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Preface

The subject area of “Deep Eutectic Solvents” was inaugurated for research and application just 15 years ago, in Abbott’s paper (with coworkers) of 2003 in Chemical Communications. Since then, publications on this subject proliferated in an exponential mode, their number increasing 1.6-fold annually, there being already some 200 publications that appeared in the first quarter of 2018. Of the total number of publications. only 3.2% are in non-English languages and 4.0% are patents, the other papers are in scientific journals and deal with the preparation, properties, and applications of these neoteric solvents. In retrospect, it appears timely to summarize what has been achieved in this area and this book is a result.

Chapter 1 deals with the role of solvents in general in chemical laboratory practice and in the chemical industry in particular. Recent trends are to replace conventional organic solvents with neoteric ones devoid of the hazards involved with the former, including room temperature ionic liquids (RTILs) and supercritical fluids. They then specify the requirements from solvents to be considered as being “green”, i.e., to be ecologically friendly and safe, nontoxic, biodegradable, and to be prepared easily from readily available low-cost materials. Deep eutectic solvents are liquid mixtures at ambient conditions of (generally) two components that are themselves not necessarily liquid under such conditions. Therefore, a short presentation of solid–liquid phase diagrams and the means of their determination is placed here in order to illustrate the “deep eutectic” aspect of the solvents that are the subject of this book.

Chapter 2 shows the great variety of the deep eutectic solvents (DESs), i.e., mixtures that are liquid at ambient conditions and can be considered to act as “green” solvents as specified in the previous chapter. Natural deep eutectic solvents (NADES) are a subclass, the components of which are of natural origin and need not be synthesized. The prototype of the DESs is the 1:2 choline chloride/urea mixture (commercially available as Reline) and many other DESs based on a choline salt or its analogs have been described. Most of the DESs of which there are reports in the literature comprise alkyl-substituted ammonium or phosphonium salts on the one hand and amides or substances with hydroxyl groups (alkanols, polyols, carboxylic acids) on the other at a definite molar ratio, and may be called conventional deep eutectic solvents. These DESs are ionic liquids, being based on salts of various types, and may be considered to be a subgroup of the well-established room temperature ionic liquids (RTILs). There are, however, a substantial number of nonconventional DESs, involving metal salts, metal salt hydrates, and zwitterionic amino acids which are also ionic. On the other hand, nonionic DESs involving sugars and carboxylic acids also share properties and applications with the conventional ones, and are dealt with here.

Chapter 3 describes the physical and chemical properties of the deep eutectic solvents. The solid–liquid phase diagrams of DESs are dealt with, but surprisingly, perhaps, complete diagrams are available for only a fraction of the systems that are deemed to be deep eutectic solvents (some DESs, however, are low transition temperature mixtures (LTTMs) that form glasses on cooling rather than crystalline solids). The thermodynamic properties include vapor–liquid equilibria, i.e., vapor pressures (that are very low), enthalpies of vaporization, boiling points, and critical points, but these are rather unimportant for actual applications. The heat capacity and surface tension of the DESs are of greater relevance. The volumetric properties: the density, thermal expansibility, and compressibility are presented, as are the transport properties: viscosity, electrical conductivity, diffusion coefficients, and thermal conductivity. Other physical properties that are included are the refractive index and polarizability, the electrical permittivity, and the magnetic susceptibility. The chemical properties of DESs are their liquid structures, as obtained by diffraction experiments and computer simulations, their solvatochromic indices that are relevant to their ability to solvate solutes, their basicity or acidity, and hydrophilicity or hydrophobicity. The ability of DESs to absorb gases is dealt with as are their electrochemical properties (electrochemical potential window) and capacitance. Finally, the important issues that pertain to the DESs being "green", i.e., their toxicity (cytotoxicity and phytotoxicity, as well as hazard to humans) and biodegradability are discussed.

Chapters 4 and 5 deal with the reported applications of deep eutectic solvents, with illustrative examples (certainly not an exhaustive set) of reports to the end of 2017, with a few interesting ones from the beginning of 2018. The applications described in Chap. 4 include the use of DESs as reaction media, including ionothermal synthesis of metal-based inorganic compounds based on dissolved metal oxides in the solvents, as well as catalyzed or non-catalyzed synthesis of organic compounds and enzymatic catalyzed synthesis of biomolecules. The processing of biomass (lignocellulose) and the production of biodiesel in DESs have received widespread attention and are dealt with. Deep eutectic solvents have been used for the electrodeposition of metals on the one hand and on their electro-polishing on the other. Nanotechnology is another area for which widespread applications have been reported, including nanosized metallic particles and magnetic oxides used as catalysts, carbon nanotubes and graphene sheets, and porous molecularly imprinted polymers.

The applications described in Chap. 5 involve extraction and sorption by the DESs. The desulfurization and denitrification of fuels is one of the fields of application and extraction of or from hydrocarbons, such as aliphatic–aromatic separations or breaking of azeotrope mixtures is another. The extraction of bioactive ingredients from plant materials by DESs has received a great deal of attention as has the extraction of metal specie for analytical purposes. The sorption of obnoxious gases, mainly carbon and sulfur dioxides, appears to be an economically and ecologically attractive alternative to the existing methods and is described in detail.

The last chapter, Chap. 6, summarizes the trends and prospects for applications of deep eutectic solvents, in sustainable chemistry, in materials and nanotechnology, and in analytical chemistry, sorption and extraction. The addition of unconventional deep eutectic solvents to the arsenal of common DESs is another promising development.

Jerusalem, Israel Yizhak Marcus
April 2018

Contents

Chapter 1
Introduction

Deep eutectic solvents (DESs) are a certain class of liquids at ambient conditions (that have freezing points below, say, 25 °C) that are binary compositions of two components, each of which has a melting point above that of the deep eutectic solvent, hence they are eutectics. Deep eutectic solvents are a subgroup of room temperature ionic liquids (RTILs), but are binary mixtures contrary to ordinary RTILs that are single substances. Being generally ionic in nature, deep eutectic solvents should have appreciable electrical conductivities, but nonionic deep eutectic solvents have also been described. As solvents, they should be able to dissolve a variety of solutes, be these organic substances, metal oxides, or substances of other kinds. The deep eutectic solvents also should be noninflammable, nontoxic, and friendly to the environment ('green', biodegradable) in order to be useful for industrial processes. The freezing point of 25 °C is set as an arbitrary upper limit to deep eutectic solvents to be dealt with in this book.

1.1 Solvents for Processing and in the Laboratory

Much of chemistry takes place or is carried out in a liquid solution. This is the case in nature: geochemical reactions and physiology in plants and living organisms, in industry: textile, paper, food, biomass processing, hydrometallurgy, bulk chemicals, and pharmaceuticals, and in the laboratory: synthesis, purification, and analysis. Therefore, solvents are required that have the desired properties for the processes to be carried out on the one hand and that do not have disadvantageous properties on the other.

There are several features of liquids that make them suitable as solvents. A solvent should have an appropriate liquid range, i.e., it should be liquid at ambient temperatures and pressures and over a suitable range of these conditions. It should be available at commercial quantities at the purity required for the envisaged process, or be readily purified for this purpose, and be inexpensive. It should be

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recyclable (generally, but not necessarily, by distilling it out from the process mixture, after the product has been recovered) and when disposed-of should be environmentally friendly. Tunability is a desired aspect, in that by changing conditions (the temperature or pressure) or by addition of co- or anti-solvents the solubilities of the desired product and of undesired by-products and residual raw materials can be controlled. Several attributes of prospective solvents should be avoided: these include high viscosity that impedes ready flow, high volatility, flammability, and toxicity to humans and the environment.

Water is, of course, a very widely utilized solvent, because of its advantageous properties and minimal detrimental ones. It is readily available at the required purity, it is cheap, it has a convenient liquid range, it is readily recycled, and has good solvent properties for a wide variety of solutes. It is also nontoxic, nonflammable, and environmentally friendly. It may even be utilized under increased pressures at elevated temperatures, beyond its normal boiling point, and even at supercritical conditions. Water is, of course, the primary solvent for physiological processes as well as for many geochemical ones.

However, water is a poor solvent at ambient conditions for nonpolar substances, for many permanent gases, for most industrial polymers, and for those solid materials that have such large crystal energies that cannot be overcome by the solvation energies and the entropy changes involved in the dissolution. Furthermore, water is highly reactive towards many solutes and cannot be used if such solutes are required to be unchanged by the solvent itself during the process. Therefore, alternative solvents have been extensively used in industry and in the laboratory, that have better solvent properties regarding such prospective solutes for which water is inadequate as a solvent.

Organic liquids have for a long time served for this purpose, both dipolar and hydrogen bonded ones and nonpolar solvents as well, for different classes of solutes. Their main role is their ability to solvate the particles (molecules or ions) of the solutes. Their general properties have been summarized in several monographs, e.g., [1, 2], and those properties conducive to their solvating abilities have also been summarized [2]. For some applications, it has been found that aqueous/organic solvent mixtures and nonaqueous mixtures of organic solvents perform better than individual ones, for example for pharmaceutical solutes [3]. General and solvating ability properties of such mixtures have also been summarized [4]. Although such organic solvents are generally readily available commercially in high purity, their costs have to be taken into account for industrial applications. Furthermore, such solvents may be too volatile, toxic, flammable, and detrimental to the environment, so that special precautions have to be undertaken in their utilization. The present general trend in the industry is to avoid the commonly employed organic solvents and to replace them with solvents that are not volatile, nontoxic, nonflammable, and environmentally friendly.

Supercritical solvents, in particular, supercritical carbon dioxide (SCD) [5–7] and supercritical water (SCW) [8–10], but also, to a smaller extent, other supercritical fluids, have been proposed for a variety of applications. These include the sorption and separation of gases (SCD) and the total oxidation and elimination of environmentally hazardous substances (SCW). The chemicals comprising these solvents are cheap and readily available, but appreciable costs in energy for obtaining the required elevated temperature and/or pressure as well as corrosion problems detract from the attractiveness of supercritical solvents for large-scale uses.

Ionic liquids as solvents include molten salts at elevated temperatures and have in the past been promoted for certain applications, including coolants and moderating agents for nuclear reactors, nuclear fuel reprocessing, and metallurgical applications. Their application as solvents is restricted to solutes that withstand the elevated temperatures involved, and this excludes most organic solutes. However, in the last 20 years, the class of room temperature ionic liquids (RTILs) has gained enormous interest regarding their properties [11] and uses as solvents for a host of applications [12–14]. A great variety of room temperature ionic liquids, based on imidazolium, pyrrolidinium, pyridinium, and nonsymmetrical quaternary ammonium and phosphonium cations, are now commercially available at moderate costs. They are generally used at ambient conditions, but their properties are tunable by the choice of the temperature of application and the cation/anion combination and/or modification by inclusion of further polar and protic groups in their building stones [15] as well as by the use of cosolvents, e.g., water. Another means for production of room temperature ionic liquids is the use of large complex anions, such as chloroaluminates, $Al_2Cl_7^-$, that decrease the freezing points of the salts by diminishing their lattice energies, making them liquid at ambient conditions [16]. Room temperature ionic liquids are generally nonvolatile, but may have inconvenient viscosities unless used above ambient conditions. They still may be toxic and flammable, as well as difficult to recycle, so that their costs must be taken into account for industrial purposes.

The search for alternative solvents has not abated since the advent of the room temperature ionic liquids, and one possible candidate has been suggested by Abbott et al. [17] in 2003: the eutectic combination of choline chloride and urea. The melting points of the components are 302 °C for choline chloride ($HOC_2H_4N(CH_3)_3^+Cl^-$) and 133 °C for urea ($O{=}C(NH_2)_2$), whereas for the 1:2 eutectic the melting point is 12 °C, making the liquid mixture an attractive solvent. The depression of the freezing point involves hydrogen bonding, where one component urea, provides the hydrogen bond donation ability and the other component, providing the hydrogen bond accepting ability through its chloride anion. The choline chloride may be substituted by other quaternary ammonium salts or by salts with a hydrogen bond accepting moiety other than the chloride anion and the urea by other hydrogen bond donating substances. A eutectic may then be formed that melts below ambient temperature, hence constitutes a usable liquid solvent. It was found that the choline chloride/urea pair at the eutectic composition, as well as similar pairs, have large ionic conductivities and manageable viscosities, and form immiscible biphasic liquid systems with solvents that are incapable of donation of hydrogen bonds, giving rise to a host of applications [17]. This discovery opened the field of deep eutectic solvents that is the subject of this book.

1.2 Green Solvents

The concept of ‘green solvents’ pertains to the wider area of ‘green chemistry’, for which 12 principles have been established. These are as follows:

(1) Waste prevention: synthesis and processing should not leave waste materials to clean-up and dispose.
(2) Safety: no toxic materials should result from the process.
(3) Hazard prevention: avoidance of the formation of materials or processes that are hazardous.
(4) Preference for renewable feedstock: avoidance of depleting raw materials from mining or fossil fuels.
(5) Preference for catalytic reactions: catalysts are preferable to stoichiometric reagents.
(6) Avoidance of temporary modifications: derivatives require additional reagents for the regeneration of the desired products.
(7) Atom economy should be maximized: wasted atoms should be avoided.
(8) Safe solvents need to be used: minimal quantities of recyclable solvents are preferred.
(9) Energy efficiency is to be maximized: ambient temperatures and pressures should be preferred.
(10) Degradable products and reagents are preferred: the materials should not accumulate in the environment.
(11) In-time control: monitoring of reactions for the elimination of undesired by-products.
(12) Minimization of the potential for accidents: explosion, fire, and pollution possibilities of processes must be kept in mind.

In view of these principles, the chemical community is proceeding in recent years toward sustainable industrial processes, for which summit conferences are organized, annual **Green Chemistry** and Engineering Conferences take place, and Green Chemistry and Sustainable Chemistry and Engineering journals and series are published.

More than 10^7 tons of organic solvents are produced each year for industrial purposes [18], but most of these do not conform to the requirements of ‘green chemistry’. Industry has, indeed, in recent years, followed the slogan “pollution prevention pays” [19] by reduction of the amounts of solvents that are used in the processes and by their recycling, so that much smaller amounts are disposed into the environment. As a consequence, the demand for ‘green solvents’ has proliferated, meeting the essential criteria listed above [20].

Water is the ‘greenest solvent’ imaginable, as mentioned in Sect. 1.1: it is readily available at the required purity, it is cheap, it is readily recycled, nontoxic, nonflammable, and environmentally friendly. However, even water, widely used as a solvent in a variety of industrial applications, should be avoided as much as possible, because of the hazard of return of contaminated water to the natural sources: underground reservoirs, rivers, and lakes. Apart from water, there are few solvents from natural sources, and employment of these, mainly hydrocarbons from the refining of fossil fuels, contradicts principle (4) of “green chemistry”. Alternative solvents may include supercritical water [8, 9] and carbon dioxide [21], ionic liquids [12–14], and fluorous phases [22]. Synthetic solvents are sought that, in addition to their desired positive properties, such as availability at low costs, dissolution abilities of the prospective solutes and the required widths of their spectroscopic and electrochemical windows, avoid the undesirable features of toxicity, flammability, loss through volatility, and environmental incompatibility.

Several metrics for the environmental health and safety properties of solvents exist that deal with process safety, human health, and the environment [23]. Several guiding specifications have been adopted by industry. The Pfizer guide provides a simple comparison of common solvents, deeming them “preferred”, “usable”, or “undesirable”. The GSK guide focuses on small molecule organic solvents in the pharmaceutical industry and is most useful when choosing among known alternatives [24]. The Sanofi solvent selection guide provides a clear rank (recommended, problematic, hazardous, or highly hazardous) to each solvent which includes a number of bio-derived and less common solvents [25]. A further solvent selection guide is available in [26].

The process safety aspects include the flash point, the vapor pressure, explosion risk (peroxide formation potential), auto-ignition temperature, static charge formation, self-reaction potential, and corrosiveness. The health aspects include carcinogenicity, mutagenicity, reprotoxicity, skin absorption, acute toxicity, and respiratory and eye irritation, as well as prolonged occupational exposure hazard. The environmental aspects include water contamination, ozone depletion, bioaccumulation, energy demand for distillation, photoreactive potential, and non-degradability.

Room temperature ionic liquids (RTILs) have been widely promoted in recent years as ‘green solvents’. A recent publication [27] shows that ~80% of papers dealing with solvents for green technologies pertain to room temperature ionic liquids (RTILs), ~15% pertaining to supercritical carbon dioxide, and only ~5% pertaining to other ‘green solvents’. Industrial applications of room temperature ionic liquids have been described [28, 29] and their properties have been summarized [11].

One of the main features of room temperature ionic liquids is their low volatility, so that loss to the environment and its pollution by the vapors of room temperature ionic liquids is minimized. Other hazards of room temperature ionic liquids may be minimal, but some have flashpoints below 200 °C, examples being: 1-ethyl-3-methylimidazolium ethyl sulfate (157.0 °C), 1-hexyl-3- methylimidazolium chloride (178.5 °C), 1-butyl-3-methyl-imidazolium methyl sulfate (102 °C) [30]. These temperatures are diminished when the room temperature ionic liquids are heated for a moderately prolonged time [31]. In spite of their very low vapor pressures, room temperature ionic liquids are combustible rather than nonflammable [32] and may auto-ignite at >400 °C [33].

Room temperature ionic liquids are not devoid of toxicity, as recent discussions on applications of ionic liquids in the food and bioproducts industries reveal [34, 35]. Thus, although the imidazolium-based RTILs are the most popular choice, this choice occurs despite clear indications about their toxicity. Room temperature ionic liquids with lower toxicity, such as cholinium saccharinate, were synthesized [36] and had lower eco-toxicity levels toward crustaceans, when compared to most common ionic liquids, a fact related to the natural origin of the ions. The use of renewable natural compounds for the synthesis of room temperature ionic liquids, such as amino acids, lipid-like compounds, or those involving acids from natural origin is emerging.

The low vapor pressures of room temperature ionic liquids make them much less susceptible to air pollution than common organic solvents. However, room temperature ionic liquids are not per se innocuous environmentally, and relevant issues of room temperature ionic liquids, including environmental behavior and toxicity, and routes for designing nontoxic room temperature ionic liquids and the techniques that might be adopted for the removal/recovery of room temperature ionic liquids have been discussed [37]. Of major concern are their fate, transport, and transformations in terrestrial and aquatic systems. The adsorption of room temperature ionic liquids on soils and sediments has been investigated [38]. The biodegradation of room temperature ionic liquids, including methods for its assessment, the trends observed for structurally related room temperature ionic liquids, and applications of biodegradable ionic liquids in synthetic chemistry have been reviewed [39]. Room temperature ionic liquids that are classified as readily biodegradable require a $\geq 60\%$ biodegradation level in 28 days and full biodegradation should yield completely nontoxic products.

A further issue that pertains to the use of room temperature ionic liquids as solvents is their considerable viscosity at ambient conditions. Water and common organic solvents: *n*-hexane, methanol, tetrahydrofuran, and acetonitrile have at 25 °C dynamic viscosities η/mPa•s < 1. On the other hand, typical room temperature ionic liquids have at 25 °C viscosities η/mPa•s of 15.0 for 1-ethyl-3-methylimidazolium hexafluorophosphate, 35.6 for 1-butyl-4-methylpyridinium dicyanamide, 30.0 for 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate, and 245 for octyl tributylphosphonium dicyanamide, and even larger viscosities for other members of these classes of room temperature ionic liquids [11].

All these considerations are relevant also to the deep eutectic solvents that are dealt with in this book, and are discussed in turn at the appropriate places.

1.3 Solid–Liquid Phase Diagrams

Solid–liquid phase diagrams present the temperatures at which crystalline solid states of aggregation of a substance or a mixture of substances are at equilibrium with liquid states, i.e., the melting/freezing points of either single substances or as a function of the composition in the case of mixtures. In the case of a binary mixture there may occur a eutectic, that is, a composition that has a lower melting point than any other composition, including the neat components. On the other hand, a crystalline compound may be formed between the two components, and this has its own characteristic melting point. If the liquid formed on fusion of this compound crystallizes back on cooling to this same compound it is said to melt congruently, otherwise, it melts incongruently and the original compound is not reformed on cooling the liquid melt, but either of the initial components may crystallize out. A further complication that may occur is the formation of solid solutions of the components of the mixture formed on cooling the liquid melts, rich in the one component or in the other as the overall concentration changes.

Several methods are used to obtain the solid–liquid equilibrium (SLE) diagrams of binary mixtures. Commonly, the components at given molar ratios are mixed and heated above the melting point of the mixture to form a homogeneous liquid. The mixture is allowed to cool gradually and its temperature is measured until visually a solid phase appears. This procedure may be carried out by means of a hot-stage microscope [40]. A more sophisticated method is to monitor the temperature of the cooling liquid mixture with time and to note a halt in the cooling curve that indicates equilibrium crystallization of the solid phase. A possible undercooling can be noted in such cooling curves, and on nucleation of the melt, a temperature upshot is seen toward the halt at the true freezing point. A further method that is widely employed is differential scanning calorimetry (DSC) which on heating the mixture shows an endothermic peak, the onset of which indicates the melting point and the enthalpy change of fusion is obtained from integration of the DSC curve [40]. An exothermic peak is shown by DSC on cooling the molten material, indicating the freezing point.

Simple solid–liquid phase diagrams with a single eutectic are found in many binary mixtures, and the melting points of the eutectic can be a great deal below those of the constituent compounds. The distance between the eutectic melting point and the point at the composition of the eutectic on the straight line connecting the melting points of the constituents is called the eutectic distance, Δt_m, and characterizes the success with which the melting point t_m has been diminished. This is demonstrated in Fig. 1.1 for the mixtures of α-naphthol ($t_m/°C = 95.1$) with *o*-nitroaniline ($t_m/°C = 69.6$), where a eutectic occurs ($t_m/°C = 44.0$) at a mole fraction of *o*-nitroaniline of 0.5616 [41], but its t_m is above ambient temperature. In this case, the eutectic distance is $\Delta t_m/°C = 36$.

Similar situations are observed also with inorganic materials, for instance, for salt hydrates that have melting points not far from ambient temperatures, in contrast with molten salts [11] that are outside the scope of this book. The solid–liquid phase diagram of mixtures of magnesium chloride hexahydrate ($MgCl_2{\bullet}6H_2O$, $t_m/°C = 112$) with nickel chloride hexahydrate ($NiCl_2{\bullet}6H_2O$, $t_m/°C = 30$) [42] is shown in Fig. 1.2. The eutectic at the 1:1 composition has a melting point $t_m/°C = 4$. This binary salt hydrate system may serve as a deep eutectic solvent, but has not been so described and used so far, as much as is known, and the eutectic distance $\Delta t_m/°C = 67$ is quite appreciable.

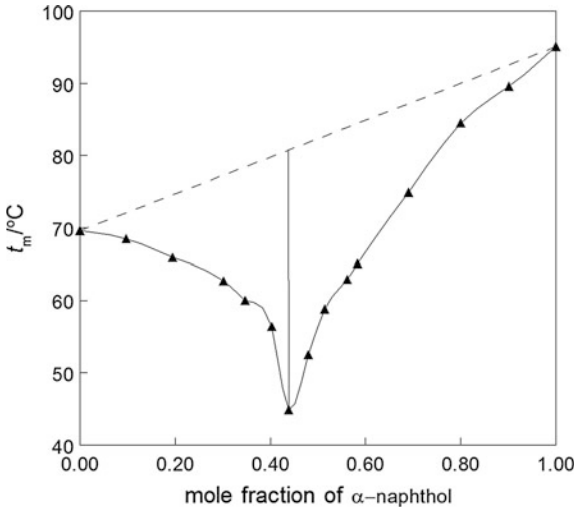

Fig. 1.1 Solid–liquid phase diagrams of the α-naphthol with *o*-nitroaniline binary systems [41]. The lines connecting the experimental points are guides to the eye and have no further significance. The dashed line connects the melting points of the components and the vertical line represents the eutectic distance

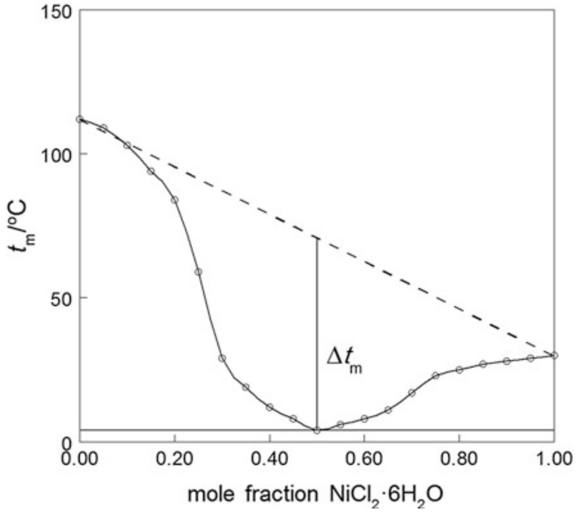

Fig. 1.2 The solid–liquid phase diagram of mixtures of $MgCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ [42]. The lines connecting the experimental points are guides to the eye and have no further significance, but the eutectic distance Δt_m is indicated as a vertical solid line up to the dashed line connecting the melting points of the components

A fairly complicated phase diagram occurs for the corresponding nitrate systems: mixtures of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$, t_m/°C = 89.5) with nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, t_m/°C = 56.7) [42, 43], shown in Fig. 1.3. A maximum in the diagram occurs at the 1:1 composition, at which a congruently melting compound is formed (t_m/°C = 87), surrounded by two minima (eutectics) with t_m/°C = 70 and 51.

An even more complicated phase diagram is obtained for solutions of magnesium chloride in water [44], in which a series of hydrates are successively at equilibrium with the solution, the dodecahydrate, octahydrate, hexahydrate, tetrahydrate, and dihydrate, as shown in Fig. 1.4.

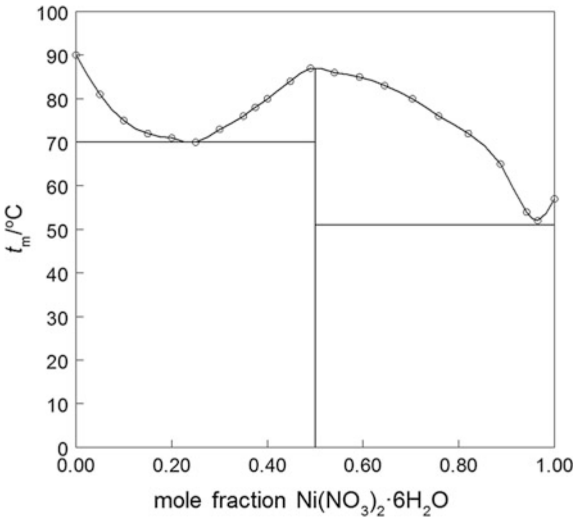

Fig. 1.3 Solid–liquid phase diagram of mixtures of $Mg(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ [42, 43]

The deep eutectic solvents dealt with in this book have the much simpler form of solid–liquid phase diagram, with a single eutectic, as shown in Fig. 1.1 for the *o*-nitroaniline/α-naphthol system, and in Fig. 1.2 for the $MgCl_2 \cdot 6H_2O/NiCl_2 \cdot 6H_2O$ system.

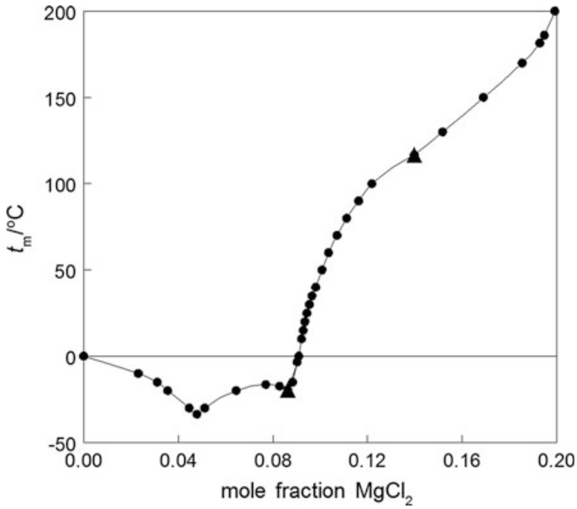

Fig. 1.4 The solid–liquid phase diagram of aqueous $MgCl_2$ [44]. The lines connecting the experimental points are guides to the eye and have no further significance. Up to the first triangle from the left, the hydrates at equilibrium with the solution are successively the dodecahydrate and the octahydrate; between the two triangles the hexahydrate is at equilibrium with the solution, and beyond the second triangle it is the tetrahydrate, that in turn reverts to the dihydrate (outside the figure)

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Chapter 2
The Variety of Deep Eutectic Solvents

The following definition is generally used in this book: deep eutectic solvents (DESs) are binary mixtures of the definite composition of two components, one of which being ionic, that yield a liquid phase at ambient conditions, ≤ 25 °C. Some cases that do not conform to this restrictive definition are, however, also included, since they have properties and uses similar to those that do. The general mode of preparation of deep eutectic solvents, if their ingredients are solids at ambient conditions, is to mix the components at the prescribed molar ratio and heat the mixture to a moderately elevated temperature (generally 60–100 °C) for a few hours until the entire mass is converted to a homogeneous clear liquid. If one of the ingredients is itself liquid at ambient conditions the other component is dissolved in it, if necessary by moderate heating for some time. A variant is to dissolve both components in water, which is then vacuum evaporated or removed by freeze-drying, and to dry the resulting deep eutectic solvent in a desiccator [1, 2].

One general mode for the formulation of a deep eutectic solvent is to have one component of the binary mixture a hydrogen bond acceptor (HBA), e.g., an ionic component with an anion such as chloride, and the other a hydrogen bond donor (HBD), such as an amide, an alcohol, or a carboxylic acid. The deep eutectic solvent keeps the identities of the components which interact via hydrogen bonding, and no covalent compound between them is formed. The optimal ratio of the hydrogen bond acceptor and hydrogen bond donor that forms the eutectic depends on the mutual hydrogen bonding abilities of the components.

The concept of natural deep eutectic solvents (NADES) involves as the hydrogen bond donor components of the binary mixtures any of the many substances from natural origins that form deep eutectic solvents with choline chloride (itself a natural product) or other hydrogen bond acceptor ingredients of natural origin. The advantage of natural deep eutectic solvents over other deep eutectic

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solvents is that the natural ones are expected to be nontoxic, biodegradable, hence more environmentally friendly, and to be prepared easily from readily available low-cost materials.

Figure 2.1 shows the structures of commonly used hydrogen bond acceptor ingredients of deep eutectic solvents and Fig. 2.2 shows the corresponding structures of the hydrogen bond donor components [3].

Some publications consider eutectic mixtures that have melting/freezing points above 25 °C as deep eutectic solvents, but here mainly those that melt/freeze below this temperature are dealt with. However, some mixtures do not crystallize on cooling but have a glass transition point rather than having a freezing/melting point. Such mixtures are termed 'low transition temperature mixtures' (LTTMs) and act like deep eutectic solvents in most respects and are dealt with here. The scope of deep eutectic solvents is extended by the addition of a third component, another hydrogen bond donor agent, as, for example, water. However, here mostly binary mixtures of one hydrogen bond acceptor agent and one hydrogen bond donor agent are dealt with.

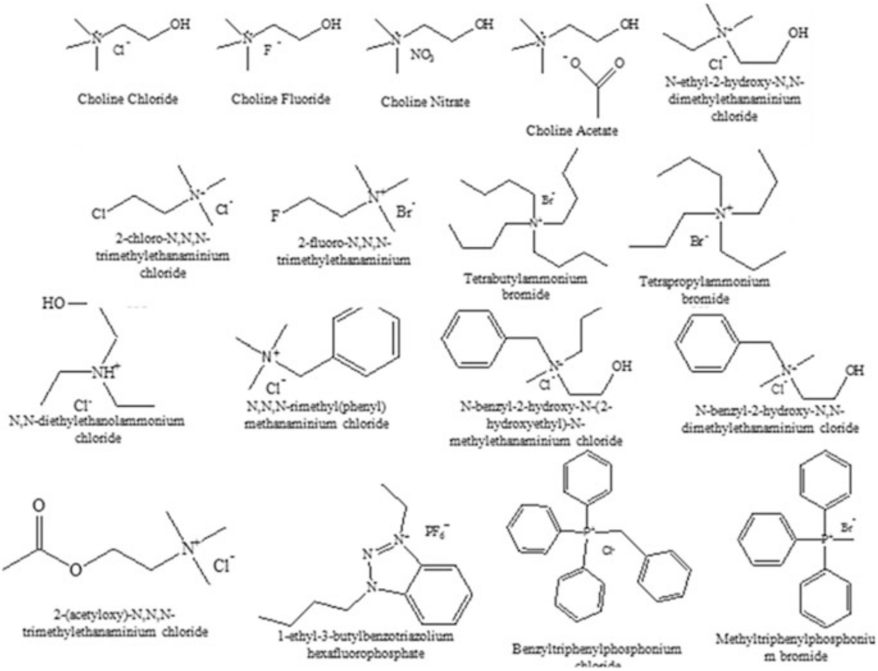

Fig. 2.1 Structures of hydrogen bond accepting components of deep eutectic solvents (from [3], by permission of the publisher, Elsevier)

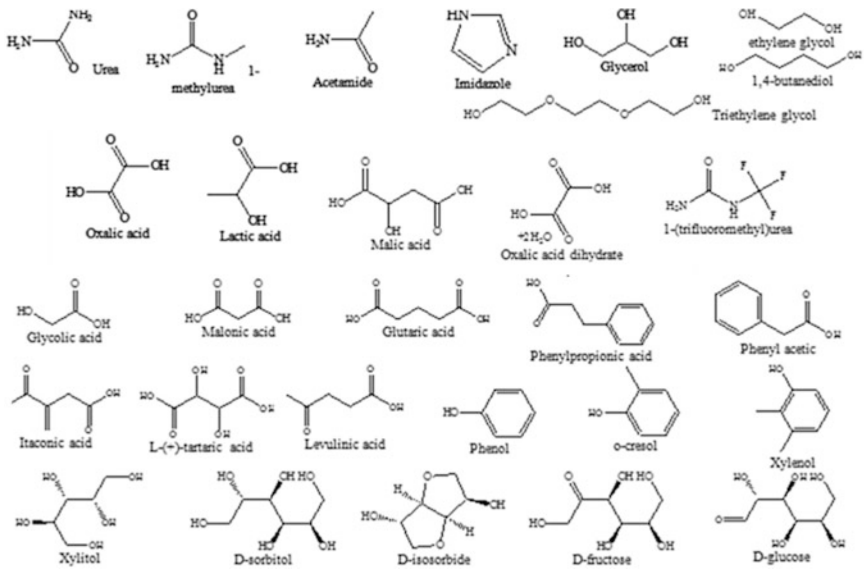

Fig. 2.2 Structures of commonly used hydrogen bond donor components of deep eutectic solvents (from [3] with permission of the publisher, Elsevier)

2.1 Deep Eutectic Solvents Based on Choline Chloride and Analogs

The first deep eutectic solvent (DES) was suggested by Abbott et al. [4]: the eutectic combination of choline chloride and urea. This deep eutectic solvent is nowadays known under the trade name “Reline” and is commercially available. However, it is simply prepared by mixing the solid components at the appropriate molar ratio, 1 choline chloride: 2 urea, heating while stirring to 80 °C, and the homogeneous transparent liquid deep eutectic solvent is thereby formed. For the 1:2 eutectic, the melting point is $t_{me}/°C = 12$ [4] (but see Sect. 3.1 for disagreeing values), making the liquid mixture an attractive solvent so that Reline is widely used as a solvent for a host of applications.

The raw materials for this particular deep eutectic solvent, Reline, are widely available natural products and are biodegradable, hence environmentally friendly, i.e., ‘green’, making this combination a NADES. Choline chloride (2-hydroxyethyl-*N*,*N*,*N*-trimethylaminium chloride ($HOC_2H_4N(CH_3)_3^+Cl^-$, CAS No. 67-48-1) is mass produced as a growth-promoting chicken feed additive at a price of ~850 USD/ton. It is a white deliquescent crystalline solid, has a molar mass of $M/\text{g mol}^{-1} = 139.62$ and has a melting point of $t_m/°C = 302$ (but it decomposes on melting). It is very hydrophilic: its octanol/water distribution constant is $\log K_W^O = -5.16$, and it is highly soluble in water: $s/\text{g dm}^{-3} > 650$ at room temperature. Choline chloride is a skin irritant and hazardous in case of ingestion, but potential chronic health effects are not known. The material is combustible but not readily flammable.

Urea ($O{=}C(NH_2)_2$, CAS No. 57-13-6) is mass produced as a nitrogen fertilizer at a price of ~200 USD/ton. It is a white crystalline solid, has a molar mass of M/g mol^{-1} = 60.06, and has a melting point of t_m/°C = 132.7. It is moderately hydrophilic: its octanol/water distribution constant is $\log K_W^O = -1.52$, and it is highly soluble in water: s/g dm^{-3} = 1080 at 20 °C. Urea is a skin irritant and hazardous in case of ingestion and inhalation, but potential chronic health effects are not known. Urea is nonflammable, but may be combustible at high temperatures.

The eutectic distance for the 1:2 choline chloride: urea eutectic combination is Δt_m/°C = 178, in view of the melting points of the ingredients: 302 and 133 °C. The hydrogen bond acceptor chloride anion of the choline salt may be exchanged for other anions that also have good hydrogen bond accepting abilities, such as nitrate (t_{me}/°C = 4) or fluoride (t_{me}/°C = 1) for the resulting deep eutectic solvent [4]. However, for a choline salt with an anion less prone to accept hydrogen bonds the melting point of the 1:1 combination is considerably above ambient: t_{me}/°C = 67 for the tetrafluoroborate salt.

Choline chloride may be substituted by other similar quaternary ammonium salts that form deep eutectic solvents with urea [3, 4]. A change of one of the methyl groups of the choline cation to an ethyl or benzyl group lowers the melting point of the quaternary ammonium salt/urea deep eutectic solvent. The chloride of 2-hydroxyethyl-ethyl-*N*,*N*–dimethylaminium has t_{me}/°C = –38 and that of 2-hydroxyethyl-benzyl-*N*,*N*–dimethylaminium has t_{me}/°C = −33. Other substitutions of choline, such as 2-acetylethyl-*N*,*N*,*N*–trimethylaminium, t_{me}/°C = –14, *N*,*N*-bis(2-hydroxyethyl)-benzyl-methylaminium, t_{me}/°C = −6, and 2-chloroethyl-*N*,*N*,*N*–trimethylaminium, t_{me}/°C = 15, are further examples [4].

Table 2.1 summarizes the compositions regarding deep eutectic solvents based on choline and its analogs, their molar masses M and their melting/freezing points t_{me}. Some amides besides urea also produce deep eutectic solvent with choline chloride, the most effective being trifluoroacetamide ($CF_3C(O)NH_2$, CAS No. 354-38-1) at a molar ratio of choline chloride: amide of 2:5, with t_{me}/°C = −43.6. The eutectic distance, in this case, is Δt_m = 184 °C [5, 6], slightly larger than for urea as a component. Some other amides than urea and trifluoroacetamide have also been tried with choline chloride, but do not produce deep eutectic solvents: they have melting points above ambient. Methyl-substituted ureas are examples: 1-methyl-, 1,2-dimethyl-, 1,1-dimethyl-urea eutectics with choline chloride have t_{me}/°C = 29, 70, 149, respectively. The eutectic of choline chloride with acetamide has t_{me}/°C = 80, with benzamide has t_{me}/°C = 129, and with thiourea has t_{me}/°C = 175 [4].

Choline chloride is an ingredient of a wide range of other deep eutectic solvents, for instance, those formed with a carboxylic acid as the hydrogen bond donating ingredient. When a monobasic acid is employed, the ratio 1:2 choline chloride: acid produces the low-melting eutectic: t_{me}/°C = 20 for phenylpropanoic acid

Table 2.1 Deep eutectic solvents based on choline chloride and its analogs formed at the indicated ratios of HBA:HBD, their molar masses M, and the melting point of the eutectics, t_{me}

HBA	HBD	M/kg mol^{-1}	t_{me}/°C	Ref.
Choline chloride	urea (1:2), Reline	0.25974	12	[4]
	Thiourea (1:3)	0.36790	<10	[5]
	trifluoroacetamide (1:2)	0.36570	–44	[6, 7]
	propanoic acid (1:2)	0.28778	<–80^{b}	[8]
	chloroacetic acid (1:2)	0.32862	<–80^{c}	[8]
	trichloroacetic acid (1:2)	0.46640	<–80^{d}	[8]
	phenylacetic acid (1:2)	0.42595	25	9
	phenylpropanoic acid (1:2)	0.43998	20	[9]
	malonic acid (1:1), Maline	0.24368	10	[9]
	glutaric acid (1:1)	0.27174	–16 (t_{ge})	[3]
	glycolic acid (1:1)	0.21507	–16 (t_{ge})	[9]
	lactic acid (1:2)	0.31978	–78	[9]
	levulinic acid (1:3)	0.48795	–11	[10]
	oxalic acid dehydrate (1:1)	0.26569	–40	[3]
	malic acid (1:1)	0.27371	–56	[9]
	Trifluoromethanesulfonic acid		< 25	[11]
	p-toluenesulfonic acid (1:2)	0.52007	<–80^{e}	[8]
	ethylene glycol (1:2), Ethaline	0.26376	–66	[12]
	diethylene glycol (1:3)	0.45738	< –20	[13]
	triethylene glycol (1:3)	0.58953	-19.8	[14]
	glycerol (1:2), Glyceline	0.32380	–40	[15]
	1,2-propanediol (1:3)	0.36732	< –20	[16]
	1,4-butanediol (1:2)	0.31986	–32	[2, 9, 10]
	2,3-butanediol (1:3)	0.40938	< –20	[16]
	PEG 200 (1:2)	0.53902	< 25	[17]
	furfuryl alcohol (1:3)	0.43392	–36	[10]
	xylitol (1:1)	0.29177	LRT^{a}	[19, 20]
	d-sorbitol (1:1)	0.32179	9	[7]
	d-isosorbide (1:2)	0.43190	LRT^{a}	[19, 20]
	xylose (1:1)	0.28915	LRT^{a}	[21]
	fructose (2:1)	0.43237	10	[3]
	glucose (2:1)	0.43237	15	[3]
	Sucrose (1:1)	0.48132	LRT^{a}	[21]
	phenol (1:3)	0.42195	–20	[3, 22]
	o-cresol (1:3)	0.43597	–24	[3, 22]
	p-cresol (1:2)	0.33699	<20	[23]
	2,3-xylenol (1:3)	0.50613	18	[3, 22]
	4-chlorophenol (4:5)	0.29972	< 20	[3, 22]
	2-methoxyphenol^{f} (1:3)	0.51144	<20	[24]

(continued)

Table 2.1 (continued)

HBA	HBD	M/kg mol^{-1}	t_{me}/°C	Ref.
	ethanolamine (1:2)	0.27168	< –20	[25]
	triethanolamine (1:2)	0.43800	LRT	[31]
Choline acetate	urea (1:2)	0.28334	18	[4]
	glycerol (1:1.5)	0.30175	13	[32]
Choline bromide	levulinic acid (1:4)	0.53240	10.7	[4]
Choline fluoride	urea (1:2)	0.24329	1	[4]
Choline nitrate	urea (1:2)	0.28630	4	[4]
Me_3-(2-ClEt)N^+Cl^-	urea (1:2)	0.27619	15	[4]
Me_2Et-(2-HOEt)N^+Cl^-	urea (1:2)	0.27377	–38	[4]
Me_2Bz-(2-HOEt)N^+Cl^-	urea (1:2)	0.33574	–33	[4]
	levulinic acid (1:2)	0.44794	< 20	[33]
	xylose (1:1)	0.36585	–30[b]	[34]
	ribose (1:1)	0.36585	–28[b]	[34]
	glucose (1:1)	0.39588	–7[b]	[34]
	mannose (1:1)	0.39588	–16[b]	[34]
	fructose (1:1)	0.39588	–47[b]	[34]
Acetylcholine$^+Cl^-$	urea (1:2)	0.26627	–14	[4]
	imidazole (1:3)	0.38590	–66	[35]
	Triazole (1:1)	0.25073	–65	[35]
	xylose (1:1)	0.33179	–11[b]	[34]
	ribose (1:1)	0.33179	–49[b]	[34]
	glucose (1:1)	0.36382	–7[b]	[34]
	mannose (1:1)	0.36382	–45[b]	[34]
	fructose (1:1)	0.36382	–49[b]	[34]
	2-methoxyphenol[f] (1:3)	0.55408	<20	[24]

[a] LRT = liquid at room temperature. [b] Glass transition temperatures t_{ge}/°C = –64. [c] t_{ge}/°C = –40. [d] t_{ge}/°C = –53. [e] t_{ge}/°C = –55. [f] Guaiacol

($C_6H_5C_2H_4CO_2H$, CAS No. 501-52-0), but when a dibasic acid is used, the ratio is 1:1, e.g., with malonic acid ($CH_2(CO_2H)_2$, CAS No. 141-82-2) t_{me}/°C = 10 [7]. The deep eutectic solvent with malonic acid is commercially called "Maline". However, some other carboxylic acids produce with choline chloride eutectics with melting points above ambient: so do phenylacetic acid, t_{me}/°C = 25, oxalic acid, t_{me}/°C = 34, and succinic acid, t_{me}/°C = 71 among others [7]. With glutaric acid (1,3-propanedicarboxylic acid, CAS No. 110-94-1) a low transition temperature mixtures (LTTMs), t_{ge}/°C = –16, is produced, where t_{ge} is the glass transition temperature, i.e., the deep eutectic solvent is a liquid above this temperature but does not crystallize. Oxalic acid dihydrate (CAS No. 6153-56-6) forms with choline chloride at a 1:1 ratio a low transition temperature mixtures, t_{ge}/°C = −40.2 [3], contrary to the anhydrous oxalic acid.

Hydroxy- and keto-carboxylic acids may produce with choline chloride low-melting deep eutectic solvents. Levulinic acid (4-ketopentanoic acid $CH_3C(O)CH_2CH_2CO_2H$, CAS No. 123-76-2) of natural origin has been promoted as an ingredient of deep eutectic solvents, the 1:3 choline chloride: levulinic acid deep eutectic solvent has a $t_{me}/°C = -11.2$ [8]. With other hydroxylic acids considerably lower melting eutectics are produced, thus with the monocarboxylic glycolic acid ($HOCH_2CO_2H$, CAS No. 79-14-1) $t_{ge}/°C = -16$ (glass transition), with lactic acid (2-hydroxypropanoic acid, $CH_3CH(OH)CO_2H$, CAS No. 50-21-5) at a 1:2 ratio $t_{me}/°C = -78$ and with the dicarboxylic malic acid (2-hydroxybutanedioic acid, $HCO_2CH(OH)CH_2CO_2H$, CAS No. 617-48-1) at a 1:1 ratio $t_{me}/°C = -56$ [7]. Two carboxylate groups are seen to be needed to hydrogen bond with the chloride anion. On the other hand, citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, $HO_2CCH_2C(OH)(CO_2H)CH_2CO_2H$, CAS No. 77-92-9) produces with choline chloride a eutectic melting above ambient: $t_{me}/°C = 69$ [7]. The deep eutectic solvent formed by choline chloride with glycolic, oxalic, malonic, and glutaric acids at 1:1 molar ratios and with levulinic acid at a 1:2 ratio have also been described in [9], but without their melting points, only glass transition temperatures <-12 °C having been reported.

Some of these carboxylic acids are natural products, hence they form with choline chloride natural deep eutectic solvents (NADES). Malonic acid, the hydrogen bond donating agent in Maline, was listed as one of the top 30 chemicals to be produced from biomass by the US Department of Energy. Its reference price is USD 7400/ton, i.e., it is rather expensive. In food and drug applications, malonic acid can be used to control acidity, either as an excipient in pharmaceutical formulation or natural preservative additive for foods. Glutaric acid is naturally produced in the body during the metabolism of some amino acids. It is used in the production of polymers such as polyesters and polyamides, the odd number of carbon atoms being useful in decreasing polymer elasticity. Its reference price is USD 4300/ton, less expensive than malonic acid. The glutaric acid may cause irritation to the skin and eyes and it may be harmful by ingestion, inhalation, or skin absorption. Levulinic acid occurs naturally in papaya and rice bran, among other natural products. Its largest application is its use in the manufacturing of DALA a biodegradable herbicide used in South Asia. Another key application is its use as ethyl levulinate in cosmetics, fragrances, and perfumes. The reference price for levulinic acid is USD 3500/ton and this substance is relatively nontoxic. Lactic acid occurs naturally in sour milk and is produced by bacterial fermentation of sugar and starch. Its reference price is USD 1300/ton, its annual production is 300,000 tons globally, and it is used in cosmetics to adjust acidity and for its disinfectant and keratolytic properties.

Polyols have been used to produce deep eutectic solvents with choline chloride, foremost among which is ethylene glycol (1,2-ethanediol, HOC_2H_4OH, CAS No. 107-21-1), forming at the 1:2 molar ratio the deep eutectic solvent, commercially available and called “Ethaline”, $t_{me}/°C = -66$. Very useful is also glycerol (1,2,3-propanetriol, $HOCH_2CH(OH)\text{-}CH_2OH$, CAS No. 56-81-5), forming at the 1:2 ratio the so-called “Glyceline”, $t_{me}/°C = -40$. Also useful is 1,4-butanediol

(OHC_4H_8OH, CAS No. 110-63-4) at a ratio of 1:3 forming deep eutectic solvents with t_{me}/°C = −32 [2, 7, 8]. Other polyols, derived from sugars, are also effective with choline chloride: furfuryl alcohol (2-furylmethanol, CAS No. 98-00-0) at a 1:3 ratio has t_{me}/°C = −36 [10] or −35.8 [8] and d-sorbitol (hexahydroxyhexane, CAS No. 50-70-4) at the 1:1 ratio has t_{me}/°C = 8.6 [6]. Two further polyols are mentioned in [11] that form deep eutectic solvents with choline chloride, i.e., mixtures that are liquid at room temperature: xylitol (pentahydroxypentane, CAS No. 87-99-0) at a 1:1 ratio and d-isosorbide (CAS No. 652-67-5) at a 1:2 ratio, but the melting points were not reported [12]. Sugars, such as d-fructose and d-glucose, also form deep eutectic solvents with choline chloride at 1:2 molar ratios, with t_{me}/°C = 10 and 15, respectively [3].

As for the carboxylic acids, some of the polyol hydrogen bond donors are natural products that form with choline chloride natural deep eutectic solvents. Glycerol, the hydrogen bond donor component of Glyceline, is obtained from the hydrolysis of fats and oils in the manufacture of soap at a reference price of USD 500/ton on a >1 million tons scale annually. Glycerol serves as a humectant, solvent, and sweetener in food and beverages, and is also used as filler in commercially prepared low-fat foods. Xylitol is naturally found in low concentrations in the fibers of many fruits and vegetables as well as fibrous material such as corn husks and sugar cane bagasse. Industrial production of xylitol, at a reference price of USD 3000/ton, starts from a hemicellulose extracted from hardwoods or corncobs, which is hydrolyzed and catalytically hydrogenated. Xylitol has no known toxicity in humans and is used as a sweetener. Sorbitol is obtained by reduction of glucose at a reference price of USD 500/ton. It is used as a sweetener and has no toxicity to humans. Furfuryl alcohol is manufactured industrially at a reference price of USD 1500/ton by the catalytic reduction of furfural, which is obtained from corncob and sugar cane bagasse. It is used as a solvent and as a chemical intermediate for furan resins in thermoset polymer matrix composites, cements, adhesives, and coatings. It is irritating to eyes, skin, and respiratory tract and harmful if inhaled or swallowed. The two sugars mentioned above, are, of course, nontoxic ingredients of natural deep eutectic solvents.

Another kind of hydrogen bond donors for deep eutectic solvents with choline chloride are phenols at a 1:3 mol ratio. With phenol itself (CAS No. 108-95-2) the deep eutectic solvents based on choline chloride has t_{me}/°C = −20.1, with *o*-cresol (2-methylphenol, CAS No. 95-48-7) it has t_{me}/°C = −23.8, and with 2,3-xylenol (2,3-dimethylphenol, CAS No. 526-75-0) it has t_{me}/°C = 17.7 [3, 13]. The phenols are toxic and this should be considered if they are to be employed.

The hydrogen bond donor agent producing with choline chloride a deep eutectic solvent needs not be an organic substance: calcium chloride hexahydrate provides water as the hydrogen bond donor agent, and various molar ratios of it with the choline chloride have freezing temperatures below ambient, ranging from the 1:4 mixture, t_{me}/°C = 16.8 to the 1:10 mixture, t_{me}/°C = 24.1 [14].

It should be noted in Table 2.1 that some of the hydrogen bond donor components of the deep eutectic solvents are themselves liquid at ambient temperatures and that some of the eutectic temperatures are very low indeed, down to more than

90 °C below ambient (25 °C), i.e. t_{me}/°C < −65, for example, those with ethylene glycol and lactic acid. In cases where no melting or glass transition points have been reported but physical properties or applications have been reported down to a certain temperature t/°C, this is denoted as <t in the appropriate column.

2.2 Deep Eutectic Solvents Based on Other -Onium Salts

Quaternary ammonium salts other than those of choline or its analogs have been used as hydrogen bond accepting ingredients (HBA) of deep eutectic solvents. However, non-quaternary alkylammonium salts have also been used for this purpose. Symmetrical tetraalkylammonium salts are not useful as room temperature ionic liquids (RTILs), of which deep eutectic solvents are a subcategory, because they have melting points much above ambient. However, when suitable hydrogen bond donating substances (HBD) are added, they do form low-melting eutectics. In many cases, the hydrogen bond donating ingredient employed was a liquid at ambient conditions, so that the solid salt hydrogen bond acceptor and the liquid hydrogen bond donor could be shaken together in an incubator shaker at 80 °C for 2 h, and the colorless homogeneous transparent liquid deep eutectic solvents was formed.

Ethylammonium chloride ($C_2H_5NH_3^+Cl^-$, CAS No. 557-66-4) forms a deep eutectic solvent at a 1:4 ratio with glycerol having a melting point (read from a figure) of t_{me}/°C = −58 [15]. With urea and trifluoroacetamide, it forms deep eutectic solvents at 2:3 ratios having melting points (read from a figure) of t_{me}/°C = 30 and 20, respectively [16]. Alkylammonium bromides form deep eutectic solvents at a 1:2 molar ratio with glycerol: ethylammonium bromide ($C_2H_5NH_3^+Br^-$, CAS No. 593-55-5) t_{me}/°C = −6, propylammonium bromide ($C_3H_7NH_3^+Br^-$, CAS No. 4905-83-3) t_{me}/°C = −4, and butylammonium bromide ($C_4H_9NH_3^+Br^-$, CAS No. 15567-09-6) t_{me}/°C = −10 [17]. Another example of a non-quaternary ammonium salt is *N*,*N*-diethylethanolammonium chloride ($(C_2H_5)_2(HOC_2H_4)NH^+Cl^-$, CAS No. 14426-20-1) that at 1:2 mol ratios with ethylene glycol forms a deep eutectic solvent with t_{me}/°C = −31.0 and with glycerol it forms one with t_{me}/°C = −1.3 [18]. This tertiary salt also forms deep eutectic solvents at a 1:1 ratio with malonic acid and with zinc nitrate hexahydrate as the hydrogen bond donating agents, but their freezing points were not specified [19].

Tetraethylammonium chloride ($(C_2H_5)_4NCl$, CAS No. 56-34-8) forms a deep eutectic solvent at a 1:4 molar ratio with levulinic acid, with t_{me}/°C < −60, i.e., a freezing point not detectable in the range $-60 \leq t_m/°C \leq 80$ [20]. Tetraethylammonium bromide ($(C_2H_5)_4NBr$, CAS No. 71-91-0) forms deep eutectic solvent at 1:4 molar ratios with ethylene glycol, t_{me}/°C = −24.4, and with triethylene glycol (3,6-dioxa-1,8-octanediol, $HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH$, CAS No. 112-27-6) and levulinic acid, all with t_{me}/°C < −60 [20]. With 1,2-dimethyl-urea ($O{=}C(NHCH_3)_2$, CAS No. 98-31-1) it forms a deep eutectic solvent at an unspecified molar ratio with t_{me}/°C in the range 20–25.

Tetrapropylammonium bromide ($(C_3H_7)_4NBr$, CAS No. 1941-30-6, TPAB) forms deep eutectic solvents with some polyols [20, 21]: ethylene glycol, glycerol, and triethylene glycol. Several ratios of the components were tested, and the lowest melting eutectics were obtained with 1:4 TPAB:ethylene glycol, t_{me}/°C = −23, 1:3 TPAB:triethylene glycol, t_{me}/°C = −19, 1:3 TPAB:glycerol, t_{me}/°C = −16 [21]. With levulinic acid TPAB and tetrapropylammonium chloride, ($(C_3H_7)_4NCl$, CAS No. 5810-42-4) form low transition temperature mixtures at 1:4 molar ratios t_m/°C < −60 [20].

Tetrabutylammonium chloride ($(C_4H_9)_4NCl$, CAS No. 75-57-0, TBAC) also forms deep eutectic solvents with ethylene glycol, glycerol, and triethylene glycol: 1:3 TBAC:ethylene glycol, t_m/°C = −31, 1:3 TBAC:triethylene glycol, t_m/°C = −13, and 1:4 TBAC:glycerol, t_m/°C = −43 [22]. With levulinic acid, TBAC forms a low transition temperature mixture at 1:4 molar ratios t_m/°C < −60 [20]. With urea at a 1:4 molar ratio, the melting point of the eutectic is just above ambient, 27 °C [23]. With levulinic acid, TBAC forms a low transition temperature mixture at 1:4 molar ratios t_m/°C < −60 [24], and with propanoic acid ($CH_3CH_2CO_2H$, CAS No. 79-09-4), phenylacetic acid ($C_6H_5CH_2CO_2H$, CAS No. 103-82-2), ethylene glycol, and polyethylene glycol (PEG400, CAS No. 25322-68-3) it forms deep eutectic solvents with t_m/°C < 15 [25].

Tetrabutylammonium bromide ($(C_4H_9)_4NBr$, CAS No. 1643-19-2, TBAB) forms deep eutectic solvents with carboxylic acids at a 1:1 molar ratio, whether mono- or dicarboxylic. The deep eutectic solvents with acetic acid have t_{me}/°C = −18.5, with propanoic acid t_{me}/°C = −19.1, with oxalic acid t_{me}/°C = −22.2, and with malonic acid t_{me}/°C = −18.0. With formic acid, a deep eutectic solvent is formed too, but its eutectic melting point was not determined [26]. TBAB forms deep eutectic solvents also with ethanolamine (2-aminoethanol, $H_2NC_2H_4OH$, CAS No. 141-43-5), t_{me}/°C = 0.4 [14], but with diethanolamine ($HN(C_2H_4OH)_2$, CAS No. 111-42-2) and triethanolamine ($N(C_2H_4OH)_3$, CAS No. 102-71-6) the melting points are much lower: −67.8 and −76.6 °C, respectively [27].

Tetrahexylammonium bromide ($(C_6H_{11})_4NBr$, CAS No, 4328-13-6) forms at molar ratios of 1:2 deep eutectic solvents with ethylene glycol and with glycerol, but their freezing points were not determined [28]. Benzyltrimethylammonium chloride ($C_6H_5CH_2N(CH_3)_3^+Cl^-$, CAS No. 53-93-9) forms with levulinic acid a low transition temperature mixture at 1:4 molar ratios t_m/°C < −60 [15]. It forms with *p*-toluene sulfonic acid ($CH_3C_6H_4SO_3H$, CAS No. 104-15-4) a deep eutectic solvent at 1:2 molar ratio, t_{me}/°C = −1, and with oxalic acid a deep eutectic solvent at 1:1 molar ratio, t_{me}/°C = 2, but with citric acid at a 1:1 molar ratio the freezing point is above ambient, 31 °C [29]. Benzyltrimethylammonium methanesulfonate ($C_6H_5CH_2N(CH_3)_3^+\ CH_3SO_3^-$) mixed at a 1:1 ratio with *p*-toluene sulfonic acid monohydrate ($CH_3C_6H_4SO_3H{\cdot}H_2O$, CAS No. 6192-52-5) forms a clear colorless deep eutectic solvent after mixing at 60 °C for 10 min, having a melting point (read from a figure) of t_{me}/°C = −5 [30]. Benzyltriprophylammonium chloride ($C_6H_5CH_2(C_3H_7)_3N^+Cl^-$, CAS No. 5197-87-5) forms low transition temperature mixtures with several hydrogen bond donating agents: ethylene glycol, glycerol, phenol, and lactic acid at 1:3 mol ratios. They have $t_m/°C < -90$, except that with lactic acid that has $t_{me}/°C = -56.3$ [31].

Tetramethyl-, tetraethyl-, and tetrabutylammonium chlorides form low transition temperature mixtures with lactic acid at a 1:2 ratio that do not crystallize on cooling but form glasses, with glass transition temperatures of −69, −71, and −66 °C, respectively [32]. Guanidine carbonate mixed with malic acid at a 2:1 ratio probably forms guanidinium malate when heated for prolonged periods at 70 °C, and then forms a deep eutectic solvent with ethylene glycol, useful for the capture of carbon dioxide [33].

Of the quaternary phosphonium salts, mainly methyltriphenylphosphonium bromide ($CH_3P(C_6H_5)_3Br$, CAS No. 1779-49-3) has been used to obtain deep eutectic solvents. With the polyols ethylene glycol $t_{me}/°C = -46$, with triethylene glycol $t_{me}/°C = -8$, and with glycerol $t_{me}/°C = -5$, all at the 1:3 ratio [3]. With trifluoroacetamide, it forms a deep eutectic solvent at an unspecified molar ratio with $t_{me}/°C = -69.3$, and with levulinic acid, it forms a deep eutectic solvent at a 1:4 molar ratio with $t_m/°C < -60$ [20]. Benzyltriphenylphosphonium chloride ($C_6H_5CH_2(C_6H_5)_3PCl$, CAS No. 1100-88-5) forms eutectics with glycerol (1:5) with $t_{me}/°C = 50.4$ and with ethylene glycol (1:3) with $t_{me}/°C = 47.9$, i.e., above ambient, so they are not proper deep eutectic solvents [34]. However, with glycerol a deep eutectic solvent is formed at a 1:16 HBA:HBD ratio, $t_{me}/°C = -22.0$ and the corresponding allyltriphenylphosphonium bromide ($CH_2{=}CHCH_2(C_6H_5)_3PBr$, CAS No. 1560-54-9) forms with glycerol a deep eutectic solvent at a 1:14 ratio with $t_{me}/°C = -23.8$ [35]. The symmetrical tetrabutylphosphonium bromide ($(C_4H_0)_4PBr$, CAS No. 3115-68-2) forms with levulinic acid at a 1:4 molar ratio a deep eutectic solvent with $t_m/°C < -60$ [20]. Such deep eutectic solvents based on the phosphonium salts have definite toxicity toward bacteria and possibly also larvae of aquatic organisms [36].

Deep eutectic solvents based on these -onium hydrogen bond acceptors (HBA) mixed with various hydrogen bond donors (HBD) at appropriate ratios are summarized in Table 2.2. In cases, where no melting or glass transition points have been reported but physical properties or applications have been reported down to a certain temperature $t/°C$, this is denoted as $<t$ in the appropriate column.

2.3 Unconventional Deep Eutectic Solvents

Prior to the advent of the choline chloride/urea deep eutectic solvent, stoichiometric mixtures of halide salts of organic cations and certain metal halides were found to have melting points below ambient, i.e., to be room temperature ionic liquids. Examples of such moieties are 1-ethyl-3-methylimidazolium chloride mixed at a 1:1 ratio with aluminum chloride forming the tetrachloroaluminate (CAS No. 80432-05-9) $t_m/°C = 8$ and mixed at a 1:2 ratio forming the heptachlorodialuminate (1-ethyl-3-methylimidazolium$^+Al_2Cl_7^-$), $t_m/°C = -98$ [37]. However,

Table 2.2 Deep eutectic solvents based on –onium salts as hydrogen bond acceptors, at ratios of HBA:HBD as noted, their molar masses M, and the melting point of the eutectics, t_{me}

HBA	HBD	Ratio HBA:HBD	M/kg mol^{-1}	t_{me}/°C	Ref.
$Me_4N^+Cl^-$	acetic acid	1:4	0.34980	< –20	[25]
	decanoic acid	2:9	0.88477	26[f]	[49]
	lactic acid	1:2	0.28975	–69[a]	[47]
$EtNH_3N^+Cl^-$	glycerol	1:4	0.44990	–58	[27]
	urea	2:3	0.34326	30	[28]
	trifluoroacetamide	2:3	0.50220	20	[28]
$EtNH_3N^+Br^-$	glycerol	1:2	0.31017	–6	[29]
	2-methoxyphenol[f]	1:3	0.33430	<20	[24]
$Et_2(HOEt)NH^+Cl^-$	ethylene glycol	1:2	0.27779	–31.0	[30]
	glycerol	1:2	0.33765	–1.3	[30]
	Triethylene glycol	1:4	0.60083	–16.6	[14]
$Et_3MeN^+Cl^-$	acetic acid	1:2	0.27178	< –20	[25]
$Et_4N^+Cl^-$	acetic acid	1:2	0.28589		[25]
	butanoic acid	1:2	0.33808	< 25	[50]
	hexanoic acid	1:2	0.45024	< 25	[50]
	octanoic acid	1:2	0.50632	< 25	[50]
	decanoic acid	2:3	0.51031	24[f]	[49]
	levulinic acid	1:4	0.63014	< –60	[36]
	lactic acid	1:2	0.34586	–71[a]	[47]
$Et_4N^+Br^-$	ethylene glycol	1:4	0.45844	–24	[36]
	glycerol	1:2	0.31017	–6	[29]
	triethylene glycol	1:4	1.06632	< –60	[36]
	levulinic acid	1:4	0.67460	< –60	[36]
	1,2-dimethylurea			20-25	[36]
$PrNH_3{}^+Br^-$	glycerol	1:2	0.32420	–4	[36]
$Pr_4N^+Cl^-$	acetic acid	1:6	0.58211	< –20	[25]
	butanoic acid	1:2	0.39803	< 25	[50]
	hexanoic acid	1:2	0.45411	< 25	[50]
	octanoic acid	1:2	0.51019	< 25	[50]
	decanoic acid	2:5	0.65216	15[f]	[49]
	dodecanoic acid	1:2	0.62235	25[f]	[49]
	levulinic acid	1:4	0.68624	< –60	[36]
	ethanolamine	1:4	0.46613	< –20	[25]
$Pr_4N^+Br^-$ (TPAB)	ethylene glycol	1:4	0.51454	–23	[36]
	glycerol	1:3	0.53653	–16	[36]
	triethylene glycol	1:3	0.90838	–19	[36]
	butanoic acid	1:2	0.28248	< 25	[50]
	hexanoic acid	1:2	0.33856	< 25	[50]
	levulinic acid	1:4	0.73070	< –60	[36]

(continued)

Table 2.2 (continued)

HBA	HBD	Ratio HBA:HBD	M/kg mol^{-1}	t_{me}/°C	Ref.
$BuNH_3^+Br^-$	glycerol	1:2	0.33823	–10	[29]
$DcNH_3^+ Br^-$ [e]	hexafluoroisopropanol	1:2	0.57431	–25	[51]
$DoNH_3^+ Br^-$ [e]	hexafluoroisopropanol	1:2	0.60235	–29	[51]
$TdNH_3^+ Br^-$ [e]	hexafluoroisopropanol	1:2	0.63039	–33	[51]
$Bu_4N^+Cl^-$ (TBAC)	urea	4:1	1.17174	27	[39]
	ethylene glycol	1:3	0.46413	–31	[38]
	glycerol	1:4	0.64628	–43	[38]
	triethylene glycol	1:3	0.92004	–13	[38]
	PEG 400	1:2	1.07792	<15	[42]
	acetic acid	1:2	0.39802	< –20	[25]
	propanoic acid	1:2	0.42608	<15	[40]
	butanoic acid	1:2	0.45414	< 25	[50]
	hexanoic, octanoic ac.	1:2		< 25	[52]
	decanoic acid	1:2	0.94144	–12.0	[53]
	dodecanoic acid	?		<25	[54]
	phenylacetic acid	1:2	0.55022	< 15	[40]
	levulinic acid	1:4	0.74236	< –60	[36]
	lactic acid	1:2	0.45808	–66[a]	[47]
	aspartic acid	1:9	1.47540	25.0	[55]
	glutamic acid	1:10	1.74880	28.8	[55]
	arginine	1:6	1.32270	25.0	[55]
	serine	1:8	1.11822	25.0	[56]
	threonine	9:1	2.62038	20.2	[56]
	methionine	11:1	3.20633	19	[56]
	α-tocopherol	1:4	2.00034	–50	[57]
$Bu_4N^+Br^-$ (TBAB)	formic acid	1:1	0.36839	LRT[c]	[41]
	acetic acid	1:1	0.38242	–19	[41]
	propanoic acid	1:1	0.39645	–19	[41]
	butanoic acid	1:2	0.49859	< 25	[50]
	hexanoic acid	1:2	0.55467	< 25	[50]
	octanoic acid	1:2	0.61075	< 25	[50]
	decanoic acid	1:2	0.66683	< 25	[50]
	oxalic acid	1:1	0.41240	–22	[41]
	malonic acid	1:1	0.42643	–18	[41]
	levulinic acid	1:4	0.78681	0.4	[58]
	ethylene glycol	1:2	0.44651	< 25	[59]
	PEG 200, 600	1:2		< 20	[60]
	sulfolane	1:7	1.16356	< 25	[61]
	ethanolamine	1:6	0.68885	–68	[42]
	diethanolamine	1:6	0.95321	–77	[42]

(continued)

Table 2.2 (continued)

HBA	HBD	Ratio HBA:HBD	M/kg mol^{-1}	t_{me}/°C	Ref.
	triethanolamine	1:3	0.76994	< –60	[42]
$Hx_4N^+Br^-$	ethylene glycol	1:2	0.55872	LRT^c	[43]
	glycerol	1:2	0.61876	LRT^c	[43]
$Hp_4N^+Cl^-$	decanoic acid	1:2	0.83623	–16.7	[62]
$MeOc_3N^+Cl^-$	alkanols, alkanediols	1:2		LRT^c	[63]
	decanoic acid	1:2	0.74870	9.0	[62]
$Oc_4N^+Cl^-$	decanoic acid	1:2	0.84688	2.0	[53]
	perfluorodecanoic acid	1:2	1.53050	LRT^c	[53]
$Oc_4N^+Br^-$	decanoic acid	1:2	0.89233	9.0	[62]
$BzMe_3N^+Cl^-$	acetic acid	1:2	0.65013	< –20	[25]
	levulinic acid	1:4	0.65013	< –60	[27]
	tosylic acid^b	1:2	0.53009	–1	[44]
	oxalic acid	1:1	0.27572	2	[44]
	glycerol	1:2	0.36987		[64]
$BzMe_3N^+MeSO_3^-$	tosylic acid^b	1:1	0.41764	–5	[45]
$BzEt_3N^+Cl^-$	acetic acid	1:2	0.34787	–20	[25]
	oxalic acid	1:1	0.31781	5	[65]
	citric acid	1:1	0.41989	26	[65]
	tosylic acid	1:2	0.57204	2	[65]
$BzPr_3N^+Cl^-$	ethylene glycol	1:3	0.45606	< –90	[66]
	glycerol	1:3	0.54612	< –90	[66]
	phenol	1:3	0.55218	< –90	[66]
	lactic acid	1:3	0.54009	–56	[66]
$Bu_4P^+Br^-$	levulinic acid	1:4	0.80377	< –60	[67]
	ethylene glycol	1:2	0.46347	< 25	[59]
$MePh_3P^+Br^-$	ethylene glycol	1:3	0.54343	–46	[3]
	glycerol	1:3	0.63349	–24	[3]
	1,2-propanediol	1:4	0.66162		[68]
	Triethylene glycol	1:4	0.95790	–18.2	[14]
	triethylene glycol	1:3	0.99934	–8	[3]
	acetic acid	1:4	0.59742	< –20	[25]
	levulinic acid	1:4	0.82166	< –60	[36]
	trifluoroacetamide	1:8	1.26154	–69	[36]
$EtPh_3P^+ I^-$	ethylene glycol	1:6	0.79067	< 30	[69]
	sulfolane	1:4	0.89893	< 30	[69]
$AllylPh_3P^+Br^-$	glycerol	1:14		–24	[70]
	diethylene glycol	1:4	0.80774	<20	[71]
	triethylene glycol	1:10		–19.5	[14]
$BenzylPh_3P^+Cl^-$	glycerol	1:5		50	[74]
		1:16		–22	[70]

(continued)

Table 2.2 (continued)

HBA	HBD	Ratio HBA:HBD	M/kg mol^{-1}	t_{me}/°C	Ref.
	ethylene glycol	1:3		48	[74]
	triethylene glycol	1:8		–19.5	[14]
$Me_3S^+TFSI^-$ [c]	formamide	1:1	0.40307	–20	[72]
	trifluoroacetamide	2:1	0.82910	LRT[c]	[72]
$C(NH_2)_3^+Cl^-$	ethanolamine	1:2	0.21769	< –20	[25]
$C(NH_2)_3^+$ malate	ethylene glycol			LRT[c]	[48]
$Emim^+Cl^-$ [e]	ethylene glycol	2:1, 1:1, 1:2		< 20	[72]
LidDec[d]	decanoic acid	1:1		–66[c]	[73]

[a] Glass transition temperature. [b] *p*-toluenesulfonic acid. [c] Liquid at room temperature. [d] LidDec = lidocaine decanoate. [e] Dc = decyl, Do = dodecyl, Td = tetradecyl. [e] 1-ethyl-3-methylimidazolium chloride. [f] Read from a small figure

these mixtures constitute a single molten salt, hence are not proper deep eutectic solvents, for which the two initial components retain their separate identities.

Proper deep eutectic solvents are formed when the metal halide is the hydrogen bond acceptor and a suitable hydrogen bond donor is added: a mixture of zinc chloride and urea at a 2:7 mol ratio has t_{me}/°C = 9, with acetamide ($CH_3C(O)NH_2$, CAS No. 60-35-5) at a 1:4 mol ratio it has t_{me}/°C = −16. In the eutectic mixtures, zinc is present in the cationic species, e.g., $[ZnCl(urea)]^+$, as shown by mass spectrometry. With ethylene glycol (1,2-ethanediol) at a 1:4 mol ratio, zinc chloride has t_{me}/°C = −30, and with 1,6-hexanediol at a 1:4 mol ratio it forms a deep eutectic solvent t_{me}/°C = −23 [38, 39]. Similarly, 2-chloroethyl trimethylammonium chloride ($ClC_2H_4N(CH_3)_3^+Cl^-$, Cas No. 999-81-5) produces with zinc chloride at a 1:2 molar ratio a deep eutectic solvent melting at 23 °C [40], but this may be a chlorozincate room temperature ionic liquid rather than a deep eutectic solvent in which each ingredient retains its identity. Zinc nitrate hexahydrate with urea at a mole ratio of 2:1 forms a deep eutectic solvent with a melting point of 9 °C that remains stable (does not lose water) up to 50 °C [41]. Choline chloride forms a deep eutectic solvent with calcium chloride hexahydrate at several molar ratios, the lowest melting of which is at a 1:2 molar ratio, t_m/°C = 2.70 [42]. Other metal halides also form with asymmetrical quaternary ammonium salts low-melting mixtures having melting points below 25 °C [43]. There is no certainty, however, that in all these cases proper deep eutectic solvents are formed, i.e., mixtures in which the components retain their identities, rather than ionic liquids that are single components, made up from a cation and an anion. Potassium carbonate forms low transition temperature mixtures with glycerol at molar rations 1:4–1:6 that are liquid at 10 °C, but do not crystallize on cooling and have glass transition temperatures (that for the 1:4 ratio of −38 °C) [44]. Potassium and ammonium thiocyanates form with amides low-melting eutectics that can be used as solvents for the absorption of sulfur dioxide [45]. Several deep eutectic solvents have been prepared, based on lithium bis[trifluoromethylsulfonyl]imide as the hydrogen bond acceptor component and amides (urea [46], acetamide [47], *N*-methylacetamide [48]) as the hydrogen bond donor components. To this category could be added the deep eutectic solvents formed by trimethylsulfonium bis[trifluoromethylsulfonyl]imide as the hydrogen bond acceptor and formamide or trifluoroacetamide as the hydrogen bond donor component, although trimethylsulfonium is not a metal cation [49]. Table 2.3 summarizes the compositions and melting points of the low-melting mixtures formed from metal salts (or their hydrates) and organic substances. In cases, where no melting or glass transition points have been reported but physical properties or applications have been reported down to a certain temperature t/°C, this is denoted as $<t$ in the appropriate column.

Certain amino acids have served as the hydrogen bond acceptor component of deep eutectic solvents with several hydrogen bond donor component, such as urea, 1,2-ethanediol, and carboxylic acids. In many cases, glass formation was observed as the temperature was decreased, but no freezing to a crystalline solid took place [50, 51]. Exceptions to this general trend are the 1:1 mixture of *l*-proline (pyrrolidine-2-carboxylic acid, CAS No. 147-85-3) and oxalic acid (HCO_2CO_2H, CAS No. 144-62-7), t_{me}/°C = −14.5 [52] and trimethylglycine ($(CH_3)_3NCH_2CO_2H$, CAS No. 107-43-7, betaine) and mandelic acid ($C_6H_5CH(OH)CO_2H$, CAS No. 90-64-2) t_{me}/°C = 13 [53]. Trimethylglycine (betaine) at 1:2 ratios forms with glycolic acid ($HOCH_2CO_2H$, CAS No. 79-14-2) a deep eutectic solvent t_{me}/°C = −36, with phenylacetic acid a deep eutectic solvent t_{me}/°C = −7, and with 2-furoic acid (furan-2-carboxylic acid, CAS No. 88-14-2) a deep eutectic solvent with t_{me}/°C = 11 [53]. When the hydrogen bond donor component is a carboxylic acid, the zwitterionic amino acid is taken to be protonated, so that an ionic deep eutectic solvent is produced.

On the other hand, amino acids have also been suggested as the hydrogen bond donor component of deep eutectic solvents, with tetrabutylammonium chloride as the hydrogen bond acceptor component. In such cases, rather large ratios of the salt to the hydrogen bond donating agent yield the low-melting compositions, but at near ambient temperatures or somewhat above them. The deep eutectic solvent formed with aspartic acid at 9:1 HBA:HBD has t_m/°C = 25.1, that with glutamic acid at 10:1 ratio has t_m/°C = 28.9, that with arginine at 6:1 ratio has t_m/°C = 25.1 [54], that with serine at 8:1 ratio has t_m/°C = 24.9, that with threonine at 9:1 ratio has t_m/°C = 20.2, and that with methionine at 11:1 ratio has t_m/°C = 19.1 [55].

Water could well be a hydrogen bond donor ingredient to form deep eutectic solvents with suitable hydrogen bond acceptor components, such as certain salts and ionic liquids. Alkyl-(2-hydroxyethyl)-dimethylammonium bromide ionic liquids, where alkyl = C_nH_{2n+1} with n = 2, 3, 4 and 6, form with water at a 1:2 mol ratio deep eutectic solvents [56]. For n = 2 (ethyl) [57] t_{me} = −25.1 °C and for the other n values t_{me} is somewhat higher, up to −13 °C. It is to be noted that in the case n = 1, i.e., of alkyl being methyl, choline bromide, water has not been mentioned as forming a deep eutectic solvent with this salt. Water forms a deep eutectic solvent also with ethyl-(2-hydroxyethyl)-dimethylammonium tetrafluoroborate at a 1:3 mol ratio, t_{me} = −27.2 °C [57]. Thus, although stronger hydrogen bond acceptor anions such as chloride, acetate, and fluoride are required for the conventional deep eutectic solvent formation with amides, carboxylic acids, and

Table 2.3 Deep eutectic solvents formed between metal salts and organic substances and the melting point of the eutectics, t_{me}

Metal salt	Organic substance	Molar ratio	t_{me}/°C	Ref.
$LiClO_4$	Acetamide	1:4	n.a.	[89]
	Propionamide	1:4	n.a.	[89]
$LiNO_3$	N-methylacetamide	1:2	–75	[90]
$LiPF_6$	N-methylacetamide	1:5	–52	[90]
LiTFSI[a]	urea	1:3.6	–37.6	[86]
	acetamide	1:4	–67	[87]
	N-methylacetamide	1:2	–72	[90]
K_2CO_3	ethylene glycol	1:10	-122[b]	[150]
	glycerol	1:4 – 1:6	< 10	[83]
		1:10	-91[b]	[150]
KSCN	acetamide	1:3	5	[85]
	caprolactam	1:3	0	[85]
NH_4SCN	acetamide	1:3	5	[85]
	caprolactam	1:3	–10	[85]
	urea	2:3	24	[85]
$MgCl_2{\cdot}6H_2O$	choline chloride	1:1	16	[91]
$CaCl_2{\cdot}6H_2O$	choline chloride	1:2	2.7	[66]
$ZnCl_2$	urea	2:7	9	[78]
	acetamide	1:4	–16	[78]
	1,2-ethanediol	1:4	–30	[78]
	1,6-hexanediol	1:4	–23	[78]
	chloroethyltrimethylammonium$^+$Cl$^-$	1:2	23	[44]
	choline chloride	2:1	23-25	[82]
	bromopropyltrimethylammonium$^+$Br$^-$	2:1	22-24	[82]
$Zn(NO_3)_2{\cdot}6H_2O$	choline chloride	1:1	<25	[31]
	diethylethanolammonium$^+$Cl$^-$	1:1	<25	[92]
$SnCl_2$	benzyldimethylethanolammonium$^+$Cl$^-$	2:1	17	[82]
	2-acetyloxytrimethylammonium chloride	2:1	20	[74]
$AlCl_3$	urea	1:1	<25	[78]
	acetamide	1:1	–63[c]	[78]
$FeCl_3$	benzyldimethylethanolammonium$^+$Cl$^-$	2:1	21	[82]
	tetrabutylphosphonium bromide	1:2	15.7	[70]
$CrCl_3{\cdot}6H_2O$	urea	2:1	9	[81]
$FeCl_3$	benzyldimethylethanolammonium$^+$Cl$^-$	2:1	21	[82]
	tetrabutylphosphonium bromide	1:2	15.7	[70]

[a] lithium bis[trifluoromethylsulfonyl]imide. [b] Glass transition temperature

polyols, for water as the hydrogen bond donor even mild hydrogen bond accepting anions, such as bromide and tetrafluoroborate, suffice for deep eutectic solvent formation.

Water features also as the hydrogen bond donor component with more conventional ionic liquids, The deep eutectic solvent formed with 1-butyl-3-methylimidazolium *p*-toluenesulfonate has t_{me}/°C = −36 at the water mole fraction $x_W = 0.70$ (read from a figure) [58]. *N*-hexyl-3-methylpyridinium *p*-toluenesulfonate forms with water a deep eutectic solvent that has t_{me}/°C = −10.0 at $x_W = 0.879$ [59]. The deep eutectic solvent formed between water and 1-butyl-3-methylpyridinium dicyanamide has t_{me}/°C = −28 at $x_W = 0.76$ (read from a figure) [60, 61]. The deep eutectic solvent formed between water with 1-butyl-1-methylpiperidinium thiocyanate has t_{me}/°C = −56 at $x_W = 0.66$ [62] and that with 1-butyl-1-methylpyrrolidinium thiocyanate has t_{me}/°C = −92 at $x_W = 0.69$ [63]. These values were read from a figure with non-random two-liquid (NRTL)-modeled lines leading to the eutectic point, whereas the experimental points themselves do not necessarily lead to them. Complete solid–liquid phase diagrams (reaching from the pure components to the eutectic) were reported in figures also for the deep eutectic solvents formed between water with 1-butyl-1-methylpyrrolidinium dicyanamide, t_{me}/°C = −31 at $x_W = 0.77$, with its trifluoromethylsulfonate, t_{me}/°C = −30 at $x_W = 0.60$, and with its tricyanomethanide, t_{me}/°C = 13 at $x_W = 0.42$ [64]. Incomplete diagrams were shown there also for mixtures of water with other ionic liquids, but no eutectic points could be deduced from them. Complete phase diagrams, but where NRTL-modeled lines lead to the eutectic point rather than the experimental points themselves, were reported for water with 1-alkyl-1-methylmorpholinium bromide, where alkyl = C_nH_{2n+1} with $n = 3$, 4, and 5 [65]. The eutectic points (read from figures) have t_{me}/°C = −33 at $x_W = 0.82$ for $n = 3$, t_{me}/°C = −42 at $x_W = 0.82$ for $n = 4$, and t_{me}/°C = −73 at $x_W = 0.69$ for $n = 5$. For the corresponding water and 1-pentyl-1-methylpiperidinium bromide system, t_{me}/°C = −28 at $x_W = 0.75$ was derived from the NRTL-modeled lines [65].

Table 2.4 summarizes the deep eutectic solvents formed between water and organic salts and ionic liquids.

With monohydric alkanols, on the other hand, no real deep eutectic solvents are formed with room temperature ionic liquids, the observed eutectic temperatures being only 1–6 °C lower than the freezing points of the alkanols themselves. This was reported for 1-butyl-3-methylimidazolium *p*-toluenesulfonate with 1-octanol and with 1-decanol and presumably holds also with ethanol, 1-butanol, and 1-hexanol, although no complete phase diagrams were shown for these three alkanols [58]. The same is the case for 1-hexyl-3-methylpyridinium *p*-toluenesulfonate for these five alkanols [59] and for 1-butyl-1-methylpiperidinium thiocyanate with 1-alkanols $C_nH_{2n+1}OH$, $n = 8$, 9, 10, and 12 [62].

It is interesting to note that fairly deep eutectic liquids are formed between benzene, devoid of hydrogen bond donating properties, and two ionic liquids: t_{me}/°C = −27 at benzene mole fractions $x_B = 0.65$ for 1-hexyl-3-methylpyrrolidinium thiocyanate and t_m/°C = –13 at $x_B = 0.55$ for 1-butyl-1-methylpiperidinium thiocyanate (where

Table 2.4 Deep eutectic solvents formed between water as the hydrogen bond donor component and organic salts and ionic liquids as hydrogen bond acceptor components and the melting point of the eutectics, t_{me}

HBA Cation	HBA Anion	x_W	t_{me}/°C	Ref.
ethyl-(2-hydroxyethyl)-dimethylammonium	bromide	0.642	–25.1	[98]
	BF_4^-	0.737	–27.2	[98]
propyl-(2-hydroxyethyl)-dimethylammonium	bromide	0.65	–31	[97]
butyl-(2-hydroxyethyl)-dimethylammonium	bromide	~0.65	–22	[97]
hexyl-(2-hydroxyethyl)-dimethylammonium	bromide	~0.65	–13	[97]
1-butyl-3-methylimidazolium	tosylate	0.70	–36	[99]
1-butyl-3-methylpyridinium	$N(CN)_2^-$	0.76	–28	[101]
1-hexyl-3-methylpyridinium	tosylate	0.879	–10.0	[100]
1-butyl-1-methylpiperidinium	thiocyanate	0.66	–56	[103]
1-butyl-1-methylpyrrolidinium	thiocyanate	0.69	–92	[104]
	$N(CN)_2^-$	0.71	–37	[105]
	$N(CN)_2^-$	0.75	–40	[107]
	$CF_3SO_3^-$	0.60	–30	[105]
	$CF_3SO_3^-$	0.60	–28.5	[107]
	$C(CN)_3^-$	0.42	13	[105]
	$C(CN)_3^-$	0.52	–31	[107]
	$B(CN)_4^-$	0.43	6	[107]
1-propyl-1-methylmorpholinium	bromide	0.82	–0.33	[106]
1-butyl-1-methylmorpholinium	bromide	0.82	–42	[106]
1-pentyl-1-methylmorpholinium	bromide	0.69	–73	[106]
1-pentyl-1-methylpiperidinium	bromide	0.75	–28	[106]

t_{me}/°C = 5.5 for benzene itself and 22.2 and 31.1 for the two ionic liquids, respectively) [66]. Benzene (subscript $_B$) also forms with N-butylquinolinium bis (trifluoromethylsulphonyl)imide (t_m/°C = 56.4), a deep eutectic having t_{me}/°C = −8.3 at $x_B = 0.746$ [67] and with *N*-butylpyridinium bis[(trifluoromethyl)sulphonyl]imide (t_m/°C = 18.2), a deep eutectic having t_{me}/°C = –22.9 at $x_B = 0.642$ [68].

A further group of binary mixtures that nominally can be termed 'deep eutectic solvents', but are not generally recognized as such, are mixtures of ice with certain salt hydrates or mixtures of two salt hydrates. Some salt hydrates that melt congruently, i.e., crystallize unchanged on cooling their melts, yield deep eutectic solvents with water. They feature such properties that commonly used or proposed deep eutectic solvents should have: they are definitely nonflammable, they are nontoxic (heavy metal salts, such as $Cd(NO_3)_2{\cdot}4H_2O$, are avoided), they are inexpensive (expensive metal salts, such as $CsF{\cdot}H_2O$, are avoided), and are readily reconstituted after use. Several lithium and magnesium salt hydrates, among a variety of other salts, are prone to yield deep eutectic solvents with ice. As for many other deep eutectic solvents, one of the components (water) is liquid at ambient conditions and the eutectic temperatures may reach very low values. A large body of information is available in the compilations by Linke and Seidel [69, 70] and by Kirgintsev et al. [71], generally in the form of solid/liquid equilibrium at certain temperatures at compositions given as w = g anhydrous salt per 100 g saturated aqueous solution. The mole fraction of the n-hydrate (that with n molecules of water per formula unit of the anhydrous salt) is calculated, using the molar mass of the anhydrous salt, M/g mol^{-1}, and that of water, 18.015 g mol^{-1}, as

$$x(\text{salt} \cdot n\text{H}_2\text{O}) = (1+n)(w/M)/[(w/M)+(100-w)/18.015] \tag{2.1}$$

The molar ratios of the components are generally not ratios of integers, unlike most of the deep eutectic solvents with choline chloride, its analogs, and other -onium salts as the hydrogen bond acceptor components. The eutectic distances, Δt_{me}/°C, are not as large as those for, say, choline chloride with urea, 178. Nevertheless, for some salt hydrates, they reach as much as Δt_{m}/°C = 137 for ice/$\text{Mg(ClO}_4)_2{\cdot}6\text{H}_2\text{O}$ and 113 for ice/$\text{KOH}{\cdot}\text{H}_2\text{O}$ [72]. If related to the unhydrated salts the eutectic distances, $\Delta t_{\text{m},}$ are much more appreciable.

Table 2.5 summarizes the formation of deep eutectic solvents between water and salt hydrates.

Mixtures of magnesium chloride hexahydrate ($\text{MgCl}_2{\cdot}6\text{H}_2\text{O}$) with nickel chloride hexahydrate ($\text{NiCl}_2{\cdot}6\text{H}_2\text{O}$) [73] can also be called deep eutectic solvents, see Chap. 1, Fig. 1.3. The melting points of the components are t_{m}/°C = 112 for $\text{MgCl}_2{\cdot}6\text{H}_2\text{O}$ and 30 for $\text{NiCl}_2{\cdot}6\text{H}_2\text{O}$, and the eutectic at the 1:1 composition has a melting point t_{m}/°C = 4 and the distance Δt_{m}/°C = 67 is quite appreciable. Ammonium nitrate forms with manganese and zinc nitrate hexahydrates deep eutectic solvents with large melting point distances of the eutectics [74]. With $\text{Mn(NO}_3)_2 6\text{H}_2\text{O}$ (t_{m}/°C = 25.8) at the ammonium nitrate mole fraction of 0.450, the eutectic has t_{me}/°C = 4.6 and Δt_{me}/°C = 100.0 (given t_{m}/°C = 169 for NH_4NO_3 [75]) and for $\text{Zn(NO}_3)_2 6\text{H}_2\text{O}$ (t_{m}/°C = 36.4) at the ammonium nitrate mole fraction of 0.447 the eutectic has t_{me}/°C = 12.7 and Δt_{me}/°C = 109.7.

Mixtures of the incongruently melting calcium chloride hexahydrate with a few other salt hydrates also form deep eutectic solvents [76]. With 0.35 mol fraction calcium bromide hexahydrate t_{me}/°C = 14, with 0.25 mol fraction calcium nitrate tetrahydrate t_{m}/°C = 13 and with 0.17 mol fraction magnesium nitrate hexahydrate t_{m}/°C = 9 (in the latter two cases these are not necessarily the eutectic points) [73].

The deep eutectic solvents described in this and the previous sections are all more or less hydrophilic, they absorb water from the atmosphere and are soluble in water. For certain uses, hydrophobic (deep eutectic) solvents would be useful and such have been proposed in recent years. Certain tetraalkylammonium halides form hydrophobic deep eutectic solvents with decanoic acid ($\text{C}_9\text{H}_{17}\text{CO}_2\text{H}$, CAS No. 334-48-5) at 1:2 molar ratios: tetrabutylammonium chloride t_{me}/°C = −12.0, tetraheptylammonium chloride ($(\text{C}_7\text{H}_{13})_4\text{NCl}$, CAS No. 10247-90-2) t_{me}/°C = −16.7, tetraoctylammonium chloride ($(\text{C}_8\text{H}_{15})_4\text{NCl}$, CAS No. 13125-07-3) t_{me}/°C = 2.0, and bromide ($(\text{C}_8\text{H}_{15})_4\text{NBr}$, CAS No. 14866-33-2) t_{me}/°C = 9.0, and methyltricotylammonium

Table 2.5 Deep eutectic solvents formed between congruently melting salt hydrates with ice as the hydrogen bond donor component, the melting points of the salt hydrates, t_{msh}, of the eutectics, t_{me}, the eutectic composition (mole fraction of the salt hydrate, $x_{eutectic}$, and the eutectic distance, Δt_{me} [114]

Salt hydrate	t_{msh}/°C of salt	t_{me}/°C of eutectic	$x_{eutectic}$	Δt_{me}/°C
$Al(NO_3)_3•9H_2O$	71.0	–27.2	0.36	53
$CaBr_2•6H_2O$	38.2	–22.2	0.59	45
$Ca(NO_3)_2•4H_2O$	47.7	–28.7	0.38	45
$Ca(ClO_4)_2•6H_2O$	45.5	–74.6	0.39	90
$Co(NO_3)_2•6H_2O$	55.8	–26.2	0.42	49
$FeCl_3•6H_2O$	36.8	–55.0	0.36	68
$KF•4H_2O$	18.5	–40.2	0.39	47
$KOH•H_2O$	126.8	–65.2	0.38	113
$K_2HPO_4•4H_2O$	13.0	–13.5	0.40	19.4
$LiCH_3CO_2•2H_2O$	57.8	–16.1	0.17	26
$LiNO_3•3H_2O$	29.5	–22.9	0.31	32.1
$LiClO_3•3H_2O$	8.1	–40.2	0.32	43
$LiClO_4•3H_2O$	95.1	–18.2	0.21	38
$LiI•2H_2O$	75.0	–69.0	0.45	100
$Mg(CH_3CO_2)_2•4H_2O$	57.2	–29.2	0.31	50
$MgBr_2.6H_2O$	164.4	–42.7	0.38	105
$MgCl_2.6H_2O$	116.2	–33.6	0.34	73
$Mg(NO_3)_2.6H_2O$	89.5	–4.1	0.40	40
$Mg(ClO_4)_2•6H_2O$	154.8	–68.6	0.44	137
$MnCl_2.4H_2O$	57.8	–25.6	0.44	51
$Mn(NO_3)_2.6H_2O$	25.8	–36.2	0.45	48
$NaCH_3CO_2•3H_2O$	57.8	–18.2	0.35	38
$NaOH•H_2O$	65.1	–28.2	0.19	41
$NiCl_2.6H_2O$	30.2	–45.3	0.39	57
$Ni(NO_3)_2•6H_2O$	56.7	–34.1	0.41	57
$Zn(NO_3)_2•6H_2O$	36.4	–32.0	0.41	46

chloride ($CH_3(C_8H_{15})_3NCl$, CAS No. 10247-90-2) t_{me}/°C = −0.1, and bromide ($CH_3(C_8H_{15})_3NBr$, CAS No. 35675-80-0) t_{me}/°C = 9.0 [77]. These deep eutectic solvents being hydrophobic, i.e., immiscible with water, can be used for solvent extraction purposes.

Lidocaine (2,6-dimethylcyclohexyl-2-diethylaminoglycylamide, CAS No. 137-58-6) forms with decanoic acid lidocaine decanoate and with further 1, 2, or 3 molecules of decanoic acid this salt forms hydrophobic deep eutectic solvents with unspecified freezing temperatures [78]. These hydrophobic deep eutectic solvents can be used to form a biphasic system with water and to extract various solutes from aqueous media. On the other hand, deep eutectic solvents prepared from tetrabutylammonium chloride and hexanoic, octanoic, decanoic, and dodecanoic acids, although hydrophobic, are not sufficiently stable in water to serve for extraction in biphasic systems [79].

2.4 Nonionic Deep Eutectic Solvents

The definition of the deep eutectic solvents presented at the beginning of this chapter, namely "Deep eutectic solvents (DESs) are binary mixtures of definite composition of two components, one of which being ionic, that yield a liquid phase at ambient conditions" precludes the inclusion of nonionic deep eutectic solvents in this exposition. However, many such moieties have been described in the literature and deserve consideration here, perhaps under the changed subtitle: low transition temperature mixtures (LTTMs). They are characterized by low iconicity, hence by low electrical conductivity, but such solvents appear to be compatible with enzymatic reactions. Most of them consist of naturally originating components and may be classified as NADES. They are of several types: polyalcohols (including sugars) with carboxylic acids, zwitterionic amino acids with non-protonating hydrogen bond donating components, and mixtures of amides. For only very few of the nonionic mixtures described in the literature as deep eutectic solvents have the actual freezing points of the eutectics been reported, although in some cases the glass transition temperatures have been, but in any case, these mixtures are liquid near ambient temperatures. In addition to binary mixtures, some ternary mixtures have also been dealt with in this context and are mentioned here.

The sugars glucose, fructose, and sucrose in 1:1 combination with malic, maleic, and citric acids feature in [1, 80, 81] and in [1] also other sugars and sugar alcohols: xylitol, adonitol (ribitol), and sorbitol are considered. The 1:1 mixtures of citric acid with glucose and adonitol are dealt with in [82]. The 1:1 mixture of fructose with malic acid is used in [83] for extraction purpose and with citric and tartaric acids in [84] as tools for bioavailability. The latter two acids in 1:1 combination with glucose are considered and the glass transition points, 9.8 and −18.3 °C are reported in [85] whereas the polarities of the mixtures are reported in [86]. Menthol (racemic 5-methyl-2-(propan-2-yl)cyclohexan-1-ol, CAS No. 89-78-1) produces eutectic solvents with carboxylic acids at various molar ratios: 1:1 with acetic acid, 1:2 with pyruvic and lactic acids, and 2:1 with lauric (dodecanoic) acid. Their glass transition points are −7.8, −58.8 and −6.8, −61.1, and 7.1 and 13.8 °C, respectively, with two such points detected by thermal analysis for two of the mixtures. Other physical properties, the density and viscosity, and their temperature dependences are also reported in [87]. Menthol forms deep eutectic solvents with several other carboxylic acids (benzoic acid, phenylacetic acid, and ibuprophen CAS No. 15687-27-1) at 3:1 molar ratios [88].

Two zwitterionic amino acids: proline and betaine (trimethylglycine) have received considerable attention as components of deep eutectic solvent mixtures. When mixed with stoichiometric amounts of carboxylic acids, they form ionic liquids that are outside the scope of this section, but with excess acid or with nonacidic hydrogen bond donors they may produce nonionic deep eutectic solvents. Binary mixtures of proline and of betaine with sugars (glucose, mannose, maltose, sucrose) and with sugar alcohols (sorbitol, xylitol) produce nonionic natural deep eutectic solvents [1, 85, 89], as they do with glycerol, and betaine does so with ethylene glycol [47]. Mixtures of betaine and/or carnitine (3-hydroxy-4-trimethyl-aminobutyric acid, CAS No. 541-15-1) with ethylene glycol [89] and with phenol [90] form deep eutectic mixtures that do not freeze down to −60 and −80 °C, respectively. The 2:5 proline mixture with glycerol forms a deep eutectic solvent [91] as does betaine with 1:1, 1:2, and 1:3 glycerol [92]. Non-hydroxylic hydrogen bond donors, namely amides, have also been used with the zwitterionic amino acids to produce nonionic deep eutectic solvents. Thus, 1:1 mixtures of betaine with 1-methylurea and of proline with acetamide yield such solvents [91]. The glass transition temperatures of mixtures of betaine with urea at molar ratios of 1:1–2:5 are below −40 °C [93]. The 1:2 mixture of betaine with urea has been used as a deep eutectic solvent in combination with an aqueous salt solution for the biphasic extraction of proteins [94]. Twelve sulfobetaines (e.g., $(CH_3)_2C_4H_9NC_3H_6SO_3$) form with camphorsulfonic acid (CAS No. 35963-20-3) deep eutectic solvents with low iconicity [95].

Nonionic deep eutectic solvents are also produced by mixtures of two amides. Caprolactam forms such solvents at a 3:1 ratio with urea and at a 1:1 ratio with acetamide, whereas 1:2 urea/acetamide mixtures also form such eutectics, with melting points of 30, 18, and 48 °C and very small electric conductivities [96]. These three mixtures are also mentioned in [97]. The latter mixture has a glass transition point of −67 °C, but its dynamic properties were studied only at >55 °C [98].

Ternary nonionic deep eutectic solvents have also received attention, mainly based on zwitterionic amino acids. The mixture proline/glycerol/sucrose at a 4:9:1 molar ratio is a sustainable efficient extraction medium [99]. The mixtures comprised of betaine/glycerol/glucose at a 4:20:1 molar ratio [100] and betaine/ethylene glycol/water at a molar ratio of 1:2:1 [101] have also been found useful for the extraction of natural products. Solvents consisting of betaine with urea, methylurea, glucose, sorbitol, glycerol, or ethylene glycol and with water as the third component form with an aqueous salt solution a biphasic system useful for the extraction of proteins [102]. Mixtures of 2:3 acetamide and urea melt too high for being useful, but 1 mass of this mixture with 2 masses of PEG 300 (polyethylene glycol with a mean molar mass of 300 g mol^{-1}) is a eutectic melting at 32 °C, i.e., forming a nonionic eutectic solvent [103].

The nonionic deep eutectic solvents dealt with in this book are summarized in Table 2.6. In cases, where no melting or glass transition points have been reported but physical properties or applications have been reported down to a certain temperature *t*/°C, this is denoted as <*t* in the appropriate column.

Table 2.6 Some non-ionic low transition temperature solvents for which glass transition temperatures, t_g, have been reported

HBA	HBD	Ratio HBA:HBD	t_g/°C	Ref.
0.6 acetamide + 0.4 urea	PEG400	13:1	32[a]	[143]
proline	oxalic acid	1:1	–14.5	[144]
	glycolic acid	1:1	–30.7	[145]
	lactic acid	2:1	–36.7	[144]
	malic acid	1:3	–44.4	[144]
	malic acid		–8.2	[145]
betaine	urea	1:2	–42.5	[134]
	ethylene glycol	1:4	< –60	[132]
	phenol	1:3	< –80	[131]
	2-furoic acid	1:2	11[a]	[96]
	phenylacetic acid	1:2	–7[a]	[96]
	oxalic acid	1:1	–17.2	[144]
	glycolic acid	1:2	–36[a]	[96]
	lactic acid	2:1	–46.9	[144]
	mandelic acid	1:1	13[a]	[96]
	malic acid	1:3	–20.0	[144]
	levulinic acid	1:2	< 30	[146]
dimethyldodecyl-N-oxide	phenylacetic acid	1:1	–34	[68]
dimethyloctadecyl-N-oxide	phenylacetic acid	1:1	20	[68]
N-methylmorpholine-N-oxide	phenylacetic acid	1:1	–21	[68]
N-dodecylmorpholine-N-oxide	phenylacetic acid	1:1	–27	[68]
carnitine	ethylene glycol	1:4	< –60	[132]
	phenol	1:3	< –80	[131]
menthol	acetic acid	1:1	–7.8	[131]
	$C_nH_{2n+1}COOH$ (n =3,5,7,9)	1:1	< 25	[52]
	octanoic acid	?	<25	[54]
	dodecanoic acid	2:1	7.1	[128]
	lactic acid	1:2	–61.1	[128]
	levulinic acid	1:1	< 25	[52]
	pyruvic acid	1:1	–58.8	[128]
glucose	citric acid	1:1	9.8	[147]
	tartaric acid	1:1	–18.3	[147]
sucrose	citric acid	1:1	–14.0	[147]
$BuMe_2N(C_2H_6)SO_3$	camphorsulfonic acid	1:2	13[a]	[136]
$Bu_3N(C_2H_6)SO_3$	camphorsulfonic acid	1:2	9[a]	[136]
$DoMe_2\ N(C_2H_6)SO_3$	camphorsulfonic acid	2:3	–1[a]	[136]
Octanoic acid	Dodecanoic acid	3:1	9.0[a]	[148]
Nonanoic acid	Dodecanoic acid	3:1	9.0[a]	[148]
Decanoic acid	Dodecanoic acid	2:1	18.0[a]	[148]

[a] Melting temperature, t_m/°C

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Chapter 3
Properties of Deep Eutectic Solvents

The practical application of deep eutectic solvents naturally depends on their properties, including their phase diagrams, thermodynamic properties, volumetric properties, transport properties, electrochemical properties, optical and spectroscopic properties, their chemical properties (polarity) and structures, and their toxicity and ecological behavior. These are dealt with in turn in this chapter.

3.1 Solid–Liquid Phase Diagrams

In view of the deep eutectic solvents being eutectics, it may be surprising that rather few complete phase diagrams of the systems leading to these eutectics have been published. In some cases, the eutectic is deep and sharp in the sense that the composition range of its occurrence is very narrow, as illustrated in Chap. 1 in Fig. 1.2 for the α-naphthol with *o*-nitroaniline mixtures (this system is not a deep eutectic solvent, because the eutectic temperature is above ambient). On the other hand, there are systems for which the composition near the eutectic is rather extensive (a shallow diagram). This has the advantage that the composition of the binary mixture needs not to be very precisely defined for functioning as a deep eutectic solvent.

In many cases, no full solid–liquid phase diagrams have been reported but only the freezing points of certain ratios of the hydrogen bond accepting salt component (HBA) and hydrogen bond donating component (HBD) or mole fractions of the latter. In other cases, the freezing points at compositions rich in the HBA component and those rich in the HBD component have been reported (in some cases in tables, in others in figures), but data near the eutectic point are missing. In such cases, instead, the existing data have been modeled, generally by means of the nonrandom two-liquid (NRTL) method on both sides of the eutectic, and the meeting point of the modeled curves is deemed to represent the eutectic composition and temperature.

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Choline chloride is the basis of many deep eutectic solvents, but its fusion properties cannot be measured directly because it decomposes at elevated temperatures. These properties had, therefore, to be estimated indirectly, from its solubility in mixtures involving also a second, a hydrogen bond donating, component. The resulting melting point was 597 ± 7 K and the molar enthalpy of fusion was 4.3 ± 0.6 kJ mol^{-1} [1]

The phase diagram of the primary deep eutectic solvents, 1:2 choline chloride and urea ("Reline") [2] is shown in Fig. 3.1. Note that there are no data for $x_{urea} < 0.35$ (except for pure choline chloride) nor for $x_{urea} > 0.85$ (except for pure urea); hence, the curves are guides to the eye and have no further significance. The mixtures being hygroscopic, they absorb water from the atmosphere, but the sample studied under the measurement conditions were found to contain <1 wt% water by NMR analysis. The eutectic temperature for the 1:2 mixture was reported as t_m/°C = 12 [2]. However, it was subsequently found by Chemat et al. [3] to be 12.70 °C for the 1:2 mixture whereas Morrison et al., using DSC, found that the onset of melting of the solid 1:2 mixture appeared at 17.1 °C [4]. A more complete phase diagram for $x_{urea} > 0.85$ was reported (in a small figure) by Kim and Park [5] in general agreement with the data of Abbott et al. [2] and Morrison et al. [4], but divergent values were obtained for $x_{urea} < 0.4$. No value of the eutectic temperature was reported there [5], however. Still more recently, Meng et al. [6] stressed the fact that the mixture readily absorbs water from a moist atmosphere, and that for the dry 1:2 system, the eutectic temperature was appreciably higher: t_m/°C = 25 [6]. This result was obtained both by direct microscopic observation and by differential scanning calorimetry (DSC). A eutectic point having t_m/°C = 12 corresponded to 6 wt% of water in the mixture, and even lower eutectic points were attained with more water absorbed, near 0 °C for 10 wt% water [6]. Although dried starting materials were employed in the primary report on the choline chloride/urea system

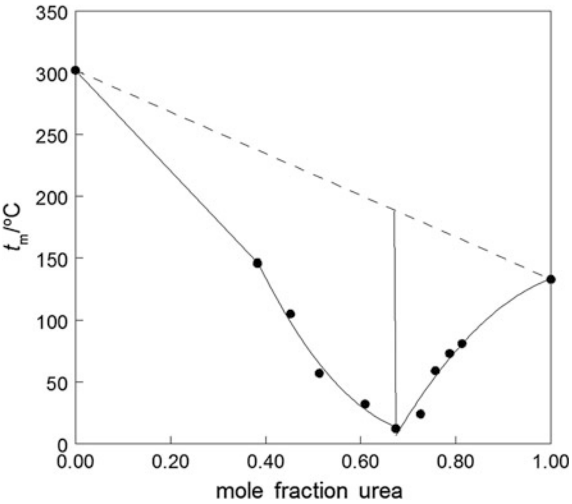

Fig. 3.1 Solid–liquid phase diagram of the choline chloride/urea binary system [2]. The lines connecting the experimental points are guides to the eye and have no further significance. The dashed line connects the melting points of the components, and the vertical line represents the eutectic distance

and NMR analysis showed <1 wt% water in the mixture leading to the usually quoted eutectic temperature of 12 °C [2], there remains appreciable uncertainty regarding this value in view of the subsequent reports [4, 6].

For the "Ethaline" systems involving choline chloride and ethylene glycol (EG), the freezing points were reported for only three compositions: x_{EG} =0.636 with t_{m}/°C = −33.3, x_{EG} =0.667 with t_{m}/°C = −6.0, and x_{EG} =0.714 with t_{m}/°C = 4.2. Similarly, for choline chloride and glycerol (Gl) "Glyceline", the freezing points are at x_{Gl} =0.500 t_{m}/°C = 8, x_{Gl} =0.667 t_{m}/°C = −36.2, and x_{Gl} =0.750 t_{m}/°C = −32.7 [7]. These data were plotted in a not very clear phase diagram, together with the freezing points of the end members, in [8]. However, a detailed phase diagram was shown in a figure in [9] for mixtures of choline chloride with glycerol, in essential agreement with the values reported in [7].

In the case of choline chloride/malonic acid ("Maline") mixtures, the lack of nucleation prohibited the construction of a phase diagram for this system using differential scanning calorimetry [3]. Acetylcholine chloride reaches with glycerol an even lower eutectic temperature than for choline chloride, at x_{Gl} =0.800 with t_{m}/°C ∼ −73, as read from the figure, and other ammonium salts (ethylammonium chloride, chloroethyl trimethylammonium chloride, and tetrapropylammonium bromide) at mole ratios of 1:3 with glycerol also have freezing points lower than the 1:2 choline chloride: glycerol system [9]. For the systems involving choline chloride and trifluoroacetamide (TFA), the freezing points were reported for only three compositions: x_{TFA} =0.636 with t_{m}/°C = 2.7, x_{TFA} =0.667 with t_{m}/°C = −30.0, and x_{TFA} =0.714 with t_{m}/°C = −43.6 [5]. Fairly detailed phase diagrams of the mixtures of choline chloride with carboxylic acids were reported in [10]. The phase diagram of the binary mixture of choline chloride with *o*-cresol is shown in Fig. 3.2, constructed from data in [11].

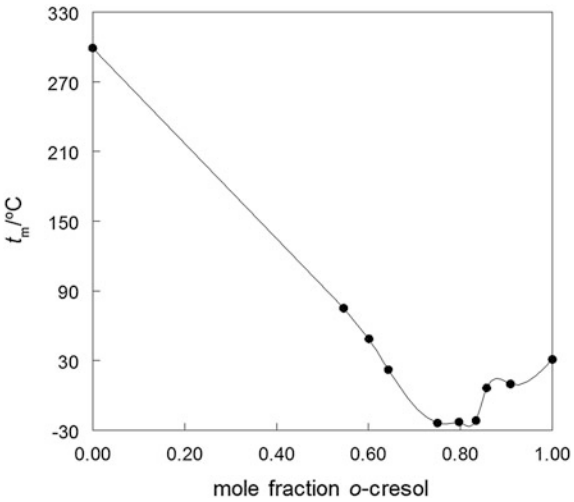

Fig. 3.2 Phase diagram of the binary mixtures of choline chloride with *o*-cresol, from data in [11]

For the systems involving tetrabutylammonium chloride and ethylene glycol (EG) or glycerol (Gl), the freezing points were reported for only three compositions each. For ethylene glycol, the freezing points were at x_{EG} =0.667 t_m/°C = −30.1, x_{EG} =0.750 t_m/°C = −30.9, and x_{EG} =0.800 t_m/°C = −16.8. For glycerol, the freezing points were at x_{Gl} =0.750 t_m/°C = −41.6, x_{Gl} =0.800 t_m/°C = −42.6, and x_{Gl} =0.833 t_m/°C = −42.8 [12]. Also reported there were the freezing points of four mixtures of the tetrabutylammonium chloride salt with triethylene glycol (TEG): x_{TEG} = 0.500 t_m/°C = 17.1, x_{TEG} = 0.333 t_m/°C = 2.4, x_{TEG} = 0.250 t_m/°C = −12.7, x_{TEG} = 0.200 t_m/°C = −9.6. The glass transition temperatures for mixtures with all these three hydrogen bond donating components are 30–40 °C lower than the melting points [12]. The data for the mixtures with ethylene glycol and glycerol were plotted in a not very clear phase diagram, together with the freezing points of the end members, in [8]. The detailed phase diagram of tetrabutylammonium chloride and α-tocopherol (vitamin E, CAS No. 59-02-9) as the hydrogen bond donating component was reported in [13] where an eutectic at the mole ratio 4:1 HBA: HBD having t_m/°C = −50 was found. The diagram is rather shallow at larger tocopherol contents and the freezing point reaches 4 °C for pure tocopherol.

For the systems involving methyltriphenylphosphonium bromide and ethylene glycol (EG), glycerol (Gl), or triethylene glycol (TEG), the freezing points were reported for only three compositions each [7]. The data are: x_{EG} = 750 t_m/°C = −46.31, x_{EG} =0.800 t_m/°C = −49.4, and x_{EG} =0.833 t_m/°C = −48.6, x_{Gl} =0.667 h t_m/°C = 3.4, x_{Gl} =0.750 t_m/°C = −5.6, and x_{Gl} =0.800 t_m/°C = 15.8, and x_{TEG} = 750 t_m/°C = –8.3, x_{TEG} =0.800 t_m/°C = –18.9, and x_{TEG} =0.833 t_m/°C = −21.6. Plots of the data have not been reported.

On the other hand, complete solid–liquid phase diagrams have been reported for ionic liquids based on the 1-butyl-1-methylpyrrolidinium cation with several anions as the hydrogen bond accepting component and water (W) as the hydrogen bond donating one [14]. The deep eutectic solvent that was produced for the salt with the trifluoromethylsulfonate anion had t_m/°C = −28.5 at x_W = 0.60, the one with tetracyanoborate anion had t_m/°C = 6 at x_W = 0.43, that with the tetracyanomethanide anion had t_m/°C = –31 at x_W = 0.52, and that with the dicyanamide anion had t_m/°C = −40 at x_W = 0.75, but for the latter two systems, incomplete phase diagrams were reported. Furthermore, a phase diagram was reported [14] for the ternary system of the choline chloride + resorcinol (1:4) mixture (melting above ambient temperature) with water, forming a deep eutectic solvent at x_W = 0.8163 having t_m/°C = −8.4, as shown in Fig. 3.3.

Phase diagrams of the deep eutectic solvents formed between ice and salt hydrates are more readily obtained from the data in the Linke and Seidell compilation [15], the Krigintsev et al. compilation [16], and in subsequent publications [17]. Just one example is shown in Fig. 3.4, which is for the calcium perchlorate hexahydrate/ice system, with data from [18]. The solid–liquid phase diagram of mixtures of the two salt hydrates $MgCl_2 \cdot 6H_2O$ and $NiCl_2 \cdot 6H_2O$ is shown in Fig. 1.2 in Chap. 1.

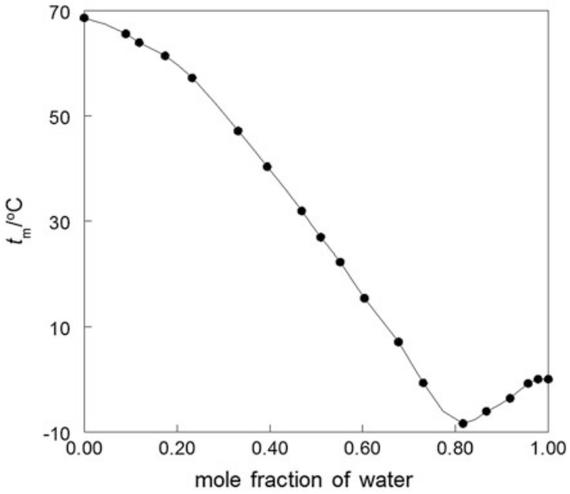

Fig. 3.3 Solid–liquid phase diagram of the choline chloride + resorcinol (1:4)/water ternary system [14]. The lines connecting the experimental points are guides to the eye and have no further significance

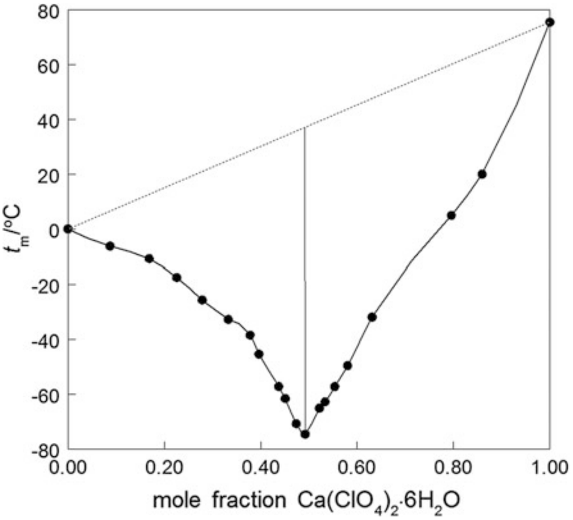

Fig. 3.4 Phase diagram of aqueous calcium perchlorate hexahydrate: • experimental values from [18], —— connecting lines (not modeled). The eutectic distance of Δt_m/°C = 137 is shown

3.2 Thermodynamic Properties

The thermodynamic properties of deep eutectic solvents include beyond the freezing points of the eutectics (See Chap. 2 and the section above) also such data as the vapor pressures, boiling points, critical constants, the enthalpy change of melting/freezing, the heat capacities of the liquids, and their surface tensions. The volumetric properties: the densities and the related expansibilities and compressibilities are dealt with in the next section.

3.2.1 Vapor–Liquid Equilibria

Very little attention has been given the vaporization of the deep eutectic solvents, their boiling points, and their critical constants. In fact, there is general agreement that the vapor pressures of the neat deep eutectic solvents (contrary to their mixtures with water) at ambient temperatures are low or even negligible. Only recently have the vapor pressures of the deep eutectic solvents formed by choline chloride with polyols at 25 °C been studied. They were predicted to be of the order of pPa to nPa; for example, p/pPa = 85 for ethylene glycol, 204 for glycerol, 10.6 for diethylene glycol, and 19 for triethylene glycol as the hydrogen bond donating agents [19]. Actual measurements of the vapor pressures of deep eutectic solvents have again only recently been made, and only at considerably above ambient temperatures, 70–120 °C. The values of p/Pa at 70 °C being 2.14 for choline chloride/glycerol, 0.336 for choline chloride/urea, 2.16 for diethylethanolammonium chloride/glycerol, 0.138 for diethylethanolammonium chloride/urea, and 0.832 for methyltriphenylphosphonium bromide/glycerol [20].

Mirza et al. [21] devoted a study to the estimation of the boiling point and critical constants, using the method proposed by Valderrama and Robles [22] among others. According to this method, using group contributions, the boiling point of deep eutectic solvents would be

$$T_\mathrm{b}/\mathrm{K} = 198.2 + \Sigma n_i T_{\mathrm{b}i} \tag{3.1}$$

Here n_i is the number of the i groups in the molecule and $T_{\mathrm{b}i}$ is their group contribution (in K), listed for 31 commonly occurring groups and for variants of 11 among them when present in rings. The estimated boiling points of 27 deep eutectic solvents based on choline chloride with various hydrogen bond donating components and in addition those of 12 deep eutectic solvents based on other hydrogen bond accepting components were presented in a table [21]. These estimated boiling points range from 75.3 °C for the 2:3 mixture of ethyl trimethylammonium chloride with trifluoromethanesulfonamide ($F_3CSO_2NH_2$) to 389.8 °C for the 1:1 mixture of choline chloride with fructose. The estimated critical temperatures, T_c/K, are 1.25–1.55 (most commonly 1.36) times higher than the estimated boiling points T_b/K, requiring the input of another listed 42 group contributions, and the critical pressures and critical volumes also result [21]. These quantities were used (with a non-specified procedure) to estimate the densities of the 39 deep eutectic solvents at 40 °C for comparison with experimental values, with fair agreement, generally within 10%, with better agreement than another density estimation method [23] produced. Since, however, the densities of deep eutectic solvents can be readily measured directly, this cumbersome estimation does not fulfill a very useful function.

The normal boiling points T_b of deep eutectic solvents are generally not relevant for their applications, but represent the upper limit of their usage, if they do not decompose below these T_b. Therefore, the critical temperatures T_c that are on the average about $^4/_3(T_b/\mathrm{K})$ [21] are not quantities that are relevant to their applications, but have found use for the estimation of other properties that have not been measured as functions of the temperature.

A path for the estimation of the critical temperatures is described in [24] alternative to the group additivity method followed by Mirza et al. [21]. The surface tensions σ of liquids over a temperature range are related to their critical temperatures T_c according to the Eötvös and the Guggenheim relationships (see Sect. 3.2.4). These relationships may be inverted in order to deduce the critical temperatures from $\sigma(T)$ and $\rho(T)$ data that are available in the literature, which are linear over a wide temperature range. Thus, the critical temperature T_c^E according to the Eötvös expression is

$$T_c^E = T/\left[1 - \sigma(T)V(T)^{2/3}/A_0\right] \tag{3.2}$$

and T_c^G according to the Guggenheim expression is

$$T_c^G = T/[1 - \sigma(T)/\sigma_0]^{9/11} \tag{3.3}$$

where extrapolation to the nominal temperature $T = 0$ yields, respectively, $A_0 = \sigma(0)V(0)^{2/3}$ and $\sigma_0 = \sigma(0)$. The critical temperatures of deep eutectic solvents, calculated either from the group contributions [21, 25] or from the surface tensions [24] are shown in Table 3.1. The agreement of the values from the various sources and methods, ranging from 500 to 1000 K is unfortunately poor, but values of $T_c > 1000$ K are probably incorrect.

Table 3.1 The critical temperatures of deep eutectic solvents: T_c^{Ma} from [21], T_c^{Mb} from [25], and T_c^G and T_c^E from [24]

HBA	HBD	HBD/HBA	T_c^{Ma}/K	T_c^{Mb}/K	T_c^G/K	T_c^E/K
Choline$^+$Cl$^-$	Ethylene glycol	1:2	602	611	669	836
	Glycerol	1:2	681	981	605	832
	1,3-butanediol	1:3	638			
	Triethylene glycol	1:2	662^b			
	Fructose	2:1	757	903	564	869
	Glucose	2:1	887	887	1191	
	Ethanolamine	1:7			790	1486
	Urea	1:2	644			
	Trifluoroacetamide	1:2	589			
	Malonic acid	1:2	739	666^b		
	Lactic acid	1:2	681			
	Phenol	1:2	651			
Acetylcholine$^+$Cl$^-$	Urea	1:2	667			
EtNH$_3^+$Cl$^-$	Urea	2:3	582			

(continued)

Table 3.1 (continued)

HBA	HBD	HBD/HBA	T_c^{Ma}/K	T_c^{Mb}/K	T_c^{G}/K	T_c^{E}/K
	Acetamide	2:3	544			
	Trifluoroacetamide	2:3	532			
$Et_2(HOEt)NH^+Cl^-$	Ethylene glycol	1:4	612	667	651	982
	Glycerol	1:2	641	696	728	1158
$Pr_4N^+Br^-$	Ethylene glycol	1:4			677	1068
	Glycerol	1:3			720	1159
	Triethylene glycol	1:3			701	1146
$Bu_4N^+Cl^-$	Ethylene glycol	1:3			650	1002
	Glycerol	1:5			769	1312
	Triethylene glycol	3:1			635	963
$Bu_4N^+Br^-$	Glycerol	1:4			558	609
	Ethanolamine	1:4			919	2072
	Aspartic acid	1:9			563	720
	Glutamic acid	1:10			518	633
	Arginine	1:6			708	1044
$MePh_3P^+Br^-$	Ethylene glycol	1:4	708	989	642	906
	Glycerol	1:3	832	996	631	914
	Ethanolamine	1:8			724	1289
$BezylPh_3P^+Br^-$	Glycerol	1:19			613	894
$AllylPh_3P^+Br^-$	Glycerol	1:14			512	671
	Diethylene glycol	1:4	898[a]		748	980
	Triethylene glycol	1:4	738[a]		581	768

[a] From [144]

[b] From [145]

3.2.2 Solid–Liquid Equilibria

The freezing temperatures of most of the deep eutectic solvents dealt with here have been reported (see Chap. 2 and Sect. 3.1), but there is very little information regarding the heat change of the freezing process. Glass transition temperatures may have been reported for those deep eutectic solvents that do not crystallize on sufficient cooling. The integral of the endothermic peak of the differential scanning calorimetry curve on slow heating the solid mixtures forming the deep eutectic solvents provided the heat change of the melting for the archetypical 1:2 choline chloride/urea deep eutectic solvent. However, two different melting points and related molar enthalpies of fusion have been reported: the one is 17 °C and 6.15 kJ mol^{-1} [4] and the other is 25 °C and 8.05 kJ mol^{-1} [6]. These values are appreciably smaller than the molar enthalpies of fusion of the components: $\Delta_f H/\mathrm{kJ\ mol^{-1}} = 29.75$ estimated for choline chloride (it could not be measured because of decomposition near the melting point) [8] and 14.79 for urea [26]. Values for other deep eutectic solvents could not be found, although those for the components are readily available.

3.2.3 Heat Capacity

The molar heat capacities of deep eutectic solvents have received considerably more attention than their enthalpies of fusion and values are available for a small variety of them over a certain temperature range. They have been measured by differential scanning calorimetry and follow the expression:

$$C_{\mathrm{P}}/\mathrm{J\,K^{-1}\,mol^{-1}} = a_1 + a_2(T/\mathrm{K}) + a_3(T/\mathrm{K})^2 + a_4(T/\mathrm{K})^{-2} \tag{3.4}$$

with the coefficients shown in Table 3.2 taken from [27]. A few additional values have also been reported [28, 29]. The molar heat capacity increases with the temperature and with the molar mass of the deep eutectic solvent [28], and in view of this the values reported for the tetrabutylammonium chloride/urea system [29] appears to be completely out of line and may require revision.

It was noted that the water content of the deep eutectic solvents (absorbed from the atmosphere) affects the heat capacity, and data are available also for solutions of deep eutectic solvents in water [28, 29]. The heat capacity of the deep eutectic solvent formed between choline chloride and malonic acid at a 1:2 molar ratio (“Maline”) could not be determined experimentally (possibly due to its high viscosity) but was estimated computationally [30]. At 25 °C, the computed value is

Table 3.2 Molar heat capacity, C_{P}/J $\mathrm{K^{-1}}$ $\mathrm{mol^{-1}}$, of deep eutectic solvents at 298.15 K and the coefficients of Eq. (3.4) from [27] or as noted

HBA	HBD	C_{P}(298 K)	a_1	a_2	10^3a_3	10^7a_4
Choline$^+$Cl$^-$	Urea	180.2[a]	247.4	−0.5633	1.141	
	Ethylene glycol	185.1[a]	181.9	−0.1936	0.737	
	Glycerol	235.7[a]	302.8	−0.6783	1.531	
	Triethylene glycol	299.0	8552	−34.27	40.17	−0.1427
	Fructose	311.5	12,140	−45.83	50.12	−0.2332
	Glucose	327.5	−891	6.562	−8.879	44.48
	Malonic acid	226.9	829.5	−2.695	3.584	−1.045
	Citric acid	422.0	3869	−14.75	18.11	−5.877
	Oxalic acid	270.8	2930	−10.70	12.27	−4.984
	Phenol	219.3	1274	−4.09	4.717	−2.259
$Et_2(HOEt)NH^+Cl^-$	Ethylene glycol	202.0[b]	107.1	0.319		

(continued)

Table 3.2 (continued)

HBA	HBD	C_P(298 K)	a_1	a_2	10^3a_3	10^7a_4
	Glycerol	247.8[b]	133.1	0.385		
$Bu_4N^+Cl^-$	Glycerol	281.2	−1387	6.827	−7.366	−2.255
	Urea	590.1[c]	32,260	−12.57	140.3	−0.595
	Ethylene glycol	288.3	−686.8	4.296	−4.899	1.154
	Malonic acid	299.8	−6344	31.21	−39.76	7.735
	Triethylene glycol	445.0	819.2	−1.293	1.757	−1.285
$MePh_3P^+Br^-$	Malonic acid	336.9	−1214	6.965	−8.427	1.988
	Glycerol	328.5	−544.6	3.708	−4.064	1.146
	Ethylene glycol	237.6	−2300	10.64	−12.20	4.003
Betaine	Ethylene glycol[e]	618.9	−1011.4	8.858	−0.0114	
L-Carnitine	Ethylene glycol[e]	679.2	−1051.3	9.067	−0.0109	

[a] Extrapolated from linear relationship between 303.15 and 353.15 K from [28]
[b] Extrapolated as in footnote[a]
[c] From [29]
[d] At 308.15 K, the melting point being 300.3 K
[e] Molar ratio 1:3 [146]

C_P/J K^{-1} mol^{-1} = 229, intermediate between the values for the deep eutectic solvents with ethylene glycol 209 and with glycerol 259, contrary to expectations in view of its larger molar mass. The computed values for the latter two deep eutectic solvents are 12 and 9% larger than the (extrapolated) experimental values (Table 3.2), however.

3.2.4 Surface Tension

A considerable body of information exists regarding the surface tension σ of deep eutectic solvents, the values diminishing linearly with increasing temperatures, as shown in Table 3.3 for choline chloride-based deep eutectic solvents and other ammonium- and phosphonium-based ones.

The Eötvös and Guggenheim empirical expressions were used by Mjalli et al. for the correlation of the surface tensions of deep eutectic solvents based on glycerol and ethylene glycol hydrogen bond donating components with choline chloride, diethylethanolammonium chloride, and methyltriphenylphosphonium bromide as the hydrogen bond accepting components [25]. Both methods require the critical temperature T_c of the deep eutectic solvent in the following manner:

Table 3.3 Surface tensions, σ/mN m^{-1}, of deep eutectic solvents at 25 °C and their temperature coefficients (dσ/dt)/mN m^{-1} °C^{-1}

HBA	HBD	HBA: HBD	σ	dσ/dt	Ref.
Choline chloride	Urea	1:2	52.0		[147]
	Ethylene glycol	1:2	48.91	−0.0932	[25]
	Ethylene glycol	1:2	48.0		[147]
	Glycerol	1:2	56.0		[147]
	Glycerol	1:2	58.05	−0.1353	[148]
	Glycerol	1:2	57.24	−0.0896	[25]
	1,4-butanediol	1:3	47.17		[25]
	Fructose	2:1	74.0	−0.200	[88]
	Glucose	2:1	71.57	−0.0524	[149]
	Glucose	2:1	71.71	−0.0516	[25]
	Phenylacetic acid	1:2	41.86[a]		[10]
	Malonic acid	1:1	65.98[a]		[10]
	Malonic acid	1:1	65.7		[147]
	Ethanolamine	1:7	49.18	−0.0694	[150]
Ethylammonium Br	Glycerol	1:2	57.6		[151]
Propylammonium Br	Glycerol	1:2	51.7		[151]
Butylammonium Br	Glycerol	1:2	44.9		[151]
Diethylethanolammonium$^+$Cl$^-$	Ethylene glycol	1:4	47.51	−0.0956	[25]
	Glycerol	1:5	59.35	−0.1132	[25]
	Glycerol	1:2	54.54	−0.0888	[148]
	Trifluoroacetamide	1:2	40.27		[152][c]
Tetrapropylammonium$^+$Br$^-$	Ethylene glycol	1:4	47.05	−0.0877	[153]
	Glycerol	1:3	53.12	−0.0883	[153]
	Triethylene glycol	1:3	46.57	−0.0814	[153]
Tetrabutylammonium$^+$Cl$^-$	Ethylene glycol	1:3	40.49	−0.0817	[12]
	Glycerol	1:5	47.35	−0.0700	[12]
	Triethylene glycol	3:1	40.22	−0.0849	[12]
	Glutamic acid	10:1	37.6[b]	−0.1375	[154]
	Aspartic acid	9:1	38.5[b]	−0.1150	[154]
	Arginine	6:1	40.4[b]	−0.0750	[154]
	Serine	8:1	68.34	−0.0103	[155]
	Threonine	9:1	40.60	−0.1050	[155]
	Methionine	11:1	39.89	−0.1070	[155]
Tetrabutylammonium$^+$Br$^-$	Glycerol	1:4	36.57	−0.1409	[148]
	Ethanolamine	1:4	35.83	−0.0392	[150]
MethyltriphenylP$^+$Br$^-$	Ethylene glycol	1:4	51.29	−0.1056	[152][c]
	Glycerol	1:3	58.94	−0.1259	[152][c]
	Glycerol	1:3	54.35	−0.0883	[148]

(continued)

Table 3.3 (continued)

HBA	HBD	HBA:HBD	σ	$d\sigma/dt$	Ref.
	Triethylene glycol	1:5	49.85		[152][c]
	Ethanolamine	1:8	50.27	−0.0828	[150]
BenzyltriphenylP$^+$Br$^-$	Glycerol	1:16	53.24	−0.1205	[148]
AllyltriphenylP$^+$Br$^-$	Glycerol	1:14	41.57	−0.1409	[148]
LiTFSI[d]	Acetamide	1:4	46.8		[156]

[a] The temperature was not specified but is probably 25 °C

[b] At 40 °C

[c] The same data were repeated in [157]

[d] Lithium bis[trifluoromethyl)sulfonyl]imide

$$\sigma V^{2/3} = A(1 - T/T_c) \tag{3.5}$$

for the Eötvös correlation, where V is the molar volume of the deep eutectic solvents and

$$\sigma = \sigma_0(1 - T/T_c)^{11/9} \tag{3.6}$$

for the Guggenheim correlation, where A and σ_0 are constants obtained for a reference temperature. The critical temperatures T_c, in turn, have been discussed earlier in this chapter, as derived from group contributions.

For the nonconventional deep eutectic solvents based on salt hydrates, there are only few data for the concentrated aqueous solutions that are relevant for them. At moderate concentrations, the surface tension varies linearly with the concentration, but there is no guarantee that this linearity persists to the eutectic composition. The following data could still be found in the literature for salts listed in Table 2.4 pertaining to 25 °C. The sets of the three values of the surface tensions σ/mN m^{-1}, their temperature derivatives ($d\sigma/dT$)/mN m^{-1} K^{-1}, and the relevant molalities are: KF 86.3, unspecified, 7.10 m (extrapolated beyond 4.0 m) [31]; KOH 97.9, −0.19, 17.01 m (interpolated for 25 °C) [32]; NaOH 82.62, −0.077, 6.51 m (interpolated for 25 °C) [33]; $MgCl_2$ 87.6, unspecified, 4.09 m [34]; $Mg(NO_3)_2$ 88.0, unspecified, 5.29 [35]; $Zn(NO_3)_2$ 85.58, −0.122, 5.51 m [36]. In these cases as for the conventional deep eutectic solvents, $d\sigma/dT$ is negative and the surface tension σ is >10 mN m^{-1} larger than that of water, i.e., the ions are driven away from the surface layer.

3.3 Volumetric Properties

3.3.1 Density and Expansibility

The density of deep eutectic solvents is readily measured and should be available for most of the useful deep eutectic solvents. For the conventional deep eutectic solvents based on choline chloride, its analogs, and other ammonium and phosphonium hydrogen bond accepting components, the densities at 25 °C are shown in Table 3.4, as are the coefficients of the linear temperature dependence functions, $\rho = a - b(t/^\circ\mathrm{C})$. In a few cases noted in the table, a quadratic expression in the temperature was reported. Also presented in the table are the isobaric expansibilities, $\alpha_\mathrm{P} = \rho^{-1}(\partial\rho/\partial T)_P = b/\rho(25\ ^\circ\mathrm{C})$. The densities of these deep eutectic solvents are mostly within the range 1.1–1.3 g cm^{-3} and the isobaric expansibilities are within the range −0.55 to −0.65 kK^{-1}; values outside these ranges (except for a few density values <1.0) should be considered with due caution. For example, the entries in Table 3.4 for the choline chloride/urea deep eutectic solvent at 25 °C are sufficiently consistent, but nonconforming values have also been reported: $\rho/\mathrm{g\ cm}^{-3}$ = 1.20, 1.212, and 1.25 [37].

Table 3.4 Densities, $\rho/\mathrm{g\ cm}^{-3}$, of deep eutectic solvents at 25 °C, their temperature dependencies, $\rho/\mathrm{g\ cm}^{-3} = a - b(t/^\circ\mathrm{C})$, and their isobaric thermal expansibilities $10^3\alpha_\mathrm{P}/\mathrm{K}^{-1}$

HBA	HBD	HBA:HBD	$\rho/\mathrm{g\ cm}^{-3}$	a	10^3b	$10^3\alpha_\mathrm{P}/\mathrm{K}^{-1}$	Ref.
Choline chloride	Urea	1:2	1.1981	1.2125	0.577	0.482	[158]
	Urea	1:2	1.1974	1.2119	0.582	0.486	[159]
	Urea	1:2	1.1979	1.2103	0.523	0.437	[160]
	Ethylene glycol	1:2	1.1171	1.1314	0.572	0.512	[26]
	Ethylene glycol	1:2	1.1182	1.1327	0.579	0.518	[25]
	Ethylene glycol	1:2	1.1141	[a]			[161]
	Ethylene glycol	1:2	1.1166	1.1305	0.557	0.499	[162]
	Triethylene glycol	1:2	1.1285	1.1445	0.638	0.565	[145]
	Glycerol	1:2	1.1913	1.2051	0.552	0.463	[153]
	Glycerol	1:2	1.1924	1.2063	0.557	0.467	[25]
	Glycerol	1:2	1.1916	[b]			[162]
	Glycerol	1:2	1.2070	1.2195	0.5	0.41	[33]
	1,4-butanediol	1:3	1.0610				[163]
	Furfuryl alcohol	1:3	1.1351	1.3318	0.660	0.581	[164]
	Fructose	2:1	1.1177	1.1324	0.589	0.527	[88]
	Fructose	1:1	1.272	1.286	0.54		[165]
	Fructose	2:1	1.2779	1.3081	1.179	0.907	[40]
	Glucose	2:3	1.2672	1.2801	0.516	0.407	[36]
	Glucose	2:1	1.2422	1.267	1.000	0.805	[40]

(continued)

Table 3.4 (continued)

HBA	HBD	HBA:HBD	ρ/g cm^{-3}	a	10^3b	$10^3\alpha_P$/K^{-1}	Ref.
	Glucose	2:1	1.2423			0.414	[145]
	Glucose	1:1	1.273	1.286	0.54		[165]
	Mannose	1:1	1.278	1.293	0.60		[165]
	Ribose	1:1	1.267	1.280	0.54		[165]
	Xylose	1:1	1.257	1.272	0.60		[165]
	Levulinic acid	1:2	1.1380	1.1544	0.658	0.578	[166]
	Levulinic acid	1:2	1.1384	1.3499	0.710	0.631	[167]
	Levulinic acid	1:3	1.1380	1.3440	0.369	0.607	[164]
	Levulinic acid	1:4	1.1354				[168]
	Malonic acid	1:1	1.4000	1.4500	2.0	1.43	[57]
	Malonic acid	1:1	1.0660	[c]			[161]
	Oxalic acid	1:1	1.2998	1.3473	1.9	1.46	[57]
	Ethanolamine	1:7	1.0661	1.0843	0.73	0.685	[146]
	Triethanolamine	1:2	1.3296	1.3746	1.8	1.35	[158]
	Trifluoroacetamide	1:2	1.4851	1.2773	1.9	1.28	[158]
	Phenol	1:3	1.0921	[d]			[10]
	Phenol	1:2	1.0948	1.1150	0.811	0.741	[169]
	o-cresol	1:3	1.0707				[11]
	p-cresol	1:2	1.0681	1.0880	0.800	0.749	[169]
	p-chlorophenol	1:2	1.1988	1.2206	0.870	0.726	[169]
	Guaiacol	1:3	1.1504	1.1664	0.639	0.555	[170]
Choline bromide	Levulinic acid	1:4	1.2073				[168]
Acetylcholine Cl	Levulinic acid	1:2	1.1406	1.3642	0.750	0.665	[113]
	Imidazole	1:3	0.9906	1.1402	0.502	0.507	[171]
	1,2,4-triazole	1:1	1.0341	1.1293	0.454	0.439	[171]
	Guaiacol	1:3	1.1477	1.1611	0.537	0.468	[170]
Ethylammonium Br	Glycerol	1:2	1.358				[151]
Propylammonium Br	Glycerol	1:2	1.328				[151]
Butylammonium Br	Glycerol	1:2	1.293				[151]
Et_2NHCl	Guaiacol	1:3	1.0959	1.1109	0.682	0.622	[170]
$Et_2(HOEt)NHCl$	Ethylene glycol	1:2	1.0987	1.1149	0.618	0.562	[39]
	Ethylene glycol		1.0999	1.1152	0.6	0.55	[172]
	Ethylene glycol	1:3	1.0995	1.1157	0.636	0.578	[40]
	Triethylene glycol	1:4	1.118[g]				[173]
	Glycerol	1:2	1.1131	1.1881	0.599	0.538	[39]
	Glycerol		1.1766	1.1938	0.6	0.51	[172]
	Glycerol	1:4	1.2051	1.2209	0.629	0.522	[40]

(continued)

Table 3.4 (continued)

HBA	HBD	HBA: HBD	ρ/g cm^{-3}	a	10^3b	$10^3\alpha_P$/K^{-1}	Ref.
	Glycerol	1:2	1.1709		0.66	0.564	[40]
	Malonic acid	1:1	1.2201	1.2726	2.1	1.72	[57]
Et$_4$NCl	Levulinic acid	1:2	1.0939	1.3036	0.704	0.652	[113]
	Levulinic acid	1:4	1.1020				[168]
Et$_4$NBr	Ethylene glycol	1:4	1.1596				[168]
	Triethylene glycol	1:4	1.1468				[168]
	Levulinic acid	1:2	1.1736	1.3977	0.752	0.649	[113]
	Levulinic acid	1:4	1.1669				[168]
Pr$_4$NCl	Levulinic acid	1:4	1.0759				[168]
Pr$_4$NBr	Ethylene glycol	1:4	1.1339	1.1509	0.682	0.601	[153]
	Glycerol	1:3	1.1924	1.2214	0.664	0.557	[153]
	Triethylene glycol	1:3	1.1426	1.1681	0.700	0.613	[153]
	Triethylene glycol	1:4	1.1204				[168]
	Ethylene glycol	1:4	1.1314				[168]
Bu$_4$NCl	Ethylene glycol	1:3	1.0263	1.0423	0.639	0.623	[12]
	Ethylene glycol	1:2	0.9890			0.684	[174]
	Glycerol	1:5	1.1417	1.1579	0.650	0.569	[12]
	Glycerol	1:4	1.1714	1.1891	0.6	0.51	[148]
	Triethylene glycol	1:2	1.0043	1.0197	0.618	0.615	[12]
	PEG 400	1:2	1.0771			0.625	[174]
	Propanoic acid	1:2	1.1183			0.632	[174]
	Phenylacetic acid	1:2	1.0401			0.678	[174]
	Decanoic acid	1:2	0.9168				[94]
	Levulinic acid	1:2	1.0310	1.2432	0.712	0.700	[113]
	Levulinic acid	1:4	1.0484				[168]
	Glutamic acid	10:1	0.9630^{e}	0.9791	0.601	0.624	[154]
	Aspartic acid	9:1	0.9582^{e}	0.9875	0.584	0.609	[154]
	Arginine	6:1	1.0042^{e}	1.0223	0.603	0.600	[154]
	Serine	8:1	0.9906	1.0056	0.600	0.606	[155]
	Threonine	9:1	0.9393	0.9562	0.677	0.721	[155]
	Methionine	11:1	0.9393	0.9741	0.637	0.678	[155]
Bu$_4$NBr	Ethylene glycol	1:4	1.0762				[168]
	Levulinic acid	1:2	1.0972	1.3121	0.721	0.666	[113]
	Glycerol	1:4	1.1748	1.1898	0.6		[148]
	Glycerol	1:4	1.1507				[175]
	Triethylene glycol	1:4	1.0976				[168]
	Levulinic acid	1:4	1.1061				[168]
	Ethanolamine	1:4	1.0547	1.0729	0.73	0.692	[150]
Hx$_4$NBr	Ethylene glycol	1:2	1.0045	1.0204	0.633	0.630	[176]

(continued)

Table 3.4 (continued)

HBA	HBD	HBA: HBD	ρ/g cm^{-3}	a	10^3b	$10^3\alpha_P$/K^{-1}	Ref.
	Glycerol	1:2	1.0426			0.627	[176]
Hp_4NCl	Decanoic acid	1:2	0.8907				[94]
Oc_4NCl	Decanoic acid	1:2	0.8889				[94]
Oc_4NBr	Decanoic acid	1:2	0.9298				[94]
$BenzylMe_3NCl$	*p*-toluenesulfonic acid	1:1	1.1904	1.385	0.653	0.548	[177]
	Oxalic acid	1:1	1.1940	1.391	0.661	0.553	[177]
$BenzylPr_3NCl$	Ethylene glycol	1:3	1.06^f			0.580	[178]
	Glycerol	1:3	1.13^f			0.550	[178]
	Phenol	1:3	1.058^f			0.620	[178]
	Lactic acid	1:3	1.118^f			0.641	[178]
$MePh_3PBr$	Ethylene glycol	1:4	1.393	1.42	1.1	0.79	[179]
	Ethylene glycol	1:4	1.2327	1.2504	0.709	0.575	[39]
	Glycerol	1:1.75	1.233	1.25	0.7	0.57	[179]
	Glycerol	1:3	1.2969	1.3132	0.651	0.502	[39]
	Glycerol	1:3	1.2889	1.3156	0.700	0.543	[40]
	Glycerol	1:3	1.2964	1.3139	0.7	0.54	[148]
	Triethylene glycol	1:5	1.1860				[163]
	Trifluoroacetamide	1:8	1.123	1.31	0.7	0.62	[179]
	Ethanolamine	1:8	1.1007	1.1209	0.81	0.736	[150]
$BenzylPh_3P^+Cl^-$	Glycerol	1:16	1.2407				[180]
	Triethylene glycol	1:8	1.140^g				[181]
$BenzylPh_3P^+Br^-$	Glycerol	1:16	1.2337	1.2512	0.7	0.57	[27]
$AllylPh_3P^+Br^-$	Glycerol	1:14	1.2630	1.2805	0.7	0.55	[27]
	Glycerol	1:14	1.2649				[175]
	Diethylene glycol	1:10	1.1563	1.1745	0.728	0.630	[182]
	Triethylene glycol	1:10	1.1555	1.1611	0.746	0.646	[182]
	Triethylene glycol	1:10	1.1555	1.1742	0.749	0.648	[183]

[a] ρ/g cm^{-3} = 1.187 + 0.055 × 10^{-3}(T/K) − 1.004 × 10^{-6}(T/K)^2
[b] ρ/g cm^{-3} = 1.227 + 0.309 × 10^{-3}(T/K) − 1.435 × 10^{-6}(T/K)^2
[c] ρ/g cm^{-3} = 1.303 − 0.200 × 10^{-3}(T/K) − 0.690 × 10^{-6}(T/K)^2
[d] ρ/g cm^{-3} = 1.10 + 0.54 × 10^{-3}(T/K) − 1.886 × 10^{-6}(T/K)^2
[e] At 30 °C
[f] Read from the figure, because the presented numerical coefficients are erroneous

Nonionic deep eutectic solvents include those based on *N*-oxides hydrogen bond acceptors (HBA) with 1:1 phenylacetic acid, the densities at 25 °C being ρ/g cm^{-3} = 1.156 for dodecyldimethyl-*N*-oxide HBA, 0.977 for octadecyldimethyl-*N*-oxide HBA, 1.156 for *N*-methylmorpholinium-*N*-oxide HBA, and 0.995 for *N*-dodecylmorpholinium-*N*-oxide HBA [38].

Several attempts have been made to predict the densities of deep eutectic solvents, although their measurement is readily carried out, so that the prediction does not appear to be very useful. Shahbaz et al. used artificial intelligence and group contribution methods for such predictions [39], applied to glycerol and ethylene glycol hydrogen bond donating components with choline chloride, diethylethanolammonium chloride, and methyltriphenylphosphonium bromide as the hydrogen bond accepting components. Data at five temperatures in the range 25–85 °C were used as the training set for the neural network and ten other temperatures within this range were used for validation of the predictions. The group contribution method depended on the estimated critical points of the components and used the measured density at 25 °C as a reference for the estimation of the densities at higher temperatures. Mjalli et al. [25] showed that a combination of Eqs. (3.4) and (3.6) yields the expression:

$$\rho = C(T_c - T)^{1/3} \tag{3.7}$$

where C is a constant obtained from the density at a reference temperature for the prediction of the densities at other temperatures. This method appeared to be superior to the use of the modified Rackett expression for this purpose [25, 40].

The densities of less conventional deep eutectic solvents have also been reported and for the mixtures involving a salt hydrate and ice, a comprehensive listing of the densities and isobaric expansibilities at 25 °C is presented in Table 3.5. The values were obtained from the two-parameter expression reported by Apelblat [41]:

$$\rho(T, w) = \rho_W(T) / \left[1 - \rho_W(T)\left(Aw + Bw^2\right)\right] \tag{3.8}$$

Table 3.5 Densities ρ of eutectics of salt hydrates with ice at their anhydrous salt mass fractions w, their molar volumes V, and their isobaric expansibilities α_P at 25 °C [41]

Salt hydrate	t_m/°C of eutectic	$w_{eutectic}$	ρ/g cm^{-3}	V/cm^3 mol^{-1}	$10^3\alpha_P$/K^{-1}
$Al(NO_3)_3 \cdot 9H_2O$	−27.2	0.399	1.375	387.9	0.35
$CaBr_2 \cdot 6H_2O$	−22.2	0.695	2.118	135.8	0.54
$Ca(NO_3)_2 \cdot 4H_2O$	−28.7	0.527	1.540	202.0	0.39
$Ca(ClO_4)_2 \cdot 6H_2O$	−74.6	0.548	1.556	280.3	0.40
$Co(NO_3)_2 \cdot 6H_2O$	−26.2	0.512	1.613	221.4	0.41
$FeCl_3 \cdot 6H_2O$	−55.0	0.420	1.339	288.6	0.34
$KF \cdot 4H_2O$	−40.2	0.242	1.277	155.8	0.33
$KOH \cdot H_2O$	−65.2	0.488	1.502	76.5	0.38
$K_2HPO_4 \cdot 4H_2O$	−13.5	0.563	1.400	108.3	0.73
$LiCH_3CO_2 \cdot 2H_2O$	−16.1	0.201	1.102	299.3	0.28
$LiNO_3 \cdot 3H_2O$	−22.9	0.171	1.202	190.9	0.31
$LiClO_3 \cdot 3H_2O$	−40.2	0.371	1.284	189.7	0.33
$LiClO_4 \cdot 3H_2O$	−18.2	0.282	1.191	316.9	0.30

(continued)

Table 3.5 (continued)

Salt hydrate	t_m/°C of eutectic	$w_{eutectic}$	ρ/g cm^{-3}	V/cm^3 mol^{-1}	$10^3\alpha_P$/K^{-1}
$LiI \cdot 2H_2O$	−69.0	0.670	1.961	101.9	0.50
$Mg(CH_3CO_2)_2 \cdot 4H_2O$	−29.2	0.380	1.164	294.5	0.30
$MgBr_2 \cdot 6H_2O$	−42.7	0.472	1.573	247.9	0.40
$MgCl_2 \cdot 6H_2O$	−33.6	0.280	1.254	270.9	0.32
$Mg(NO_3)_2 \cdot 6H_2O$	−4.1	0.440	1.414	238.6	0.36
$Mg(ClO_4)_2 \cdot 6H_2O$	−68.6	0.582	1.520	297.3	0.40
$MnCl_2 \cdot 4H_2O$	−25.6	0.523	1.637	146.9	0.42
$Mn(NO_3)_2 \cdot 6H_2O$	−36.2	0.495	1.689	180.6	0.43
$NaCH_3CO_2 \cdot 3H_2O$	−18.2	0.380	1.203	179.5	0.31
$NaOH \cdot H_2O$	−28.2	0.207	1.223	158.3	0.31
$NiCl_2 \cdot 6H_2O$	−45.3	0.397	1.498	218.2	0.38
$Ni(NO_3)_2 \cdot 6H_2O$	−34.1	0.417	1.465	248.6	0.37
$Zn(NO_3)_2 \cdot 6H_2O$	−32.0	0.502	1.595	232.5	0.41

Here $\rho_W(T)$ is the density of water at the temperature T, w is the mass fraction of the (anhydrous) salt in the aqueous mixture, corresponding to the eutectic in the present context, and A and B are temperature-independent constants listed for the salts of interest and many others. The mass fractions w are related to the mole fractions x of the eutectic listed in Table 2.4 as

$$w = x/[x + (1-x)M_W/M_S] \tag{3.9}$$

where M_W is the molar mass of water, 18.015 g mol^{-1}, and M_S is that of the anhydrous salt.

Most density values for 25 °C for the relevant concentrated aqueous salt solutions reported in the literature agree within 2% with those from Eq. (3.8). However, a few density values and their temperature dependencies not agreeing with those derived from Eq. (3.8) and shown in Table 3.5 have also been reported. The density of aqueous $Ni(NO_3)_2$ from [42] extrapolated from 4.0 to 5.5 molal is 12% larger and that for aqueous $Mg(CH_3CO_2)_2$ from [43] extrapolated from 302.95 to 298.15 K is 7% larger than the values listed in Table 3.5, but on the whole the values in Table 3.5 for the eutectic compositions should be valid.

The isobaric thermal expansibilities α_P shown in Table 3.5 were calculated as

$$\alpha_P = [\rho(308.15\,\mathrm{K}) - \rho(288.15\,\mathrm{K})]/[20\rho(298.15\,\mathrm{K})] \tag{3.10}$$

The densities at any temperature are calculated from that at the reference temperature 25 °C, $\rho(25)$, and the isobaric thermal expansibility according to:

Table 3.6 Densities ρ of eutectics of deep eutectic solvents involving metal salts and organic substances and their isobaric expansibilities α_P at 25 °C

Metal salt	Organic substance	ρ/g cm^{-3}	$10^3\alpha_P$/K^{-1}	Ref.
$ZnCl_2$	Urea	1.63		[184]
	Acetamide	1.36		[184]
	1,2-ethanediol	1.45		[184]
	1,6-hexanediol	1.38		[184]
$Zn(NO_3)_2 \cdot 6H_2O$	Choline chloride	1.482	1.35	[57]
	Diethylethanolammonium$^+$Cl$^-$	1.220	1.64	[57]
$CaCl_2 \cdot 6H_2O$	Choline chloride	1.381	0.36	[185]
$CrCl_3 \cdot 6H_2O$	Urea	1.646	1.7	[186]
LiTFSI	Acetamide	1.401		[156]
K_2CO_3	Glycerol	1.474	0.42	[187]
	Glycerol (1:10)	1.2590	0.434	[188]
	1,2-ethanediol (1:10)	1.2561	0.532	[188]
KSCN	Acetamide	1.207	0.564	[189]
	Caprolactam	1.155	0.578	[189]
NH_4SCN	Acetamide	1.090	0.613	[189]
	Caprolactam	1.084	0.559	[189]
	Urea	1.259	0.487	[189]

$$\rho(T) = \rho(25)[1 - \alpha_P((t/^\circ C) - 25)] \tag{3.11}$$

The densities of a few other nonconventional deep eutectic solvents based on metal salts have been determined as shown in Table 3.6, all following the linear dependence $\rho = a - b(t/^\circ C)$.

3.3.2 *Compressibility*

Little has been published regarding the compressibilities of deep eutectic solvents, and the available information is mainly confined to deep eutectic solvents based on choline chloride and is summarized in Table 3.7. The adiabatic (isentropic) compressibility $\kappa_S = 1/\rho u^2$ is obtained from the density ρ and the speed of sound u. The isothermal compressibility $\kappa_T = \rho^{-1}(\partial\rho/\partial P)_T$ is obtained from the pressure dependence of the density or else from the adiabatic compressibility as $\kappa_T = \kappa_S + TV\alpha_P^2/C_P$, where V is the molar volume M/ρ, M is the molar mass, and ρ and α_P are from Table 3.4 and the molar heat capacity C_P is from Table 3.2.

The adiabatic (isentropic) compressibility of deep eutectic solvents composed of salt hydrates and water has been reported for sufficiently concentrated aqueous solutions of only a few of the salts listed in Table 2.4 as forming deep eutectic solvents. The κ_S values at 25 °C were calculated from the reported data and are

Table 3.7 The compressibility and internal pressure of deep eutectic solvents based on choline chloride and on allyltriphenylphosphonium bromide with several HBD components at 25 °C

HBD component	κ_S/GPa^{-1}	Ref.	κ_T/GPa^{-1}	Ref.	P_{int}/MPa	$(\partial \kappa_T/\partial T)_P$/TPa^{-1}K^{-1}
Choline chloride HBA						
Urea			0.208	[158]	626	0.34
	0.179	[93]	0.202		644	
	0.180^{a}	[94]	0.203^{a}		652	
Ethylene glycol			0.287	[190]	518	0.51
	0.238	[93]	0.269		553	
Glycerol			0.245	[191]	568	0.72
	0.186	[93]	0.208		669	
Levulinic acid	0.287	[50]	0.337^{b}		511	1.18^{c}
Fructose	0.205	[93]	0.300		901	
Glucose	0.094	[93]	0.167		1436	
Allyltriphenylphosphonium bromide HBA						
Diethylene glycol			2.30	[182]	81.6	
Triethylene glycol			3.10	[182]	52.4	

[a] At 303.15 K

[b] The molar heat capacity is not known, estimated as 220 J K^{-1} mol^{1} in view of other acids in Table 3.2

[c] For κ_S

Table 3.8 The compressibility of deep eutectic solvents based on salt hydrates with ice at 25 °C

Salt hydrate	κ_S/GPa^{-1}	$(\partial \kappa_S/\partial T)_P$/TPa^{-1} K^{-1}	Ref.
$Ca(NO_3)_2 \cdot 4H_2O$	0.205^{a}	0.42	[192]
$KF \cdot 4H_2O$	0.288		[193]
KOH	0.123		[194]
$LiNO_3 \cdot 3H_2O$	0.293^{b}	1.44^{d}	[195]
$Mg(CH_3CO_2)_2 \cdot 4H_2O$	0.212	3.51^{d}	[192]
$MgCl_2 \cdot 6H_2O$	0.295		[193]
$Mg(NO_3)_2 \cdot 6H_2O$	0.206		[193]
$NaOH \cdot H_2O$	0.217		[193]
$Zn(NO_3)_2 \cdot 6H_2O$	0.196^{c}	0.54	[192]

[a] There are also values 0.203 GPa^{-1} [196] and 0.206 GPa^{-1} [197]

[b] There is also value 0.262 GPa^{-1} [196]

[c] There is also value 0.199 GPa^{-1} [36]

[d] From data in [196]

shown in Table 3.8. The corresponding isothermal compressibilities κ_T could not be evaluated from $\kappa_T = \kappa_S + TV\alpha_P^2/C_P$, due to the lack of the molar heat capacities of the solutions of the eutectic compositions. As a rule of thumb, the κ_T are ~10% larger than the κ_S. In the case of $Ca(NO_3)_2 \cdot 4H_2O$, the partial molar heat capacities were reported as functions of the molality at 58.4 °C [44], so that with the mole fraction of the (anhydrous) salt at the eutectic composition of 0.38, the molar heat capacity of the solution could be evaluated as 120.9 J K^{-1} mol^{-1}; hence, the isothermal compressibility is $\kappa_T = 0.230$ GPa^{-1}, indeed 8% larger than the κ_S extrapolated to this temperature.

A quantity related to the compressibility is the internal pressure of the deep eutectic solvents, regarded as a single substance, obtained as $P_{int} = T\alpha_P/\kappa_T$. Its values, derived from the entries for κ_T in Table 3.7, are shown there too. For the choline chloride-based deep eutectic solvents for which there are κ_T data, the internal pressure P_{int} is commensurate with (but some 20% larger than) common polar organic solvents [45] and room temperature ionic liquids [46].

3.4 Transport Properties

3.4.1 Viscosity

The viscosity η of deep eutectic solvents is their key transport property that has implications for their electrical conductivity. The viscosity diminishes greatly with increasing temperatures and generally follows the Vogel–Fulcher–Tammann (VFT) expression:

$$\ln(\eta/1\text{mPa s})\_ = A_\eta + B_\eta/\left(T - T_{0\eta}\right) \tag{3.12}$$

In many cases, however, the temperature dependence follows the Arrhenius expression, wherein Eq. (3.12) $T_{0\eta} = 0$. The viscosity of the conventional deep eutectic solvents with ammonium- and phosphonium-type hydrogen bond accepting components and various hydrogen bond donating ones at 25 °C is shown in Table 3.9 along with the parameters of the VFT expression, A_η, B_η, and $T_{0\eta}$. The viscosities of a large number of such deep eutectic solvents were reported in [47] over the temperature range from 293.15 to 333.15 K at 5 K intervals; many of the data for 298.15 K are shown in Table 3.9. The coefficient B_η represents the activation energy for the flow, $B_\eta = E_\eta/R$. It should be noted that there is not, in general, very good agreement between the values at 25 °C reported by different authors for a given deep eutectic solvent, in some cases even within a factor of two. This depends, in part, on the water content of the deep eutectic solvents tested, since water drastically diminishes the viscosity of the material [48, 49].

The viscosity of choline-based deep eutectic solvents was modeled by Mjalli and Naser [50] in terms of the modified VFT expression. The parameter A_η depends on the mole fraction of the hydrogen bond accepting salt whereas B_η and $T_{0\eta}$ remain

Table 3.9 The viscosity, η/mPa s, of conventional deep eutectic solvents at 25 °C and parameters for the VFT correlation expression

DES HBA	DES HBD	Ratio	η/mPa s	A_η	B_η	T_0/K	E_η/kJ mol	Ref.
Choline Cl	Urea	1:2	829	−2.409	854	204.6		[159]
	Urea	1:2	748	−15.818	6674	0	55.49	[3]
	Urea	1:2	1571	−18.163	7581	0	63.03	[198]
	Ethylene glycol	1:2	44.4	−2.15	863	153		[199]
	Ethylene glycol	1:2	40					[50]
	Glycerol	1:2	329	−2.485	1036	173.0		[162]
	Glycerol	1:2	302	−9.263	4469	0	37.12	[148]
	Triethylene glycol	1:2	839	−2.260	4849	0	40.31	[57]
	Triethylene glycol	1:3	66					[50]
	1:4-butanediol	1:4	55					[50]
	Phenol	1:3	446	−2.10	702	179.1		[11]
	Phenol	1:2	99.8	0.0495	972	170.5		[169]
	o-cresol	1:3	77.7					[11]
	p-cresol	1:2	102.0	0.0034	1875	115.9		[169]
	p-chlorophenol	1:2	123.2	0.0796	892	176.8		[169]
	Xylose	1:1	920	−3.823	1382	168.3		[165]
	Xylose	1:1	51	−24.71		0	71.02	[200]
	Ribose	1:1	1564	−3.888	1468	167.6		[165]
	Glucose	3:2	7968	−21.27	9020	0	75.59	[149]
	Glucose	1:1	6310	−15.35	7180	0	59.73	[201]
	Glucose	1:1	1586	−3.853	1406	172.8		[165]
	Glucose	1:1	644	−30.45		0	91.52	[200]
	Fructose	2:1	11312	−13.90	6940	0	57.70	[88]

(continued)

Table 3.9 (continued)

DES HBA	DES HBD	Ratio	η/mPa s	A_η	B_η	T_0/K	E_η/kJ mol	Ref.
	Fructose	1:1	653	−3.958		169.1		[165]
	Mannose	1:1	1068	−3.673	1324	173.8		[165]
	Xylitol	1:1	7540	−17.64	7920	0	65.86	[201]
	Sorbitol	1:12	19470	−18.73	8530	0	70.91	[201]
	Sucrose	1:1	79590	−30.87		0	104.50	[200]
	Glycolic acid	1:1	548	−11.034	5157	0	42.58	[48]
	Glycolic acid	1:1	399					[174]
	Lactic acid	1:1	400					[105]
	Oxalic acid	1:1	8953	−17.279	7842	0	65.20	[48]
	Oxalic acid	1:1	458	−2.240	4610	0	38.32	[57]
	Malonic acid	1:1	1350	−11.615	5612	0	46.66	[48]
	Malonic acid	1:1	829	−2.304	4961	0	41.25	[57]
	Glutaric acid	1:1	1936	−11.640	5727	0	47.62	[48]
	Levulinic acid	1:2	102	−5.190	1783	116.5	39.93	[202]
	Levulinic acid	1:2	256	−9.703	4051	31.8	33.68	[174]
	Levulinic acid	1:2	216	−10.839	4834	0	40.19	[48]
	Trifluoroacetamide	1:2	77.3	−2.175	3898	0	32.40	[57]
	Citric acid	1:1	3852	−30.53		0	96.15	[200]
	Tartaric acid	1:1	2389	−33.4		0	102.08	[200]
	Ethanolamine	1:7	39.6					[47]
	$Zn(NO_3)_2 \cdot 6H_2O$	1:1	107	−2.078	3835	0	31.88	[57]
	$CrCl_3 \cdot 6H_2O$	1:2	4671					[50]
Acetylcholine Cl	Levulinic acid	1:2	115	−1.758	642	199.5	48.82	[202]

(continued)

Table 3.9 (continued)

DES HBA	DES HBD	Ratio	η/mPa s	A_η	B_η	T_0/K	E_η/kJ mol	Ref.
	Imidazole	1:3	464			0	48.48	[171]
	Triazole	1:1	441	−15.336	6388	0	53.11	[171]
Guanidinium hydrochloride	Ethanolamine	1:2	78.3					[47]
Ethylammonium Br	Glycerol	1:2	307[c]					[151]
Propylammonium Br	Glycerol	1:2	398[c]					[151]
Butylammonium Br	Glycerol	1:2	421[c]					[151]
Diethylethanolammonium Cl	Glycerol	1:2	433					[47]
Benzyltrimethylammonium Cl	Glycerol	1:2	716.6					[47]
	Acetic acid	1:2	113.0					[47]
	Oxalic acid	1:1	1335	−16.450	7050	0	58.62	[177]
	p-toluenesulfonic acid	1:1	10830	−19.142	8477	0	70.48	[177]
Benzyltripropylammonium Cl	Ethylene glycol	1:3	228	−4.01	1295	161	10.77	[178]
	Glycerol	1:3	3095	−4.93	1619	173	13.46	[178]
	Phenol	1:3	378	−2.63	748	211	6.22	[178]
	Lactic acid	1:3	4216	−3.43	1046	209	8.70	[178]
Et_2ethanolammonium Cl	Ethylene glycol	1:2	50.6	−2.450	847	165.3		[172]
	Glycerol	1:2	513	−2.042	875	192.6		[172]
	Glycerol	1:2	425	−10.543	4948	0	41.14	[148]
	Malonic acid	1:1	541	−2.302	4832	0	40.17	[57]
	$Zn(NO_3)_2 \cdot 6H_2O$	1:1	163	−2.051	3798	0	31.57	[57]
Triethylmethylammonium Cl	Ethylene glycol	1:2	41.7					[47]
	Glycerol	1:2	236.6					[47]
	Lactic acid	1:2	117.5					[47]

(continued)

Table 3.9 (continued)

DES HBA	DES HBD	Ratio	η/mPa s	A_η	B_η	T_0/K	E_η/kJ mol	Ref.
	Levulinic acid	1:2	96.4					[47]
Tetraethylammonium Cl	Glycerol	1:2	310^d					[203]
	Levulinic acid	1:2	93	−1.439	560	204.4	47.06	[202]
	Octanoic acid	1:3	65.9					[47]
Tetraethylammonium Br	Levulinic acid	1:2	106	−1.254	518	210.3	49.67	[202]
Tetrapropylammonium Cl	Ethanolamine	1:4	55.1					[47]
	Acetic acid	1:6	32.7					[47]
Tetrapropylammonium Br	Ethylene glycol	1:3	70.3	−9.512	4104	0	34.12	[153]
	Glycerol	1:3	739	−14.890	3409	0	53.29	[153]
	Triethylene glycol	1:3	90.0	−9.051	4040	0	33.59	[153]
Tetrabutylammonium Cl	Ethylene glycol	1:3	85.6	−8.757	3936	0	32.72	[12]
	Ethylene glycol	1:2	120	−5.006	1743	120.3		[174]
	Glycerol	1:3	816	−14.355	6279	0	52.21	[12]
	Triethylene glycol	4:1	90500^a	−8.330	6380	0	53.05	[12]
	PEG 400	1:2	175	−3.039	1224	149.0		[174]
	Acetic acid	1:2	20.9					[47]
	Propanoic acid	1:2	154	−3.605	1211	158.1		[174]
	Phenylacetic acid	1:2	288	−1.475	666	204.9		[174]
	Levulinic acid	1:2	87	−1.627	587	201.9	46.78	[202]
	Decanoic acid	1:2	265					[50]
	Aspartic acid	9:1	1790	−15.211	6769	0	56.28	[154]
	Glutamic acid	10:1	3578	−13.642	6507	0	54.10	[154]
	Arginine	6:1	24,540	−15.908	7757	0	64.50	[154]

(continued)

Table 3.9 (continued)

DES HBA	DES HBD	Ratio	η/mPa s	A_η	B_η	T_0/K	E_η/kJ mol	Ref.
	Serine	8:1	325,000			0	60.95	[155]
	Threonine	9:1	22,990	−5.711	4697	0	39.07	[155]
	Methionine	11:1	330,000	−9.776	6703	0	55.73	[155]
Tetrabutylammonium Br	Glycerol	1:4	869	−13.202	5954	0	49.50	[148]
	Ethanolamine	1:6	51.8					[47]
	Acetic acid	1:2	256.8					[47]
	Levulinic acid	1:2	252	−2.829	921	188.0	56.11	[202]
Tetrahexylammonium Br	Ethylene glycol	1:2	172	−3.673	1405	168.9		[176]
	Glycerol	1:2	813	−3.474	1366	164.2		[176]
Tetraheptylammonium Cl	Decanoic acid	1:2	173					[50]
Methyltrioctylammonium Cl	Decanoic acid	1:2	783					[50]
Tetraoctylammonium Cl	Decanoic acid	1:2	473					[50]
Tetraoctylammonium Br	Decanoic acid	1:2	636					[50]
Tetraoctylammonium Br	Decanoic acid	1:2	640					[177]
Methyltrioctylammonium Br	Decanoic acid	1:2	577					[50]
Trimethylsulfonium bis(trifluoromethylsulfonyl)imide	Formamide	1:1	6.6	−1.478	390	182	3.24	[204]
	Trifluoroacetamide	2:1	20	−1.959	595	178	4.95	[204]
Methyltriphenylphosphonium Br	Ethylene glycol	1:4	106	−11.81	4881	0	40.58	[179]
	Ethylene glycol	1:3	110.5					[47]
	1,3-propanediol	1:4	119.5					[47]
	Glycerol	1:1.75	4449	−17.60	7713	0	64.46	[179]
	Glycerol	1:3	2190	−17.467	7501	0	62.37	[148]
	Glycerol	1:4	1748					[47]

(continued)

Table 3.9 (continued)

DES HBA	DES HBD	Ratio	η/mPa s	A_η	B_η	T_0/K	E_η/kJ mol	Ref.
	Acetic acid	1:4	118.5					[47]
	Levulinic acid	1:3	957					[47]
	Trifluoroacetamide	1:8	172	−13.68	5614	0	46.68	[179]
Allyltriphenylphosphonium Br	Glycerol	1:14	866	−14.524	6347	0	52.76	[148]
Benzyltriphenylphosphonium Cl	Ethylene glycol	1:3	1430	−14.69	6546	0	54.43	[179]
	Glycerol	1:5	5490	−16.37	7448	0	61.93	[179]
	Glycerol	1:16	1299	−15.071	6631	0	55.13	[148]
Betaine	Levulinic acid	1:2	981					[203]
Li bis(trifluoromethylsulfonyl)imide	Acetamide	1:4	100					[156]
	N-Me-acetamide	1:4	40		961	164	7.99	[122]
KSCN	Acetamide	1:3	44^b	0.336	438	224		[189]
	Caprolactam	1:3	1082^b	1.660	397	252		[189]
NH_4SCN	Acetamide	1:3	20^b	0.751	210	250		[189]
	Caprolactam	1:3	294^b	0.286	578	230		[189]
	Urea	2:3	28^b	1.667	186	248		[189]

[a] At 50 °C
[b] At 40 °C
[c] At 20 °C
[d] Extrapolated

independent of it, but B_η is temperature-dependent. Altogether seven coefficients were presented for the description of the composition (near the eutectic point) and the temperature dependence of the viscosity of nine selected deep eutectic solvents. More recently, Haghbakhsh et al. [51] modeled the viscosity of deep eutectic solvents according to the free volume theory coupled with association equations of state.

Salt hydrates forming deep eutectic solvents with ice form concentrated aqueous salt solutions at 25 °C. The concentration dependence of the relative viscosity η/η_W (where η_W is the viscosity of water and at 25 °C $\eta_W = 0.8903$ mPa s) can be represented by the extended Jones–Dole expression:

$$\eta/\eta_W = 1 + Ac^{1/2} + Bc + Dc^2 \tag{3.13}$$

where c is the molar concentration. Equation (3.13) is generally valid without the last term up to 1 mol dm^{-3} concentrations. Whereas the A coefficients of Eq. (3.13)

Table 3.10 Viscosity of aqueous salts at 25 °C that form eutectics as salt hydrates with ice

Salt	$m_{eutectic}$	η/mPa s	A	B	Ref.
$Ca(NO_3)_2 \cdot 4H_2O$	6.80	10.31	−6.28[e], −6.87[f]	533[e], 2752[f]	[53, 205]
$FeCl_3 \cdot 6H_2O$	4.46	9.07			[206]
$KF \cdot 4H_2O$	7.10	2.17			[207]
$KOH \cdot H_2O$	17.01	6.57			[208]
$LiNO_3 \cdot 3H_2O$	6.23	1.75	−5.17[a], −4.63[b],	1712[a], 1530[b]	[209, 210]
$123LiI \cdot 2H_2O$	15.14	2.17			[211]
$Mg(CH_3CO_2)_2 \cdot 4H_2O$	4.99	86.2	−13.89	5421	[43]
$MgBr_2 \cdot 6H_2O$	4.86	4.77			[212]
$MgCl_2 \cdot 6H_2O$	4.09	4.87	−5.73[c], −5.70[f]	2170[c], 2173[f]	[205, 213, 214]
$Mg(NO_3)_2 \cdot 6H_2O$	5.29	7.6	−5.35[d]	2173[d]	[43, 212]
$Mg(ClO_4)_2 \cdot 6H_2O$	6.23	7.10			[212]
$Mn(NO_3)_2 \cdot 6H_2O$	6.49	~7.7			[210]
$MnCl_2 \cdot 4H_2O$	8.72	30.0			[215]
$NaOH \cdot H_2O$	6.51	4.06			[208]
$NiCl_2 \cdot 6H_2O$	5.07	8.07	−6.52	2564	[205]
$Ni(NO_3)_2 \cdot 6H_2O$	5.51	8.08			[42]
$Zn(NO_3)_2 \cdot 6H_2O$	5.51	6.97			[42]

Where multiple entries are shown for η they were derived from the references shown in sequence

[a] Ref. [209]

[b] Ref. [216]

[c] Ref. [213]

[d] Ref. [43]

[e] Ref. [53], the full VFT equation needed with $T_0 = 170$ K

[f] Ref. [205]

can be evaluated from theory and the B coefficients are available for individual ions [52], hence for their combinations as salts, the D coefficients are scarce in the literature. The relevant concentrations of the deep eutectic solvents forming salts are above the validity of Eq. (3.13) without the term in the square of the concentration. Still, numerical values for the viscosity of aqueous salt solutions at the molalities corresponding to the mole fractions of the salt hydrates forming deep eutectic solvents with ice are available for many of these salts at 25 °C, and are well represented by a cubic expression in the molality above 1 mol (kg water)$^{-1}$. Interpolation or extrapolation to the needed molalities shown in Table 3.10 then yield the viscosities presented there. These are generally <10 times the viscosity of water at 25 °C, except for the magnesium acetate and manganese chloride solutions that are more viscous. The temperature dependence of the viscosity of these concentrated salt solutions follows, where reported, the Arrhenius equation, i.e., Eq. (3.12) with $T_{0\eta} = 0$, except for one report regarding calcium nitrate [53], where $T_{0\eta} = 170$ K is required for expressing the temperature dependence of the viscosity.

There are a few reports regarding the viscosity of other nonconventional deep eutectic solvents: those involving metal salts with organic substances and mixtures of ionic liquids (morpholinium and piperidinium bromides) with water, and of amino acids with hydroxycarboxylic acids (proline and glycolic and malic acids [54]). The temperature dependence, when measured, follows the Arrhenius expression, i.e., Eq. (3.12) with $T_{0\eta} = 0$, except for the deep eutectic solvents involving inorganic thiocyanates. Table 3.11 summarizes the available data.

It should be noted that the deep eutectic solvents (except those involving salt hydrates with ice) are rather viscous, having dynamic viscosities at room temperature at least 30 times that of water at ambient conditions, but for most of them, the viscosities are some hundreds fold larger than that of water, up to a few times 10^5 as large (Tables 3.9 and 3.11).

Table 3.11 The viscosity of deep eutectic solvents involving metal salts with organic substances, cyclic quaternary ammonium salts with water, and nonionic deep eutectic solvents

Salt	Other components	Ratio	η(25 °C)/ mPa s	$10^5\eta_0$/ mPa s	E_η/ kJ mol^{-1}	Ref.
$ZnCl_2$	Choline chloride	2:1	227,000	3.95	55.7	[217]
	Choline chloride	2:1	85,000			[184]
	Urea	1:3.5	11,340		85	[184]
	Acetanide	1:4	1800		85	[184]
	Ethylene glycol	1:4			85	[184]
	1,6-hexanediol	1:6			85	[184]
$Zn(NO_3)_2 \cdot 6H_2O$	Choline chloride	1:1	107	8.0[b]	31.9	[57]
	$Et_2EtOHNHCl$	1:1	163	7.8[b]	31.6	[57]

(continued)

Table 3.11 (continued)

Salt	Other components	Ratio	η(25 °C)/ mPa s	$10^5\eta_0$/ mPa s	E_η/ kJ mol^{-1}	Ref.
$AlCl_3$	Urea	1:1	240			[218]
	Acetamide	1:1	60			[218]
$CrCl_3 \cdot 6H_2O$	Choline chloride	2:1	4800[a]		54.2[c]	[186]
	Urea	2:1	2600[a]			[186]
$CaCl_2 \cdot 6H_2O$	Choline chloride	2:1	78	9.0[b]	5.35	[185]
K_2CO_3	Ethylene glycol	1:6	166	0.263	77.6	[219]
	Glycerol	1:4	16,520		44.5	[219]
KSCN	Acetamide	1:3	122	[d]		[189]
	Caprolactam	1:3	8984	[d]		[189]
NH_4SCN	Acetamide	1:3	57	[d]		[189]
	Caprolactam	1:3	1322	[d]		[189]
	Urea	2:3	67	[d]		[189]
$MePr_2MorBr$[e]	Water	1:4	27	6.20	32.1	[220]
MeBuMorBr[e]	Water	1:4	33	3.60	33.9	[220]
MePeMorBr[e]	Water	1:3.5	104	0.55	41.04	[220]
MePePipBr[e]	Water	1:3	58	0.66	39.6	[220]
Proline	Glycolic acid	1:1	8080			[113]
	Malic acid	1:3	15,100			[113]
Menthol	Benzoic acid	3:1	44	17.8	27.6	[221]
	Phenylacetic acid	3:1	30	12.0	13.7	[221]
	Ibuprofen	3:1	80	0.88	28.2	[221]

[a] At 20 °C

[b] η_0/mPa s (not $10^5\eta_0$)

[c] Ref. [44]

[d] The full VFT expression is needed

[e] Mor = morpholinium, Pip = piperidinium

3.4.2 *Electric Conductivity*

The specific electrical conductivity of conventional deep eutectic solvents increases greatly with increasing temperatures and generally follows the Vogel–Fulcher–Tammann (VFT) expression:

$$\ln\left(\kappa/1\text{mS cm}^{-1}\right) = A_\kappa + B_\kappa/(T - T_{0\kappa}) \tag{3.14}$$

where B_κ is a negative quantity. In many cases, however, the temperature dependence follows the Arrhenius expression, wherein Eq. (3.14) $T_{0\kappa} = 0$. The specific conductivities of the conventional deep eutectic solvents at 25 °C are shown in Table 3.12 along with the parameters of the VFT expression, A_κ, B_κ, and $T_{0\kappa}$. The coefficient B_κ represents the activation energy for the conductivity, $-B_\kappa = E_\kappa/R$. The molar conductivities of the deep eutectic solvents are obtained by multiplication of the specific conductivities by the molar volumes: $\Lambda = \kappa V = \kappa M/\rho$ (see Table 2.1 for M values and Table 3.4 for ρ values).

Considerably less information is available regarding the specific conductivities of deep eutectic solvents based on salt hydrate/ice combinations. The data for these deep eutectic solvents at room temperature are essentially the conductivities of concentrated aqueous solutions, whereas most literature data deal with dilute solutions and the infinite dilution molar conductivities. Information regarding the electrical conductivity of concentrated solutions of some lithium salts pertaining to their uses in batteries is available [55, 56] but does not apply to salts forming deep eutectic solvents. Still, information is available for some of the relevant solutions at the molalities m pertaining to the eutectic compositions at 25 °C, as shown in Table 3.13. Some data had to be converted to the molar concentration $c = m\rho/(1 + mM_{\text{anhyd}})$ of the eutectic, where M_{anhyd} is the molar mass of the anhydrous salt, and ρ and M_{anhyd} are expressed in terms of kg dm^{-3} and kg mol^{-1}. The data are then inter- or extrapolated in second power polynomials of the reported κ or Λ in the variables m or c, as the cases may be.

The Walden product of the molar conductivity and the viscosity has been discussed for electrolyte solutions in a variety of solvents. Abbott et al. [10] pointed out that in the case of deep eutectic solvents the Walden product is inversely proportional to the radius of the anion of the hydrogen bond accepting component associated with the hydrogen bond donating component (pertaining to carboxylic acids). However, the product of the conductivity with the fluidity, which is the inverse of the viscosity, is more informative in the case of ionic liquids and deep eutectic solvents that are themselves the solvents. These products are compared with the corresponding products of aqueous KCl solutions that are considered to be completely ionically dissociated, for the estimation of the degree of ionic dissociation of room temperature ionic liquids or deep eutectic solvents. Plots of ln Λ against $\ln(\eta^{-1})$ of individual deep eutectic solvents over a certain temperature range were shown by Bahadori et al. [57], Cardellini et al. [58], Abbott et al. [59], and Rengsti et al. [60]. Examples of such plots are shown in Fig. 3.5, where values above the straight line denote ionic liquids with full ionicity, those below the line are partly ionically associated.

3.4.3 Self-diffusion

Another transport property of deep eutectic solvents that ought to be known is the self-diffusion of the three components making up the deep eutectic solvents: those of the cation and anion of the hydrogen bond accepting ingredient and that of the hydrogen bond donating ingredient. Such information is obtained from NMR

Table 3.12 The specific electrical conductivity, κ, of deep eutectic solvents at 25 °C and parameters for the VFT correlation expression

DES HBA	DES HBD	Ratio	κ/mS cm^{-1}	A_κ	B_κ	$T_{0\kappa}$/K	E_κ/kJ mol^{-1}	Ref.
Choline Cl	Urea	1:2	0.199[b]					[222]
	Urea	1:2	2.31[c]					[57]
	Trifluoroacetamide	1:2	2.48					[57]
	Trifluoroacetamide	1:2	2.86[b]					[222]
	Ethylene glycol	1:2	7.61[a]					[223]
	Ethylene glycol	1:2	7.33					[224]
	Ethylene glycol	1:2	0.64	0.618	−744	159	−6.09	[148]
	Glycerol	1:2	1.047[a]					[223]
	Glycerol	1:2	1.75					[224]
	Glycerol	1:2	1.02	5.3×10^4	−3238	0	−26.92	[148]
	Triethylene glycol	1:2	1.41					[225]
	Triethylene glycol	1:3	1.78					[226]
	1:4-butanediol	1:4	1.606[a]					[223]
	Phenol	1:3	3.14					[11]
	o-cresol	1:3	1.21					[11]
	Xylitol	1:1	1.15	1063	−1107	136	−9.20	[227]
	Phenylacetic acid	1:2	0.48					[10]
	Phenylpropanoic acid	1:2	0.32					[10]
	Oxalic acid	1:1	0.42					[10]
	Oxalic acid	1:1	1.88	13.27	−3708	0	−30.83	[57]
	Malonic acid	1:1	0.88					[10]
	Malonic acid	1:1	0.91	16.35	−3724	0	−30.96	[57]
	Levulinic acid	1:2	0.81	536	−720	187	−5.99	[202]
	$Zn(NO_3)_2 \cdot 6H_2O$	1:1	9.28	9.07	−1989	0	−16.54	[57]

(continued)

Table 3.12 (continued)

DES HBA	DES HBD	Ratio	κ/mS cm^{-1}	A_κ	B_κ	$T_{0\kappa}$/K	E_κ/kJ mol^{-1}	Ref.
	Water	1:1.6	1.76	9.02		0	−20.87	[228]
Acetylcholine Cl	Urea	1:2	0.017^b					[222]
	Levulinic acid	1:2	0.67	1488	−1013	167	−8.42	[202]
Ethylammonium Cl	Urea	2:3	0.348^b					[222]
	Acetamide	2:3	0.688^b					[222]
	Trifluoroacetamide	2:3	0.390^b					[222]
Ethylammonium Br	Glycerol	1:2	1.99					[151]
Propylammonium	Glycerol	1:2	1.11					[151]
Butylammonium	Glycerol	1:2	0.88					[151]
Diethylethanolammonium Cl	Ethylene glycol	1:2	5.12					[224]
	Glycerol	1:2	0.75					[224]
	Glycerol	1:2	0.25					[226]
	Glycerol	1:2	0.78	8.6×10^4	−3482	0	−28.95	[148]
	Malonic acid	1:1	1.13	12.01	−3494	0	−29.05	[57]
	$Zn(NO_3)_2 \cdot 6H_2O$	1:1	7.05	9.07	−2094	0	−17.41	[57]
Tetraethylammonium Cl	Levulinic acid	1:2	1.05	248	−527	202	−4.38	[202]
Tetraethylammonium Br	Levulinic acid	1:2	0.98	266	−533	203	−4.43	[202]
Tetrapropylammonium Br	Ethylene glycol	1:3	2.89	1.493×10^4	−2545	0	−21.16	[153]
	Glycerol	1:3	0.249	1.890×10^6	−4724	0	−39.28	[153]
	Triethylene glycol	1:3	0.888	2.444×10^4	−3048	0	−25.34	[153]
Tetrabutylammonium Cl	Ethylene glycol	1:2	0.957	198	−820	134	−6.81	[174]
	PEG 400	1:2	0.124	13	−541	172	−4.50	[174]
	Propanoic acid	1:2	0.274	75	−672	169	−5.59	[174]

(continued)

Table 3.12 (continued)

DES HBA	DES HBD	Ratio	κ/mS cm^{-1}	A_κ	B_κ	$T_{0\kappa}$/K	E_κ/kJ mol^{-1}	Ref.
	Phenylacetic acid	1:2	0.091	38	−568	194	−4.72	[174]
	Levulinic acid	1:2	0.45	255	−805	171	−6.69	[202]
Tetrabutylammonium Br	Glycerol	1:4	0.123	1.3×10^6	−4822	0	−40.09	[148]
	Levulinic acid	1:2	0.22	138	−547	214	−4.55	[166]
Benzyltripropylammonium Cl	Ethylene glycol	1:3	0.87	302	−901	144	−7.49	[178]
	Glycerol	1:3	0.079	390	−970	184	−8.07	[178]
	Phenol	1:3	0.274	39.6	−372	222	−3.09	[178]
	Lactic acid	1:3	0.017	189	−783	214	−6.51	[178]
Trimethylsulfonium bis(trifluoromethylsulfonyl)imide	Formamide	1:1	16.20	398	−381	179	−3.17	[204]
	Trifluoroacetamide	2:1	7.86	699	−552	175	−4.59	[204]
Methyltriphenylphosphonium Br	Ethylene glycol	1:4	2.07	12.15	−1900	0	−15.80	[179]
	Glycerol	1:1.75	1.08	4.78×10^4	−3190	0	−2652	[179]
	Glycerol	1:3	0.060	$3.04\text{x}10^7$	−5978	0	−49.70	[148]
	Trifluoroacetamide	1:8	3.42	2124	−1917	0	−15.94	[179]
Allyltriphenylphosphonium Br	Glycerol	1:14	0.056	2.62×10^6	−5269	0	−43.81	[148]
	Diethylene glycol	1:4	1.405	1256	−2038	0	−16.95	[166]
	Triethylene glycol	1:4	0.739	7559	−2757	0	−22.93	[166]
	Triethyleneglycol	1:10	0.464					[225]
Benzyltriphenylphosphonium Cl	Ethylene glycol	1:3	0.50	1.0×10^{-32}	21642	0	+180.96	[179]
	Glycerol	1:5	0.02	6.9×10^{-4}	997	0	+8.29	[179]
	Glycerol	1:16	0.070	1.35×10^6	−5001	0	−41.58	[148]
	Triethyleneglycol	1:8	0.212					[225]
Li bis(trifluoromethylsulfonyl)imide	Urea	1:3.6	0.23					[229]

(continued)

Table 3.12 (continued)

DES HBA	DES HBD	Ratio	κ/mS cm^{-1}	A_κ	B_κ	$T_{0\kappa}$/K	E_κ/kJ mol^{-1}	Ref.
	Acetamide	1:4	1.07					[156]
	N-Methylacetamide	1:4	1.35	780	−852	164	−7.08	[122]
KSCN	Acetamide	1:3	5.35[b]			203		[181]
	Caprolactam	1:3	0.215[b]			224		[181]
NH_4SCN	Urea	2:3	2.05[b]			218		[181]
	Acetamide	1:3	15.6[b]			197		[181]
	Caprolactam	1:3	0.595[b]			212		[181]

[a] At 20 °C

[b] At 40 °C

[c] At 30 °C

Table 3.13 The specific electrical conductivity, κ, at 25 °C of deep eutectic solvents based on salt hydrate/ice eutectics

Salt	m_{eutectic}	κ/mS cm^{-1}	Ref.
$Al(NO_3)_2 \cdot 9H_2O$	3.12	0.150	[230]
$Ca(NO_3)_2 \cdot 4H_2O$	6.80	0.112, 0.068	[230]
$KOH \cdot H_2O$	17.01	0.441	[231]
$KF \cdot 4H_2O$	7.10	0.362, 0.305	[232, 233]
$LiClO_3 \cdot 3H_2O$	6.53	0.149	[234]
$LiClO_3 \cdot 3H_2O$	3.69	0.161	[233]
$LiNO_3 \cdot 3H_2O$	6.23	0.169, 0.168	[233, 235]
$LiI \cdot 2H_2O$	15.14	0.133	[233]
$MgCl_2 \cdot 6H_2O$	4.09	0.197, 0.141, 0.141	[213, 230, 236]
$Mg(NO_3)_2 \cdot 6H_2O$	5.29	0.115, 0.110	[230, 236]
$Mg(ClO_4)_2 \cdot 6H_2O$	6.23	0.061	[230]
$NiCl_2 \cdot 6H_2O$	5.07	0.124, 0.092	[236, 237]

measurements on the one hand and from molecular dynamics computer simulations on the other hand. The so far reported information is, however, confined to four choline chloride-based deep eutectic solvents only and is summarized in Table 3.14. The temperature dependence of the self-diffusion coefficient D_i (of the ith ingredient) followed the Arrhenius expression, when it was reported: $\ln D_{\mathrm{I}} = \ln D_{\mathrm{I}^\circ} + E_{\mathrm{D}}/RT$, where E_{D} is the activation energy for the diffusion. The

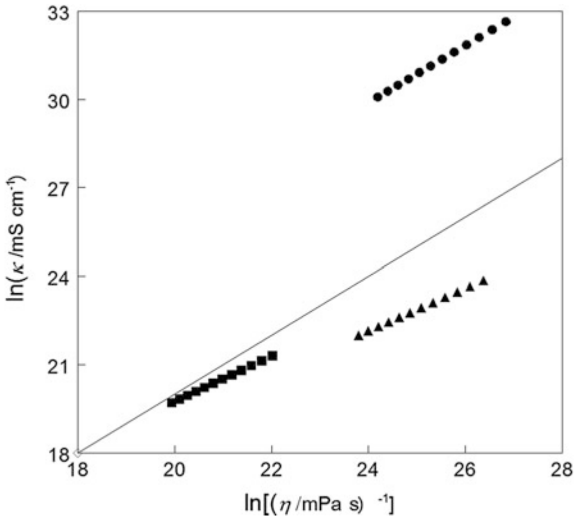

Fig. 3.5 Logarithmic plots of the specific conductivities against the fluidities of 1:1 choline chloride/malonic acid (circles), 1:2 choline chloride/trifluoroacetamide (squares), and 1:1 *N*,*N*-diethylethanolammonium chloride/malonic acid (triangles)

Table 3.14 The self-diffusion coefficients of the ingredients of choline chloride-based deep eutectic solvents at 25 °C

DES	Species	$10^{12}D$/m s^{-1}	E_D/kJ mol^{-1}	Method	Ref.
Reline	Cholinium$^+$	3.5	−47.8	NMR	[147]
	Urea	6.6	−45.0	NMR	[147]
Ethaline	Cholinium$^+$	26.2	−37.1	NMR	[147]
		18.1		Simulation	[30]
		17.6		Simulation	[70]
	Chloride$^-$	25.0		Simulation	[30]
		30.0		Simulation	[70]
	Ethylene glycol	47.7		NMR	[147]
		37.5		Simulation	[30]
		38.0		Simulation	[70]
Glyceline	Cholinium$^+$	3.8	−41.2	NMR	[238]
		3.8	−42.0	NMR	[147]
		3.0		Simulation	[30]
	Chloride$^-$	4.6		Simulation	[30]
	Glycerol	5.2	−42.0	NMR	[238]
		5.1	−41.9	NMR	[147]
		4.5		Simulation	[30]
Maline	Cholinium$^+$	0.64	−44.4	NMR	[147]
	Malonic acid	0.60	−33.6	NMR	[147]

rate of diffusion correlates with the free volume fraction, V_f, in the deep eutectic solvents:

$$V_f = [V-(V_{HBA} + V_{HBD})]/V \tag{3.15}$$

where $V = M/\rho$ is the molar volume of the deep eutectic solvents, and V_{HBA} and V_{HBD} are the molar volumes of the ingredients. All these volumes increase with the temperature, but the free volume appears to increase more, hence enabling increased diffusion.

3.4.4 Thermal Conductivity

A transport property of deep eutectic solvents for which hardly anything has been published so far is the thermal conductivity. One report [61] presents a few values for deep eutectic solvents at 20 °C: λ/W m^{-1} K^{-1} = 0.217 for 1:2 ethylammonium bromide/glycerol, 0.209 for 1:2 propylammonium bromide/glycerol, and 0.207 for 1:2 butylammonium bromide/glycerol, i.e., only slightly dependent on the alkyl chain length of the cation. Another report deals with choline chloride/glycerol deep eutectic solvents at 1:2. 1:3. And 1:4 molar ratios which have thermal conductivities at 25 °C (read from a figure) of λ/W m^{-1} K^{-1} = 0.15, 0.20, 0.35, respectively, increasing with the temperature [264]. These values are all smaller than that for glycerol itself, λ/W m^{-1} K^{-1} = 0.285, a fact attributed to the salts disrupting the dense hydrogen-bonded structure of the glycerol, therefore conducive to good thermal conductivity.

3.5 Other Physical Properties

3.5.1 Refractive Index

The refractive index n_D at the sodium D-line frequency of deep eutectic solvents has been reported in many publications as summarized in Table 3.15 for the values observed at 25 °C. The agreement between values of n_D reported for given deep eutectic solvents by several authors is fair, but it is doubtful whether a deep eutectic solvent can be identified by its refractive index value. The values of n_D for most of the deep eutectic solvents are between 1.46 and 1.51, but values larger than the latter were observed for deep eutectic solvents involving phenyl groups in either of the components. The temperature dependence of n_D is linear and has been reported in most of the references cited in Table 3.15. The molar refraction R_D of the deep eutectic solvents is according to the Lorentz–Lorenz expression:

$$R_D = (M/\rho)\left(n_D^2 - 1\right)/\left(n_D^2 + 2\right) = V\left(n_D^2 - 1\right)/\left(n_D^2 + 2\right) \qquad (3.16)$$

It reflects mainly their molar volumes because of the narrow range of the n_D values. The polarizability α of the deep eutectic solvents is obtained from the molar refraction as:

$$\alpha = (3/4\pi N_A)R_\infty \approx 3.92 \times 10^{-31}\left(R_D/\mathrm{cm}^3\,\mathrm{mol}^{-1}\right) \qquad (3.17)$$

The numerical coefficient pertains to the replacement of the infinite frequency molar refraction R_∞ by that of the commonly used one at the sodium D line, R_D. The polarizability of most of the deep eutectic solvents is therefore according to the above information $0.010 \le \alpha/\mathrm{nm}^3$ per particle ≤ 0.013, commensurate with that of ionic liquids.

The refractive indices and molar refractions of the concentrated aqueous solutions that constitute the eutectic salt hydrate/ice deep eutectic solvents have not been reported. The available data pertain to concentrations below those of the deep eutectic solvents and mostly to salts other than those yielding the deep eutectic solvents (except KF, $MgCl_2$, $Ca(NO_3)_2$ and a few others) [62]. The numerical values derivable from the Tammann–Tait–Gibson model applied to the refractive indices [63] do not help here either. However, given the fact that the polarizabilities of the constituting ions do not vary appreciably from their crystalline state to their aqueous solutions and given the additivity of the molar refractions of the ions and the water in the deep eutectic solvents, it is possible to calculate the molar refraction of the solution at 25 °C at the composition that forms the eutectic. The molar refractions of the ions R_{D^+} and R_{D^-} taken from [64] with that of water, $R_{DW} = 3.84\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$, yield the molar refraction of the solution of the salt hydrate $C_pA_q \cdot nH_2O$ at 25 °C, corresponding to the deep eutectic solvents at its eutectic mole fraction x_e:

$$R_{De} = x_e(pR_{D^+} + qR_{D^-} + nR_{DW}) + (1 - x_e)R_{DW} \tag{3.18}$$

The resulting molar refractions of these liquid deep eutectic solvents at room temperature, shown in Table 3.16, are much smaller than those of the deep eutectic

Table 3.15 The refractive index and molar refractivity of deep eutectic solvents at 25 °C

HBA	HBD	HBA: HBD	V/ cm^{3}mol	n_D	R_D/ cm^{3}mol	Ref.
Choline chloride	Urea	1:2	217.32[a]	1.5044[a]	64.39	[239]
	Urea	1:2	216.79	1.5117	65.02	[240]
	Ethylene glycol	1:2	236.11	1.4682	65.66	[241]
	Ethylene glycol	1:2	236.11	1.4611	64.80	[163]
	Ethylene glycol	1:2	236.11	1.4691	65.77	[242]
	Glycerol	1:2	271.80	1.4868	78.14	[241]
	Glycerol	1:2	271.80	1.4852	77.93	[163]
	Glycerol	1:2	271.80	1.4829	77.61	[48]
	Glycerol	1:2	271.80	1.4779	76.92	[243]
	Glycerol	1:2	271.80	1.4853	77.94	[242]
	1,4-butanediol	1:3	301.47	1.4656	83.43	[163]
	Fructose	2:1	387.33	1.5198	117.71	[88]
	Glucose	2:3	341.20	1.6669	126.99	[149]
	Levulinic acid	1:2	428.78	1.4619	117.81	[166]
	Levulinic acid	1:2	428.78	1.4690	119.41	[167]
	Lactic acid	1:9		1.4432		[240]
	Phenylacetic acid	1:2		1.526		[9]
	Phenylpropanoic acid	1:2		1.522		[9]
	Malonic acid	1:1	197.95	1.478	56.03	[9]
	Malonic acid	1:1	197.95	1.4871	56.94	[48]
	Malonic acid	1:1	197.95	1.4861	56.84	[240]
	Oxalic acid	1:1	182.41	1.4865	52.42	[48]
	Malic acid	1:1		1.4813		[240]
	Malic acid	1:1		1.4866		[242]
	Ethanolamine	1:7		1.4791		[150]

(continued)

Table 3.15 (continued)

HBA	HBD	HBA: HBD	V/ cm^{3}mol	n$_D$	R_D/ cm^{3}mol	Ref.
Acetylcholine Cl	Levulinic acid	1:2	464.69	1.4580	126.80	[166]
Ethylammonium Br	Glycerol	1:2	228.40	1.497	66.83	[151]
Propylammonium Br	Glycerol	1:2	244.13	1.495	71.19	[151]
Butylammonium Br	Glycerol	1:2	261.59	1.492	75.89	[151]
Me_3NHBr	Levulinic acid	1:2	399.20	1.4502	107.33	[166]
$Et_2(HOEt)NHCl$	Ethylene glycol	1:2	252.84	1.4650	67.97	[163]
	Ethylene glycol	1:2	252.84	1.4677	70.25	[159]
	Glycerol	1:2	303.34	1.4853	27.28	[33]
	Glycerol			1.4856		[172]
Et_4NCl	Levulinic acid	1:2	469.92	1.4326	129.33	[166]
Et_4NBr	Levulinic acid	1:2	475.90	1.4711	133.05	[166]
Pr_4NBr	Ethylene glycol	1:4	453.78	1.4677	126.07	[153]
	Glycerol	1:3	449.96	1.4872	129.46	[153]
	Triethylene glycol	1:3	795.01	1.4747	223.71	[153]
Bu_4NCl	Ethylene glycol	1:3	452.24	1.4635	124.67	[12]
	Ethylene glycol	1:2	406.53	1.4661	112.53	[174]
	Propylene glycol	1:2		1.4710		[174]
	Glycerol	1:5	646.73	1.4768	182.67	[12]
	Triethylene glycol	3:1		1.4848		[12]
	Propanoic ac	1:2	381.01	1.4554	103.45	[174]
	Phenylacetic acid	1:2	529.01	1.5082	157.75	[174]
	Levulinic acid	1:2	607.47	1.4561	165.17	[166]
	Serine	8:1		1.4813		[155]
	Threonine	9:1		1.4852		[155]
	Methionine	11:1		1.4824		[155]
Bu_4NBr	Levulinic acid	1:2	611.32	1.4696	170.44	[166]
	Ethanolamine	1:4		1.4881		[150]
BenzylMe3NCl	*p*-toluenesulfonic acid	1:1	445.30	1.5465	141.11	[177]
	Oxalic acid	1:1	230.92	1.5174	69.91	[177]
	Citric acid	1:1		1.4642		[177]
BenzylEt3NCl	*p*-toluenesulfonic acid	1:2		1.5470		[89]
	Oxalic acid	1:1		1.5156		[89]
	Citric acid	1:1		1.5307		[89]
BenzylPr3NCl	Ethylene glycol	1:3	430.01	1.4965	164.53	[178]
	Glycerol	1:3	483.31	1.5036	186.87	[178]
	Phenol	1:3	522.41	1.5471	214.52	[178]

(continued)

Table 3.15 (continued)

HBA	HBD	HBA: HBD	V/ cm^3mol	n_D	R_D/ cm^3mol	Ref.
	Lactic acid	1:3	483.50	1.4926	183.92	[178]
Bu_4PBr	Ethylene glycol	1:2		1.4872		[244]
$MePh_3PBr$	Ethylene glycol	1:4	491.20	1.5530	157.19	[163]
	Ethylene glycol	1:4	491.20	1.5584	158.45	[179]
	Glycerol	1:1.75	420.42	1.5677	137.48	[179]
	Glycerol	1:3	488.46	1.4589	133.51	[163]
	Triethylene glycol	1:5	934.29	1.5178	283.02	[163]
	Trifluoroacetamide	1:8		1.4834		[179]
	Ethanolamine	1:8		1.5024		[150]
$AllylPh_3PBr$	Diethylene glycol	1:4		1.5430	42.52	[182]
	Triethylene glycol	1:4		1.5297	51.18	[182]

[a] At 30 °C

solvents based on organic components shown in Table 3.15. This is due to the large water content of the salt hydrate/ice-based deep eutectic solvents, because of the small value of the molar refraction of the water, R_{DW}, noted above. Given the large molar volumes V of the salt hydrate/ice-based deep eutectic solvents presented in Table 3.5, inversion of the Lorentz–Lorenz expression (3.16) then yields quite low values of the refractive indices of these solutions: $n_D = [V + 2R_D)/(V - R_D)]^{1/2}$, also shown in Table 3.16.

3.5.2 *Permittivity and Susceptibility*

Hardly anything has been reported regarding the dielectric permittivity and the magnetic susceptibility of deep eutectic solvents. These mixtures, being highly ionic, should cause some difficulties concerning the measurement of their static permittivity, and indeed only estimates have been reported. The value $\varepsilon_0 = 14.34$ was estimated [65] for Reline (1 choline chloride: 2 urea) at 25 °C, increasing with the temperature, contrary to the behavior of common organic solvents. Values in the range $12.8 \leq \varepsilon_0 \leq 29.4$ at 20 °C were estimated for 1:4 molar ratios of salts with acetamide (the salts are LiBr, $LiNO_3$, $LiClO_4$, $NaClO_4$, NaSCN, and KSCN). These estimated values are considerably smaller than those of acetamide at its melting point, $\varepsilon_0 \sim 64$ at 81 °C [66].

The magnetic susceptibility of deep eutectic solvents appears not to have been reported. Except when paramagnetic ions are involved, the magnetic susceptibility should be additive and prorated for the diamagnetic susceptibilities of the ingredients of the deep eutectic solvents. For common organic solvents, the molar volume diamagnetic susceptibility is proportional to the molar refraction:

Table 3.16 The molar refractivity of the aqueous salt hydrate-based deep eutectic solvents at 25 °C and their derived refractive indices

Salt hydrate	$x_e(\text{salt} \cdot n\text{H}_2\text{O})$	R_{De}	n_{De}
$Al(NO_3)_3 \cdot 9H_2O$	0.36	25.74	1.265
$CaBr_2 \cdot 6H_2O$	0.59	30.42	1.366
$Ca(NO_3)_2 \cdot 4H_2O$	0.38	16.66	1.127
$Ca(ClO_4)_2 \cdot 6H_2O$	0.39	21.82	1.119
$Co(NO_3)_2 \cdot 6H_2O$	0.42	21.53	1.150
$FeCl_3 \cdot 6H_2O$	0.36	21.23	1.113
$KF \cdot 4H_2O$	0.39	10.25	1.101
$KOH \cdot H_2O$	0.38	6.64	1.134
$K_2HPO_4 \cdot 6H_2O$	0.40	17.60	1.257
$LiCH_3CO_2 \cdot 2H_2O$	0.17	6.87	1.035
$LiClO_3 \cdot 3H_2O$	0.32	10.19	1.082
$LiClO_4 \cdot 3H_2O$	0.21	8.15	1.039
$LiI \cdot 2H_2O$	0.45	29.27	1.486
$Mg(CH_3CO_2)_2 \cdot 4H_2O$	0.31	15.79	1.082
$MgBr_2 \cdot 6H_2O$	0.38	20.17	1.125
$MgCl_2 \cdot 6H_2O$	0.34	16.00	1.090
$Mg(NO_3)_2 \cdot 6H_2O$	0.40	19.58	1.126
$Mg(ClO_4)_2 \cdot 6H_2O$	0.44	23.22	1.120
$MnCl_2 \cdot 4H_2O$	0.44	17.92	1.190
$Mn(NO_3)_2 \cdot 6H_2O$	0.45	23.32	1.202
$NaCH_3CO_2 \cdot 3H_2O$	0.35	11.61	1.099
$NaOH \cdot H_2O$	0.19	4.85	1.046
$NiCl_2 \cdot 6H_2O$	0.39	18.68	1.132
$Ni(NO_3)_2 \cdot 6H_2O$	0.41	20.93	1.130
$Zn(NO_3)_2 \cdot 6H_2O$	0.41	20.84	1.138

$$-\chi/10^{-6}\mathrm{cm}^3\,\mathrm{mol}^{-1} = 2.46 \times 10^{-5}\left(R_D/\mathrm{cm}^3\,\mathrm{mol}^{-1}\right) \tag{3.19}$$

and may, thus, be derived from the entries in Table 3.15 for the deep eutectic solvents based on organic ingredients.

3.6 Chemical Properties

3.6.1 Liquid Structure

The liquid structure of deep eutectic solvents has received little attention, and whatever was reported was just recently. Extended X-ray absorption fine structure (EXAFS) has been applied for the study of the liquid structure of room temperature ionic liquids, but required a metal atom to be a part of the ions constituting the ionic liquid [67]. Although several classes of deep eutectic solvents do incorporate a metal atom in the binary mixtures, EXAFS appears so far not to have been applied to the investigation of their liquid structures, although it has been applied to metal salt solutes in them.

Molecular dynamics computer simulations have been applied to mixtures of choline chloride and urea by Sun et al. [68]. In order to accommodate urea molecules, most chloride anions are positioned near hydrogen atoms associated with the oxygen atoms of the cations. The distribution of other cations around the given cation becomes very disordered, and other cations move farther from a given cation, a tendency which disrupts the long-range ordered structure of choline chloride. It was concluded that at the ratio of 2 urea per 1 salt unit (Reline), the cation–anion, cation–urea, and anion–urea interaction energies are only modest, conducive to the low melting point of the eutectic mixture. A more recent molecular dynamics study of the bulk structure of Reline was reported by Kaur et al. [69].

An improved force field was employed by Ferreira et al. [70] in the molecular dynamics study of the structure of Ethaline (1:2 choline chloride/ethylene glycol) over a wide temperature range (25–100 °C). The average coordination number of the chloride was 4 at all temperatures. Most of the hydrogen bonds existed among the ethylene glycol molecules themselves ($\sim 50\%$) and from these to the chloride anion ($\sim 25\%$). A molecular dynamics simulation was also applied by Shen et al. [71] to the deep eutectic solvent consisting of choline iodide and glycerol at the 1:3 molar ratio. The main interest in that study was the behavior of the deep eutectic solvent ingredients near the walls of nanotubes in which the deep eutectic solvents were confined, but some attention was directed also to the bulk of the deep eutectic solvent (at 60 °C). Further molecular dynamics studies of the hydrogen-bonded structures of choline chloride-based deep eutectic solvents are those of Perkins et al. [30], dealing with Reline, Ethaline, Glyceline, and Maline, and of Monhemi et al. [72] dealing with Reline. The first of these studies confirmed the hydrogen bonding between the chloride anion and the hydrogen bond donating component, but indicated also interactions between the polyol molecules and in the case of Maline also between the malonic acid and the hydroxyl group of the choline [30]. The other study showed that in the case of Reline the urea is strongly bound to the chloride anion and therefore does not exhibit its usual denaturing effect on a protein (lipase enzyme) [72]. Molecular dynamics was applied to the X-ray and neutron scattering data of a deep eutectic solvent comprising lithium perchlorate as the hydrogen bond accepting component and acetamide and propionamide as the hydrogen bond donating components. Nanoscale spatial heterogeneity was found for these solvents [73]. First-principle molecular dynamics was applied to Reline, finding micro-heterogeneous domains in the liquid with the formation of preferred hydrogen-bonded aggregates [74].

Neutron diffraction was applied to the Reline deep eutectic solvent by Hammond et al. [75], employing deuteron/proton substitution do obtain the partial structure factors and partial radial distribution functions after application of empirical potential structure refinement methods. The anticipated three-dimensional hydrogen-bonded network was revealed, involving not only urea but also the choline hydroxyl group acting as hydrogen bond donors. Neutron scattering and broadband dielectric spectroscopy were used on Glyceline, which has a much smaller viscosity than glycerol. The glycerol hydrogen-bonding network dominates the structure and the collective dynamics of Glyceline [76]. Two-dimensional Fourier transform infrared spectroscopy was applied to deep eutectic solvents with trifluoroacetamide as the hydrogen bond donating component and various hydrogen bond accepting components: chlorides of choline, chlorocholine, tetramethyl-, tetraethyl-, and benzyltrimethylammonium cations. Microheterogeneity was found for all these liquids, increasing as the symmetry of the cation diminishes [77].

3.6.2 Solvatochromic Indices

Information regarding the chemical properties of deep eutectic solvents is available from results of using various solvatochromic probes. Their use is based on the premise that suitably selected probes act as stand-ins for more general solutes, the solvent properties concerning which are to be ascertained. The absorption (sometimes fluorescence) spectra of the solvatochromic probes are generally measured at 25 °C. The polarity of the deep eutectic solvents is probed by means of the Dimroth–Reichardt betaine 1,6-diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, the absorption peak of which is noted as $E_T(30)$. Its normalized value, E_T^N, is defined as

$$E_T^N = \left[E_T(30)(\text{solvent}) - E_T(30)\left(\text{Si}(\text{CH}_3)_4\right)\right] / \left[E_T(30)(\text{water}) - E_T(30)\left(\text{Si}(\text{CH}_3)_4\right)\right] \quad (3.20)$$

Values of E_T^N of several commonly used deep eutectic solvents: Reline, Ethaline, and Glyceline [78–80] are shown in Table 3.17. In strongly acidic deep eutectic solvents, a variant probe, $E_T(33)$, based on 2,5-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate, had to be used, related to the more usual probe as $E_T(30) = 0.9953\, E_T(33) - 8.11$ [81].

Other indices are the Kamlet–Taft π^* that measures the combined polarity and polarizability of solvents, α that measures their hydrogen bond donation ability, and β that measures their hydrogen bond acceptance ability. These were obtained by the use of the probes 4-nitroaniline and *N*,*N*-diethyl-4-nitroaniline in the deep eutectic solvents, combined with their $E_T(30)$ values. The values had to be read from a figure [79, 80, 82], to within ±0.02 units, and are shown in Table 3.17 too. Somewhat differing numerical values were reported in [83], where the deep eutectic solvents contained a small amount of water. Wrong expressions were used in [84] for obtaining the π^* and β values for Reline, so values disagreeing with those in Table 3.17 resulted. The Catalan indices *SP* for polarizability, SdP for dipolarity, SA for acidity, and SB for basicity [85] are also shown in Table 3.17 for these three deep eutectic solvents, Reline, Ethaline, and Glyceline. Nile Red was used in [86]

Table 3.17 Solvatochromic indices of commercially available choline chloride-based deep eutectic solvents

Index	Reline	Ethaline	Glyceline
E_T^N	0.81 [78]	0.82 [78]	0.84 [78]
	0.84 [83]	0.82 [83]	0.85 [83]
	0.81 [81]	0.83 [81]	0.84 [81]
π^*	1.21 [226]	1.16 [226]	1.18 [226]
	1.19 [83]	1.11 [83]	1.16 [83]
	1.14 [81]	1.07 [81]	1.11 [81]
α	0.65 [82]	0.82 [82]	0.78 [82]
	0.86 [83]	0.90 [83]	0.89 [83]
	1.42[a] [81]	1.47[a] [81]	1.49[a] [81]
β	0.48 [82]	0.55 [82]	0.55 [82]
	0.56 [83]	0.64 [83]	0.54 [83]
	0.50 [81]	0.57 [81]	0.52 [81]
SP	0.88 [85]	0.82 [85]	0.85 [85]
SdP	0.76 [85]	0.97 [85]	0.87 [85]
SA	0.67 [85]	0.55 [85]	0.59 [85]
SB	0.36 [85]	0.38 [85]	0.43 [85]

[a] Using 2,5-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's dye 33) as the probe

as a probe for measuring the polarity of deep eutectic solvents, resulting in values for 1:2 choline chloride/1,2-propanediol ~1:2 choline chloride/glycerol >1:1 choline chloride/malic acid, but these cannot be readily compared with the values of E_T^N or π^*.

The solvatochromic indices E_T^N (Eq. (3.20)) and the Kamlet–Taft π^*, α and β have also been determined for several other deep eutectic solvents, as shown in Table 3.18 [83, 87].

The values of these solvatochromic indices that have been reported for deep eutectic solvents are generally between those of methanol and water among common solvents and commensurate with those of room temperature ionic liquids. This means that these deep eutectic solvents are highly polar and polarizable, and have good hydrogen bond donation and acceptance abilities toward solutes.

3.6.3 Acidity/Basicity

Another quantity that characterizes the chemical solvent properties of deep eutectic solvents is their acidity. This quantity is measured by the use of pH probes and instruments calibrated with aqueous buffer solutions, hence "apparent pH" values result that cannot be assigned physical meanings beyond their empirical values. The reported data are for 25 °C are shown in Table 3.19. The measured apparent pH diminishes linearly with increasing temperatures [88], their temperature dependence

Table 3.18 Solvatochromic indices of deep eutectic solvents other than Reline, Ethaline, and Glyceline

Solvent HBA	Solvent HBD	E_T^N	Ref.	π^*	Ref.	α	Ref.	β	Ref.
Choline chloride	Acetic acid			1.10	[81]			0.53	[81]
	Glycolic acid	0.36	[196]	1.08	[81]	0.49^a	[196]^a	0.50	[81]
	Malic acid	0.79	[196]	1.08	[81]	1.39^a	[196]^a	0.42	[81]
	Levulinic acid	0.35	[196]	1.00	[81]	0.51^a	[196]^a	0.57	[81]
$Et_4N^+Cl^-$	Butanoic acid			0.92	[87]	0.99	[199]	0.76	[87]
	Hexanoic acid			0.86	[87]	0.97	[199]	0.85	[87]
	Octanoic acid			0.81	[87]	0.96	[199]	0.87	[87]
$Pr_4N^+Cl^-$	Butanoic acid			0.93	[87]	0.94	[199]	0.84	[87]
	Hexanoic acid			0.85	[87]	0.91	[199]	0.92	[87]
	Octanoic acid			0.80	[87]	0.90	[199]	0.96	[87]
$Pr_4N^+Br^-$	Butanoic acid			0.93	[87]	1.07	[199]	0.80	[87]
	Hexanoic acid			0.87	[87]	1.02	[199]	0.86	[87]
$Bu_{4-}N^+Cl^-$	Butanoic acid			0.86	[87]	0.92	[199]	0.99	[87]
	Hexanoic acid			0.81	[87]	0.90	[199]	1.02	[87]
	Octanoic acid	0.69	[196]	0.76	[81]	1.41^a	[196]	0.99	[81]
				0.69	[87]	0.94	[199]	1.19	[87]
	Decanoic acid	0.65	[196]	0.73	[81]	1.36^a	[196]	0.97	[81]
				0.86	[87]	0.85	[199]	1.28	[87]
	Dodecanoic acid	0.69	[196]	0.71	[81]	1.45^a	[196]	1.04	[81]
	Levulinic acid			1.06	[81]			0.82	[81]
$Bu_4N^+Br^-$	Butanoic acid			0.93	[87]	1.02	[199]	0.81	[87]
	Hexanoic acid			0.92	[87]	1.02	[199]	0.93	[87]
	Octanoic acid			0.84	[87]	0.98	[199]	1.09	[87]
	Decanoic acid			0.71	[87]	0.95	[199]	1.05	[87]

[a] Using 2,5-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's dye 33) as the probe

being about $-0.02\ K^{-1}$ on the average. A few of the deep eutectic solvents for which pH data have been reported are notably basic: potassium carbonate/glycerol is an obvious example, but choline chloride/urea and choline chloride/triethanolamine are further examples [249]. On the other hand, quite a number of deep eutectic solvents are highly acidic according to their apparent pH values being ≤ 1.0: those involving acids such as choline chloride/malonic acid and choline chloride/citric acid, diethylethanolammonium chloride/malonic acid, and benzyltrimethyl- and benzyltriethylammonium chloride/malonic, oxalic, and citric acids [89–91]. The same observation holds for deep eutectic solvents involving zinc nitrate hexahydrate as the hydrogen bond donating component. Other deep eutectic solvents are more nearly neutral, according to their apparent pH values shown in Table 3.19. Bromphenol blue was the indicator used for probing the Brønsted acidity of organic acids in Reline, Ethaline, and Glyceline [92]. The pK_a values in the deep eutectic solvents were 0.2–0.5 unit larger than in water (they are somewhat less strongly acidic).

The acidity of a carboxylic acid in a deep eutectic solvent (Ethaline) is less pronounced than in aqueous solutions, their pK_a being 0.2–0.5 units larger [93]. This was established by means of measurements with the bromphenol blue indicator and electrometrically with a glass electrode (yielding slightly smaller pK_a values). These acid/base properties should play important roles in the applications of deep eutectic solvents.

Another measure of the acidity of highly acid solvents is their Hammett acidity function, H_0, measured with an indicator such as 4-nitroaniline. For this indicator, the function is determined as

$$H_0 = 0.99 + \log(I_{\mathrm{NA}}/I_{\mathrm{NAH^+}}) \tag{3.21}$$

where I_{NA} and $I_{\mathrm{NAH^+}}$ are the light absorption intensities of the neutral and protonated forms of the indicator. The following values of H_0 obtained for deep eutectic solvents consisting of 1:2 choline chloride + hydrogen bond donating (HBD) component have been reported: for the following HBDs, they are as follows: urea 1.73 [84], *p*-toluene sulfonic acid 0.87, trichloroacetic acid 0.96, monochloroacetic acid 1.46, and propanoic acid 2.23 [91]. The smaller H_0 is, the more acidic is the solvent.

3.6.4 Hydrophilicity/Hydrophobicity

Deep eutectic solvents, being ionic, are generally highly hydrophilic and miscible with water. For some applications, immiscibility with water is desirable, in order to produce a biphasic system for the solvent extraction of certain solutes. For this purpose, hydrophobic deep eutectic solvents are needed, and several such solvents have been reported. Mixtures of certain quaternary ammonium salts as the hydrogen bond accepting component and decanoic acid as the hydrogen bond donating one at 2:1 molar ratios have been suggested for this purpose [94]. Lidocaine (*N*-(2,6-dimethylphenyl)-diethylacetamide) decanoate with decanoic acid also constitutes a hydrophobic deep eutectic solvent [95] that may be used for the extraction of metal ions from aqueous solutions. The hydrophobicity, measured as the water content in the deep eutectic solvents after mixing the deep eutectic solvents with water, increases in the hydrogen bond accepting series: tetrabutylammonium chloride < trioctylammonium chloride < trioctylammonium bromide < tetraheptylammonium chloride < tetraoctylammonium bromide < tetraoctylammonium chloride. Methyltrioctylammonium chloride produces hydrophobic deep eutectic solvents with a variety of alcoholic hydrogen bond donating agents [96] as well as acidic hydrogen bond donating agents [97]. No quantitative measures of the hydrophobicity of these deep eutectic solvents were reported, however. In other cases, hydrophobicity is counterproductive for the intended application in extraction experiments [98] with toluene as one of the phases and for levulinic acid as the hydrogen bond donating agent. For deep eutectic solvents with choline chloride, benzyldimethyl-ethanolammonium chloride, and tetrabutylammonium chloride as the hydrogen bond accepting agents, the last named is too hydrophobic relative to the others and is lost to the toluene phase. On the other hand, tetrabutylammonium chloride is not sufficiently hydrophobic to form water-stable deep eutectic solvents with aliphatic carboxylic acids up to dodecanoic acid, and dissolves in water in a biphasic system [99]. Tetraoctylammonium chloride (or bromide) with decanoic acid or perfluorodecanoic acid formed hydrophobic deep eutectic solvents that were modeled by perturbed-chain statistical associated fluid theory (PC-SAFT) with regard to carbon dioxide solubilities, but no further indication of their hydrophobicities was reported [100].

3.6.5 Gas Solubility

The solubility of gases in deep eutectic solvents, in particular of carbon and sulfur dioxides, is another characterization of their chemical properties. The capacity of the deep eutectic solvents for the absorption of a gas at a given temperature and partial pressure of the gas is of importance. It may be expressed as the molality of the gas in the deep eutectic solvents: moles gas per 1 kg deep eutectic solvent, as well as the Henry law constant k_H (the lower it is, the higher the solubility). These solubility values and the enthalpy of dissolution of the gas are characterizing quantities. The vapor pressure of the deep eutectic solvents is negligible with regard to the applied pressures; therefore, the gas phase is pure carbon dioxide at equilibrium with the saturated solution, and its fugacity is equated to its pressure, P_{gas}. Hence:

$$k_{H(x)} = \lim(x_{gas} \to 0)P_{gas}/x_{gas} \tag{3.22}$$

on the mole fraction scale and

$$k_{H(m)} = \lim(m_{gas} \to 0)P_{gas}/m_{gas} \tag{3.23}$$

on the molality scale. The units of $k_{H(x)}$ generally employed are MPa, those of $k_{H(m)}$ are MPa kg mol^{-1}, and interconversion between them is via the molar mass M/kg mol^{-1} of the deep eutectic solvents: $k_{H(x)} = k_{H(m)}/M$. The saturation molality of the gas in the deep eutectic solvents at a partial pressure of the gas of P_{gas} is obtained as $m = P_{gas}/k_{H(m)}$. The molar enthalpy of solution, $\Delta_{sol}H$, may serve for the evaluation of the solubility at other temperatures. $\Delta_{sol}H$ *is* obtained from:

$$\Delta_{sol}H/\mathrm{kJ\,mol^{-1}} = R(\mathrm{d}\ \ln k_{H(m)}/\mathrm{d}T^{-1}) \tag{3.24}$$

Table 3.19 The apparent pH of deep eutectic solvents at 25 °C

HBA	HBD	HBA: HBD	pH	Ref.
Choline chloride	Urea	1:2	10.22	[245]
	Trifluoroacetamide	1:2	2.36	[57]
	Triethanolamine	1:2	10.66	[57]
	Triethylene glycol	1:3	4.30	[246]
	Glycerol	1:2	7.63	[245]
	Glycerol	1:1	4.7	[90]
	Xylitol	5:2	4.3	[90]
	Fructose	2:1	6.75	[88]
	Fructose	5:2	4.7	[90]
	Glucose	2:1	7.00	[149]
	Glucose	5:2	5.3	[90]
	Sucrose	4:1	4.7	[90]
	Malonic acid	1:1	−0.3	[90]
	Citric acid	1:1	−0.3	[90]
	$Zn(NO_3)_2 \cdot 6H_2O$	1:1	1.00	[57]
$Et_2(HOEt)NHCl$	Triethylene glycol	1:1	1.42	[246]
	Malonic acid	1:1	0.98	[57]
	$Zn(NO_3)_2 \cdot 6H_2O$	1:1	0.52	[57]
$BenzylMe_3NCl$	*p*-toluenesulfonic acid	1:1	−1.39	[177]
	Oxalic acid	1:1	−0.93	[177]
	Citric acid	1:1	−0.06	[177]
$BenzylEt_3NCl$	*p*-toluenesulfonic acid	1:1	−1.5	[89]
	Oxalic acid	1:1	−0.8	[89]
	Citric acid	1:1	1.0	[89]
Pr_4NBr	Ethylene glycol	1:4	4.64	[153]
	Glycerol	1:3	5.96	[153]
	Triethylene glycol	1:3	5.22	[153]
$MePh_3PBr$	Ethylene glycol	1:4	6.30	[179]
	Glycerol	1:1.75	6.87	[179]
	Triethylene glycol	1:4	4.64	[246]
	Trifluoroacetamide	1:8	2.68	[179]
$BenzylPh_3PCl$	Triethylene glycol	1:8	5.20	[246]
$AllylPh_3PBr$	Diethylene glycol	1:4	1.40	[228]
	Triethylene glycol	1:4	1.25	[228]
	Triethylene glycol	1:10	1.92	[246]
K_2CO_3	Glycerol	1:5	13.24	[187]

Up to moderate pressures, ≤ 30 MPa, the pressure dependence of the saturation capacities, mole fractions, or molalities of the gas in the various deep eutectic solvents is linear. The solubility of the gas in the deep eutectic solvents diminishes as the temperature is increased in all the cases, as manifested in the negative molar enthalpies of solution of the gas. The deep eutectic solvent expands at a given temperature on absorption of the gas.

The solubility of carbon dioxide in deep eutectic solvents has recently been reviewed [101, 102] with some additional data [103–106]. It is commensurate with its solubilities in room temperature ionic liquids, which have been suggested as solvents for its removal from flue gases. The solubility of sulfur dioxide in deep eutectic solvents has also been reviewed in [101] with some additional data [107–110].

Little has been published regarding the solubility of other gases in deep eutectic solvents. The solubility of methane, hydrogen, carbon monoxide, and nitrogen in Reline was modeled by means of the NRTL and COSMO-RS models. The experimental data are available only in small-scale figures, showing the mole fraction of the gas in the saturated solution as a function of the pressure (above 0.6 MPa) at a given temperature [111].

The solubility of gases in deep eutectic solvents was modeled by means of several equations of state or modifications of them for deep eutectic solvents [74, 100, 106, 112–114].

A detailed description of the application of deep eutectic solvents for the removal of gases by their dissolution in them is presented in Sect. 5.5.

3.6.6 Electrochemical Properties

Electrochemical properties, including the applicable potential window width of deep eutectic solvents and the capacitance of double layers involving deep eutectic solvents, have been reported in relatively few publications. Cyclic voltammetry is generally employed for the determination of the electrochemical potential window (EPW) with the non-reacting glassy carbon working electrode. An extensive list of such windows for deep eutectic solvents based on various choline salts and diverse hydrogen bond donating agents was reported by Li et al. [115] and is shown in Table 3.20. For a given hydrogen bond donating component, methylurea, the widths become narrower in the sequence of choline salts $Cl^- > ClO_4^- > BF_4^- > Br^- \sim NO_3^- > I^-$. No generalization regarding the effect of the hydrogen bond donating component can be made on the other hand. There are, however, conflicting reports indicating much narrower potential windows for some of these deep eutectic solvents. The EPW of the 1:2 choline chloride/urea deep eutectic solvents (Reline) is relatively narrow, 2.4 V (−1.2 to +1.2 V vs. Ag reference) compared with other ionic liquids [116]. This window becomes narrower, diminishing from 2.7 V at 25 °C to 2.2 V as the temperature is increased to 90 °C [117]. When glassy carbon electrodes are used the potential windows are wider than when

Table 3.20 The electrochemical potential windows of choline salt-based deep eutectic solvents according to [115]

HBA anion	HBD	E_{anode}/V	$E_{cathode}$/V	EPW/V
Chloride	Urea	−2.75	1.54	4.29
	Methylurea	−3.06	1.66	4.72
	Ethylene glycol	−2.35	1.26	3.61
	1,4-butanediol	−2.57	1.33	3.90
	Glycerol	−2.21	1.38	3.59
	Xylitol	−2.67	1.66	4.33
	Oxalic acid	−0.92	1.24	2.16
	Malonic acid	−2.55	1.70	4.25
Bromide	Urea	−2.09	1.23	3.32
	Methylurea	−1.76	0.82	2.58
	Ethylene glycol	−1.35	0.77	2.12
	1,4-butanediol	−1.14	0.58	1.72
	Glycerol	−2.36	1.16	3.52
	Xylitol	−2.67	1.66	4.35
	Malonic acid	−2.38	1.03	2.41
Iodide	Urea	−0.89	0.36	1.25
	Methylurea	−1.73	0.36	2.09
	Ethylene glycol	−2.38	0.30	2.68
	Glycerol	−2.17	0.42	2.59
	Oxalic acid	−2.32	0.44	2.76
Nitrate	Methylurea	−1.76	0.76	2.52
Perchlorate	Methylurea	−2.49	2.04	4.53
Tetrafluoroborate	Methylurea	−1.66	2.03	3.69

platinum electrodes are used: for choline chloride-based deep eutectic solvents they are EPW= 2.64 V with 1:1 malonic acid, 2.10 V with 1:1 oxalic acid, 2.52 V with 1:2 triethanolamine, 2.02 V with 1:1 zinc nitrate hexahydrate, and 3.32 V with 1:2 trifluoroacetamide [57]. For *N*,*N*-diethylethanolammmonium chloride with 1:1 malonic acid, the window is 2.82 V and with 1:1 zinc nitrate hexahydrate, it is 2.42 V. Further EPW values for deep eutectic solvents were reported in [118]. Much wider potential stability windows were obtained for deep eutectic solvents based on lithium salts with *N*-methylacetamide (NMA). For the lithium hexafluorophosphate and the bis(trifluoromethanesulfonate)imide (LiTFSI) salts 1:4 NMA deep eutectic solvents, the window was 4.7 V and for the nitrate salt, it was 5.3 V [118]. However, electrochemical decomposition of choline chloride-based deep eutectic solvents has been noted [119] in long-term electrolysis experiments, contrary to short cyclic voltammetry ones, generally employed for the determination of the potential window. The decomposition (oxidation at a non-soluble anode) may lead to chlorinated and/or toxic volatile products, voiding the claim of “green” solvents regarding these deep eutectic solvents [54]. Caveat!

The double layer capacitance of 1:2 choline chloride/glycerol (Glyceline) has been measured at platinum, gold, and glassy carbon electrodes by cyclic voltammetry, being 7.8 μF cm^{-2} within 0.2 units [120]. With liquid mercury electrodes, the capacitance of 1:2 choline chloride-based deep eutectic solvents measured at the point of zero charge is $C/\mu\text{F cm}^{-2} = 51.2$ for urea (Reline), 32.9 for ethylene glycol (Ethaline), and 26.5 for 1,3-propylene glycol [121]. The 1:4 LiTFSI/NMA system could be charged at 2 V up to a specific capacitance of ca. 150 F g^{-1} [122]. Deep eutectic solvents produced from trimethylsulfonium bis(trifluoromethanesulfonate) imide with trifluoroacetamide or formamide could be charged at 2 V up to 214 or 357 F g^{-1} as electrochemical double layer capacitors [123]. An electrolyte consisting of 1:2 choline chloride/glycerol (Glyceline) had a specific capacitance of 78.7 F g^{-1} enhanced to 92.9 F g^{-1} by addition of 0.33 mol fraction γ-butyrolactone [124].

The behavior of deep eutectic solvents based on choline chloride and urea, glycerol, phenylacetic acid, malonic acid, and levulinic acid as hydrogen bond donation components under static and dynamic external electrical fields was studied by means of molecular dynamics simulations in [125]. Only moderate dipolar reorientation took place under the applied fields ($E < 2.5$ V nm^{-1}) because of the large intrinsic fields in these fluids.

3.7 Toxicity and Biodegradability

Deep eutectic solvents are generally claimed to be “green”, one attribute of which is their having very low toxicity, especially in comparison with common organic solvents and room temperature ionic liquids. The claimed low toxicity is not entirely true, and certain deep eutectic solvents have non-negligible toxicity for humans. This may have a deleterious effect when these are considered for large-scale industrial uses, but any existing toxicity may be beneficial for their antiseptic and therapeutic uses.

Hayyan and coworkers were the first to pose the question on whether deep eutectic solvents were benign or toxic [126] and then studied the cytotoxicity of these solvents [127–130] as did several other groups. Although Reline, Ethaline, Glyceline, and choline chloride/triethylene glycol deep eutectic solvents were found to be nontoxic toward four kinds of bacteria (both gram-positive and gram-negative ones), their cytotoxicity toward brine shrimps, a primitive aquatic arthropod found in lakes, was much larger than that of the individual components [126]. On the other hand, methyltriphenylphosphonium bromide-based deep eutectic solvents with ethylene glycol, triethylene glycol, and glycerol as the hydrogen bond donating components did have toxic effects against the abovementioned bacteria, in addition to their cytotoxicity toward brine shrimps [127]. The acute toxicity for mice of these four kinds of phosphonium salt deep eutectic solvents was found to be non-negligible and combined in vitro and in vivo toxicity profiles of deep eutectic solvents were carried out and contributed to potential therapeutic uses of them [128]. The cytotoxicity profiles of natural deep eutectic solvents, based on choline chloride with glucose, fructose, sucrose, glycerol, and malonic acid in the presence of water was investigated in [129] and the one with malonic acid proved to be the most cytotoxic. These solvents interact with the phospholipid cell membranes and their accumulation defines their cytotoxicity. The cytotoxicity of the first two of these solvents as well as one formed from diethylethanolammonium chloride and triethylene glycol was further studied in [130] with respect to their anticancer potential.

Deep eutectic solvents based on zwitterionic betaines were studied regarding their toxicity by Cardellini and coworkers. Trimethylglycine forms deep eutectic solvents that are liquid at room temperature with 2-furoic acid, phenylacetic acid, mandelic acid, and glycolic acid [58]. Their cytotoxicity toward eukaryotic model cells was evaluated and found to be due to their dehydrating activity, comparable to the low cell toxicity of calcium chloride. Similar results were found for deep eutectic solvents produced by camphoric acid and various betaines that have, however, low ionicity [131].

The toxicity of choline chloride-based deep eutectic solvents toward fungi and fish, using ethylene glycol, glycerol, urea, malonic acid, and two metal salts $ZnCl_2$ and $Zn(H_2O)_6(NO_3)_2$ as the hydrogen bond donating agents was tested in [132]. The acute oral toxicity test of Glyceline in rats showed it to be nontoxic (median lethal dose of 7.7 g kg^{-1}) [133]. This deep eutectic solvent might therefore be used as a carrier for the administration of drugs. The metal-containing solvents were more toxic than the others and Ethaline proved essentially harmless. In a subsequent study regarding toxicity toward fungi and fish, the solvents tested included also another acidic component, *p*-toluenesulfonic acid, which showed toxicity between those of metal-containing ones and those based on alcohols, sugars, or urea [134]. The deep eutectic solvents at their eutectic compositions showed toxicities different from those of their components or non-eutectic mixtures thereof, signifying that they might be treated as specific substance. The cytotoxicity toward fish cell lines and phytotoxicity (wheat) of solvents based on choline chloride with glycerol, glucose, and oxalic acid was tested in [135]. The former two exhibited low toxicity whereas the one with oxalic acid showed moderate toxicity. Additional deep eutectic solvents, using malic, citric, and lactic acids as well as fructose, xylose, and mannose were tested with fish cell lines, exhibiting low cytotoxicity [136]. Further tests with choline chloride-based deep eutectic solvents involving acetic, citric, lactic, and glycolic acids showed them to be “moderately toxic”, their toxicity being dominated by the concentration of the acid [137]. Deep eutectic solvents based on choline acetate were less toxic than the corresponding Reline, Ethaline, and Glyceline based on choline chloride toward bacteria, plant cells, and hydra [138]. Some aspects of the toxicity and biodegradability of choline-based deep eutectic solvents were discussed in [139].

The antiseptic and fungicidal aspects of the deep eutectic solvents may be considered an asset, providing that their toxicity toward higher organisms is minimal. Broad antiseptic effects of the 1:1 cholinium geranate/geranic acid (3,7-dimethyl-2,6-octadienoic acid) deep eutectic solvent against bacteria, fungi, and viruses was demonstrated in [140] and suggested for skin treatment. The nonionic deep eutectic solvents composed of 1:1 sucrose/citric acid and 1:1:1 fructose/glucose/malic acid were tested for their antimicrobial effects in photodynamic therapy upon dilution [141]. However, when biocatalysis in deep eutectic solvents by enzymes that are not isolated from but incorporated in viable microorganisms is desired, the cytotoxic properties of these solvents is a disadvantage. This could be overcome by a freeze-drying procedure, as had been applied in the case of *Escherichia coli* TG1.pPBG11 bacteria incorporated into Glyceline [93]. Maline was found to be effective for inhibiting the growth and β-lactamase production by *Bacillus cereus* EMB20 [142]. Selected issues related to the toxicity of deep eutectic solvents were reviewed in [143]. The question whether deep eutectic solvents are more toxic than their ingredient or less toxic depends on the individual solvents and has no general answer.

The biodegradability of deep eutectic solvents was studied in [132] and in [135], the conclusion is that they are generally biodegradable, but a dissenting opinion was published in [138], and the necessity to study this aspect further was voiced in [137].

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Chapter 4
Applications of Deep Eutectic Solvents

Since their advent in 2003, deep eutectic solvents have found applications in numerous fields where their properties as solvents, permitting the dissolution of a large variety of solutes, and their being "green", i.e., ecologically friendly as described in Chap. 1, gave them advantages over more conventional solvents. It is possible in the present chapter to present only examples of the numerous applications that have been proposed over less than a score of years that have passed since the first publication regarding the deep eutectic solvents. Deep eutectic solvents (among other neoteric ones) have recently been reviewed for their use as green and sustainable solvents in chemical processes [1].

An application that cannot be classified under the headings of the following sections nor under those in Chap. 5 is the preparation of solid composite electrolytes for lithium/lithium-ion batteries. The deep eutectic solvent comprises 1:4 lithium bis(trifluorometanesulfonyl)imide as the hydrogen bond acceptor and *N*-methylacetamide as the hydrogen bond donor. This liquid was mixed with 1:8.7 tetraethoxysilane and formic acid in a sol–gel process, to form the so-called eutectogel as the battery electrolyte that is thermally stable to 130 °C and electrochemically stable up to 4.8 V [2].

4.1 Applications as Reaction Media

The use of deep eutectic solvents as reaction media is predicated on their being able to dissolve the reactants and any catalyst that is to be used, on their not being consumed in the reaction, on the ability to recover the product(s) of the reaction, and on the ability to recycle the solvent and catalyst, if used. With these conditions in mind, deep eutectic solvents have been chosen due to their being inexpensive, readily produced, and readily (bio)degradable, i.e., being "green". When

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commercially available DESs have been used as reaction media, they are noted in the following by their commercial names, as referred to in Chap. 2: Reline, Ethaline, Glyceline, and Maline.

Several reports for the use of deep eutectic solvents in the synthesis of inorganic materials have been published, many of them under the heading of “ionothermal synthesis”. Metal oxides are soluble in DES based on choline chloride: Reline, Ethaline, and Maline [3]. The latter shows the largest solubility of metal oxides, being >0.5 mass% at 50 °C for V_2O_5, CrO_3, MnO, Mn_2O_3, FeO, and Co_3O_4, and >1.4 mass% for Cu_2O, CuO, and ZnO. Appreciable but lower solubilities are manifested in Maline by CoO, Fe_3O_4, V_2O_3, Fe_2O_3, and NiO. In Reline appreciable solubilities have V_2O_3, CrO_3, and ZnO, whereas in Ethaline the solubilities of metal oxides are generally small, except for Cu_2O and ZnO. The solutions have the metal ions complexed with chloride anions and may be used for the preparation of other complexes and compounds based on the metal ions. In a previous paper [4], solubilities at 50 °C of CuO, Fe_3O_4, and ZnO in Maline, and in choline chloride 1:1 with oxalic acid and 1:2 with phenylpropanoic acid were reported. When $CuCl_2{\cdot}2H_2O$ is dissolved in a series of DES (at 0.02 mol dm^{-3}), it forms transparent colored solutions ranging from yellow (in Ethaline) through yellowish-green (in Reline), blue (in Ethaline with added NH_3) to purplish blue (in Ethaline with added ethylenediamine) [5]. Lead oxide is added to the 3d elements dealt with above, and the solubilities of ZnO, Cu_2O, and PbO_2 in Reline at 60 °C, which are considerably larger than those of other metal oxides present in electric arc furnace dust, are described [6, 7] and this DES may be used for their processing.

Ionothermal synthesis of various inorganic materials in deep eutectic solvents that are liquid at room temperature has often been reported. A feature of the ionothermal synthesis is the structure directing ability of the eutectic solvent mixture, besides acting as the solvent. A list of such applications is presented in Table 4.1.

Eutectic mixtures based on choline chloride with various urea derivatives (1,3-dimethylurea, 2-imidazolone (1,2-ethyleneurea), and tetrahydro-2-pyrimidinone (1,3-propyleneurea)) have been employed for the production of aluminum phosphates [8], the urea derivative decomposed during the reaction and provided the template for the desired structure of the product. A layered gallium phosphate was prepared in an eutectic mixture consisting of choline chloride and imidazolidone [9] or tetrahydro-2-pyrimidinone [10] as a solvent and as a structure directing agent. Cobalt aluminophosphates were prepared by ionothermal synthesis in eutectic mixtures of choline chloride with succinic and glutaric acids (at 1:1 ratios) and with citric acid (at a 1:2 ratio) [11].

Novel vanadium fluorides and oxyfluorides were synthesized in a deep eutectic solvent based on choline chloride and 1,3-dimethylurea or 2-imidazolone (1,2-ethyleneurea) in the presence of hydrogen fluoride [12]. However, these template producing solvents are not proper deep eutectic solvents as defined in this book, since they are not liquid at room temperature and because a component of the solvent, the urea derivative, is consumed in the structure directing reaction. Only the eutectic formed from tetramethylammonium bromide and 1,3-dimethylurea,

Table 4.1 Ionothermal synthesis of inorganic materials in deep eutectic solvents

Deep eutectic solvent	Product	Ref.
Reline	MPO_4 (M = Mn, Fe, Co)	[295]
	Nanostructured nickel compounds	[296]
	Aluminum phosphate	[218]
	Cu(I) in chloride media	[297]
	Surface-modified silica particles	[298]
	Fe_2O_3 (haematite) nanospindles	[216]
	Fe_3O_4 magnetic nanoparticles	[299]
	Mg–A; layered double oxides	[300]
	$CoFe_2O_4@B_2O_3–SiO_2$	[28]
Ethaline	Nickel phosphide nanoparticles	[301]
	Nickel phosphide coatings	[302]
	Nickel oxide nanostructured films	[218]
Maline	Iron(III) hexacyanoferrate nanospheres	[251]
Choline chloride/oxalic acid	Oxalate-bridged lanthanide(III) chains	[303]
	Oxalate-bridged gadolinium polymers	[304]
Choline chloride/diethylene glycol	Zinc oxide nanoparticles	[224]
Choline chloride/pyrazole	Tin(II) phosphite alone and Mn-doped	[305]
Choline chloride/imidazolidone	Gallium phosphate, layered	[9]
Ethylammonium chloride/oxalic acid	Zirconium phosphate open framework	[306]
Me_4NCl/urea	Zirconium fluorophosphates	[307]
Me_4NCl/1,6-hexanediol	Sodalite, zeolite ZSM-39	[308]
Et_4NCl/pentaerythritol	Silicalite-1	[308]
Pr_4NBr/pentaerythritol	Silicalite-1, zeolite ZSM-5	[308]
Pr_4NBr/oxalic acid	Layered α-$Zr(HPO_4)_2 \cdot H_2O$	[306, 309]

among those tested in the study [8], has a melting point ≤ 25 °C and is a proper deep eutectic solvent.

There is an extensive list of reports dealing with the production of organic compounds in deep eutectic solvents, a subject that has also been reviewed in several publications [13–23]. These all stress the “green” aspect of the deep eutectic solvents: environmental friendliness, sustainability, biodegradability, as well as their direct utility in metal-catalyzed or non-catalyzed organic reactions. Biocatalysis by means of enzymes was another feature that was pointed out in these reviews [14, 16] and elsewhere [24–26].

The reactions that were reported as using deep eutectic solvents were Lewis acid-catalyzed dehydration of carbohydrates, hydrogenation of olefins, isomerization, cycloaddition to terminal azides and alkynes, and cross-coupling [16] as well as replacement, condensation and oxidation, and reduction reactions [18]. The synthesis of heterocyclic compounds as well as esterification and halogenation reactions in deep eutectic solvents featured in [23]. The hydrogen bond accepting (HBA) components of the deep eutectic solvents dealt with in these reviews included choline chloride, ethylammonium chloride, and betaine (trimethylglycine) hydrochloride and the commonly used hydrogen bond donating (HBD) components included urea, ethylene glycol, glycerol, oxalic acid, malonic acid, and lactic acid [17], but many other HBA and HBD agents have also been used in deep eutectic solvents for organic reactions.

Reline is featured in a majority of the detailed reports on the use of deep eutectic solvent that are summarized in Table 4.2, which are but a sampling of the existing relevant publications. Some special features in the use of deep eutectic solvents as reaction media for organic synthesis is the use of ultrasound [27, 28], highly acidic

Table 4.2 Examples of organic reactions in deep eutectic solvents

Deep eutectic solvent	Reaction/product	Ref.
Reline	Bromination of a substituted quinone	[310]
	N-arylphthalimide derivatives	[311]
	Amino acid dithiocarbamates	[312]
	Peptide synthesis, chymotrypsin-catalyzed	[39]
	Oxazole synthesis, ultrasound-assisted	[27]
	Tricyanovinylated aromatics	[40]
	Redox isomerization of allyl alcohols to carbonyls	[31]
	Imine and hydrobenzamide synthesis	[313]
	Butyl acetate, lipase-catalyzed	[41]
	Disubstituted isoxazoles and isoxazolines	[314]
	Substituted pyridines	[315]
	Stereoselective reactions	[35]
	Aminoimidazoles	[316]
	Stereoselective organocatalyzed reactions	[36]
	Enantioselective aldol reaction	[37]
	Regio- and stereoselective synthesis	[38]
	Peroxidation reactions	[42]
	Benzofused seven-membered heterocycles	[317]
	Dihydroquinazolinones, catalytic synthesis	[28]
	Crude heavy oil hydrogenation with MoO_3	[56]

(continued)

Table 4.2 (continued)

Deep eutectic solvent	Reaction/product	Ref.
Ethaline	Butyl acetate, lipase-catalyzed	[41]
	Peroxidation reactions	[42]
Glyceline	Butyl valerate, lipase-catalyzed	[13]
	N-arylphthalimide derivatives	[311]
	Biocatalyzed reactions, transesterification	[14]
	Peptide synthesis, chymotrypsin-catalyzed	[39]
	Redox isomerization of allyl alcohols to carbonyls	[40]
	Butyl acetate, lipase-catalyzed	[41]
	Stereoselective reactions	[35]
	Aminoimidazoles	[316]
	Stereoselective organocatalyzed reactions	[36]
	Enantioselective aldol reaction	[37]
	Peroxidation reactions	[42]
	Cycloisomerization of a terminal alkyne	[31]
Maline	*N*-arylphthalimide derivatives	[311]
	Butyl valerate, lipase-catalyzed	[13]
Choline chloride 1:1 fructose	Stereoselective reactions	[35]
	Stereoselective organocatalyzed reactions	[36]
Choline chloride 1:2 lactic acid	Redox isomerization of allyl alcohols to carbonyls	[31]
Choline chloride + levulinic, + oxalic, or + *p*-toluenesulfonic acids	Cellulose nanocrystal production	[30]
Choline chloride + xylitol or + isosorbide	Peptide synthesis, chymotrypsin-catalyzed	[39]
Ethylammonium chloride + acetamide	Butyl valerate, lipase-catalyzed	[13]
+ urea, + ethylene glycol, + glycerol	Peroxidation reactions, biocatalyzed	[42]
Betaine hydrochloride + glycerol	Biocatalyzed reactions, transesterification	[14]
Betaine monohydrate + glycerol	Interaction with palmitic acid	[15]
Benzyltrimethylammonium methylsulfonate + *p*-toluene sulfonic acid	Esterification of carboxylic acids with alcohols	[30]

media [29, 30], metal catalysis [16, 17, 19, 31–34], stereo- or enantioselectivity [35–38], and biocatalysis [20, 24, 39–43].

Catalysis by the deep eutectic solvents themselves or as enzyme-friendly media has been stressed in some further publications, where, for instance, *Candida* *antarctica* lipase A (CALA) and *Escherichia coli* TG1/pPBG11 are active in deep eutectic solvents [25, 44]. The activity, stability, and structure of the enzyme lactase from *Bacillus* HR03 in betaine-based natural deep eutectic solvents were studied in [26].

The eutectic solvent prepared from 1:2 choline chloride with zinc chloride is the solvent as well as the catalyst for transesterification reactions for biodiesel production [45]. It was also effective for the cycloaddition reaction of organic nitriles with sodium azide [46] and for acylation of secondary alcohols, phenols, and naphthols [47]. Deep eutectic solvents consisting of choline chloride with urea, glycerol, or *p*-toluene sulfonic acid act as both solvents and catalysts [48]. Deep eutectic solvents consisting of benzyltrimethylammonium chloride with *p*-toluene sulfonic acid, citric acid, or oxalic acid act as both solvent and catalyst in the esterification of acetic acid with butanol [49] or with 2-ethylhexanol [50]. Selective alkylation of imines and quinolines with organolithium reagents could be carried out fast at room temperature and in the presence of air in Glyceline solvent [51].

Deep eutectic solvents are also used for the preparation of heterogeneous catalysts used in catalytic reactions. Metallic gold with a large surface area is featured in several publications. Gold nanowire networks were prepared in Reline and in Ethaline, and were used in the catalytic reduction of 4-nitroaniline [52]. Monodisperse gold microparticles were prepared in Maline and used in the reduction of 4-nitrophenol [53]. Gold nanoparticles on a titania support were prepared in Reline and used in the selective hydrogenation of butadiene as catalysts [54]. Gold nanofoams were prepared in Ethaline and used in the reduction of aromatic nitro-compounds [55]. Molybdenum oxide catalyst for the upgrading of heavy crude oil was dissolved in Reline [56]. Reline was used for the preparation of nickel and nickel nitride nanoparticles used in catalytic reactions [57]. A sulfonic acid functionalized nanocatalyst based on a magnetic Fe_3O_4 on silica and titania surfaces was prepared in Reline [58]. A palladium catalyst with a pyridinophosphine ligand, usable in cross-coupling reactions, was successfully prepared in Reline [59]. A cross-dehydrogenative coupling reaction using copper oxide impregnated on magnetite as catalyst was carried out in Ethaline [60].

In those cases in which either the hydrogen bond accepting (HBA) or the hydrogen bond donating (HBD) component of the deep eutectic solvent is a monomer capable of polymerization, functional polymeric materials can result from free-radical polymerization, in this kind of solvent as well as of the solvent itself. An example of the monomeric HBA is choline methacrylate bromide at 2:1 with malonic acid and an example of the monomeric HBD is acrylamide at 1:2 with choline chloride forming the solvent [61]. Choline chloride was polymerized with methacrylic acid (1:2) while incorporating magnetite in order to produce a magnetic molecularly imprinted polymer for the selective recognition and separation of bovine hemoglobin [62]. Deep eutectic solvents were also used as reaction media for the production of molecularly imprinted polymers of which the solvent was not a monomer [63].

4.2 Biomass and Biodiesel Processes

Biomass from vegetation consists mainly of cellulose, with hemicellulose and lignin being minor components. The processes that are involved aim at decomposition of the biomass to sugars on the one hand and at esterification of the polysaccharides to useful products, such as cellulose acetate films or to fuels. For this purpose, the cellulose, hemicellulose, and lignin have to be solubilized in suitable solvents, and deep eutectic solvents have been suggested as neoteric "green" solvents for this purpose. The use of deep eutectic solvents for the fractionation of lignocellulosic biomass was reviewed in [61, 64] and along with ionic liquids in [65].

Molten salt hydrates have since many years been studied for their dissolving abilities of cellulose. Although these melts by themselves are not the eutectics dealt with in Chaps. 2 and 3, they readily are turned to the eutectics on dilution with the appropriate amount of water. This may have as a consequence the gelation of the dissolved cellulose, or its remaining in solution, depending on the salt, the temperature, and the concentration. The presence of small strongly hydrated cations (Li^+, Ca^{2+}, Zn^{2+}) and highly polarizable anions (I^-, SCN^-, ClO_4^-) is conducive to the dissolution of cellulose from biomass.

Zinc chloride hydrates featured in several of the investigations of cellulose dissolution. The tetrahydrate, $ZnCl_2{\cdot}4H_2O$, is liquid at room temperature and is highly acidic (more than neat phosphoric acid) [66]. It forms a eutectic with water at a mole ratio of 2.17 water per unit $ZnCl_2{\cdot}4H_2O$ with a melting point of −62 °C [67], but its use for the preparation of cellulose aerogels did not specify the composition of the salt hydrate solvent nor the temperature at which the dissolution of the cellulose was effected [68, 69]. The tetrahydrate was said to be able to swell cellulose but without forming a clear solution [70]. Other reports on the use of aqueous zinc chloride for the dissolution of cellulose did not specify a definite hydrate, but just salt hydrate melts. Dissolution of cellulose in aqueous 70 mass% zinc chloride has been described [71]. Conversion of cellulose to isosorbide mentioned molten hydrated zinc chloride (at mole fractions of $ZnCl_2 \geq 0.66$) as a solvent that solubilized cellulose due to interactions between the ionic species and hydroxyls, breaking the hydrogen-bonded network of the cellulose [72]. The presence of vicinal hydroxyl groups on the glucopyranoside rings of the cellulose was essential for the formation of the zinc chloride complex [70, 73]. The solubility of cellobiose increased with the aqueous zinc chloride concentration, this salt being more efficient than LiCl [74]. Cellulose dissolved to a clear solution in 68 mass% aqueous zinc chloride, from which solution cellulose-based films were readily prepared [75]. Aqueous zinc chloride, at concentrations above 29.6 mass%, effectively dissolves starch, another manifestation of a polysaccharide biomass [76].

Aqueous calcium thiocyanate is another medium commonly used for the dissolution of cellulose, although no information could be found on eventual eutectic formation from the salt hydrates with water. A solution boiling between 135 and 150 °C dissolves bleached cotton or wood pulp when heated to 80–100 °C, the fiber gradually passing into a colloidal solution, but solutions boiling above or below these limits are not solvents for cellulose [77]. A 59 mass% solution dissolved cellulose at 120 °C, the solution turning to a porous gel on cooling [78]. A solution of calcium thiocyanate in water at 59 mass%, a composition corresponding to the hexahydrate, produced aerogels on the dissolution of the cellulose [69]. A lower concentration, $\geq$48.5 mass%, corresponding to the tetra- (or lower) hydrate was able to dissolve cellulose [79] and changes in the structure of wood pulp take place at 55 mass% concentration of this salt [80], whereas NaSCN at 60 mass% was rather ineffective for the dissolution [81].

Aqueous lithium salts are other media used for the dissolution and processing of cellulose. Molten lithium perchlorate trihydrate and iodide dihydrate, which do form deep eutectic solvents (see Chap. 2), yield transparent but viscous solutions of cellulose [82, 83]. In addition to these lithium salts, also the molten thiocyanate dihydrate dissolves cellulose [84]. Molten lithium acetate, chloride, and nitrate are not effective for the dissolution, although they do cause swelling of the cellulose [72, 84, 85]. On the contrary, molten lithium bromide hydrate, or the aqueous solution at 54–60 mass%, is quite effective for this purpose [86, 87].

Dissolution of cellulose in hydroxide media is possible but less effective than the aqueous salt media mentioned above. Dissolution in 8.5 mass% aqueous sodium hydroxide required hydrothermal and ethanol–acid pretreatments [88] and when applied to rice husks aqueous alkalis are able to dissolve the lignin (and the silica) but not the cellulose, whereas the latter can be dissolved in aqueous tetrapropyl- and tetrabutylammonium hydroxide [89].

No dissolution but in some cases fine dispersion and swelling was observed in several molten salt hydrates, including $LiCH_3CO_2{\cdot}2H_2O$, $LiNO_3{\cdot}3H_2O$, $Na_2S{\cdot}H_2O$, $NaCH_3CO_2{\cdot}3H_2O$, $MgCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}18H_2O$, and $Zn(NO_3)_2{\cdot}6H_2O$. The dissolution of cellulose in molten salt hydrates, summarized in Table 4.3, was reviewed in [90, 91], where the solvents were also used as reaction media for carboxymethylation and for acetylation of the dissolved cellulose.

Conventional deep eutectic solvents have also been tested as pretreatment agents of cellulose for various processes. Glyceline pretreatment was more effective than the use of Reline or the choline acetate/glycerol eutectic for subsequent enzymatic hydrolysis [91]. Reline was used, however, for studying the dissolution of cellulose fibers or their chemical derivatization [92]. Hydrothermal pretreatment of date palm residues served for the reduction of the recalcitrance of this biomass for dissolution in Glyceline and subsequent enzymatic digestion [93]. Microwave assistance was useful for the fractionation of lignocellulose in choline chloride/lactic acid deep eutectic solvent [94]. Lignin could be solubilized in a deep eutectic solvent consisting of betaine/lactic acid and be subsequently transformed into uniform nanoparticles [95]. Lignocellulosic biomass processing was tested with some deep eutectic solvents, such as those using betaine or choline chloride as the hydrogen bond accepting components and lactic, malic, oxalic, and other acids as the hydrogen bond donating components [96–98]. Of these, only the 1:2 betaine/lactic acid and 1:10 choline chloride/lactic acid were markedly effective, and only lignin but not starch nor cellulose were dissolved. In a two-stage process, using choline

Table 4.3 Processing of biomass in aqueous/molten salt hydrates

Salt	Process	Ref.
Zinc chloride	Cellulose aerogel preparation	[68, 69]
	Swelling of cellulose	[70]
	Dissolution of cellulose	[71]
	Conversion of cellulose to isosorbide	[72]
	Dissolution of cellobiose	[74]
	Dissolution and film production from cellulose	[75]
	Dissolution of starch from biomass	[76]
Calcium thiocyanate	Dissolution of cotton and wood pulp	[77]
	Dissolution of cellulose, porous gel formed on cooling	[78]
	Cellulose aerogel preparation	[69]
	Dissolution of cellulose	[79]
	Structure change of wood pulp	[80]
Lithium bromide	Dissolution of cellulose	[86, 87]
Lithium iodide	Dissolution of cellulose	[82, 83]
Lithium perchlorate	Dissolution of cellulose	[82, 83]
Lithium thiocyanate	Dissolution of cellulose	[84]
Sodium hydroxide	Dissolution of pretreated cellulose	[88]
	Dissolution of lignin	[89]
Pr_4NOH, Bu_4NOH	Dissolution of cellulose	[89]

chloride/oxalic acid in the first stage and Reline in the second, rice straw was effectively pretreated for enzymatic hydrolysis [99].

Biodiesel, referring to diesel fuel based on vegetable oil or animal fat, consists of methyl, ethyl, or propyl esters of long-chain alkyl carboxylic acids. It is typically made by chemically reacting lipids, such as vegetable oil, soybean oil, or animal fat (tallow), in a suitable solvent with an alcohol. A by-product of such reactions is glycerol that should be separated from the fuel, and deep eutectic solvents have been proposed for this task. The 1:1 mixtures of glycerol with choline chloride (i.e., not Glyceline, the 1:2 mixture), chloroethyltrimethylammonium chloride, and ethylammonium chloride were effective for the removal of the glycerol on biodiesel production from soybean and rapeseed oils [100]. Glyceline was tested for this purpose for biodiesel produced from palm oil [101]. More effective than Glyceline for this purpose were Ethaline and the choline chloride/trifluoroacetamide deep eutectic solvents [102] or those based on methyltriphenylphosphonium bromide with ethylene glycol or triethylene glycol [103]. Artificial neuron networks were employed in order to predict the efficiency of the removal of glycerol from the produced biodiesel and showed that phosphonium-based solvents were superior in this respect to ammonium-based ones [104]. Indeed, allyltriphenylphosphonium bromide/*p*-toluenesulfonic acid was the preferred medium for the esterification of oleic acid with glycerol to produce di- and triclycerides [105].

Another aspect of biodiesel production is the catalyst used for the esterification reaction. The same phosphonium solvent, namely, allyltriphenylphosphonium bromide/*p*-toluenesulfonic acid served well as a catalyst for the production of the methyl ester from crude palm oil [106]. Low-grade crude palm oil with a high fatty acid content could be effectively processed in diethylethanolammonium chloride/*p*-toluenesulfonic acid deep eutectic that acted both as solvent and as catalyst for the transesterification [107]. Whereas the glycerol-based deep eutectic solvents, Glyceline and methyltriphenylphosphonium bromide/glycerol, were not very effective for the elimination of glycerol from the biodiesel [101–103], they proved effective for the removal of the residual potassium hydroxide catalyst employed for the transesterification reaction [108].

Most of these reports dealt with biodiesel production from crude palm oil, but there are, of course, many other vegetable oil and animal fat sources for biodiesel fuel production. It ought to be mentioned that the waste glycerol from the biodiesel production is valuable as a component of deep eutectic solvents [109]. Rapeseed oil was treated in Glyceline as the solvent with a calcium oxide [110] or with sodium hydroxide catalyst [111] for the production of biodiesel. The oil from the Indian beech tree *Pongamia pinnata* was trans-esterified by methanol in the presence of sodium hydroxide catalyst in the 1:2 choline chloride/oxalic acid deep eutectic solvent [112]. Soybean oil was used for biodiesel preparation by transesterification with propanol or butanol, rather than the commonly used methanol, in choline chloride/glycerol and /ethylene glycol solvents at various compositions and with sodium alkoxide catalysis [113]. The 1:2 choline chloride/zinc chloride mixture is liquid at 25 °C and is an effective solvent for the preparation of biodiesel from soybean oil [114]. The high Lewis acidity of the mixture is conducive for the transesterification reaction. The influence of the type and purification of animal fat on the quality of the biodiesel produced from it in Ethaline was studied in [115].

Enzymatic catalysis was also applied to biodiesel production in deep eutectic solvents. *Millettia pinnata* seed oil was treated in a choline acetate/glycerol deep eutectic solvent with a suitable enzyme as the catalyst to produce biodiesel [116] the acetate eutectic being more effective than the commonly used chloride one. This was not the case for the enzymatic preparation of biodiesel from soybean oils, where the chloride eutectic was more efficient than the acetate one [117]. Both rapeseed oil and used acidic cooking oil were the sources for the enzymatic synthesis of biodiesel in Reline and Glyceline as solvents [118]. Yellow horn seed oil was the source for enzyme-catalyzed preparation of biodiesel in deep eutectic solvents, assisted by microwave irradiation, Glyceline proving to be the most efficient among the choline chloride-based solvents tested [119].

A microalgal biomass could be pretreated with aqueous choline chloride/oxalic acid (40 vol% water) or aqueous Ethaline (24 vol% water) to recover the lipid content for subsequent conversion to biodiesel [120]. The role of the water was to reduce the viscosity of the deep eutectic solvent. The same biomass was treated in a 1:3 choline chloride/acetic acid eutectic solvent to extract the lipid and convert it to diesel oil in a one-step process [121], this composition being more effective than those with formic, oxalic, and malonic acids.

Table 4.4 Biodiesel preparation in deep eutectic solvents

DES HBA	DES HBD	Ratio	Additional feature	Ref.
Choline Cl	Urea	1:2	Enzymatic catalysis	[118]
	Ethanediol	1:2	Glycerol removal	[99]
	Ethanediol	1:2	Addition of water	[120]
	Ethanediol	1:2	Na alkoxide catalysis	[113]
	Glycerol	1:1	Glycerol removal	[99]
	Glycerol	1:2	Glycerol removal	[101]
	Glycerol	1:2	CaO catalysis	[110]
	Glycerol	1:2	NaOH catalysis	[111]
	Glycerol	1:2	Na alkoxide catalysis	[113]
	Glycerol	1:2	Enzymatic catalysis	[117]
	Glycerol	1:2	Enzymatic catalysis	[118]
	Glycerol	1:2	Enzymatic catalysis, microwave asst.	[119]
	Acetic acid	1:3		[121]
	Oxalic acid	1:1		[120]
	CF_3CONH_2	1:2	Glycerol removal	[102]
	$ZnCl_2$	1:2	Lewis acidity catalysis	[114]
Choline acetate	Glycerol	1:2	Enzymatic catalysis	[116]
$EtNH_3Cl$	Glycerol	1:1		[99]
$Et_2EtOHNHCl$	pTSA[a]		*p*-toluene sulfonic acid catalysis	[118]
$ClEtMe_3N$ Cl	Glycerol	1:1	Glycerol removal	[99]
$MePh_3P$ Br	Ethanediol		Glycerol removal	[103]
	TEG[b]		Glycerol removal	[103]
$AllylPh_3P$ Br	pTSA[a]		*p*-toluene sulfonic acid catalysis	[106]

[a] *p*-toluene sulfonic acid
[b] triethylene glycol

The use of deep eutectic solvents for biodiesel production was reviewed in [122] and more recently in [123] and the results are summarized in Table 4.4.

4.3 Metal Electrodeposition and Electropolishing

From their earliest use as solvents, the deep eutectic fluids were found to dissolve metal oxides (see Sect. 4.1), and then the route to their use as electrolytes for metal electroplating was opened. Two deep eutectic solvents, now commercially available but readily prepared from their ingredients: Reline and Ethaline, have by far found the widest applications, as shown in Tables 4.5 and 4.6.

Electrochemical methods of investigation, cyclic voltammetry, and chronoamperometry have been extensively used for studying the electrodeposition of metals from deep eutectic solvents. The rate of nucleation is one aspect that has been studied, and its effect on the morphology of the deposited metals has been determined.

Table 4.5 Metals, metal alloys, and metal composites electrodeposition from Reline

Metal(s)	Additional features	Ref.
Ag	Mechanism of nucleation	[318]
	Thin film, nanoparticles	[129]
	Comparison with aqueous process	[124]
	Underpotential deposition	[130]
Au	Thin film, nanoparticles	[318]
	Shape-controlled nanocrystals	[131]
Au–Mn	Spectroscopic characterization	[319]
Co, Co–Sm	Magnetic deposits	[143]
Co–Pt	Magnetic film	[144]
Co–Sm	Magnetic film, nanowires	[132]
Cu	Also Al_2O_3, SiC composites	[152]
	Cu(I) stabilization in solution	[297, 320]
	Nanoporous film	[133]
	Dissolution of CuO	[321]
	Underpotential deposition	[322]
	Structural characterization	[164]
Cu–Ga	Precursor for $CuGaS_2$	[147, 148]
	Precursor for $Cu(InGa)S_2$	[149]
Cu–Ga–In	Precursor for $Cu(InGa)S_2$	[150, 323]
Cu–In	Precursor for $CuInSe_2$	[324]
Cu–Sn–Zn	Precursor for CZTS solar cells	[151]
Cu–Zn	Dissolution of CuO, ZnO	[325]
	Alloy film	[134]
Ga	Electrodeposition	[147]
In	Subsequent phosphoridation to InP	[326, 327]
Ni	Nanostructures	[135]
	Electrodeposition	[328]
	Electrodeposition	[173]
	Electrodeposition of nanostructures	[329]
Pb	Dissolution of PbO, submicrometer wires, powder	[330, 331]
	Dissolution of PbO, PbO_2, $PbSO_4$	[155]
	Nanoparticle aggregation	[332]
Pd	Nanoparticles	[136]
	Nanoparticles, thin film	[129]
	Shape control of deposited crystals	[333]
Pt	Nanoflowers for catalysis	[137]
	Nanocrystals	[138]
Sm	Electrodeposition	[143]
Sn	Electrodeposition	[163]
Zn	Metal nucleation	[334]

(continued)

Table 4.5 (continued)

Metal(s)	Additional features	Ref.
	Brightening by amine additives	[175]
	Composite with graphene oxide	[335]
	Deposition from dissolved arc furnace dust	[336]
Zn–Co	Electrodeposition	[337]
Zn–Mn	Boric acid additive	[338]
	Electrodeposition	[339]
	Electrodeposition	[340]
Zn–Ni	Electrodeposition	[341]
Zn–Sn	Effects of additives	[156]
Zn–Ti	Electrodeposition	[342]

Table 4.6 Metals, metal alloys, and metal composites electrodeposition from Ethaline

Metal(s)	Additional features	Ref.
Ag	Application of quartz microbalance	[343]
	Thin film, nanoparticles	[129]
	Underpotential deposition	[130]
	Composites with Al_2O_3 and SiC	[153]
	Iodine-assisted extracted from ores	[125]
	Nanoparticles on a glassy carbon support	[187]
Ag–Co	Magnetic multilayers	[145]
As	Electrodeposition	[344]
Au	Thin film, nanoparticles	[297]
	Iodine-assisted extracted from ores	[125]
	Au^+ speciation	[181]
Bi	From chlorometalate salts	[345]
Bi–Sn	From chlorometalate salts	[345]
	Effect of boric acid	[346]
Cd–Zn	Coatings	[347]
Co–Cr	Structure, corrosion resistance	[348]
Co–Fe	Magnetic films	[146]
Co–Fe–Ni	Films	[139]
Co–Ni	Concentration dependence	[349]
Co–Ni–Sn	Microstructure, use as cathode	[349]
Co–Sm	Films	[350]
Co–Sn	Microstructure, use as cathode	[351]
	Enhanced corrosion resistance	[352]
Cu	Composites with Al_2O_3 and SiC	[152]
	Dissolution of CuO	[321]

(continued)

Table 4.6 (continued)

Metal(s)	Additional features	Ref.
	Electrodeposition	[353]
	Galvanic replacement growth kinetics	[182]
	Superhydrophobic film	[354]
Cu–Sn	Electrodeposition	[355]
Cu–Zn	Iodine-assisted recovery from complex mixtures	[125]
Fe	Films, magnetic properties	[140]
	Concentration dependence	[356]
Ga–As	Iodine-assisted recovery from complex mixtures	[125]
In	Electrodeposition	[357]
Ni	Nanostructured films	[141]
	Concentration dependence	[349]
	Bright deposits, effect of additives	[176]
	Composite with SiO_2	[154]
	Comparison with aqueous bath	[358]
Ni–P	Coatings	[302]
Ni–Sn	Microstructure, use as cathode	[157]
Pb	Reduction of PbO to porous lead	[359]
	Reduction of PbO	[360]
	Reduction of PbO	[361]
	Recycling from perovskites	[362]
Pd	Thin film, nanoparticles	[129]
Sn	Effect of complexing agents	[157]
	Thin film, nanoparticles	[142]
	Application of quartz microbalance	[343]
	From chlorometalate salts	[345]
	Electrodeposition	[163]
Sn–Sb	Alloy powder	[363]
Zn	Brightening by amine additives	[175]
	Comparison with aqueous bath	[126]
	Effect of tartrate ions	[158]
	Mechanism of deposition	[364]
	Deposition of alumina support	[365]
	Effect of electrode potential	[366]
	Effect of amine additives	[159]
	Deposition of Ti/TiO_2	[367]
	Porous TiO_2 templates	[368]
Zn–Ni	Effect of additives	[160]
Zn–Sn	Speciation of zinc and tin ions	[369]
	Use for corrosion protection	[161]
	Effect of additives	[156]
Zn–Ni–Sn	Electrodeposition	[370]

Comparisons of the performance of deep eutectic solvents as the electrolytes with that of corresponding aqueous electrolytes have been made [124–127], and the advantages and drawbacks of each process have been discussed. The potential windows of deep eutectic solvents are wider (see Sect. 3.6.6) than those of aqueous electrolytes and the evolution of hydrogen at the cathode is absent in the former solvents. The effect of ultrasound on the electrodeposition of copper from Glyceline and from aqueous solutions, increasing the current densities, was studied [127], the differences being due to the different viscosities. The "green" nature of the deep eutectic solvents is an advantage [126], and the reduction in the amount of wastewater is another, but drag-out due to the higher viscosity of the deep eutectic solvent (in particular of Reline, but also of Ethaline) is a disadvantage. The rate of nucleation, both for anodic dissolution of silver and for cathodic deposition in Reline, is smaller than in aqueous solutions [124]. In the case of nickel electrodeposition, the viscosity and conductivity in Ethaline solvent were not the rate-limiting factors compared with aqueous solutions under the same conditions of temperature and concentration [125]. However, the speciation of the nickel in the two kinds of solvents is different, leading to different morphologies of the deposited metal: that in Ethaline being nanocrystalline, hence bright, compared with the microcrystalline morphology, hence matt appearance, of the deposit from aqueous solutions. Nickel was electrodeposited from an Ethaline solution on a stainless steel mesh with a controllable pore size for efficient oil/water separation [128].

In many cases, special morphologies of the deposited metals and alloys were the consequence of the choice of the deep eutectic solvents for the electrodeposition. Thin films consisting of nanoparticles or nanowires, or having nano-porosity have been the targeted deposits for many investigations [129–142]. Some such deposited metals are particularly effective as catalysts [131, 137]. Magnetic metal and alloy deposits have resulted in a number of studies of the use of deep eutectic solvents [132, 140, 143–146]. Precursors for photovoltaic compounds involving gallium and indium together with copper have been deposited from deep eutectic solvents [147–151], and composites involving alumina, silica, and silicon carbide were targeted in other studies [152–154]. Various additives to the deep eutectic solvent have been used to affect the deposited metal or alloy, and their effects have been studied [155–161].

Although Reline and Ethaline have been by far the most widely used deep eutectic solvents for the electrodeposition of metals and alloys, a few studies involved other solvents of this kind. Glyceline featured in the electrodeposition of cobalt [162] and of copper [127]. Choline chloride was also the hydrogen bond accepting component of the deep eutectic solvent formed with propylene glycol as the hydrogen bond donating agent for the electrodeposition of tin [163] and with oxalic and malonic acids for the electrodeposition of copper [164]. The deep eutectic solvent composed of 1:2 choline chloride/$CrCl_3 \cdot 6H_2O$ served well for the electrodeposition of thick, adherent, and crack-free films of chromium [165, 166]. Choline acetate was preferred over choline chloride as the component of the deep eutectic solvent for the electrodeposition of α-brass (copper–zinc alloy) as a bright coating. The choline acetate contained 20 mass% of water and triethanolamine was added for obtaining the most suitable solvent [167]. Another chloride-free deep eutectic solvent that has been suggested is that based on choline dihydrogencitrate with ethylene glycol, used for the electrodeposition of copper [168].

Electropolishing of metal deposits is a process opposing the electrodeposition, in that it dissolves anodically oxide layers produced on metal coatings exposed to the atmosphere. The brightening of electrodeposited coatings can also be effected by the use of certain additives to the deep eutectic solvents that affect the dissolved metal species. Ethaline has been used effectively for the electropolishing of stainless steel [169–172] and the surface was characterized. Bright deposits of nickel [173] and a cobalt–platinum alloy [144] were obtained from Reline and of niobium [174] from Ethaline by electrochemical polishing. Ethylenediamine and ammonia were effective brightening agents for the electrodeposited zinc from Reline and from Ethaline [175]. Four additives: nicotinic acid, methylnicotinate, 5,5-dimethyl hydantoin, and boric acid were tested for obtaining bright nickel deposits from Ethaline [176]. The former two direct the crystal growth to the 111 orientation while the latter two direct it to the 220 orientation. The electrolytic removal of the iron-rich layer from nickel-based hot isostatic press consolidation was achieved in Ethaline [177].

A galvanic replacement reaction in Ethaline enabled the fabrication of nickel nanostructures on a copper-based template by reduction of $NiCl_4^{2-}$ [178]. Electro-less galvanic deposition of metallic silver on copper from Ethaline was studied in [179, 180], and the deposits were characterized using acoustic impedance spectroscopy, scanning electron (SEM), and atomic force (AFM) microscopies. Bright gold on nickel was produced by electro-less galvanic deposition from a solution of AuCN in Ethaline [181]. Galvanic replacement of copper was studied in [182].

The subject of electrodeposition of metals and alloys from deep eutectic solvents was reviewed early in the course of using deep eutectic solvents in [183, 184] and more recently in [185], where electropolishing was also dealt with. A caveat regarding the electrochemical decomposition of choline chloride-based deep eutectic solvents was published in [186]. Over longer periods of electrolysis in Ethaline several decomposition products were found, such as 2-methyl-1,3-dioxolane and chlorinated products, such as chloromethane and chloroform.

4.4 Applications in Nanotechnology

In this section are initially discussed non-electrochemical procedures for the preparation of nanostructured metals and alloys in deep eutectic solvents; the electrochemical procedures having been dealt with in the previous section [129–142, 187]. Subsequently are dealt with nonmetallic nanostructured substances prepared in deep eutectic solvents, such as metal oxides, other inorganic compounds, carbon nanotubes and graphene sheets, and nanofibers of organic polymers.

Silver nanoparticles, of narrow size distribution around 4.5 nm, were prepared and dispersed in Reline by laser ablation of a metallic silver plate [188]. Reports on other non-electrochemical nanostructured metals dealt with gold. Shape-controlled (star-shaped) gold nanoparticles were prepared in Reline by reduction of $HAuCl_4$ with ascorbic acid at room temperature [189]. A low energy sputter deposition of gold in Reline resulted in spherical gold nanoparticles of 5 nm diameter that tended to self-assemble at the surface of the liquid and in the bulk as well [190]. The self-assembly of the gold nanoparticles in Reline was also studied in [191, 192]. Gold microparticles with surface roughness of controlled monodisperse diameters of 1–5 μm were prepared in the Maline deep eutectic solvent by reduction of $HAuCl_4$ with ascorbic acid at 50 °C [53]. High-index facetted gold nanocrystals with enhanced electrocatalytic activities were produced in Reline [193]. Gold nanowire networks with average widths of 17 and 23 nm were prepared by reduction of $HAuCl_4$ with $NaBH_4$ in Reline and in Ethaline [52]. Gum Arabic was used to stabilize gold nanosheets [194] and nanoparticles [195], the deep eutectic solvent in the latter study consisting of 4:1:1 choline chloride, glycerol, and gallic acid (3,4,5-trihydroxybenzoic acid) and $HAuCl_4$ was the source of the gold. Gold nanofoams were produced in Ethaline by reduction of $HAuCl_4$ on a zinc foil [55]. Gold nanoparticles supported on functionalized nanosilica were produced in Reline for use as an electrochemical enzymatic glucose biosensor [196]. Titania-supported gold nanoparticles were prepared in 2:3 choline chloride/urea mixtures (not the 1:2 mixture, Reline) [54]. Gold–palladium core–shell nanoparticles were prepared on a graphite rod in a deep eutectic solvent [197]. Most of the applications of the gold nanoparticles described in this paragraph were in catalysis, although in one case, the gum Arabic stabilized nanoparticles, were used as an X-ray contrast agent [195].

Carbon nanotube-supported platinum–cobalt nanocrystallites were prepared in Ethaline, which showed enhanced methanol electrooxidation performance [198]. High-index facetted platinum concave nanocubes were grown on multi-walled carbon nanotubes in Reline [199]. Self-supported films consisting of nickel–molybdenum microspheres were produced electrochemically in Ethaline [200].

The preparation of inorganic oxide nanostructures in deep eutectic solvents has received an extensive amount of work. Mesoporous silica spheres, useful as packing materials in size-exclusion chromatography, were prepared in deep eutectic solvents consisting of Reline (with possible presence of arginine) [201] and in 1:1 ammonium fluoride as the hydrogen bond accepting component and ethylene glycol, 1,2-butanediol, or glycerol as the hydrogen bond donating one [202]. Self-organized titania "nanobamboos" were prepared in a deep eutectic solvent consisting of 1:1 choline chloride and succinic acid by anodic dissolution of titanium. The "nanobamboos" are nanotubes decorated with periodic exterior rings [203]. Titania nanosized powder was produced by anodization of titanium in Reline or in Ethaline in the presence of tetrabutylammonium bromide and ethanol [204]. The synthesis of nanostructured titania in deep eutectic solvents as well as in room temperature ionic liquids was recently reviewed in [205]. The synthesis of nanoparticles of Mn_3O_4 was accomplished in an all-in-one system: Ethaline as solvent, reactant, and template [206]. A deep eutectic solvent resulted from choline chloride and tin(IV) chloride that was used for the preparation of tin/tin dioxide/carbon composites as electrodes for supercapacitors [207].

The preparation of magnetic nanoparticles based on iron oxides in deep eutectic solvents received a great deal of attention. Spherical magnetic Fe_3O_4 nanoparticles were prepared in Reline [208] and in Reline, Ethaline or 1:1 choline chloride/oxalic acid [209] by co-precipitation of hydrated iron(II) and iron(III) chlorides as solutes. A combined oxidative precipitation and ionothermal method was employed for the production of magnetic Fe_3O_4 nanoparticles in Reline or Ethaline [210]. Magnetic nanoparticles of Fe_3O_4 were coated by Reline using 3-iodopropyltrimethoxy-silane as a binder, for use as a catalyst [211]. Magnetic nanoparticles of Fe_3O_4 were also prepared in Ethaline [212] and Reline [213]. A core–shell nanoreactor consisting of $Fe_3O_4@SiO_2$ in Reline involving HSO_3^- sorbed on the silica and $NaNO_3$ was prepared ultrasonically assisted in [213]. A catalyst consisting of $CoFe_2O_4@B_2O_3–SiO_2$ as a hybrid magnetic composite nanostructure was prepared ultrasonically assisted in Reline [28]. Porous nanosheets, where much of the iron was replaced by cobalt to yield $Co_{2.7}Fe_{0.3}O_4$, were prepared in Reline by co-precipitation of hydrated cobalt(II) and iron(III) chlorides [214]. The iron in ferrite could also be replaced partly by M = Mg, Co, or Ni to produce MFe_2O_4 nanoparticles in 1:1 choline chloride/maleic acid deep eutectic solvent [215]. Haematite (Fe_2O_3) nanospindles were prepared in a one-step synthesis in Reline [216]. Microwave assistance was used in the preparation of Fe_2O_3 nanoparticles in Reline [217]. A prominent use of this magnetic nanostructure is as readily removed heterogeneous catalysts [180, 183–185]; other uses include that as readily recoverable adsorbents of Cu^{2+} [208] or Cd^{2+} and Pb^{2+} [209] or of organic wastes [214], or for storage of Li as a lithium electrode [216].

Other nanostructured metal oxides prepared in deep eutectic solvents include NiO as a film electrodeposited from a choline chloride-based electrolyte [218] or as nanocrystals of NiO with high-energy facets prepared in Reline [219] or mesoporous flower-like NiO electrodes prepared in Reline [220]. Nanostructures of ZnO, including twin cones and nanorods, were prepared by dissolution of ZnO in Reline and precipitation of it by an anti-solvent containing ethanol [221] and a similar procedure was used for the preparation of mesoporous ZnO nanosheets [222] and of Cu^{2+}-doped ZnO nanocrystals [223]. Ionothermal precipitation was used to obtain highly dispersive ZnO nanoparticles in Ethaline [224]. These ZnO-based materials showed good photocatalytic performance. Nanocrystalline SnO_2, of $\sim$4 nm grain size, used as anodes for lithium-ion batteries, was prepared from tin(II) chloride hydrate dissolved in deep eutectic solvents by precipitation with hydrazine hydrate [225]. An ionothermal method was used in choline chloride-based deep eutectic solvents to produce mesoporous SnO_2 structures involving two crystalline phases: orthorhombic and tetragonal [226]. Nanostructured ceria, CeO_2, was prepared in Reline that allowed morphology and porosity control [227].

Other nanostructured inorganic materials prepared in deep eutectic solvents belong mainly to two groups: binary sulfides and analogous materials and salts of oxyacids. An exception is CuCl nanoparticles, prepared in Reline at room temperature by reduction of copper(II) chloride with ascorbic acid in the presence of polyvinylpyrrolidone [228]. Another exception is the ionothermal synthesis of nanoparticles of nickel phosphide with a core/shell structure in Ethaline [229]. The core is amorphous and is covered by shells of crystalline Ni_3P of various thickness. Such structures can be used for lithium storage in anodes of lithium batteries. Nanoparticles of BiOCl sensitized by Bi_2S_3 were prepared in a deep eutectic solvent and can be used as photocatalysts [230].

Self-supported porous Ni_3S_2 films were prepared in Ethaline on nanoporous copper [231], serving as electrocatalysts for hydrogen evolution reactions. The double sulfide $CuInS_2$ in the form of chalcopyrite-structured nanorods was prepared in Reline, assisted by microwave heating [232]. Nanoparticles of the triple sulfide Cu_2ZnSnS_4, known as CZTS used in photovoltaic devices, were prepared in Reline with thiourea as the sulfur source, acting as both solvent and template [233]. Porous $NiCo_2S_4$ was prepared by solvothermal synthesis in a deep eutectic solvent consisting of thiourea and polyethylene glycol (PEG 200) [234]. Mesoporous Ni–Mo sulfides supported on carbon were prepared in deep eutectic solvents consisting of choline chloride and glucose [235]. The self-assembly of nanoparticles of PbS to star-like microscale superstructures was studied in Reline as the deep eutectic solvent [236]. These films of PbS composed of highly oriented nano/microrods were prepared in Reline on a glass substrate by ionothermal synthesis [237]. A variety of binary metal sulfides is produced in a two-stage process in choline chloride/thioacetamide denoted as a deep eutectic solvent precursor (DESP). In the first stage, a metal salt is dissolved in the solvent at a low temperature and in the second stage, the metal–DESP complex is transformed to the binary metal sulfide by heating [238].

Various nano-particulate calcium phosphates, hydroxyapatites, and fluoroapatites were prepared in deep eutectic solvents. Monetite ($CaHPO_4$) nanoparticles were prepared in a one-step low-temperature reaction using an all-in-one (reactant, solvent, template) deep eutectic solvent consisting of 1:1 choline chloride/calcium chloride hexahydrate [239]. Amorphous calcium phosphate nanoparticles (with non-specified chemical formulae), evolving to calcium deficient hydroxyapatites (CDHA), were prepared in Reline and also in Ethaline and Glyceline [240–242]. The effects of reaction time, temperature, and natures of the precursors and the solvent were studied in these investigations. Mineral substituted hydroxyapatite was prepared in a choline chloride/thiourea deep eutectic solvent [243]. On the other hand, nanocrystalline hydroxyapatite powder was prepared in Reline [244] as was the analogous fluoroapatite [245]. Bioactive fluoroapatite nanoparticles were prepared in a choline chloride–calcium chloride medium [246]. Emphasis in these studies was placed also on the recovery of the deep eutectic solvent for reuse in the synthetic processes.

A few other nanoparticles of salts of oxyacids were prepared in deep eutectic solvents. These include spindle-like nanoparticles of lithium manganese phosphate, prepared ionothermally in Ethaline by microwave heating [247, 248]. Ferroelectric barium titanate nanoparticles were prepared in 1:1 choline chloride/malic acid [249] and spindle-like nanotubes of bismuth vanadate were prepared in Reline [250] ionothermally. Non-oxyacid salt nanoparticles that were prepared in deep eutectic solvents include nanospheres with controlled sizes of Prussian blue, prepared in 1:1 choline chloride/malic acid by addition of $FeCl_3 \cdot 6H_2O$ and $K_4Fe(CN)_6 \cdot 3H_2O$ to the deep eutectic solvent [251]. Nanostructured electropolymerized poly(methylene blue) films were prepared in Ethaline [252].

Carbon nanotubes (CNTs) are another kind of materials prepared in deep eutectic solvents, which may be single-walled or multi-walled or composites with other substances. Polycondensation of resorcinol with formaldehyde in Ethaline, containing a small amount of water introduced with the formaldehyde, yielded the desired multi-walled carbon tubes after heat treatment with ready recycling of the Ethaline solvent [253]. Single-walled and double-walled carbon nanotubes were prepared by polycondensation of furfuryl alcohol in the highly acidic 1:1 choline chloride/*p*-toluenesulfonic acid deep eutectic solvent [254]. A deep eutectic solvent comprising choline chloride and acrylic acid was used both as a solvent and as the reactant to form HNO_3-functionalized carbon nanotube composites with poly (acrylic acid) that were macroporous [255]. Multi-walled carbon nanotube composites with nickel were electrodeposited from Reline containing nickel chloride on a copper substrate [256]. Carbon nanotubes prepared separately were subsequently functionalized by treatment with $KMnO_4$ or with HNO_3 in two phosphonium-based deep eutectic solvents: 1:1 methyltriphenylphosphonium bromide/glycerol and 1:16 benzyltriphenylphosphonium chloride/glycerol [257]. The resulting material was used for the absorption of arsenic species from water. A different deep eutectic solvent, comprised of 1:1 tetrabutylammonium bromide/glycerol was used to functionalize carbon nanotubes with KMnO4 for producing a material efficiently removing mercury species from water [258]. Magnetic multi-walled carbon nanotubes (MMWCNTs) were dispersed in a deep eutectic solvent comprised of 1:2 choline chloride/resorcinol for microextraction purposes [259]. MMWCNTs were also covered with Reline to form magnetic bucky gels for similar purposes [260]. Reline was also used for the electrodeposition of nickel on carbon nanotubes [261]. Multi-walled carbon nanotubes were treated in Reline with nitric acid and then with $PdCl_2$ and $SnCl_2$ solutions in Reline to produce the PdSn alloy supported on the nanotubes by sonication to be used as catalysts [262]. Allyltriphenylphosphonium bromide/glycerol was the deep eutectic solvent used to functionalize carbon nanotubes for the removal of mercury from water [263]. Ethaline was used for the synthesis of carbon nanotubes functionalized with redox-active poly(methylene blue) [264].

Another form of nanostructured carbon is graphene, and this was produced in deep eutectic solvents too. The interface between graphene and deep eutectic solvents consisting of choline chloride with urea, glycerol, malonic, levulinic, or phenylacetic acids was elucidated in [265]. Various such solvents (Reline, Ethaline, Glyceline, 1:2 choline chloride/di- and triethylene glycol, Maline, and methyltriphenylphosphonium bromide/glycerol, among several others) were used to reduce graphene oxide, formed by oxidation with $KMnO_4$, to produce functionalized graphene with hydrophilic groups [266]. Magnetic graphene oxide nanoparticles were prepared in Ethaline or Glyceline by incorporation of Fe_3O_4 treated with 3-aminopropyltriethoxysilane in the core/shell structures, which were used for the extraction of proteins [267]. Carboxamide functionalized graphene oxide complexed with copper nanoparticles as a catalyst was prepared in Glyceline [34]. Graphene oxide treated with choline chloride/NaH_2PO_4 as a deep eutectic solvent was a high potency flame retardant [268]. Magnetic graphene oxide nanoparticles coated with a deep eutectic solvent (Glyceline or choline chloride/ phenol or /tetrahydro-tetramethylnaphthol-2) using ultrasound assistance was used for drug pre-concentration [269]. Fresh seaweed was converted to functionalized graphene nanosheets (doped with Fe_3O_4) in a deep eutectic solvent comprising choline chloride/$FeCl_3{\cdot}6H_2O$ [270], which could be used as electrocatalysts. Graphene sheets derived from seaweeds were treated with deep eutectic solvents, comprising choline chloride and a metal (iron(III), zinc, or tin(II)) chloride, and were used for the removal of fluoride from water [271]. Functionalized graphene oxide nanoparticles dispersed by ultrasonication in 1:3 choline chloride/triethylene glycol and in 1:4 and 1:5 methyltriphenylphosphonium bromide/ethylene glycol deep eutectic solvents were proposed as new heat transfer fluids with enhanced thermal conductivity [272].

Mesoporous silica (SBA-15) was used as a support for deep eutectic solvents to be used as catalysts. The solvent consisting of *N*-methylpyrrolidine hydrochloride/ zinc chloride was thus immobilized on mesoporous silica in [273, 274]. Nanoflowers consisting of copper phosphate on which *C. antarctica* lipase B enzyme was immobilized were prepared in Reline and in ethylammonium chloride/ ethylene glycol deep eutectic solvents [275].

Nanostructured polymeric materials were prepared advantageously in deep eutectic solvents both electrochemically and otherwise. Conducting polyaniline films were prepared electrochemically in 1:2 choline chloride/1,2-propanediol deep eutectic solvent [276]. The films were nano-particulate and could be doped/dedoped reversibly, exhibiting fast charge transport across the film. Several other choline-based mixtures: Reline, Ethaline, and Glyceline, could also be used for the electrochemical preparation of polyaniline [277] the morphology, stability, and electrochromism of the products having also been studied. These three deep eutectic solvents were used for the electrochemical deposition of the conducting poly(3,4-ethylenedioxythiophene) film on glassy carbon electrodes [278], that could be used for sensing ascorbic acid, dopamine, and uric acid. Elastin-like recombinamers were prepared in Reline from several pentapeptides [279], their conformation in the collapsed state being stable even in the presence of water. The preparation of porous molecularly imprinted polymers (MIP) in various deep eutectic solvents for analytical purposes was described in [201].

Natural materials were transformed into nanofibers in deep eutectic solvents, for example, wood cellulose [280] and paper and board cellulose [281] that were pretreated in Reline before undergoing nanofibrillation. Cellulose was converted to nanofibrils by treatment with deep eutectic solvents comprising either ammonium thiocyanate/urea or guanidinium chloride/urea [282]. Silylated cellulose nanofibrils that were hydrophobic and super-absorbing aerogels were prepared in Reline [283]. Agar was advantageously made electro-spinnable in Reline [284] compared with aqueous media, producing elastic nanofibers. Unbleached mechanical wood pulp was converted to nanofibers by treatment with a deep eutectic solvent made from triethylammonium chloride and imidazole [285]. Chitin nanofibers were prepared in a 1:2 choline chloride/thiourea deep eutectic solvent but not in Reline [286]. Lysozyme from hen eggs was transformed into nanofibers in a deep eutectic solvent involving choline chloride and acetic acid [287]. Guanine-rich oligonucleotide quadruplexes have the potential to control the bottom-up synthesis of nanoarchitectures, and two such oligonucleotides were prepared in Reline [288]. Nanocrystalline cellulose could be prepared in deep eutectic solvents comprising choline chloride and oxalic, *p*-toluenesulfonic, or levulinic acids, by mechanical disintegration of the primarily produced nanofibers from wood cellulose [29]. Cellulose nanocrystals were also produced from cotton by treatment with choline chloride/oxalic acid dihydrate deep eutectic solvent [289]. The cellulose nanocrystals produced in choline chloride/oxalic acid dihydrate deep eutectic solvent could then be used to stabilize marine diesel oil-in-water emulsions [290].

Microemulsions in the “pre-ouzo” state were obtained in the absence of a surfactant and water in Reline and 1:4 choline chloride/ethylene glycol deep eutectic solvents [291]. These fluctuations in the nonhomogeneous liquid were not due to an amphiphilic effect. Deep eutectic solvents consisting of alkylammonium chloride or bromide (alkyl = ethyl, propyl, butyl, or pentyl) and ethylene glycol or glycerol are nanostructured, as shown by X-ray scattering, and consequently, phospholipids form bilayer phases or vesicles in them [292]. Bucky gels, consisting of Reline and magnetic multi-walled carbon nanotubes, were prepared by treating carbon nanotubes with nitric acid, then adding $FeCl_2$ and $FeCl_3$ and co-precipitating Fe_3O_4 with the nanotubes by addition of a base [260]. They could be used as dispersive solid extractants for the determination of trace organochlorine pesticides.

The field of nanotechnological applications of deep eutectic solvents was reviewed in [293] and [294]. These solvents can be used to prepare well-defined nanomaterials, shape-controlled nanoparticles, films, metal-organic frameworks, colloidal assemblies, hierarchically porous carbons, and DNA/RNA architectures. They act as supramolecular templates as well as reactants. The moderate to large viscosities of the deep eutectic solvents are conducive to the ability of nanoparticle dispersions to be formed, retaining the large surface area-to-volume ratios conducive to catalytic activity, rather than allowing rapid growth to macrocrystalline moieties. These modes of operation of deep eutectic solvents make them useful in nanotechnology, additional to their low costs, ready availability, and “green” nature.

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Chapter 5
Deep Eutectic Solvents in Extraction and Sorption Technology

Deep eutectic solvents have been used extensively for the extraction and separation of a great variety of substances from diverse media. Several review papers deal with the development of deep eutectic solvents for using them for extraction purposes [1–3]. Deep eutectic solvents have been tailor-made for extractive purposes by combining choline chloride, betaine, or proline with glycerol or sucrose, forming sustainable and effective extraction media [4]. Solid-phase extraction media were produced on silica supports by chloroethyltrimethylammonium chloride (chlorocholine)/urea [5] and by choline chloride with various commonly used hydrogen bond donating agents modifying graphene and graphene oxide [6]. Special techniques have been used for extraction with deep eutectic solvents, namely, dispersive microextraction and anti-extraction. In the former of these, the deep eutectic solvent was water-immiscible 1:2 choline chloride/4-chlorophenol, which was injected by aid of a dispersive agent (acetonitrile) into the aqueous solution from which the analytes were extracted into the centrifugally sedimented layer of the cloudy mixture produced [7]. The other method involved choline chloride, tetramethylammonium chloride, or tetraethylammonium chloride with phenol to first extract phenolic compounds from neutral oil, but the entrained oil in the deep eutectic solvent was subsequently removed by an alkane (hexane) anti-solvent [8].

Biphasic aqueous/immiscible solvent extraction systems involving deep eutectic solvents have been proposed in several publications. Hydrophobic deep eutectic solvents have been prepared for this purpose, for instance, one based on menthol with a carboxylic (acetic, pyruvic, lactic, or lauric) acid [9]. Tetraalkylammonium chlorides (alkyl: butyl, heptyl, octyl), tetraoctylammonium bromide, and methyltrioctylammonium chloride or bromide form with decanoic acid hydrophobic deep eutectic solvents that can be used in biphasic extraction [10]. The water-immiscible deep eutectic solvent phase is produced in situ when choline chloride and 4-chlorophenol at a 1:2 molar ratio are dissolved in the aqueous medium and heated. This phase separates out from the cloudy mixture and contains the analytes to be separated [11]. Polypropylene glycol with a mean molar mass of 400 g mol^{-1} (PPG-400) has been used with the otherwise hydrophilic deep eutectic solvents

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composed of choline chloride with urea, acetic, glycolic, lactic, or citric acid to produce the water-immiscible phase in a biphasic extraction system [12]. Aqueous biphasic systems involving deep eutectic solvents based on choline chloride with urea, ethylene glycol, glycerol, and lactic acid and on betaine with urea are mentioned as analytical applications in [13] and that based on choline chloride with sugars is mentioned in [14], in spite of the hydrophilic nature of the components. The solute (vanillin, β-ionone, or tocopherol) partitioning in biphasic systems based on choline chloride/or betaine/levulinic acid deep eutectic solvents and on mixtures of heptane and an alkanol or acetonitrile, using the predictive thermodynamic model COSMO-RS, was described in [15].

The performance of a polyethylene sulfone ultrafiltration membrane was improved by impregnation of it with a 1:2 tetrabutylammonium chloride/decanoic acid deep eutectic solvent [16].

5.1 Desulfurization and Denitrification of Fuels

The desulfurization of liquid fuels and oils is a major area of investigation to which deep eutectic solvents have been turned. The removal of sulfur compounds, in particular, thiophene and dibenzothiophene from model and simulated hydrocarbon fuels, was studied in [17–26]. Liquid fuel modeled by *n*-heptane containing thiophene was extracted by deep eutectic solvents comprising tetrabutylammonium bromide with 1:4 ethylene glycol or triethylene glycol and with 1:7 sulfolane and by methyltriphenylphosphonium bromide with 1:4 ethylene glycol. The sulfolane-containing mixture proved to be the most efficient for the removal of the thiophene [17]. Liquid fuel modeled by *n*-octane containing thiophene, benzothiophene, or dibenzothiophene was extracted by deep eutectic solvents comprising 1:1 tetrabutylammonium bromide with formic, acetic, propanoic, oxalic, malonic, or adipic acids, of which the one involving formic acid proved to be the most efficient for the removal of the sulfur compounds [18]. Dibenzothiophene was extracted from a liquid fuel modeled by a mixture of *i*-octane, *n*-decane, *c*-hexane, and toluene by the deep eutectic solvent 1:2 tetrabutylammonium bromide/polyethyleneglycol PEG-200 [19]. Extraction of dibenzothiophene from model oil simulated by *n*-octane was achieved with a deep eutectic solvent consisting of choline chloride/trifluoromethanesulfonic acid at various molar ratios [20]. Extraction of benzothiophene and/or methylthiophene from model oil simulated by *n*-octane was studied with deep eutectic solvents in which tetrabutylammonium, tetramethylammonium, or choline chlorides served as the hydrogen bond accepting components and ethylene glycol, tetraethylene glycol, polyethylene glycol (unspecified molar mass), glycerol, and malonic acid as the hydrogen bond donating components [21, 22]. The combination of tetrabutylammonium chloride with ethylene glycol [21] or with polyethylene glycol [22] was the most efficient extractant. Glyceline or 2:3 choline acetate/glycerol featured in a microextraction study of the removal of dibenzothiophene from liquid fuels modeled by *n*-octane or *n*-dodecane [23]. Choline chloride analogs with butyl, octyl, dodecyl, and benzyl groups replacing one methyl group attached to the nitrogen combined with 1:1 iron (III) chloride were used as deep eutectic solvents for the desulfurization of the model fuel *n*-octane [24]. Deep eutectic solvents consisting of 1:2 tetrahexylammonium bromide with ethylene glycol or glycerol were used for the extraction of thiophene from hexane and octane, and the results were correlated by means of the nonrandom two liquid (NRTL) model [25]. Glyceline was used with dodecane and biodiesel to extract dibenzothiophene and its oxidation product, and the spent deep eutectic solvent was regenerated for further extraction cycles [26]. Nonconventional deep eutectic solvents, composed of 1:2 tetrabutylphosphonium bromide and anhydrous iron(III) chloride (t_m = 15.7 °C), were used for desulfurization of *n*-octane as well as of commercial diesel fuels [27, 28]. A commercial gasoline was desulfurized by means of extraction with *N*-butylpyridinium bromide/malonic acid deep eutectic solvent. Other dicarboxylic acids, succinic, glutaric, and adipic acids, were also tested as the hydrogen bond donation agents, but were less efficient [29].

Oxidative/extractive desulfurization processes were described in [26, 30–37]. Choline or tetrabutylammonium chlorides with *p*-toluenesulfonic acid deep eutectic solvents were used to remove benzothiophene from *n*-octane and real fuels after oxidation with hydrogen peroxide [30]. Deep eutectic solvents comprising 1:2 choline chloride/carboxylic acids (formic to pentanoic) were used with a model oil (unspecified) to remove thiophene derivatives by photochemical air oxidation catalyzed by isobutanal [31]. Deep eutectic solvents comprising 1:2 choline chloride/polyols as well as Reline and Maline were used with hydrogen peroxide and phosphotungstic acid catalysis to remove thiophene derivatives from *n*-octane, the PEG 200 hydrogen bond donating (HBD) agent [32] or the glycerol HBD [26] being the most effective. Ethaline was the deep eutectic solvent used with hydrogen peroxide oxidative extraction using a vanadium substituted phosphotungstate catalyst for the desulfurization of a model fuel composed of isooctane and toluene [33]. An unconventional deep eutectic solvent, consisting of zinc chloride as the hydrogen bond accepting component and phenylpropanoic acid as the HBD component, and hydrogen peroxide were used for the oxidative extractive desulfurization of *n*-octane as the model fuel with no additional catalyst being required [34]. A deep eutectic solvent consisting of 1:2 tetrabutylammonium chloride and oxalic acid proved to be a useful extractant for the oxidative desulfurization of diesel oil with hydrogen peroxide with practical recycling of the extractant [35]. Another deep eutectic solvent consisting of 1:2 zinc chloride and propanoic acid was used for the oxidative extraction with hydrogen peroxide of dibenzothiophene from octane as the model oil, with good results even after five cycles of use [36]. Still another extractant consisted of 1:2 proline with *p*-toluenesulfonic acid for the hydrogen peroxide oxidative desulfurization of model diesel oil with recycling of the extractant [37].

Catalytic oxidative desulfurization of liquid fuels, using polyoxometalate catalysts and extraction with deep eutectic solvents, was studied in [38–40]. Tris[triethyl(3-propylsulfonic acid)ammonium)] phosphotungstae, $[Et_3(C_3H_7SO_3H)N^+]_3PW_{12}O_{40}{}^{3-}$, was the catalyst in 1:2 choline chloride/acetic acid deep eutectic solvent for the oxidative desulfurization of diesel oil with hydrogen peroxide [38]. A cholinium-sodium polymolybdate catalyst/solvent was used for the oxidative desulfurization of fuel oils with oxygen [39]. A different cholinium-alkali metal iodo-polymolybdate catalyst was prepared in Reline and was used for the oxidative desulfurization of octane model diesel oil with hydrogen peroxide and extraction with 1-butyl- or 1-octyl-3-methylimidazolium tetrafluoroborate [40].

Polymer-based deep eutectic solvents consisting of 1:2 tetrabutylammonium chloride/polyethylene glycols PEG 200 and PEG 600 were effective for the desulfurization of a simulated diesel fuel consisting of *c*-hexane, *i*-octane, *n*-decane, and toluene [41]. Magnetic deep eutectic solvents consisting of 1:2:1 choline chloride/phenol/iron(III) chloride or 1:4:1 choline chloride/ethylene glycol/iron(III) chloride were used for ultrasonic-assisted microextraction of thiophene from *n*-heptane, the former solvent being nearly 100% effective [42].

The extractive denitrification of liquid fuels by deep eutectic solvents has been studied considerably less than their desulfurization. The nitrogen compounds studied in [43] included "basic" or five-membered rings: pyrole, indole, indoline, carbazole, and benzocarbazole, and "non-basic" or six-membered rings: pyridine, quinoline, and benzoquinoline. A large variety of deep eutectic solvents (a total of 94) were tested for extraction capacity and selectivity. Ammonium-based solvents had higher selectivity but lower capacity than phosphonium-based ones that had lower selectivities but larger capacities. The denitrification of *n*-hexadecane as a model fuel was subsequently studied in greater detail, using 1:2 tetrabutylammonium and tetrabutylphosphonium bromides/ethylene glycol as the solvents [44]. Both deep eutectic solvents were effective extractants, but the phosphonium-based one was somewhat better. A deep eutectic solvent comprising 1:2 choline chloride/phenylacetic acid was also very effective for removing cyclic organo-nitrogen compounds from *n*-heptane [45].

The variety of deep eutectic solvents used for the desulfurization of liquid fuels or for the extraction of thiophene and its derivatives (mainly dibenzothiophene) from alkanes simulating such fuels is summarized in Table 5.1.

Table 5.1 Deep eutectic solvents used for the desulfurization of liquid fuels

Hydrogen bond accepting (HBA) component	Hydrogen bond donating (HBD component	Ref.
Choline chloride	1,2-ethanediol (Ethaline)	[33, 42]
	Gycerol (Glyceline)	[30]
	Polyethylene glycol	[23, 26]
	Carboxylic acids	[31, 38, 45]
	Urea, malonic acid	[32]
	Trifluoromethanesulfonic acid	[20]
	p-toluenesulfonic acid	[21]
Choline acetate	Glycerol	[23]

(continued)

Table 5.1 (continued)

Hydrogen bond accepting (HBA) component	Hydrogen bond donating (HBD component	Ref.
Choline polymolybdate		[39, 40]
Alkyldimethyl(OHC_2H_4)N^+ Cl^-	$FeCl_3$	[24]
Tetrabutylammonium chloride	1,2-ethanediol	[22, 44]
	Polyethylene glycol	[30, 41]
	p-toluenesulfonic acid	[35]
Tetrabutylammonium bromide	1,2-ethanediol, sulfolane	[17]
	Polyethylene glycol	[19]
	Carboxylic acids	[18]
Tetrahexylammonium bromide	1,2-ethanediol, glycerol	[25]
Tetrabutylphosphonium bromide	1,2-ethanediol	[44]
	$FeCl_3$	[27, 28]
Methyltriphenylphosphonium bromide	1,2-ethanediol, sulfolane	[17]
Proline	*p*-toluenesulfonic acid	[37]
N-butylpyridinium bromide	Malonic acid	[29]
Zinc chloride	Carboxylic acids	[34, 36]

5.2 Extraction of/from Hydrocarbons and Oils

The removal of phenol and phenolic compounds from oils by means of deep eutectic solvents has received some attention. Deep eutectic solvents based on choline chloride with various hydrogen bond donating components as well as a nonionic ternary solvent, 1:1:1 glucose/fructose/sucrose, were differently effective for the extraction of the phenolic compounds tyrosol, hydroxytyrosol, oleacein, and oleocanthal from virgin olive oil [46]. The extraction of phenol itself from hydrocarbon fuels was accomplished by in situ conversion of the phenol with a quaternary ammonium salt to a deep eutectic solvent immiscible with the fuel. The salts that were effective were choline, tetramethylammonium, and tetraethylammonium chlorides [47, 48]. With toluene simulating the fuel, the phase equilibria were studied in [47] and the mass transfer dynamics of the process were studied in [48]. Deep eutectic solvents based on 1:3 betaine/phenol and carnitine (3-hydroxy-4-trimethylaminobutanoic acid)/phenol extracted phenol from toluene as a model oil [49]. The extraction of various phenolic compounds from vegetable sources was reviewed in [50]. On the other hand, deep eutectic solvents having 2:1 mixtures of phenols (phenol, chlorophenol, and resorcinol) as the hydrogen bond donating agent with choline chloride sorbed on magnetic bucky gels were used for the microextraction of aromatic hydrocarbons from water and urine samples [51]. The phenolic content of model oil (toluene and phenol) or of coal tar oil was extracted by deep eutectic liquids, formed with a salt comprising bis(triethylammonium bromide) groups separated by di-, tri-, or tetramethylene bridges, which could be separated from the oil [52].

The extractive separation of other polar compounds from alkanes by means of deep eutectic solvents was studied in [53–55]. Ethanol was separated from *n*-hexane by means of Maline or 1:1 choline chloride/oxalic acid deep eutectic solvents [53]. 1-Pentanol, 2-pentanone, butanoic acid, and ethyl acetate were separated from cyclohexane by extraction with Ethaline, and curcumine and β-carotene were likewise separated from decane [54]. Quinoline was separated from toluene and heptane by extraction with methyltriphenylphosphonium bromide/ethylene glycol or glycerol [55]. Quinoline and indoline were also extracted from toluene + heptane mixtures by 1:4 methyltriphenylphosphonium bromide/ethylene glycol [56]. Polar compounds were separated from one another by extraction with deep eutectic solvents: for example, phenyl ethanol from its acetate or propanoate ester and butanol from butyl acetate by extraction with Glyceline [57] or ethanol was separated from methyl ethyl ketone by extraction with Glyceline or with tetraethylammonium chloride/glycerol [58].

The separation of aliphatic from aromatic hydrocarbons by extraction with deep eutectic solvents has received considerable attention [59–72]. The variety of deep eutectic solvents that have been used for the extraction of solutes from hydrocarbons, for the separation of aliphatic and aromatic hydrocarbons, or the breaking of azeotropic mixtures involving hydrocarbons is summarized in Table 5.2.

Table 5.2 Deep eutectic solvents used for the extraction of hydrocarbons

Hydrogen bond accepting (HBA) component	Hydrogen bond donating (HBD) component	Ref.
Choline chloride	Urea (Reline)	[55, 56, 59, 78]
	1,2-ethanediol (Ethaline)	[57, 58, 62, 66–68, 73]
	1,2-propanediol	[75]
	Gycerol (Glyceline)	[67, 75, 77]
	Aliphatic carboxylic acids	[53, 54, 62, 66, 68, 73–75]
	Aromatic carboxylic acids	[76]
	Phenols	[51]
	Glucose	[69]
Benzylcholine chloride	Levulinic acid	[74]
Tetraethylammonium chloride	1,2-ethanediol	[71]
	Glycerol	[58, 71]
	Aromatic carboxylic acids	[76]
	Phenol	[47, 48]
Tetrabutylammonium chloride	1,2-ethanediol	[71]
	Levulinic acid	[74]
	Phenol	[47, 48]

(continued)

Table 5.2 (continued)

Hydrogen bond accepting (HBA) component	Hydrogen bond donating (HBD) component	Ref.
Tetrabutylammonium bromide	1,2-ethanediol	[65]
	Sulfolane	[72]
Tetrahexylammonium chloride	1,2-ethanediol, glycerol	[71]
Tetrahexylammonium bromide	1,2-ethanediol, glycerol	[64]
Methyltriphenylphosphonium bromide	1,2-ethanediol, glycerol	[55, 56]
Ethyltriphenylphosphonium bromide	1,2-ethanediol, sulfolane	[61]
Tetrabutylphosphonium bromide	1,2-ethanediol, sulfolane	[60]
	Levulinic acid	[63]
Betaine, carnitine	Phenol	[49]
Glucose + fructose + sucrose		[46]

Specific pairs of hydrocarbons are dealt with in the following papers. Benzene and *n*-hexane are separated by means of extraction of the former by 1:4 or 1:6 methyltriphenylphosphonium bromide/ethylene glycol [59] or by 1:2 choline chloride/glycerol or lactic acid [62]. The latter paper also deals with mixtures of ethyl acetate and hexane, from which the former component is extracted into the deep eutectic solvent. The liquid–liquid equilibrium data for ternary mixtures involving benzene, hexane, and a deep eutectic solvent are described in [71], the latter component consisting of tetramethyl-, tetraethyl-, tetrabutyl-, or tetrahexylammonium chloride with ethylene glycol or glycerol. Ethylbenzene was separated from *n*-octane by extraction with a deep eutectic solvent composed of tetrabutylammonium bromide with ethylene glycol or pyridine or both [70]. Benzene was effectively separated from *n*-hexane by extraction with 1:2 tetrahexylammonium bromide with either ethylene glycol or glycerol [64]. Benzene was removed efficiently from cyclohexane by extraction with 1:7 tetrabutylammonium bromide/sulfolane, having been selected by a screening study of 40-deep eutectic solvents using the COSMO-RS method [73]. Toluene is separated from *n*-heptane by extraction with 1:4 deep eutectic solvents consisting of a variety of hydrogen bond accepting components and lactic acid, ethylene glycol, or triethylene glycol as the hydrogen bond donating one as well as with Reline and Maline. The selectivity for toluene is enhanced by short side chains, a small central atom, and a large anion of the hydrogen bond accepting component [66]. Tetrabutylphosphonium bromide with levulinic acid was used to separate toluene from its mixtures with *n*-hexane or cyclohexane [63]. The extractive separation of ethylbenzene from *n*-octane was effectively carried out with a ternary deep eutectic solvent consisting of tetrabutylammonium bromide with both ethylene glycol and pyridine, whereas with only ethylene glycol the selectivity was high but the distribution ratio was low and vice versa with only pyridine [65].

Somewhat more generalized aromatic/aliphatic extractive separation studies aimed at, among other targets, the separation of aromatics from naphtha. Tetrabutylphosphonium bromide [60] or ethyltriphenylphosphonium iodide [61] with ethylene glycol or sulfolane was the deep eutectic solvents used for the determination of the phase equilibria for toluene and heptane mixtures as model compounds. The aromatic substances benzene, toluene, and pyridine were extracted selectively from *n*-hexane by a 1:1 eutectic of choline chloride/glucose [69]. Reline and Glyceline were the deep eutectic solvents used for the extraction of toluene and pyridine, representing aromatics, from *n*-hexane and *n*-butanol, representing aliphatics [67]. Several choline chloride-based deep eutectic solvents (with ethylene glycol, glycerol, and levulinic, phenylacetic, and malonic acids, and urea) were tested for the extractive separation of aromatics from gasoline [68]. The combination of choline chloride with levulinic acid was the most effective one and had the most suitable physical properties. The extractive separation of aromatic from aliphatic hydrocarbons using deep eutectic solvents was recently reviewed critically in [70]. The COSMO-RS method was found to be effective for the screening of ternary aromatic + aliphatic + deep eutectic solvent systems. The latter solvents can compete successfully with room temperature ionic liquids and with organic solvents that have been proposed for the envisaged separations.

Extractive separation studies similar to the above ones are those of azeotropic mixtures or of isomers. Choline chloride/ethylene glycol or glycerol or levulinic acid deep eutectic solvents were used to break the *n*-heptane/ethanol azeotrope [73]. The azeotrope between *n*-heptane and toluene could be broken by the use of one out of several deep eutectic solvents: 1:2 choline, benzylcholine, and tetrabutylammonium chlorides with levulinic acid [74]. The COSMO-RS method was applied for prediction of the tie lines in the phase diagrams. A similar approach was used for the breaking of the azeotropes between ethanol and *n*-hexane, *n*-heptane, and *n*-octane by Reline, choline chloride/1,2-propanediol, or/lactic acid, but here the predictions of the COSMO-RS method did not agree well with the experimental results [75]. Choline, tetramethyl-, and tetraethylammonium chlorides formed with benzene-di- and benzene-tricarboxylic acids eutectic solvents that were used for the separation of the isomers of these acids by liquid–liquid distribution [76]. The quaternary ammonium salt could be regenerated using isopropanol as an anti-solvent.

Extraction with deep eutectic solvents has also found some use in the petroleum industry. Reline and Glyceline were used for heavy oil recovery from brine-flooded reservoirs [77]. Reline was also used as an agent separating bitumen from oil shales; although it is immiscible with the hydrocarbons, due to its density it keeps the solid (sand) and two liquid phases (Reline and naphtha) apart [78]. Ethaline has been proposed as an inhibitor of asphaltene precipitation from crude oil [79].

5.3 Extraction of Metal Species

A quite different mode for the use of deep eutectic solvents in extraction applications is the selective extraction of metal ions, mainly for analytical purposes. Copper, iron, nickel, and zinc can be determined in fish and other marine biological samples by digestion with a choline chloride/oxalic acid solvent [80, 81]. Lead and cadmium in edible oils were pre-concentrated for microextraction by deep eutectic solvents consisting of Reline, Ethaline, or choline chloride/oxalic acid for subsequent analytical determination [82]. Alkali metal ions (Li, Na, K) and transition metal ions (Mn, Fe, Cu, Ni, Cu, Zn) were extracted by means of the hydrophobic deep eutectic solvent consisting of lidocaine decanoate/decanoic acid from aqueous solutions for subsequent analytical determination [83]. Chromium(III) and (VI) could be selectively extracted from aqueous environmental samples, based on an ultrasound-assisted emulsification and microextraction method, with deep eutectic solvents consisting of choline chloride/phenol at several molar ratios, or tetrabutyl- or methyltrioctylammonium chloride/decanoic acid [84]. Copper was determined in sediment samples by extraction with Reline or with choline chloride/oxalic acid deep eutectic solvents [85]. Lead was extracted from blood samples by a carrier-mediated hollow fiber liquid extraction method using Reline [86]. A deep eutectic solvent consisting of 1:2 choline chloride/lactic acid was used to leach metal ions from NdFeB magnets, and Fe and Cu were separated from Nd and Dy in this solvent by extraction with liquid trioctylmethylammonium thiocyanate in toluene [87]. A variety of elements could be determined in agricultural soil samples by extraction with a choline chloride/oxalic acid deep eutectic solvent [88]. Aluminum was determined in water and food samples by ultrasound-assisted emulsification and microextraction with the 1:4 choline chloride/phenol deep eutectic solvent [89].

A different use of deep eutectic solvents for the extraction of metal ions is for recovery rather than analysis. The recovery of cobalt from a choline chloride/lactic acid deep eutectic solvent for battery recycling by means of extraction with several organic extractant/diluent systems has been studied [90]. The recovery of cadmium, cobalt, palladium, rhenium, and zinc in the system comprising of Aliquat 336 [methyl-tri(octyl/decyl)ammonium chloride] in an aromatic diluent + wet choline chloride/lactic acid was studied as a function of the water content of the deep eutectic solvent phase [91]. The recovery of lead and zinc from electric arc furnace dust was described using choline-based solvents [92, 93]. Rare earth elements may be leached and recovered from coal byproducts (not further specified) by Reline [94]. These processes have not reached viable industrial use so far.

A further use of deep eutectic solvents is for the removal of toxic metallic elements from food. Choline chloride-based natural deep eutectic solvents (NADES) were effective for the removal of cadmium from rice flour, and the best solvent was the 1:1:2 mixture with tartaric acid and water, combined with 1% saponin surfactant [95].

5.4 Extraction of Bioactive Materials

A great deal of research has been directed toward the extraction of bioactive species from natural sources by means of deep eutectic solvents, as recently reviewed [96–98]. Deep eutectic solvents based on choline chloride, betaine, and proline with various hydrogen bond donating agents were tested for the extraction of alkaloids (efficiently) and anthraquinones (less so) from herbal medicines. The extraction of flavonoids, saponins, and phenolic acids was also tested, and the extractability with different solvents was correlated with their chemical and physical properties: hydrogen bonding, polarity, acidity, and viscosity [96]. Choline chloride-based deep eutectic solvents with various hydrogen bond donating agents were also used for leaching of alkaloids, flavonoids, and catechins from plant materials (tea leaves) after mechanochemical treatment [97]. Deep eutectic solvents based on choline chloride (mainly) were also reviewed regarding their extraction of bioactive compounds, including flavonoids, polysaccharides, proteins, and some other compounds from both plant and animal sources [98].

Many more specific studies regarding the extraction of bioactive molecules from various sources by means of deep eutectic solvents have also been published. Natural deep eutectic solvents consisting of choline chloride/sugars or polyols as well as some others have been used for the extraction of phenolic compounds from safflower seed oil [99]. Deep eutectic solvents consisting of sugars and polyols as the hydrogen bond donating agents with choline chloride and some other hydrogen bond accepting agents were used for the extraction of flavonoids from Chinese herbs [100]. Reline, Ethaline, Glyceline, and choline chloride/thiourea were the deep eutectic solvents tested for the extraction of the antimalarial compound glaucarubinone from the roots of an American tropical tree, the first of these solvents being the most effective [101].

Phenolic compounds were extracted from industrial byproducts involving onions, olives, tomatoes, and pears with deep eutectic solvents made up from a sugar (glucose and fructose) and a hydroxycarboxylic acid (lactic and citric) [102]. Polyphenols and furanocoumarins were extracted from *Ficus carica* L (fig leaves) by a nonionic deep eutectic solvent made up from equimolar amounts of d-fructose, xylitol, and glycerol [103]. Chrysoidine dyes, chrysoidine G, astrazon orange, and astrazon orange R, were extracted from food samples with choline chloride-based deep eutectic solvents assisted by ultrasound, the 1:3 choline chloride/ethylene glycol one being the most efficient [104]. Polygodial was extracted from *Pseudowintera colorata* (Horopito) leaves by 1:2 tetrabutylammonium chloride/1-dodecanol, which performed better than some other deep eutectic solvents tested [105].

Chinese herbs yielding traditional Chinese medicines were subjected to extraction with deep eutectic solvents in order to separate their active ingredients. The 1:1 choline chloride/1,2-propanediol solvent containing some water was used for the microwave-assisted extraction of both hydrophilic and hydrophobic compounds from the roots of Chinese red sage [106]. Choline chloride, betaine, and proline served as the hydrogen bond accepting component with various hydrogen bond donating agents for the extraction of flavonoid glycosides and aglycones from another kind of Chinese herb, *Platycladi cacumen* [107]. The major flavone *C*-glycosides were extracted from *Cymbidium kanran* with several deep eutectic solvents, the 1:4 choline chloride/dipropylene glycol solvent being the most efficient [108]. The flavonoid quercetin was extracted from *Ginkgo biloba* with deep eutectic solvents based on choline chloride with polyols (1:2 to 1:5 with ethylene glycol, glycerol, and 1,4-butenediol), the one with 1:3 choline chloride/glycerol being the most efficient [109]. The flavonoid rutin, occurring in citrus fruit, was extracted from a Chinese medicinal herb with a ternary deep eutectic solvent consisting of methyltriphenylphosphonium bromide/formic acid/chalcone (1,3-diphenylprop-2-en-1-one) [110]. Rutin may be made more bioavailable by its administration as a solution in natural deep eutectic solvents. Those solvents, based on proline with either choline chloride or glutamic acid proved to be the most effective, in terms of the solubility of rutin in them, among other solvents based on amino acids or sugars [111, 112]. Anthraquinones were extracted from rhubarb root with hydrophobic deep eutectic solvents based on choline chloride, decyl-, dodecyl-, or tetradecylammonium bromide with highly acidic hexafluoroisopropanol as the hydrogen bond donating component from aqueous salt solutions [113]. Polyprenyl acetates were extracted from *Ginkgo biloba* leaves by a deep eutectic solvent comprising 1:2:3 methyltrioctylammonium chloride/1-octanol/octanoic acid [114]. Bioactive compounds were extracted from *Artemisia* plants: artemisinin from *Artemisia annua* with 1:4 methyltrioctylammonium chloride/1-butanol [115] and rutin, quercetin, and scoparone from *Artemisiae scorpariae* with 1:2 choline chloride/formic acid (the most effective form among several other such solvents) [116].

Catechins were extracted from green tea by a variety of both ionic and nonionic eutectic solvents, and 4:20:1 betaine/glycerol/glucose proved to be the most effective one [117]. The harmful ochratoxin A that contaminated wheat and derived products could be determined effectively by extraction with Reline or Glyceline [118]. Ferulic, caffeic, and cinnamic acids were subjected to ultrasound-assisted microextraction with Ethaline or Glyceline from olive, almond, sesame, and cinnamon oils (simulated by *n*-hexane) for subsequent HPLC-UV determination [119]. Volatile compounds, such as nicotine and solanone, were isolated from tobacco by means of microwave-assisted microextraction with Reline or Ethaline [120]. Glyceline was used in a flow method for the extraction of procainamide from human saliva for spectrofluorimetric determination [121]. Ethaline was used for the ultrasonic-assisted extraction of sesamol from sesame oils [122].

The hydrophobic deep eutectic solvents tetrabutylammonium chloride or menthol with a carboxylic acid (acetic, pyruvic, levulinic, butanoic, hexanoic, octanoic, and dodecanoic acids) were used in two-phase aqueous extractions to remove pesticides (acetamprid, imidacloprid, nitenpyram, and thiamethoxam) from aqueous environments [123]. Volatile carboxylic acids (acetic, propanoic, and butanoic) can be extracted from aqueous solutions by means of hydrophobic deep eutectic solvents consisting of tetraalkylammonium chloride or bromide (alkyl = butyl, heptyl, or octyl) with decanoic acid [10]. Maline was tested for the extraction of 2-phenylethanol (fragrance material) from aqueous solutions, but turned out to be inferior to several room temperature ionic liquids for this purpose [124].

Special techniques, involving solid-phase extraction, were developed for the extraction of certain solutes using deep eutectic solvents. Ultra-trace analysis of organochlorine pesticides was accomplished by means of dispersive solid-phase extraction with deep eutectic solvents based on choline chloride with phenol, acetic acid, glycerol, or urea sorbed on magnetic multi-walled carbon nanotube composites [125]. A mixture of choline chloride and itaconic acid (2-methylidenesuccinic acid) was polymerized and grafted on silica-covered magnetic microspheres and applied for solid-phase extraction of trypsin [126]. The 1:2 betaine/ethylene glycol deep eutectic solvent was either sorbed on mesoporous silica or reacted with the monomer 3-aminopropyltriethoxysilane to form the molecularly imprinted polymer, used in solid-phase extraction and purification of levoflaxin from green bean extracts [127]. Graphene modified by choline chloride-based deep eutectic solvents (Ethaline, Reline, and Glyceline) was used for solid-phase (imbedded in a pipette tip) extraction of the drug sulfamerazine from river water [128]. A deep eutectic solvent as an acceptor phase in a three-phase hollow fiber liquid-phase microextraction was used for extraction and pre-concentration of steroidal hormones from biological fluids. The deep eutectic solvents acceptor phase comprised 1:4 choline chloride or methyltriphenylphosphonium bromide or iodide with ethylene glycol [129].

Low transition temperature mixtures (LTTMs) based on sodium acetate were used for the extraction of antioxidants from red grape pomace, the most efficient mixture being the 1:5 sodium acetate/lactic acid mixture [130]. Microwave-assisted pretreatment of the microalgae *Phaeodactylum tricornutum* with deep eutectic solvents composed of choline chloride with carboxylic acids (oxalic or levulinic) was effective for subsequent extraction of lipids from the algae [131]. Benzoylurea residuals in water samples were determined by dispersive microextraction based on freezing temperature control, using 1:1 methyltrioctylammonium chloride/1-dodecanol deep eutectic solvent [132].

Proteins and other polymeric biomolecules constitute a special class of solutes, the extraction of which in aqueous two-phase systems (ATPS) by deep eutectic solvents having been studied. Reline as well as other quaternary ammonium halide/urea mixtures was used for the extraction of bovine serum albumin from an aqueous phase containing K_2HPO_4 [133]. Such an aqueous phase was also used for the extraction of this protein with Glyceline [134]. Ternary deep eutectic solvents based on betaine/hydrogen bond donating agent (urea, methylurea, ethylene glycol, glycerol, sorbitol, and glucose)/water at certain molar ratios were used for ATPS extraction of bovine serum albumin, trypsin, and ovalbumin [135]. Natural deep eutectic solvents based on citric acid with choline chloride, betaine, and in particular with fructose were effective for the extraction of gluten for immunoassay [136]. Tetrabutylammonium bromide/polyols or PEG 600 (polyethylene glycol with a mean of 14 $-C_2H_4O-$ groups) was used in ATPS for the extraction of DNA [137] and RNA [138]. Magnetic graphene oxide modified with choline chloride-based deep eutectic solvents (Reline, Ethaline, Glyceline, or with glucose) was used for solid-phase extraction of proteins (bovine serum albumin, ovalbumin, bovine hemoglobin, and lysozyme) [139, 140].

The variety of deep eutectic solvents that have been used for the extraction of bioactive solutes from natural materials is summarized in Table 5.3.

Table 5.3 Deep eutectic solvents used for the extraction of bioactive solutes from natural materials

Hydrogen bond acceptor	Hydrogen bond donor	Ref.
Choline chloride	Urea (Reline)	[101, 118, 120, 125, 128, 133, 139, 140]
	Thiourea	[101]
	1,2-ethanediol (Ethaline)	[101, 104, 119, 120, 122, 128, 139, 140]
	Gycerol (Glyceline)	[101, 118, 119, 121, 125, 128, 134, 139, 140]
	Polyols	[99, 100, 106, 108]
	Sugars	[99]
	Phenol	[125]
	Formic acid	[116]
	Levulinic acid	[109, 131]
	Oxalic acid	[131]
	Itaconic acid	[126]
	Citric acid	[136]
Tetrabutylammonium$^+$ Cl$^-$	Dodecanol	[105]
	Carboxylic acids	[123]
Tetrabutylammonium$^+$ Br$^-$	Polyols, PEG	[137, 138]
$MeOc_3N^+$ Cl$^-$	Butanol	[115]
	Dodecanol	[132]
	Octanol + octanoic acid	[114]
Tetradecylammonium$^+$ Br$^-$	Hexafluoroisopropanol	[113]
$MePh_3P^+$ bromide	Formic acid/chalcone	[110]
Proline	Various	[107, 111, 112]
Betaine	1,2-ethanediol	[127]
	Glycerol, glucose	[117]
	Citric acid	[136]
	Various	[107, 111, 112, 135]
Menthol	Carboxylic acids	[122]
Glucose	Lactic, citric acid	[102]
Fructose	Lactic, citric acid	[102, 136]
	Xylitol + glycerol	[103]
Sodium acetate	Lactic acid	[130]

5.5 Sorption of Obnoxious Gases

The capture in liquids of obnoxious gases, such as the main greenhouse gas carbon dioxide and the pollutant sulfur dioxide, has received much attention in recent years [141]. Aqueous ethanolamine is employed as an efficient agent for the capture of carbon dioxide [142] but has several drawbacks. These include corrosion problems, high solvent volatility, and in particular large costs of its thermal regeneration from the carbamate generated from the carbon dioxide. Ionic liquids have been proposed for this purpose too [143], having extremely low volatility, but are costly to manufacture and generally not ecologically advantageous. Deep eutectic solvents emerged recently as being free from most of these disadvantages [144]. They are inferior to aqueous ethanolamine in their carbon dioxide sorption capacity, but have been claimed to compete with it economically, taking the cyclic process of sorption/regeneration together.

The capacity of a solvent for the capture of a gas, the mass of the dissolved gas at equilibrium per unit mass of solvent at a given temperature and partial pressure of the gas, is a key quantity to be reported. The capacity may be expressed as the molality of the gas in the deep eutectic solvent: moles of gas per 1 kg solvent, at a given temperature and gas pressure. Further characterizing quantities that have been reported are the Henry law constant (the lower it is, the higher the solubility) and the molar enthalpy of dissolution of the gas. The quantities expressing the solubility of gases in solvents have been dealt with in more detail in Sect. 3.6.5.

The first report on the dissolution of a gas in a deep eutectic solvent, Glyceline, just stated that when carbon dioxide at 50 bar pressure is dissolved and the pressure is released, vigorous degassing takes place, but this phenomenon was not further quantified [145]. The first quantitative study of the solubility of a gas in a deep eutectic solvent was that of Li et al. [146], who measured the solubility of carbon dioxide in Reline. The results of this and similar studies were recorded as g gas/g solvent, converted to molality, m_{gas} = mol gas/kg solvent, to mol gas/mol solvent, or to the mole fraction $x_{\mathrm{gas}}(P, T)$ in the saturated solution at the employed gas partial pressure P and temperature T.

Ali et al. [147] have recently analyzed the operating conditions for an industrial process for the capture of carbon dioxide in a deep eutectic solvent and its subsequent release and compared it advantageously with the current industrial process [142]. The solubility of carbon dioxide in a deep eutectic solvent diminishes as the temperature is raised, and therefore the release of the carbon dioxide and the regeneration of the solvent for a further cycle are affected by a definite temperature swing.

The solubility of carbon dioxide in a variety of deep eutectic solvents is presented in Table 5.4 in terms of the Henry's law constants on the molality basis, $k_{\mathrm{H}(m)}$ at 40 °C for choline chloride-based solvents (there not being sufficient comparative data at 25 °C, although these are all liquid, some rather viscous, at this temperature) and at 25 °C for solvents based on other quaternary ammonium salts or phosphonium salts. The 40 °C temperature is characteristic for the process of the

Table 5.4 H's law constants for the solubility of carbon dioxide in deep eutectic solvents, at 40°C for choline chloride-based solvents and at 25°C for the other solvents

Hydrogen bond acceptor	Hydrogen bond donor	Ratio	$k_{H(m)}$ (MPa kg mol^{-1})	$-\Delta_{sol}H$ (kJ mol^{-1})	Ref.
Choline chloride	Urea	1:2	0.245^{a}	17.2	[146]
			0.578^{a}	14.9	[157]
			0.334	17.0	[174]
			0.393		[163]
			0.439		[156]
	1,2-ethanediol	1:2	0.271	19.4	[175, 176]
			0.390		[163]
	1,2-propanediol	1:2	0.263^{b}		[177]
	1,3-propanediol	1:4	0.443	18.8	[175]
	1,3-butanediol	1:2	0.344		[174]
	1,4-butanediol	1:4	0.418	9.9	[175]
	2,3-butanediol	1:4	0.344	9.8	[175]
	Diethyleneglycol	4:1	0.394	14.4	[178]
	Triethyleneglycol	4:1	0.372	14.4	[178]
	Glycerol	1:2	0.170	22.7	[163, 179]
			0.170	17.0	[174]
			0.294^{b}		[163]
	Furfuryl alcohol	1:3	0.354	11.67	[180]
	Fructose	1:1	0.605^{i}		[152]
	Phenol	4:1	0.336	12.3	[178]
	Phenylacetic acid	1:2	0.148	3.11	[149]
	Malic acid	1:1	0.476		[177]
		1:1	0.592^{i}		[152]

(continued)

Table 5.4 (continued)

Hydrogen bond acceptor	Hydrogen bond donor	Ratio	$k_{H(m)}$ (MPa kg mol^{-1})	$-\Delta_{sol}H$ (kJ mol^{-1})	Ref.
	Lactic acid	1:2	0.95[a]	15.5	[150]
			0.400		[175]
			1.29	15.50	[181]
		1:1	0.643[i]		[152]
	Citric acid	1:1	0.576[i]		[152]
	Levulinic acid	1:2	0.145	4.9	[167]
		1:3	0.262	15.35	[180]
Tetramethylammonium Cl	Acetic acid	1:4	2.45		[173]
	Lactic acid	1:2	9.90[g]		[173]
Triethylmethylammonium Cl	Acetic acid	1:2	2.44		[173]
	1,2-ethanediol	1:2	2.23		[173]
	Glycerol	1:2	8.82		[173]
	Lactic acid	1:2	3.04		[173]
	Levulinic acid	1:2	2.39		[173]
Tetraethylammonium Cl	Acetic acid	1:2	1.95		[173]
	Lactic acid	1:2	9.62[g]		[173]
	Levulinic acid	1:3	2.04[h]		[173]
Tetraethylammonium Br	Levulinic acid	1:3	2.36[h]		[173]
Triethylbutylammonium AcO	Water	1:1	8.89[d]		[173]
Triethylbutylammonium Mal[c]	Water	1:6	4.67[d]		[173]
Tetrabutylammonium Cl	Lactic acid	1:2	7.23[g]		[173]
	Levulinic acid	1:3	1.85[h]		[173]
Tetrabutylammonium Br	Acetic acid	1:2	2.83		[173]

(continued)

Table 5.4 (continued)

Hydrogen bond acceptor	Hydrogen bond donor	Ratio	$k_{H(m)}$ (MPa kg mol^{-1})	$-\Delta_{sol}H$ (kJ mol^{-1})	Ref.
	Levulinic acid	1:3	2.10[h]		[173]
Benzyltriethylammonium Cl	Acetic acid	1:2	2.56		[173]
BenzyldiethylEtOHN[e] Cl	Acetic acid	1:2	3.28		[173]
Acetylcholine Cl	Levulinic acid	1:3	1.79[h]		[173]
Choline prolinate	PEG200	1:1	1.80[f]		[173]
Methyltriphenylphosphonium Br	1,2-propanediol	1:4	10.0		[173]
	Glycerol	1:4	17.9		[173]
	Levulinic acid	1:3	12.5		[173]

[a] Recalculated from reported $k_{H(x)}$ values
[b] At 30 °C
[c] Mal = malonate
[d] Converted from reported $k_{H(x)}$ in [154]
[e] Benzyldiethyl-2-ethanolammonium
[f] Converted from reported $k_{H(x)}$ in [182]
[g] Converted from reported $k_{H(x)}$ in [183] at 35 °C
[h] At 30 °C [184]
[i] Interpolated between 35 and 45 °C

capture of carbon dioxide from flue gases. The saturation molalities are related to the Henry's law constants as m =0.1 MPa/$k_{\mathrm{H}(m)}$, the partial pressure of the carbon dioxide being 0.1 MPa (1 bar, ∼1 atm). The molar enthalpies of solution for the gas dissolution process are also shown in Table 5.4 when available, serving for the evaluation of the solubility at other temperatures.

Considerably less information is available regarding the solubility of sulfur dioxide in deep eutectic solvents. Although the sorption of sulfur dioxide in these solvents is linear with its partial pressure [148], the lines do not pass through the origin, and hence Henry's law appears not to be valid at the large concentrations of sulfur dioxide that were found. Therefore, the data are reported in Table 5.5 as saturation molalities at 1 bar (0.1 MPa) partial pressure rather than as Henry's law constants.

Deep eutectic solvents have been proposed for the purpose of separation of mixtures of gases, but there is hardly any information related to the solubilities of gases other than carbon dioxide and sulfur dioxide in these solvents. The solubility of nitrogen in 1:2, 1:3, and 1:4 choline chloride/phenylacetic acid has been reported

Table 5.5 Solubility of sulfur dioxide in deep eutectic solvents at 1 bar pressure and 40 °C

HBA	HBD	Ratio	m (mol kg^{-1})	Ref.
Choline chloride	Urea	1:2	4.50	[159]
	Thiourea	1:1	8.76	[159]
	1,2-ethanediol	1:2	6.22	[159]
	Glycerol	1:2	4.00	[148]
	Glycerol	1:1	10.05^{a}	[153]
	Malonic acid	1:1	4.31	[159]
	Levulinic acid	1:3	4.45	[185]
Acetylcholine chloride	Levulinic acid	1:3	4.84	[185]
Tetraethylammonium Cl	Levulinic acid	1:3	5.67	[185]
Tetraethylammonium Br	Levulinic acid	1:3	5.78	[185]
Tetrabutylammonium Cl	Levulinic acid	1:3	4.63	[185]
Tetrabutylammonium Br	Levulinic acid	1:3	5.19	[185]
	Caprolactam	1:1	3.93	[186]
Trimethylaminoacetate	1,2-ethanediol	1:1	5.71	[161]
Trimethylamino-2-OH- butyrate	1,2-ethanediol	1:1	5.70	[161]
Imidazole	Glycerol	1:2	2.52	[187]
2-Et-3-Me-imidazolium Cl	1,2-ethanediol	1:2	18.0^{b}	[188]
Ammonium thiocyanate	Urea	2:3	4.40	[189]
	Acetamide	1:3	5.32	[189]
	Caprolactam	1:3	5.79	[189]
Potassium thiocyanate	Acetamide	1:3	5.73	[189]
	Caprolactam	1:3	6.60	[189]

[a] At t =77 °C
[b] At t =20 °C

[149]. The interpolated saturation molality in the 1:2 mixture (eutectic) at 40 °C and 0.1 MPa partial pressure is 0.106 mol kg^{-1}, the Henry law constant is 0.943 MPa kg mol^{-1}, and the molar enthalpy of solution is −5.63 kJ mol^{-1}, the solubility of sulfur dioxide being ~50% larger than the values for carbon dioxide, Table 5.4. Ammonia was absorbed by deep eutectic solvents based on 1:3:5 choline chloride/resorcinol/glycerol, reaching 10.6 mol/kg solvent at 20 °C, reduced to 7.5 mol/kg solvent at 40 °C [150]. Ethaline was used in a thin layer on the electrode in an amperometric device for monitoring oxygen contents in atmospheres, at 2.0–26.5 °C [151]. Whereas nitrogen dioxide was reduced at a similar potential as oxygen, no interference by N_2, CO, CO_2, NO, SO_2, and H_2S was observed. No implications regarding the solubilities of these gases in the deep eutectic solvent were reported, however. The solubility of CO_2, CH_4, H_2, CO, and N_2 in Reline deep eutectic solvent was predicted—although in many cases unsatisfactorily—using NRTL and COSMO-RS models [151]. The absorption of nitrogen, besides carbon dioxide, in the natural deep eutectic solvents (NADES) consisting of 1:1 choline chloride with fructose, and malic, citric, or lactic acids at 25–55 °C is reported in [152], where molecular dynamics simulations were used to model the absorption.

The solubility of the gases that were studied in the deep eutectic solvents diminishes as the temperature is increased, manifested by the negative molar enthalpies of solution of the gas, Table 5.4. The pressure dependence of the saturation capacities of the gas in the various deep eutectic solvents is linear up to moderate pressures, 30 MPa. Therefore, absorption of the gas in the deep eutectic solvents at a relatively low temperature permits its subsequent release at a higher temperature by diminishing the pressure or, in the case of sulfur dioxide, by bubbling of nitrogen [153] for recycling the solvent.

In some cases, the gas solubility has been studied with regard to the composition of the solvent, in terms of the ratios of the hydrogen bond accepting and hydrogen bond donating components that do not correspond to the eutectic, but no generalization can be deduced from the published data. The solubility of carbon dioxide in the non-eutectic 1:3 choline chloride/phenylacetic acid mixture is ~50% larger than in the eutectic 1:2 mixture, but no such difference was noted for the solubility of nitrogen [151]. In a molecular dynamics study, the solubility of sulfur dioxide in the non-eutectic 1:1 choline chloride/glycerol mixture was stated to be larger than in the eutectic [153].

Deep eutectic solvents based on triethylbutylammonium acetate, propionate, butyrate, malonate, succinate, phthalate, malate, and citrate as the hydrogen bond acceptor and water as the hydrogen bond donor at mole ratios from 1:1 to 1:6 that exhibit very low glass transition temperatures (<−49 °C) have been used to absorb carbon dioxide [154]. Guanidinium malate (prepared from the carbonate with malic acid)/ethylene glycol deep eutectic solvent was used in [155] for the capture of carbon dioxide and addition of arginine improving the absorption ability. The sorption of carbon dioxide at 25 °C in, for example, 1:1 triethylbutylammonium butyrate/H_2O is 1.32 mol carbon dioxide per kg of solvent at 0.044 MPa partial pressure. The carbon dioxide reacted with the water to form the bicarbonate anion. However, no information on release of the carbon dioxide and recycling the solvent was provided.

On the other hand, the effect of water on the sorption of carbon dioxide by conventional deep eutectic solvents is deleterious, water serving as an anti-solvent, inducing the release of the gas. Water has the beneficial effect of decreasing the viscosity in the case of Reline, permitting faster absorption, but it reduces the equilibrium solubility. For instance, the saturation mole fraction of carbon dioxide in this solvent at 35 °C and 2.5 MPa pressure diminishes from 0.120 to 0.110 to 0.097 as the mass fraction of water increases from 0.0185 to 0.0910 to 0.183 [156]. In another report, at this temperature and at 0.1 MPa pressure, the saturation mole fraction of carbon dioxide in the solvent diminishes from 0.0030 to 0.0020 to 0.0011 as the mass fraction of water increases from 0.0106 to 0.0909 to 0.308 [157]. At the same temperature and with a mass fraction of water of 0.200, the saturation molality of carbon dioxide in Ethaline and Glyceline diminishes by 4.5 and 1.5%, respectively [158].

The mechanism of the dissolution of carbon dioxide in the deep eutectic solvent is generally regarded as being physical absorption of the nonpolar but highly polarizable gas in interstices in the hydrogen-bonded structure of the liquid solvent. This is manifested by the ready removal of the carbon dioxide as the pressure on the gas-saturated solvent is diminished and the temperature is increased. Bubbling nitrogen through the loaded solvent can also be used, since although at the lower temperature carbon dioxide is absorbed slightly better than nitrogen, this is reversed at a somewhat higher temperature [152]. This mechanism contrasts with the carbamate formation that takes place in aqueous ethanolamine that is the present industrial practice, which is energetically expensive for its reversal and for regeneration of the solvent.

In the case of the dissolution of sulfur dioxide in deep eutectic solvents, there is some evidence that the solute may interact specifically with molecular groups in the solvent. Nevertheless, the sulfur dioxide can be displaced from choline chloride-based solvents by nitrogen bubbling [159] and ^{1}H NMR analysis indicated that the sorption process in the caprolactam/acetamide deep eutectic solvent is of physical nature [160]. However, with solvents based on betaines as hydrogen bond accepting components (trimethylglycine or l-carnitine) and 1,2-ethanediol as the hydrogen bond donating component, ^{1}H and ^{13}C NMR spectra indicated interaction of the sulfur dioxide with the $–CO_2^-$ group of the solvent [161].

The solubility of carbon dioxide in deep eutectic solvents was modeled by means of the Peng–Robinson equation of state [162] for a variety of such solvents or by a modification of it [163] for Reline and Ethaline. The perturbed-chain statistical associated fluid theory (PC-SAFT) was applied for the modeling [164] of solvents composed of tetraalkylammonium chloride/lactic acid (alkyl = methyl, ethyl, butyl). This method was also employed for modeling the carbon dioxide solubility in tetraoctylammonium chloride (or bromide) with decanoic acid (or perfluorodecanoic acid) forming hydrophobic deep eutectic solvents [165]. Molecular dynamics simulations were used for the study of the interfacial properties of systems involving Reline, Glyceline, and Maline as the solvents and carbon dioxide and sulfur dioxide as the dissolving gases [166] and in a study of the liquid/vapor interface on dissolution of carbon dioxide in the choline chloride/levulinic acid deep eutectic solvent [167]. The dissolution of sulfur dioxide in deep eutectic solvents was modeled using the cubic plus association equations of state and the nonrandom two liquid (NRTL) and UNIQUAC models [168].

The physicochemical properties and the gas separation applications of deep eutectic solvents have been recently reviewed [169], as have the solubilities of the gases [170, 171]. The value of these solvents as "green" solvents and attractive media for the capture of carbon dioxide was reviewed in [172], and their screening for this purpose was reviewed in [173].

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Chapter 6
Trends and Prospects for Deep Eutectic Solvents

6.1 Sustainable Chemistry

The trends regarding the chemical industry for the twenty-first century are along several paths [1]. One trend is the replacement of fossil raw materials (oil, natural gas) or mined minerals with renewable sources, such as biomass or recycled wastes. Sustainable processes for the valorization of waste biomass by its conversion to biofuels (biodiesel) via green processes are currently in the forefront of research. Trends in the minimization of industrial wastes and their treatment for a sustainable environment are also currently of importance [2]. The advent of neoteric solvents has been an important step in this direction, deep eutectic solvents playing a major role in this process. Another trend is the replacement of stoichiometric processes by catalytic ones, in particular, those involving enzymes, and heterogeneous catalysis replacing homogeneous one for the purpose of recycling the catalyst. Deep eutectic solvents are involved in this trend too. The use of mechano-chemistry, ultrasound, and microwaves as energy inputs rather than the application of external heat is another trend used in the synthesis of organic materials [3].

Deep eutectic solvents, also called low-transition temperature mixtures, have been deemed to be "the organic reaction medium of the century" [4]. These solvents may play the role of an active catalyst besides serving as the solvent for the reaction. For example, the deep eutectic solvents formed between choline chloride and zinc chloride or trimethylcyclohexylammonium methanesulfonate and *p*-toluenesulfonic acid use their acidic natures for the catalysis of the esterification of long-chain and aromatic carboxylic acids with alkanols. These are illustrations of one of the many organic reactions that have been and can be carried out in deep eutectic solvents, including alkylation, cyclization, condensation, redox, and organometallic reactions [4]. A large portion of the publications dealing with deep eutectic solvents pertain to a choline salt as one of the components. The application of such salts in organic transformations has been recently reviewed [5], including reactions catalyzed by choline (cholinium) chloride without or with metallic Lewis

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acids or carboxylic acids or by choline hydroxide, or reactions involving oxidizing agents. Such ionic liquids are said to be “the future solvents of the chemical and allied industry” because of their “green” properties. The use of deep eutectic solvents in polymerization reactions has recently been reviewed too [5], noting that a monomeric component of the solvent itself may undergo polymerization, or else the liquid serves just as a solvent for the reaction. As examples, acrylic or methacrylic acid, acting as the hydrogen bond donor of the deep eutectic mixture with choline chloride, can thus be polymerized. Another example is the polymerization of hydroxyethylmethacrylate in the choline chloride/ethylene glycol deep eutectic solvent [6]. These methods of polymerization should become more extensively used because of the “greenness” of the deep eutectic solvents.

Biomass treatment in deep eutectic solvents has come to the forefront of technical innovation along two paths: biocatalysis by such solvents that are compatible with enzymes and biodiesel production from lignocellulose. Enzymes, such as lipases, proteases, epoxide hydrolases, and peroxidases can be used in deep eutectic solvents, such as choline-based ones, or their mixtures with water [6]. Highly polar substrates, such as carbohydrates and nucleosides, can be treated in deep eutectic solvents, in those cases when water cannot be used because it may hydrolyze the products. Pretreatment and saccharification of lignocellulose can thus be carried out in deep eutectic solvents in order to produce biodiesel liquid fuel [7]. The tunability and biodegradability of deep eutectic solvents is stressed in [8], where organocatalysis (basic or acidic) and biotransformations in these solvents are dealt with. “Given their promising features, it may be expected that many applications in these areas will appear in the coming years” is a conclusion of this report. In another recent review [9], the eco-friendly and sustainable aspects of deep eutectic solvents are emphasized and many organic synthetic reactions are described. The recent progress concerning deep eutectic solvents in biocatalysis is discussed in [10], where the understanding of how these solvents affect the biocatalytic reaction is said to lead to new applications.

Biomass valorization into valuable chemicals is attracting much attention in recent years, and deep eutectic solvents play a leading role in this direction. Biodiesel, a liquid fuel resulting from the transesterification of vegetable oils or animal fats in deep eutectic solvents has gained tremendous attention in recent years [11]. These solvents act also as cosolvents, catalysts, and extracting agents, and choline chloride/zinc chloride is an example of a solvent and acid catalyst. Lipase is an active enzyme for biodiesel production in, e.g., choline chloride/glycerol solvent, and this solvent is also effective for the extraction of glycerol from crude biodiesel. The recycling of the deep eutectic solvents is also dealt with in this review [11]. Lignocellulosic biomass is a source of lignin that can be valorized and the biomass can be pretreated and fractionated into its components (cellulose, hemicellulose, and lignin) in these solvents [12]. Starch is relatively soluble in some deep eutectic solvents, e.g., choline chloride/malic acid and lignin is quite soluble in certain deep eutectic solvents (e.g., betaine/lactic acid), but cellulose is hardly soluble in deep eutectic solvents so that the biomass can be fractionated. Degradation of the cellulose to 5-hydroxymethylfurfural (HMF) is a target of an application described in detail [12].

On a quite different level is the relation of natural deep eutectic solvents to biochemical and physiological processes. Such solvents (NADES) can act as cryoprotective agents, preventing the formation of ice crystals in cells. In some insects and even in a vertebrate living thing (frog), their intervention is useful. An example is the combination urea/glucose/amino acids in frogs [13]. The formation of non-water-soluble compounds, such as rutin, quercetin, cinnamic acid, carthamin, taxol, ginkgolide B, and 1,8-dihydroxyanthaquinone in plants has been explained by the role that natural deep eutectic solvents play in their formation and transport [14]. This unexpected activity/stability is explained by the large and strong hydrogen bond network formed in such solvent mixtures. These eutectic mixtures may also explain the holding of water in plants against its evaporation in very arid areas. Molecularly imprinted polymers (MIPs) are of increasing interest due to their specific binding sites and molecular recognition ability. Their production in deep eutectic solvents has been compared with that in room temperature ionic liquids in [15].

The use of deep eutectic solvents for biocatalysis has recently been reviewed [16]. These solvents may have a significant effect on selectivity, stability, and activity of enzymes through their H-bond basicity, ion kosmotropicity, amphiphilicity, hydrophobicity, polarity, and viscosity. “In particular, the combination of reaction and separation will be of interest in the future as here the potential of deep eutectic solvents can be exploited to full extent.” Deep eutectic solvents “have been used as media, solvents/cosolvents or as catalysts for various biological processes, it seems clear that they possess enormous potential for beneficial applications in the future” [17]. This quote is taken from a recent review of the applications in biotechnology and bioengineering—promises and challenges, where, however, it is stressed that the safety (toxicity) concern of these mixtures must be sufficiently addressed.

6.2 Materials and Nanotechnology

The many applications described in Sect. 4.4 point to the expected development foreseen for the use of deep eutectic solvents in the field of nanotechnology. Novel materials or materials with novel properties produced in deep eutectic solvents for their use in heterogeneous catalytic activities are one aspect of the emerging trends. These new nanomaterials, gold nanowire networks, are good candidates for future applications in catalysis [18]. The high viscosity of the Ethaline deep eutectic solvent helps the synthesis of gold nanofoams, “a synthetic strategy that may open a new avenue to the DES-assisted synthesis of inorganic nanofoams and functional devices” [19]. Turning from metals to oxides, it was suggested that “as a burgeoning field, the development of DESs assisted routes for the synthesis of TiO_2 nanomaterials offers both opportunities and challenges for future developments in nanomaterials synthesis." [20]. Iron oxides as "green materials for the photo-electrochemical splitting of water", produced by a microwave-assisted solvothermal methodology in Reline [21] are another example of prospective uses of deep eutectic solvents. Formation of "functional materials, including noble metals, porous carbonaceous materials, transition metal compounds" in deep eutectic solvents (DES) should "inspire scientists to use DES as a powerful tool to push the frontiers of materials, energy and environmental science" is proposed in [22].

Another trend in the use of deep eutectic solvents for the production of nanomaterials is the all-in-one-pot synthetic methods. The choline chloride/$CaCl_2 \cdot 6H_2O$ reaction medium provided "calcium-active sites, and electrosteric stabilization required for formation and growth control of fluoroapatite nanoparticles … introducing and developing a simple, rapid, and sustainable method toward green and economical synthesis of fluoroapatite nanobiomaterials" [23]. In a one-step process, pyrolysis of a mixture of seaweed granules and choline chloride/$FeCl_3$ deep eutectic solvent was employed as a source of iron, as a template, and as a catalyst for the production of Fe_3O_4/Fe-doped graphene nanosheets [24].

The prospects for using deep eutectic solvents in analogy with the already established use of room temperature ionic liquids in nanotechnology have been summarized a few years ago in [25].

Eutectogels (ETGs) have recently been introduced as a new class of solid composite electrolytes and been prepared easily via a sol–gel route in the deep eutectic solvent constituted by lithium bis(trifluoromethane)sulfonamide with *N*-methylacetamide. These solid composite electrolytes demonstrate an acceptable thermal and electrochemical stability and high ionic conductivity at room temperature. The Li/$LiFePO_4$ half cells assembled with ETGs deliver a stable and reversible specific capacity for over 60 cycles. There are good prospects for the application of ETGs in lithium ion or metal batteries, hence opening up new horizons toward safer, cheaper and more performant devices [26]. A ternary mixture of 2:3:1 choline chloride/urea/glycerol has been used to form a novel gel polymer electrolyte from phthaloylated starch that forms a bioelectrolyte with appreciable conductivity [27].

6.3 Analytical Chemistry, Sorption and Extraction

There are many prospects for natural deep eutectic solvents in analytical chemistry, where they may be used for sample preparation as solvents, as extracting agents, or as reaction media [28], and may further be used in liquid chromatography. Gluten may be extracted from foods for its subsequent determination by using natural deep eutectic solvents, such as the water-diluted citric acid/fructose combination with sonification [29]. Environmentally friendly and nonpolluting solvent pretreatment of palm oil samples for polyphenol analysis using choline chloride based deep eutectic solvents [30] and speciation, pre-concentration and determination of selenium (IV) and (VI) species in water and food samples with choline chloride/phenol

[31] are other examples of the emerging use of such solvents in analytical chemistry. The present applications of deep eutectic solvents in analytical chemistry and trends in these applications are reviewed in [32].

Indirect applications of deep eutectic solvents for a sustainable environment, which may show trends in future applications, are illustrated by the use of such solvents for the preparation of efficient sponges for selective removal of oils from water. Hydrophobic, super-absorbing aerogels result from cellulose nanofibrils pretreated by Reline and then silylated, which have the desired properties [33].

Deep eutectic solvents were expected to play a major role in the extraction of bioactive compounds from various sources for analytical purposes [34]. An overview as well as challenges and opportunities regarding the application of deep eutectic solvents for the extraction of phenolic compounds extraction are presented in [35].

The capture of carbon dioxide in deep eutectic solvents as alternatives to the capture in organic amines or in room temperature ionic liquids is gaining attention. It is possible to develop novel deep eutectic solvents with promising absorption capacity, but more studies are needed to determine the absorption mechanism and to clarify how these sorbents can be adjusted and fine-tuned to be best tailored as optimized media for carbon dioxide capture [36].

6.4 Unconventional Deep Eutectic Solvents

Most of the studies regarding the use of deep eutectic solvents heretofore have used conventional combinations of a hydrogen bond accepting salt (such as choline chloride, tetrabutylammonium chloride, or methyltriphenylphosphonium bromide) and an organic hydrogen bond donating agent (such as urea, ethylene glycol, glycerol, or malonic acid), and some such solvents are commercially available (Reline, Ethaline, Glyceline, Maline). Their applications have been described in Chaps. 4 and 5, and trends regarding these applications are presented above.

More recently, nonconventional deep eutectic solvents that need not be ionic have been added to the tool kit of reaction media and extractants. These include natural deep eutectic solvents (NADES) based on zwitterionic amino acids (betaine, proline), solvents based on lidocaine, menthol, or glucose with carboxylic acids, or mixtures of long-chain carboxylic acids. Deep eutectic solvents based on water as the hydrogen bond donating agents with *N*-alkyl heterocyclic salts or with inorganic salt hydrates as the accepting agents have also been introduced, and their applications are promising but still pending.

However, a deep eutectic solvent based on betaine with polypropylene glycol 400 has recently been introduced for aqueous biphasic extraction systems used in pigment partitioning [37]. The use of the deep eutectic solvent formed by menthol with dodecanoic acid for the extraction of the lower alkanols from aqueous solutions has recently been proposed [38]. Deep eutectic solvents comprising mixtures of two long-chain carboxylic acids have recently been promoted as hydrophobic extracting agents [39].

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