

# Chapter 1

## Introduction

This book deals with ionic liquids, i.e., with single substances in their liquid state of aggregation that are dissociated into ions to a major extent. Because of the enormous amount of information that is available regarding this subject, the book does not deal with mixtures of ionic liquids nor with their solution (as electrolytes) in molecular solvents. Furthermore, the information presented here is in no way exhaustive, it is rather illustrative of the subjects dealt with and deals mostly with what was published in readily accessible literature to the end of 2014. The book emphasizes the properties of the ionic liquids and does not deal with their reactions and possible applications.

The properties of ionic liquids, because they are dissociated to a major extent into ions, depend on those of the constituting cations and anions. Therefore, Chap. 2 of the book is devoted in part to the properties of isolated ions that do not interact with their environment. These properties comprise their mass and charge, their standard thermodynamics of formation, and their entropy and heat capacity under standard conditions. The sizes of ions, once they are in a condensed phase, depends on their being constrained by their neighboring particles due to the repulsion of their outer electron shells. These properties of the individual constituting ions of ionic liquids are assumed to be ‘portable’ when they form the ionic liquid, some of them being subject to changes induced by the mutual interactions of the ions.

Ionic liquids comprise, as the chapter headings indicate, high-temperature molten salts, network-forming ionic liquids, low-temperature molten salts, and room temperature ionic liquids (RTILs). The interest of researchers in high-temperature molten salts, dealt with in Chap. 3, peaked in the 1950s and 1960s of the last century in connection of their possible use in the metallurgical industry and in nuclear fuel reprocessing. An introductory text [1], several multi-author monographs [2–4], a handbook [5] and data compilation [6], and a series of ‘advances’ from vol. 1 [7] to vol. 6 [8] were published. The interest in high-temperature melting salts has waned since then, but information is still accruing, summarized in the proceedings of international conferences, e.g., that of the 17th, held in Las Vegas in 2010 or of EUCHEM conferences held regularly up to date.

Network-forming molten salts, described in Chap. 4, are based on relatively low-melting zinc halides and on molten slags, i.e., high-melting borates, silicates, and germanates. Their structures involve polyhedral anions that share corners, sides, or faces, among which small cations are dispersed. These substances in the liquid state are in thermodynamic equilibrium, but they tend to form glasses rather than to crystallize when sufficiently cooled, such glasses being outside the scope of this book.

Low-melting ionic liquids, discussed in Chap. 5, have melting points characteristically  $<250$  °C and share many properties with the high-melting salts. They involve many substances in which either cation or anion is organic, e.g., tetraalkylammonium or carboxylate, but also purely inorganic salts. A special class of such low-melting ionic liquids are salt hydrates, in which the cation is hydrated, which on cooling from the liquid state may crystallize congruently (to a salt with the same composition as the melt) but need not do so. Salt hydrates have been suggested as thermal energy storage materials.

Room temperature ionic liquids (RTILs), the subject of Chap. 6, have become en vogue from the beginning of the present century, the number of publications dealing with them increasing exponentially since then and several books dealing with RTILs have by now been published, from an introduction [9] to further in depth discussions [10–12]. These substances are liquid at  $<100$  °C and a large variety of them have become commercially available by now, but new ones with various functionalities are being synthesized all the time. Again, due to the enormous variety of RTILs, only a small sub-group of them is dealt with here, namely aprotic RTILs with no added functionality in their cations and with a restricted variety of anions.

Certain inorganic salts, such as  $\text{HgI}_2$ ,  $\text{AsBr}_3$ , and  $\text{AlCl}_3$ , have low melting points ( $<250$  °C) but they do not dissociate appreciably to ions in the molten state. Since they do not constitute ionic liquids, such salts are outside the scope of this book.

Once the ions are combined to form ionic liquids with whatsoever melting points, the properties of such liquids become the subject of this book, ranging from their structures to thermodynamic, transport, electrical and optical properties as well as chemical properties as appropriate. Structures are determined by diffraction methods (with x-rays and neutrons) and similar techniques (EXAFS) and computer simulations. Thermodynamic properties include the liquid range, from the melting to the (normal) boiling point, or up to the critical point when relevant, the energetic changes involved in the phase changes, heat capacities, and surface tensions. Volumetric properties, such as density, thermal expansibility, and compressibility are presented. The cohesive energy and cohesive energy density of the liquid salt are also included. The transport properties include self-diffusion, viscosity, electrical conductivity, and thermal conductivity. The electrical and optical properties include the permittivity, the refractive index, and molar refraction. The chemical properties involve those that affect the abilities of the ionic liquids to act as solvents, hence their solvation abilities, mutual solubilities with water, as the most important representative of molecular liquids, their hydrophilicity and hydrophobicity, where relevant, and the solubility of carbon dioxide and some other solutes in them.

These properties are compiled in tables and are annotated: in many cases with reference to previous critical compilations and reviews, where references to the original literature may be found, and augmented with references to more recent references or those otherwise not included in the compilations and reviews. The selection of the data included in the tables is the responsibility of the author of this book, and it was attempted to select the data critically. No attempt was made, however, to be exhaustive of the profusion of available data nor was it attempted to be comprehensive at all. The data that are presented in the Tables are discussed in terms of the physicochemical effects behind these data. Where appropriate, methods to predict such data from other information on the ionic liquids or their constituent ions or at least to make appropriate correlations with such information were presented.

## 1.1 List of Symbols

Chemical species and units of physical quantities are denoted by Roman type characters, whereas physical quantities that can be expressed by numerical values are denoted by Greek or *italics* characters. Mathematical symbols have their usual meaning and are not listed here. The same symbol is used for an extensive property of a system and for the molar quantity of a constituent of the system. The SI systems of physical units is used throughout, but some extra-SI ones commonly used in the physicochemical literature are also included where they simplify the notation. These include the symbols °C for centigrade temperatures ( $T/K - 273.15$ ).

### Principal Latin Characters

$A$	Helmholz energy, molar Helmholtz energy (in $\text{J mol}^{-1}$ )
$a_X$	thermodynamic activity of species X
$B(T)$	Tait expression temperature-dependent parameter
$B_x$	activation energy for process x ( $\eta$ , $\kappa$ , $A$ , or $D$ )
$ce$	cohesive energy (in $\text{kJ mol}^{-1}$ )
$ced$	cohesive energy density (in MPa)
$C_P$	molar heat capacity at constant pressure (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$C_V$	molar heat capacity at constant volume (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$c_X$	molar concentration of species X (in $\text{M} = \text{mol}\cdot\text{dm}^{-3}$ )
$C^{z+}$	a generalized cation
$D$	diffusion coefficient (in $\text{m}^2\cdot\text{s}^{-1}$ )
$d$	interionic distance (in nm)
$E$	energy, molar energy (in $\text{J}\cdot\text{mol}^{-1}$ )
$e$	elementary charge ( $1.6022 \times 10^{-19}$ C)
$E_T^N$	normalized polarity index
$F$	Faraday constant ( $9.6485 \times 10^4$ C $\cdot\text{mol}^{-1}$ )
$G$	Gibbs energy, molar Gibbs energy (in $\text{J}\cdot\text{mol}^{-1}$ )

$g(r)$	pair correlation function
$GP$	Gordon parameter
$H$	enthalpy, molar enthalpy (in $\text{J}\cdot\text{mol}^{-1}$ )
$h$	solvation (hydration) number
$I$	radiation scattering intensity
$I$	moment of inertia
$k_B$	Boltzmann constant ( $1.3807 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$ )
$K_H$	Henry's law constant
$m$	number of segments
$M_X$	molar mass of species X (in $\text{kg}\cdot\text{mol}^{-1}$ )
$N_A$	Avogadro's number ( $6.0221 \times 10^{23} \text{ mol}^{-1}$ )
$N_{\text{co}}$	coordination number
$n_D$	refractive index at the sodium D line
$P$	pressure (in Pa)
$p$	vapor pressure (in Pa)
$P_W^{\text{O}}$	octanol/water partition constant
$P_\sigma$	parachor
$R$	gas constant ( $8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$r_{\text{corr}}$	linear correlation coefficient
$R_D$	molar refractivity at the sodium D line (in $\text{m}^3\cdot\text{mol}^{-1}$ )
$r_X$	radius of particle of species X (in nm)
$S$	entropy, molar entropy (in $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ )
$S(q)$	structure factor in $q$ (reciprocal length) space
$T$	temperature (in K)
$t$	transference number
$U$	Potential interaction energy in the system (in J)
$u$	speed of sound (in $\text{m}\cdot\text{s}^{-1}$ )
$u(r)$	potential energy function
$V$	volume, molar volume (in $\text{m}^3\cdot\text{mol}^{-1}$ )
$v_X$	microscopic volume of species X (in $\text{nm}^3$ )
$x_X$	mole fraction of species X
$y$	packing fraction
$Z$	lattice parameter
$Z_X$	atomic number of element X
$z_X$	charge number of ionic species X (taken algebraically)

### Principal Greek Characters

$\Delta_x$	change of quantity for process x
$\alpha$	Kamlet-Taft hydrogen bond donation ability of solvent
$\alpha_P$	isobaric thermal expansibility (in $\text{K}^{-1}$ )
$\alpha_X$	polarizability of species X (in $\text{m}^{-3}$ )
$\beta$	Kamlet-Taft electron pair donation ability of solvent
$\delta$	chemical shift of NMR signal (in ppm)

$\delta_H$	Hildebrand solubility parameter (in $\text{MPa}^{1/2}$ )
$\epsilon, \epsilon_s,$	relative static permittivity
$\epsilon_0$	permittivity of empty space ( $8.8542 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}$ )
$\eta$	dynamic viscosity ( $\text{Pa} \cdot \text{s}$ )
$\theta_D, \theta_E$	Debye or Einstein temperature
$\kappa$	specific conductance ( $\text{S} \cdot \text{m}^{-1}$ )
$\kappa_S, \kappa_T$	adiabatic (isentropic), isothermal compressibility (in $\text{Pa}^{-1}$ )
$\Lambda$	molar conductivity (in $\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$ )
$\lambda$	wavelength of radiation
$\lambda_{\text{th}}$	thermal conductivity (in $\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ )
$\nu_I$	stoichiometric coefficient (number of ions I per formula)
$\pi^*$	Kamlet-Taft polarity/polarizability of solvent
$\rho$	density (in $\text{kg} \cdot \text{m}^{-3}$ )
$\sigma$	surface tension (in $\text{N} \cdot \text{m}^{-1}$ )
$\sigma_I$	softness parameter of ion I
$\Phi$	fluidity (reciprocal of viscosity) (in $\text{Pa}^{-1} \text{ s}^{-1}$ )
$\chi$	molar (diamagnetic) susceptibility (in $\text{m}^3 \cdot \text{mol}^{-1}$ )
$\omega$	frequency of an electromagnetic wave (in $\text{s}^{-1}$ )

### Principal Subscripts

+, -	of cation, anion
0	of a unit quantity
0	characteristic temperature in VFT equation
b	of boiling (at atmospheric pressure)
c	critical
els	contribution from electrostriction
f	of formation
g	of glass transition
h	of a hole
hyd	pertaining to hydration
I	pertaining to the ion I
int	internal
intr	intrinsic value
L, latt	of lattice
m	of melting
r	reduced quantity
s	of sublimation
sd	of solid
solv	of solvation
v	of vaporization
vd	of void space, of cavity

## Principal Superscripts

- \* characteristic quantity
- ° standard thermodynamic function (for  $T = 298.15$  K, for  $P = 0.1$  MPa)

A chemical substance or ion is generally referred to in the text by its name or formula, but in tables and as subscripts abbreviations are generally employed. The symbol  $I^{z\pm}$  denotes a generalized ion,  $C^+$  or  $M^{z+}$  denote a cation, and  $A^-$  and  $X^{z-}$  denote an anion. The abbreviations cr for crystal, g for gas, ig for ideal gas, l for liquid denote the state of the ion or substance described. The common abbreviations of alkyl chains, Me = methyl, Et = ethyl, Pr = 1-propyl, Bu = 1-butyl, Pe = 1-pentyl, Hx = 1-hexyl, Oc = 1-octyl, Dc = 1-decyl, Do = 1-dodecyl, Td = 1-tetradecyl, and also Ph = phenyl are employed.

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