Chapter 7
Life and the Need for a Solvent

Life as we know it consists of chemical interactions that take place in the liquid state, yet the requirement that life be liquid-based is not normally part of anyone's definition of a living system. Thus, we cannot state categorically that life in either a solid or gaseous state is impossible. There are, however, compelling theoretical advantages for the complex chemical interactions that compose the living state to occur in a liquid medium. These include (1) an environment that allows for the stability of some chemical bonds to maintain macromolecular structure, while (2) promoting the dissolution of other chemical bonds with sufficient ease to enable frequent chemical interchange and energy transformations from one molecular state to another; (3) the ability to dissolve many solutes while enabling some macromolecules to resist dissolution, thereby providing boundaries, surfaces, interfaces, and stereochemical stability; (4) a density sufficient to maintain critical concentrations of reactants and constrain their dispersal; (5) a medium that provides both an upper and lower limit to the temperatures and pressures at which biochemical reactions operate, thereby funneling the evolution of metabolic pathways into a narrower range optimized for multiple interactions; and (6) a buffer against environmental fluctuations.

For a substance to be an effective solvent for living processes, its physical properties in the liquid state must be matched to those of the environment in which it occurs. Those relevant properties include the requirement that it be liquid at the prevailing temperatures and pressures on the planetary body in question. These properties include the melting and boiling point of the solvent, but also its critical temperature and pressure. The critical temperature of a compound is that temperature beyond which the liquid phase cannot exist, no matter how much pressure is applied to it. The critical pressure of a substance is the pressure required to liquefy a gas at its critical temperature. A suitable solvent must also have sufficient physical buffering capacity, which can be specified by its enthalpy of fusion (melting) and vaporization (kJ/mol) describing the amount of energy needed to change 1 mol of the substance from solid to liquid at its melting point and from liquid to gas at its boiling point, respectively. A large temperature range for the liquid state is favorable. For those reactions that depend on the making and breaking of ionic and hydrogen bonds, and
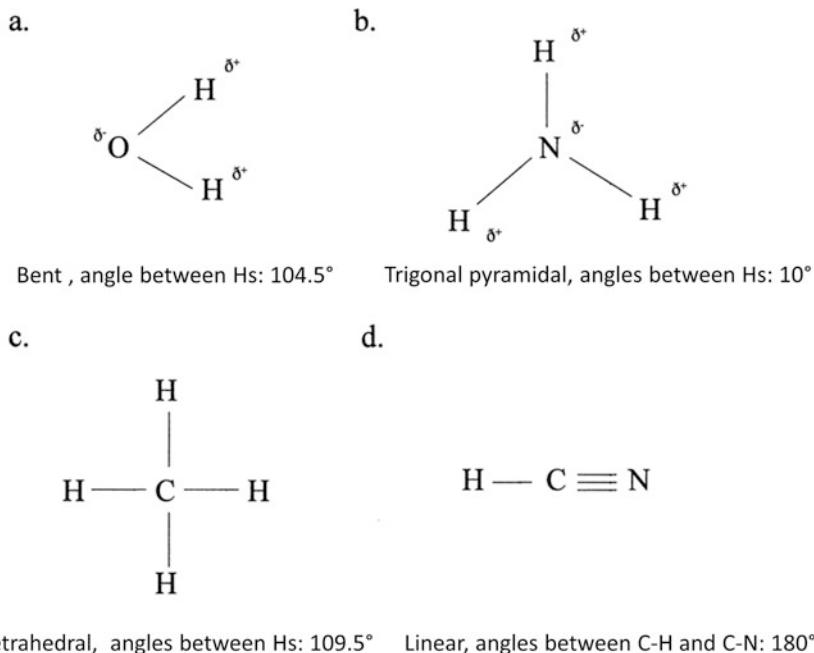
a.

Bent , angle between Hs: 104.5°

b.

Trigonal pyramidal, angles between Hs: 10°

c.

d.

Tetrahedral, angles between Hs: 109.5°   Linear, angles between C-H and C-N: 180°

Fig. 7.1 Structure of some molecules that are discussed here as a solvent; (**a**) water, (**b**) ammonia, (**c**) methane, and (**d**) hydrocyanic acid

for maintaining appropriate macromolecular configurations, a measure of the solvent's polarity is important. The common measure is the dipole moment in debye (D, $1 \text{ D} = 3.335 \times 10^{-30}$ cm), which describes the polarity of a molecule and is dependent on charge and distance. The more polar the compound the higher is its dipole moment, but if the geometry of the molecule is symmetrical (e.g. CH_4, Fig. 7.1c), the charges are balanced and the dipole moment equals zero. The maintenance of appropriate diffusion rates depends on both density and viscosity. Viscosity, the quantity that describes a fluid's resistance to flow, is very much dependent on temperature and is measured in poise (P, dyne s/cm^2) or pascal seconds (Pa s; 1 Pa s $=$ 10 poise). To the extent that electrical conductivity is relevant to a particular living process, the dielectric constant is also pertinent. The dielectric constant (dimensionless) is the ratio of the permittivity of a substance to the permittivity of free space and describes the extent to which a material concentrates electric flux (permittivity is the proportionality constant between electric displacement and electric field intensity). The physical properties for a variety of inorganic candidate solvents are provided in Table 7.1.

First, we will discuss why water is such an excellent solvent for the environmental conditions of Earth. Then, we will discuss other possible solvents that could replace water under environmental conditions either similar to or vastly different from those existing on Earth. Finally, we will discuss how the nature of a solvent could

Table 7.1 Some physical properties of water and other polar compounds relevant to their solvent capabilities

Property	H_2O	NH_3	HCN	HF	H_2S	H_2SO_4	H_2O_2	N_2H_4
Molecular weight	18.02	17.03	27.02	20.01	34.08	98.08	34.01	32.05
Density (g/ml)	0.997	0.696	0.684	0.818	1.393	1.83	1.443	1.004
Melting point (°C at 1 bar)	0.00	−77.73	−13.3	−83.4	−85.5	10	−0.4	1.6
Boiling point (°C at 1 bar)	100.0	−33.33	26.0	20.0	−59.6	337	150.2	113.5
Liquid range (°C at 1 bar)	100	44.4	39.3	103.4	25.9	327	151	111
Critical temp. (°C)	374	132	184	188	100	NA	455	380
Critical pressure (bar)	215	111	54	64.8	88	NA	215	14.2
Enthalpy of fusion (kJ/mol)	6.0	5.7	8.4	4.6	2.4	10.7	12.50	12.7
Enthalpy of vaporization (kJ/mol)	40.7	23.3	25.2	30.3	18.7	NA	51.6	41.8
Dielectric constant (ε)	80.1	16.6	115	83.6	5.9	101	89(?)	51.7
Viscosity (10^{-3} P)	9.6	2.7 (at −34°C)	2.0	~4.3	4.3	260	11.4	9.8
Dipole moment (D)	1.85	1.47	2.99	1.83	0.98	2.7	2.01	1.9
Surface tension (10^{-3} J/m^2)	71.99	19.8	18.1	NA	NA	NA	79.7	66.39
Relative probability of occurrence[a]	1	0.25	0.14	NA	1.31	0.42	NA	0.26

Note: Data from CRC (2001), Firsoff (1963), Merck Research Labs (1996), Moeller (1957); http://www.trimen.pl/witek/ciecze/oldliquids.html and http://www.flexwareinc.com/gasprop.htm. NA = not available
[a]Relative probability of liquids on bodies >1000 km in diameter around any star in our stellar neighborhood as provided by Bains (2004)

determine the chemical characteristics of a living system, including the nature of its origin and evolution.

7.1   Water as the Universal Solvent for Life on Earth

Water is usually portrayed as the universal solvent for life as we know it, because of various properties that make it a very good solvent for the environmental conditions of Earth. Probably, the most important property of water is its polar structure (Fig. 7.1a). This polarity allows liquid water molecules to stick to each other via hydrogen bonding, providing it with polymer-like properties. The hydrogen bonding also raises the freezing and boiling point of water to much higher temperatures than would otherwise be expected from a molecule with a molecular weight as low as
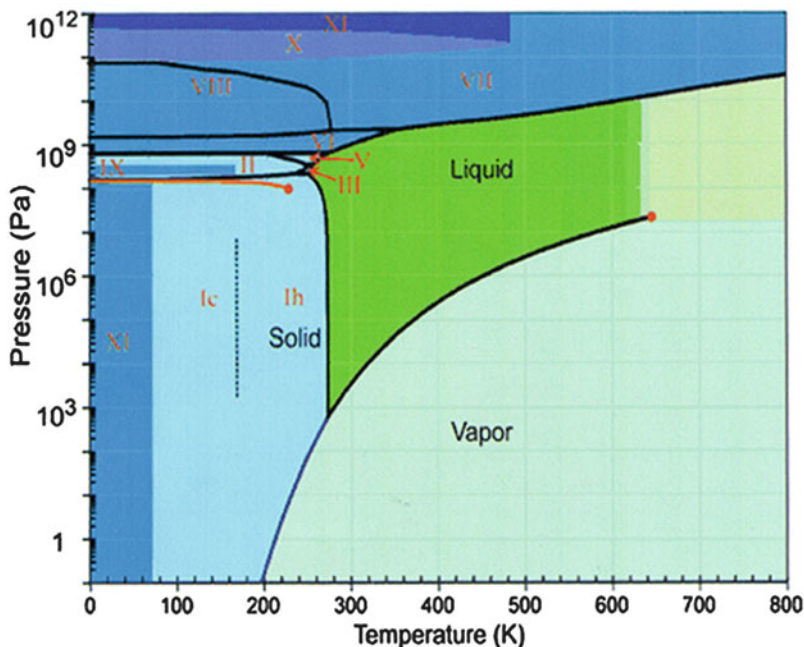
Fig. 7.2 Phase diagram for water. Stability fields for the solid, liquid, and gas phases as shown. All the different solid phases of ice involve hydrogen bonding of water molecules to four neighboring water molecules (from Chaplin 2003). Notice that the triple point is located very close to Earth's average temperature allowing all three phases to coexist under a wide variety of climatic conditions

18 g/mol. Water is a liquid in a temperature range of 0–100 °C (at 1 bar pressure). The triple point of water at which all three phases—solid, liquid, and gas—coexist is also located within this temperature range, very close to Earth's average temperature (Fig. 7.2). Thus, water in the liquid form allows for the wide variety of climatic conditions, differentiated habitats, and complex chemical and physical interactions found on Earth. And because life on Earth has evolved as a system that operates in liquid water, the temperature at which water is a liquid determines the range of temperatures at which living processes can proceed normally. The dynamic properties of life cease below the freezing point of aqueous solutions, and are destroyed at temperatures above their boiling point. This empirical fact lends credence to the supposition that life is fundamentally a liquid-based process. Some tardigrades (hydrophilous micrometazoans) have been recorded to survive temperatures below −250 °C and as high as 151 °C (Cavicchioli 2002), but this kind of survival occurs only in a dormant state.

The superiority of water as a good solvent for ionic and polar covalent bonds is a function of its high dipole moment (1.85 D), which quantifies the electric charges at its poles. Thus, water readily dissolves molecules such as salts that serve as co-factors for many metabolic reactions and mediate bioelectrical processes, as well as monomeric organic compounds with abundant polar groups such as sugars

and amino acids that need to be capable of intracellular and transcellular mobility. On the other hand, water is not a good solvent for molecules with non-polar covalent bonds, such as those of hydrophobic organic molecules like lipids, which serve as the core of cellular membranes, and proteins embedded in the membrane core. Large biomolecules are thus able to maintain stable stereochemical configurations—a property essential for their biological activity—because of the stability of covalent carbonyl, peptide, glycosidic, phosphatidyl, and disulfide bonds in an aqueous solvent. Another advantage of water is that it offers organic non-polar compounds a way to be concentrated.

There are challenges, however. First, many organic synthesis reactions involve dehydration, which is inhibited in the presence of water, hence requiring energetically expensive and elaborately catalyzed reactions. Secondly, water is very reactive and therefore damaging to many biomolecules, including high-energy phosphatidyl compounds that break down easily, and many cellular macromolecules, particularly the nucleic acids (Feinberg and Shapiro 1980). Water does not support protein folding, because it disrupts the hydrogen bonds (Baross et al. 2007). Specific repair mechanisms have evolved to counter the damaging reactivity of water with DNA, and metabolic evolution has evolved generally under the limitations imposed by water on biochemical processes.

One of the most biologically favorable properties of water is its role as a thermal moderator. The reason is that (1) water's high heat capacity allows it to be available over a wide range of temperatures (from 0 °C to 100 °C at 1 bar pressure), and (2) water is a good heat insulator. For example, the heat of vaporization, the amount of energy required to change from the liquid into the vapor phase, requires 40.7 kJ/mol (at a pressure of 1 bar), compared to 23.3 kJ/mol for ammonia and 18.7 kJ/mol for H_2S (Table 7.1). This high heat of vaporization stabilizes an organism's intercellular temperatures and promotes consistent chemical reaction rates. This same property also accounts for the cooling capacity of water evaporated from the surface of animals living in air, a mechanism important in the dissipation of excess heat.

The property of water to act as a heat insulator can be quantified by its dielectric constant, which is relatively high compared to most other potential solvents (Tables 7.1 and 7.2). Taken together, the wide temperature range at which water stays liquid and its insulating properties allow organisms immersed in liquid water to be very well protected from temperature fluctuations. This property is readily observable in the tendency of the oceans of the Earth to maintain moderate temperatures and counteract extreme temperature climatic fluctuations (though the floating of water ice on top of liquid water is counterproductive). Water also provides stability against environmental fluctuations in a chemical sense. Water dissociates into a proton (H+), which is usually attached to a water molecule as a hydronium ion (H_3O^+), and an anion (OH^-), providing acid and base characteristics further increasing the solubility of compounds immersed in water. Drastic changes in pH, which could easily be detrimental to life, can be prevented by the presence of naturally and widespread occurring buffers such as carbonate and phosphate. The presence of acid and base possibilities also leads to neutralization reactions, in which the cation of the

Table 7.2 Comparison of physical properties for water, organic, and non-polar compounds relevant to their solvent capabilities

Property	H_2O	CH_4	C_2H_6	CH_3OH	$HCONH_2$	N_2
Molecular weight	18.015	16.04	30.07	32.04	45.04	28.01
Density (g/ml)	0.997	0.426 at $-164°C$	0.572 at $-107°C$	0.793	1.13	0.85
Melting point (°C at 1 bar)	0.00	-182	-172	-94	3	-210
Boiling point (°C at 1 bar) °	100.0	-161.5	-89	65	211	-196
Liquid range (° C at 1 bar) °	100	18	65	159	208	14
Critical temp. (°C)	374	-82.6	$+32.3$	240	NA	-147
Critical pressure (bar)	215	45.4	47.8	78	NA	33.3
Enthalpy of fusion (kJ/mol)	6.0	0.94	2.7	2.2	8.44	0.71
Enthalpy of vaporization (kJ/mol)	40.7	8.2	14.7	40.5	60.1 at $25°C$	5.56
Dielectric constant (ε)	80.1	1.7	1.9	354 at $13°C$	110	1.45
Viscosity (10^{-3} P)	9.6	0.009 at $20°C$	0.011 at $20°C$	5.9	33	2.04
Dipole moment (D)	1.85	0.0	0.0	1.6	3.4	0
Surface tension (10^{-3} J/m^2)	71.99	NA	NA	22.1	57.03	10.53
Relative probability of occurrence[a]	1	0.62	1.25	NA	NA	1.96

Notes: Data from CRC (2001), Goldsmith and Owen (2003), Firsoff (1963), Moeller (1957), Merck Research Labs (1996); http://www.trimen.pl/witek/ciecze/old liquids.html and http://www.flexwareinc.com/gasprop.htm

NA not available

[a]Relative probability of liquids on bodies >1000 km in diameter around any star in our stellar neighborhood as provided by Bains (2004)

base combines with the anion of the acid to form a salt, and the anion of the base combines with the cation of the acid to form a molecule of the solvent. Salts dissociate in their solvent, in this case water, into charged ions, increasing the reactivity of the solution as well as its conductivity. The usefulness of this electrolytic property is enhanced by the low viscosity of water. Ions can flow within and circulate efficiently through the solvent and participate in reactions within a reasonable time frame.

The role of water as a climatic stabilizer is an immensely important property for all organisms. Associated with that property is its unusual capacity to decrease in density as it freezes below its maximum density at 4 °C. This has obvious advantages for life in Earth's oceans and lakes, because the lighter water ice floats and acts as insulator for organisms beneath its surface and prevents the complete freezing of a body of water from the bottom to the top. This advantage is more important for

multicellular forms of life than for microbial life, because microbes can more easily employ adaptive strategies against freezing such as surviving in a spore state. This peculiar property of water has a disadvantage as well, in that ice crystals pierce the cellular membranes due to the expansion of water as a solid. This is the basis for frost damage to plants, for example. However, this property is only valid for ice I (Fig. 7.2), while ice II or any other form of ice is denser than liquid water (Baross et al. 2007). Thus, on a planet much more massive than Earth, ice would sink in water. Another peculiar property of water is its high surface tension, which reflects the tendency of water to form droplets due to greater cohesion among adjacent water molecules than between water and the molecules of air with which it is in contact. The surface tension of water is very high with a value of 71.99 mN/m at 25 °C (CRC 2001), compared to most other liquids. The surface tension of other potential solvents at their respective temperature of liquidity is not very well known though. This property is not directly related to the solvent's ability to transport nutrients, but is likely to be relevant to the origin of life. Organic compounds may have been concentrated in small water droplets that enhanced the probability of a reaction sequence leading to prebiotic molecules (Gusev 2002).

The unusual properties of water have more recently been a focus of investigation. Morawietz et al. (2016) suggested that the 4 °C density maximum is caused by weak van der Waals forces that modulate the flexibility of the water´s hydrogen bond network. Wernet et al. (2004) and Nilsson and Pettersson (2015) hypothesized that many of the seemingly anomalous properties can be explained by water having two different types of structures: a tetrahedral geometry and a more random, disordered orientation of hydrogen bonds. According to that hypothesis, water at moderate temperatures would be a mix of both varieties, with the water molecules being more densely packed in the disordered structure. The discovery of high and low-density amorphous forms of water ice and their transition from one into the other appears to support the existence of two distinct liquid forms (Perakis et al. 2017). Many apparent anomalies of water, such as its high heat capacity, could be explained: when energy in the form of heat is applied to the low-density tetrahedral structures, many of them would be converted to the higher density disordered arrangement rather than increasing their kinetic energy (thus the temperature) of the water molecules. If this hypothesis is proven to be correct, observations for the existence of metastable bulk liquid water down to temperatures of about 227 K might be explainable as well (Sellberg et al. 2014).

One important environmental advantage of water is that in an Earth-type environment it is self-shielding against ultraviolet radiation. Ultraviolet photons dissociate water molecules, releasing oxygen and hydrogen into the atmosphere. If that happens, some of the oxygen atoms will form ozone molecules, which are an excellent absorber for UV radiation, thus shielding the planetary surface from this detrimental form of high energy.

Another important property for any candidate to be qualified as a vital solvent in a scheme of organic chemistry leading to biology is that it has to be related to that scheme (Firsoff 1963). A solvent may be as good as water in an Earth-type environment, but if it does not form any ions that could advantageously enter into

biochemical reactions, it is of little interest. With respect to water, hydration and dehydration reactions are widespread in the biochemistry of Earth's organisms. Examples include the formation of peptide bonds between amino acids via dehydration synthesis reactions and the breakdown of complex sugars by hydration hydrolysis.

If life requires proteins, which are essential biomolecules for life on Earth, water is an ideal solvent. Proteins fold to a unique, globular conformation, which tightly packs over 80% of the peptide groups and non-polar side chains. This marginally higher stability of proteins in the folded state, which allows both stability and solubility, would be very difficult to reproduce in alternative solvents (Pace et al. 2004). However, Benner et al. (2004) pointed out that many organic molecules that are parts of a carbon-based metabolism display problematic reactivity with water, citing the difficulty with carbon dioxide cycling as an example. At a symposium on the biological importance of water, Daniel et al. (2004a) wondered about the biological functions of water at the molecular level and whether water is truly irreplaceable for the function of living systems. Terran organisms are very well adapted to water and other solvents are usually very toxic to them. The toxicity of these solvents is determined by their ability to permeate the cell membrane, which results in the leakage of macromolecules, including proteins and RNA (Isken and de Bont 1998). However, some bacteria tolerate other solvents at very high concentrations by membranes that limit the diffusion of solvents into the cell and by specialized efflux mechanisms that remove solvents that have diffused into the cell (Baross et al. 2007).

Perhaps the most important property of a life-sustaining solvent is that it has to occur in large quantities on the planetary surface or wherever the life-sustaining reactions are to occur. With oxygen the most common element on Earth, and hydrogen the most common element in the Universe, water would be expected to be common on Earth. Water is also known from spectral analysis to be a common molecule in the Universe, and thus may be the obvious choice as a solvent elsewhere as well. However, many properties that make water such a good solvent are directly linked to the environmental conditions existing on Earth as discussed above. Thus, considering environmental conditions unlike those on Earth may require the participation of some other types of solvents. This notion will be explored in the coming sections.

7.2 Inorganic Polar Solvents as Alternatives to Water

In their assessment of the limits of organic life in planetary systems, the National Research Council (Baross et al. 2007) found no compelling reason to limit the environment for life to water as a solvent, although terran life is constrained to use carbon as the scaffolding element for most of its biomolecules. Several potential candidates could replace water as a polar solvent on other worlds. For example, Benner (2002) suggested sulfuric acid (H_2SO_4) as a possibility for Venus, and

ammonia (NH_3) as a possibility for Jupiter. Most of the potential solvent candidates are liquids at lower temperatures than water. Hydrazine, N_2H_4, which is a liquid from 2 °C to 114 °C at 1 bar pressure, is one of the few exceptions. There is, however, overlap with the thermal range of liquidity for water in some cases (e.g. HCN, HF). Chemical reactions occurring within these solvents would proceed at a much slower pace than on Earth, typically by a factor of 2 for every 10 °C decrease in temperature (Jakosky 1998). However, the key to developing a suitable chemistry at a given temperature lies in selecting chemical reactions suited to that temperature. For example, those reactions involving unstable and highly reactive free radicals have very low activation energies (Feinberg and Shapiro 1980) and would be suited for low temperature organisms. Also, lower temperatures and an abundance of nitrogen could open up new possibilities, such as polymeric chains of nitrogen atoms. Bonds of nitrogen to nitrogen are weaker than carbon to carbon bonds, and are less abundant on Earth. Some of them are very reactive under Earth conditions (e.g. hydrazine). At lower temperatures, however, these compounds would be more stable and may be suitable for the construction of complex molecules. Many planetary bodies within our Solar System have much colder surface temperatures than Earth, and planets and moons at these temperature ranges may be much more common than Earth-type bodies in the Universe.

In order to qualify as a suitable candidate for a polar solvent, the solvent has to be easily available and plentiful, as well as suitable for at least a hypothetical scheme that could lead to prebiotic chemisty. If not plentiful in the Universe, there has to be some kind of fractionation mechanism that could conceivably enrich the particular solvent on a planetary body. In the following we discuss the polar inorganic solvent candidates, which we rank according to the likelihood that they could replace water as the life-supporting solvent in certain types of environments. We further discuss methanol and formamide as the most promising polar organic compounds for alternative forms of life.

7.2.1 Ammonia

The idea of life based on ammonia as a solvent has received a considerable amount of attention. For example, Haldane (1954) pointed out ammonia analogues to water and suggested the possibility of building proteins, nucleic acids and polypeptides within a liquid ammonia solvent. Raulin et al. (1995) suggested that "ammono" analogues of terran biomolecules in which oxygen atoms are replaced by NH groups might yield an equally viable pseudo-biochemistry. Life on Earth exploits compounds containing the $C = O$ carbonyl unit. In ammonia, $C = O$ units would have to be replaced by $C = N$ units, but given this adjustment Benner et al. (2004) argued that metabolism in liquid ammonia is easily conceivable. Baross et al. (2007) argued that the $C = N$ bond would be equally satisfactory for supporting carbon-carbon bond forming reactions. Firsoff (1963) went into some detail showing similarities of synthesis reactions in water-based, ammonia-based and water-ammonia mixtures.

An especially interesting example provided by him is the synthesis of proteins from amino acids through a peptide bond. In a water system two glycine molecules combine with the release of water (Eq. 7.1):

$$(7.1)$$
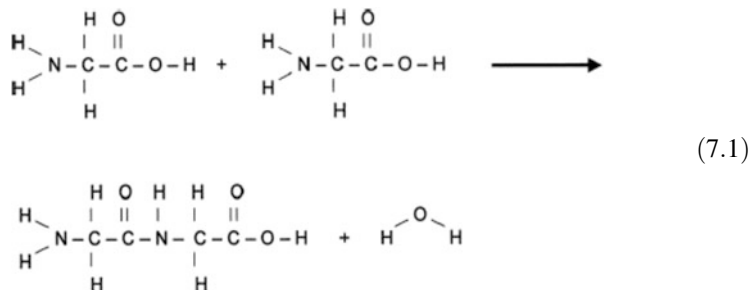
If reaction (7.1) would take place in a water-ammonia mixture the COOH group would be replaced with a $CONH_2$ group and reaction (7.2) would be the result. In this reaction (7.2) the peptide bond is preserved and ammonia is released instead of water:

$$(7.2)$$
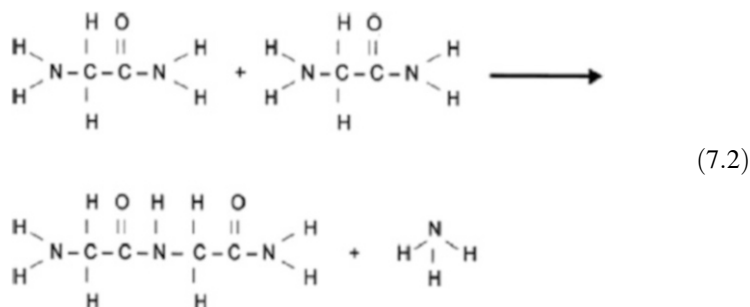
Firsoff (1963) speculated that the preservation of the peptide bond may be a relic of an ammono-organic scheme on Earth in the early stages of evolution.

In a pure ammonia solvent without the presence of oxygen, the carboxyl group could be replaced with a $-CH(NH_2)NH_2$ group and the peptide bond with a $-CH(NH_2)-NH-$ group. Similar analogues can be shown for the phosphate bonds in the nucleic acids (Firsoff 1963). A further parallel is that ammoniation reactions in ammonia as solvent are directly analogous to hydration reactions with water in which a salt and the solvent are produced. This leads to an important environmental consequence that minerals in a near-surface or subsurface "hydrosphere" would contain ammonia in their crystal structure just as Earth's rocks contain water. Although there appear to be chemical pathways leading from ammonia to prebiotic macromolecules, water is a more powerful solvent than ammonia based on its physical and chemical properties. Ammonia has a structure comparable to water (Fig. 7.1b) but a lower dipole moment and is thus less efficient at dissolving polarized compounds. Ammonia's heat of vaporization and heat of fusion are

lower than that of water (although the heat of fusion is nearly equal, Table 7.1). Thus, ammonia is not as good at moderating temperature as water, but is still sufficient to have a stabilizing effect on climatic conditions. The surface tension of ammonia is only about one third of water; thus ammonia is not likely to concentrate organic macromolecules in microscopic interfaces as well as water. Ammonia dissociates into nitrogen and hydrogen, and does not afford any protection from UV light when compared to the dissociation of water. Thus any origin of life in ammonia would have to occur in some kind of protected environment. Ammonia, however, makes up for this disadvantage by its ability to dissolve alkali metals without reaction, which is of biological relevance because alkali metals can act as catalysts. Also, salt solutions in liquid ammonia have usually a greater electrical conductivity than an aqueous solution of the same salt (Mee 1934). Ammonia is about four times less viscous than water, thus dissolved particles and ions have a less difficult time to find and react with each other. Ammonia self-dissociates as water does but to a much lower degree (1.9×10^{-33} at $-50\,°C$ compared to 10^{-14} at $25\,°C$ for water). Ammonia dissociates to NH_4^+ (equivalent to H_3O^+ of water) and the anion NH_2^-. It can further dissociate to form two more base anions, NH^{2-} and N^{3-}, thus acid-base reactions do occur in an ammonia system but to a much lower degree.

Ammonia is liquid at lower temperatures than water and has a smaller range in which it stays liquid, thus life would have to adapt to a smaller temperature window to survive on such a world. However, the temperature range over which ammonia is liquid for some relevant planetary surface pressures is greater than for water. For example, at a pressure of 60 bar ammonia is liquid from $196°$ to $371°K$ (Baross et al. 2007). Since solid ammonia is denser than liquid ammonia, there is no mechanism for preventing liquid ammonia from completely freezing during a cold spell. This is no problem for microbial life since it could have adapted to survive any cold spell or cyclic freezing in a spore state. However, survival of multicellular organisms in such an environment would be less likely. Further, chemical reactions would generally be expected to progress at a slower pace, lengthening life spans, and therefore decreasing the rate at which competition and adaptive radiation would drive evolution (Schulze-Makuch and Irwin 2006). Microbial life in ammonia might not be as differentiated or as well adapted compared to water-based life on Earth. Further, liquid ammonia cannot co-exist with free oxygen, thus aerobic metabolism would be inconsistent with ammonia as a solvent.

Liquid ammonia could, on the other hand, present an opportunity for microbial life on the more numerous colder bodies in the Solar System as well as for Jovian-size planets where the boiling point of ammonia could be as high as ammonia's critical temperatures of $+132.4°C$ (given the extreme pressures). Ammonia and water are definitely related solvents, as indicated by the fact that life sustaining organic macromolecules such as proteins, amino acids and nucleic acids contain both OH and NH_2 functional groups in various combinations and proportions with which ammonia could easily interact. Aspinall et al. (2002) suggested that phosphate, a vital element for life on Earth, can be replaced by ammonophosphate analogues that are stable in water and ammonia, can lose protons to hold multiple negative charges, and can form stable amide-like bonds with carbon molecules.

Bains (2004) hypothesized that movement of electrons ("electricity") rather than protons ("proticity") would be a reasonable energy transaction for ammonium supported life. Different hydrocarbons become miscible with ammonia depending on temperature and pressure conditions. The formation of ammonia-philic and ammonia-phobic phases (analogous to hydrophilic and hydrophobic phases in water) is clearly conceivable in liquid ammonia at temperatures well below its boiling point at standard pressures (Baross et al. 2007).

Interestingly, several enzymes of terran organisms remain active down to temperatures of about $-100°C$ (Bragger et al. 2000). In the likely subsurface oceans of the Galilean satellites, and possibly also at Titan and Triton, some ammonia dissolved in water may act as antifreeze, lowering the temperature at which water can stay liquid and thus possibly support life (Fortes 2000). Alternatively, any ammonia solvent in this type of environment should not be expected to be pure either. Water in the form of ice or icebergs would dissolve in liquid ammonia, thus the occurrence of water groups such as OH^- and O^{2-} should be expected within an ammonia solvent, if it indeed is capable of supporting life. Any ammonia-water mixture would be very basic, though. A 1.7% ammonia solution has a pH of 11.6 (Budavari et al. 1996) and it isn't clear how well life could adapt to this high basicity. On Earth, life is much more capable of withstanding and adapting to extreme acidities than basicities. However, there are not many natural environments on Earth with high pH-values (mostly soda lakes); thus there may have been no need for the evolution of organisms on Earth to develop this type of adaptation. Therefore, high pH may not be a fundamental obstacle for life. There is certainly enough ammonia in our Solar System, and in comets and the interstellar medium of the Universe in general, to sustain the possibility that living systems could thrive in a solvent of ammonia, or an ammonium-water mixture, within the appropriate thermal limits.

7.2.2   Hydrocyanic Acid

The structure of hydrocyanic acid, with a triple bond between the carbon and the nitrogen, is quite different from the structure of water, ammonia and methane (Fig. 7.1d). It is an excellent ionic solvent with a dipole moment of 2.8 D compared to 1.85 D for water and 1.47 D for ammonia. Also, as a thermal moderator it is about equal to water and superior to ammonia, with (1) a heat of fusion of 8.41 kJ/mol and heat of vaporization of 25.2 kJ/mol, and (2) a dielectric constant of 114.9. The range of temperature at which HCN remains a liquid is somewhat small, but it extends up to 26 °C allowing chemical reactions to proceed at a reasonable pace. Hydrocyanic acid dissociates into H^+ and CN^- with sulfuric and hydrochloric acids remaining acids in liquid HCN while cyanides are bases (Firsoff 1963). Cyan compounds are generally toxic to aqueous life in Earth's oceans and fresh water reservoirs.

However, the toxicity only indicates the occurrence of reactions that are competitive with water-based biochemistry and the ease with which water groups can be replaced by CN. CN bonds are of fundamental importance in proteins and other organic substances, and the substitution of CN for OH would yield HCN-analog compounds. Some compounds valuable for life such as metals are insoluble or only soluble to a small extent in HCN, while other compounds such as certain salts (e.g. potassium thiocyanite, permanganate) are highly soluble and give highly conductive solutions (Moeller 1957).

Hydrocyanic acid is not as abundant as water in the Universe but has been detected in comets and at planetary bodies such as Jupiter and Titan, and in the interstellar medium (Brown 1984; Lunine et al. 1999). Hydrocyanic acid not only offers protection from UV radiation, but can even combine with itself in alkaline solutions to form amino acids with the assistance of UV photons (7.3).

$$3HCN + 2H_2O + UVlight \rightarrow C_2H_5O_2N + CN_2H_2 \qquad (7.3)$$

In addition to glycine, this reaction produces cyanamide (CN_2H_2), which can link amino acids together as the first step in the formation of proteins. Another promising pre-biotic pathway was offered by Matthews and Moser (1966), who suggested the direct synthesis of protein ancestors (heteropolypeptides) from hydrogen cyanide and water without the intervening formation of amino acids. Also of interest is that the important purine adenine ($C_5H_5N_5$) is a pentamer of HCN. A biochemistry based on hydrocyanic acid would likely be quite different from one based on either water or ammonia, and that is perhaps the primary reason why HCN did not receive much consideration as a solvent for life. HCN cannot interact as well with Earth-type organic macromolecules as ammonia. Its relatively small thermal window of liquidity, and its limited ability to dissolve some biologically important compounds are disadvantages for HCN as a solvent for living systems. However, it is intriguing that when dissolved in water HCN spontaneously reacts to form heterogeneous oligomers, which upon standing hydrolyze to release a variety of molecules of biological significance such as purines, pyrimidines, urea, and amino acids (Cleaves et al. 2008). To the extent that Earth provides a natural laboratory for comparing HCN with H_2O, with temperatures covering the range at which both compounds are liquid, HCN clearly is not competitive with water as a solvent, either because of its much lower abundance, or because the nature of biomolecules that would be stable and reactive in a hydrocyanic acid medium are not metabolically competitive with those that function in water. However, with its relatively high molecular weight of 27 g/mol, it could be the solvent of choice on a planetary body where most of the lighter molecules may have steamed off at some stage of atmospheric evolution. In such an atmosphere, cyanogen (C_2N_2) could be expected as an atmospheric constituent, which might provide energizing reactions analogous to oxidation in Earth's atmosphere (Firsoff 1963).

7.2.3 Hydrofluoric Acid

The solvent properties for hydrofluoric acid and water are very similar. The dipole moment and the dielectric constant are basically the same, while the heat of fusion and heat of vaporization of HF is only slightly lower (Table 7.1). Thus, hydrofluoric acid is an excellent temperature moderator and solvent. The temperature range at which HF remains liquid is a bit larger than for water and extends much lower ($-83°C$ to $+20°C$). Two hydrofluoric acid molecules dissociate into HF_2^- and H^+. Due to their non-polar nature most hydrocarbon compounds are insoluble in hydrofluoric acid, but many of them are polymerized, decomposed or lead to conducting solutions with complex cations, where the organic molecule bonds to the proton of HF (Firsoff 1963). Conceivably, F^- or HF_2^- could replace OH^-, and F_2^{2-} could replace O^{2-} in oxides. Fluorination could thus replace oxidation as the primary energy-yielding reaction, and would be more efficient due to the greater bonding energy of fluorine. As a result, free fluorine would be one of the atmospheric gases, and would likely have the same fate as oxygen had in the early Earth atmosphere (being such a very reactive element it would quickly be bound to surface rocks and removed from the atmosphere). The primary problem with hydrofluoric acid as a primary solvent is the low cosmic abundance of fluorine. Further, organofluorine compounds are extremely rare, at least in terran biochemistry (Budisa et al. 2014). The abundance of fluorine in the Solar System was estimated to be about 1000 times less than that of carbon, nitrogen or oxygen (Anders and Grevesse 1989). It is difficult to envision any fractionation mechanism that could enrich hydrofluoric acid to such a sufficient extent to become the primary solvent on a planetary body. One possibility is that all molecular oxygen could be used up in oxidation reactions on the planetary surface and that fluorine gas would be released from F-rich magmas later in the history of the planetary body. However, due to its low cosmic abundance and the unlikelihood of an efficient fractionation mechanism, we rank HF as an alternative solvent lower than ammonia and hydrocyanic acid in spite of the advantageous properties of the hydrofluoric acid molecule.

7.2.4 Hydrogen Sulfide, Sulfur Dioxide and Sulfuric Acid

Hydrogen sulfide remains a liquid at colder temperatures than any other candidate solvent introduced in Table 7.1, but its temperature range as a liquid is only 26 °C. Hydrogen sulfide does not moderate temperatures very well, given its low heat of fusion, heat of vaporization and dielectric constant. It is not particularly efficient as an ionic solvent, given its low dipole moment, but it does dissolve many substances, including many organic compounds. Similarly to water hydrogen sulfide dissociates into H^+ and SH^-. In a biochemical scheme with H_2S as solvent, the SH^- anion could simply replace the hydroxyl group in organic compounds. Hydrogen sulfide is a relatively common compound in the Universe, usually associated with volcanic

activity on planetary bodies. H_2S could be a conceivable solvent on Io, the volcanically most active planetary body in the Solar System (Schulze-Makuch 2010; Irwin and Schulze-Makuch 2011). A subsurface layer of hydrogen sulfide could turn liquid when overhead lava warms the subsurface layer up to its range of liquidity (Table 7.1), then "spores" could become activated, reproduce, and perpetuate an exotic subsurface microbial ecosystem.

In this type of environment another sulfur solvent, sulfur dioxide, may compete with hydrogen sulfide. Sulfur dioxide is a solvent with a dipole moment of 1.6, remains a liquid at temperatures from -75 °C to -10 °C, and could be retained preferentially on massive planetary bodies due to its high molecular weight of 64 g/mol. However, due to the double bond in sulfur dioxide the development of a biochemical scheme would be more complicated for SO_2 than for H_2S, because rearrangements would be needed. Also, SO_2 is not a proton-based solvent. Proton-based solvents have the advantage that organic macromolecules such as nucleic acids are constructed via hydrogen bonds and are able to exchange materials with the solvent or change their formation for biological purposes without having to overcome a high-energy barrier. Interestingly, sulfates including sulfuric acid (H_2SO_4) are insoluble in sulfur dioxide, and would thus be rock material in a pool of sulfur dioxide.

Sulfuric acid has been suggested as a possible candidate for a life-supporting solvent within 1 AU (astronomical unit) of a star like our Sun (Fig. 7.3). Benner (2002) suggested sulfuric acid (H_2SO_4) as a possibility for Venus, where the atmosphere is rich in it. Sulfuric acid has a huge liquidity range, from 10°C to 337°C, a dielectric constant and dipole moment larger than water, and an extremely high viscosity (Table 7.1). The prospect of pure sulfuric acid as a life-sustaining solvent would require a biochemistry very different from the one with which we are familiar. The $C = C$ bond is reactive as a base in strong acids and could support metabolism as an analog to the $C = O$ unit (Baross et al. 2007), a reactivity shown to work in some terran biochemistry like that used by plants to synthesize fragrant molecules (Kreuzwieser et al. 1999). Sulfuric acid mixes well with water, and if life exists in the atmosphere of Venus (Sagan 1961; Grinspoon 1997; and Schulze-Makuch et al. 2002b, 2004), it would be expected to be adapted to a sulfuric-acid water mixture. This possibility is explored further in Sect. 8.3.

7.2.5   Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) has a larger liquidity range than water (from -0.4 to 150.2°C), but mirrors water in many other properties (Table 7.1). As a pure compound, hydrogen peroxide does not qualify as a good solvent for life, because it is a strong oxidizer and would oxidize most carbon compounds rapidly to carbon dioxide. Thus, it is not compatible with biochemistry as we know it. However, mixtures of H_2O_2 and H_2O present an intriguing possibility, as suggested by Houtkooper and Schulze-Makuch (2007). Such a mixture would freeze at
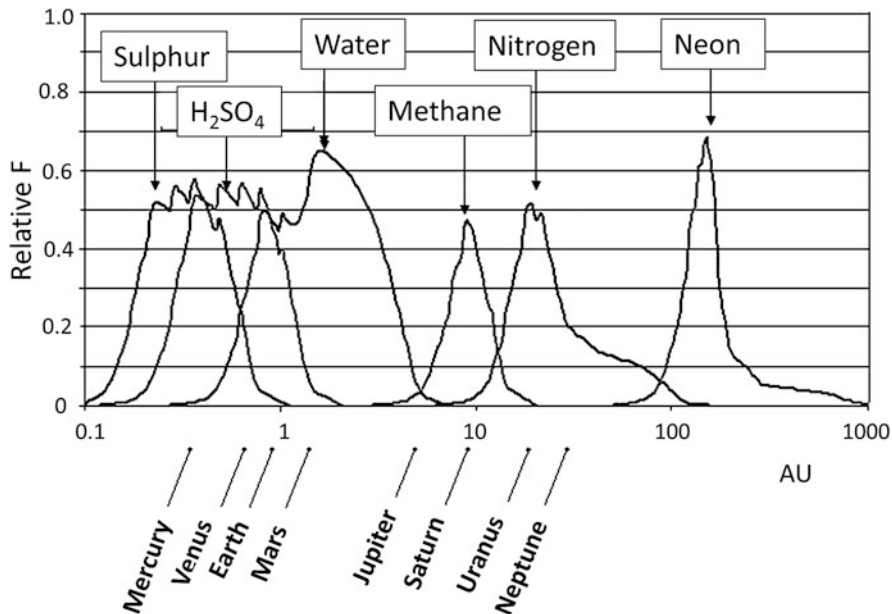
Fig. 7.3 Probability distribution for occurrence of different liquids as a function of distance from a Sun-like star. The x-axis represents distance and the y-axis represents the added probability of surface and subsurface liquid. Figure courtesy of William Bains, following the method described in Bains (2004)

temperatures significantly below the freezing point of water, because the lower eutectic point lies at $-56.5\ °C$ for a mixture with 61.2 weight % H_2O_2 (Foley and Giguère 1951). Also, mixtures with a high H_2O_2 concentration tend to supercool (Giguère and Secco 1954), and would thus not produce icy crystals that could pierce cellular membranes. H_2O_2–H_2O mixtures are slightly acidic, with a pH of 4.5 for the 60 weight % mixture. Because of the lower water vapor partial pressure in equilibrium with the liquid, H_2O_2–H_2O mixtures tend to be hygroscopic compared to water alone, which would offer the opportunity for an organism to scavenge water molecules from the atmosphere in an arid environment. Houtkooper and Schulze-Makuch (2007) hypothesized that organisms on Mars might use a H_2O_2–H_2O mixture as a mechanism of adaptation to Martian environmental conditions. They pointed out that such a biochemistry would explain the observations made during the Viking life detection experiments amazingly well (see also Sect. 10.1). There are various terrestrial analogs for the utilization of H_2O_2, including microbes that use H_2O_2 in their metabolic pathways, such as *Acetobacter peroxidans* (Tanenbaum 1956). Of course, the tendency for peroxides to form free radicals that are highly reactive would require the evolution of counteractive mechanisms for protecting cellular material in a peroxide-rich environment.

7.2.6   Hydrazine

Hydrazine (N_2H_4) is a liquid at a temperature range from 2 °C to 114 °C and thus one of the very few solvent candidates that has a larger temperature range and a larger absolute temperature at which it stays a liquid than water. Hydrazine is an excellent polar solvent with a dipole moment of 1.9 comparable to water. Its dielectric constant (51.7) and viscosity (9.8×10^{-3} P) are also very similar to water. Based on its physical properties it would be an excellent solvent candidate as an alternative to water. Hydrazine, however, is a very reactive molecule and decomposes extremely fast in the presence of oxygen, making it an ideal rocket fuel. This property suits it poorly to serve as a solvent in the presence of oxygen. Because of its high reactivity, it would be expected to make a better solvent at low temperatures in an anoxic environment, for driving biochemical reactions at a reasonable speed. However, at temperatures below 2 °C hydrazine is a solid and therefore not a suitable solvent. Furthermore, hydrazine is not an abundant molecule, and thus does not appear to be a promising solvent candidate despite its favorable physical properties.

7.3   Other Solvents as Alternatives to Water

Organic and non-polar compounds are usually not considered good candidates as alternative biological solvents. However, Carrea et al. (1995), Cabral (2001), and Klibanov (2001) have shown that terran enzymology can operate in a variety of non-aqueous solvents, and even in completely non-polar solvents such as benzene, diphenyl ether, or straight-chain hydrocarbons from heptane to hexadecane. Furthermore, the fungus *Fusarium alkanophilum* is known to be able to thrive in a hydrocarbon environment, extracting metabolic water from light hydrocarbons (Marcano et al. 2002). Also, many organic reactions fundamental to biochemistry can occur in nonaqueous solvents (Benner et al. 2004; Bragger et al. 2000). Table 7.2 provides some solvent-related physical properties of polar and non-polar hydrocarbons, and the non-polar compound dinitrogen. These compounds are relatively common in the Universe, and some of them are primary liquid compounds on at least one planetary body of our Solar System (e.g., methane and ethane on Titan, dinitrogen on Triton). Except for the notable exceptions of methanol (CH_3OH) and formamide ($HCONH_2$), which are discussed below in more detail, nearly all of these potential solvents are liquid at temperatures much lower than water (as most of the polar substitutes for water are).

7.3.1   Inorganic Non-Polar Compounds

Liquid nitrogen is probably the most promising non-polar inorganic compound. Liquid nitrogen boils at −196 °C and thus can occur in our Solar System in the

liquid state only on the icy satellites of the outer Solar System (Fig. 7.3). Temperature and pressure conditions should be right for Triton to have liquid nitrogen in its subsurface. Even a liquid nitrogen ocean may be a possibility (Bains 2004). Though it is very abundant, dinitrogen does not have properties that would be considered as suitable for life from a terran perspective (Table 7.2). However, Bains (2004) hypothesized that silanols could dissolve in liquid nitrogen on very cold planetary bodies at concentrations sufficient to be precursors of life. Nitrogen may also occur in mixtures such as many of the other solvent candidates. While the surface liquids on Titan are a mixture of methane and ethane, substantial amounts of nitrogen from the atmosphere are thought to be dissolved into the hydrocarbon mixture, which would alter its properties significantly (Bains 2004; Lorenz and Lunine 1997; Thompson et al. 1992).

7.3.2   *Organic Polar Compounds*

Hydrocarbon compounds are generally non-polar but can be made into polar molecules by replacing H with an OH group in a hydrocarbon molecule. Two of them, methanol and formamide, have some potential as a suitable solvent for life in particular.

7.3.2.1   **Methanol**

Methyl alcohol or methanol (CH_3OH) is an excellent polar solvent with a dipole moment of 1.68 D compared to 1.85 D of water and 1.47 D of ammonia. It is also a better temperature moderator than water based on its extremely high dielectric constant and heat of vaporization (Table 7.1), and remains a liquid in the wide temperature range from $-94\ ^\circ C$ to $+65\ ^\circ C$. It may also be a relatively common compound in the Universe as it has been found in the interstellar medium and in comets (Goldsmith and Owen 2003). Liquid hydrocarbon compounds are known to exist on Titan in large quantities, but methanol has not been found there. However, Tang et al. (2006) suggested the presence of pools or even oceans of methanol on early Mars. They pointed out that the gray hematite found on Mars could have been produced in a thermal system of organic compounds such as methanol that was generated from the photochemical oxidation of methane, since methane is thought to have been abundant in the early Martian atmosphere.

   If methanol was present in reasonable quantities on the early Earth, it could have promoted organic synthesis such as the formation of sugars (Eisch et al. 2004). Methanol was delivered to the early Earth via comets, but visualizing an efficient production mechanism is challenging, because the oxidation of methane to methanol occurs at very low efficiencies due to the high C-H bond strength in methane. However, it could have occurred at much higher rates through iron or copper containing zeolites (Hammond et al. 2012). Methanol mixes well with water. The

mixture has a eutectic temperature of 157 K. Thus, methanol could have been a valuable ingredient under early Earth conditions, and perhaps also in extraterrestrial locations, both as an antifreeze during cold spells and by promoting organic synthesis reactions (Schulze-Makuch and Houtkooper 2015).

7.3.2.2 Formamide

Another potential solvent is formamide ($HCONH_2$, Table 7.2). This compound has more than double the liquidity range of water and stays liquid at much higher temperatures. It is one of the few compounds with a peptide bond that has been found in the interstellar medium. It has a high surface tension to concentrate solutes, and a higher dipole moment and a larger dielectric constant than water. Benner et al. (2004) pointed out that many chemical species that are thermodynamically unstable in water with respect to hydrolysis, are spontaneously synthesized in formamide. This includes ATP from ADP and inorganic phosphate, peptides from amino acids, and even oligoribonucleotides (Schoffstall et al. 1982; Schoffstall and Liang 1985; Saladino et al. 2012). Formamide can be formed through electrical discharges in an atmosphere containing hydrogen, carbon, and nitrogen, and also through meteorite impacts (Ferus et al. 2015). Formamide itself is hydrolyzed by water and can thus only exist in a dry environment. However, desert environments have been proposed as potential sites for the prebiotic synthesis of ribose (Ricardo et al. 2004) and many synthesis reactions of organic macromolecules would be thermodynamically favorable in desert pools of formamide (Baross et al. 2007). Since desert environments are not thought to have been common on the early Earth, a Martian origin for terran life has been suggested (Benner and Kim 2015). However, though formamide is formed by the reaction of hydrogen cyanide and water, both of which are abundant, formamide itself does not appear to be abundant in the Solar System, nor probably elsewhere in the Universe.

7.3.3 Organic Non-Polar Compounds

Traditionally, it has been assumed that liquids other than water are unsuitable for the complex catalysis that is essential for biochemistry, especially non-polar organic compounds (Bains 2004). Membranes of terran organisms, which are submerged in the polar solvent, water, are amphiphilic with their polar (hydrophilic) heads exposed to the solvent and their non-polar (hydrophobic) tails oriented toward each other, away from the solvent. They interact with the polar solvent to take up nutrients, respond to intracellular signals, and discard wastes. If a non-polar solvent could support life, the chemical orientation of membranes would have to be fundamentally different. In this case, the heads immersed in the solvent would have to be non-polar in order to interact with the hydrocarbon solvent. However, broad empirical experience has demonstrated that organic reactivity in hydrocarbon solvents is

no less versatile than in water, and many enzymes derived from organisms on Earth are believed to catalyze reactions by having an active site that is not hydrophilic (Benner et al. 2004). Also, a hydrocarbon solvent may actually improve chances for the origin of life, inasmuch as extensive experience with organic synthesis reactions has shown that the presence of water greatly diminishes the chance of constructing nucleic acids. Thus, the assemblage of organic macromolecules that could give rise to life appears to be much more straightforward in a hydrocarbon environment. A hydrocarbon solvent would also provide protection against UV radiation, as hydrocarbon smog emanating from the liquid solvent would absorb some of the UV radiation and thus offer a significant degree of protection. Hydrocarbons as the primary solvents on a planetary body are not beyond the realm of possibility. Saturn's moon Titan may provide a strong case in point. Spectroscopic results indicate the presence of methane rain on Titan (Lorenz 2000; Lunine et al. 1983) and the presence of liquid lakes on Titan's surface has been confirmed by the Cassini-Huygens mission (Stofan et al. 2007). In a non-polar hydrocarbon solvent such as methane or ethane, cellular membranes would likely be hydrophobic on the outside and hydrophilic at their cores. Thus, if a hydrocarbon liquid such as methane or ethane, or a mixture of both, could support life as a primary solvent, the resulting organisms would likely be quite different from those on Earth. In a solvent such as ethane a putative organism would be able to use hydrogen bonding more effectively, because the bonds would have the appropriate strengths for low temperatures.

Methanogenesis could be an energy-yielding strategy in this type of environment. For example, photochemically produced acetylene, which is a solid under Titan's surface conditions (Lorenz 2000), could be reduced with the help of hydrogen in the atmosphere to methane (Eq. 7.4)

$$C_2H_2 + 3H_2 \rightarrow 2CH_4 \qquad\qquad (7.4)$$

In fact, methane is detected at a lighter isotopic fractionation than would be expected from Titan formation theory (Lunine et al. 1999), which could indicate activity of living organisms (Abbas and Schulze-Makuch 2002; Schulze-Makuch and Grinspoon 2005). Essential building blocks of life such as sugars, proteins and nucleic acids could exist in such organisms as well. However, given the vastly different environment from which that form of life would originate, it appears more likely that another solution to the make-up of life would have been found. Baross et al. (2007) suggested that the environment of Titan meets the absolute requirements for life, which include thermodynamic disequilibrium, abundant carbon containing molecules and heteroatoms, and a fluid environment—further concluding that "this makes inescapable the conclusion that if life is an intrinsic property of chemical reactivity, life should exist on Titan."

7.3.4   Supercritical Fluids: Carbon Dioxide

Supercritical fluids could also play a role as a life sustaining solvent on other worlds. The properties of supercritical fluids are usually quite different from those of regular fluids. Supercritical water, for example, is relatively non-polar and acidic. There are some advantages to supercritical fluids, especially for carbon dioxide and water, which include: (1) high solubility of gases within supercritical mixtures, (2) miscibility of gases such as O_2 and H_2 in supercritical fluids, (3) high diffusion rates and variable density, and (4) high dissolving power (Baross et al. 2007). Ikushima (1997) advanced the case for supercritical fluids as an appropriate medium for chemical and biochemical processes under certain conditions. One cited example was the synthesis of esters from acryl donors and terpene alcohols by lipase in *Candida cylindracea*, which in supercritical carbon dioxide caused drastic conformational changes that enabled active sites to catalyze stereoselective synthesis. Reactivity was found to be susceptible to small changes in pressure or temperature near the critical point of the supercritical fluid. Shkrob and Sauer (2001) showed that high-mobility CO_2-multimer anions in supercritical carbon dioxide form stable complexes with water, aliphatic alcohols, alkyl halides, and alkyl nitriles.

An example of how supercritical CO_2 might support living processes can be seen in the recent discovery of subsurface accumulations of liquid carbon dioxide under Earth's oceans (Inagaki et al. 2006). The low density liquid CO_2 has been found to be trapped by a surface pavement and subpavement cap of CO_2 hydrate ($CO_2 \times 6H_2O$). As the density of liquid CO_2 increases with depth, it becomes denser than sea water, opening up the possibility of many reservoirs of liquid carbon dioxide on the sea floor (House et al. 2006). Most amazing was the detection of 10^7 cells/ml at the liquid CO_2/CO_2-hydrate interface (Inagaki et al. 2006), which is quite remarkable given the potentially hostile nature of CO_2 (Nealson 2006). Carbon dioxide is usually described as a non-polar solvent, given the zero molecular dipole moment and its low dielectric constant. However, strong theoretical and recent experimental evidence indicates that CO_2 can participate in hydrogen-bonding interactions, and thus has polar attributes (Raveendran et al. 2005). Industrially, supercritical carbon dioxide is increasingly promoted as an environmentally benign alternative to conventional organic solvents (Raveendran et al. 2005) and is used in biotechnological applications to catalyze reactions that do not occur in water (Budisa and Schulze-Makuch 2014). Carbon dioxide is a very common compound on many planets, including our neighbors Venus and Mars. Supercritical carbon dioxide could occur in a number of these extraterrestrial locations, such as in the subsurface of Venus. It certainly deserves more attention as a potential life-sustaining solvent.

7.4   Quantitative Assessment of Solvent Candidates

In this section we will attempt to make a quantitative assessment regarding the suitability of a compound as an alternative solvent for life. There are some properties that are advantageous for life independently of the biochemistry of the living organism. Abundance is a definite advantage and may be the primary reason why life on Earth uses water as the universal solvent. Local abundance is most important for the solvent to be available for life processes, but overall cosmic abundance is relevant as well. If a compound is cosmically very rare a suitable fractionation mechanism has to be available to provide the compound in sufficient quantity. Aside from abundance, the most important property is being in a liquid state at the prevailing temperature of the local environment. The enthalpy of fusion and vaporization indicates how good a heat insulator the solvent is, and the dipole moment of the compound gives a general measure of its ability to dissolve other compounds (for life based on non-polar polymeric chemistry this criterion would be applied differently; for the present analysis that possibility will be disregarded).

A quantitative estimate of the feasibility that a given solvent could be effective in a particular planetary environment is shown in Table 7.3. The metric is obtained by assigning +1 to four favorable characteristics—cosmic abundance, local abundance, enthalpy of vaporization, and dipole moment; by assigning −1 for unfavorable instances of the same characteristics; and by assigning 0 to cases that fall between clearly favorable and unfavorable characteristics. A fifth property—liquid at prevailing local temperature—is of such obvious importance that +2 is assigned for favorable cases, −2 for cases in which the solvent cannot be liquid at the prevailing temperature, and 0 for intermediate or unknown situations. The range of temperatures at which a solvent candidate is in the liquid state (at a pressure of 1 bar) is given in Fig. 7.4. Adding the assigned points for each of the five characteristics yields a single composite value for each solvent on each planetary body shown in Table 7.4.

This estimate is obviously crude and speculative to a large degree, and we certainly have not considered all possible solvents. A more precise and systematic analysis may emerge from further research, a consideration of other relevant variables, and a more highly differentiated system of weighting the different factors. Nonetheless, some generalizations can be gleaned from even this preliminary analysis. These include the inference that water is the best solvent on warmer bodies, but methanol may be superior on some colder worlds; that ammonia or ammonia-water mixtures (with ammonia being the "antifreeze" for water) may be an important solvent on the colder worlds as well [also supported by Leliwa-Kopystyński et al. (2002)]; and that despite some favorable properties, hydrocyanic acid, hydrofluoric acid, and hydrogen sulfide do not appear particularly advantageous under any conditions.

With respect to specific planetary bodies, Table 7.4 suggests the following: (1) water is clearly the best solvent for Earth; (2) water is also the best solvent, perhaps in combination with ammonia and methanol, beneath the surface of the icy

Table 7.3 Feasibility of selected solvents for particular planetary environments

Solvent	Earth					Icy satellites					Gas giants				
	C	L	T	E	D	C	L	T	E	D	C	L	T	E	D
H_2O	+	+	++	+	0	+	+	0	+	0	+	−	0	+	0
NH_3	+	−	−−	0	0	+	−	++	0	0	+	+	0	0	0
HCN	0	−	++	0	+	0	−	−−	0	+	0	−	0	0	+
HF	−	−	0	0	0	−	−	++	0	0	−	−	0	0	0
H_2S	−	0	−−	−	−	−	−	++	−	−	−	0	0	−	−
CH_3OH	0	−	++	0	+	0	−	++	0	+	0	−	0	0	+
C_2H_6	0	−	−−	−	−	0	−	++	−	−	0	−	0	−	−
	Io (near subsurface)					Titan surface					Titan subsurface				
Solvent	C	L	T	E	D	C	L	T	E	D	C	L	T	E	D
H_2O	+	−	0	+	0	+	0	−−	+	0	+	0	−−	+	0
NH_3	+	−	0	0	0	+	0	−−	0	0	+	+	++	0	0
HCN	0	−	−−	0	+	0	0	−−	0	+	0	0	−−	0	+
HF	−	−	0	0	0	−	−	−−	0	0	−	−	0	0	0
H_2S	−	+	++	−	−	−	0	−−	−	−	−	0	++	−	−
CH_3OH	0	−	0	0	+	0	0	0	0	+	0	0	++	0	+
C_2H_6	0	−	0	−	−	0	+	++	−	−	0	+	++	−	−

Cosmic abundance (C): += major component on planetary bodies or in interstellar space; −= found only in trace amounts
Local abundance (L): += major constituent in local environment; −= trace amounts or less in local environment
Thermal range (T): ++= liquid at prevailing local temperature; −−= liquid outside of prevailing local temperature
Enthalpy of vaporization (E): +≥40 kJ/mol; −≤ 20 kJ/mol
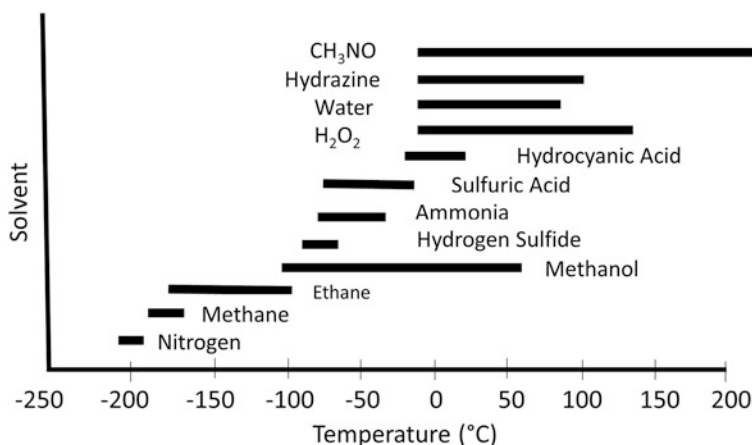Dipole moment (D): +≥2; −≤1

Fig. 7.4 Temperature ranges for selected solvent candidates to occur in the liquid state (at 1 bar)

Table 7.4 Summary assessment of selected solvent candidates for certain planetary environments

Solvent	Earth	Icy satellites	Gas giants	Io (near subsurface)	Titan surface	Titan subsurface
H_2O	+4	+3	+1	+1	+1	0
NH_3	−1	+1	+2	0	0	+3
HCN	+1	−1	0	−1	0	0
HF	−2	−1	0	−2	−3	0
H_2S	−4	−3	−3	0	−4	−2
CH_3OH	+1	+1	0	0	+1	+2
C_2H_6	−4	−2	−3	−3	0	0

satellites; (3) the gas giant planets do not favor any particular solvent except possibly water and ammonia within a particular thermal and pressure range; (4) the special circumstances of Io make it difficult for any solvent to function there, though some combination of water and H_2S might work beneath the surface; (5) Titan's surface is inhospitable for any other than organic solvents; while (6) the subsurface of Titan could function with a combination of organic solvents, ammonia, and water.

   In conclusion, Table 7.4 suggests that other solvents may be more favorable under the many environmental conditions likely to be found on other worlds that differ from those on the Earth's surface. A good example is Titan, where water is in the solid state and ethane and methane are liquids, making them more suitable solvents. Over a large range of circumstances, however, it does appear that water is an adequate if not preferred solvent. Nevertheless, many more possibilities are worthy of investigation, such as the solvent dinitrogen, which would receive a favorable rating for Triton, a very cold icy satellite.

7.5 Some Additional Thoughts

Except for the fundamental thermodynamics of its constituent molecules, there is probably no property of a living system that is more important for determining its characteristics than the nature of the solvent in which the system originated and evolved. Since the solvent determines the thermal limits within which chemical reactions can take place, the type of molecules that dissolve and do not dissolve, and the nature of the chemical interactions that can occur, both among the molecules and between them and the solvent, it follows that the total chemical makeup of the living system is a consequence of the solvent in which it occurs.

   If our Solar System is any indication, Earth-like planets are relatively rare, while planetary bodies that are either smaller and much colder, or larger and gaseous, are more frequently occurring. Both conditions render water useless as a solvent, but raise the prospects that an alternative solvent could be an effective medium for energy flow through chemically complex systems. Among the candidates are compounds that are not rare. Even those that are cosmically uncommon, like the sulfur-based solvents, may occur at critical densities under specialized circumstances (as on

the volcanic planetoid, Io). In each case, however, the alternative solvent will almost surely foster a very different biochemistry from that which thrives in an aqueous environment. It is by no means apparent that exotic biochemical systems unfamiliar to us are less plausible under exotic conditions. As defined earlier, the essence of life has to do with complexity, energy flow, and information—none of which is limited in principle to the biochemical system with which we are familiar on Earth. In searching for life beyond Earth, we would therefore be well advised to expect the unusual.

The possibility does remain that the thermodynamic properties of any molecule that could undergo complex reactions and be assembled into stable macromolecular form is strictly constrained to conditions under which only water is an adequate solvent. Until research on complex chemical interactions in solvents other than water becomes more common, this possibility cannot be ruled out. If it should turn out that only water is an adequate solvent, the implication would be that life is likely to be restricted to water-abundant planetary bodies such as Earth, Mars and Europa. Even if this were the case, the astronomical number of planetary bodies that surely exist in the Universe, combined with the abundance of water throughout the Cosmos, makes it possible that life even as we do know it may be widespread. Our hunch, however, is that the nature of life is broader and more pervasive than most of us imagine.

7.6 Chapter Summary

Water is an ideal solvent for the complex chemical systems that constitute life on Earth, because of its broad thermal range of liquidity corresponding to Earth's average temperature and atmospheric pressure, and because of other characteristics that make it both an excellent physical buffer and advantageous medium for complex chemical interactions among the biomolecules that have evolved under the physico-chemical conditions prevailing on Earth.

On other worlds where temperatures and pressures are different, other solvents are more likely to be found in the liquid state. Many of them have properties that make them adequate, if not advantageous, as solvents for complex chemical systems. This includes, in particular, polar solvents like ammonia, hydrocyanic acid, and methanol. Under specialized conditions, others such as hydrogen sulfide and sulfur dioxide, could serve as solvents as well. Likewise, non-polar solvents like methane and ethane can be stable liquids under some conditions. While each of these could in principle host complex biochemical interactions, the nature of the molecules that would thrive in a given solvent would be dependent on the nature of that solvent. On worlds where the physicochemical conditions require that a solvent other than water provide a liquid medium, the conditions for the origin of biomolecules and the evolution of their variations and transformations would be different, and likely would result in the elaboration of a biochemical system different from that known to us from the one example of life on Earth.