

Yizhak Marcus

Ions in Water and Biophysical Implications

From Chaos to Cosmos

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Preface

It is so often stated that water is a ubiquitous liquid on earth and a general solvent for many kinds of solutes that such statements sound as clichés. Nevertheless, they are correct and merit discussion. Other common statements are that the properties of water are unique among liquids and are difficult to understand: “No one really understands water. It’s embarrassing to admit it, but the stuff that covers two-thirds of our planet is still a mystery. Worse, the more we look, the more the problems accumulate: new techniques probing deeper into the molecular architecture of liquid water are throwing up more puzzles.” (Ball 2008). Unfortunately, to date this situation keeps being rather true and should be accorded a more comprehensive treatment.

On the other hand, ions are found in a large variety of environments. These include a non-environment where the ions are isolated in vacuum, as generated for example in a mass spectrometer. Ions in a gaseous phase include clusters of ionized water vapour relating to cloud formation. Ions in condensed phases may occur in solids, whether crystalline or disordered (glasses) but also in liquids, including room temperature ionic liquids or molten salts at higher temperatures. In such condensed phases the ions are in close vicinity to one another with strong coulombic interactions between their charges that tend to order the ions (at least over short distances in liquids) with alternating positive and negative charges.

Ions also exist in liquid solutions in a variety of solvents, whether non-aqueous, aqueous, or mixed. When ions are placed in a solvent, by the dissolution of an electrolyte capable of extensive ionic dissociation, the properties of such solutions cannot be estimated simply as weighted sums of the properties of the individual components, solvent and ions. This results from the strong interactions between the ions and the solvent molecules, which merit intensive investigation in order to comprehend the properties of such solutions. The ions tend to be solvated in solution with a solvation shell around them, the solvent separating the ions from one another, their mutual distance apart depending on their concentration. For a binary electrolyte, consisting of one cation C and one anion A at a molar concentration c their average distance apart is inversely proportional to the cube root of the concentration: $d_{C-A}^{av} = (2cN_A)^{-1/3}$ (Marcus 2009). If each of the ions has one solvent molecule attached to it in the space between them, there is hardly space for a further solvent molecule between the solvated ions at a concentration of 1 mol per litre. Therefore, the

properties of dilute and mildly concentrated solutions differ considerably. Moreover, electrolyte solutions may be homogeneous but also colloidal dispersions and their properties vary from those in the bulk to those near surfaces. The interactions of ions at solution surfaces, whatever the phase at the other side of the surface—a gas, an immiscible liquid, a solid (e.g., an electrode), or dispersed colloidal particles (including biopolymers)—are also a subject that requires attention.

Both biological systems and their physiology are based on the water that is present in all living things, which is essential to life, as well as on solutions of ions in the water. Furthermore, these solutions exist in rather heterogeneous situations, in the vicinity of surfaces of organic substances that are partly hydrophilic and partly hydrophobic and which may carry charges on their ionisable groups. Therefore, the biophysical implications of such solutions are consequences of the above-mentioned interactions. There exists thus a wide spread of topics that should be dealt with in a book such as the present one.

The term “entropy”, meaning “transformation” in Greek, was introduced by Clausius for this well known but perhaps less well understood thermodynamic quantity. This entity is often interpreted as “disorder” in a system, equivalent to “chaos”, but also as “lack of knowledge” in terms of information theory (Ben-Naim 2008). It is the purpose of this book to fill the gap in ordered knowledge about the above mentioned topics of ions in water, and lead the reader from “chaos” to “cosmos”, which means in Greek “order” and “harmony”. Therefore, “from chaos to cosmos” is an apt subtitle for this book, in particular because ions in aqueous solutions relating to biophysical phenomena are classified as “chaotropic” or “kosmotropic”. The justification of the use of these terms in the context of biological systems is critically assessed in this book. The author does not belong to the biophysics research establishment, hence his efforts to bring order to the use of such terms such as chaotropic and kosmotropic ions and the Hofmeister effect and series is like tilting at windmills. Still, he is confident that the suggestions made in this book may infiltrate into this establishment and might be accepted in the long run.

This book, being written by a single author, cannot be a comprehensive treatise on the subject of ions in water. It does present the author’s physicochemical point of view, but is annotated with a large number of references to the original literature. In the present millennium already some 700 books have been published that have “water” in their title, but only very few have bearing on the present spread of problems. Some, indeed “ancient”, books on aqueous electrolyte solutions, however, should be mentioned here, because they contain the physicochemical basis for the present discussions: the books by Harned and Owen (1958) and by Robinson and Stokes (1965). More recently the books by Conway (1981) and by Marcus (1985) and a special journal issue edited by Harding (2001) bear directly on the problems dealt with here. Other books are mentioned in the chapters dealing with the specific topics.

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List of Symbols

Symbol Description (Units (SI))

Acronyms

<i>cmc</i>	Critical micelle concentration
EoS	Equation of state
ITIM	Identification of truly interfacial molecules
MC	Monte Carlo computer simulation
MD	Molecular dynamics computer simulation
<i>PVT</i>	Pressure-volume-temperature
SAFT	Statistical associated fluid theory
SHG	Second harmonic generation spectroscopy
SPT	Scaled particle theory
<i>STI</i>	Surface tension increment
VLE	Vapour/liquid equilibrium
VSFG	Visible sum frequency generation spectroscopy

Symbols for units (not in the general SI list) Roman font

m	Molality ($\text{mol kg solvent}^{-1}$)
M	Molarity (mol dm^{-3})

Universal constants in *italics* font

<i>e</i>	Unit electrical charge: 1.602177×10^{-19} (C)
<i>F</i>	Faraday's constant: 9.64853×10^4 (C mol^{-1})
<i>k_B</i>	Boltzmann's constant: 1.380658×10^{-23} (J K^{-1})
<i>N_A</i>	Avogadro's number: 6.022136×10^{23} (mol^{-1})
<i>R</i>	Gas constant: 8.31451 ($\text{J K}^{-1} \text{mol}^{-1}$)
ϵ_0	Permittivity of vacuum: 8.854188×10^{-12} ($\text{C}^2 \text{J}^{-1} \text{m}^{-1}$)

Symbols for physical quantities in Roman *italics* font

<i>A</i>	Helmholz energy, molar (kJ mol^{-1})
<i>a</i>	Attractive parameter in an EoS ($\text{J}^2 \text{Pa}^{-1} \text{mol}^{-2}$)
<i>B</i>	Virial coefficient (m^3)
<i>b</i>	Scattering length (nm)
<i>b</i>	Co-volume parameter in an EoS (m^3)
<i>C_P</i>	Heat capacity at constant pressure, molar ($\text{J K}^{-1} \text{mol}^{-1}$)
<i>C_V</i>	Heat capacity at constant volume, molar ($\text{J K}^{-1} \text{mol}^{-1}$)
<i>c</i>	Concentration, molar scale (mol dm^{-3})
<i>D</i>	Diffusion coefficient ($\text{m}^2 \text{s}^{-1}$)
<i>d</i>	Interatomic distance (nm)
<i>E</i>	Energy, molar (kJ mol^{-1})
<i>e_{HB}</i>	Energy of an H-bond per mole of bonds (kJ mol^{-1})
<i>f</i>	Fugacity (kPa)
<i>f_i</i>	Fraction of water molecules with <i>i</i> H-bonds
<i>G</i>	Gibbs energy, molar (kJ mol^{-1})
<i>g</i>	Kirkwood dipole orientation parameter
<i>g(r)</i>	Pair correlation function
<i>H</i>	Enthalpy, molar (kJ mol^{-1})
<i>h_i</i>	Hydration number, ionic
<i>I</i>	Ionic strength (mol dm^{-3})
<i>I</i>	Intensity of scattered or absorbed radiation
<i>K</i>	Equilibrium constant ($\text{dm}^3 \text{mol}^{-1}$)
<i>K^O_w</i>	Octanol/water partition coefficient
<i>K_w</i>	Ion product of water ($\text{dm}^6 \text{mol}^{-2}$)
<i>k</i>	Variable, function of diffraction angle (m^{-1})
<i>k</i>	Rate constant (s^{-1})
<i>L_g</i>	Ostwald coefficient of gas solubility
<i>M</i>	Mass, molar (kg mol^{-1})
<i>m</i>	Mass, molecular (kg)
<i>m</i>	Molality (mol kg^{-1})
<i>N</i>	number of components
<i>N</i>	Number of molecules or ions
<i>N_{co}</i>	Coordination number
<i>n</i>	Refractive index (at specified frequency)
<i><n_{HB}></i>	Average number of H-bonds per water molecule
<i>P</i>	Pressure (MPa)
<i>P_i</i>	Internal pressure (MPa)
<i>p</i>	Vapor pressure (kPa)
<i>p(event)</i>	Probability of an event
<i>r</i>	Radial distance from a particle (nm)
<i>r_i</i>	Radius, ionic (nm)
<i>S</i>	Entropy, molar ($\text{J K}^{-1} \text{mol}^{-1}$)

$S(k)$	Structure factor
s	Solubility (mol dm^{-3})
T	Temperature (absolute) (K)
T_1	Spin-lattice nmr relaxation time (s)
t	Temperature (centigrade) ($^{\circ}\text{C}$)
t_i	Transference number, ionic
U	Configurational energy of system, molar (kJ mol^{-1})
u	Sound velocity (m s^{-1})
u_i	Mobility, ionic ($\text{m s}^{-1} \text{V}^{-1}$)
V	Volume, molar (m^3)
v	Specific volume ($\text{m}^3 \text{kg}^{-1}$)
v	Velocity, molecular (m s^{-1})
x	Mole fraction of specified component or species
Y	Generalized thermodynamic function or solvatochromic parameter
y	Activity coefficient, molar scale
Z	Compressibility factor PV/RT
Z	Lattice parameter
z	Charge number, algebraic

Symbols for physical quantities in Greek *italics*

α	Kamlet-Taft H-bond donation ability index
α	Polarizability, molecular (m^{-3})
α_P	Expansibility, isobaric (K^{-1})
β	Kamlet-Taft H-bond acceptance ability index
γ	Activity coefficient, molal scale
δ	NMR chemical shift (ppm)
δ_H	Hildebrand solubility parameter ($\text{MPa}^{1/2}$)
ϵ_r	Relative permittivity
ζ	Reciprocal of the friction coefficient
η	Dynamic viscosity (mPa s^{-1})
θ	Angle between two dipoles or three atoms ($^{\circ}$)
θ_{ca}	Contact angle between a solid and a sessile drop ($^{\circ}$)
κ_S	Compressibility, adiabatic (GPa^{-1})
κ_T	Compressibility, isothermal (GPa^{-1})
Λ	Conductivity, molar ($\Omega^{-1} \text{m}^2 \text{mol}^{-1}$)
λ_i	Conductivity, ionic equivalent ($\Omega^{-1} \text{m}^2 \text{mol}^{-1}$)
μ	Dipole moment (C m)
μ	Chemical potential (kJ mol^{-1})
ν	Wave number (cm^{-1})
ξ	Correlation length (m)
π^*	Kamlet-Taft polarity/polarizability index
ρ	Density (kg m^{-3})
σ	Diameter, molecular (nm)

τ	Relaxation or correlation time (ps)
φ	Volume fraction
φ	Osmotic coefficient
χ	Number of H-bonds of any given water molecule
ω	Frequency (s^{-1})
ω	Pitzer's acentric factor

Sub- and superscripts

*	Pure substance or scaling parameter
°	Standard state
∞	Infinite dilution
ass	Association
c	Critical
D	Dielectric or Debye, or self diffusion
E	Excess thermodynamic quantity
f	Of formation (thermodynamic quantity)
g	Of a gas
^{ig}	Ideal gas
i	Of an individual ion
r	Reduced, divided by the critical quantity
v	Of vaporization
w	Of water
σ	Saturation (VLE equilibrium)

Chapter 1

Water

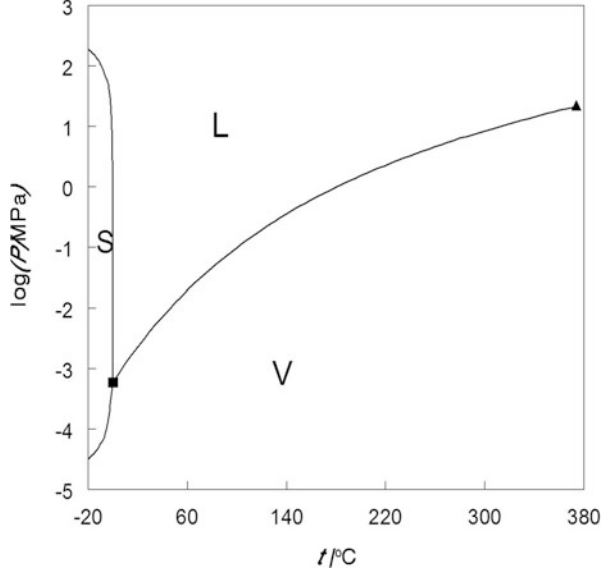
Water is a ubiquitous liquid substance in our world, is essential for life as we know it, and has by all accounts striking properties that set it aside from other liquids. It has therefore been investigated from many points of view and the results have been published in innumerable papers in journals and in many books. Some 70 years ago Dorsey (1940) published a compendium of data on the water substance and Eisenberg and Kauzmann (1969) published a book on the structure and properties of water. A collective set of volumes, edited by Franks (1972) some 40 years ago, was devoted to water and solutions in it. Since then numerous more books and review articles have been devoted to the properties of water, both for itself and as a solvent for various substances, including electrolytes and their constituent ions. The recent review by Malenkov (2006) of the structure and dynamics of liquid water covers the developments in these subjects since the earlier books mentioned above. Recent works on the properties of water are the collection of review papers edited by Pratt (2002) and the book by Ben-Naim (2009) on understanding water.

1.1 Liquid Water

1.1.1 The Properties of Water in the Liquid State

The limits of existence of water in a thermodynamically stable liquid state extend from the triple point, at which it is in equilibrium with ice I, the solid state of water under ordinary pressures, to the critical point, at which the distinction between liquid and vapour phases vanishes. The former limit, the triple point, is at $0.01\text{ }^{\circ}\text{C}$ ($T_t = 273.16\text{ K}$) and $P_t = 0.61166\text{ kPa}$. The latter limit, the critical point, is at $374.93\text{ }^{\circ}\text{C}$ ($T_c = 647.096\text{ K}$) and $P_c = 22.064\text{ MPa}$. Liquid water also exists in a meta-stable sub-cooled state, theoretically down to the glass transition point, 139 K , but experimentally to 232 K ($-41\text{ }^{\circ}\text{C}$) before spontaneous nucleation and freezing sets in. Liquid water is at equilibrium with water vapour along the so-called saturation curve, $p_{\sigma}(T)$, where p_{σ} is the vapour pressure, but it exists as a liquid also at higher external pressures. Wagner and Pruss (2002) reported the IAPWS 1995 formulation

Fig. 1.1 A part of the phase diagram of water, showing the domains of the solid (iceI, *S*), the liquid (*L*), and the vapour (*V*). The square denoted the triple point and the triangle the critical point. (From data in (Dorsey 1940))



for the thermodynamic properties of water; it seems to be so far the last word on the subject. The expression for the saturation (equilibrium) vapour pressure of liquid water, $p_\sigma(T)$, takes the following form:

$$\ln\left(\frac{p_\sigma}{P_c}\right) = (1 - \theta)^{-1} [a_1\theta + a_2\theta^{1.5} + a_3\theta^3 + a_4\theta^{3.5} + a_5\theta^4 + a_6\theta^{7.5}] \quad (1.1)$$

where $\theta = 1 - T/T_c$ and with the following coefficients: $a_1 = -7.8595$, $a_2 = 1.84408$, $a_3 = -11.78665$, $a_4 = 22.68074$, $a_5 = -15.96187$, and $a_6 = 1.801225$. The relevant part of the phase diagram of water is shown in Fig. 1.1.

The properties of water are important for the understanding of the effects ions have on it. The molecular properties pertain to isolated water molecules in the ideal gas state. Some of these properties are shown in Table 1.1 for ordinary water, H_2O , and also for heavy water, D_2O , where known. The properties of these substances as liquids are, of course, also of large significance in the context of this book and are shown in Table 1.1 too.

The thermophysical and thermodynamic properties of liquid water as well as its chemical properties, all depend on the temperature and the pressure. The thermophysical and thermodynamic properties include the density ρ , the molar volume $V = M/\rho$, the isothermal compressibility $\kappa_T = \rho^{-1}(\partial\rho/\partial P)_T = -V^{-1}(\partial V/\partial P)_T$, the isobaric expansibility $\alpha_P = -\rho^{-1}(\partial\rho/\partial T)_P = V^{-1}(\partial V/\partial T)_P$, the saturation vapour pressure p_σ , the molar enthalpy of vapourization $\Delta_v H$, the isobaric molar heat capacity C_P , the Hildebrand solubility parameter $\delta_H = [(\Delta_v H - RT)/V]^{1/2}$, the surface tension γ , the dynamic viscosity η , the relative permittivity ϵ_r , the refractive index (at the sodium D-line) n_D , and the self-diffusion coefficient D . These are shown in Table 1.2, at the ambient pressure of 0.1 MPa (1 bar, 0.986923 atm) as a function

Table 1.1 Properties of light and heavy water. (Jasnsco and Van Hook 1974; Marcus 1985, 1998)

Molecular properties	H ₂ O	D ₂ O
O–H(D) bond length, (pm)	95.72	95.75
H–O–H angle, (°)	104.523	104.474
Moment of inertia, ($I_A/10^{-30}$ kg m ²)	0.10220	0.18384
Moment of inertia, ($I_B/10^{-30}$ kg m ²)	0.19187	0.38340
Moment of inertia, ($I_C/10^{-30}$ kg m ²)	0.29376	0.56698
Hydrogen bond length, (pm)	276.5	276.6
Dipole moment, (μ/D)	1.834	1.84
Electrical quadrupole moment, ($\theta/10^{-39}$ C m ²)	1.87	
Polarizability, ($\alpha/10^{-30}$ m ³)	1.456	1.536
Collision diameter, (σ/pm)	274	
Potential energy minimum, (u/k_B)/K	732	
O–H(D) bond energy at 0 K, (kJ mol ^{−1})	44.77	
Proton (deuteron) affinity, (kJ mol ^{−1})	762	772
Symmetrical stretching frequency, (cm ^{−1})	3656.65	2671.46
Asymmetrical stretching frequency, (cm ^{−1})	3755.79	2788.05
Bending frequency, (cm ^{−1})	1594.59	1178.33
Zero point vibrational energy, (kJ mol ^{−1})	55.31	40.44
<i>Thermodynamic properties</i>		
Triple point, K (°C)	273.15 (0.00)	276.97 (3.82)
Normal boiling point, K (°C)	373.15 (100.00)	374.57 (101.42)
Critical temperature, K (°C)	647.3 (374.1)	644.1 (370.9)
Critical pressure, (MPa)	22.12	21.86
Molar mass, ($M/\text{kg mol}^{-1}$)	0.018015	0.020031
Van der Waals volume, ($V_{\text{vdW}}/\text{cm}^3 \text{ mol}^{-1}$)	12.4	12.4
Van der Waals surface area, ($A_{\text{vdW}}/10^4 \text{ m}^2 \text{ mol}^{-1}$)	22.6	22.6
Ideal gas heat capacity, ($C_p/\text{J K}^{-1} \text{ mol}^{-1}$)	33.578	34.238
Ideal gas entropy, ($S/\text{J K}^{-1} \text{ mol}^{-1}$)	188.72	198.23
Enthalpy of vapourization, (kJ mol ^{−1})	44.04	45.46
<i>Properties of the liquid at 25 °C</i>		
Isobaric heat capacity, ($\text{J K}^{-1} \text{ mol}^{-1}$)	75.27	84.52
Isochoric heat capacity, ($\text{J K}^{-1} \text{ mol}^{-1}$)	74.48	83.7
Isothermal compressibility, (GPa^{-1})	0.457	0.4678
Isobaric expansibility, (10^{-3} K^{-1})	0.2572	0.1911
Surface tension, (mN m^{-1})	71.97	71.85
Viscosity, (mPa.s)	0.890	1.103
Magnetic susceptibility, ($\chi/10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)	−12.9	
Relative permittivity, (ϵ_r)	78.46	78.06
($\partial \ln \epsilon_r / \partial T$) _P (10^3 K^{-1})	−4.59	−4.64
($\partial \ln \epsilon_r / \partial P$) _T (GPa^{-1})	0.471	
Self-diffusion coefficient, ($D/10^{-9} \text{ m}^2 \text{ s}^{-1}$)	2.299	2.109
Cooperative relaxation time (at 20 °C), (τ/ps)	9.55	12.3
Refractive index at Na D line	1.33250	1.32841

of the temperature, in the range relevant for liquid water, i.e., at $0^\circ\text{C} \leq t \leq 100^\circ\text{C}$, where the vapour pressure is $p_\sigma \approx 1\text{atm} = 0.101325\text{ MPa}$.

Finally, some chemical properties of water, such as the polarity and solvatochromic indices, are listed in Table 1.3 for 25°C . The self-ionic-dissociation, of water is the most important chemical property of water. Its equilibrium constant, K_w ,

Table 1.2 Thermophysical and thermodynamic properties of water at ambient pressure (0.1 MPa) and varying temperatures ($0^{\circ}\text{C} \leq t \leq 100^{\circ}\text{C}$)

t ($^{\circ}\text{C}$)	ρ (g cm^{-3})	V ($\text{cm}^3 \text{ mol}^{-1}$)	α_p (mK^{-1})	κ_T (GPa^{-1})	p_{σ} (kPa)	$\Delta_v H$ (KJ mol^{-1})	C_p ($\text{J K}^{-1} \text{ mol}^{-1}$)	δ_H ($\text{MPa}^{1/2}$)	γ (mN m^{-1})	η (mPa s)	ε_r	n_D	D^a ($10^{-9} \text{m}^2 \text{ s}^{-1}$)
0	0.99984	18.019	-0.0681	0.5089	0.611	45.03	75.98	48.71	75.62	1.792	87.81	1.33395	1.099
10	0.99970	18.021	+0.0880	0.4781	1.228	44.67	75.52	48.46	74.20	1.307	83.99	1.33374	1.525
20	0.99820	18.048	0.2068	0.4585	2.338	44.24	75.34	48.13	72.75	1.002	8.027	1.33298	2.023
25	0.99705	18.069	0.2572	0.4525	3.169	44.04	45.29	47.96	71.96	0.890	78.46	1.33250	2.299
30	0.99565	18.095	0.3032	0.4477	4.245	43.84	75.27	47.79	71.15	0.798	76.67	1.33195	2.594
40	0.99222	18.157	0.6853	0.4424	7.381	43.46	75.28	47.44	69.55	0.653	73.22	1.33066	3.238
50	0.98804	18.234	0.4576	0.4417	12.35	43.09	75.31	47.07	67.90	0.547	69.90	1.32909	3.956
60	0.98320	18.324	0.5231	0.4450	19.92	42.74	75.38	46.71	66.17	0.467	66.73	1.32730	4.748
70	0.97777	18.425	0.5837	0.4516	31.18	42.40	75.47	46.33	64.41	0.4041	63.70	1.32526	5.615
80	0.97180	18.538	0.6411	0.4614	47.38	42.09	75.60	45.96	62.60	0.354	60.81	1.32302	6.557
90	0.96532	18.663	0.6962	0.4743	70.12	41.79	75.75	45.58	60.74	0.313	58.05	1.32061	7.574
100	0.95836	18.799	0.7501	0.4902	101.325	41.50	75.95	45.20	58.85	0.278	55.41	1.31805	8.667

^aFrom (Eastale et al. 1989)

Table 1.3 Chemical properties of light and heavy water at 25 °C

Property	H ₂ O	D ₂ O
Dimrot-Reichard polarity index, ($E_T(30)/\text{kcal mol}^{-1}$)	63.1	62.5
Normalized Dimrot-Reichard polarity index, (E_T^N)	1.000	0.991
Kamlet-Taft polarity/polarizability, (π^*)	1.09	
Kamlet-Taft electrom pair donicity, (β)	0.47	
Kamlet-Taft hydrogen bond donicity, (α)	1.17	
Gutmann donor number	18.0	
Gutmann-Maier acceptor number	54.8	
Marcus softness parameter, (μ)	0.00	
Ion product, pK_W (Pentz and Thornton 1967)	13.996	14.860

Table 1.4 Some temperature dependent chemical properties of water

$t(^{\circ}\text{C})$	$\kappa(\mu\text{S m}^{-1})^a$	$pK_{W(m)}^b$	S_y
0	1.19	14.944	0.4883
10	2.33	14.535	0.4960
20	4.20	14.167	0.5046
25	5.48	13.996	0.5091
30	7.06	13.833	0.5139
40	11.1	13.535	0.5241
50	16.7	13.262	0.5351
60	24.0	13.016	0.5470
70	33.4	12.796	0.5599
80	45.5	12.598	0.5739
90	59.9	12.420	0.5891
100	76.4	12.260	0.6056

^aFrom Light (1984)^bFrom Harned and Owen (1958)

for the ion product resulting from the autoprotolysis, has been studied extensively by many authors, and the book by Bates (1973) may be consulted for details. Table 1.4 shows pK_W , the negative of the logarithm of the ion product equilibrium constant, (on the molal scale, $\text{mol (kg water)}^{-1}$). Also relevant are the specific conductance κ , and the limiting slope of the Debye-Hückel expression for the activity coefficients of 1:1 electrolytes S_y (on the molar, M, scale). The values of these properties are shown for $0^{\circ}\text{C} \leq t \leq 100^{\circ}\text{C}$ in Table 1.4.

Such data are available also in the compendium by Riddick et al. (1986) on the properties of solvents and in the book by Marcus “Ion Solvation” (1985) among other sources. The latter book also summarizes interpolation functions for some of these variables. Some of these data are also available there for heavy water, D₂O and for sub-cooled liquid water, down to -35°C , and heated liquid water along the saturation line to the critical point and at elevated pressures.

1.1.2 Water as a Structured Liquid

There exists consensus among researchers that water is a highly structured liquid due to an extensive network of hydrogen bonds (HBs). However, no agreement exists

on how the structure is to be defined and on how the extent of hydrogen bonding is to be measured or computed. Only recently have the intermolecular distances $d(\text{O}_\text{W}-\text{O}_\text{W})$, $d(\text{O}_\text{W}-\text{H}_\text{W})$, and $d(\text{H}_\text{W}-\text{H}_\text{W})$ (pertaining to the water oxygen and hydrogen atoms) and the orientations of the water molecules been determined satisfactorily in liquid water by diffraction measurements and computer simulations (Head-Gordon and Hura 2002).

The molecular structure of liquids, as measured by x-ray and neutron diffraction, is presented in the first place as the structure factors $S(k)$. The diffraction methods yield the intensities I of the diffracted beams at various angles θ at a fixed wavelength λ of the radiation for the defined variable k :

$$k = \lambda^{-1} 4\pi \sin\left(\frac{\theta}{2}\right) \quad (1.2)$$

The structure factors are then obtained as

$$S(k) \approx \frac{I(k) - I(0)}{I(\infty) - I(0)} \quad (1.3)$$

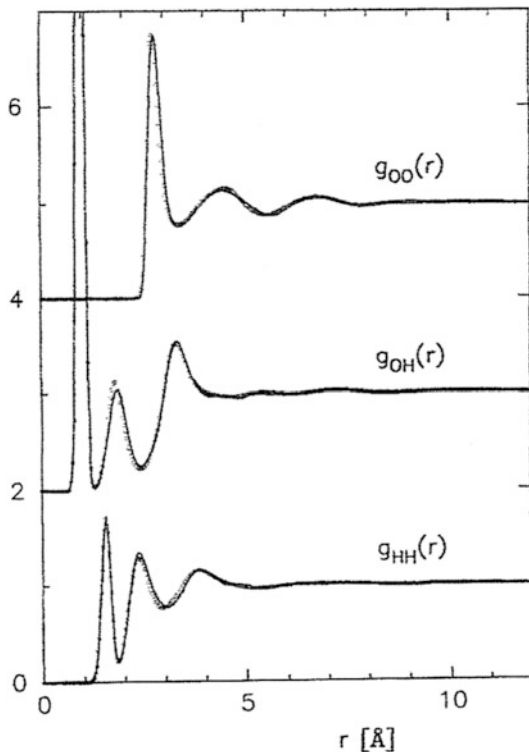
This expression uses the intensities measured at very small angles $I(0)$ and at very large angles $I(\infty)$ to normalize the intensities and eliminate the effect of the incoherent scattering on the relative intensities. Note that $\lim_{k \rightarrow 0} S(k) = \rho k_\text{B} T \kappa_\text{T} \sim 0.01$ (nominally $S(0) = 0$) where ρ is the number density of the diffracting atoms, and also that $S(\infty) = 1$.

The structure factor is related to the radial distribution function of the liquid $n(r)$ and, in turn, to the pair correlation function $g(r)$ of the diffracting atoms, see below. The former of these quantities is the probability of finding a particle in a spherical shell of thickness dr at a distance r from a given particle. At large distances there are no interactions between the particles so that $dn(r \rightarrow \infty, dr) = \rho 4\pi r^2 dr$, is proportional to the number density of the particles. At short distances, where attraction and repulsion forces between the particles play a role, the presence of a given particles at the origin affects the probability for another one to be in a volume element at the distance r from it: they are correlated. Hence the pair correlation function is defined by the conditional probability of finding another particle at a distance r from a given one:

$$dn(r, dr) = g(r) \rho 4\pi r^2 dr \quad (1.4)$$

Since there is no correlation between the particles at large distances from each other $g(r \rightarrow \infty) = 1$. On the other hand, at very small distances the large repulsion of the electronic shells of the atoms prevent their overlapping and $g(r < \sigma) = 0$, where σ is the diameter of the particles. Integration of Eq. (1.4) from σ to any distance r yields the number of neighbouring molecules around the particle at the origin, i.e., the coordination number up to that distance. Generally $g(r)$ peaks at $r = \sigma + \varepsilon$, i.e., at a distance slightly beyond σ , and “undulates” further out reaching unity asymptotically, but practically beyond 3σ and possibly up to 5σ . The coordination numbers reach plateaus (have small slopes) at $r \sim \sigma$, that is the first coordination shell, and possibly also for the second shell at $r \sim 2\sigma$.

Fig. 1.2 The three partial pair correlation functions: $g(\text{O}_\text{W}-\text{O}_\text{W}, r)$, $g(\text{O}_\text{W}-\text{H}_\text{W}, r)$, and $g(\text{H}_\text{W}-\text{H}_\text{W}, r)$, for water at ambient conditions. (Reproduced from (Soper 2000) with kind permission of © The American Institute of Physics)



The structure factors yield after Fourier transformation the total pair correlation function $g(r)$:

$$g(r) = (2\pi^2\rho r)^{-1} \int_0^\infty (S(k) - 1)k \sin(kr) dk \quad (1.5)$$

Here “total” means that $g(r)$ pertains to all the diffracting atoms. Application of x-ray diffraction results in the structure of liquid water, in terms of $g(\text{O}_\text{W}-\text{O}_\text{W}, r)$, since only the oxygen atoms, but not the hydrogen atoms, diffract x-rays. This function resembles to some extent that of liquid argon, a non-structured liquid by all accounts (Fisenko et al. 2008), as demonstrated by Marcus (1996). There is, thus, more in the notion of the structure of water than what is measurable by $g(r)$, which is dominated by the strong repulsion of molecules that are too closely packed together.

Special techniques, isotope substitution in neutron diffraction with empirical potential structure refinement, permit partial pair correlation functions to be obtained. The three partial pair correlation functions: $g(\text{O}_\text{W}-\text{O}_\text{W}, r)$, $g(\text{O}_\text{W}-\text{H}_\text{W}, r)$, and $g(\text{H}_\text{W}-\text{H}_\text{W}, r)$, provide more information on the molecular structure of water as discussed below. Those for water at ambient conditions are shown in Fig. 1.2 (Soper 2000).

Table 1.5 The “structuredness” of some highly hydrogen-bonded solvents at 25 °C compared with other common electrolytic solvents

Solvent	<i>Stiffness</i> ($\delta_H^2 - P_i$)/ MPa	<i>Order</i> ($\Delta\Delta_{\text{vap}}S/R$)	$\Delta C_p/V$ (J K ⁻¹ cm ⁻³)	KDOCP (g)	<i>Openness</i> (1 - V_X/V)
Water	2,129	7.82	2.31	2.90	0.076
1,2-Ethanediol	548	21.20	0.92	2.08	0.091
Glycerol	541	39.50	1.41	2.13	0.034
2-Ethanolamine	490	23.20	0.67	2.25	0.090
Formamide	1,014	7.58	1.56	1.67	0.091
Methanol	570	6.26	0.92	2.82	0.243
Acetonitrile	186	4.38	0.74	0.74	0.236
N, N-Dimethylformamide	101	4.00	0.74	1.03	0.249
Dimethyl sulphoxide	187	5.07	0.89	1.04	0.140

The first peak in the $g(\text{O}_W\text{--O}_W, r)$ function pertains to nearest water molecule neighbours, the second peak to next-nearest-neighbours, etc. The extent of the correlation (the height of the peak) is seen to diminish with increasing distances. The very large first peak in $g(\text{O}_W\text{--H}_W, r)$ pertains to the O–H covalent bond and is not relevant to the structure of water, but the second and further peaks yield information on the mutual orientation of the water molecules and on the hydrogen bonding. The latter item can also be retrieved from $g(\text{H}_W\text{--H}_W, r)$.

Before going into the details of the hydrogen bonding, there are other features of structured liquids in general and of water in particular that ought to be discussed. The notion of “structuredness” that was introduced by Marcus (1992) relates to more subtle interactions characterizing bulk properties of a liquid. Following Caldin and Bennetto (1971), Marcus described the structuredness of liquids in terms of the “stiffness”, “order”, and “openness” of a liquid in general.

The work that must be expended in order to create a cavity in a liquid measures its stiffness. Such a cavity is required in order to accommodate a molecule of the liquid itself, condensing into it from the vapour, or of a solute particle. This work per unit volume of the cavity can be obtained from the thermodynamic quantities characterizing the liquid: its molar enthalpy of vapourization $\Delta_v H$, its molar volume V , its isobaric expansibility α_p , its isothermal compressibility κ_T , and its vapour pressure p_σ , all at the temperature of interest T . These yield the difference between the cohesive energy density $ced = \delta_H^2 = [\Delta_v H - RT]/V$ and the internal pressure $P_i = T\alpha_p/\kappa_T - p_\sigma$. The ced is the square of the Hildebrand solubility parameter. According to Marcus (1999):

$$\text{stiffness} = \delta_H^2 - P_i = [(\Delta_v H - RT)/V] - T(\alpha_p/\kappa_T) - p_\sigma \quad (1.6)$$

Water is a very stiff liquid, with $\delta_H^2 - P_i = 2,129$ MPa at 25 °C, much beyond other liquids, even those with a hydrogen bonded network, Table 1.5.

The deficit of the molar entropy of a liquid with respect to the same substance in the ideal gas phase is a measure of the “order” existing in the liquid. Trouton’s constant, $\Delta_{\text{vap}}S(T_b) = \Delta_v H(T_b)/T_b$ is the negative of this deficit, where T_b is the

normal boiling point at atmospheric pressure (0.101325 MPa) and $\Delta_v S$ and $\Delta_v H$ are the molar entropy and enthalpy of vapourization. Trouton's constant of an ordered liquid is $\Delta_{\text{vap}} S(T_b)/R > 12$. The value for water is 13.15, but it shares this property with a great many other liquids that are ordered (Marcus 1992). However, water vapour at the boiling point is associated and thus has a lower entropy than it would have in the ideal gas state. For a more refined criterion for order possible association in the vapour phase is taken into account according to Marcus (1996) by equating order with $\Delta \Delta_v S/R$. This eliminates liquids, such as normal alkanes, that are deemed to be unordered and vapour phase association:

$$\begin{aligned} \text{order} = \Delta \Delta_v S/R &= [\Delta_v S_{\text{liquid}}(T, P^\circ) - \Delta_v S_{\text{alkane}}(T, P^\circ)]/R \\ &+ (P^\circ/R)d(B_{\text{liquid}} - B_{\text{alkane}})/dT \end{aligned} \quad (1.7)$$

In this expression $\Delta_v S(T, P^\circ) = S(\text{vapour}, T, P^\circ) - S(\text{liquid}, T, P^\circ)$ is the molar entropy difference between the vapour and the liquid at the standard pressure $P^\circ = 0.1$ MPa and the temperature of interest, T . The comparison of $\Delta_v S(T, P^\circ)$ of the test liquid is with this quantity of a saturated alkane having the same skeleton as the molecules of the liquid. For this purpose, non-carbon atoms are converted: halogen $-X$ to $-\text{CH}_3$, ethereal oxygen $-\text{O}-$ to $-\text{CH}_2-$, carbonyl $>C=O$ to $-\text{CH}(\text{CH}_3)-$, etc. as appropriate. The temperature derivative of the difference between the second virial coefficients B of the vapours of the liquid of interest and of the alkane takes into account association of the vapour.

This criterion for the existence of “order” in a given liquid is $\Delta \Delta_v S/R > 2$, and at 25 °C water has $\Delta \Delta_v S/R = 7.94$, larger than many liquids deemed structured by any criterion (Marcus 1998). However, this quantity is by no means larger than for all structured liquids, see Table 1.5. When the “order density” in a structured liquid is expressed by division of $\Delta \Delta_v S$ by V , the molar volume of the liquid, water ($\Delta \Delta_v S/V = 3.23 \text{ J K}^{-1} \text{ cm}^{-3}$) becomes quite similar to 1,2-ethanediol (3.15) and 2-ethanolamine (3.21), having a somewhat lower value than glycerol (4.20), but a higher one than formamide (1.58) and methanol (1.28).

The molar heat capacity at constant pressure of a liquid, $C_P(l)$, is the amount of energy that must be invested in order to increase its temperature. This energy is consumed by re-ordering the liquid molecules in addition to that going into internal degrees of freedom. The latter amount of energy is taken into account by subtraction of the ideal gas quantity. Hence, a further measure of the order in liquids is the heat capacity density (Marcus 1996):

$$\text{order} = \frac{\Delta C_P}{V} = \frac{C_P(l) - C_P(\text{i.g.})}{V(l)} \quad (1.8)$$

Structured liquids have values of $(\Delta C_P/V)/\text{J K}^{-1} \text{ cm}^{-3} > 0.6$, that for water being 2.32, larger than the values of some other structured liquids, see Table 1.5. This is due to the small molar volume of water and mainly to the extensive hydrogen bonded network that absorbs the energy.