

Part One
Fundamentals of Chemistry in Nonaqueous Solutions:
Electrochemical Aspects

1

Properties of Solvents and Solvent Classification

Three types of liquid substances, i.e. molecular liquids, ionic liquids and atomic liquids, can serve as *solvents*. They dissolve *solutes* that are solid, liquid or gaseous and form *solutions*. Molecular liquid solvents are the most common and include, besides water, many organic solvents and some inorganic solvents, such as hydrogen fluoride, liquid ammonia and sulfur dioxide. Ionic liquid solvents are mostly molten salts and usually used at relatively high temperatures. Nowadays, however, various room-temperature ionic liquids (or simply called 'ionic liquids') are being designed and used as a kind of 'green solvents'.¹⁾ There are only a few atomic liquid solvents at room temperatures, metallic mercury being a typical example. Besides these liquid solvents, supercritical fluids are sometimes used as media for chemical reactions and separations (see footnote 1).

Apart from Chapter 13, which deals with electrochemistry in new solvents (supercritical fluids, ionic liquids, etc.), this book mainly considers molecular liquid solvents. Thus, the term 'solvents' means molecular liquid solvents. Water exists abundantly in nature and has many excellent solvent properties. If water is appropriate for a given purpose, it should be used without hesitation. If water is not appropriate, however, some other solvent (or ionic liquids) must be employed. Molecular solvents other than water are generally called *nonaqueous solvents*. Nonaqueous solvents are often mixed with water or some other nonaqueous solvents, to obtain desirable solvent properties. These mixtures of solvents are called *mixed solvents*.

1) 'Green' chemistry is the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products (Anastas, P.T., Warner, J.C. (1998) *Green Chemistry, Theory and Practice*, Oxford University Press, New York, p. 11). Under the framework of green chemistry, efforts are being made to find environmentally benign media (green solvents) for chemical processes; among such media are harmless

nonaqueous solvents, immobilized solvents, ionic liquids, supercritical fluids, aqueous reaction systems and solvent-free reaction systems. For the recent situation, see, for example, Abraham, M.A., Moens, L. (eds) (2002) *Clean Solvents: Alternative Media for Chemical Reactions and Processing*, Oxford University Press, New York; Nelson, W.M. (2003) *Green Solvents for Chemistry: Perspectives and Practice* (Green Chemistry Series), Oxford University Press, New York.

Table 1.1 Physical properties of organic solvents and some inorganic solvents of electrochemical importance.

Solvent	Abbreviated symbol	Bp (°C)	Fp (°C)	Vapor pressure ^a (mmHg)	Density ^a (g cm ⁻³)	Viscosity ^a (cP)	Conductivity ^a (S cm ⁻¹)	Relative permittivity ^a (D)	Dipole moment ^a (D)	Toxicity ^b
(1) Water		100	0	23.8	0.9970	0.890	6×10^{-8}	78.39	1.77	
Acids										
(2) Hydrogen fluoride		19.6	-83.3	—	0.9529	0.256	1×10^{-4}	84.0	1.82	0.5
(3) Formic acid		100.6	8.27	43.1	1.2141	1.966	6×10^{-5}	58.5 ₁₆	1.82 ₃₀	5
(4) Acetic acid	HOAc	117.9	16.7	15.6	1.0439	1.130	6×10^{-9}	6.19	1.68 ₃₀	10
(5) Acetic anhydride		140.0	-73.1	5.1	1.0749	0.783 ₃₀	5×10^{-9}	20.7 ₁₉	2.82	5
Alcohols										
(6) Methanol	MeOH	64.5	-97.7	127.0	0.7864	0.551	1.5×10^{-9}	32.7	1.71	200.T
(7) Ethanol	EtOH	78.3	-114.5	59.0	0.7849	1.083	1.4×10^{-9}	24.6	1.74	1000.C(A4)
(8) 1-Propanol	1-PrOH	97.2	-126.2	21.0	0.7996	1.943	9×10^{-9}	20.5	1.71	200.C(A3)
(9) 2-Propanol	2-PrOH	82.2	-88.0	43.3	0.7813	2.044	6×10^{-8}	19.9	1.66 ₃₀	200.C(A4)
(10) Methyl cellosolve (i)		124.6	-85.1	9.7	0.9602	1.60	1.1×10^{-6}	16.9	2.04	5
(11) Cellosolve (ii)		135.6	<-90	5.3	0.9252	1.85	9×10^{-8}	29.6 ₂₄	2.08	5
Ethers										
(12) Anisole (methoxybenzene)	PhOMe	153.8	-37.5	3.54	0.9893	0.895	1×10^{-13}	4.33	1.245	NE
(13) Tetrahydrofuran (iii)	THF	66.0	-108.4	162	0.8892 ₂₀	0.460	—	7.58	1.75	50.C(A3)
(14) 1,4-Dioxane (iv)		101.3	11.8	37.1	1.028	1.087 ₃₀	5×10^{-15}	2.21	0.45	20.C(A3).T
(15) Monoglyme (1,2-dimethoxyethane) (v)	DME	84.5	-69	48 ₂₀	0.8637	0.455	—	7.20	1.71	NE
(16) Diglyme (vi)		159.8	-64	3.4	0.9384	0.989	—	—	1.97	NE

Ketones												
(17) Acetone	Ac	56.1	-94.7	231	0.7844	0.303	5×10^{-9}	20.6	2.7 ₂₀	500,C(A4)		
(18) 4-Methyl-2-pentanone	MIBK	117.4	-84	18.8	0.7963	0.546	$<5 \times 10^{-8}$	13.1 ₂₀	—	50,T		
(19) Acetylacetone	Acac	138.3	-23.2	8.6 ₂₃	0.9721	0.694	1×10^{-8}	25.7 ₂₀	2.78 ₂₂	NE		
Nitriles												
(20) Acetonitrile	AN	81.6	-43.8	88.8	0.7765	0.341 ₃₀	6×10^{-10}	35.9	3.53	20,C(A4),T		
(21) Propionitrile	PrN	97.4	-92.8	44.6	0.7768	0.389 ₃₀	8×10^{-8}	28.9 ₂₀	3.50	Very toxic		
(22) Butyronitrile	BuN	117.6	-111.9	19.1	0.7865	0.515 ₃₀	—	24.8 ₂₀	3.50	Very toxic		
(23) Isobutyronitrile		103.8	-71.5	—	0.7656	0.456 ₃₀	—	20.4 ₂₄	3.61	Very toxic		
(24) Benzoinitrile	BN	191.1	-12.7	1.28 ₂	1.0006	1.237	5×10^{-8}	25.2	4.01	Very toxic		
Amines												
(25) Ammonia		-33.4	-77.7	—	0.681 ₋₃₄	0.25 ₋₃₄	5×10^{-11}	23.0 ₋₃₄	0.93	25		
(26) Ethylenediamine	en	116.9	11.3	13.1 _{26.5}	0.8931	1.54	9×10^{-8}	12.9	1.90	10,C(A4)		
(27) Pyridine	Py	115.3	-41.6	20	0.9782	0.884	4×10^{-8}	12.9	2.37	1,C(A3)		
Amides												
(28) Formamide	FA	210.5	2.5	1 ₇₀	1.1292	3.30	$<2 \times 10^{-7}$	111 ₂₀	3.37 ₃₀	10		
(29) N-Methylformamide (vii)	NMF	180-185	-3.8	0.4 ₄₄	0.9988	1.65	8×10^{-7}	182.4	3.86	NE		
(30) N,N-Dimethylformamide (viii)	DMF	153.0	-60.4	3.7	0.9439	0.802	6×10^{-8}	36.7	3.24	10,C(A4),T		
(31) N-Methylacetamide (ix)	NMA	206	30.5	1.5 ₅₆	0.9500 ₃₀	3.65 ₃₀	2×10^{-7}	191.3 ₃₂	4.27 ₃₀			
(32) N,N-Dimethylacetamide (x)	DMA	166.1	-20	1.3	0.9363	0.927	10^{-7}	37.8	3.79	10,C(A4)		
(33) N-Methylpropionamide		104 _{16mm}	-30.9	94 ₁₀	0.9305	5.22	8×10^{-8}	176	—			
(34) Hexamethylphosphoric triamide (xi)	HMPA	233	7.2	0.07 ₃₀	1.020	3.10	2×10^{-7}	29.6	5.37	Toxic, C(A3),T		
(35) N-Methyl-2-pyrrolidone (xii)	NMP	202	-24.4	0.3	1.026	1.67	1×10^{-8}	32.2	4.09 ₃₀	NE		
(36) 1,1,3,3-Tetramethylurea	TMU	175.2	-1.2	—	0.9619	1.395	$<6 \times 10^{-8}$	23.60	3.50			

(Continued)

Table 1.1 (Continued)

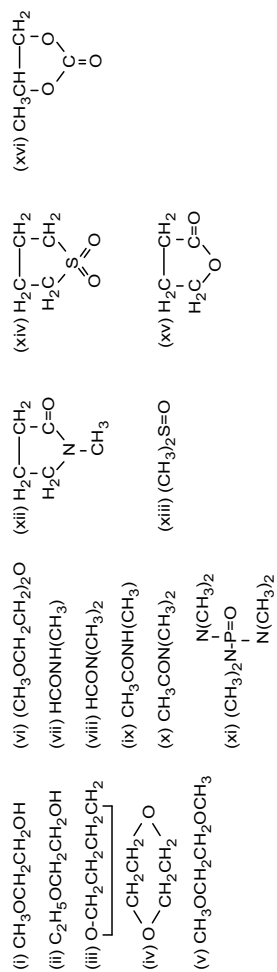
Solvent	Abbreviated symbol	Bp (°C)	Fp (°C)	Vapor pressure ^a (mmHg)	Density ^a (g cm ⁻³)	Viscosity ^a (cP)	Conductivity ^a (S cm ⁻¹)	Relative permittivity ^a	Dipole moment ^a (D)	Toxicity ^b
Sulfur compounds										
(37) Sulfur dioxide		-10.01	-75.46		1.46 ₋₁₀	0.429 ₀		15.6 ₀	1.62	2, C(A4)
(38) Dimethyl sulfoxide (xiii)	DMSO	189.0	18.5	0.60	1.095	1.99	2 × 10 ⁻⁹	46.5	4.06	NE
(39) Sulfolane (xiv)	TMS	287.3	28.5	5.0 ₁₁₈	1.260 ₃₀	10.3 ₃₀	<2 × 10 ⁻⁸ ₃₀	43.3 ₃₀	4.7 ₃₀	
(40) Dimethylthioformamide	DMTF	70 _{1mm}	-8.5		1.024 ₂₇	1.98	—	47.5	4.4	
(41) N-Methyl-2-thiopyrrolidinone	NMTP	145 _{15mm}	19.3		1.084	4.25	—	47.5	4.86	
Others										
(42) Hexane		68.7	-95.3	151.3	0.6548	0.294	<10 ⁻¹⁶	1.88	0.085	50.T
(43) Benzene		80.1	5.5	95.2	0.8736	0.603	4 × 10 ⁻¹⁷	2.27	0	0.5,C(A1),T
(44) Toluene		110.6	-95.0	28.5	0.8622	0.553	8 × 10 ⁻¹⁶	2.38	0.31	50,C(A4),T
(45) Nitromethane	NM	101.2	-28.6	36.7	1.1313	0.614	5 × 10 ⁻⁹	36.7	3.17	20,C(A3)
(46) Nitrobenzene	NB	210.8	5.76	0.28	1.1983	1.62 ₃₀	2 × 10 ⁻¹⁰	34.8	4.00	1,C(A3),T
(47) Dichloromethane		39.6	-94.9	436	1.3168	0.393 ₃₀	4 × 10 ⁻¹¹	8.93	1.55	50,C(A3)
(48) 1,2-Dichloroethane	DCE	83.5	-35.7	83.4 ₂₀	1.2464	0.73 ₃₀	4 × 10 ⁻¹¹	10.37	1.86	10,C(A4)
(49) γ -Butyrolactone (xv)	γ -BL	204	-43.4	3.2	1.1254	1.73		39.1	4.12	
(50) Propylene carbonate (xvi)	PC	241.7	-54.5	1.2 ₅₅	1.195	2.53	1 × 10 ⁻⁸	64.92	4.94	
(51) Ethylene carbonate	EC	248.2	36.4	3.4 ₉₅	1.3383	1.9 ₄₀	5 × 10 ⁻⁸ ₄₀	89.8 ₄₀	4.9	
(52) Methyl acetate	MA	56.9	-98.0	216.2	0.9279	0.364	3 × 10 ⁻⁶ ₂₀	6.68	1.72	200
(53) Ethyl acetate		77.1	-83.6	94.5	0.8946	0.426	<1 × 10 ⁻⁹	6.02	1.82	400

Except for the column of 'Toxicity', the data in this table are mainly from Ref. [3], though some are from Ref. [1].

^aUnless otherwise stated, the data are at 25 °C. The temperatures other than 25 °C are shown as subscript.

^bThe numerical value shows the TLV as time-weighted average (TWA), i.e. the maximum permissible vapor concentration that the average person can be exposed for 8 h per day, 5 days per week without harm, in ppm (cm³ of solvent vapor per 1 m³ of air) [29, 30a, 31]. The mark 'C' shows that the solvent is or is suspected to be carcinogenic and A1.

A3 and A4 show 'confirmed human carcinogen', 'confirmed animal carcinogen with unknown relevance to humans' and 'not classifiable as a human carcinogen', respectively. The mark 'T' shows the solvent has been listed in Title III of the Clean Air Act Amendments of 1990 as a hazardous air pollutant. NE stands for 'not established'.



There are a great many kinds of neat nonaqueous solvents. Substances that are solid or gaseous at ambient temperatures also work as solvents, if they are liquefied at higher or lower temperatures. For mixed solvents, it is possible to vary the mixing ratio and thus the solvent properties continuously. Therefore, if both nonaqueous and mixed solvents are included, the number of solvents really is infinite.

When a nonaqueous solvent is to be used for a given purpose, a suitable one must be selected from the infinite number available. This is not easy, however, unless there are suitable guidelines available on how to select solvents. In order to make solvent selection easier, it is useful to classify solvents according to their properties. The properties of solvents and solvent classification have been dealt with in detail in the literature [1, 2]. In this chapter, these problems are briefly discussed in Sections 1.1 and 1.2, and then the influences of solvent properties on reactions of electrochemical importance are outlined in Section 1.3.

Organic solvents and some inorganic solvents for use in electrochemical measurements are listed in Table 1.1, with their physical properties.

1.1 Properties of Solvents

Physical and chemical properties that are important in characterizing solvents as reaction media are listed in Table 1.2 and are briefly discussed in Sections 1.1.1 and 1.1.2. The data of solvent properties have been compiled in Refs [2–4] for a number of solvents. In addition to these properties, structural aspects of solvents are outlined in Section 1.1.3 and the effects of toxicity and the hazardous properties of solvents are considered in Section 1.1.4.

1.1.1 Physical Properties of Solvents

Each of the physical properties in Table 1.2 has its own significance.²⁾ The boiling point, T_b , and the melting (or freezing) point determine the liquid range of solvents. The vapor pressure is a fundamental vaporization property, and it is also important when considering the problem of toxicity and other hazards of solvents (Section 1.1.4). The heat of vaporization, $\Delta_v H$, determines the cohesive energy density, c , defined by $c = (\Delta_v H - RT)/V_m$, and the solubility parameter, δ , is defined by $\delta = c^{1/2} = [(\Delta_v H - RT)/V_m]^{1/2}$, where V_m is the molar volume. The cohesive energy density is a measure of the ‘stickiness’ of a solvent and is related to the work necessary to create ‘cavities’ to accommodate solute particles in the solvent. Conversely, the solubility parameter proposed by Hildebrand is useful in predicting the solubilities of nonelectrolyte solutes in low-polarity solvents. In many cases, two liquid substances with similar δ values are miscible, while those with dissimilar

²⁾ See Refs [1–3] or advanced textbooks of physical chemistry.

Table 1.2 Physical and chemical properties of solvents.

Physical properties	<i>Bulk properties:</i> boiling point, melting (or freezing) point, molar mass, density, viscosity, vapor pressure, heat capacity, heat of vaporization, refractive index, relative permittivity, electric conductivity; <i>molecular properties:</i> dipole moment, polarizability
Chemical properties	Acidity (including the abilities as proton donor, hydrogen bond donor, electron pair acceptor and electron acceptor) ^a ; basicity (including the abilities as proton acceptor, hydrogen bond acceptor, electron pair donor and electron donor) ^a

^aThe terms ‘acidity’ and ‘basicity’ are used in somewhat wider ways than usual (see text).

δ values are immiscible.³⁾ The heat of vaporization at the boiling point, $\Delta_v H(T_b)$ in kJ mol^{-1} , determines Trouton’s constant, $(\Delta_v S(T_b)/R)$, which is equal to $\Delta_v H(T_b)/T_b$. Solvents with $\Delta_v S(T_b)/R \leq 11.6$ are usually nonstructured (e.g. $\Delta_v S(T_b)/R = 7.2$ for acetic acid, 10.2 for hexane, 10.5 for benzene and 10.9 for acetone), while those with $\Delta_v S(T_b)/R \geq 12$ are structured (e.g. $\Delta_v S(T_b)/R = 12.5$ for methanol and 13.1 for water). The viscosity (η) influences the rate of mass transfer in the solvent and therefore the conductivity of electrolyte solutions.

The relative permittivity, ϵ_r , influences the electrostatic interactions between electric charges. If two charges, q_1 and q_2 , are placed in a vacuum at a distance r from each other, the electrostatic force F_{vac} between them is expressed by Eq. (1.1):

$$F_{\text{vac}} = \frac{q_1 q_2}{4\pi\epsilon_0 r^2} \quad (1.1)$$

where ϵ_0 is the permittivity of a vacuum and $\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$. F_{vac} is a repulsive force if q_1 and q_2 are of the same sign, while F_{vac} is an attractive force if they

3) The primary role of solvents is to ‘dissolve’ substances. There is an old principle – ‘like dissolves like’. In general, polar solvents can dissolve polar substances, while nonpolar solvents can dissolve nonpolar substances. The following table shows the relationship between the polarities of solvents and solutes and their mutual solubilities:

obtained by dissolution. The energetic stabilization depends on the energies of three interactions, i.e. solute–solvent, solute–solute and solvent–solvent interactions. When both the solvent and the solute are nonpolar, all of the three interactions are weak. In that case, the energy gained by the entropy of mixing of the solvent and the solute plays an important role

Solvent A	Solute B	Interaction			Mutual solubility
		A ... A	B ... B	A ... B	
Nonpolar	Nonpolar	Weak	Weak	Weak	High
Nonpolar	Polar	Weak	Strong	Weak	Low
Polar	Nonpolar	Strong	Weak	Weak	Low
Polar	Polar	Strong	Strong	Strong	High

The necessary condition for dissolution of a substance is that energetic stabilization is

in the high mutual solubility. For the dissolution of electrolytes, see Section 2.1.

are of opposite sign. If the two charges are placed in a solvent of relative permittivity ϵ_r and at a distance r , the electrostatic force F_{solv} between them is expressed by Eq. (1.2):

$$F_{\text{solv}} = \frac{q_1 q_2}{4\pi\epsilon_0\epsilon_r r^2} = \frac{F_{\text{vac}}}{\epsilon_r} \quad (1.2)$$

Because ϵ_r is larger than ~ 1.8 for most solvents (1.84 for *n*-pentane and 1.88 for *n*-hexane are examples of lowest ϵ_r values), the electrostatic interaction between charges is always weakened by solvents. As discussed in Chapter 2, the relative permittivity of a solvent has a decisive influence on the electrostatic solute–solute and solute–solvent interactions as well as on the dissolution and dissociation of electrolytes. Thus, it is used in classifying solvent polarity or solvating capability. Solvents of high permittivities ($\epsilon_r \geq 15$ or 20) are called *polar solvents*, while those of low permittivities are called *apolar* or *nonpolar solvents* (Section 1.2). Many of the solvents listed in Table 1.1 are polar solvents, because the solvents for electrochemical use must dissolve and dissociate electrolytes. The relative permittivities of *N*-methylformamide (NMF) and *N*-methylacetamide (NMA) are exceptionally high, at 182 and 191, respectively. This is because the molecules of these solvents mutually interact by hydrogen bonding and are linearly arranged, causing high permittivities (Section 1.1.3). However, some nonpolar solvents, e.g. hexane and benzene ($\epsilon_r \sim 2$), are now also used in electrochemical measurements, as will be discussed in Section 8.4.

If a solvent is placed in a low-frequency electric field ($< 10^7$ Hz), its molecules are polarized in two ways: one is the *induced polarization*, which is due to the atomic and electronic displacements, and the other is the *orientational polarization*, which is due to the alignment of the permanent dipoles. They both contribute to the *static permittivity*, ϵ_s , which is equal to ϵ_r in Table 1.1. However, if the frequency of the electric field is increased, the orientational polarization is lost in the microwave region (10^9 – 10^{11} Hz) because the permanent dipoles need some time to rotate or reorient. The permittivity after this Debye (rotational) relaxation is the *infinite frequency permittivity* and is denoted by ϵ_∞ (Figure 1.1). Then, after the resonant transition in the IR region, the polarization occurs only due to electronic displacement. The permittivity then obtained is the *optical permittivity* and is denoted by ϵ_{op} . After the transition in the UV region, no polarization occurs and the permittivity becomes equal to unity. Table 1.3 shows the values of ϵ_s , ϵ_∞ and ϵ_{op} for some solvents. It also shows the values of the Debye relaxation time, τ_D , and the longitudinal relaxation time, τ_L ; τ_D is obtained experimentally by such methods as dielectric relaxation spectroscopy [5] and τ_L is obtained by the relation $\tau_L = (\epsilon_\infty/\epsilon_s)\tau_D$ [6]. For H-bonding solvents such as alcohols and water, the Debye relaxation process is more complicated. Table 1.4 shows the data for the sequential relaxation of such solvents. For example, monoalcohols give three relaxation processes: the first (slowest) one (τ_1) is attributed to the winding chain formed by association, the second one (τ_2) is attributed to the rotation of monomers and molecules situated at the chain end and the third one (τ_3) is attributed to the hindered rotation of molecules within the H-bonded system. Solvents that undergo one Debye relaxation are called ‘Debye’ solvents, while those that undergo sequential relaxations are called ‘non-Debye’ solvents. For PC and DMF, some confusion is observed whether their behavior is Debye or non-Debye. According to the recent studies, these dynamic properties of solvents have remarkable influences on various electrochemical processes such as

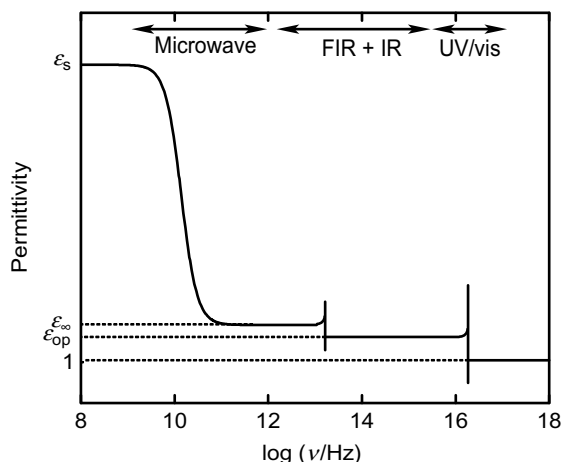


Figure 1.1 Dielectric dispersion spectra for a polar solvent with a single Debye relaxation process in the microwave region and two resonant transmissions in the IR and UV ranges [5b].

ion solvation, homogeneous and heterogeneous electron-transfer reactions and ionic migrations, as discussed in Sections 2.2.2, 4.13, 7.2.1, 8.2.2 and 8.3.1.

The refractive index, n_D , defined as the ratio of light speed at the sodium D-line in a vacuum to that in the medium, is used in obtaining the polarizability, α , of

Table 1.3 Solvent dielectric and related properties at 25°C.^a

Solvent	$\epsilon_s (= \epsilon_r)$	ϵ_{op}	ϵ_∞	$\epsilon_{op}^{-1} - \epsilon_s^{-1}$	τ_D (ps)	τ_L (ps)
Debye solvents						
AN	37.5	1.80	2	0.528	3.3	~0.2
Ac	21	1.84	2	0.495	3.3	0.3
DMSO	46.7	2.18	5.7	0.438	19.5	2.4
HMPA	29.6	2.12	3.3	0.438	80	8.9
NB	35.7	2.40	4.1	0.389	45.6	5.2
Py	13.3	2.27	2.3	0.365	6.9	1.2
THF	7.58	1.97	2.3	0.376	3.3	1.0
Non-Debye solvents						
EtOH	24.5	1.85	4.2	0.499	130	22
FA	110	2.09	7.0	0.469	37	2.35
MeOH	32.7	1.76	5.6	0.628	48	8.2
NMF	182	2.04	5.4	0.485	123	3.7
1-PrOH	20.4	1.92	2.2	0.472	390	42
Debye or non-Debye (?) solvents (different viewpoints exist)						
DMF	36.7	2.04	4.5	0.472	11.0	1.3
PC	65	2.02	4.1	0.480	43	2.7

^aFrom McManis, G.E., Golovin, M.N. and Weaver, M.J. (1986) *J. Phys. Chem.*, **90**, 6563; Barthel, J., Bachhuber, K., Buchner, R., Gill, J.B. and Kleebauer, M. (1990) *Chem. Phys. Lett.*, **167**, 62; Galus, Z. (1995) *Advances in Electrochemical Science and Engineering*, vol. 4 (eds H. Gerischer and C.W. Tobias), Wiley-VCH Verlag GmbH, Weinheim, p. 222.

ϵ_s : static permittivity; ϵ_{op} : optical permittivity; ϵ_∞ : infinite frequency permittivity; $(\epsilon_{op}^{-1} - \epsilon_s^{-1})$: solvent Pekar factor; τ_D : Debye relaxation time and τ_L : longitudinal relaxation time.

Table 1.4 Dielectric relaxation parameters of water and lower alcohols determined by femtosecond terahertz pulse spectroscopy at 25°C.^a

Solvent	ϵ_s	τ_1 (ps)	ϵ_2	τ_2 (ps)	ϵ_3	τ_3 (ps)	ϵ_∞
Water	78.36	8.24	4.93	0.18			3.48
MeOH	32.63	48	5.35	1.25	3.37	0.16	2.10
EtOH	24.35	161	4.15	3.3	2.72	0.22	1.93
1-PrOH	20.44	316	3.43	2.9	2.37	0.20	1.97

^aFrom Kindt, J.T. and Schmuttenmaer, C.A. (1996) *J. Phys. Chem.*, **100**, 10373.

solvent molecules. The relationship between α and n_D is given by $\alpha = (3V_m/4\pi N_A)(n_D^2 - 1)/(n_D^2 + 2)$, where N_A is the Avogadro constant and V_m is the molar volume.⁴⁾ Solvent molecules with high α values tend to interact easily with one another or with other polarizable solute particles by dispersion forces.⁵⁾

Most solvents consist of molecules that are intrinsic dipoles and have permanent dipole moments (μ). If such molecules are placed between the two plates of a capacitor as a vapor (or as a dilute solution in a nonpolar liquid), they are oriented by the electric field. Then, the orientational polarization and the induced polarization occur simultaneously, as described above. If ϵ_r is the relative permittivity of the vapor, there is a relationship

$$\frac{\epsilon_r - 1}{\epsilon_r + 2} = \frac{4\pi N_A}{3V_m} \left(\alpha + \frac{\mu^2}{3k_B T} \right) \quad (1.3)$$

where k_B is the Boltzmann constant. By plotting the relation between $V_m(\epsilon_r - 1)/(\epsilon_r + 2)$ and $1/T$, the value of μ is obtained simultaneously with the value of α , although a more accurate value of μ is obtainable from the Stark splitting of microwave lines.

The dipole moment is also used to assess the solvent polarity: solvents with high dipole moments (e.g. $\mu \geq 2.5$ D, 1 D = 3.33564×10^{-30} C m) are called *dipolar solvents*, while those with low dipole moments are called *apolar* or *nonpolar solvents*. Many solvents with high ϵ_r values also have high μ values (see Table 1.1). However, the μ value of water (1.77 D) is lower than expected from its high solvating abilities. The dipole moment

4) Examples of n_D values: methanol 1.326, water 1.332, AN 1.341, hexane 1.372, PC 1.419, DMF 1.428, DMSO 1.477, benzene 1.498, Py 1.507, NB 1.550 and DMTF 1.576 (Table 3.5 in Ref. [2a]). For all solvents, the value of n_D is between 1.2 and 1.8. There is a relationship $\epsilon_{op} \sim n_D^2$.

5) Dispersion forces (instantaneous dipole-induced dipole interactions): Even in atoms and molecules with no permanent dipole moment, the continuous movement of electrons results, at any instant, in small dipole moments, which fluctuatingly polarize the electronic system of the neighboring atoms or molecules. This coupling causes the electronic movements to be synchronized in such a way that a mutual

attraction results (Ref. [1a], p. 13). The dispersion forces, which are universal for all atoms and molecules, are proportional to the products of the polarizabilities (α) of the two interacting species but are short range in action. Among the intermolecular forces, the dispersion forces are often stronger than the dipole-dipole and dipole-induced dipole forces, though they are weaker than the hydrogen bonding. Due to the dispersion forces, benzene exists as a liquid at normal temperatures, and hydrogen and argon are condensed to liquids at low temperatures. See, for example, Israelachvili, J.N. (1992) *Intermolecular and Surface Forces*, 2nd edn, Academic Press, London, Chapter 6.

tends to underestimate the polarity of small solvent molecules because it depends on the distance between the positive and negative charge centers in the molecule.

Many efforts have been made to correlate solute–solvent and solute–solute interactions in solutions with such polarity scales as relative permittivity and dipole moment, but these have often been unsuccessful. The chemical properties of solvents, as described below, often play more important roles in such interactions.

1.1.2

Chemical Properties of Solvents

Here, we mean by ‘chemical properties’ the acidity and basicity of solvents. Furthermore, we use the terms ‘acidity’ and ‘basicity’ in a somewhat broader sense than usual. The ability to accept an electron is included in the acidity of solvents, in addition to the abilities to donate a proton and a hydrogen bond and to accept an electron pair, while the ability to donate an electron is included in the basicity of solvents, along with the abilities to accept a proton and a hydrogen bond and to donate an electron pair. Conventionally, acidity and basicity are defined by the proton-donating and proton-accepting capabilities by the Brønsted acid–base concept and the electron pair-accepting and electron pair-donating capabilities by the Lewis acid–base concept. However, a solvent with a strong proton-donating ability usually has strong hydrogen bond-donating, electron pair-accepting and electron-accepting abilities. Moreover, a solvent with a strong proton-accepting ability usually has strong hydrogen bond-accepting, electron pair-donating and electron-donating abilities. Inclusion of electron-accepting and electron-donating abilities in acidity and basicity, respectively, is also justified by the fact that the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for molecules of various solvents are linearly correlated with the donor and acceptor numbers (see below), respectively [7].

As outlined in Section 1.3, the solvent acidity and basicity have a significant influence on the reactions and equilibria in solutions. In particular, differences in reactions or equilibria among the solvents of higher permittivities are often caused by the differences in solvent acidity and/or basicity. Because of the importance of solvent acidity and basicity, various empirical parameters have been proposed to express them quantitatively [1a, 2].⁶ Examples of the solvent acidity scales are Kosower’s Z values [8], Dimroth and Reichardt’s E_T scale [1a, 9], Mayer, Gutmann and Gerger’s acceptor number (AN) [10, 11], Kamlet and Taft’s α parameter [12] and Catalán and Díaz’s SA parameter [13]. On the other hand, examples of the solvent basicity scales are Gutmann’s donor number (DN) [11, 14], Kamlet and Taft’s β parameter [12] and Catalán *et al.*’s SB parameter [15]. Besides the acidity and basicity parameters, empirical solvent polarity/polarizability parameters such as the π^* scale [16] have also been proposed. The correlations between these empirical parameters have been

⁶ The parameters for solvent acidity and basicity are included in the parameters of solvent ‘polarity’. Here, the solvent polarity is defined as solvent’s overall solvation capability (solvation power) for solutes, which in turn depends on the action of all possible, specific and

nonspecific, intermolecular interactions between solute ions or molecules and solvent molecules [17]. As reviewed in Ref. [18], the quantitative measures of solvent polarity are numerous.

studied in detail [2, 19]. Moreover, to relate these parameters to solvent effects on various physicochemical quantities in solutions, linear solvation energy relationships (LSER) [20], as expressed by Eq. (1.4), are often employed:

$$XYZ = XYZ_0 + a \cdot \alpha + b \cdot \beta + s \cdot \pi^* + \dots \quad (1.4)$$

where XYZ is the given quantity, XYZ_0 is the quantity at $\alpha = \beta = \pi^* = 0$ and a , b and s are the coefficients for α , β and π^* , respectively. In the same way, for AN and DN , a semiempirical multiparameter relationship has been given for the solvent effects on physicochemical quantities:

$$\Delta G_S - \Delta G_R = a(DN_S - DN_R) + b(AN_S - AN_R) + c(\Delta G_{vp}^{\circ S} - \Delta G_{vp}^{\circ R})$$

Here, ΔG is the Gibbs energy for the quantity under consideration and ΔG_{vp}° is the standard molar Gibbs energy of vaporization; the sub- and superscripts S and R denote solvents S and R , respectively, and a , b and c are coefficients.

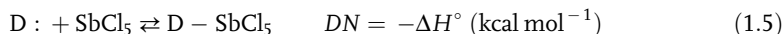
In this book, we only use the acceptor number, AN , and the donor number, DN , because they are the most popular in the field of electrochemistry and convenient to use.⁷⁾

7) Kamlet and Taft's parameters (α for solvent hydrogen bond donor (HBD) acidities, β for solvent hydrogen bond acceptor (HBA) basicities and π^* for solvent dipolarity/polarizability) are dealt with in Chapter 13, in sections on supercritical fluids and ionic liquids. These parameters are evaluated by using UV/vis spectral data of solvatochromic compounds as follows: α , β and π^* values for cyclohexane ($c\text{-C}_6\text{H}_{12}$) being defined as equal to zero [1a]. (1) β scale: The enhanced solvatochromic shifts, $\Delta\Delta\bar{\nu}$, are determined in HBA solvents for 4-nitroaniline relative to homomorphous N,N -diethyl-4-nitroaniline. Both standard compounds can act as HBA substrates (at the nitro-oxygen) in HBD solvents, but only 4-nitroaniline can act as an HBD substrate (at NH_2 group) in HBA solvents. Taking the $\Delta\Delta\bar{\nu}$ value at 2800 cm^{-1} for HMPA (a strong HBA solvent) as $\beta = 1.00$, β values for HBA solvents are

obtained. (2) α scale: The enhanced solvatochromic shifts, $\Delta\Delta\bar{\nu}$, are determined in HBD solvents for 4-nitroanisole and the pyridinium- N -phenolate betaine dye, and taking the $\Delta\Delta\bar{\nu}$ value of 6240 cm^{-1} for methanol (a strong HBD solvent) as $\alpha = 1.00$, α values for HBD solvents are obtained. (3) π^* scale: Solvent effects on the $\pi \rightarrow \pi^*$ electronic transitions of positively solvatochromic nitroaromatics of the type $\text{D-C}_6\text{H}_4\text{-A}$, where D and A stand for electron donor (e.g. NMe_2) and electron acceptor (e.g. NO_2) groups, respectively (e.g. 4-nitroanisole and N,N -dimethylamino-4-nitroaniline). The relation $\pi^*(S) = [\bar{\nu}(S) - \bar{\nu}(c\text{-C}_6\text{H}_{12})] / [\bar{\nu}(\text{DMSO}) - \bar{\nu}(c\text{-C}_6\text{H}_{12})]$, where $\bar{\nu}(S)$ is the wavenumber of the maximum of the long-wavelength solvatochromic absorption band of the indicator in solvent S ($\pi^*(\text{DMSO}) = 1.00$), is used. The values obtained by somewhat modified methods are shown below.

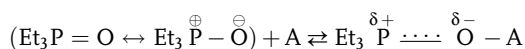
Solvents	α	β	π^*	Solvents	α	β	π^*
Gas phase	0.00	0.00	-1.23	NM	0.22	0.06	0.75
Cyclohexane ($c\text{-C}_6\text{H}_{12}$)	0.00	0.00	0.00	HMPA	0.00	1.00	0.87
Dichloromethane	0.13	0.10	0.73	DMF	0.00	0.69	0.88
NB	0.00	0.30	0.86	NMF	0.62	0.80	0.90
Py	0.00	0.64	0.87	FA	0.71	0.48	0.97
THF	0.00	0.55	0.55	EtOH	0.86	0.75	0.54
Ac	0.08	0.48	0.62	MeOH	0.98	0.66	0.60
PC	0.00	0.40	0.83	Acetic acid	1.12	0.45	0.64
DMSO	0.00	0.76	1.00	2,2,2-Trifluoroethanol	1.51	0.00	0.73
AN	0.19	0.40	0.66	Water	1.17	0.47	1.09

The donor number, DN [11, 14], of solvent D (Lewis base) is determined calorimetrically as the negative value of the standard enthalpy change, $-\Delta H^\circ$ (in kcal mol^{-1}), for the 1 : 1 adduct formation between solvent D and antimony pentachloride (SbCl_5), both being dilute, in 1,2-dichloroethane (DCE) at 25°C (Eq. (1.5)).



The values of DN are listed in Table 1.5 in increasing order. The solvent basicity increases with the increase in the DN value. The DN value for DCE (reference solvent) is zero.

The acceptor number, AN [10, 11], of solvent A (Lewis acid) is obtained by measuring the ^{31}P -NMR chemical shift ($\Delta\delta$, ppm) of triethylphosphine oxide ($\text{Et}_3\text{P}=\text{O}$, a strong Lewis base) in solvent A:



The ^{31}P -NMR chemical shift of $\text{Et}_3\text{P}=\text{O}$ is also measured in hexane ($\Delta\delta(\text{hexane})$) and in DCE containing SbCl_5 ($\Delta\delta(\text{SbCl}_5 \text{ in DCE})$). Here, by definition, $AN = 0$ for hexane and $AN = 100$ for SbCl_5 in DCE. Then, the AN of solvent A is obtained by Eq. (1.6).

$$AN = 100 \times \frac{\Delta\delta(\text{A}) - \Delta\delta(\text{hexane})}{\Delta\delta(\text{SbCl}_5 \text{ in DCE}) - \Delta\delta(\text{hexane})} = 2.348[\Delta\delta(\text{A}) - \Delta\delta(\text{hexane})] \quad (1.6)$$

The values of AN are also included in Table 1.5.⁸⁾ The solvent acidity increases with the increase in the AN value. Here, it should be noted that neither DN nor AN can be correlated with the relative permittivity of the corresponding solvents.

Lewis acids are electron pair acceptors and Lewis bases are electron pair donors. However, according to the hard and soft acids and bases (HSAB) concept [21], Lewis acids are classified into hard and soft acids, while Lewis bases are classified into hard and soft bases. Hard acids interact strongly with hard bases, soft acids with soft bases.

The HSAB concept also applies to solvent–solute interactions. Therefore, we have to know whether the solvent is hard or soft as a Lewis acid and a Lewis base. Water is a hard acid and a hard base. In general, hydrogen bond donor solvents are hard acids and solvate strongly to hard-base anions (i.e. small anions such as OH^- , F^- , Cl^- and anions with a negative charge localized on a small oxygen atom (CH_3O^- , CH_3COO^- , etc.)). On the other hand, for solvents having electron pair donor atoms such as O, N and S, the softness increases in the order $\text{O} < \text{N} < \text{S}$. Here, examples of solvents with an O atom are water, alcohols, ketones and amides, those with an N atom are nitriles, amines and pyridine and those with an S atom are thioethers and

8) Riddle and Fowkes [22] considered that the acceptor numbers determined by the NMR method are partly due to the van der Waals forces between $\text{Et}_3\text{P}=\text{O}$ and solvent molecules and attributed somewhat large AN values of strongly basic solvents such as pyridine to it. They proposed new acceptor numbers, cor-

rected for the influence of the van der Waals forces, as follows: hexane 0.0, Py 0.5, THF 1.9, DMA 5.7, DMF 6.6, Ac 8.7, DMSO 10.8, NM 14.8, AN 16.3, FA 32.2, MeOH 41.7, CH_3COOH 49.3, W 52.4, CF_3COOH 111.0 (compare with the AN values in Table 1.5).

Table 1.5 Chemical properties of organic solvents of electrochemical interest.

Solvent ^a	DN	AN	pK _{SH}	ε _r	Solvent	DN	AN	pK _{SH}	ε _r
(48) 1,2-Dichloroethane (DCE)	0	16.7	—	10.4	(6) Methanol (MeOH)	(19)	41.3	17.2	32.7
(42) Hexane	(0)	0.0	1.88	1.88	(3) Formic acid	(19)	83.6	6.2	58.5 ₁₆
(43) Benzene	0.1	8.2	2.27	2.27	(13) Tetrahydrofuran (THF)	20.0	8.0	—	7.6
(45) Nitromethane (NM)	2.7	20.5	—	36.7	(4) Acetic acid (HOAc)	(20)	52.9	14.45	6.2
(46) Nitrobenzene (NB)	4.4	14.8	—	34.8	(15) 1,2-Dimethoxyethane (DME)	23.9	10.2	—	7.2
(5) Acetic anhydride	10.5	—	14.5	20.7 ₁₉	(28) Formamide (FA)	(24)	39.8	16.8 ₂₀	111.0
(24) Benzotrile	12.0	—	—	25.2	(30) N,N-Dimethylformamide (DMF)	26.6	16.0	29.4	36.7
(20) Acetonitrile (AN)	14.1	18.9	33.3	35.9	(35) N-Methyl-2-pyrrolidone (NMP)	27.3	13.3	25.6	32.2
(39) Sulfolane (TMS)	14.8	—	25.5	43.3	(32) N,N-Dimethylacetamide (DMA)	27.8	13.6	23.9	37.8
(14) 1,4-Dioxane	14.8	10.8	—	2.21	(36) Tetramethylurea (TMU)	29.6	—	—	23.6
(50) Propylene carbonate (PC)	15.1	18.3	—	66.1	(38) Dimethyl sulfoxide (DMSO)	29.8	19.3	33.3	46.5
Diethyl carbonate (DEC)	16.0	—	—	2.8	(27) Pyridine (Py)	33.1	14.2	—	12.9
(51) Ethylene carbonate (EC)	16.4	—	—	89.6	(34) Hexamethylphosphoric triamide (HMPA)	38.8	10.6	20.6	29.6
(52) Methyl acetate (MA)	16.5	10.7	—	6.7	(7) Ethanol (EtOH)	(32?)	37.9	19.1	24.6
(23) Butyronitrile (BuN)	16.6	—	—	20.3	(8) 1-Propanol (1-PrOH)	37.3	19.4	—	20.5
(17) Acetone (Ac)	17.0	12.5	32.5	20.7	(9) 2-Propanol (2-PrOH)	(36?)	33.6	21.1	19.9
(53) Ethyl acetate	17.1	9.3	22.8	6.0	(29) N-Methylformamide (NMF)	(49?)	32.1	10.74	182.4
(49) γ-Butyrolactone (γ-BL)	(18)	17.3	—	39	Trifluoroacetic acid	105.3	—	—	8.55
(1) Water	18(G)–33(L) ^b	54.8	14.0	78.4					

Donor number (DN), acceptor number (AN) and autoprotolysis constants (pK_{SH}) (with relative permittivities (ε_r)).^aFor the numbers before the solvent names, see Table 1.1.^bG means gas and L means liquid.

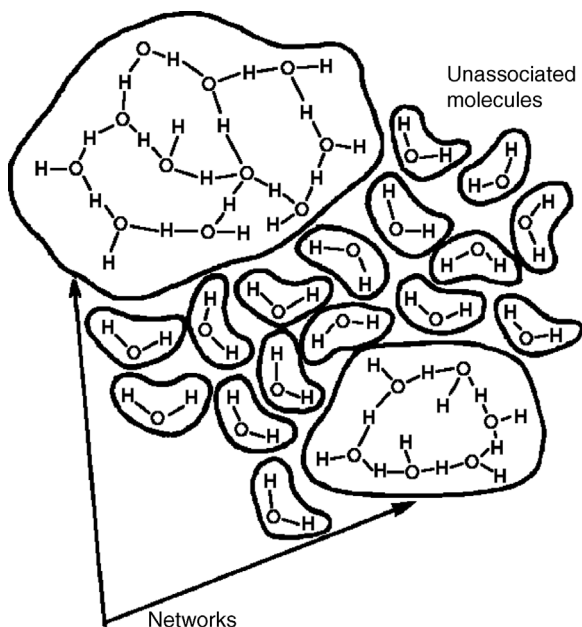


Figure 1.2 The three-dimensional structure of water. (Nemethy, G. and Scheraga, H.A. (1962) *J. Chem. Phys.*, **36**, 3382.)

thioamides. Hard-base solvents solvate strongly to hard-acid cations (Na^+ , K^+ , etc.), while soft-base solvents easily solvate to soft-base cations (Ag^+ , Cu^+ , etc.). Antimony pentachloride (SbCl_5), used in determining the donor number of solvents, is in between a hard acid and a soft acid. However, the donor number is considered to be the scale of solvents as hard bases. Recently, some scales have been proposed for the softness of solvents [23].⁹⁾

1.1.3

Structural Aspects of Solvents

The physical and chemical properties of solvents are closely related to their structures. Water molecules have strong hydrogen-bonding ability and considerable parts of them are combined with one another to form three-dimensional networks (Figure 1.2) [24]. A water molecule held in a network does not stay there long and is liberated as a free molecule; the lifetime of an individual hydrogen bond is of

9) For example, Marcus [23] proposed the μ scale for the softness of solvents. If the Gibbs energy of transfer of species i from water to solvent S is expressed by $\Delta G_i^\circ(i, W \rightarrow S)$ (in kJ mol^{-1}), μ is defined by $\mu = \{ (1/2)[\Delta G_i^\circ(\text{Na}^+, W \rightarrow S) + \Delta G_i^\circ(\text{K}^+, W \rightarrow S)] - \Delta G_i^\circ(\text{Ag}^+, W \rightarrow S) \} / 100$. This scale is based on the fact that the size of the soft acid, Ag^+ (0.115 nm in radius), is

between the sizes of the hard acids, Na^+ (0.102 nm) and K^+ (0.138 nm). Examples of the μ values are as follows [2]: AN 0.34; DMF 0.11, DMTF 1.35; DMSO 0.22; FA 0.09; NB 0.23; NM 0.03; NMP 0.13, NMTP 1.35; PC -0.09; Py 0.64. Here, DMTF and NMTP are soft bases, and Py and AN are between soft and hard.

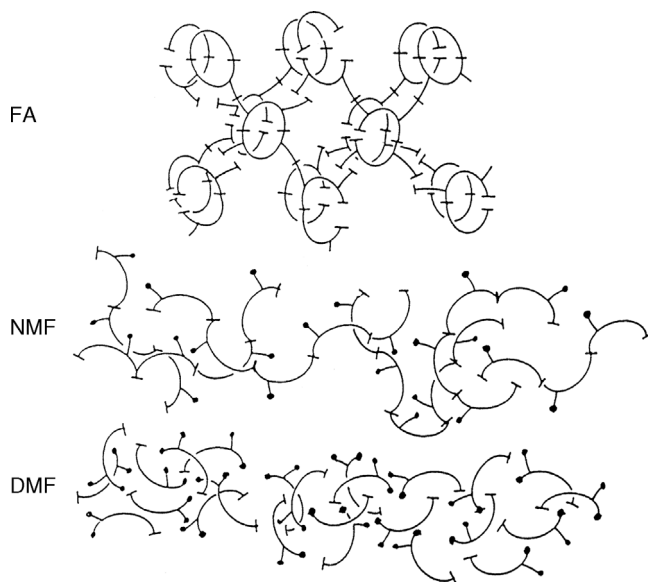


Figure 1.3 The liquid structures of FA, NMF and DMF [27a].

●— Methyl group; \curvearrowright H-bond ($-\text{NH}\cdots\text{O}=\text{CH}-$).

the order of 0.6 ps [25]. However, the network formation by hydrogen bonding is responsible for various anomalous physical properties of liquid water, including high boiling and melting points, high values of heat of vaporization, surface tension, compressibility and viscosity and peculiar density change with temperature [26]. Due to the network formation, molecules and ions, which are large in size, are often difficult to dissolve in water unless they have hydrophilic site(s).

Studies of solvent structure are usually carried out by analyzing radial distribution functions that are obtained by X-ray or neutron diffraction methods. Monte Carlo (MC) or molecular dynamics (MD) calculations are also used. Studies of the structure of nonaqueous and mixed solvents are not extensive yet, but some of the results have been reviewed. Pure and mixed solvents included in the reviews [27] are FA, NMF, DMF, DMSO, AN, 2,2,2-trifluoroethanol, EtOH, DMF/AN and 2,2,2-trifluoroethanol/DMSO. For example, Figure 1.3 schematically shows the liquid structures of FA, NMF and DMF. In FA, chain structure and ring-dimer structure are combined by hydrogen bonding to form three-dimensional networks, causing high melting and boiling points and high viscosity of FA.¹⁰⁾ In NMF, linear but short chain structures predominate, giving it a high permittivity. DMF is not hydrogen bonding and most DMF molecules exist as monomers. Thus, the melting and boiling points and the viscosity of DMF are lower than those of FA and NMF. For other solvents, see Ref. [27].

¹⁰⁾ The results of X-ray diffraction and molecular dynamics at high pressure and high temperature show that the pressure increase en-

hances ring dimer formation at the expense of linear chain structure, but the temperature increase gives an opposite effect [28].

1.1.4

Toxicity and Hazardous Properties of Solvents

There have been recent concerns that many solvents are toxic or hazardous to human health and/or the environment. The latest situation has been discussed in detail in Refs [29–31]. Especially, the *International Chemical Safety Cards (ICSCs)* [31], which is freely available on Web, provides very useful information on the safety and toxicity of many individual solvents.

Effects on human health usually occur by exposure to solvents or by the uptake of solvents through the lungs or skin. General effects that are caused by acute exposure to high solvent concentrations are dysfunctions of the central nervous system (CNS); symptoms such as dizziness, euphoria, confusion, nausea, headache, vomiting, paresthesia, increased salivation, tachycardia, convulsions, and coma can occur, depending on the situation. Besides these general effects, specific effects by particular solvents are also observed. Among these are nonimmunological hepatotoxicity (halogenated hydrocarbons, EtOH, DMF), nephrotoxicity (halogenated hydrocarbons, toluene, dioxane, ethylene glycol), reproductive toxicity (CS₂, benzene, nitrobenzene), hemopoietic toxicity (benzene metabolites), neurotoxicity (hexane, EtOH, styrene), ocular toxicity (MeOH) and immunological allergies to various solvents. More seriously, carcinogenic solvents are considered to induce malignant tumor; even among the solvents listed in Table 1.1; benzene (A1: confirmed human carcinogen) and dichloromethane, HMPA, NB, NM, 1-PrOH, Py and THF (A3: confirmed animal carcinogen with unknown relevance to humans) are suspected to have carcinogenic effect on humans. Threshold limit values (TLVs), listed in the last column of Table 1.1, are the values of time-weighted average (TWA, the definition of which is in the footnote of the table) taken from Ref. [31], in which other information on the safety and toxicity of solvents is also available. Because of the complicated nature of carcinogenesis, it is often difficult to define TLVs for carcinogens.

Many solvents in common use are volatile organic compounds (VOCs),¹¹⁾ and various environmental problems are caused by their evaporation. In the lower atmosphere, VOCs participate in photochemical reactions to form, to varying degrees, ground-level ozone and other oxidants that affect health, as well as cause damage to materials, crops and forests. Ozone impairs normal functioning of the lungs and reduces the ability to perform physical activity. Some solvents are listed as hazardous air pollutants (HAPs): they are toxic and/or carcinogenic and are associated with serious health effects such as cancer, liver or kidney damage, reproductive disorders and developmental or neurological problems. They also have detrimental environmental effects on wildlife and degrade water or habitat quality. The ‘T’ symbol in the last column of Table 1.1 shows that the solvent has been listed as an HAP. The solvents known as chlorofluorocarbons (CFCs) generally do not contribute to ground-level ozone formation but cause stratospheric ozone depletion.

11) A volatile organic compound is defined by the Environmental Protection Agency (EPA) as any compound of carbon, excluding carbon monoxide, carbon

dioxide, carbonic acid, metallic carbides or carbonates and ammonium carbonate, which is emitted or evaporated into the atmosphere.

In the stratosphere, these gradually release chlorine and other halogens into the atmosphere; these are effective in destroying the ozone layer that protects us from damage by ultraviolet light. The production and use of many CFCs have been banned and new chemicals are used instead. Recently, there has been serious contamination of water and soil with hazardous solvents, but this is not discussed here. In the laboratory, there are potential hazards of accidental spillage of organic solvent of low boiling point, which may be highly inflammable.

In recent years, many efforts have been made to avoid problematic effects of solvents, and many international and national regulations have been established (see Chapter 19 of Ref. [29]); toxic solvents are being replaced with nontoxic or less toxic ones and environmentally hazardous solvents with harmless ones. The use of 1,3-dimethyl-2-imidazolidinone, 1,3-dimethylpropyleneurea or 1,1,3,3-tetramethylurea instead of HMPA is one such example. The search for new, environmentally benign reaction media is the subject of current research. As such media, electrochemical and nonelectrochemical uses of supercritical fluids, room-temperature ionic liquids and fluorinated solvents are becoming frequent (see Chapter 13). In nonelectrochemical fields, many reactions that have been carried out in nonaqueous solvents are now performed in aqueous systems or nonsolvent systems.

1.2 Classification of Solvents

The classification of solvents has been dealt with in various books on nonaqueous solvents [32, 33]. In the classification of solvents, it is usual to use some solvent properties as criteria. In order to discuss solvent effects on chemical reactions, it is convenient to use relative permittivities and acid–base properties as criteria.

Type	1	2	3	4	5	6	7	8
Relative permittivity	+	+	+	+	–	–	–	–
Acidity	+	+	–	–	+	+	–	–
Basicity	+	–	+	–	+	–	+	–

In 1928, Brønsted [34] used these criteria and classified solvents into the above eight types. In the table, plus (+) means high or strong and minus (–) means low or weak. Various improved methods of classification have been proposed since; in this book, we follow the classification by Kolthoff [32] (Table 1.6).¹²⁾ According to his

12) In Ref. [33c], solvents are classified as follows: *protic solvents* (amphiprotic hydroxylic solvents such as water, methanol and glycols; amphiprotic protogenic solvents such as CH₃COOH and HF; protophilic H-bond donor solvents such as FA, NMF and NH₃); *dipolar aprotic solvents* (aprotic protophilic solvents such as DMF, DMSO and Py; aprotic protophobic

solvents such as AN, Ac, NM and PC; low-permittivity electron donor solvents such as diethyl ether, dioxane and THF); *low-polarity and inert solvents* (low-polarity solvents of high polarizability such as CH₂Cl₂, CHCl₃ and benzene; inert solvents such as *n*-hexane and cyclohexane).

Table 1.6 Classification of solvents (Kolthoff) [32].

	No.	ϵ_r, μ	Acidity ^b	Basicity ^b	Examples ^a
Amphiprotic solvents					
Neutral	1a	+	+	+	Water (78); MeOH (33); ethylene glycol (38)
	1b	–	+	+	<i>t</i> -BuOH (11)
Protogenic	2a	+	++	±	H ₂ SO ₄ ; HF; HCOOH (58)
	2b	–	++	±	CH ₃ COOH (6)
Protophilic	3a	+	±	++	NMF (182); DMSO (46) ^c ; tetramethylurea (24); FA (111); NH ₃ (23)
	3b	–	±	++	En (13); tetramethylguanidine (12)
Aprotic solvents					
Dipolar protophilic ^d	4a	+	– (±)	++ (+)	DMF (37); DMSO (46) ^c ; NMP (32); HMPA (30)
	4b	–	–	++ (+)	Py (13); THF (8); ether (4)
Dipolar protophobic ^d	5a	+	– (±)	–	AN (36); PC (65); NM (37); TMS (43); Ac (21)
	5b	–	–	–	MIBK (13); methylethylketone (17)
Inert	5c	–	–	–	Aliphatic hydrocarbons (~2); benzene (2); CCl ₄ (3); DCE (10)

^aThe symbol + is for $\epsilon_r \geq 15$ or $20, \mu \geq 2.5$ D and – is for $\epsilon_r < 15$ or $20, \mu < 2.5$ D. In parentheses in the column ‘Examples’ are shown approximate values of ϵ_r .

^bThe symbol + is for the case comparable to water, ++ for the case much stronger than water, ± for the case somewhat weaker than water and – for the case much weaker than water.

^cDMSO is an amphiprotic solvent because its autoprotolysis occurs slightly ($pK_{SH} \sim 33$) and the lyate ion (CH₃SOCH₂[–]) is somewhat stable. However, DMSO is classified as an aprotic solvent. The rough criteria for aprotic solvents are $pK_{SH} > 22$ and $AN < 20$.

^dSome solvents with $\epsilon_r < 15$ (or $\mu < 2.5$ D) are also classified as ‘dipolar’. For the reason, see text.

classification, solvents are roughly divided into two groups, *amphiprotic solvents* and *aprotic solvents*.¹³⁾

Amphiprotic solvents have both acidic and basic properties in terms of the Brønsted acid–base concept. If we denote an amphiprotic solvent by SH, it donates a proton by $SH \rightleftharpoons S^- + H^+$ and accepts a proton by $SH + H^+ \rightleftharpoons SH_2^+$. Overall, the autoprotolysis (autoionization) occurs by $2SH \rightleftharpoons SH_2^+ + S^-$. The extent of autoprotolysis is expressed by the autoprotolysis constant, $K_{SH} = a_{SH_2^+} \times a_{S^-}$, the values of which are also included in Table 1.5 as pK_{SH} values (for more details, see Table 6.6).

Using water as reference, an amphiprotic solvent with an acidity and a basicity comparable to those of water is called a *neutral solvent*, the one with a stronger acidity and a weaker basicity than water is called a *protogenic solvent* and the one with a weaker acidity and a stronger basicity than water is called a *protophilic solvent*. The solvent with relatively strong acidity usually has in its molecule a hydrogen atom that is joined to

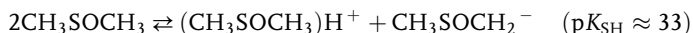
13) There is an opinion that the term ‘aprotic’ should be reserved for solvents with no hydrogen atom (e.g. SO₂ and BF₃). However, it is

more popular to use ‘aprotic’ for solvents that are very weak in proton-donating and hydrogen bond-donating abilities.

an electronegative atom such as oxygen (O), nitrogen (N) or halogen (X). Because of the electron pair donor capacity of the electronegative atom, a solvent with relatively strong acidity also has some basicity. Actually, there are no acidic solvents without some basicity.

Aprotic solvents, on the other hand, do not have a hydrogen atom joined to electronegative atom. Generally, the hydrogen atom(s) of an aprotic solvent is joined only to a carbon atom. Therefore, aprotic solvents have very weak proton-donating and hydrogen bond-donating abilities. Concerning the basicity, however, some aprotic solvents are stronger, although some are much weaker, than water. Aprotic solvents with strong basicity are said to be *protophilic*, while those with very weak basicity are said to be *protophobic*. The molecules of protophilic aprotic solvents have an oxygen atom or a nitrogen atom, on which negative charge is located. Among the aprotic solvents, those with relatively high permittivities ($\epsilon_r \geq 15$ or 20) or large dipole moments ($\mu \geq 2.5$ D) are often called *dipolar aprotic solvents*. As shown in Table 1.6, some aprotic solvents with $\epsilon_r < 15$ or $\mu < 2.5$ D (e.g. Py, THF, diethyl ether, MIBK) are classified as dipolar solvents. This is because, due to their acidic or basic properties, they behave like dipolar solvents. Solvents with low relative permittivities (or dipole moments) and very weak acidic and basic properties are called *inert solvents*.

The distinction between amphiprotic and aprotic solvents is not always clear. For instance, dimethyl sulfoxide (DMSO) is usually considered aprotic, but it undergoes an autoprotolysis as follows:



where $(\text{CH}_3\text{SOCH}_3)\text{H}^+$ is a lyonium ion and $\text{CH}_3\text{SOCH}_2^-$ is a lyate ion. Thus, DMSO may be considered to be an amphiprotic solvent.¹⁴⁾ It is usual, however, to include solvents with $\text{p}K_{\text{SH}} > 22$ as aprotic solvents. On the other hand, the values of acceptor number are often less than 10 for inert solvents, between 10 and 20 for dipolar aprotic solvents and 25 or more for neutral or protogenic amphiprotic solvents.

1.3

Effects of Solvent Properties on Chemical Reactions: An Outline

Chemical reactions in solutions are often affected drastically by the solvents used. The main objective of this book is to correlate the properties of solvents and the solvent effects on various chemical processes relevant to electrochemistry. The most important solvent properties in considering solvent effects are the solvent permittivity and the solvent acidity and basicity. If the permittivity of one solvent is high ($\epsilon_r > 30$) and that of the other is low ($\epsilon_r < 10$), the difference in a chemical process in the two solvents is usually attributable to the influence of permittivity. However, the

14) The lyate ion of DMSO ($\text{CH}_3\text{SOCH}_2^-$) is called *dimsyl ion*. Its alkali metal salts are fairly stable and have been used as titrant in DMSO [32a].

Table 1.7 Acid–base properties of solvents and the characteristics of reactions

Solvents with weak (strong) acidity	Solvents with weak (strong) basicity
(1) Solvation to small anions is difficult (easy) <ul style="list-style-type: none"> • Small anions are reactive (nonreactive) 	(1) Solvation to small cations is difficult (easy) <ul style="list-style-type: none"> • Small cations are reactive (nonreactive)
(2) Proton donation from solvent is difficult (easy) <ul style="list-style-type: none"> • pH region is wide (narrow) on the basic side • Strong bases are differentiated (leveled) • Very weak acids can (cannot) be titrated 	(2) Proton acceptance by solvent is difficult (easy) <ul style="list-style-type: none"> • pH region is wide (narrow) on the acidic side • Strong acids are differentiated (leveled) • Very weak bases can (cannot) be titrated
(3) Reduction of solvent is difficult (easy) <ul style="list-style-type: none"> • Potential region is wide (narrow) on negative side • Strong reducing agent is stable (unstable) in the solvent • Substances difficult to reduce can (cannot) be reduced 	(3) Oxidation of solvent is difficult (easy) <ul style="list-style-type: none"> • Potential region is wide (narrow) on positive side • Strong oxidizing agent is stable (unstable) in the solvent • Substances difficult to oxidize can (cannot) be oxidized

difference in a chemical process in two high-permittivity solvents (e.g. $\epsilon_r > 30$) is often attributable to the influence of the acidity or basicity of the two solvents rather than the influence of permittivity. General tendencies of the effects of solvent acid–base properties on chemical processes are summarized in Table 1.7. For example, the items on the left-hand column of the table should be read as follows:

1. A solvent with weak acidity is a weak hydrogen bond donor and solvates only very weakly to small anions (F^- , Cl^- , OH^- , CH_3COO^- , etc.). Thus, small anions are very reactive in it. In contrast, a solvent with strong acidity easily solvates to small anions by hydrogen bonding and weakens their reactivity.
2. In a solvent with weak acidity, the solvent molecule cannot easily release a proton. Thus, the pH region is wider on the basic side than in water; some strong bases, whose strengths are leveled in water, are differentiated; some very weak acids, which cannot be determined by neutralization titration in water, can be determined. In contrast, in a solvent with strong acidity, a proton is easily released from the solvent molecule. Thus, the pH region is narrow on the basic side; strong bases are easily leveled; neutralization titrations of very weak acids are impossible.
3. A solvent with weak acidity is a weak electron acceptor and is more difficult to reduce than water. Thus, in it, the potential window is wider on the negative side than in water; some strong reducing agents that are not stable in water can survive; some substances that are difficult to reduce in water can be reduced. In contrast, a solvent with strong acidity easily accepts electrons and is reduced. Thus, in it, the potential window is narrow on the negative side; strong reducing agents easily reduce the solvent; some substances, which can be reduced in water, cannot be reduced until the reduction of the solvent.

Water has high permittivity and moderate acidity and basicity. Thus, in water, many cations and anions are easily solvated (hydrated) and many electrolytes are highly soluble and dissociate into ions. Water has fairly wide pH and potential ranges and a convenient liquid temperature range. Of course, water is an excellent solvent. However, as in Table 1.7, the reaction environment can be expanded much wider than in water by using a solvent with weak acidity and/or basicity. This is the reason why dipolar aprotic solvents, which are either protophilic or protophobic, are used in a variety of ways in modern chemistry.

Although water is an excellent solvent and the most popular, it has somewhat anomalous properties that come from the hydrogen-bonding ability of water to form three-dimensional networks (Figure 1.2, Section 1.1.3). Large molecules and ions are often difficult to dissolve in water, unless they have hydrophilic site(s). Therefore, water is not suitable as a medium for reactions involving large hydrophobic molecules or ions. In contrast, most dipolar aprotic solvents are nonstructured or only weakly structured and can dissolve many large hydrophobic molecules and ions. This is another major reason why dipolar aprotic solvents are often used instead of water.

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