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Electrochemistry in Nonaqueous Solutions

Second, Revised and Enlarged Edition

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Contents

Preface to the First Edition

A majority of chemical reactions are carried out in solution. The use of a solvent as reaction medium makes it easy to control reaction conditions such as temperature, pressure, pH, rate of mass transfer and concentration of reactant. Water is the most popular solvent. However, by using appropriate nonaqueous solvents, substances that are insoluble in water can be dissolved, substances that are unstable in water remain stable and chemical reactions that are impossible in water become possible. The reaction environments are markedly wider in nonaqueous solvents than in water.

The widespread use of nonaqueous solvents, especially dipolar aprotic solvents, began in the 1950s in various fields of pure and applied chemistry and has contributed greatly to advances in chemical sciences and technologies. From the very beginning, electrochemistry in nonaqueous solutions has played an important role in exploring new chemical possibilities as well as in providing the methods to evaluate static solvent effects on various chemical processes. Moreover, many new electrochemical technologies have been developed using nonaqueous solvents. Recently, electrochemistry in nonaqueous solutions has made enormous progress: the dynamic solvent effects on electrochemical processes have been greatly elucidated and solvent effects are now understood much better than before. On the other hand, however, it is also true that some useful solvents have properties that are problematic to human health and the environment. Today, efforts are being made, under the framework of 'green chemistry', to find environmentally benign media for chemical processes, including harmless nonaqueous solvents, immobilized solvents, ionic liquids, supercritical fluids, aqueous systems and even solventless reaction systems. For electrochemical purposes, replacing hazardous solvents with harmless solvents, ionic liquids and supercritical fluids appears to be promising.

This book was written to provide readers with some knowledge of electrochemistry in nonaqueous solutions, from its fundamentals to the latest developments, including the current situation concerning hazardous solvents. The book is divided into two parts. Part I (Chapters 1–4) contains a discussion of solvent properties and then deals with solvent effects on chemical processes such as ion solvation, ion complexation, electrolyte dissociation, acid–base reactions and redox reactions. Such solvent effects are of fundamental importance in understanding chemistry in nonaqueous solutions; furthermore, their quantitative evaluations are often carried out by means of electrochemical techniques. Part II (Chapters 5–12) mainly deals with the use of electrochemical techniques in nonaqueous solutions. In Chapter 5, the fundamentals of various electrochemical techniques are outlined in preparation for the following chapters. In Chapters 6–9, the applications of potentiometry, conductimetry, polarography, voltammetry and other new electrochemical techniques in nonaqueous solutions are discussed by focusing on the chemical information they provide. Chapters 10 and 11 examine methods of selecting and purifying the solvents and electrolytes of electrochemical importance. Finally, in Chapter 12, some practical applications of nonaqueous solvents in modern electrochemical technologies are discussed. These include their use in batteries, capacitors and display devices, and such processes as electrolytic refining, plating, synthesis and polymerization. The applicability of ionic liquids and supercritical fluids as environmentally benign media for electrochemical technology is also dealt with.

Most chemists are familiar with chemistry in aqueous solutions. However, the common sense in aqueous solutions is not always valid in nonaqueous solutions. This is also true for electrochemical measurements. Thus, in this book, special emphasis is placed on showing which aspects of chemistry in nonaqueous solutions are different from chemistry in aqueous solutions. Emphasis is also placed on showing the differences between electrochemical measurements in nonaqueous systems and those in aqueous systems. The importance of electrochemistry in nonaqueous solutions is now widely recognized by nonelectrochemical scientists – for example, organic and inorganic chemists often use cyclic voltammetry in aprotic solvents to determine redox properties, electronic states and reactivities of electroactive species, including unstable intermediates. This book will therefore also be of use to such nonelectrochemical scientists.

I obtained most of the information included in this book from the publications of many scientists in this field. I would like to express my sincere thanks to all of them. I also would like to thank my coworkers for their cooperation, the editorial and production staff of Wiley-VCH for their help and support and my wife for her assistance and patience.

Matsumoto *Kosuke Izutsu*
December 2001

Preface to the Second Edition

The second edition consists of three parts: Part I (Chapters 1–4) is for electrochemical aspects of the fundamentals of chemistry in nonaqueous solutions, Part II (Chapters 5–12) deals with the electrochemical techniques and their applications in nonaqueous solutions and Part III (Chapters 13 and 14) is concerned with the electrochemistry in new solvent systems. Chapter 13 is on the electrochemistry in clean solvents and special emphasis is placed on supercritical fluids and (room-temperature) ionic liquids. Chapter 14 is on the electrochemistry at the liquid–liquid interfaces and, in addition to charge transfers at the interface between water and organic solvents, those at the interface between water and ionic liquid are also discussed. Since the publication of the first edition, considerable efforts have been made in pursuing green solvents that are benign to human health and the environment. Especially, the movement in the field of ionic liquids has been remarkable and the rapid progress is still continuing. Most of the ionic liquids are nonvolatile, nonflammable, less toxic, chemically and thermally stable and good solvents for both organic and inorganic materials. Due to their aprotic properties, many ionic liquids can replace aprotic organic solvents, particularly for use in electrochemistry. Moreover, the immiscibility of ionic liquids with water makes possible their applications to the water/ionic liquid interfaces in various ways, including electrochemical uses.

Besides the addition of the two new chapters, each of the Chapters 1–12 has been updated and revised. Especially, the revision in Chapter 12 is considerable because the use of nonaqueous solutions in modern electrochemical technologies is steadily increasing.

Although some nonaqueous solvents that are hazardous to human health and the environment cannot be used or should be used with great care, the needs for the electrochemical use of less hazardous solvents, including supercritical fluids and ionic liquids, are increasing. Thus, the knowledge of electrochemistry in nonaqueous solutions is also increasing its importance.

Finally, I wish to thank the editorial and production staff at Wiley-VCH Verlag GmbH, for their help and support in making this edition.

Musashino, Tokyo
August 2009

Kosuke Izutsu

Books, reviews and data compilations on nonaqueous solvents and the chemistry, especially electrochemistry, in nonaqueous solutions are shown below:

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42 Endres, F., Abbott, A.P. and MacFarlane, D.R. (eds) (2008) *Electrodeposition from Ionic Liquids*, Wiley-VCH Verlag GmbH, Weinheim.

Examples of books dealing with the fundamentals of electrochemistry:

1 Rossiter, B.W. and Hamilton, J.F. (eds) (1986) *Electrochemical Methods, Physical Methods of Chemistry*, vol. II, 2nd edn, John Wiley & Sons, Inc., New York.

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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*.

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[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]	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	$9\times10^{-9}{}_{18}$	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	$<5\times10^{-8}$	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) Benzonitrile	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}	$5\times10^{-11}{}_{-34}$	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	$<2\times10^{-7}$	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}	$2\times10^{-7}{}_{40}$	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-pyrrolidinone (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	$<6\times10^{-8}$	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}	$<2\times10^{-8}{}_{30}$	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}	$5\times10^{-8}{}_{40}$	89.8_{40}	4.9	
(52) Methyl acetate	MA	56.9	−98.0	216.2	0.9279	0.364	$3\times10^{-6}{}_{20}$	6.68	1.72	200
(53) Ethyl acetate		77.1	−83.6	94.5	0.8946	0.426	$<1\times10^{-9}$	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].

[a] Unless otherwise stated, the data are at 25°C. The temperatures other than 25°C are shown as subscript.

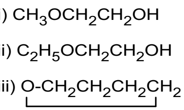
[b] The numerical value shows the TLV as time-weighted average (TWA), i.e. the maximum permissible vapor concentration that the average person can be exposed for 8 h per day, 5 days per week without harm, in ppm (cm^3 of solvent vapor per 1 m^3 of air) [29, 30a, 31]. The mark 'C' shows that the solvent 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’.

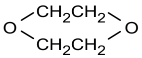
(i) $CH_3OCH_2CH_2OH$

(ii) $C_2H_5OCH_2CH_2OH$

(iii)



(iv)



(v) $CH_3OCH_2CH_2OCH_3$

(vi) $(CH_3OCH_2CH_2)_2O$

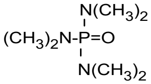
(vii) $HCONH(CH_3)$

(viii) $HCON(CH_3)_2$

(ix) $CH_3CONH(CH_3)$

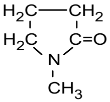
(x) $CH_3CON(CH_3)_2$

(xi)



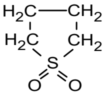
$$(CH_3)_2N\text{-}\underset{\displaystyle N(CH_3)_2}{\overset{\displaystyle N(CH_3)_2}{P}}{=}O$$

(xii)

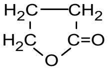


(xiii) $(CH_3)_2S{=}O$

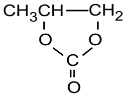
(xiv)



(xv)



(xvi)



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

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

Table 1.2 Physical and chemical properties of solvents.

Physical properties	*Bulk properties*: boiling point, melting (or freezing) point, molar mass, density, viscosity, vapor pressure, heat capacity, heat of vaporization, refractive index, relative permittivity, electric conductivity; *molecular properties*: 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]

[a] The 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):

$$F_{vac} = \frac{q_1 q_2}{4\pi\varepsilon_0 r^2} \tag{1.1}$$

where ε_0 is the permittivity of a vacuum and $\varepsilon_0 = 8.854 \times 10^{-12}\,\mathrm{F\,m^{-1}}$. 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:

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 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 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):

$$F_{\mathrm{solv}} = \frac{q_1 q_2}{4\pi\varepsilon_0\varepsilon_r r^2} = \frac{F_{\mathrm{vac}}}{\varepsilon_r} \tag{1.2}$$

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 ($\varepsilon_r \geq 15$ 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 ($\varepsilon_r \sim 2$), 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 $\varepsilon_{\mathrm{op}}$. 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 $\varepsilon_{\mathrm{op}}$ 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 $\tau_L = (\varepsilon_\infty/\varepsilon_s)\tau_D$ [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

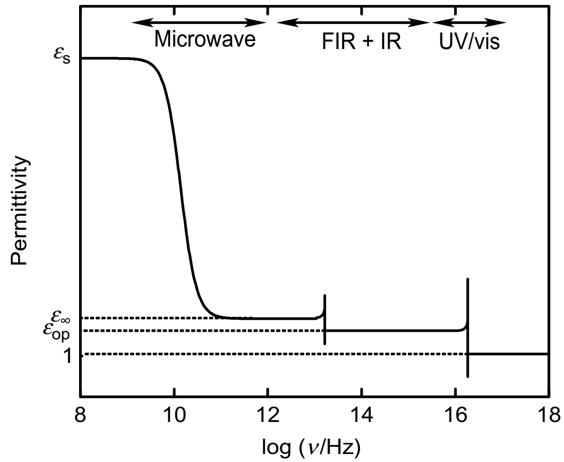

Figure 1.1 Dielectric dispersion spectra for a polar solvent with a single Debye relaxation process in the microwave region and two resonant transmissions in the IR and UV ranges [5b].

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	ε_s (= ε_r)	ε_{op}	ε_∞	$\varepsilon_{op}^{-1} - \varepsilon_s^{-1}$	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

[a] From 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; ($\varepsilon_{op}^{-1} - \varepsilon_s^{-1}$): 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

[a] From 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 poralizable 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

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

where k_B is the Boltzmann constant. By plotting the relation between $V_m(\varepsilon_r - 1)/(\varepsilon_r + 2)$ 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

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[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 $\varepsilon_{op} \sim n_D^2$.

[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.