Lecture notes in English for the

Chemistry of non-aqueous solutions, melts and extremely concentrated aqueous solutions

(code of the course KMN131E-1)

Pál Sipos

University of Szeged, Faculty of Science and Informatics

Institute of Chemistry

Department of Inorganic and Analytical Chemistry

Szeged, 2020.

MAGYARORSZÁG KORMÁNYA
Európai Unió
Európai Szociális Alap
BEFEKTETÉS A JÖVŐBE

Content

Course description – aims, outcomes and prior knowledge

Chemists usually prefer working in fluid systems, in particular with liquids, that is, with solutions. The rationale of this is rather simple: unlike in solid and gaseous systems, in the liquid state the reaction conditions (pressure, temperature or pH) are relatively readily controllable. In liquids, the rate of mass transfer is rapid (as opposed to, *e.g.*, in solids) and the concentration of the reactants can be much higher than, *e.g.*, in gases.

In the majority of the textbook cases presented during the university studies, the liquid medium can be characterized as follows:

1. the solvent is most often water (aqueous solutions)
2. to avoid theoretical complications, the concentration of the solutes is almost always low (that is, the solutions are dilute) and
3. in order to avoid practical (experimental) hardships, the temperature, pressure and pH are ambient (atmospheric pressure, around room temperature, and the pH is in the readily controllable 2-12 region).

During this course, we will look at systems for which at least one of these conditions is not fulfilled. Accordingly, the course will cover the general aspects of the chemistry of

1. non-aqueous solvents (organic and inorganic molecular liquids) [1]
2. molten salts (high temperature melts of inorganic salts) [2,3]
3. ionic liquids (room temperature melts of organic salts) [4]
4. supercritical fluids [1]
5. extremely concentrated aqueous electrolyte solutions [5]

The course is concerned with advanced level chemistry and as such, it is intended to be presented to Chemistry MSc students. Sound knowledge of advanced level organic, inorganic, physical and analytical chemistry is required, therefore the completion of the following courses is perquisite for enrolling to the present course:

1. Advanced Inorganic Chemistry, theory (KMN114E-1)
2. Advanced Organic Chemistry, theory (KMN204-E)
3. Advanced Organic Chemistry, practical (KMN204-G)
4. Advanced Physical Chemistry, theory (KBN037E)
5. Modern Techniques in the Instrumental Analysis, theory (KMN110E)
6. Modern Techniques in the Instrumental Analysis, practical (KMN110G)

Chapter 1 Chemistry of non-aqueous solutions

Water is an ideal solvent for several reactions because of its advantageous properties, just to mention a few: (i) it is cheap, readily available in large quantities and in high purity; (ii) at atmospheric pressure, it remains in the liquid state between 0 and 100 ^{o}C, that is, close to ambient conditions; (iii) it has reasonably low viscosity (agitation is easy); (iv) it has relatively low vapor pressure; (v) non-toxic (though *ca.* 6 liters of water is the usual lethal dose for an average adult human); (vi) good solvent for a large number of solutes, *etc*. For this reason, water is clearly the most popular solvent in the chemical laboratories, and in water an enormous number of chemical reactions can take place without major complications.

There are, however, cases, when water needs to be replaced with some other solvents, for the following reasons:

- It is often the case, that the solute is not sufficiently soluble in water (*e.g.*, several small molecular apolar organic compounds or polar macromolecules, like cellulose);
- It may cause difficulties, *e.g.*, in certain pharmaceutical applications, that a given solute is too weak base or too weak acid in water. For example, hardships experienced during the acid-base titration of alkaloids in water; in this case, most often glacial acetic acid has to be used instead of water, in which the alkaloids, that are too weak bases in water, become stronger bases and can be titrated with $HClO_4$;
- There are solutes which may enter into redox reaction with water, *e.g.*, Na metal readily reacts with water, and is oxidized to Na^+; however, metallic Na can be dissolved physically, without redox reaction in liquid ammonia (formation of solvated electron) or in Hg (formation of Na-amalgam);

- There are chemical reactions, which do not take place in water but do take place in other solvents. For example, silver-halides, like AgI, are precipitates (ionic compounds with low solubility, that is much less than, say, 1 millimol per liter) and do not dissolve in presence of excess halide. However, in solvents like acetone, DMSO or DMF, the formation of the $Ag_4I_6^{2-}$ complex was observed and the solubility of this compound was found to be in the order of *ca.* 1 mol L^{-1}.

On the basis of the chemical properties of the solvent, we can define molecular liquids (comprising of molecules), ionic liquids (comprising of ions; they may be molten salts and room temperature molten salts, see Chapters 2 and 3) and atomic liquids (for example, amalgams, where the solvent is liquid mercury.) The atomic liquids as solvents and amalgams are out of the scope of this course. Molecular liquids may be used as solvents in pure form, but quite often (for example, in several liquid chromatographic applications) solvent mixtures are employed, giving a further variable in the hand of the experimentalists. In this course, we will mainly deal with pure solvents, but in some cases, the properties of selected solvent mixtures will also be discussed. In Chapter 1, we will focus on molecular liquids.

It is important to note here, that several of the molecular liquids are volatile and/or are of high toxicity. In the literature, the acronym VOC stands for volatile organic compounds, and common compounds like benzene, CCl_4, $CHCl_3$, *etc.* belong to this group. Because of their volatility and toxicity (environmental unfriendliness), chemists permanently look for alternatives to be able to avoid using VOCs as solvents. Some examples:

- non-aqueous solvents with low toxicity – when the solvent is selected, it’s toxicity and environmental impact is considered in the first place;

- immobilized solvents – in this case the solvent is immobilized to a large inner surface solid support and has limited chance to “escape”;
- ionic liquids – their volatility (vapor pressure) is extremely small but there are concerns regarding their toxicity in some cases (Chapter 3);
- super critical CO_2 – this approach uses CO_2 at $T > 31.0\ ^{o}C$ and $p > 72.8$ atm, in which the compound is in the so-called super-critical state (Chapter 4);
- novel approaches with water – in this approach, the reactants are chemically altered in a way, that the target reaction can take place in water;
- reactions without solvent - here the reactants directly interact in absence of solvent, for example one of the reactant is the solvent, or both.

1.1 Physical properties of the molecular liquids

The most important physical properties of the molecular liquids are compiled in Table 1.1.

1. *Melting point, boiling point* – they determine the temperature range, where the solvent can be used; it is desirable, that this range includes the ambient conditions.

2. *Vapor pressure* – it is connected with toxicity, and flammable liquids with high vapor pressure are hazardous (explosive when mixed with air).

3. *Heat of evaporation* – $\Delta_v H$, from which the cohesive energy density can be calculated as $c = (\Delta_v H - RT)/V_m$. The quantity c determines the „stickiness" of the solvent, which is the energy required to create a „cavity" inside the solvent (here V_m is the molar volume). From the cohesive energy density, one may obtain the solubility parameter, $\delta = c^{1/2}$, which is suitable for the estimation of the solubility of non-electrolytes – two solvents are miscible, if their δ values are similar.

4. *Trouton's constant* – defined as $\Delta_v H(T_b)/T_b$ and is determined by the heat of evaporization and the boiling point. If it is < 11.6 kJ/mol, the solvent has not-ordered structure (*e.g.*, hexane: 10.2 kJ/mol, benzene: 10.5 kJ/mol, acetone: 10.9 kJ/mol, acetic acid: 7.2 kJ/mol). If it is > 12.0 kJ/mol, the solvent has ordered structure (*e.g.*, water: 13.1 kJ/mol, methanol: 12.5 kJ/mol).

5. *Viscosity, density* – these properties determine the mobility of the solute particles as well as the energy needed for the agitation of the reaction mixture – from chemical engineering point of view, both are very important.

6. *Heat capacity* – determines the energy needed to input for the heating of the reaction mixture,

Table 1.1 Physical properties of some organic and inorganic solvents; abbreviations used in this Table will be used throughout the text, on the basis of the data published in [1].

Solvent	**Abbr. symbol**	**Bp (°C)**	**Fp (°C)**	**Vapor pressure1) (mmHg)**	**Density1) (g/cm^{-3})**	**Viscosity1) (cP)**	**Conductivity1) (S cm^{-1})**	**Rel. permit-tivity1)**	**Dipole moment1) (D)**	**Toxicity2)**
1) Water		100	0	23,8	0,9970	0,890	6 x 10^{-8}	78,39	1,85	-
Acids										
2) Hydrogen fluoride		19,6	-83,3	-	0,9529	0,256	1 x 10^{-4}	84,0	1,82	-
3) Formic acid		100,6	8,27	43,1	1,2141	1,966	6 x 10^{-5}	58,5$_{16}$	1,82$_{30}$	5
4) Acetic acid	HOAc	117,9	16,7	15,6	1,0439	1,130	6 x 10^{-9}	6,19	1,68$_{30}$	10
5) Acetic anhydride		140,0	-73,1	5,1	1,0749	0,783$_{30}$	5 x 10^{-9}	20,7$_{19}$	2,82	5
Alcohols										
6) Methanol	MeOH	64,5	-97,7	127,0	0,7864	0,551	1,5 x 10^{-9}	32,7	2,87$_{20}$	200, T
7) Ethanol	EtOH	78,3	-114,5	59,0	0,7849	1,083	1,4 x 10^{-9}	24,6	1,66$_{20}$	1000
8) 1-Propanol	1-PrOH	97,2	-126,2	21,0	0,7996	1,943	9 x 10^{-9}	20,5	3,09$_{20}$	200
9) 2-Propanol	2-PrOH	82,2	-88,0	43,3	0,7813	2,044	6 x 10^{-8}	19,9	1,66$_{30}$	400
10) Methyl cellosolvei)		124,6	-85,1	9,7	0,9602	1,600	1,1 x 10^{-6}	16,9	2,04	25
11) Cellosolveii)		135,6	<-90,0	5,3	0,9252	1,850	9 x 10^{-8}	29,6$_{24}$	2,08	100
Ethers										
12) Tetrahydrofuraniii)	THF	66	-108,4	162	0,8892$_{20}$	0,460	-	7,58	1,75	200
13) 1,4-Dioxaneiv)		101,3	11,8	37,1	1,028	1,087$_{30}$	5 x 10^{-15}	2,21	0,45	25, T
14) Monoglyme v)	DME	84,5	-69,0	48$_{20}$	0,8637	0,4550	-	7,2	1,71	-
15) Diglymevi)		159,8	-64,0	3,4	0,9384	0,9890	-	-	1,97	-

Tab 1.1 (continued)

Solvent	Abbr. symbol	Bp (°C)	Fp (°C)	Vapor pressure1) (mmHg)	Density1) (g/cm^{-3})	Viscosity1) (cP)	Conductivity1) (S cm^{-1})	Relative permit-tivity1)	Dipole moment1) (D)	Toxicity2)
Ketones										
16) Acetone	Ac	56,1	-94,7	231,0	0,7844	0,303	5 x 10^{-9}	20,6	2,7	750
17) 4-Methyl-2-pentanone	MIBK	117,4	-84,0	18,8	0,7963	0,546	< 5 x 10^{-8}	$13{,}1_{20}$	-	-
18) Acetylacetone	Acac	138,3	-23,2	$8{,}6_{23}$	0,9721	0,694	1 x 10^{-8}	$25{,}7_{20}$	2,78	-
Nitriles										
19) Acetonitril	AN	81,6	-43,8	88,8	0,7765	$0{,}341_{30}$	6 x 10^{-10}	35,9	3,53	40, T
20) Propionitrile	PrN	97,4	-92,8	44,6	0,7768	$0{,}389_{30}$	8 x 10^{-8}	$28{,}9_{20}$	3,50	Very toxic
21) Butyronitrile	BuN	117,6	-111,9	19,1	0,7865	$0{,}515_{30}$	-	$24{,}8_{20}$	3,50	Very toxic
22) Isobutyronitrile		103,8	-71,5	-	0,7656	$0{,}456_{30}$	-	$20{,}4_{24}$	3,61	Very toxic
23) Benzonitrile	BN	191,1	-12,7	$1{,}0_{28,2}$	1,0006	1,237	5 x 10^{-8}	25,2	4,01	-
Amines										
24) Ammonia		-33,4	-77,7	-	$0{,}681_{-34}$	$0{,}25_{-34}$	5 x 10^{-11}	$23{,}0_{-34}$	0,93	-
25) Ethylenediamine	en	116,9	11,3	$13{,}1_{26,5}$	0,8931	1,54	9 x 10^{-8}	12,9	1,90	10
26) Pyridine	Py	115,3	-41,6	20,0	0,9782	0,884	4 x 10^{-8}	12,9	2,37	5
Amides										
27) Formamide	FA	210,5	2,5	$1{,}0_{70,0}$	1,1292	3,3	< 2 x 10^{-7}	$111{,}0_{20}$	3,37	20
28) N-Methylformamide vii)	NMF	180-185	-3,8	$0{,}4_{44}$	0,9988	1,65	8 x 10^{-7}	182,4	3,86	10
29) N,N-Di-Me-formamide viii)	DMF	153,0	-60,4	3,7	0,9439	0,802	6 x 10^{-8}	36,7	3,24	10, T
30) N-Me-acetamideix)	NMA	206,0	30,5	$1{,}5_{56}$	$0{,}9500_{30}$	$3{,}65_{30}$	2 x 10^{-7}	$191{,}3_{32}$	4,27	-
31) N,N- Di-Me-acetamidex)	DMA	166,1	-20,0	1,3	0,9363	0,927	1 x 10^{-7}	37,8	3,79	10

Tab 1.1 (continued)

Solvent	Abbr. symbol	Bp (°C)	Fp (°C)	Vapor pressure[1] (mmHg)	Density[1] (g/cm^{-3})	Viscosity[1] (cP)	Conductivity[1] (S cm^{-1})	Relative permit-tivity[1]	Dipole moment[1] (D)	Toxicity[2]
32) N-Methylpropionamide		$104,0_{16\ \mathrm{mm}}$	-30,9	$94,0_{10}$	0,9305	5,22	8×10^{-8}	176,0	-	-
33) Hexamethylphosphoric triamide[xi]	HMPA	233,0	7,2	$0,07_{30}$	1,020	3,10	2×10^{-7}	29,60	5,37	Toxic, T, C
34) N-Methyl-2-2-pyrrolidinone[xii]	NMP	202,0	24,4	0,3	1,026	1,67	1×10^{-8}	32,20	$4,09_{30}$	-
35) 1,1,3,3-Tetramethyl-urea	TMU	175,2	-1,2	-	0,9619	1,395	$< 6 \times 10^{-8}$	23,60	3,50	-
Sulfur compounds										
36) Sulfur dioxide		-10,0	-75,5	-	$1,46_{-10}$	$0,429_{0}$	-	$15,60_{0}$	1,62	-
37) Dimethyl solfoxide[xiii]	DMSO	189,0	18,5	0,6	1,095	1,99	2×10^{-9}	46,50	4,06	-
38) Sulfolane[xiv]	TMS	287,3	28,5	$5,0_{118}$	$1,260_{30}$	$10,3_{30}$	$< 2 \times 10^{-8}$	$43,30_{30}$	$4,70_{30}$	-
39) Dimethylthioformamide	DMTF	$70,0_{1\ \mathrm{mm}}$	-8,5	-	$1,024_{27}$	1,98	-	47,50	4,40	-
40)N-Methyl-2-thiopyrrolidinone	NMTP	$145,0_{15\ \mathrm{mm}}$	19,3	-	1,084	4,25	-	47,50	4,86	
Others										
41) Hexane		68,7	-95,3	$151,3_{27}$	0,6548	0,294	$< 1 \times 10^{-16}$	1,88	0,085	300, T
42) Benzene		80,1	5,5	95,2	0,8736	0,603	4×10^{-17}	2,27	0,00	1, T, C
43) Toluene		110,6	-95,0	28,6	0,8622	0,553	8×10^{-16}	2,38	0,31	100, T

Tab 1.1 (continued)

Solvent	Abbr. symbol	Bp (°C)	Fp (°C)	Vapor pressure$^{1)}$ (mmHg)	Density$^{1)}$ (g/cm^{-3})	Viscosity$^{1)}$ (cP)	Conductivity$^{1)}$ (S cm^{-1})	Relative permittivity$^{1)}$	Dipole moment$^{1)}$ (D)	Toxicity$^{2)}$
44) Nitromethane	NM	101,2	-28,6	36,7	1,1313	0,614	5×10^{-9}	36,7	3,17	100
45) Nitrobenzene	NB	210,8	5,8	0,28	1,1983	$1{,}62_{30}$	2×10^{-10}	34,8	4,00	1, T
46) Dichloromethane		39,6	-94,9	436,0	1,3168	$0{,}393_{30}$	4×10^{-11}	8,93	1,55	500
47) 1,2-Dichloromethane	DCE	83,5	-35,7	$83{,}4_{20}$	1,2464	$0{,}73_{30}$	4×10^{-11}	10,37	1,86	1, C
48) γ-Butyrolactone[xv)]	γ-BL	204,0	-43,4	3,2	1,1254	1,73	-	39,1	4,12	-
49) Propylene carbonate [xvi)]	PC	241,7	-54,5	$1{,}2_{55}$	1,1950	2,53	1×10^{-8}	64,92	4,94	-
50) Ethylene carbonate	EC	248,2	36,4	$3{,}4_{95}$	1,3383	$1{,}9_{40}$	$5 \times 10^{-8}{}_{40}$	$89{,}8_{40}$	4,90	-
51) Methyl acetate	MA	56,9	-98,0	216,2	0,9279	0,364	$3 \times 10^{-6}{}_{20}$	6,68	1,72	200
52) Ethyl acetate		77,1	-83,6	94,5	0,8946	0,426	$< 1 \times 10^{-9}$	6,02	1,82	400

The data in this table are from Riddick, J.A., Bunger, W.B., Sakano, T.K. (Eds) Organic Solvents, Physical Properties and Methods of Purifications, 4th edn, Wiley & Sons, NewYork, 1986 and others

1) Unless otherwise stated,the data are at 25 °C. The temperatures other than 25 °C are shown as subscript.

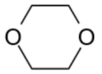
2) The numerical value shows the threshold limit value (TLV), which is defined as the maximum permissible vapor concentration that the average person can be exposed for 8 h per day, 5 days per week without harm, in ppm (cm^3 of solvent vapor per 1 m^3 of air). The mark 'T' shows the solvent has been listed in Title III of the Clean Air Act Amendments of 1990 as a hazardous air pollutant (HAP). 'C' shows that the solvent is or is suspected to be carcinogenic (Table 20.1.3 of Wypych, G. (Ed.) Handbook of Solvents, ChemTec Publishing, Toronto, 2001).

i) $CH_3OCH_2CH_2OH$

ii) $C_2H_5OCH_2CH_2OH$

iii) $O\text{-}CH_2CH_2CH_2CH_2$

iv)



v) $CH_3OCH_2CH_2OCH_3$

vi) $(CH_3OCH_2CH_2)_2O$

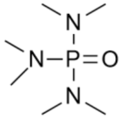
vii) $HCONH(CH_3)$

viii) $HCON(CH_3)_2$

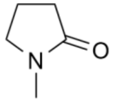
ix) $CH_3CONH(CH_3)$

x) $CH_3CON(CH_3)_2$

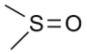
xi)



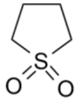
xii)



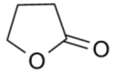
xiii)



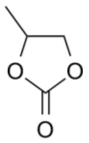
xiv)



xv)



xvi)



7. Surface tension – determines the possible foaming of the solution.

8. Electric conductivity – associated with the self-dissociation of the liquid as well as its purity.

9. Relative permittivity – if we take q_1 and q_2 electric charges, and the distance between them is r, and the attractive/repulsive force between them *in vacuo* F_{vac}, in a solvent F_{solv}, the force is defined by the Coulomb formula. ε_r is the ratio between F_{vac} and F_{solv} is defined as the relative permittivity of the solvent. For example, for water $\varepsilon_r = 78.36$ at room temperature. The presence of solvent always decreases the acting force (for example for n-hexane $\varepsilon_r = 1.88$, for n-pentane: $\varepsilon_r = 1.84$). ε_r is the measure of the polarity of the solvent, *i.e.*, for polar solvents $\varepsilon_r > 20$, for apolar solvents $\varepsilon_r < 15$. ε_r is very large for, *e.g.*, N-methylformamide, NMF (182) or for N-methylacetamid, NMA (191); this is because the solvent molecules are arranged to long chains through H-bonding interactions. The actual value of ε_r depends on the applied frequency of the applied electromagnetic field; up to *ca.* 10^9 s^{-1} (1 GHz) frequencies, the dipoles of the molecules are able to follow the fluctuations of the electric field (orientation polarization). The interaction between the permanent dipoles and the external electromagnetic field is described in terms of the so called Debye relaxation. According to this, in Debye solvents only one kind of Debye relaxation can be observed, which is the free rotation of the solvent molecules *(e.g.*, acetonitrile, DMSO, pyridine, THF). These Debye solvents comprise of isolated molecules the rotation of which is not affected by interactions with neighboring molecules. In the non-Debye solvents more than one relaxation processes can be observed. Non-Debye solvents are, *e.g.*, the water and the alcohols. In these solvents, the simultaneous free rotation as well as the hindered rotation(s) of the molecules (latters are bound in a H-bonding network) can be observed, which results in two- or more kinds of relaxation processes. For example, in water at room temperature, 90% of the molecules are bound in a H-bonded network and only 10% is free of H-bonding and freely rotating.

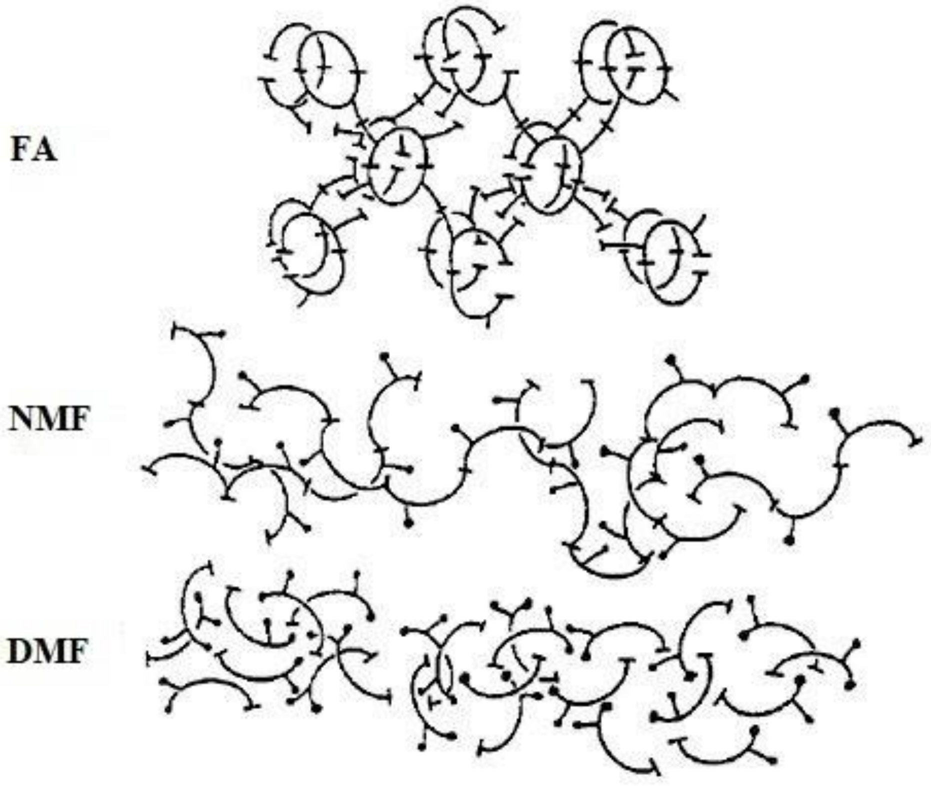


Figure 1.1 The schematic structure of FA, NMF and DMF, on the basis of the data published in [1].

Another example is the structure of formamide (FA), N-methyl-formamide (NMF) and N,N-dimethyl-formamide (DMF). FA forms chains and rings, while NMF forms short chains, both *via* H-bonds. H-bonds are not possible to be formed in DMF, therefore it consists of isolated molecules. Accordingly, FA and NMF are non-Debye solvents, while DMF is a typical Debye solvent.

10. Polarizability – it is the measure of induced polarization and is a molecular property, as opposed to relative permittivity, which is a bulk one. Induced polarization takes place when an external electromagnetic field of more than *ca.* 10^{11} s^{-1} (100 GHz) frequency is employed. If this is the case, only the electrons and the atoms within the molecule move, and the whole molecule is not able to follow the fluctuations of the electromagnetic field. The extent of the induced polarization is defined as polarizability, α, and deduced from the refractive index measured on the D-line of Na (n_D) as follows:

$$4\pi N_A \alpha = (3V_m / (n_D^2 + 2) \tag{1.1}$$

where V_m is the molar volume and N_A is the Avogadro constant. In a polarizable solvent, the solvent molecules interact strongly with each other and with polarizable solute particles through dispersion interactions.

11. Permanent dipole moment – from the relative permittivity of a solvent, ε_r, a further molecular property, the permanent dipole moment of a molecule, μ, can be derived. It can be extracted from the formula:

$$\frac{\varepsilon_r - 1}{\varepsilon_r + 2} = \frac{4\pi N_A}{3V_m}\left(\alpha + \frac{\mu^2}{3k_B T}\right) \tag{1.2}$$

where k_B is the Boltzmann constant and T is the absolute temperature. The unit of dipole moment is the Debye, 1 D = 3.33×10^{-30} C m. Solvents can be dipolar ($\mu > 2.5$ D) or apolar ($\mu < 1$ D). The dipole moment of water is $\mu = 1.85$ D. In general, the larger is ε_r, the larger is μ but this statement is valid only for large molecules.

1.2 Chemical properties of the molecular liquids – acceptor and donor numbers

One of the most important chemical properties of solvents are their basicity and acidity. The acidity of a solvent can be defined as the extent they are able to donate proton, create an H-bond and accept an electron pair. Conversely, the basicity of a solvent is the extent they are able to accept proton, accept an H-bond and donate an electron pair. The acidity of a solvent is characterized by its acceptor number, AN (not to be confused with the acronym used for acetonitrile). The larger is the acceptor number, the more acidic is the character of the solvent. The basicity of a solvent is characterized by its donor number, DN. The larger is the donor number (DN), the more basic is the character of the solvent.

The experimental determination of AN and DN is based on the following general principle. The solvent reacts with a reference donor (to obtain the solvent's AN) or acceptor (to extract the solvent's DN), and the effect that is somehow associated with the intensity of the interaction is experimentally determined.

1.2.1 DN scales

To demonstrate this principle, let us consider the solvation reaction of Ni(II) ion. In this example, it will be the reference acceptor and therefore will be used to determine the DN of a solvent. The solvates or solvate complexes formed are usually octahedral. In this complex, the d-orbitals of Ni^{2+} ion split to e_{g-} and t_{2g-} levels (crystal field splitting). The extent of this splitting (Dq, which can be measured *via* UV-Vis spectrophotometry) is the measure of the donor strength of the solvent, as we assume, that the difference between the energies of e_{g-} and t_{2g-} is proportional to the basicity of the solvent. This approach has some inherent problems: the structure of the solvates compared must be identical, which is not always the case. Moreover, if the solvent is of low basicity (small DN) and small ε_r, the coordination sphere is incomplete and/or the anion is coordinated instead of the solvent. As a result, the application of this method is limited.

A more generally accepted method is the Gutmann's donicity. It is based on the measurement of the heat of solvation. $SbCl_5$ is the reference acceptor, which is an exceptionally strong Lewis acid with only one free coordination site. When $SbCl_5$ reacts with the solvent donor molecule, $D:SbCl_5$ is formed; the larger is the heat of reaction, the stronger donor is D. Accordingly the enthalpy of this reaction, $-\Delta H(SbCl_5D)$ determined in ClH_2C-CH_2Cl at infinite dilution and is defined as the Gutmann's donicity. DN is always positive, as the formation of $SbCl_5D$ is exothermic. This is the most often used value to express basic character of a solvent.

1.2.2 AN scales

The simplest AN scale is based on the observation, that the color of various compounds in various solvents is different. This isthe so-called solvatochromic effect. In the so-called Kosower's Z-scale, the reference donor is 1-ethyl-4-carboxymethyl-pyridinium-iodide (Figure 1.2). The cation is not solvated at all, only the anion (donor) interacts with the solvent. Additionally, there is an ion-pairing reaction between the cation and the anion, the extent of which depends on the solvation of the anion. In ground state, the ion-pair consists of ions, in excited state it is more of non-ionic character, the charge transfer between the two states creates a charge transfer (CT) band. The blue shift CT band of the ion-pair (that is the shift of the absorption maximum towards the smaller λ-s or larger energies) is proportional to the solvation of the iodide ion by the solvent. The maximum λ of the CT band is by definition the Kosower Z-value.

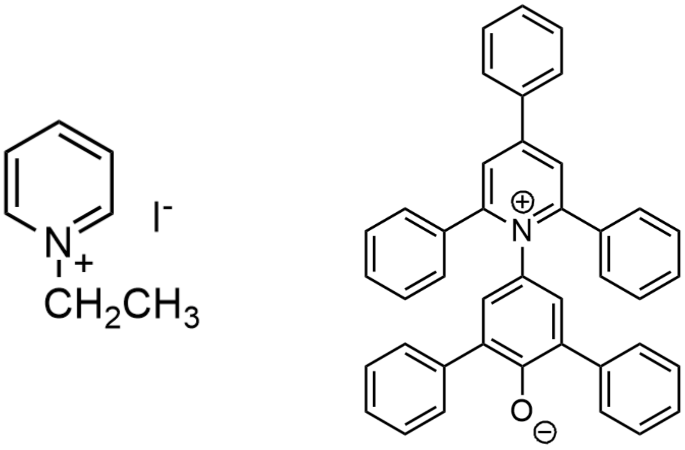


Figure 1.2 The structure of 1-ethyl-4-carboxymethyl-pyridinium-iodide (left) and pyridinium-N-phenol-betaine (right).

Experimentally more easy to determine the so called Dimroth-Reichardt’s acceptor scale in which the reference donor is pyridinium-N-phenol-betaine (Figure 1.2). The CT band of the pyridinium-N-phenol-betaine is found in the visible range of the spectrum, while that of the 1-ethyl-4-carboxymethyl-pyridinium-iodide is in the UV range. Therefore, it’s applicability is broader.

Indeed, the most generally used one is the Gutmann-Meyer-Gerger’s AN scale. They employ triethyl-phosphine-oxide (Et_3PO) as the reference donor. The ^{31}P NMR chemical shift of the P atom changes with the solvent. The stronger acceptor is the solvent, the smaller is the electron density on the phosphorous atom, and the larger is the chemical shift (δ) of the phosphorous atom in the Et_3PO on its ^{31}P-NMR spectrum. By definition AN = 0 in hexane because the Et_3PO is not solvated in this solvent. Arbitrarily, the AN of the adduct $Et_3PO:SbCl_5$ was defined as 100. The correlation between the Kosower, the Dimroth-Reichardt and the Gutmann-Meyer-Gerger AN scale is demonstrated in Table 1.2.

Table 1.2 Correlation between the Kosower (Z), the Dimroth-Reichardt (ET) and the Gutmann-Meyer-Gerger AN scale.

Solvent	**δ (^{31}P, ppm)**	**AN**	**E_T***	**Z***
Hexane	0	0	30,9	-
EtOEt	-1,64	3,9	34,6	-
Dioxane	-4,59	10,8	36,0	-
MeCOMe	-5,33	12,5	42,2	65,5
C_6H_6N	-6,04	14,2	40,2	64,0
DMF	-6,82	16,0	43,8	68,5
AN	-8,04	18,9	46,0	71,3
DMSO	-8,22	19,3	45,0	71,1
CH_2Cl_2	-8,67	20,4	46,1	64,7
$CHCl_3$	-9,83	23,1	39,1	63,2
EtOH	-15,8	37,1	51,9	79,6
H_2O	-23,35	54,8	63,1	94,6
CF_3COOH	-44,83	105,3	-	-

*in kcal/mol

The DN and AN values of the various solvents are very useful in the laboratory practice, giving rise to the so called two parameter characterization (AN and DN) of solvents. The underlying principle is that it is the chemist's (experimentalist's) primary interest to choose the solvent for a given chemical reaction appropriately. Choosing the best solvent means that this way we are able to influence or affect the properties of the solute in a chemical reaction and with the choice of the solvent, the reaction conditions can be tailored. The AN and DN values of some selected solvents are shown in Table 1.3.

Table 1.3 DN, AN and ε_r values and autoprotolysis constants (pK_{SH}) values of some selected solvents (G: gas; L: liquid); on the basis of the data published in [1].

Solvent $^{1)}$	**DN**	**AN**	**pK_{SH}**	**ε_r**	**Solvent**	**DN**	**AN**	**pK_{SH}**	**ε_r**
47) 1,2-Dichloroethane (DCE)	0	16,7		10,4	6) Methanol (MeOH)	(19)	41,3	17,2	32,7
41) Hexane	(0)	0		1,88	3) Formic acid	(19)	83,6	6,2	58,5$_{16}$
42) Benzene	0,1	8,2		2,27	12) Tetrahydrofuran (THF)	20,0	8,0		7,6
44) Nitromethane (NM)	2,7	20,5		36,7	4) Acetic acid (HOAc)	(20)	52,9	14,45	6,2
45) Nitrobenzene (NB)	4,4	14,8		34,8	14) 1,2-Dimethoxyethane (DME)	23,9	10,2		7,2
5) Acetic anhydride	10,5	-	14,5	20,7$_{19}$	27) Formamide (FA)	(24)	39,8	16,8$_{20}$	111,0
23) Benzonitrile (BN)	12,0	-		25,2	29) *N,N*-Dimethylformamide (DMF)	26,6	16,0	29,4	36,7
19) Acetonitrile (AN)	14,1	18,9	33,3	35,9	34) N-Methyl-2-pyrrolidinone (NMP)	27,3	13,3	25,6	32,2
38) Sulfolane (TMS)	14,8	-	25,5	43,3	31) N,N-Dimethylacetamide (DMA)	27,8	13,6	23,9	37,8
13) 1,4-Dioxane	14,8	10,8		2,21	35) Tetramethylurea (TMU)	29,6			23,6
49) Propylene carbonate (PC)	15,1	18,3		66,1	37) Dimethyl sulfoxide (DMSO)	29,8	19,3	33,3	46,5
Diethyl carbonate(DEC)	16,0	-		2,8	26) Pyridine (Py)	33,1	14,2		12,9
50) Ethylene carbonate (EC)	16,4	-		89,6	33) Hexamethylphosphoric triamide (HMPA)	38,8	10,6	20,6	29,6
51) Methyl acetate (MA)	16,5	10,7		6,7	7) Ethanol (EtOH)	(32?)	37,9	19,1	24,6
21) Butyronitrile(BuN)	16,6	-		20,3	8) 1-Propanol (1-PrOH)		37,3	19,4	20,5
16) Acetone (Ac)	17,0	12,5	32,5	20,7	9) 2-Propanol (2-PrOH)	(36?)	33,6	21,1	19,9
52) Ethyl acetate	17,1	9,3	22,8	6,0	28) N-Methylformamide (NMF)	(49?)	32,1	10,74	182,4
48) γ-Butyrolactone (γ-BL)	(18)	17,3		39	Trifluoracetic acid		105,3		8,55
1) (Water)	18(G)-33(L)$^{2)}$	54,8	14,0	78,4					

For example, if we want to increase the reactivity of the anion, it is advisable to use a solvent with large DN and small AN, which will strongly solvate the cation and will leave the anion intact (not solvated) and therefore more reactive. Another example is, that in case of ionic reactions, amphoteric solvents are to be used, in which the ionization and dissociation, that is the formation of ions is facilitated (see Chapter 1.4).

1.3 Classification of the solvents according to Kolthoff

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 the criteria. In this course, we will follow the classification of Kolthoff, who roughly divided the solvents into two groups, amphiprotic and aprotic solvents (Table 1.4). A further division is made on the basis of ε_r; those with $\varepsilon_r > 20$ (polar solvents) form the *a subgroup*, while those with $\varepsilon_r < 15$ (apolar solvents) form the *b subgroup.*

Table 1.4 Kolthoff's classification of solvents; on the basis of the data published in [1].

	No.	**ε_r, μ[1]**	**Acidity[2]**	**Basicity[2]**	**Examples[1]**
Amphiprotic solvents					
Neutral	1a	+	+	+	Water (78); MeOH (33); ethylene-glycol (38)
	1b	-	+	+	t-BuOH (11)
Protogenic	2a	+	++	±	H2SO4; HF; HCOOH (58)
	2b	-	++	++	CH3COOH (6)
Protophilic	3a	+	±	++	NMF (182); DMSO (46)[4]; tetramethyl urea (24); FA (111); NH_3 (23)
	3b	-	**- (±)**	++	en (13); tetramethylguanidine (12)
Aprotic solvents					
Dipolar protophilic [3]	4a	+	**-(±)**	**++ (+)**	DMF (37); DMSO (46)[4]; NMP (32); HMPA (30)
	4b	-	-	**++ (+)**	Py (13); THF (8); diethylether (4)
Dipolar protophilic [3]	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)

1) The symbol + is for $\varepsilon_r \geq 15$ or 20, $\mu \geq 2{,}5$ D and – is for $\varepsilon_r < 15$ or 20, $\mu < 2{,}5$ D. In parentheses on column 'Examples' are shown approximate values of ε_r.

2) The symbol + is for the case comparable with water, ++ for the case much stronger thanwater, ± for the case somewhat weaker than water, and – for the case much weaker than water.

3) Some solvents $\varepsilon_r < 15$ (or $\mu < 2{,}5$ D) are also classified as 'dipolar'. Fort he reason, see text.

4) DMSO is an amphiprotic solvent because its autoprotolysis occurs slightly (pK_{SH}~33) and the lyate ion ($CH_3SOCH_2^-$) is somewhat stable. However, DMSO is classified as an aprotic solvent. The rough criteria for aprotic solvents are $pK_{SH} > 22$ and AN<20.

Amphiprotic solvents

Amphiprotic solvents have both acidic and basic properties in terms of the Brönsted acid-base concept. These solvents are able to release or to accept proton, therefore at least one proton in them is attached to an atom with large electronegativity. As a result, this proton is mibile (dissociable). If we denote an amphiprotic solvent by SH, it donates proton to form S^- and it accepts proton to form SH_2^+. Overall, the following autoprotolysis reaction ($2\ SH \leftrightarrow S^- + SH_2^+$) takes place. The degree of autoprotolysis is expressed in terms of the autoprotolysis constant, $K_{SH} = [S^-][SH_2^+]$ (or alternatively, the product of the activities of S^- and SH_2^+). The pK_{SH} values of some solvents are also included in Table 1.3.

In the Kolthoff classification, water may be used as the reference solvent. An *amphiprotic* solvent having an acidity (AN) and basicity (DN) comparable to those of water is called *neutral* solvent (Group 1, for example, MeOH or t-BuOH). A solvent with stronger acidity (larger AN) and weaker basicity (smaller DN) than water is called *protogenic solvent* (Group 2, for example, HCOOH or MeCOOH). A solvent with weaker acidity (smaller AN) and stronger basicity (larger DN) than water is called *protophilic solvent* (Group 3, for example, NMF or NH_3).

Aprotic solvents

Aprotic solvents do not have hydrogen atom joined to an atom with large electronegativity. (Most often, the H-atom is attached to a carbon atom in these compounds.) Accordingly, these solvents have very weak proton donating and H-bond forming ability, their AN is therefore (usually) much smaller, than that of water. Regarding basicity, the situation is much more diverse: some aprotic solvents have larger DN, than water, others have smaller DN, than water. Aprotic solvents with strong basicity are said to be *protophilic* (Group 4, for example DMF, DMSO, Py, THF); the molecules of aprotic protophilic solvents have an O or an N atom, on which partial negative charge is located. Aprotic solvents with very weak basicity are called *protophobic* (Group 5, for example, acetonitrile, Ac, MIBK).

Among the aprotic solvents, those having high permittivities ($\varepsilon_r > 20$) or large dipole moment ($\mu > 2.5$ D) are called *dipolar aprotic solvents.* Some aprotic solvents with smaller permittivities ($\varepsilon_r < 15$) or smaller dipole moment ($\mu < 2.5$ D) are also classified as dipolar aprotic solvents (like Py, THF, MIBK, diethyl ether), this is because, due to their acidic or basic properties, they behave as dipolar solvents.

In Group 5c in the Kolthoff classification, solvents with very low relative permittivities and very weak acidity and basicity are placed. They are called *inert solvents (*for example, benzene, CCl_4, aliphatic hydrocarbons.)

Some additions to the Kolthoff classification.

1. The border between amphiprotic and aprotic solvents is not always clear. For example, DMSO is often considered as aprotic, protophilic solvent, but has a $pK_{SH} \approx 33$. This means, that the extent of autoprotolysis is very small. The practice is, that solvents with $pK_{SH} > 22$ are considered aprotic solvents.
2. Taking the AN values as basis, for inert solvents (Group 5c) AN < 10, for dipolar aprotic (Groups 4 and 5) solvents, 10 < AN < 20. and for neutral and protogenic amphiprotic solvents (Groups 1 and 2) AN > 25 can be accepted.

1.4 The effect of solvent properties on chemical reactions

Solvents play a decisive role in the chemical reactions taking place in them. In this context, solvent permittivity and solvent acidity/basicity are the most important parameters. General tendencies of the solvent acid-base properties on chemical processes are presented in Table 1.5. Water has high permittivity and moderate acidity and basicity and both cations and anions are easily solvated, electrolytes are highly soluble and dissociate to ions. With using solvents with acidity or basicity lower than that of water, the reaction environment can be expanded; this is one of the major reasons, why dipolar aprotic solvents, both protophilic and protophobic are preferred in several chemical reactions. On the other end, large molecules are not soluble in water, unless they have hydrophilic moieties; for reacting large hydrophobic molecules or ions, water is not suitable solvent. In contrast, most dipolar aprotic solvents are non-structured and can dissolve many large molecules and ions; this is why they are often used instead of water.

Table 1.5 Acid-base properties of solvents and the characteristics of reactions; on the basis of the data published in [1].

Solvents with weak (strong) acidity	**Solvents with weak (strong) basicity**
1) Solvation to small anions is difficult (easy) • Small anions are reactive (not reactive)	1) Solvation to small cations is difficult (easy) • Small cations are reactive (notreactive)
2) Proton donation from solvent is difficult (easy) • pH regionis wide (narrow) ont he basic side • Strong bases are differentiated (leveled) • Very weak acids can (cannot) be titrated	2) Proton acceptance by solvent is difficult (easy) • pH region is wide (narrow) ont he acidic side • Strong acids are differentiated (leveled) • Very weak bases can (cannot) be titrated
3) Reduction of solvent is difficult (easy) • Potential region is wide (narrow) on negative side • Strong reducing agent is stable (unstable) in the solvent • Substances difficult to reduce can (cannot) be be reduced	3) Oxidation of solvent is difficult (easy) • Potential region is wide (narrow) on positive • Strong oxidizing agent is stable (unstable) int he solvent • Substances difficult to oxidize can (cannot) be oxidized

1.5 Solvation and complexation of ions and electrolytes in non-aqueous solvents

1.5.1 The heat of dissolution

The solvation is by definition the interaction between the solute particles (ions, molecules) and the solvent. The result of the solvation is the solvated ion (or solvate complex). When the solvent is water, the special case of hydration takes place. Hydration results in the formation of hydrated ions or aqua-complexes. Solvation exert an effect on the extent of dissolution (solubility) as well as the reactions taking place in solution. These effects can be computed on the basis of the solvation energy which is the standard chemical potential of the solute in solution relative to its gaseous state.

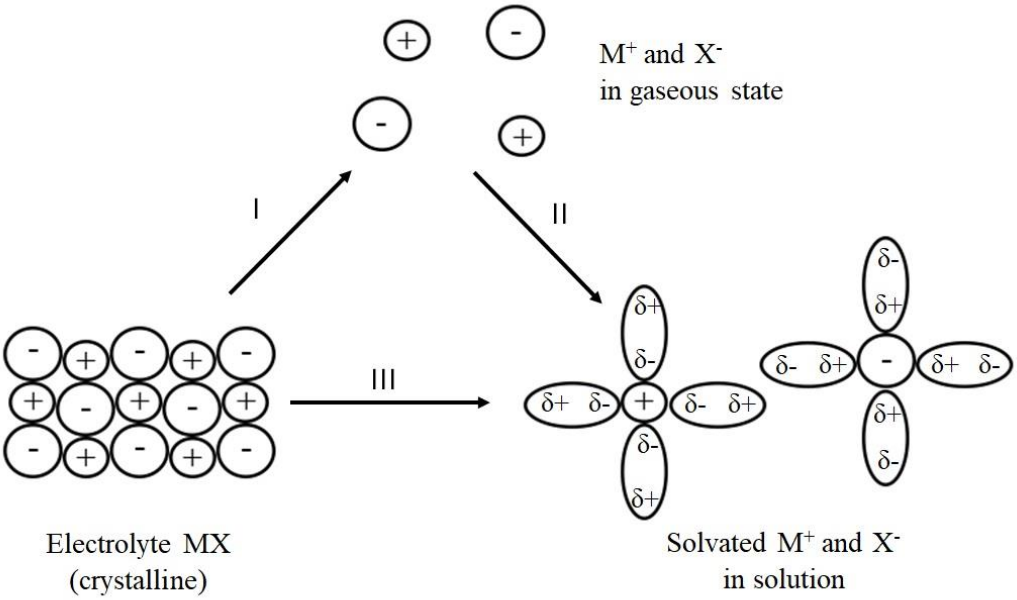


Figure 1.3 Dissolution process of an MX crystalline product on a solvent.

From Figure 1.3, it can be readily shown that the Gibbs energy of dissolution, ΔG_S^0, is the difference between the Gibbs energy of solvation ΔG_{SV}^0, and the lattice energy, ΔG_{lat}^0. The Gibbs energy of dissolution, ΔG_S^0, is directly related to the solubility product of MX:

$$\Delta G_s^o = -RT \ln K_{sp} (\mathrm{MX}) \tag{1.3}$$

Table 1.6 Thermodynamic parameters for the dissolution of lithium and sodium halides (25 ^{o}C kJ mol^{-1}) ΔH_{lat}^0 , ΔS_{lat}^0 and ΔG_{lat}^0 lattice enthalpy, entropy, and Gibbs energy of the crystalline electrolyte; ΔH_{SV}^0 , ΔS_{SV}^0 and ΔG_{SV}^0 enthalpy, entropy, and Gibbs energy of solvation of the electrolyte; ΔG_s^0 Gibbs energy of solution of the crystalline electrolyte; on the basis of the data published in [1].

Elect-rolyte	ΔH°_{lat}	$-T\Delta S^\circ_{lat}$	ΔG°_{lat}	**Water**				**Propylene carbonate (PC)**			
				ΔH°_{sv}	$-T\Delta S^\circ_{sv}$	ΔG°_{sv}	ΔG°_s	ΔH°_{sv}	$-T\Delta S^\circ_{sv}$	ΔG°_{sv}	ΔG°_s
LiF	-1040	78	-962	-1036	88	-948	14,2	-	-	-	96,2
LiCl	-861	73	-788	-899	70	-829	-40,6	-869	102	-767	22,1
LiBr	-819	72	-747	-869	66	-803	-55,6	-848	99	-749	-5,4
LiI	-762	69	-693	-825	57	-768	-75,3	-825	101	-724	-31,4
NaF	-923	78	-845	-923	82	-841	4,2	-	-	-	76,1
NaCl	-787	73	-714	-783	60	-723	-8,8	-761	83	-678	43,9
NaBr	-752	72	-680	-753	56	-697	-16,3	-741	89	-652	28,5
NaI	-702	70	-632	-710	49	-661	-28,9	-723	95	-628	4,2

If ΔG_s^0 is negative, the solubility (that is, the concentration of the solution saturated with respect to MX, $s = K_{sp}^{1/2}$) exceeds 1 M, and the given solute is well soluble in the given solvent. However, if ΔG_s^0 is positive, the solute is sparingly or not soluble in the given solvent (*e.g.*, if ΔG_s^0 = 22.8 kJ/mol, the solubility is s = 10^{-2} M).

Both the Gibbs energy of solvation ΔG_{SV}^0, and the lattice energy, $\Delta G_{lat}^0$are large negative values (Table 1.6). The difference between them (ΔG_s^0) is relatively small, and a few percents of difference between ΔG_{SV}^0, and the lattice energy, $\Delta G_{lat}^0$are may cause large changes in the solubility of the solute (compare, *e.g.*, ΔG_s^0 values of some alkali halogenides in water and in propylene-carbonate in Table 1.6.)

1.5.2 Solvation of ions, ion-solvent interactions

The solvation energy is determined by and is the sum of the contributions various types of ion-solvent interactions. The relative (approximate) fractions of the various types of interactions can be given as follows:

1.	Electrostatic interaction	≥ 80%
2.	Electron pair donor-acceptor interactions	≤ 10%
3.	Anions' interactions with H-bridge donor solvents	≤ 10%
4.	Interactions based on the HSAB theory	≤ 20%
5.	d^{10} cations' back-coordination to the solvent	≤ 10%
6.	Structure making/structure breaking	≤ 10%

The largest and most important part of the solvation energy is associated with the *electrostatic interaction* between the ion and the solvent. The electrostatic part of the free energy of solvation, ΔG_{el} can be defined as the difference of the electrostatic free energy of the ion in vacuum and in a given solvent with the permittivity of ε_r. This is described by the Born or Born-Landé equation:

$$\Delta G_{\mathrm{el}} = -\frac{N_{\mathrm{A}} z^2 e^2}{4\pi\varepsilon_0 \cdot 2r}\left(1 - \frac{1}{\varepsilon_{\mathrm{r}}}\right) = -\frac{69.4\, z^2}{r}\left(1 - \frac{1}{\varepsilon_{\mathrm{r}}}\right) \qquad (1.4)$$

where z is the charge, r the radius of the ion, ε_r is the permittivity of the solvent. ΔG_{el} rises rapidly at small ε_r (*i.e.*, in apolar solvents) with the increasing ε_r. From $\varepsilon_r > 20$, it is practically constant, which is not congruent with experimental observations; accordingly, the Born (or Born-Landé) equation is only a rough estimation.

The mean spherical approximation (MSA) is a modified form of the Born equation; assuming that ΔG_{el} is approximately equal to ΔG_{SV}^0,

$$\Delta G_{\mathrm{sv}}^{\mathrm{o}} = \frac{-N_{\mathrm{A}} z^2 e^2}{4\pi\varepsilon_0 \cdot 2(r+\delta_{\mathrm{s}})}\left(1-\frac{1}{\varepsilon_{\mathrm{r}}}\right) \tag{1.5}$$

in which the δ_s parameter takes the polarizability and the size of the solvent into consideration. In Table 1.7 the experimentally observed ΔG_{SV}^0 values of alkaline metal and halide ions are shown in water, together with the calculated ΔG_{SV}^0 values from the Born equation and from the MSA approach. It seems clear, that the MSA approach gives calculated values that are much closer to the observed ones. The Born equation always overestimates the ΔG_{SV}^0 values, while the MSA approach gives better values for large ions than for small ones.

Table 1.7 ΔG_{SV}^0 values of alkaline metal and halide ions; experimental values as well as calculated values from the Born equation and from the MSA approach are shown. r is the radius of the neat ion; on the basis of the data published in [1].

Ion	**Li^+**	**Na^+**	**K^+**	**Rb^+**	**Cs^+**	**F^-**	**Cl^-**	**Br^-**	**I^-**
r (pm)	88	116	152	163	184	119	167	182	206
Experimental	-529	-424	-352	-329	-306	-429	-304	-278	-243
Born	-779	-591	-451	-421	-373	-576	-410	-377	-333
MSA	-483	-403	-333	-316	-288	-396	-310	-291	-264

Electron pair donor-acceptor interactions contribute up to *ca.* 10% of the total solvation energy. As a general rule, cations are better solvated by solvents with high DN, while anions are better solvated by solvents with high AN. Accordingly, the solvation energy of cations increases with the increasing DN, while that of the anions increases with the increasing AN.

This correlation is clear for aprotic solvents (see Figure 1.4), but for protic solvents, deviations are seen due to H-bond formation.

Interactions of anions with H-bond forming solvents may be responsible for up to 10% of the solvation energy. Small anions (*e.g.*, F^-, Cl^-, OH^-) or anions with negatively charged O-atom (CH_3COO^-, $C_6H_5O^-$, *etc.*) are strongly solvated with solvents that form H-bonds. This is not the case for aprotic solvents, like *e.g.*, acetonitrile: in such solvents these anions are weakly solvated, therefore their reactivity is increased.

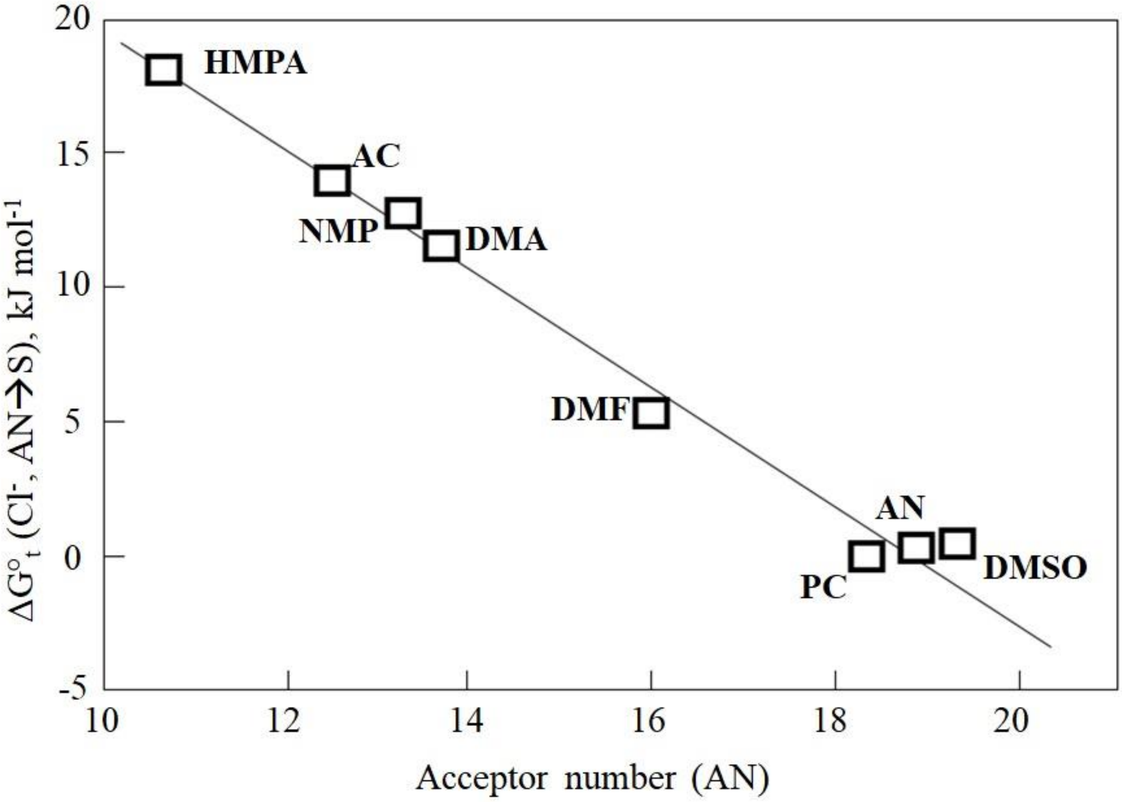


Figure 1.4 The standard Gibbs energy of transfer of the Cl^- from acetonitrile (AN) to the solvent S as a function of the acceptor number of S; on the basis of the data published in [1].

Conversely, large anions (I^-, ClO_4^-) are unable to form strong H-bond. However, if the solvent is aprotic and polarizable (DMSO, DMF, acetonitrile) it will strongly solvate them.

Interactions of the HSAB type can be as high as 20% of the total solvation energy. HSAB theory comes as the acronym for Hard and Soft Acids and Bases, and it is closely connected to the Lewis acidity and basicity concept. According to this theory, *hard* acids interact strongly with *hard* bases, *soft* acids with *soft* bases. The water is *hard* for acid and also *hard* for base; it strongly solvates the *hard* anion bases ($OH^–$, $F^–$) or the anions containing oxygen with localized charge, *i.e.*, $–O^–$ ($CH_3O^–$, $CH_3COO^–$) as well as the *hard* acid cations (Na^+, K^+). In O, N and S-containing solvents the *soft* character increases in the order of $O < N < S$. *Soft* base solvents (*e.g.*, thioethers, thioamides) solvate *soft* acids (Ag^+, Cu^+) very strongly. *Hard* solvents interact more intensely with *hard* ions, while *soft* solvents prefer *soft* ions, this is why the reduction of Ag^+ on a Hg electrode in DMF (which is a *hard* solvent) and in DMTF (dimethyl-thioformamid which is a *soft* solvent) is very much different in terms of reduction potential ($E_{1/2}$): in the *soft* solvent, the $E_{1/2}$ of the silver ion is shifted towards the more negative values in DMTF relative to DMF.

Back coordination of d^{10} *metal ions* is also an important parameter that needs to be taken into consideration upon solvation. For example, acetonitrile has small DN (14), therefore it is bound weakly to most of the metal ions. However, it solvates very strongly the Cu^+, Ag^+ and Au^+ ions. During back donation, the metal ion donates electron to the non-bonding π^* orbital of the ligand and solvates it very strongly. This is why, *e.g.*, Cu^{2+} becomes a very strong oxidant in acetonitrile: the concentration of free (unsolvated) Cu^+ becomes small, which increases the $[Cu^{2+}]/[Cu^+]$ ratio and therefore the redox potential of the Cu^{2+}/Cu^+ couple.

Finally, the *structure making* and *structure breaking* ability of a solute needs to be considered too. The underlying chemical reason of this is that the solute is capable of changing the structure of the solvent in two ways: either increasing or decreasing the ordering in the solvent. Ions which increase ordering are called structure making ions, *e.g.*, Na^+, Ca^{2+}, Zn^2, *etc.* are structure making in water. Ions that decrease the ordering, like Mg^{2+}, K^+, ClO_4^- in water, are called structure breaking solutes.

1.5.3 The structure of the solvated ions

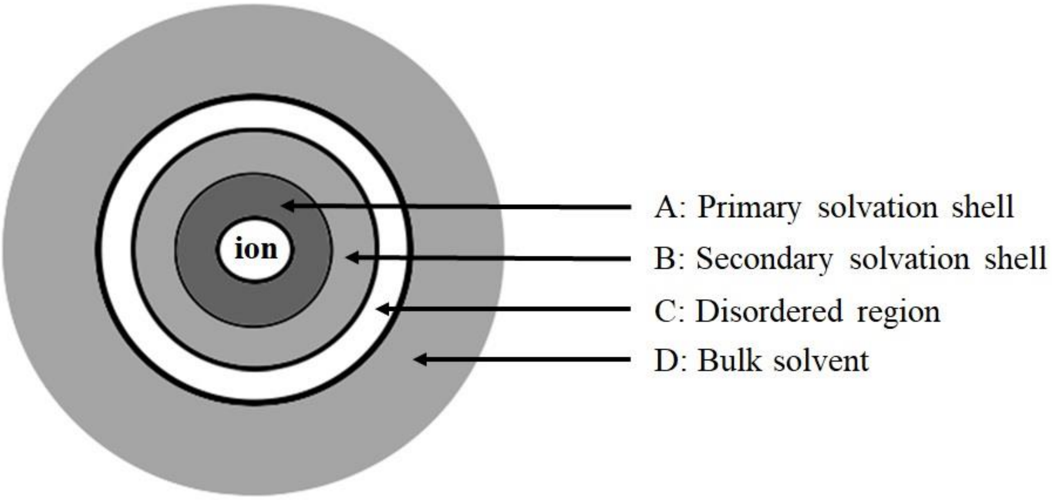


Figure 1.5 The schematic structure of a solvated ion; on the basis of the data published in [1].

The solvent molecules around the solvated ions can be classified as follows (schematically it is represented in Figure 1.5). In the *primary solvation shell* (A in Figure 1.5) there is a direct interaction between the solvent molecule and the ion, and the solvent molecules are oriented around the ion. In the *secondary solvation shell* (B in Figure 1.5) the solvent molecules are in a partially oriented structure: they are still under the influence of the ion but there is no direct interaction between them. In the so-called *disordered region* (C in Figure 1.5) the solvent molecules are in a disordered state, but some properties of them are still different from that of the *bulk of the solvent* (D in Figure 1.5).

The solvation number of an ion in a given solvent is the number of solvent molecules in the primary solvation shell. Most metal ions with donor solvents have a solvation number of 6. Small metal ions (*e.g.*, Be^{2+}) or metal ions with special geometry (*e.g.*, Pd^{2+}) the solvation number is 4. The solvation number depends on the size of the solvent molecules: large solvent molecules form small solvation number solvate, while small ones are able to form solvates with larger solvation numbers.

The experimental ways of determining solvation numbers include EXAFS (Extended X-ray Absorption Fine Structure), SXRD (Solution X-ray Diffraction), NMR (Nuclear Magnetic Resonance), FT-IR (Fourier-transformed Infrared Spectroscopy), FT-Raman (Fourier transformed Raman spectroscopy) and quantum mechanical calculations.

As an example, the determination of solvation number from FT-IR spectroscopy on the basis of the spectrum of $LiClO_4$ in acetonitrile will be analyzed. For this, the FT-IR spectra of the solution series containing increasing concentrations of $LiClO_4$ was recorded in the wavenumber region of the vibrations of the solvent (2200-2400 cm^{-1}, Figure 1.6). The C≡N stretching vibration of the free solvent molecule is found at $\nu_a = 2253\ cm^{-1}$. This is denoted as peak “a” in Figure 1.6. The C≡N stretching vibrations of the solvent molecules bound to the Li^+ is blue-shifted ($\nu_b = 2276\ cm^{-1}$) relative to that of the free solvent molecule (peak “b” in Figure 1.6.) It is clear that the intensity of peak “a” decreases with the increasing solute concentration, while that of peak “b” increases with it. The peak area (or roughly the peak height) is proportional to the concentration of the species, which has the given vibration. *Via* combining this information with the mass-balance equations, the ratio between the bound and free solvent molecules can be calculated which leads directly to the solvation number. The increase in the ν wavenumber corresponding to the C≡N stretching vibrations of the bound solvent molecules reflects the strength of the solvation. The blue shift, that is the $\Delta\nu = \nu_b - \nu_a$ for a given cation is different and follows the order of: $Na^+ < Ba^{2+} < Sr^{2+} < Ca^{2+} < Li^+$. The larger is $\Delta\nu$, the stronger is the binding (or solvation) interaction between the acetonitrile and the cation.

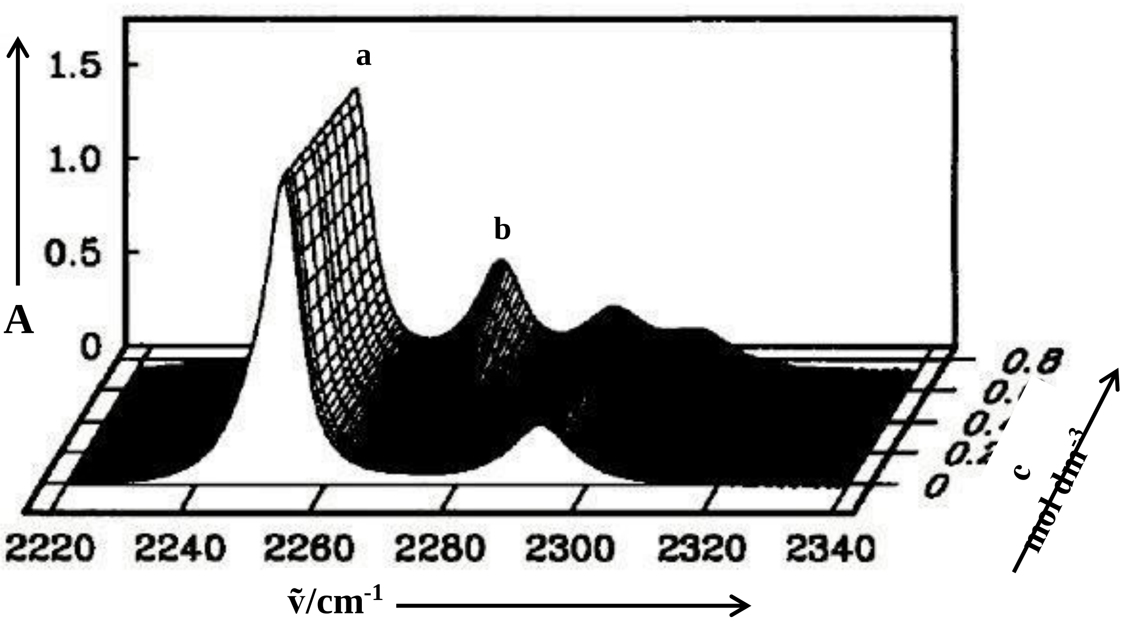


Figure 1.6 The FT-IR spectra of $LiClO_4$ in acetonitrile at various solute concentrations at 25 °C on the basis of the data published in [1].

1.5.4 The effect of solvents on the complex formation

During the complex formation between a metal ion and a ligand, two types of competitive effects needs to be considered: (i) the solvate molecules of the metal ion must be exchanged to the ligand and (ii) the solvate molecules of the ligand must be exchanged to the metal. The solvent affects and determines the forming complexes' stability and structure. To demonstrate this, the example of the Ag-halogenide complexes in protic and aprotic solvents will be analyzed. For the solubility product of AgX and for the stepwise formation of the 1:2 complex AgX_2^- the following relations hold:

$$\mathrm{Ag^+ + X^- \rightleftarrows AgX} \qquad K_{sp} = [\mathrm{Ag^+}]\,[\mathrm{X^-}] \tag{1.6}$$

$$\mathrm{Ag^+ + 2X^- \rightleftarrows AgX_2^-} \qquad \beta_2 = [\mathrm{AgX_2^-}]/([\mathrm{Ag^+}]\,[\mathrm{X^-}]^2) \tag{1.7}$$

Combining K_{sp} with β_2, $K_{sp}{\cdot}\beta_2 = [AgX_2^-]/[X^-]$ is obtained. It is plausible that the larger is the product K_{sp} with β_2, the larger is the stability constant of the (soluble) AgX_2^- complex. The effect of solvents on the formation of these AgX_2^- type complexes is shown in Table 1.8, where the K_{sp} and β_2 values obtained for AgX_2^- type complexes ($X^- = Cl^-$, Br^- and I^-) in some protic solvents (H_2O, MeOH) as well in some aprotic ones (acetonitrile, PC, DMSO). In the two protic solvents no formation of AgX_2^- can be observed. In practice this means, that the precipitate AgX does not get dissolved in an excess of X^-. However, in aprotic solvents formation of AgX_2^- is favored, and the precipitate AgX gets dissolved in an excess of X^-. The reason of this phenomenon is, that the halogenide anions are more reactive in aprotic solvents than in protic ones. Another example is, that carbohydrate complexes of metal ions in water are of low stability, while in DMSO they are of high stability, latter is due to the increased reactivity of the carbohydrates in the aprotic solvent DMSO.

Table 1.8 The solubility product of AgX (K_{sp}) and the formation constant of AgX_2^- (β_2) (X^- = Cl^-, Br^- and I^-) in some protic and in some aprotic solvents. In protic solvents, the AgX does not dissolve in the excess of the ligand (see data in the red frame) while in aprotic ones it does (see data in the green frame); on the basis of the data published in [1].

Solvent	Indifferent electrolyte		Cl^-	Br^-	I^-
H_2O	5 M $NaClO_4$	pK_{sp}	10,10	12.62.	16.35
		$\log\beta_2$	5,40	7.23	10.95
		$K_{sp}\beta_2$	$10^{-4.70}$	$10^{-5.39}$	$10^{-5.40}$
MeOH	1 M $LiClO_4$	pK_{sp}	13.0	15.2	18.2
		$\log\beta_2$	7.9	10.6	14.8
		$K_{sp}\beta_2$	$10^{-5.1}$	$10^{-4.6}$	$10^{-3.4}$
AN	0.1 M Et_4NClO_4	pK_{sp}	12.4	13.2	14.2
		$\log\beta_2$	13.1	13.8	15.2
		$K_{sp}\beta_2$	$10^{0.7}$	$10^{0.6}$	$10^{1.0}$
PC	0.1 M Et_4NClO_4	pK_{sp}	20.0	20.5	21.8
		$\log\beta_2$	20.9	21.2	22.8
		$K_{sp}\beta_2$	$10^{0.9}$	$10^{0.7}$	$10^{1.0}$
DMSO	0.1 M Et_4NClO_4	pK_{sp}	10.4	10.9	12.1
		$\log\beta_2$	11.7	12.0	13.0
		$K_{sp}\beta_2$	$10^{1.3}$	$10^{1.1}$	$10^{0.9}$

1.5.5 Solvation of ions in solvent mixtures

Relative permittivity of a mixture of two miscible solvents can be given on the basis of an equation derived from the so-called Debye-Onsager theory, *i.e.*,

$$\frac{(\varepsilon-1)(2\varepsilon+1)}{9\varepsilon}=\frac{\phi_A(\varepsilon_A-1)(2\varepsilon_A+1)}{9\varepsilon_A}+\frac{\phi_B(\varepsilon_B-1)(2\varepsilon_B+1)}{9\varepsilon_B} \qquad (1.8)$$

ε, ε_A and ε_B are the permittivity of the mixture, and components A and B, respectively, and Φ_A and Φ_B are the volume fractions of components A and B in the mixture.

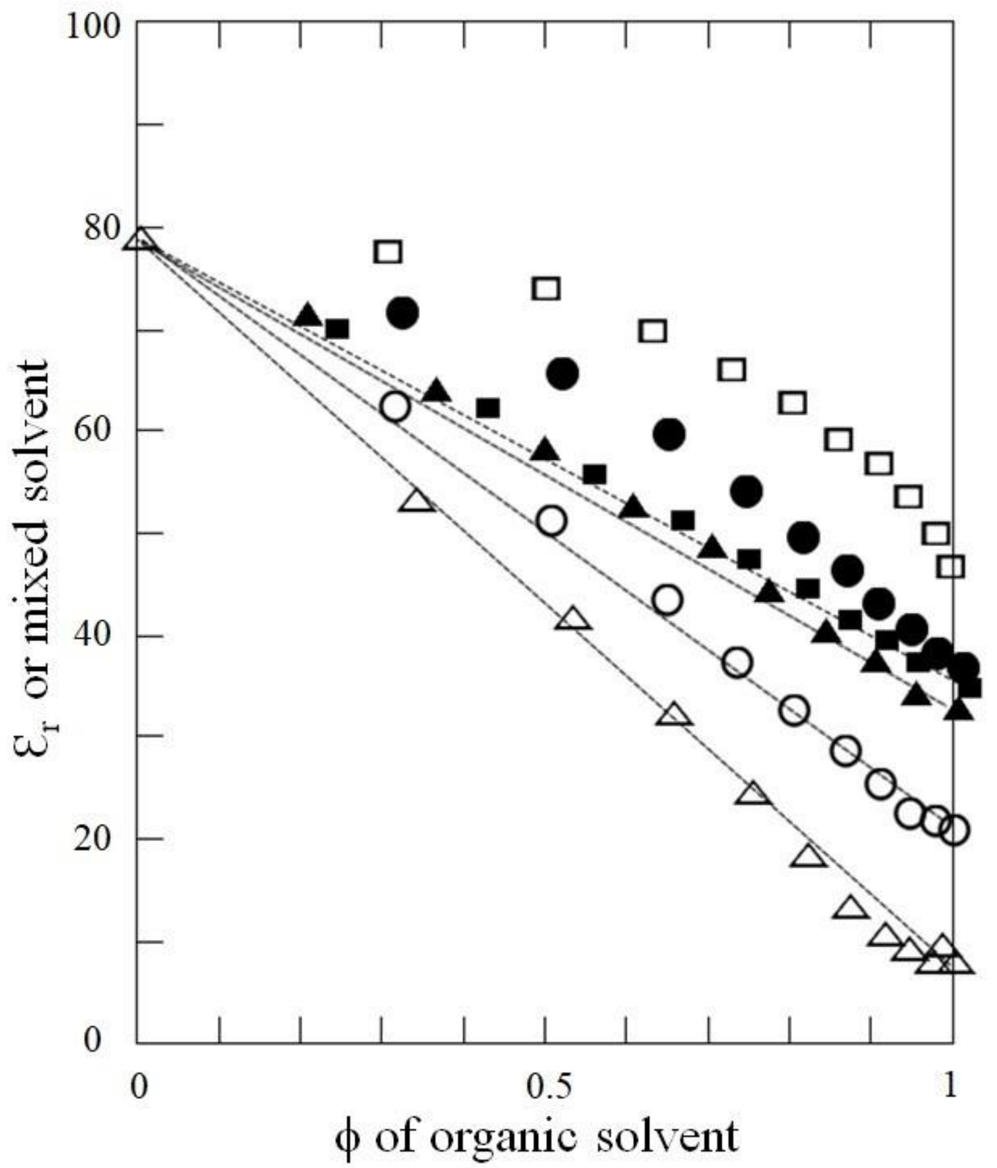


Figure 1.7 Relative permittivities of water-organic solvent mixtures plotted against their volume fractions. Solvents: open circles: acetonitrile; open triangles: MeOH; open squares: THF; filled circles: DMSO; filled triangles: DMF; filled squares: Ac on the basis of the data published in [1].

When both ε_A and ε_B are much larger than one, eqn. (1.8) is simplified to $\varepsilon = \Phi_A \varepsilon_A + \Phi_B \varepsilon_B$, that is the permittivity changes *pro rata* with the composition of the mixture. This is, however, the case only, when there is no interaction between A and B, as it is seen in Figure 1.7, where the permittivity of water-S mixtures (where S is an organic solvent miscible with water) are plotted as a function of the volume fractions of the organic component. With acetonitrile, MeOH, THF and Ac linear relationship is obtained, indicating that there is no interaction between these solvents and water. However, in H_2O-DMSO and H_2O-DMF mixtures, significant deviations from linearity are seen, which clearly shows, that these compounds interact in their mixtures.

In solvent mixtures one can observe the phenomenon of selective solvation. This means, *e.g.*, that the solvent with the larger DN is more strongly, selectively coordinated to a metal ion, than the one with the smaller DN. Accordingly, latter component determines the DN of the mixture.

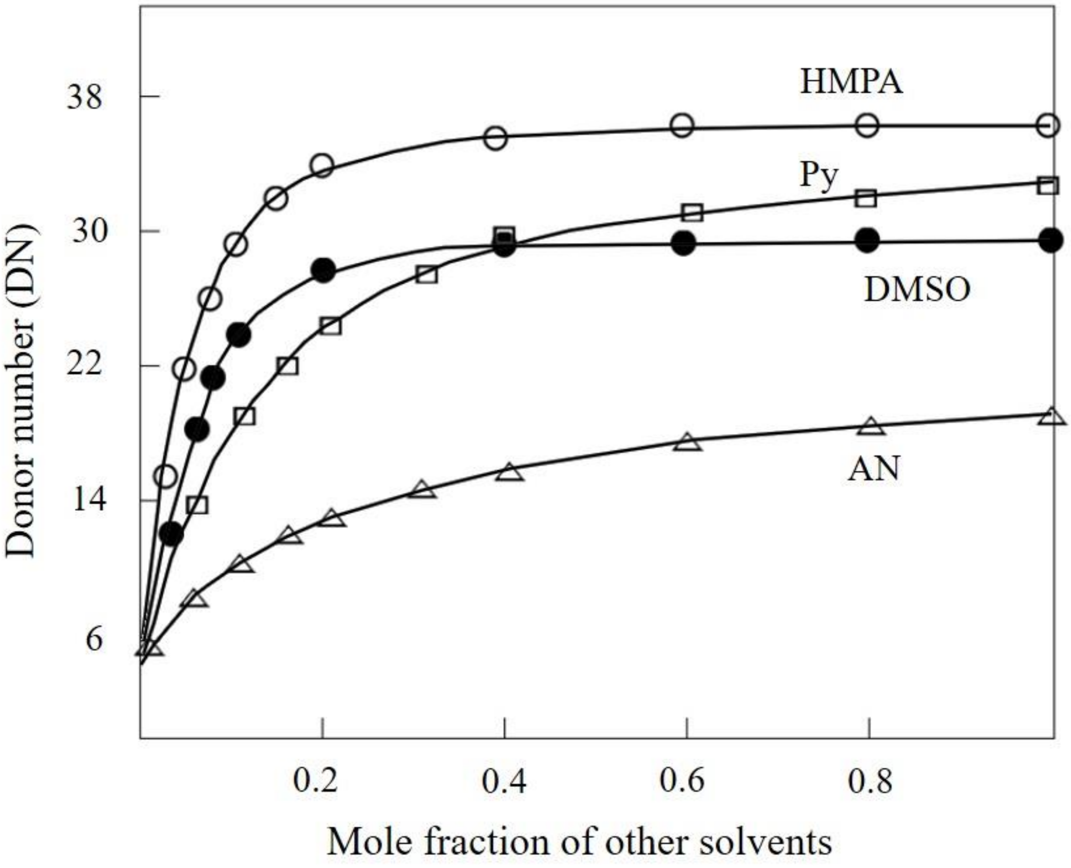


Figure 1.8 Donor numbers of mixtures of nitromethane with other solvents; on the basis of the data published in [1].

This effect is demonstrated in Figure 1.8, where the Guttman's donor number of nitromethane-S mixtures are shown (where S = HMPA, Py, DMSO and acetonitrile.) All the S-es chosen in this experiment are stronger donors, than nitromethane. From mole fractions of *ca.* 0.2, the donor number of the mixture is practically equal to that of the pure S with the higher DN. Accordingly, the S with higher DN selectively solvates the solute in the solvent mixture (recall the determination of DN in the Guttmann scale.)

1.5.6 The permittivity of solvents and the association of ions

Electrolytes may be classified as

(i) *ionophores* – this means, that they consist of ions even in the solid state (*e.g.*, NaCl)

(ii) *ionogens* – these are compounds that form ions during the dissolution/solvation and they consist of molecules *prior to* dissolution (*e.g.*, HCl).

At reasonably small (< 0.01 M) concentrations and in polar solvents ($\varepsilon_r > 40$), ionophores are in a fully dissociated state. If this is the case, then

$$\Lambda = \Lambda^{\infty} - Sc^{1/2} \tag{1.9}$$

where Λ and Λ^{∞} are the molar conductivity of the solution at $c > 0$ M and $c \to 0$ M concentrations, respectively, and S is the so called Onsager-slope. This relationship holds only for solutions, in which the dissociation of the electrolyte dissolved in it is complete.

Quite often, the complete dissociation of an electrolyte does not hold. When

(i) the solvent is not very polar or

(ii) the concentration of the electrolyte is sufficiently large, then the electrolyte is present (at least partly) in a non-dissociated state. It is told in such cases, that ion-pairs (eq. 1.10) are formed. Ion-pairs are held together by electrostatic forces between the oppositely charged ions. Such species do not contribute *e.g.*, to the ionic strength or to the conductivity of the solution and their stability is given in terms of their ion-association constant, K_A (eq. 1.11)

$$A^+ + B^- \rightleftarrows A^+B^- \text{ (ion-pair)} \tag{1.10}$$

$$K_A = [A^+B^-]/([A^+][B^-]) \tag{1.11}$$

In Figure 1.9, the logarithmic values of the ion-association constants ($\log K_A$) for tetrabutylammonium picrate (Bu_4NPic) and potassium chloride (KCl) as well as the values of $\log (cK_A)$ and the degree of ion association (α) are plotted against ($1/\varepsilon_r$). From Figure 1.9, it is clear that $\log K_A$ is inversely proportinal to ε_r. Accordingly, ion-pairing is facilitated in solvents with smaller permittivity and, conversely unfavoured in high permittivity media. The degree of association (α) depends on the product cK_A. For example, in a 0.01 M KCl solution in EtOH ($\log K_A = 2$), $\alpha = 38$ %; $\varepsilon_r = 26.4$. Compare this with a 0.01 M KCl solution (that is, the same concentration of the salt) in AcOH ($\log K_A = 6.2$) $\alpha = 99.9$ %. The relative permittivities of EtOH and AcOH are 26.4 and 6.2, respectively.

The ion-association is primarily determined by the relative permittivity of the solvent. The theoretical description of the ion-association on the basis of the relative permittivities was described by Bjerrum (1926) and Fouss (1958). Take two oppositely charged ions with charges z^+ and z^- and consider that they approach each other. With the decrsaing distance the attraction energy between the two ions increases.

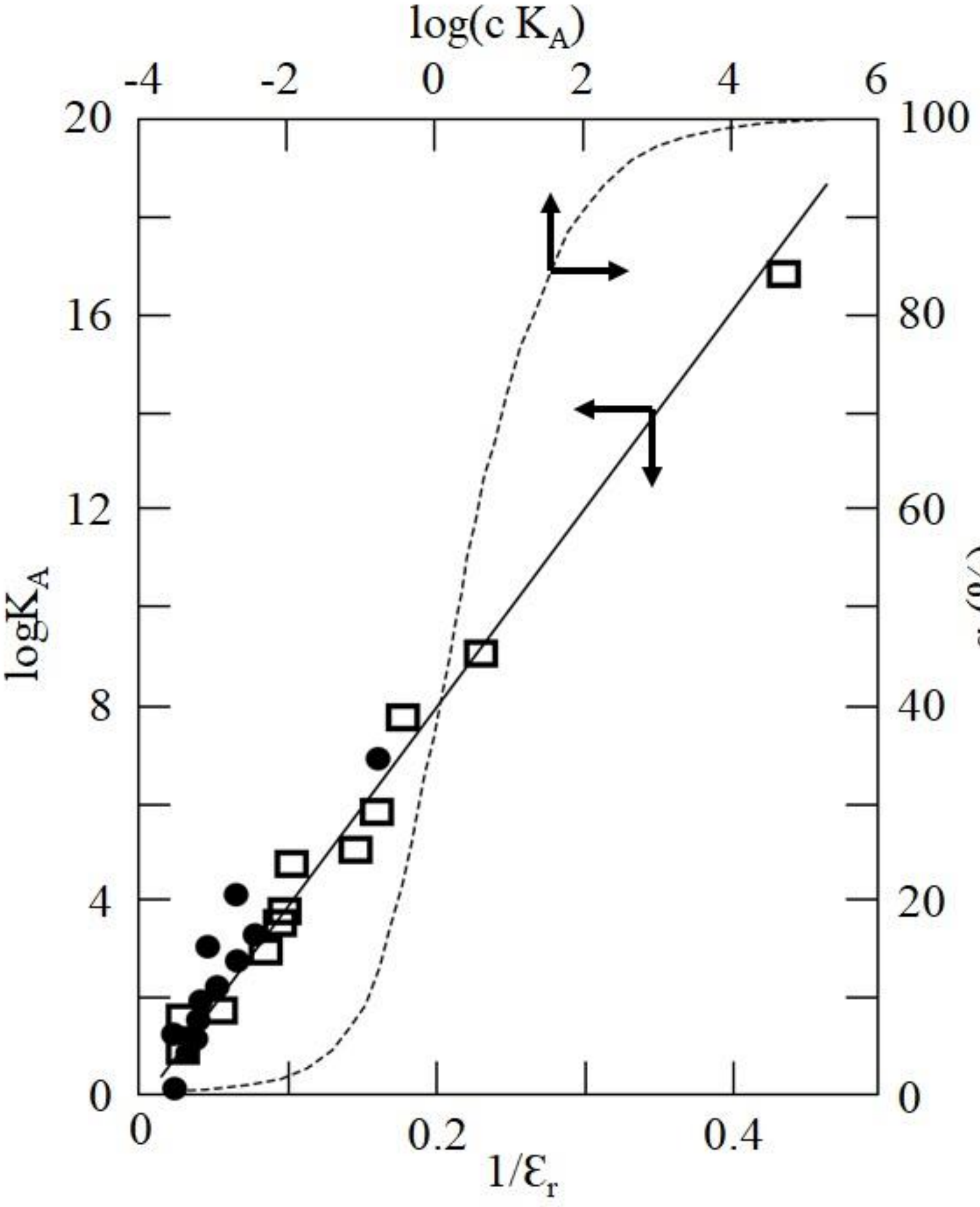


Figure 1.9 Relationship between the ion association constants (log K_A) and the reciprocal of solvent permittivity ($1/\varepsilon_r$) (solid line) and between the degree of ion association (α) and log (cK_A) (dotted curve) (open circles: Bu_4NPic in AN, NB, MeOH, Ac, Py, DCE, o-dichlorobenzene, acetic acid, chlorobenzene and benzene; closed squares: KCl in ethanolamine, MeOH, EtOH, acetic acid and H_2O-dioxane mixtures); on the basis of the data published in [1].

The electrostatic attraction energy E, at a distance of r, can be expressed as $z_+z_-e^2/4\pi e_0e_rr$ (where e is the charge of the electron). At a critical distance (q in the followings), E exceeds the Boltzmann energy of agitation ($2k_BT$) (k_B is the Boltzmann constant and T is the absolute temperature).

The possible closest approach of the two ions is the sum of their ionic radii (this is the so called distance of closest approach, *a* that is; it is physically impossible for the two ions to get closer to each other). If the ionic radii of the two ions are r_A and r_B, respectively, then $a = r_A + r_B$. According to the Bjerrum-Fouss theory, there are two scenarios:

1. if $a \leq q$, the ions do form ion-pairs, they get associated
2. if $a > q$, the ions do not form ion-pairs, they do not get associated.

If the oppositely charged ions approach each other to $a < q$ critical distance, they get „trapped”. The q critical distance can be calculated as follows:

$$q = \frac{|z_+z_-|N_A e^2}{8\pi\varepsilon_0\,\varepsilon_r RT} \tag{1.12}$$

q is inversely proportional to ε_r. In water ($\varepsilon_r = 78.4$), for 1:1 electrolytes q = 0.35 nm, for 2:2 electrolytes q = 1.4 nm. It follows, that for the overwhelming majority of the hydrated ions, $a > q$ in water. This is why in water as well as in solvents with large ε_r, the ion-association is negligible. Conversely, in solvents with small ε_r, the ions with opposite charge do form ion-pairs.

Based on this theory, both Bjerrum (eq. 13) and Fouss (eq. 14) derived a formula, that is capable of estimating the K_A association constant of an ion-pair in a solvent with relative permittivity of ε_r.

$$K_A = \frac{4\pi N_A}{1000}\int_a^q r^2\,\exp\left(\frac{2q}{r}\right)dr \tag{1.13}$$

$$\log K_A = \log(4\pi N_A a^3/3000) + 0.434|z_+ z_-|N_A e^2/(4\pi a \varepsilon_0 \varepsilon_r RT) \qquad (1.14)$$

1.5.7 The structure of the ion-pairs

The possible structures of the ion pairs forming in various solvents are shown schematically in Figure 1.10. The difference between the various forms is rather plausible. In the A^+SSB^-, the ions keep their full primary solvation shell upon association. In A^+SB^- there is at least one solvent molecule which connected both to the cation and to the anion. In A^+B^-, the ions are in direct contact.

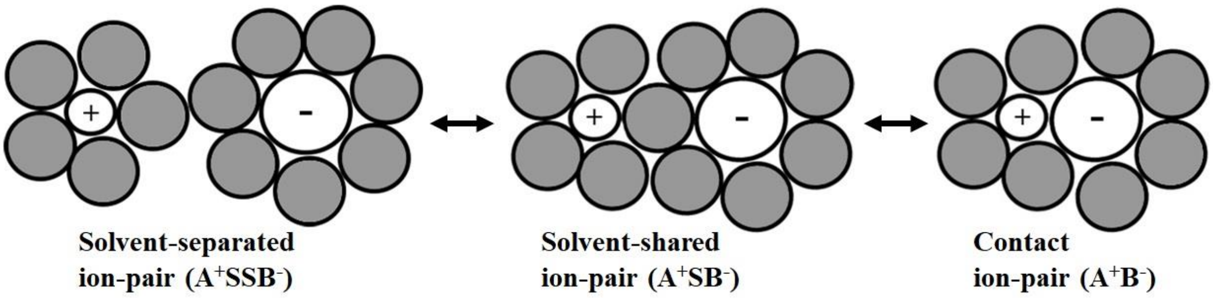


Figure 1.10 The schematic view of the structure of solvent-separated (A^+SSB^-), solvent-shared (A^+SB^-) and contact (A^+B^-) ion-pairs (S stands for a solvent molecule); on the basis of the data published in [1].

The formation of the various forms of ion-pairs takes place in a consecutive process, which can be represented by eq. (1.15). The association constants corresponding to the various consecutive equilibria are shown above the arrows in eq. (1.15). The inter-relation between K_1, K_2, K_3 and K_A is shown in eq. (1.16).

$$\mathrm{A}^{+}_{\mathrm{solv}} + \mathrm{B}^{-}_{\mathrm{solv}} \overset{K_1}{\rightleftarrows} \mathrm{A}^{+}\mathrm{SSB}^{-} \overset{K_2}{\rightleftarrows} \mathrm{A}^{+}\mathrm{SB}^{-} \overset{K_3}{\rightleftarrows} \mathrm{A}^{+}\mathrm{B}^{-} \tag{1.15}$$

$$K_{\mathrm{A}} = \frac{[\mathrm{A}^{+}\mathrm{SSB}^{-}] + [\mathrm{A}^{+}\mathrm{SB}^{-}] + [\mathrm{A}^{+}\mathrm{B}^{-}]}{[\mathrm{A}^{+}][\mathrm{B}^{-}]} = K_1(1 + K_2 + K_2K_3) \tag{1.16}$$

It is important to note here, that various experimental means are capable of detecting ("seeing") various forms of the ion-pairs. For example, conductivity is not able to distinguish between $A^+SSB^–$, $A^+SB^–$ and $A^+B^–$ as none of the three forms contribute to the conductivity of the solution. Accordingly, conductivity measurements lead to the K_A ion-association constant. Vibration spectroscopic techniques, like FT-IR or FT-Raman are sensitive for the contact ion-pairs only, therefore from such measurements, K_3 can only be extracted. Other techniques, like dielectric relaxation spectroscopy (DRS) are more sensitive to ion-pairs with larger dipole moments, therefore from DRS, (at least in principle and usually in combination with other techniques) K_1 can be estimated.

In the following, an example is presented, where distinguishing between the various types of ion-pairs was possible *via* using FT-IR measurements (Figure 1.11). In the $LiClO_4$-acetonitrile system, the relative concentrations of free ions (c_{ION}), solvent-shared ion-pairs (c_{SSIP}) and contact ion-pairs (c_{CIP}) were obtained by combining infrared and dielectric relaxation spectroscopic (DRS) measurements. As perchlorate ion does not form solvate in acetonitrile, only contact ion-pair and solvent shared ion pair can be formed in the system. In the IR spectrum of Fig. 1.11 (left), the integrated intensity of bands 1, 1' and 2 gave c_{CIP}, while that of bands a and *b* gave ($c_{ION} + c_{SSIP}$). The total ion-pair concentration, ($c_{CIP} + c_{SSIP}$), was obtained from the DRS spectra. The species distribution calculated from these results are shown in Fig. 1.11 (right). The association constant obtained this way (K_A=19.8 dm^3 mol$^{–1}$) is practically identical with that extracted from conductometric measurements (K_A=21.8 dm^3 mol$^{–1}$).

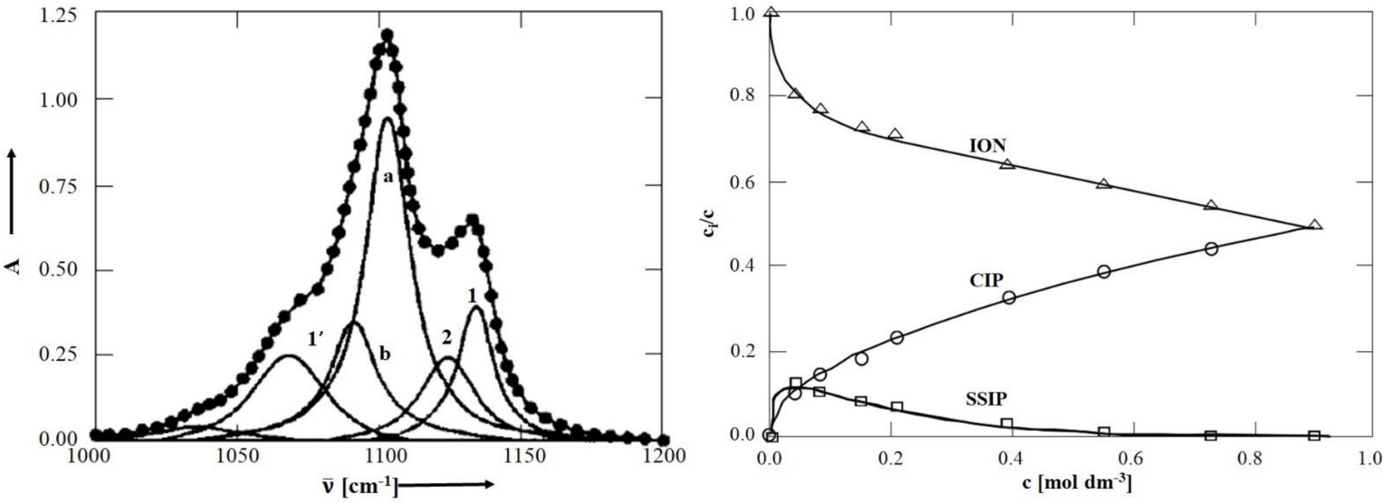


Figure 1.11 Left: Measured (points) and fitted (lines) IR spectrum in the region of the ν_3^{ClO} vibration of 0.73 M $LiClO_4$ in acetonitrile at 25 °C. Bands *a* and *b* are from the free ClO_4^-, bands 1, 1’ and 2 are from ClO_4^- in the contact ion-pair. Right: Fractions of free ions (ION), solvent-shared ion-pairs (SSIP) and contact ion-pairs (CIP) in $LiClO_4$ dissolved in acetonitrile; on the basis of the data published in [1].

1.6 Acid-base reactions in non-aqueous solvents

One of the central issues in the chemistry of non-aqueous solutions is the acid-base reactions in various solvents. This will be discussed in terms of the Brönsted-Lowry acid-base theory.

The dissociation of an HA acid to H^+ and A^- takes place in two steps:

The first step is the *ionization*, that is the formation of the solvated ion-pair consisting of H^+ and A^-. The equilibrium and the corresponding equilibrium constant, K_I, can be given as:

$$\mathrm{HA} \rightleftarrows (\mathrm{H}^+,\ \mathrm{A}^-)_{\mathrm{solv}} \qquad K_\mathrm{I} = \frac{[(\mathrm{H}^+,\ \mathrm{A}^-)]}{[\mathrm{HA}]} \tag{1.17-18}$$

The ion-pair may dissociate to separated, solvated ions; the process is called *dissociation* and the equilibrium and the corresponding equilibrium constant, K_D, can be given as:

$$(\mathrm{H}^+,\ \mathrm{A}^-)_{\mathrm{solv}} \rightleftarrows \mathrm{H}^+_{\mathrm{solv}} + \mathrm{A}^-_{\mathrm{solv}} \qquad K_\mathrm{D} = \frac{\gamma^2[\mathrm{H}^+][\mathrm{A}^-]}{[(\mathrm{H}^+, \mathrm{A}^-)]} \tag{1.19-20}$$

where γ is the activity coefficient. During the ionization, the solvent acts as a Lewis base (electron pair donor) to the H atom and as a Lewis acid (electron pair acceptor), and ionize the H and A atoms, resulting in the formation $(H^+, A^-)_{solv}$. The extent of ionization depends on the strength of the H-A bond: if it is weak, ionization occurs easily. The ionization may also become easy, if solvent molecules interact strongly with the H and A atoms. In summary, ionization is primarily determined by donor-acceptor interactions.

During dissociation, $(H^+, A^-)_{solv}$ dissociates into free ions. The dissociation process is easy if the solvent has a high permittivity and the distance of closest approach between H^+ and A^- is large enough. Thus, two important solvent properties, *i.e.* relative permittivity and donor-acceptor properties determine both the ionization and dissociation processes.

The proton dissociation constant, K_a, is large if both K_I and K_D are sufficiently large:

$$K_a = \frac{\gamma^2[\mathrm{H}^+][\mathrm{A}^-]}{[\mathrm{HA}] + [(\mathrm{H}^+,\ \mathrm{A}^-)]} = \frac{K_I K_D}{1 + K_I} \tag{1.21}$$

Accordingly, the solvents can be arranged in four major classes depending on the ease or difficulty of ionization and dissociation (Table 1.9). The acid-base properties will be discussed in the followings according to these four classes.

Table 1.9 Effect of solvents on the ionization of the HA acid and the dissociation of $(H^+,A^-)_{solv}$ ion-pair; on the basis of the data published in [1].

Solvent classification	**Ionization of HA**	**Dissociation of $(H^+, A^-)_{solv}$**
High-permittivity amphiprotic solvents	easy	easy
High-permittivity aprotic solvents	difficult or fairly easy$^{1)}$	easy
Low-permittivity amphiprotic solvents	a little difficult or easy	difficult
Low-permittivity aprotic solvents	difficult	difficult

1) Difficult in protophobic solvents, but fairly easy in protophilic solvents.

1.6.1 Acid-base reactions in amphiprotic solvents of high permittivity

In the Kolthoff classification (Table 1.4), solvents in group 1a, 2a and 3a belong to this group. Their relative permittivity is high (> 20) and they have fair or high AN and DN values. The most plausible and most important example for this group is water.

The strength of acids can be defined as follows. HA and BH^+ type acids, upon reacting with water, undergo dissociation:

$$HA + H_2O \rightleftarrows H_3O^+ + A^- \tag{1.22}$$

$$BH^+ + H_2O \rightleftarrows H_3O^+ + B \tag{1.23}$$

Strong acids in water are in completely dissociated state. Accordingly, the equilibria (1.22-23) are completely shifted to the right and as a result, HA and BH^+ practically do not exist in water (that is, the equilibrium concentration of HA and BH^+ is equal or at least tends to zero). If an acid is strong acid in water, its protons are exclusively present as H_3O^+. The water, as solvent is unable to make difference between strong acids (*e.g.*, HCl and $HClO_4$), as all of them turn completely to H_3O^+ and to the conjugated base (*i.e.*, A^- or B). This is called the *leveling effect*. As a consequence of this, the strongest acid in water is the H_3O^+. This is, because all the acids that are stronger acids, than H_3O^+, turn to H_3O^+ upon dissolution. Their strength is equal to that of H_3O^+. The water is not able to distinguish between these strong acids.

Conversely, weak acids in water are in partially dissociated state. Both HA and BH^+ exist in water, their protons are present partially as H_3O^+ and partially as HA or BH^+ forms. The protons are therefore distributed among H_3O^+ and HA/BH^+. The extent of this distribution changes from weak acid to weak acid, that is: the solvent is able to make difference between these solutes. This is called the *differentiating effect* of solvents.

The mathematical way of expressing the difference in the strength of acids is the *acid dissociation constant*:

$$K_a = \frac{a(H_3O^+)a(A^-)}{a(HA)} = \frac{\gamma^2[H_3O^+][A^-]}{[HA]} \tag{1.24}$$

$$K_a = \frac{a(H_3O^+)a(B)}{a(BH^+)} = \frac{[H_3O^+][B]}{[BH^+]} \tag{1.25}$$

The larger is K_a, the stronger is an acid. By definition, for strong acids $K_a \rightarrow \infty$.

The strength of bases can be discussed in an analogous way. A^- and B type bases upon reaction with water associate with the proton to form HA and BH^+.

$$A^- + H_2O \rightleftarrows HA + OH^- \tag{1.26}$$

$$B + H_2O \rightleftarrows BH^+ + OH^- \tag{1.27}$$

Compounds that are strong bases in water, are completely transformed to HA and BH^+ upon dissolution. Accordingly, the equilibria (1.26-27) are completely shifted to the right and as a result, A^- and B practically do not exist in water (that is, the equilibrium concentration of A^- and B is equal or at least tends to zero). If a given base is strong base in water, it turns quantitatively to OH^- and the respective conjugated acid (HA or BH^+). The water, as solvent is unable to make difference between strong bases (*e.g.*, NaOH and KOH), as both of them turn completely to OH^- and Na^+ or K^+. This is called the *leveling effect*. As a consequence of this, the strongest base in water is the OH^-. This is, because all the bases that are stronger bases, than OH^-, turn to OH^- upon dissolution. Their base strength is equal to that of OH^-. The water is therefore not able to distinguish between these strong bases.

Conversely, weak bases in water are in partially dissociated state. Both A^- and B exist in water, the concentration of A^- is commensurate with that of HA (or B with that of BH^+). The extent transformation of A^- to HA (or B to BH^+) changes from weak base to weak base, that is, the solvent is able to make difference between these solutes. Again, this is called the *differentiating effect* of solvents.

The mathematical way of expressing the difference in the strength of bases is the *base dissociation constant*:

$$K_b = \frac{a(\mathrm{HA})a(\mathrm{OH}^-)}{a(\mathrm{A}^-)} = \frac{[\mathrm{HA}][\mathrm{OH}^-]}{[\mathrm{A}^-]} \tag{1.28}$$

$$K_b = \frac{a(\mathrm{BH}^+)a(\mathrm{OH}^-)}{a(\mathrm{B})} = \frac{\gamma^2[\mathrm{BH}^+][\mathrm{OH}^-]}{[\mathrm{B}]} \tag{1.29}$$

The larger is K_b, the stronger is a base. By definition, for strong base $K_b \rightarrow \infty$.

It is well known that in water, autoprotolysis (autoionization) occurs:

$$\mathrm{H_2O + H_2O \rightleftarrows H_3O^+ + OH^-} \tag{1.30}$$

with the corresponding autprotolysis constant, $K_w = [H_3O^+][OH^-] = 10^{-13.996}$ (at 25 ^oC). In water the acidic character is manifested by the H_3O^+ ion called oxonium ion, while the basic character is carried by the OH^- ion. The acid-base equilibria in amphiprotic solvents of high permittivity (like water-like neutral solvents, *e.g.*, MeOH, EtOH, acidic protogenic solvents, *e.g.*, formic acid, or basic protophilic solvents, *e.g.*, 2-aminoethanol) can be treated by methods similar to those in aqueous solutions. In these solvents, autoprotolysis takes place yielding the *lyonium* ions and the *lyate* ions:

$$\mathrm{SH + SH \rightleftarrows SH_2^+ + S^-} \tag{1.31}$$

$$K_{\mathrm{SH}} = a(\mathrm{SH_2^+})a(\mathrm{S^-}) = \gamma^2[\mathrm{SH_2^+}][\mathrm{S^-}] \tag{1.32}$$

If the solvent is denoted by SH, then the *lyonium* ion is the SH_2^+ and the lyate ion is S^-. Replacing in eq. (1.24-29), H_2O to SH, H_3O^+ ion to SH_2^+ ion and OH^- ion S^- ion, reactions and

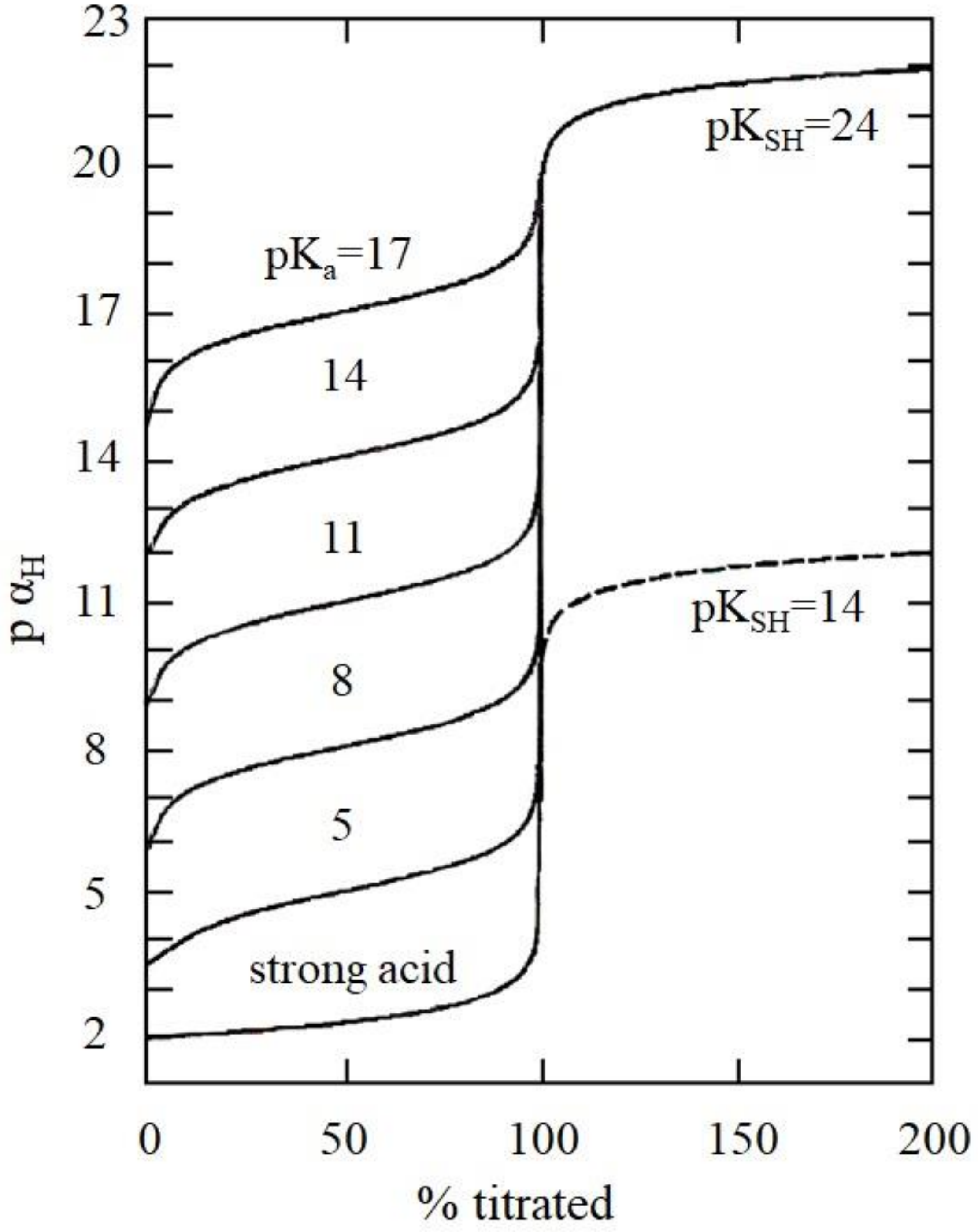


Figure 1.12 Calculated titration curves of a strong acid and weak acids of various pK_a values with a strong base, in the solvent of $pK_{SH}=24$ (with the dashed curve is for the case of $pK_{SH}=14$ (water); on the basis of the data published in [1].

equilibrium constants relating to the solvent SH can be constructed. The analogies are trivial. The strongest acid in solvent SH is SH_2^+ (lyonium ion), while the strongest base in SH is S^- (lyate ion). The strengths of the acids that are much stronger than SH_2^+ are made equivalent to that of SH_2^+, while the strengths of the bases that are much stronger than S^- are made equivalent to that of S^-. Here the acid strength of SH_2^+ differs from one solvent to another. For example, in formic acid as solvent, SH_2^+ is very strongly acidic and some strong acids in water behave as weak acids. On the other hand, in 2-aminoethanol as solvent, SH_2^+ is only weakly acidic, and some weak acids in water behave as strong acids.

The activity or (less rigorously, the concentration) of the SH_2^+ (in water, that of H_3O^+) is used for defining the pa_H (or pH) of a solution. In water, $pa_H = -\log a(H_3O^+)$, in solvent SH, $pa_H = -\log a(SH_2^+)$. From this, it can be readily deduced that the neutral pH in solvent SH is equal to $pK_{SH}/2$.

The strengths of weak acids can be compared on the basis of their K_a values, which changes from solvent to solvent. In figure 1.12, the titration curves of weak acids with various pK_a values are presented; the shape of the titration curve as well as its variation in around the end point depends on the pK_{SH} and the pK_a.

The strength of an acid depends on the solvent. The difference in the pK_a of a given acid in solvent I. and solvent II. with permittivities of $\varepsilon_{r,I}$ and $\varepsilon_{r,II}$ can be expressed with the aid of the electrostatic Born theory:

$$\mathrm{p}K_{\mathrm{a,II}} - \mathrm{p}K_{\mathrm{a,I}} = \frac{0.217 Ne^2}{RT}\left(\frac{1}{r_{\mathrm{H}}} + \frac{z_{\mathbf{B}}^2}{r_{\mathbf{B}}} - \frac{z_{\mathbf{A}}^2}{r_{\mathbf{A}}}\right)\left(\frac{1}{\varepsilon_{\mathrm{r,II}}} - \frac{1}{\varepsilon_{\mathrm{r,I}}}\right) \qquad (1.33)$$

A and B denote the acid and its conjugated base pair, respectively, while r and z are their radii and their charges, respectively. Table 1.10 shows the pK_a values of some acids and acid-base indicators in water, methanol and ethanol. The solvent effects on pK_a are smaller for BH^+-type acids than for HA^- or HA-type acids. For the BH^+-type acids, $z_A = 1$ and $z_B = 0$ in eq. (1.33), and the influence of solvent permittivity is expected to be small.

Table 1.10 Comparison of the pK_a values of some acids and acid-base indicators in water, methanol and ethanol. In the second column, the charge of the acidic form is shown; on the basis of the data published in [1].

Acids	**Charges**	**pK_a (in H_2O)**	**pK_a (in MeOH)**	**pK_a (in EtOH)**
Acetic acid	0	4.75	9.7	10.4
Benzoic acid	0	4.20	9.4	10.1
Salicylic acid	0	2.98	7.9	8.6
Phenol	0	9.97	14.2	15.3
Picric acid	0	0.23	3.8	3.9
Anilinium	+1	4.60	6.0	5.7
Methyl orange	+1	3.45	3.8	3.4
Neutral red	+1	7.4	8.2	8.2
Bromophenol blue	-1	4.1	8.9	9.5
Bromothymol blue	-1	7.3	12.4	13.2

1.6.2 Acid-base reactions in aprotic solvents of high permittivity

These are polar solvents, their acidity (AN) is small, but their basicity (DN) can be

(i) *larger than that of water* (these are the so-called *protophilic* solvents, *e.g.*, DMSO, DMF, NMP, HMPA (4a group in Table 1.4)

(ii) *smaller than that of water* (these are the so-called *protophobic* solvents, *e.g.*, acetonitrile, PC, NM, TMS, Ac (5a group in Table 1.4)

During the dissociation/dissolution of an acid, there is a solvation interaction between

1. the solvent and the H^+
2. the solvent and the undissociated acid molecule and
3. the solvent and the conjugated base pair of the acid,

The strength of acids and bases (see Table 1.11) is very much different in the various solvents depending on the relative weight of these interactions. For example, the pK_a value of acetic acid in H_2O, DMSO and acetonitrile is 4.76, 12.6 and 22.3, respectively. The solvation of the H^+ changes in the order of DMSO >> H_2O >> acetonitrile. Based on this, the AcOH would be expected to be the strongest acid in DMSO. For the solvation of CH_3COOH, not much difference is seen between the three solvents. However, the CH_3COO^- ion is solvated the most in water.

In the case of picric acid (HPic), the solvation of Pic^- in aprotic solvents is comparable to or slightly stronger than that in water. The conjugated base, Pic^- is polarizable and readily interacts with polarizable aprotic solvents by dispersion forces. Water does not interact as strongly with Pic^- by hydrogen bonding because the negative charge of Pic^- is delocalized. The resultant of these effects is, that the pK_a of picric acid is 0.38 in water, –1 in DMSO and 11.0 in AN (Table 3.4). In this case, one may attribute the largest part of the difference in pK_a to the difference in the solvation of H^+.

Table 1.11 Dissociation constants of acids in various solvents (pK_a values, 25 °C); on the basis of the data published in [1].

Solvents	**AN**	**PC**	**γ-BL**	**MN**	**DMSO**	**DMF**	**NMP**	**Py**	**MeOH**	**AcOH**	**H_2O**
Relative permittivities	35.94	64.92	39	35.87$^{3)}$	46.65	36.71	32.2	12.91	32.66	6.17$^{4)}$	78.36
Autoprotolysis constants (pK_{SH})	≥33.2	≥29.2	~29	≥24	≥33.3	≥31.6	≥24.2		16.9	14.5	14.0
Acids											
$HClO_4$	(2.1)	(1.3)		2.1	0.4	(strong)	(strong)	3.3		4.9	(strong)
HCl	8.9*	(10.9*)		8.1*	2.1	3.3	3.9	5.7	1.2	8.6	-3.7
HBr	5.5*				1.1	1.8		4.4	0.8	6.1~6.7	-4.1
HNO_3	8.9*	(10.4*)		8.8*	1.4	(decomp)	2	4.1	3.2	9.4	-1.8
H_2SO_4 (pK_{a1})	7.8*	(8.4*)		5.1*	1.4	3.1				7.2	
(pK_{a2})	25.9*			21.4	14.7	17.2					1.96
Acetic acid	22.3*	22.5*		20.5*	12.6	13.5	13.3	10.1	9.7		4.76
Benzoic acid	20.7*	19.7*		19.5*	11.0	12.3	12.3	9.8	9.4		4.19
Chloroacetic acid	15.3*			17.0*	8.9	10.1	10.9		7.8		2.88
Dichloroacetic acid	13.2*			14.1*	6.4	7	8.3		6.3		1.48
2,4-Dinitrophenol	16.0*	14.9*		15.9*	5.4	6.4	6.8	4.4	7.9		3.96
2,6-Dinitrophenol	16.5		13.7	16.0	4.9	6.1		4.8	7.7		3.70
Malonic acid (pK_{a1})	15.3*				7.2	8.0			7.5		2.88
(pK_{a2})	30.5				18.6	20.8			12.4		5.68
Methanesulfonic acid	10.0*	8.3*	8.1	(6.0)	1.6	3.0	2				
o- Nitrobenzoic acid	18.2*			16.7*	8.2	9.9	10.2		7.6		2.20
m- Nitrobenzoic acid	19.3*			17.6*	9.2	10.8	10.7		8.2		3.46
p- Nitrobenzoic acid	18.5*			17.6*	9.0	10.6	10.5		8.2		3.40
o- Nitrophenol	22.0*	20.8*		21.4*	11.0	12.2	12.6				7.17
m- Nitrophenol	23.9*	21.2*		22.2*	13.9	13.9	14.3	12.5			8.28
p- Nitrophenol	20.7*	19.7*		20.1*	11.3	12.2	12.5	9.2	11.2		7.15
Oxalic acid (pK_{a1})	14.5*		12.4*		6.2	8.6	(9.2)		6.1		1.27
(pK_{a2})	27.7				14.9	16.6			10.7		4.29

Table 1.11 (cont.)

Phenol	27.2*			(25.7)	16.5	>16	17.6		14.2		9.89
(o-)Phtalic acid (pK_{a1})	14.3*		12.4		6.2	6.7			7.4		3.0_0
(pK_{a2})	29.8				16.0	~16.5			12.1		5.4_0
(m-)Phtalic acid (pK_{a1})	19.3_4				9.8				8.6_3		3.5_4
(pK_{a2})	23.0				12.3				10.6		4.6_2
Picric acid	11.0	9.3	8.4	10.5	-1	(3.6)	(strong)	3.5	3.8		0.38
Salicylic acid	16.8*	15.2*	14.5*		6.7	8.2	8.6		7.9		2.97
p-Toluenesulfonic acid	8.7*	(6.4*)	7.1*	(5.8)	0.9	2.6	(strong)			8.4	
Trichloroacetic acid	10.6*			(7.3)		3.5			4.9	11.5	0.70
Trifluoromethanesulfonic acid	(2.6)	(2.2)		(3.0)	(strong)	(strong)					
Bases											
Ammonia	16.5	15.9		15.2	10.5	9.5			10.8	6.4	9.25
Aniline	10.7	10.1	9.1	9.1	3.6	4.4			6.0		4.63
Butylamine	18.3			16.9	11.1	10.5	10.3	5.5	11.8	8.6	10.64
Diethylamine	18.8			18.0	10.5	10.4	9.2				10.93
Diphenylguanidine	17.9	17.0	15.5	17.2	8.6	9.0	8.9				10.1
Ethylamine	18.4			17.1	11.0		10.2				10.63
Piperidine	18.9			18.2	10.6	10.4	10.4				11.12
Pyridine	12.3	11.9	10.8	12.0	3.4	3.3				6.1	5.25
Tetramethylguanidine	23.3				13.2	13.7	12.8	9.6			13.6
Tributylamine	18.1	17.5	16.6	17.8	8.4	8.6					9.9
Triethanolamine	15.9	15.9		(15.9)	7.5	7.6	7.5				7.76
Triethylamine	18.7	17.9	16.6	18.4	9.0	9.3	8.7	3.8		9.5	10.72
Bromocresolgreen$^{2)}$	18.5				7.4			5.5	9.8		4.9
Bromothymol blue$^{2)}$	22.3	17.5			11.3				12.4		7.03
Phenol red$^{2)}$	25.1				13.7		13.2		12.8		8.0
Thymol blue$^{2)}$	27.2	(20.6)			~15.3		14.5		14.0		9.2

The difference between the pK_a of, *e.g.*, the acid BH^+ in solvent S and R can be predicted on the basis of the following relationship:

$$\mathrm{p}K_\mathrm{a}(\mathrm{BH}^+,\mathrm{S}) - \mathrm{p}K_\mathrm{a}(\mathrm{BH}^+,\mathrm{R}) = \log\gamma_\mathrm{t}(\mathrm{H}^+,\mathrm{R}\rightarrow\mathrm{S}) + \log\gamma_\mathrm{t}(\mathrm{B},\mathrm{R}\rightarrow\mathrm{S}) - \log\gamma_\mathrm{t}(\mathrm{BH}^+,\mathrm{R}\rightarrow\mathrm{S}) \quad (1.34)$$

where $\log \gamma_t$ (i, R → S) is the change in the activity coefficient of species i, when it is moved from solvent R to solvent S. $\log \gamma_t$ (i, R → S) is called *transfer activity coefficient*. When i solute particle is transferred from solvent R into solvent S, the process is accompanied with an energy change; from the standard Gibbs energy (ΔG_t^0) of the transfer, the transfer activity coefficient, γ_t, can be computed:

$$\log \gamma_\mathrm{t}\,(\mathrm{i},\mathrm{R}\rightarrow\mathrm{S}) = \Delta G\mathrm{t}^\mathrm{o}(i,\ R\rightarrow S)/(2.303\,RT) \quad (1.35)$$

If $\log \gamma_t$ is negative, solvation of i is stronger in R than in S, and if it is positive, solvation of i is stronger in S than in R. $\log \gamma_t$ carries information regarding the reactivity of the solute: if, *e.g.*, $\log \gamma_t$ (i, R → S) = 3, solute i is 1000 times more reactive in R than in S. This is, for example, for the H^+ ion, when it is transferred from water to acetonitrile is as follows: $\log \gamma_t$ (H^+, H_2O → acetonitrile) = – 8.1. This is, because proton is well solvated in water but unsolvated in acetonitrile. Roughly this means, that the activity of the H^+ with a concentration of unity is equal to the activity of a $10^{-8.1}$ M solution with respect to H^+ in acetonitrile. Note, that the first member of the right hand side of eq. (1.34) is the largest among the three and usually the transfer activity coefficient of the proton determines the difference in the pK_a-s.

1.6.3 Acid-base reactions in amphiprotic solvents of low permittivity

The examples in this group include t-BuOH (neutral), HAc (protogenic), en (protophilic) (1b, 2b and 3b group in Table 1.4). Because of the amphiprotic character, ionization in these solvents is easy (see table 1.9), but because of the small dielectric constant, the dissociation is not favored. As a result of this, very often ion-pairs are formed in these solvents. Acids, which are strong acids in water, become weak in these solvents. For example, the pK_a of $HClO_4$ is very large in water, but in t-BuOH: 3.9, HAc: 4.9, en: 3.1. Because of the small ε, the conjugated base B forms ion-pair with the solvent SH, to form $(BH^+,S^-)_{solv}$ ion-pair. Even salts consisting of large ions (that is, the distance of closest approach is relatively large) are present in these solvents as ion-pairs (*e.g.*, Et_4NPic in HAc has an ion-pair dissociation constant, $K_{d,ion\text{-}pair} = 1.6 \cdot 10^{-6}$).

1.6.4 Acid-base reactions in aprotic solvents of low permittivity

In this group, solvents like, *e.g.*, pyridine (Py), THF and diethyl-ether (4b and 5 group in Table 1.4) are found. All of them are weakly solvating solvents, and ε_r is also small. Because of this, neither the ionization, nor the dissociation of an electrolyte is favored. During neutralization reactions, ion-pairs are formed, that is $B + HA \leftrightarrow BHA$. The salt often forms polymeric species, and $(BHA)_n$ is formed, which undergoes partial ionization at higher solute concentrations.

1.7 The pH scale in non-aqueous solvents

The concept of pH is widely used for the characterization of the acid-base properties of solutions. By definition, pH = – log $a(H^+)$, where $a(H^+)$ is the activity of the hydrogen ion, expressed as the product of the activity coefficient and concentration on the molal scale (see also in Section 1.6.1).

$$\mathrm{pH} = -\log a(\mathrm{H}^+) = -\log\{m(\mathrm{H}^+)\gamma_\mathrm{m}(\mathrm{H}^+)\} \qquad (1.36)$$

In dilute aqueous solutions, the pH is approximately equal to the negative logarithm of the concentration of the free hydrogen ions, or in other words that of the H_3O^+. The range within which the concentration of the oxonium ion may change in practice, is primarily determined by the autprotolysis of water. The pH of a neutral aqueous solution in the standard state is equal to 7; this is actually $pK_w/2$. In practice, the pH of most of the aqueous solutions falls between 0 and 14. Of course, there are extremely concentrated solutions, the pH of which may be smaller than 0 (*e.g.*, 37% w/w HCl) or larger than 14 (*e.g.*, 50 % w/w NaOH solution); these systems will be dealt with in Chapter 5. Nevertheless, the pK_w in water can be considered as the practical width of the pH-window of aqueous solutions. Analogously, the pH window of the amphiprotic solutions can also be related to the pK_{SH} of the solvent. This is for amphiprotic solvents fall usually between 0 and 20 (see Table 1.3). The situation for aprotic solvents is a bit more complicated. In aprotic solvents, the lyate ions ($S^–$) are often unstable, and/or the autoprotolysis does not take place at all, which is due to the lack of mobile proton in the solvent molecule. For such systems, the autoprotolysis constant cannot be defined as it is given in eq. (1.31-32), rather as $a(SH_2^+)\cdot a(OH^–)$ (for protophilic solvents) or as $a(H_3O^+)\cdot a(OH^–)$ (for protophobic solvents).

In such solvents the pK_{SH} is often higher than 20, and the width of the pH scale can be as big as 40.

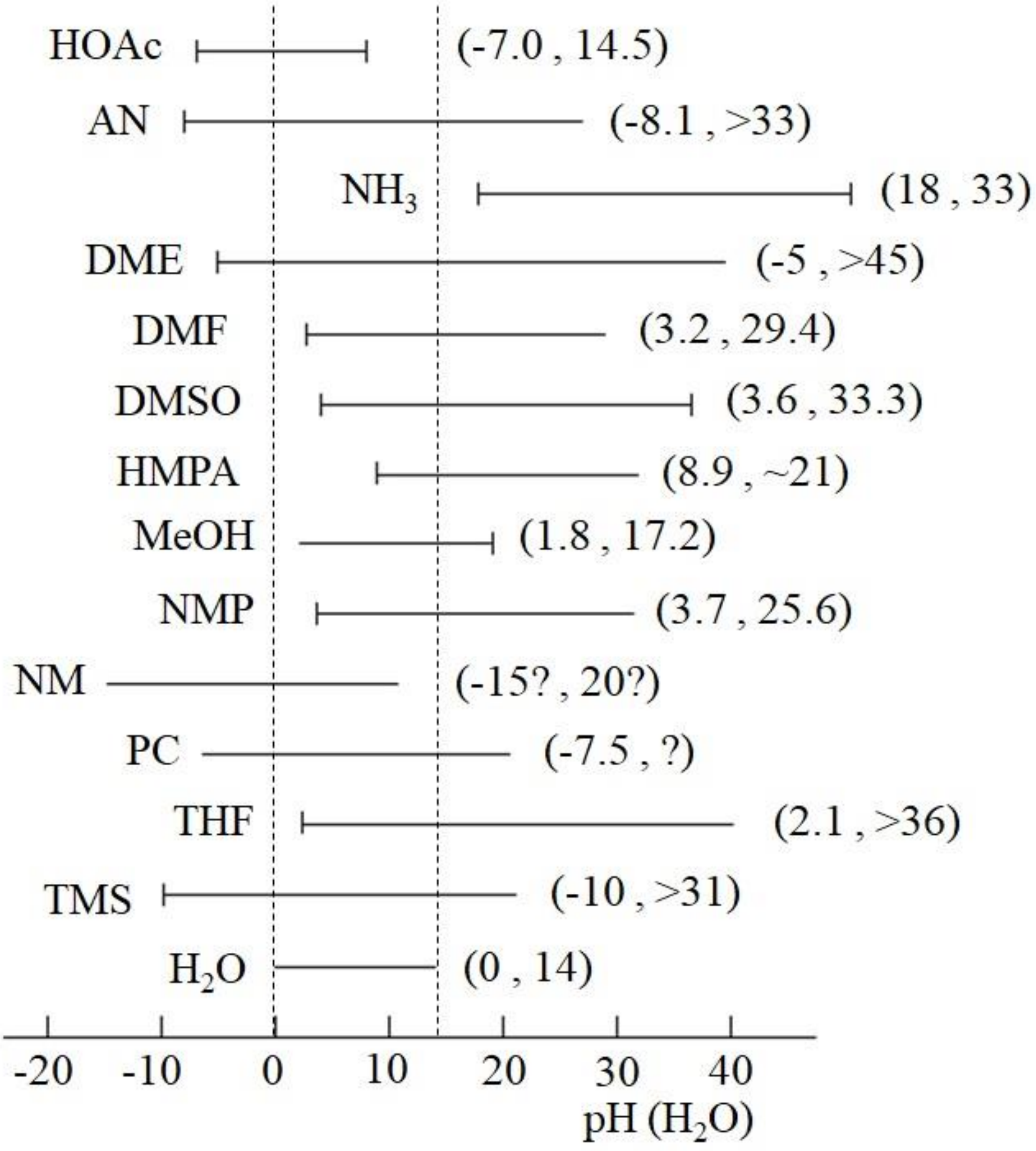


Figure 1.13 pH windows in various solvents shown by a common pH scale. The pH scale in water is used as reference. The values in parentheses correspond to the transfer activity coefficient of the proton from water to the given solvent, $-\log \gamma_t(H^+, W \rightarrow S)$ and the autoprotolysis constant of the solvent SH, pK_{SH}, respectively; on the basis of the data published in [1].

The pH of the solution of $a(H^+) = 1$ mol kg^{-1} is by definition equal to zero in each solvent. As the solvation of H^+ changes from solvent to solvent, the chemical reactivity of H^+ differs in a big way in different solvents. In order to compare the acid-base properties in various solvents, we define a common pH scale to various solvents. The reference is the water, the width of the window, as it was defined above by using the pK_{SH}, and the windows are horizontally shifted relative to each other, by the value of the transfer activity coefficient of the proton from water to the given solvent, $-\log \gamma_t(H^+, W \rightarrow S)$ (Figure 1.13). From Figure 1.13, *e.g.*, in glacial acetic acid, at $[H^+] = 10^{-7}$ mol kg^{-1} proton concentration the activity of the proton, $a(H^+)$ is the same as that at $[H^+] = 1$ mol kg^{-1} in water.

The pH-scale of solvents that are less basic than water, are extended to the left and those which are less acidic than water, are extended to the right, relative to the pH-window of water.

The pH window is shifted to the left. The pH window of solvents that differentiate acids (*e.g.*, CH_3COOH) is shifted to the left from that of the H_2O. In these solvents, the lyonium ion, SH_2^+ (*e.g.*, $CH_3COOH_2^+$, acetonium ion in glacial acetic acid) is very strong acid. Regarding basicity, they are weaker bases, than water.

Acids that are strong (and which are therefore levelled) in water, will be differentiated in such solvents; this means, that their acid strengths will become different. They can be titrated simultaneously (*e.g.*, titration of HCl and $HClO_4$ is possible in glacial acetic acid).

Bases that are weak (and which are differentiated) in water, will become strong bases in such solvents, their strength is levelled. Hence, bases that are not possible to be titrated in water, can be titrated in these solvents (*e.g.*, titration of alkaloids with $HClO_4$ in glacial acetic acid.)

The pH window is shifted to the right. The pH window of solvents (*e.g.*, DMF, DMSO, NMP, THF) that differentiate bases is shifted to the right from that of the H_2O. The lyate ion, S^- is very strong base, but these solvents are much weaker acids, than water.

Bases, which are strong (and are levelled) in water, will be differentiated in such solvents. Their basis strengths will become different; they can be titrated simultaneously.

Acids that are weak (and are differentiated) in water will become strong acids in such solvents, their strength is levelled. Therefore, acids that are not possible to be titrated in water, can be titrated in these solvents.

The pH window is extended beyond both sides of that of the water. The pH window is extended both to the right and to the left from that of the H_2O in some solvents, *e.g.*, acetonitrile, NM, DME, TMS, 4-metil-2-pentane (MIBK). All of them are protophobic, aprotic solvents. As these solvents have very weak acidity and basicity, they are not able to level the acids (low DN) and bases (low AN). The result of this is, that they are able to differentiate both acids and bases. Accordingly, their mixtures can be simultaneously titrated in these solvents. A profound example is shown in Figure 1.14, potentiometric titration curve of a mixture of acids in 4-metil-2-pentane (methyl-isobutyl-ketone, MIBK). The mixture contains HCl, $HClO_4$, acetic acid, salicylic acid and phenol. In water, HCl and $HClO_4$ are strong acids, the other three are weak acids (pK_a-s in water: acetic acid: 4.75; salicylic acid: 2.98; phenol: 9.95). The MIBK is capable of differentiating between HCl and $HClO_4$ as well as between acetic and salicylic acids.

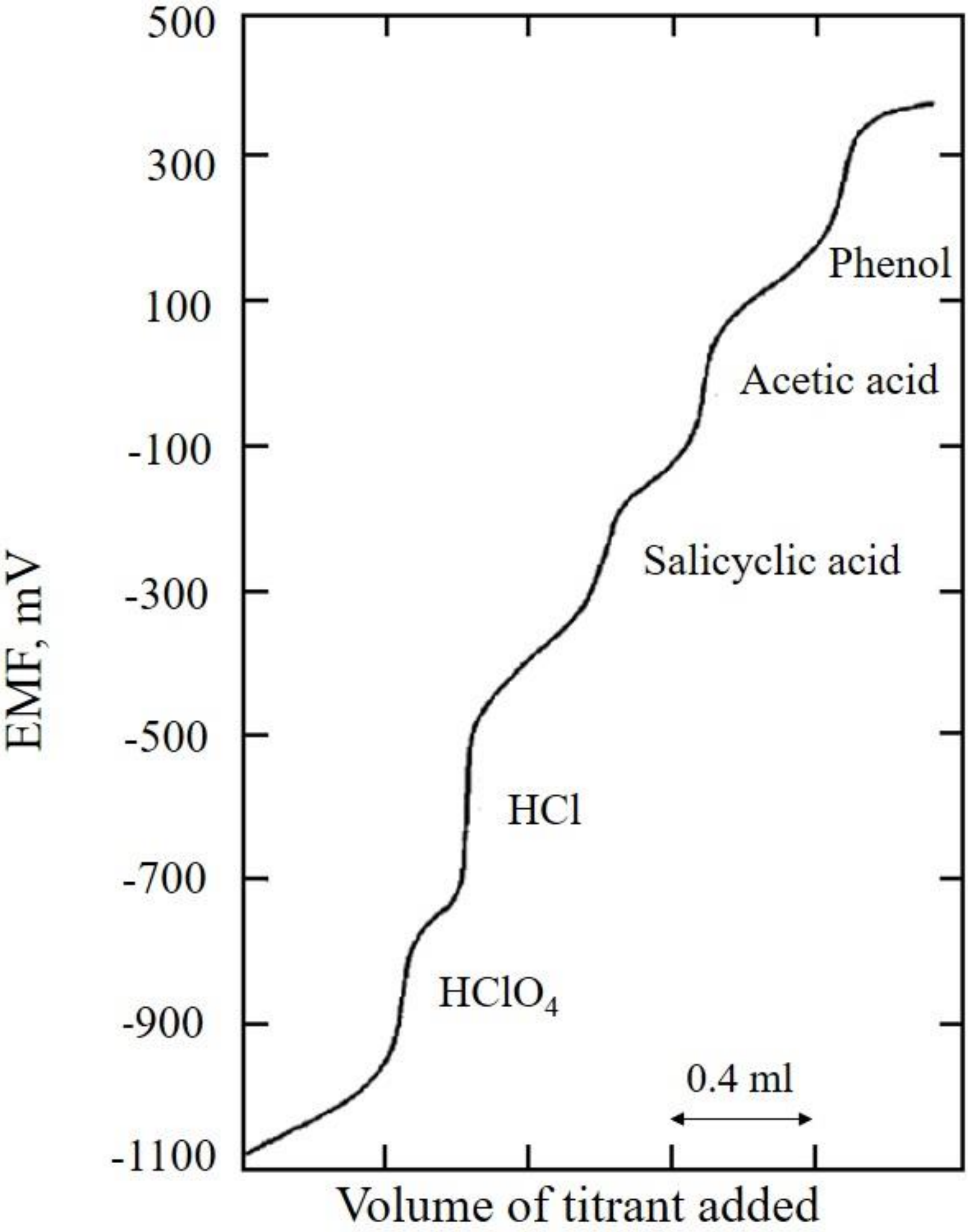


Figure 1.14 Potentiometric titration curve of a mixture of acids in 4-metil-2-pentane (methyl-isobutyl-ketone, MIBK); the mixture is titrated with 0.2M Bu_4NOH using a glass electrode-Pt electrode potentiometric system, where the cell potential is linearly dependent on the pH of the solution; on the basis of the data published in [1].

1.8 Acid-base titrations in non-aqueous solvents

The determination of a component *via* acid-base titration using a non-aqueous solvent becomes necessary, when

1. the component is not sufficiently soluble in water;
2. the component is too weak acid/base in water;
3. we would like to titrate two or more components simultaneously, but their acid/base strength is similar in water (levelled).

Upon selecting the solvent, practical considerations have to be made.

- First, it has to be considered, which of the three reasons above has to be dealt with.
- It has to be checked, if the solvent would enter into chemical (redox) reaction with the solute.
- It has to be checked, if a minimum concentration of 0.01 M of the solute can be prepared in the given solvent (this is the minimum concentration necessary for the
- The price of solvent should be reasonable.
- Sufficiently pure, *i.e.*, water-free solvents are necessary to be used (the presence of water in a non-aqueous solvent often causes the same problem as does CO_2 during the acid-base titrations in water; in other cases, see below, water does not interfere.)

Titrations in non-aqueous solutions are very popular, *e.g.*, in the field of pharmaceutical analyses. The concentration of the active ingredient in pharmaceutical products is determined very often by this method according to the *Pharmacopeia* (in Europe, 36 %, while in the USA: 24% of the analyses are done via acid base titrations in non-aqueous solutions).

Titrant solutions are (just like in aqueous solutions) strong acid or strong base solutions.

For acid titrants, the choice of the acid depends on the nature of the solvent. In amphiprotic, neutral solvents, like EtOH or MeOH, HCl is used most often. In amphiprotic, protogenic solvents, like glacial acetic acid or propionic acid, $HClO_4$ is used instead of HCl, because HCl becomes weak acid in these solvents. For aprotic solvents, most often acetonitrile or dioxane is used. In these solvents, HCl can be used as it is a strong acid.

For base titrants, the Na^+ (or R_4N^+) salt of the lyate ion is used in amphiprotic, neutral solvents, *i.e.*, NaOEt/NaOMe in EtOH/MeOH. In amphiprotic, protogenic solvents, like glacial acetic acid, NaOAc is the basis of choice. In these solvents, NaOH or R_4NOH in amphiprotic solvent must not be used because of H_2O formation. In aprotic solvents the lyate ion does not exist or tends to decompose, therefore in most of the cases R_4NOH (R = Me or Et) in the appropriate non-aqueous solvent is used. In this case, inevitably H_2O is formed, the effect of which must be checked. In some cases, the formation of water may not be problematic.

When acid-base titrations are used for the titration of acids, the solvent is often of basic character, because it increases the strength of the acids. Hence pyridine, DMF, en, *etc*. are used as solvents. The analytes that may be determined this way are, *e.g.*, amino acids – the acidity of carboxyl group (K_a) increases, while the basicity of the amino group (K_b) decreases. Another example is the titration of hydroxi-benzoic acids, where both the phenolic OH and the COOH become stronger acids than they are in water.

During titration of bases, the solvent is preferably of acidic character, as it increases the strength of the bases. Most often glacial acetic acid, occasionally propionic acid used, as solvent. Glacial acetic acid is in particular popular, because its water content can relatively readily be eliminated *via* using acetic-anhydride. The most often titrated analytes are N-containing organic bases, *e.g.*, alkaloids.

The end point of the titration can be indicated visually or instrumentally. Visual indicators, like crystal violet, operate in the same way in non-aqueous solvents as in water. For instrumental end-point detection, most often pH-sensitive glass electrode is used.

1.9 Redox reactions in non-aqueous solutions

During a redox reaction, electrons are exchanged between the reactants, oxidation and reduction take place. Oxidizing partners (oxidants) take electron(s) up, reducing partners (reductants) give electron(s) away. Oxidation and reduction may take place also on the surface of an electrode, this may be either the anode or the cathode.

The actual redox potential of a solution is equal to the cell potential of the following electrochemical cell:

$$\mathrm{Pt}|\mathrm{H}_2(p = p^0)|\mathrm{H}^+(a = 1)(\mathrm{w})\,\vdots\vdots\,\mathrm{Ox}(a_{\mathrm{Ox}}),\ \mathrm{Red}(a_{\mathrm{Red}})(\mathrm{w})|\mathrm{Pt} \qquad (1.37)$$

The potential on the left side (that half-cell is the so-called standard hydrogen electrode, SHE) is by definition 0. The equilibrium potential that appears on the inert redox (Pt) electrode on the right side in this way is equal to the cell potential of the two half cells; it is assumed, that the two sides of the liquid junction between the two half cells are equivalent and that the liquid junction potential is zero. In this case, the actual redox potential of the solution containing the oxidized and reduced form of the same compound with activities of a_{Ox} and a_{Red}, respectively, can be given by the Nernst-Peters equation, if Ox takes up n electrons to form Red:

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_{\mathrm{Ox}}}{a_{\mathrm{Red}}} \qquad (1.38)$$

where E^0 is the redox standard potential of the couple. Separating the activity coefficients and concentrations, the activity coefficients can be melted into the standard potential to obtain the $E^{0'}$ formal potential:

$$E = E^{0\prime} + \frac{RT}{nF} \ln \frac{[\mathrm{Ox}]}{[\mathrm{Red}]} \tag{1.39}$$

For the process

$$\mathrm{M}^{n+} + n\mathrm{e}^{-} \rightleftarrows \mathrm{M} \quad (\mathrm{M\colon metal}) \tag{1.40}$$

the Nernst-Peters equation reads:

$$E = E^{0}_{\mathrm{a}} + \frac{RT}{nF} \ln a\left(\mathrm{M}^{n+}\right) \tag{1.41}$$

where E^0_a is the standard electrode potential of M^{n+}/M. The standard electrode potential depends on the solvation of M^{n+}. Increasing solvation shifts the electrode potential towards the negative values. The standard electrode potentials in different solvents can be compared with the aid of the transfer activity coefficient. When the ion M^{n+} is transferred from solvent R to solvent S, the redox standard potential will change. The difference between the two standard potentials in solvents S and R, $E^0(S)$ and $E^0(R)$ can be expressed as

$$E^{0}(\mathrm{S}) - E^{0}(\mathrm{R}) = \left(\frac{RT}{nF}\right) \ln \gamma_{\mathrm{t}}(\mathrm{M}^{n+},\ \mathrm{R} \rightarrow \mathrm{S}) = \left(\frac{0.0592}{n}\right) \log \gamma_{\mathrm{t}}\left(\mathrm{M}^{n+},\ \mathrm{R} \rightarrow \mathrm{S}\right) \tag{1.42}$$

The experimental determination of the $E^0(S)$ - $E^0(R)$ difference is inherently complex. The potential of the SHE depends on the solvent, and simply changing the solvent on the right side half-cell in eq. (1.37) will introduce an uncertain liquid junction potential to the system. Hence extra thermodynamic assumptions were needed to derive the standard potential values shown in Table 1.12, where E^0 values are given relative to the potential of the SHE in water. Because of this, the values can be considered as approximations.

Table 1.12 Standard potentials of M^{n+}/M electrodes in various solvents, values referred to SHE in water at 25 °C; on the basis of the data published in [1].

Solvents$^{1)}$	**Electrode systems**								
	$H^+/(1/2)H_2$	**Li^+/Li**	**Na^+/Na**	**K^+/K**	**Rb^+/Rb**	**Cs^+/Cs**	**Ag^+/Ag**	**Tl^+/Tl**	**Cu^{2+}/Cu**
H_2O	0.000	-3.040	-2.714	-2.936	-2.943	-3.027	0.799	-0.336	0.339
MeOH	0.10	-2.99	-2.63	-2.84	-2.84	-2.94	0.87	-0.29	0.47
EtOH	0.12	-2.93	-2.57	-2.77	-2.78	-2.87	0.85	-0.26	0.58
PrOH	0.09	-2.93	-2.54	-2.75	-2.75	-2.85	0.81		0.56
TFE				-2.53			1.32		
$En(OH)_2$	0.05	-3.04	-2.74	-2.96			0.81		
Ac				-2.90	-2.90	-2.99	0.89		
PC	0.52	-2.79	-2.56	-2.88	-2.95	-3.10	0.99	-0.22	0.73
FA		-3.14	-2.80	-2.98	-3.00	-3.09	0.64		
DMF	-0.19	-3.14	-2.81	-3.04	-3.04	-3.14	0.58	-0.46	0.25$^{2)}$
DMA			-2.84	-3.06	-3.03	-3.20	0.50		
DMTF		-2.47	-2.31	-2.66		-2.88	-0.26	-0.50	
NMP	-0.26	-3.40	-2.87	-3.05	-3.03	-3.13	0.53	-0.49	
AN	0.48	-2.73	-2.56	-2.88	-2.88	-2.97	0.56	-0.25	0.65$^{2)}$
NM		-2.54	-2.45	-2.74	-2.92	-3.02	1.02		
NB	0.34	-2.65	-2.54	-2.70	-2.75	-2.87		-0.18	
DMSO	-0.20	-3.20	-2.85	-3.07	-3.05	-3.16	0.44	-0.56	0.09
TMS			-2.75	-2.98	-3.04	-3.13	0.76		0.71
HMPA				-3.10			0.32		
1,1-DCE			-2.41	-2.63	-2.64	-2.74			
1,2-DCE			-2.46	-2.67	-2.68	-2.78			

1) TFE = 2,2,2-trifluoroethane, $En(OH)_2$ = 1,2-ethanediol. For other solvents, see Table 1.1.
2) Mean value of the standard potentials for Cu^{2+}/Cu^+ and Cu^+/Cu^0.

When both the oxidized and the reduced form of a compound is in solution (*e.g.*, Fe^{3+}/Fe^{2+}), the following equilibrium takes place:

$$\mathrm{Ox} + n\mathrm{e}^- \rightleftarrows \mathrm{Red} \tag{1.43}$$

$$E = E_c^0 + \frac{RT}{nF} \ln \frac{a_{\mathrm{Ox}}}{a_{\mathrm{Red}}} \tag{1.44}$$

The solvation of the oxidized and the reduced form of the redox couple is different in different solvents. Hence, the variation in E^0_c in various solvents is due to the differences in the solvation of the oxidized and the reduced forms. Determining the variations in E^0_c from solvent to solvent is difficult for the same reason as for that of E^0_a. For these systems, it is possible (in principle) to find redox couples, for which the

$$\log \gamma_t (\mathrm{Ox},\ \mathrm{R} \rightarrow \mathrm{S}) = \log \gamma_t (\mathrm{Red},\ \mathrm{R} \rightarrow \mathrm{S}), \tag{1.45}$$

relationship holds. This means, that the transfer activity coefficient is independent on the oxidation state and is the same for the oxidized and for the reduced form. If this is the case, then the E^0_c of the given redox couple is independent of the solvent. This holds, for example, for the Fc^+/Fc^0 and the BCr^+/BCr^0 redox couples (Figure 1.15). These redox couples are considered to be much more reliable redox reference systems, than the SHE.

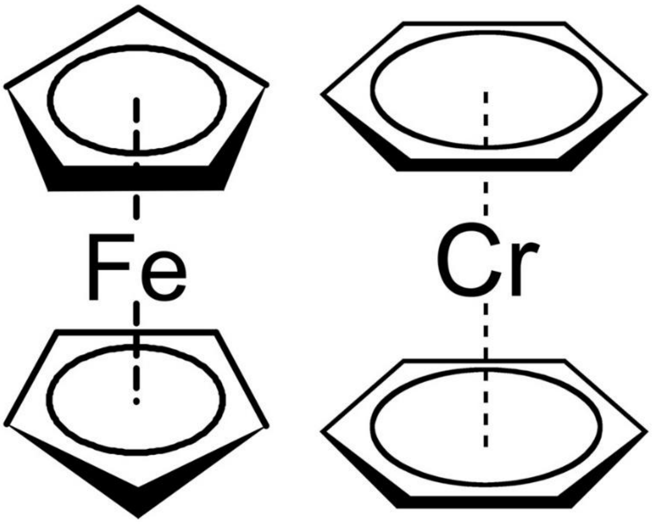


Figure 1.15 The structure of the compounds serving for redox reference purposes.

If the redox couples are metal ions, then with the increasing basicity or permittivity of the solvent, E^0_c is shifted towards the negative potentials:

$[Co(H_2O)_6]^{2+} \rightleftarrows [Co(H_2O)_6]^{3+} + e^-$ $\quad E^0_c = +1.84$ V (1.46)

$[Co(NH_3)_6]^{2+} \rightleftarrows [Co(NH_3)_6]^{3+} + e^-$ $\quad E^0_c = +0.10$ V (1.47)

Complexation exerts effects similar to this, *e.g.*, in aqueous solutions Fe^{3+} forms stronger complex with the PO_4^{3-} ion than does Fe^{2+}; this is why phosphate ions shift the redox potential of the Fe^{3+}/Fe^{2+} couple towards the negative direction. In some specific cases, the cation with the smaller positive charge is solvated more strongly. This is the case with the Fe^{2+} and Cu^+ in acetonitrile: the solvent interaction with the Fe^{2+} and Cu^+ *via* back coordination is stronger than that with Fe^{3+} and Cu^{2+}; for latters, no such specific interaction with the solvent takes place. This is why Cu^{2+} becomes strong oxidant in acetonitrile.

1.9.1 Potential windows of non-aqueous solvents

The potential window (or electrochemical window) of a solvent is the potential range, within which the solvent can be employed to perform redox reaction in it. If the actual redox potential of the solution is more negative, than the edge of this window, the solvent will get reduced; if it is more positive, it will get oxidized. For example, the water at redox potentials more negative than -0.81 V (in presence of 1 M OH^-) will get reduced according to

$$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^- \qquad E^0 = -0.81\ \text{V} \tag{1.48}$$

while at redox potentials more positive than +1.23 V (in presence of 1 M H^+) will get oxidized according to

$$2H_2O \rightleftarrows O_2 + 4\,H^+ + 4e^- \qquad E^0 = +1.23\ \text{V} \tag{1.49}$$

Both processes are well defined and the width of this potential window is 1.23 V at any pH, and shifts by 0.059 V whenever the pH changes one unit.

For solvents other than water, the situation is often complicated. For most of the solvents, it is hard, sometimes impossible to experimentally determine the potential window. The reduction reaction in amphiprotic solvents (MeOH, EtOH, *etc.*) is often analogous to that for water according to eq. (1.48). The oxidation as in eq. (1.49) is often ambiguous, and multiple parallel processes take place. In aprotic solvents, very often both the oxidation and the reduction is the resultant of several parallel processes.

Potential windows in various solvents based on a common potential scale (*vs*. Fc^+/Fc^0) obtained by voltammetry at a smooth Pt electrode is shown in Figure 1.16.

The potential window of some solvents entail more negative potential range than does water (*e.g.*, DMF, DMSO, PC, AN, *etc.*) All of them are weak acids, weaker acids than water. They can only be reduced with using strong reducing agents. This also means, that one can prepare a stable solution of a strong reducing agent using these solvents (as opposed to water). Such solvents are suitable for being used as medium for reducing compounds that have very negative reduction potential.

The potential window of other solvents is extended towards the positive potential range relative to water (for example, AcOH, CH_2Cl_2, acetonitrile, PC, NM, TMS, *etc.*) All of them are weak bases, weaker than water. They can only be oxidized with using a very strong oxidizing agent. This also means that one can prepare a stable solution of a strong oxidizing agent using these solvents (as opposed to water). Such solvents are suitable for being used as medium for oxidizing compounds that have very positive oxidation potential.

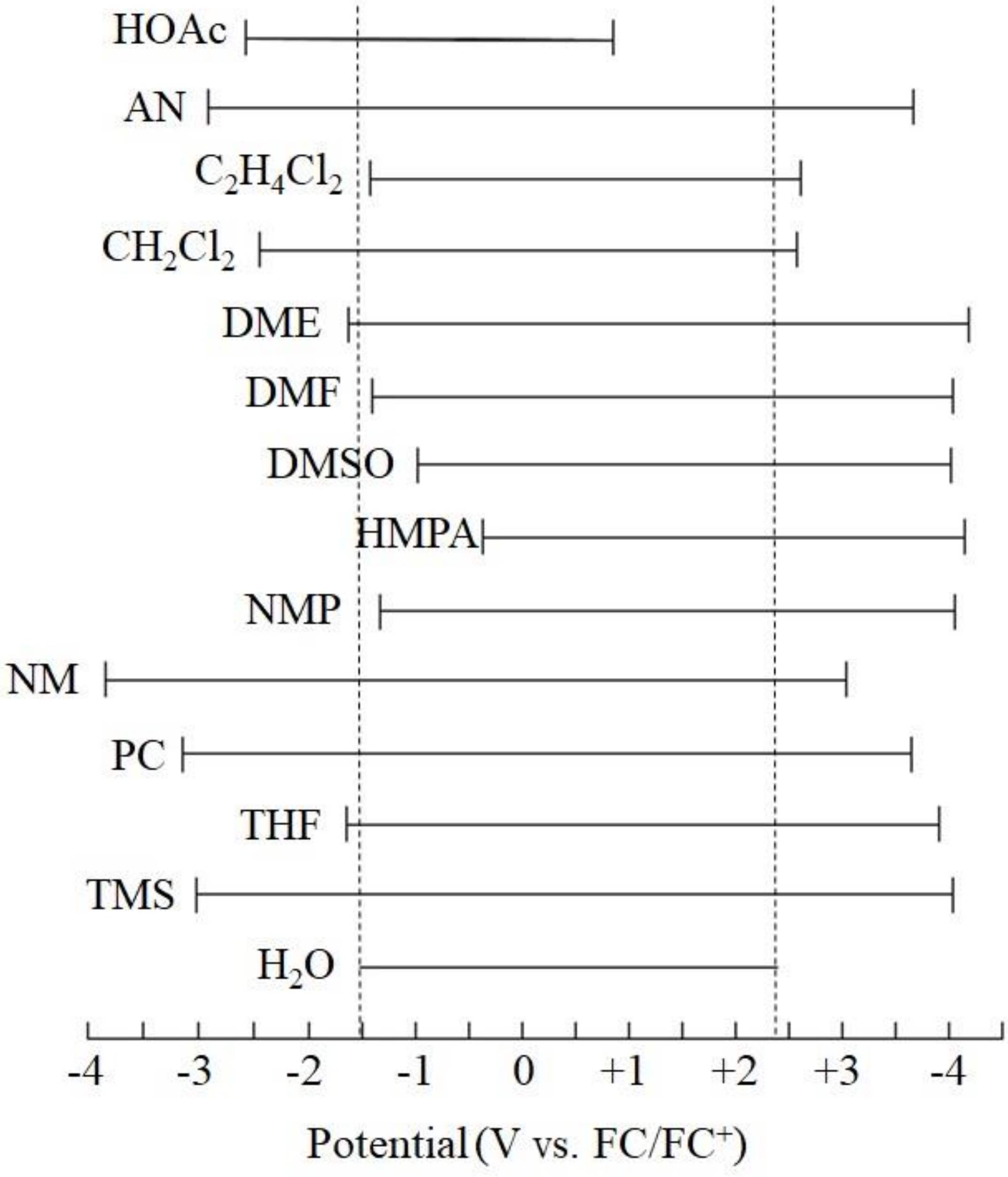


Figure 1.16 Potential windows in various solvents based on a common potential scale (*vs*. Fc^+/Fc^0). Obtained by voltammetry at a smooth Pt electrode at 10 μAmm^{-2}; on the basis of the data published in [1]

1.10 Questions and problems

1. In the chemical practice, when do we need to use non-aqueous solvents instead of water (reasons and examples)?
2. What are the most important physical properties of non-aqueous solvents, that affect their applicability in chemistry (give list, brief definitions and example, how the given property affects applicability!)
3. Define the relative permittivity of a liquid! How can we experimentally determine relative permittivity?
4. Classify non-aqueous solvents on the basis of their relative permittivity!
5. Define the Debye-relaxation! What are the Debye- and non-Debye solvents (with examples and reasons)!
6. Is the water a Debye- or a non-Debye solvent? Why? What kinds of relaxation processes can be observed in water at room temperature and based on this, characterize the structure of the liquid water at room temperature!
7. Define the acidity and basicity of a solvent!
8. Define and specify the way of determination of the Guttmann’s donor number!
9. Define and specify the way of determination of the acceptor number according to Kosower and to Diemroth-Reichardt!
10. Define and specify the way of determination of the acceptor number according to Guttmann-Meyer-Geiger!
11. Describe the properties of the amphiprotic, neutral solvents (with examples) on the basis of the classification of solvents according to Kolthoff!
12. Describe the properties of the amphiprotic, protogenic solvents (with examples) on the basis of the classification of solvents according to Kolthoff!

13. Describe the properties of the amphiprotic, protophilic solvents (with examples) on the basis of the classification of solvents according to Kolthoff!
14. Describe the properties of the aprotic, dipolar, protophilic solvents (with examples) on the basis of the classification of solvents according to Kolthoff!
15. Describe the properties of the aprotic, dipolar, protophobic solvents (with examples) on the basis of the classification of solvents according to Kolthoff!
16. Describe the properties of the aprotic, inert solvents (with examples) on the basis of the classification of solvents according to Kolthoff!
17. What is the relationship between the solubility of an electrolyte and the heat of dissolution?
18. Characterize the ion-solvent interactions, and describe the Born equation and its consequences!
19. Describe the structure of solvated ions, the solvation number, together with their definition and the ways of their determination.
20. Describe the solvation of ions in solvent mixtures!
21. What is the relationship between the permittivity of solvents and the association of ions on the basis of the Bjerrum-Fouss theory?
22. Describe the formation and structure of ion-pairs in terms of types, structure, and experimental approaches for their characterization!
23. Describe the main features of the acid base reactions in amphiprotic solvents with large dielectric constant!
24. Describe the main features of acid base reactions in aprotic solvents with large dielectric constant!
25. Describe the main features of acid base reactions in amphiprotic solvents with small dielectric constant!

26. Describe the main features of acid base reactions in aprotic solvents with small dielectric constant.
27. What is the definition of the pH scale in non-aqueous solvents? How can we apply the transfer activity coefficient for the comparison of pH values?
28. Describe the general features of acid-base titrations in non-aqueous solvents! What kind of components can be determined this way, what are the titrant solutions, how can we detect the end point?
29. What kind of components can be determined and how with using acid-base titrations in non-aqueous solutions?
30. What are the general features of redox reactions in non-aqueous solvents?
31. How can we define the potential windows for non-aqueous solvents and why are they useful?

Chapter 2 High temperature melts of inorganic compounds

2.1 Introduction

In this chapter, we will cover some aspects of the melts of inorganic compounds. These are, in general, high temperature liquids which are produced *via* the fusing of inorganic compounds, which upon melting (or up to the melting temperature), do not undergo chemical transformation and keep their chemical integrity. How high this "high temperature" can be – this depends on the type of the compound or compounds:

1. Melts of inorganic salts, *e.g.*, alkali metal halides can be prepared if the temperature is risen to 500-1200 °C, note, however, that the melting point of some organic salts can be close to the room temperature, *e.g.*, the melting point of $EtNH_3^+NO_3^-$ is 14 °C; we will cover these ionic liquids in Chapter 3;
2. Metal oxides can be melted at temperatures that are usually higher than those of the inorganic salts, that is 1500 – 3000 °C.
3. Metals are fused entailing a very wide range of temperature, *e.g.*, the melting point of the mercury is −40 °C, while that of the tungsten is 3422 °C.
4. When certain salts are mixed, the mixture's melting point may be significantly lower, than that of the pure components, for example the melting point of the eutectic mixture of $AlCl_3$/NaCl/KCl can be as low as 89 °C.

Melts are excellent "solvents" of several compounds, that are capable of "surviving" the high operating temperatures. The properties of melts (similarly to those of mixtures of molecular liquids) can be fine-tuned *via* mixing various components. For example, the melting point of $Na_3[AlF_6]$ is 1003 °C while that of the Al_2O_3 is 2000 °C. In melts containing both $Na_3[AlF_6]$ and Al_2O_3, the melting point can be brought below 1000 °C – this is used, for example, in the Hall-Herault process which is developed to manufacture aluminum *via* electrolysis (see below). Certain melts (*e.g.*, the molten alkali metal halides) are chemically stable at temperatures well over the melting point. Because of their high heat capacity, melts can be used in heat exchangers. The excellent electric conductivity of some melts can also be utilized.

In practice, molten compounds are used in a variety of fields, like in solar- and atomic power stations, production of metals (Al, Fe), glass production, fabrication of fuel cells, just to mention a few.

Table 2.1 Some physical properties of molten chloride salts; on the basis of the data published in [2].

Salt	**χ_M**	**Crystal**	**T_m(K)**	**ΔS_m(e.u.)**	**$\Delta V_m/V_l$**	**$\sigma(\Omega^{-1}cm^{-1})$**	**η(cp)**
NaCl	0.40	NaCl	1074	6.30	0.28	3.6	1.0
CuCl	1.20	Wurtzite	696	2.43	0.16	3.7	4.1
$SrCl_2$	0.55	CaF_2	1146	3.44	0.11	2.0	3.7
$CaCl_2$	0.60	$CaCl_2$	1045	6.44	0.043	2.0	3.4
$MgCl_2$	1.28	$CdCl_2$	980	9.74	0.28	1.0	2.2
$HgCl_2$	1.32	$HgCl_2$	554	9.11	0.21	$3x10^{-5}$	1.6
$ZnCl_2$	1.44	$ZnCl_2$	570	4.09	0.14	$1x10^{-3}$	$4x10^{3}$
$LaCl_3$	0.705	UCl_3	1131	11.49	0.16	1.3	6.7
YCl_3	0.66	$AlCl_3$	994	7.56	0.0045	0.39	--
$FeCl_3$	0.99	$FeCl_3$	573	17.80	0.39	0.04	--
$AlCl_3$	1.66	$AlCl_3$	466	18.14	0.47	$5x10^{-7}$	0.36
$GaCl_3$	1.68	$GaCl_3$	351	7.84	0.17	$2x10^{-6}$	1.8
$SbCl_3$	2.08	$SbCl_3$	346	8.96	0.17	$2x10^{-4}$	--

Some physical properties of molten chloride salts are collected in Table 2.1. Comparing the data in the last two columns of Table 2.1, they can be classified into 3 groups.

1. **Ionic melts**: these are molten salts with high conductivity and low viscosity, *e.g.*, NaCl, $MgCl_2$, and their melts consists of individual ions (high conductivity) which are not organized to some sort of network (low viscosity).
2. **Molecular melts**: these are molten salts with low conductivity and low viscosity, *e.g*., $HgCl_2$, $AlCl_3$, $SbCl_3$. They consist mainly of undissociated molecules (low conductivity) which are not in interaction with each other (low viscosity).
3. **Network forming melts**: molten salts with low conductivity and high viscosity, *e.g.*, $ZnCl_2$. In these, the molecules form a network (high viscosity) and they lack conducting particles (low conductivity).

2.2 Some properties of ionic melts, in particular those of molten alkali metal halides

In the ionic melts, Coulombic interactions prevail: ions with opposite charge attract, ions with identical charge repulse each other. During melting, the extent of the decrease in the ordering of the ions is much smaller, than during dissolution (Figure 2.1). The solid salts are insulators, the enhanced conductivity of melts is a clear proof of their ionic character. In ionic melts, there is no coordination chemical interaction between the ions; the system can be reasonably well modeled with hard, incompressible balls (bearing balls) in a box. Statistically, *e.g.*, cations are surrounded by anions in the immediate vicinity, and the second neighbors are mostly cations. Some association between the ions may take place (guided by Coulomb forces), as it was demonstrated by conductometric measurements of ionic melts.

In molten state, in an MX melt (see Table 2.2) the coordination number decreases (relative to the solid crystalline state). In parallel to this, due to Coulomb forces, in the melt the cation-anion distance ($d_{(l)}$ in Table 2.2) decreases relative to that in the crystalline state ($d_{(s)}$ in Table 2.2).

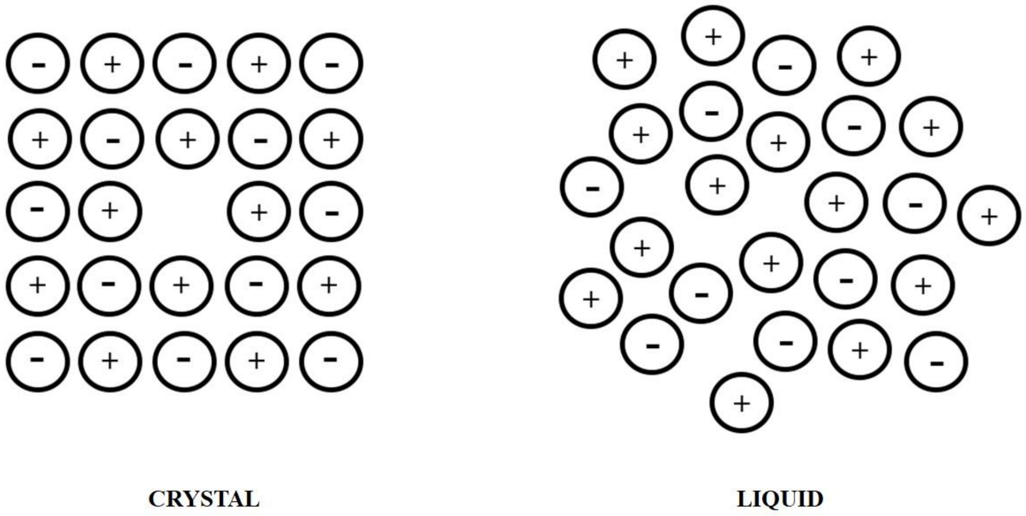


Figure 2.1 Schematic representation of the crystal and the melt of an ionic compound; on the basis of the data published in [2].

Table 2.2 The cation-anion distance and coordination number in alkali metal halides in the solid ($d_{(s)}$), liquid ($d_{(l)}$) and gaseous ($d_{(g)}$) state; on the basis of the data published in [3].

Salt	**$d_{(s)}$ (nm)**	**Coord. number**	**$d_{(l)}$ (nm)**	**Coord. number**	**$d_{(g)}$ (nm)**
LiF	0.201	6	0.195	3.7	0.153
LiCl	0.257	6	0.247	4.0	0.203
LiBr	0.275	6	0.268	5.2	0.217
LiI	0.300	6	0.285	5.6	0.239
NaF	0.231	6	0.230	4.1	0.184
NaCl	0.282	6	0.280	4.7	0.236
NaBr	0.299	-	0.298	-	0.250
NaI	0.329	6	0.315	4.0	0.271
KF	0.267	6	0.266	4.9	0.213
KCl	0.314	6	0.310	3.7	0.267
KBr	0.331	-	0.330	-	0.282
KI	0.354	-	0.353	-	0.305
RbF	0.282	-	0.273	-	0.225
RbCl	0.330	6	0.329	4.2	0.279
RbBr	0.343		0.342	-	0.295
RbI	0.367		0.366	-	0.318
CsF	0.301		0.282	-	0.235
CsCl	0.359	6	0.353	4.6	0.291
CsBr	0.362	8	0.355	4.6	0.307
CsI	0.385	8	0.383	4.5	0.332

On the basis of the compressibility of melts, the free (available) volume can be estimated as about 2% of the total volume. This can be explained by assuming, that vacancies (holes) are present in these ionic melts. Experimentally this was proven in the following way. It was estimated, that in $LiClO_3$ melts, the size of a vacancy is sufficient to accommodate a nitrobenzene molecule, but it is too large for a methanol molecule. When nitrobenzene was added to the $LiClO_3$ melt, the conductivity of the system drastically decreased: the organic molecule blocked the vacancies and prohibited the migration off the electric charges *via* hopping from vacancy to vacancy. On the contrary, addition of methanol did not cause this drop, that is: it did not fill up the holes, due to its smaller size.

Bockris and Richard made calculations to estimate the average size of a vacancy, v_i, and they found that it is directly related to the surface tension, γ, of the melt

$$v_i = 0.68\sqrt{\frac{kT}{\gamma}} \qquad (2.1)$$

where k is the Boltzmann constant and T is the absolute temperature. From this, the average number of vacancies in 1 mole of melt, N, can be computed:

$$N = \frac{\Delta V}{v_i} \qquad (2.2)$$

where ΔV is the increase in the molar volume upon melting. From this it can be estimated, that every 5th or 6th position is vacant in, *e.g.,* a molten alkali metal halide.

We already stated it, that in the MX melt, the cation-anion distance ($d_{(l)}$ in Table 2.2) decreases relative to that in the crystalline state ($d_{(s)}$ in Table 2.2).The average distance between the cations and that of the anions, on the other hand, increases, again due to Coulomb interactions. As a result of these effects, the molar volume in the molten state increases by *ca.* 25% relative to the solid crystalline state (See Table 2.2 and also Table 2.1). The value of $\Delta V_{fus}/V_s$ depends on the polarizability of the anion: it decreases with the increasing polarizabilty.

Table 2.3 Melting point (T_{fus}) and the relative increase in the molar volume ($\Delta V_{fus}/V_s$) of alkali metal halides; on the basis of the data published in [3].

Salt	T_{fus} (K)	$\Delta V_{fus}/Vs$ (%)	ΔS_{fus} (J/mol x K)
LiF	1121	29.4	24.2
LiCl	883	26.2	22.6
LiBr	823	24.3	21.3
NaF	1268	27.4	26.3
NaCl	1073	25.0	25.9
NaBr	1020	22.4	25.5
NaI	933	18.6	25.1
KF	1131	17.2	25.1
KCl	1043	17.3	25.5
KBr	1007	16.6	25.5
KI	954	15.9	25.1
RbCl	995	14.3	23.8
RbBr	965	13.5	24.2
CsCl	920	10.0	22.2

The equation of state for MX melts was first developed by Reiss, who estimated the work that is necessary to create a spherical cavity in a liquid consisting of hard balls. From this,

$$\frac{pV}{RT} = \frac{1+Y+Y^2}{(1-Y)^3} \tag{2.3}$$

where

$$Y = \frac{\pi a^3 N}{6V} \tag{2.4}$$

and N is the Avogadro constant, V is the molar volume and a is the diameter of the spheres. This theory was further developed by Fellner, Danek, Vasu and Thorne, who used these equations to predict the viscosity and conductivity of molten MX compounds (Table 2.4).

Table 2.4 Experimental and calculated viscosities and conductivities of molten alkali metal halides at T = 1.05 T_{fus}; on the basis of the data published in [3].

MX	T (K)	α (nm)	*F*	η_{exp} (cP)	η_{calc} (cP)	κ_{exp} (S/cm)	κ_{calc} (S/cm)
LiF	1174	0.195	1.46	2.05	2.33	8.80	10.03
LiCl	927	0.247	1.45	1.49	1.58	5.95	5.92
LiBr	864	0.268	1.42	1.55	1.41	4.92	4.84
LiI	758	0.285	1.47	2.19	1.68	3.96	3.41
NaF	1331	0.230	1.38	1.65	2.07	5.10	5.55
NaCl	1127	0.280	1.35	1.19	1.26	3.74	3.98
NaBr	1074	0.298	1.34	1.23	1.34	3.06	2.98
NaI	982	0.315	1.38	1.31	1.31	2.40	2.49
KF	1185	0.270	1.31	Ð	1.72	3.73	3.60
KCl	1095	0.310	1.33	1.02	1.21	2.29	2.77
KBr	1058	0.330	.130	1.04	1.32	1.74	2.02
KI	1006	0.353	1.31	1.43	1.43	1.38	1.48
RbF	1100	0.273	1.44	Ð	204	Ð	299
RbCl	1037	0.330	1.29	1.19	1.51	1.62	1.84
RbBr	1001	0.342	1.29	1.33	1.58	1.20	1.47
RbI	959	0.366	1.29	1.27	1.56	0.94	1.15
CsF	1003	0.282	1.44	Ð	208	2.53	2.63
CsCl	964	0.353	1.24	1.17	1.44	1.25	1.49
CsBr	954	0.355	1.29	Ð	1.61	0.91	1.25
CsI	939	0.385	1.26	1.66	1.70	0.73	0.88

Alkali metal halide melts can be used as solvents. They dissolve *e.g.*, noble gases which physically dissolve in them (obey the Henry law.) Other gases may get into chemical interaction with molten alkali metal halides, like, *e.g.*, $TiCl_4$ or $ZrCl_4$ interacts with KCl or NaCl *via* complex formation:

$$2\ NaCl + TiCl_4 \rightleftarrows Na_2[TiCl_6] \qquad (2.5)$$

$$2\ KCl + ZrCl_4 \rightleftarrows K_2[ZrCl_6] \qquad (2.6)$$

Davy in the middle of the XIXth century observed, that during the electrolysis of alkali metal hydroxides, the color of the melts changed, which was explained in terms of the dissolution of the metal in the melt of the compound, from which it was obtained. Later, it was also observed, that alkali metals readily dissolve in alkali metal halide melts too. For example, when Cs is dissolved in CsI (Figure 2.2), the solution turns orange-red. The absorption maximum of the dissolved alkali metal is at *ca.* 620 nm. In the melt, solvated electrons and ions are present, this causes the discoloration of the melt. In these systems, the formation of M_2^0 diatoms and M_2X^+ triplets are also possible.

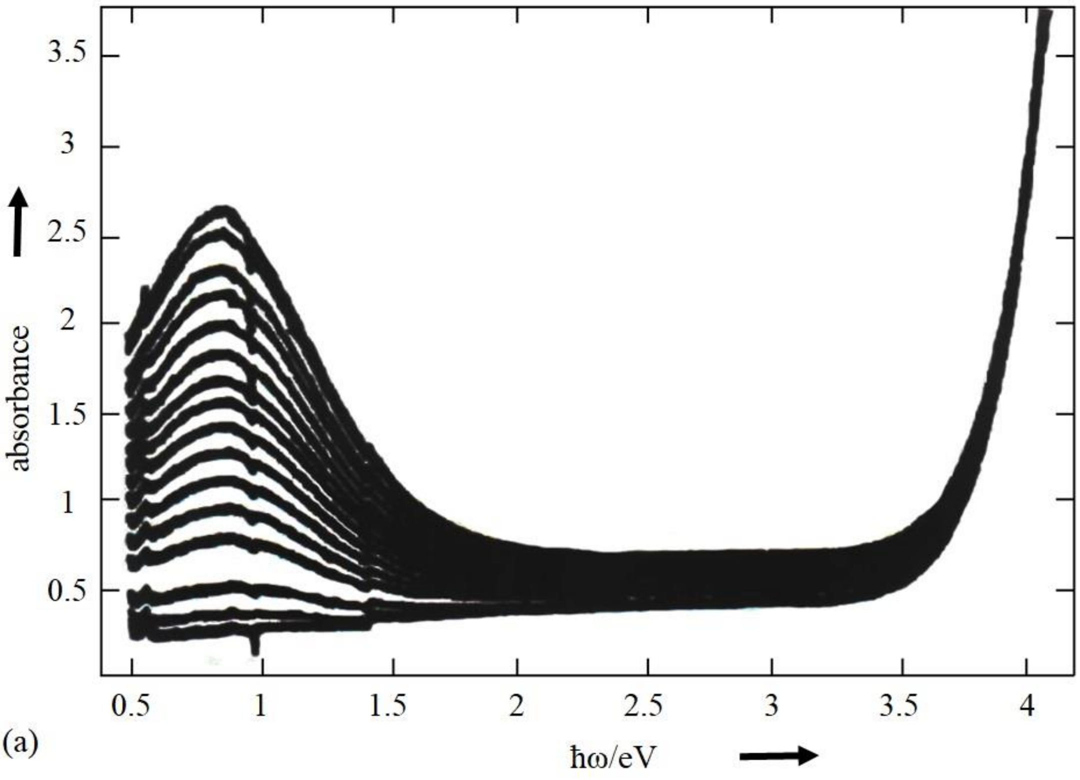


Figure 2.2 Optical absorption of CsI melt containing various amounts of dissolved Cs metal. Lowest curve: pure CsI; uppermost curve: CsI containing 3.91 mol% Cs metal; on the basis of the data published in [2].

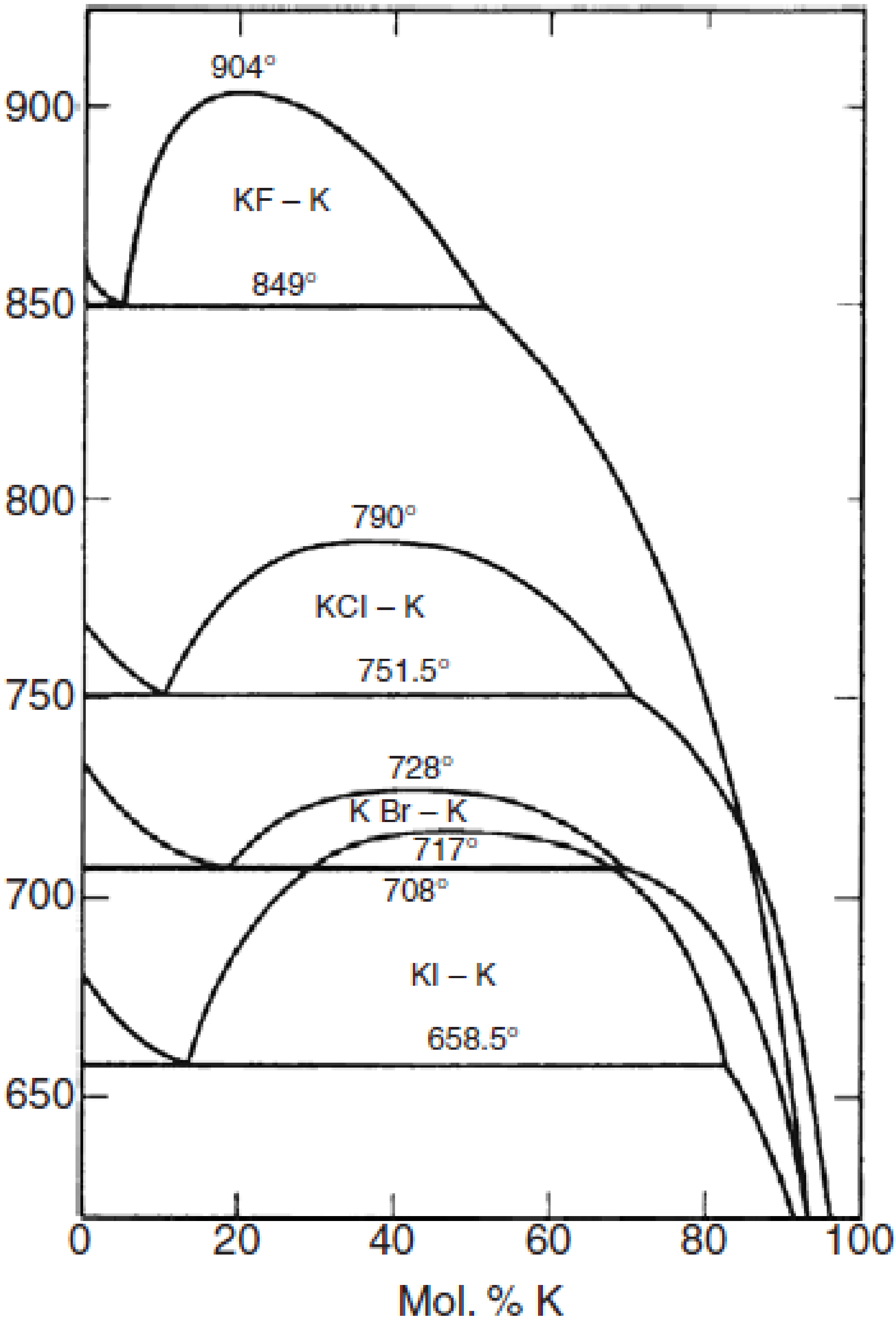


Figure 2.3 Phase diagram of the KX/K systems; on the basis of the data published in [3].

The phase diagrams of MX/M systems were determined by Bredig (Figure 2.3). He demonstrated, that there is no chemical interaction between the metal and the salt: the metal can be recovered from the melt without being chemically transformed (unlike upon the dissolution of Hg in $HgCl_2$ or Bi in $BiCl_3$; in the first case, Hg_2Cl_2, while in the second, a series of compounds, like Bi_9^{5+}, $BiCl_5^{2-}$, $Bi_2Cl_8^{2-}$, are formed.) The solubility increases in $Li^+ \rightarrow Cs^+$ and $F^- \rightarrow I^-$ direction and the metal decreases the melting point of the salt.

The dissolution of salts in MX melts is of importance in, *e.g.*, the industrial scale production of aluminum. The structure of the Al in the molten state was determined from the ^{27}Al-NMR spectra, while that in the solid state from the structure of its crystals. The Al in the solid AlF_3 crystals is present in octahedral state (each Al(III) is surrounded by 6 F^- ions). The coordination sphere is similar in the solid $Na_3[AlF_6]$ (cryolite). When NaF and $Na_3[AlF_6]$ are mixed in various proportions and are molten, a series of Al-containing species will form. The cryolite dissociates:

$$Na_3AlF_6 \rightleftarrows 3\ Na^+ + AlF_6^{3-} \qquad (2.7)$$

the AlF_6^{3-} anion further dissociates:

$$AlF_6^{3-} \rightleftarrows AlF_4^- + 2\ F^- \qquad (2.8)$$

and the products interact with the fluoride ions:

$$AlF_6^{3-} \rightleftarrows AlF_5^{2-} + F^- \qquad (2.9)$$

$$AlF_5^{2-} \rightleftarrows AlF_4^- + F^- \qquad (2.10)$$

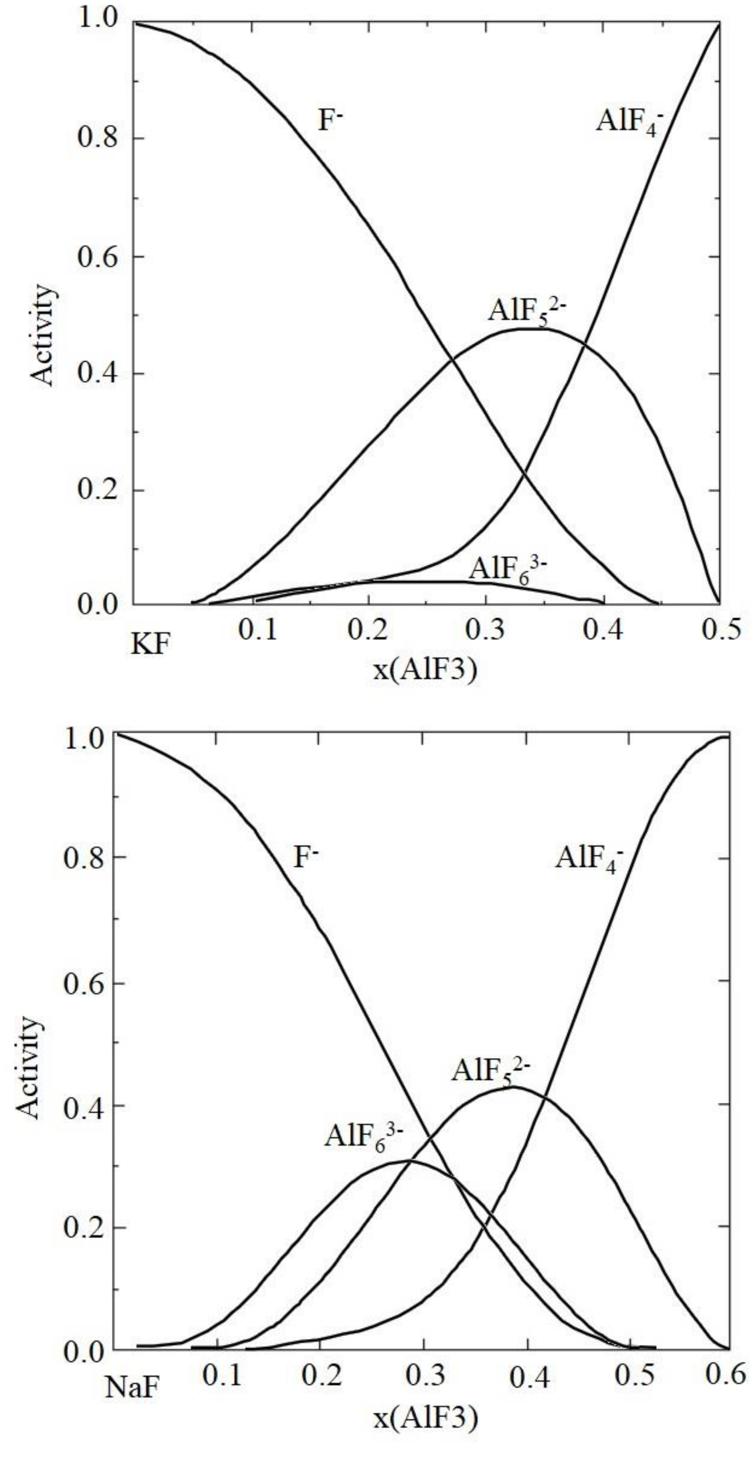


Figure 2.4 The species distribution diagram of NaF/AlF_3 (bottom) and KF/AlF_3 (top) melts from ^{27}Al NMR measurements; on the basis of the data published in [3].

The equilibria in eq. (2.8-2.10) depend on the actual concentration of the fluoride ions. The ^{27}Al NMR spectroscopy is a very useful tool for identifying the structure of the Al in melts, where a variety of coordination modes are present simultaneously. The chemical shift of Al is around 0-20 ppm in 6-coordinated, 30-50 ppm in 5-coordinated and 70-90 ppm in 4-coordinated Al-complexes. If the chemical exchange is slow between the coexisting species, the signal of the various species occurs separately on the NMR spectrum. For Al-complexes, this is very often the case. Hence, from the ^{27}Al NMR spectrum, the structure and (from the signal intensity) the concentration of these species can be obtained.

In Figure 2.4, the species distribution diagram obtained for NaF/AlF_3 and KF/AlF_3 are shown. From these diagrams it can clearly be seen, that Al(III) ions may be present in 4-, 5- and 6-coordinated state, depending on the amount of added NaF or KF. In pure AlF_3 melt, the Al is exclusively in AlF_4^- form. Upon addition of KF and NaF, the transformation to AlF_5^{2-} and AlF_6^{3-} is only partial and depends on the cation used.

These findings are of relevance in the production of aluminum metal during the Hall-Herault process. In pure cryolite melts (at T = 1000 ^oC), the AlF_6^{3-} ion is partially transformed to AlF_3, AlF_4^-, AlF_5^{2-} , AlF_6^{3-} ans $Al_2F_{11}^{5-}$.

In molten alumina (Al_2O_3, T_{fus} = 2000 ^oC) the following equilibria hold:

$$Al_2O_3 \rightleftarrows 2\ AlO^+ + O^{2-} \qquad (2.11)$$

$$Al_2O_3 \rightleftarrows AlO^+ + AlO_2^- \qquad (2.12)$$

Alumina is soluble in molten cryolite up to *ca.* 1 M at ca. 1000 ^oC. The AlF_4^- is a strong O^{2-} acceptor (see next chapter), and the following reaction takes place:

$$Al_2O_3 + AlF_4^- \rightleftarrows 3\ AlO^+ + 4\ F^- \qquad (2.13)$$

In dilute cryolite melts, reaction 2.13 is quantitatively shifted towards the right side, therefore in such melts, the Al(III) is quantitatively present in AlO^+ form. This species is reduced on the cathode according to

$$AlO^+ + 3\ e^- \longrightarrow Al + O^{2-} \qquad (2.14)$$

During the electrolysis, the processing parameters have to be set to keep the concentration of AlO^+ as high as possible. For this, the equilibrium concentration of AlF_4^- has to be maximized, which can be obtained from diagrams similar to those shown in Figure 2.4.

2.3 Acid-base reactions in melts

Melts containing mobile proton – in such systems, the acidic character is connected to the proton, and the theory which discusses these reactions is deducible from the Brönsted-Lowry acid-base theory.

Perhaps the most plausible example is the molten NH_4NO_3 (T_{fus} = 170 °C), which is often used during digestions. The dissolution of a metal-oxide takes place as follows:

$$2\ NH_4NO_3 + CaO \rightarrow Ca(NO_3)_2 + 2\ NH_3 + H_2O \qquad (2.15)$$

The process is analogous to that in water:

$$2\ HNO_3 + CaO \rightarrow Ca(NO_3)_2 + H_2O \qquad (2.16)$$

The dissolution of a metal in molten NH_4NO_3:

$$2\ NH_4NO_3 + Ca \rightarrow Ca(NO_3)_2 + 2\ NH_3 + H_2 \qquad (2.17)$$

The same process in water:

$$2\ HNO_3 + Ca \rightarrow Ca(NO_3)_2 + H_2 \qquad (2.18)$$

The dissolution of Cu in molten NH_4NO_3:

$$3\ NH_4NO_3 + Cu \rightarrow Cu(NO_3)_2 + 2\ NH_3 + N_2 + 3\ H_2O \qquad (2.19)$$

A further analogy is, that the NH_4NO_3 – NH_4Cl melt is the melt analogue of the *aqua reg*ia (HNO_3-HCl mixture in water), which is suitable for dissolving Au, Pt, Pd or for the oxidation of Mn(II) to MnO_4^- or Cr(III) to CrO_4^{2-}, *etc.*

Acid-base reactions in molten salts that does not contain proton. The example here is $HgBr_2$, where the acid-base character is associated with the exchange of the anion (bromide that is) among the various species. During the autodissociation of $HgBr_2$, the following reaction takes place:

$$2\ HgBr_2 \rightleftarrows HgBr^+ + HgBr_3^- \qquad (2.20)$$

When an acid is dissolved in molten $HgBr_2$, that is $Hg(ClO_4)_2$, upon its dissolution the cation of the solvent is generated:

$$Hg(ClO_4)_2 + HgBr_2 \rightleftarrows 2\ HgBr^+ + 2ClO_4^- \qquad (2.21)$$

Conversely, when a base is dissolved in molten $HgBr_2$, that is KBr, upon its dissolution the anion of the solvent is generated:

$$KBr + HgBr_2 \rightleftarrows K^+ + HgBr_3^- \qquad (2.22)$$

When an acid and a base react in a neutralization reaction, the solvent and a salt is produced:

$$(HgBr)ClO_4 + KHgBr_3 \rightleftarrows 2HgBr_2 + KClO_4 \qquad (2.23)$$

acid base solvent salt

Accordingly, in $HgBr_2$, acid is a compound, which upon dissolution increases the concentration of the cation of the solvent, $HgBr^+$ and base is the compound which upon dissolution increases the concentration of the anion of the solvent, $HgBr_3^-$.

Acid-base reactions in molten oxides. The chemistry of molten oxides is of immense relevance in a variety of industrial processes. Regarding their acid-base characteristics, Lux in 1939 suggested that the acidity should be associated with the exchange of the oxygen ion, O^{2-}. Following this, the quantitative characterization of acid-base equilibria *via* determining the respective dissociation constants was made by Flood. As the acid-base theory of oxide melts is a sub-section of that created by Lewis, the entire theory is often quoted the Lewis-Lux-Flood acid-base theory.

In molten oxides, the acid-base character can be described in terms of the exchange of the oxygen ion, that is, acids are those which take up (accept) and bases are those which donate (release) O^{2-} (*n.b.*, in molten $HgBr_2$, the bromide ion has an identical role.)

$$CaO \rightleftarrows Ca^{2+} + O^{2-} \qquad (2.24)$$

$$SO_4^{2-} \rightleftarrows SO_3 + O^{2-} \qquad (2.25)$$

$$\text{base} \rightleftarrows \text{acid} + O^{2-} \qquad (2.26)$$

The strength of an acid in a molten oxide can be quantitatively characterized *via* the acid dissociation constant (Flood):

$$K = \frac{a_{acid}\, a_{O^{2-}}}{a_{base}} \qquad (2.27)$$

In solution, the stronger acid expels the weaker one from its salt. Analogous process takes place in melts: SiO_2 is stronger acid than P_2O_5; hence the equilibrium is shifted to the right:

$$Ca_3(PO_4)_2 + 3\ SiO_2 \rightleftarrows 3\ CaSiO_3 + P_2O_5 \qquad (2.28)$$

In molten chromate salts the following acid-base equilibrium is established:

$$Cr_2O_7^{2-} + O^{2-} \rightleftarrows 2\ CrO_4^{2-} \qquad (2.29)$$

or in presence of nitrate ions:

$$Cr_2O_7^{2-} + 2\ NO_3^{-} \rightleftarrows 2\ CrO_4^{2-} + N_2O_5 \qquad (2.30)$$

where the base is the nitrate ion, as

$$2NO_3^{-} \rightleftarrows N_2O_5 + O^{2-} \qquad (2.31)$$

Reactions in molten oxides are involved in a variety of industrial processes, like glass- and cement industry (reaction of MOH and $M(OH)_2$ with SiO_2), production of ceramics (reaction of metal sulfates and carbonates with Al_2O_3-containing materials), digestion of oxide ores (reaction of MO and $M(OH)_2$ with $S_2O_7^{2-}$ or HSO_4^{-} ion) or sulfidic ores (reaction of FeS or Cu_2S with Na_2S), *etc.*

2.4 Questions and problems

1. Classify the molten salts on the basis of their electric conductivity and viscosity (with examples)

2. Describe the general features of the molten salts!

3. Give a general description on the alkaline-halide melts!

4. Characterize the dissolution of metals in molten salts!

5. Compare the structure of the solid and molten AlX_3 (X = Cl, Br and I)!

6. Describe the main features of acid-base reactions in melts containing mobile proton (with examples)!

7. Describe the main features of acid-base reactions in molten oxides (with examples)!

8. What are the major chemical considerations of the preparation of Al *via* electrolysis?

Chapter 3 Ionic liquids

3.1 Ionic liquids – definitions, history and discovery

Table 3.1 The list of the main features of ionic liquids; on the basis of the data published in [4].

A salt	Cation and or anion quite large
Freezing point	Preferably below 100 °C
Liquidus range	Often > 200 °C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied ≤ 30
Polarity	Moderate
Specific conductivity	Usually < 10 $mScm^{-1}$, „Good”
Molar conductivity	< 10 $Scm^2 mol^{-1}$
Electrochemical window	> 2 V, even 4.5 V, except for Brønsted acidic systems
Solvent and/or catalyst	Excellent for many organic reactions
Vapor pressure	Usually negligible

An ionic liquid is a salt consisting of ions that are poorly coordinated. These features result in these solvents, are in the liquid state below the boiling point of water, T < 100°C. Some of them are liquids even at room temperature (these are the so called room temperature ionic liquids, RTIL). In general, one of the ions in an IL has a delocalized charge. Moreover, one component is organic. These features prevent the formation of a stable crystal lattice. ILs are also called liquid electrolytes, ionic melts, fused salts, liquid salts, ionic glasses, *etc*. The expression *ionic liquids* was reinvented in the 1970’s, admittedly to make difference from molten salts [4]. The main features of the ILs are compiled in Table 3.1. Of these, perhaps the most important ones are the low vapor pressure and potential use as catalyst. Further attracting properties will be discussed later in this chapter.

Ionic liquids for the first time was prepared by Sir William Ramsay in 1876, *via* reacting an acid picoline (pyridine-carboxylic acid). As a result of this reaction, viscous liquids are formed. Ramsey used the expression „ionic liquid" for the first time for the product.

Paul Walden in 1914 reported the following reaction:

$$\mathrm{EtNH_2 + HNO_3 \rightarrow [EtNH_3^+][NO_3^-]} \qquad (3.1)$$

Walden noticed, that the melting point of this salt was very low, 14 ^{o}C. The Walden's rule for dilute electrolyte solutions the product of viscosity (η) and electric conductance (Λ) is constant:

$$\Lambda\eta = \mathrm{const.} \qquad (3.2)$$

For melts and ionic liquids, the modified Walden's rule reads as

$$\Lambda\eta^\gamma = \mathrm{const.} \qquad (3.3)$$

where $0 < \gamma < 1$, and from this it was hypothesized, that in melts, the dissociation of ions is not complete.

Next time, ionic liquids were mentioned in a patent filed in the US in 1934. In this, it was claimed, that in the melt of the chloride of an N-containing base (*e.g.*, ethyl-pyridinium, C_2py, see figure 3.1), cellulose can be dissolved below 100 ^{o} C. The viscosity of this solvent and that of the solution is reasonable and the cellulose is in chemically reactive state (*i.e.*, ether- and ester formation takes place) and therefore it is easy to use for manufacturing purposes (that is, fabricating fibers or films). In another US patent, filed in 1948, $[C_2py]Br + AlCl_3$ melt was used for the electrolytic reduction of Al. As it is shown in Figure 3.2, in a very narrow concentration range, the melting point drops significantly, to *ca.* - 50 °C, which is close to room temperature. Later the development of the related technologies was abandoned because the presence of bromide was undesirable.

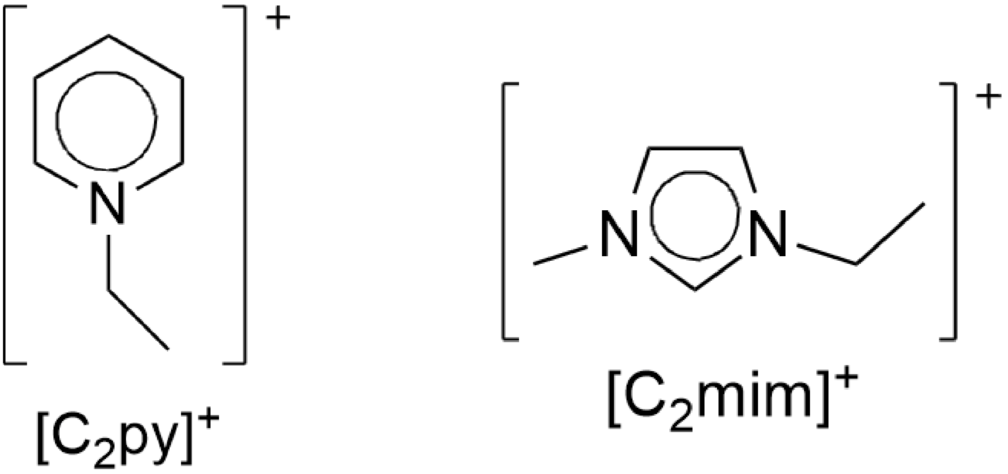


Figure 3.1 The structure of the ethyl-pyridinium, $[C_2py]^+$ and 1-ethyl-3-methylimidazolium, $[C_2mim]^+$ cations. $[C_npy]^+$ stands for the 1-alkylpyridinium cation, where the index n represents the number of carbon atoms in the linear alkyl chain, $[C_nmim]^+$ stands for the 1-alkyl-3-methylimidazolium cation, where the index n represents the number of carbon atoms in the linear alkyl chain.

In another case, in 1973 the Air Force of the US patented the use of $[C_4py]Cl + AlCl_3$ as electrolyte in dry batteries (here C_4py stands for the propyl-pyridinium ion.) They found that in broad concentration ratio range the melting point is well below room temperature, however, the pyridine containing cation was found to be sensitive to reduction, which limited the application possibilities.

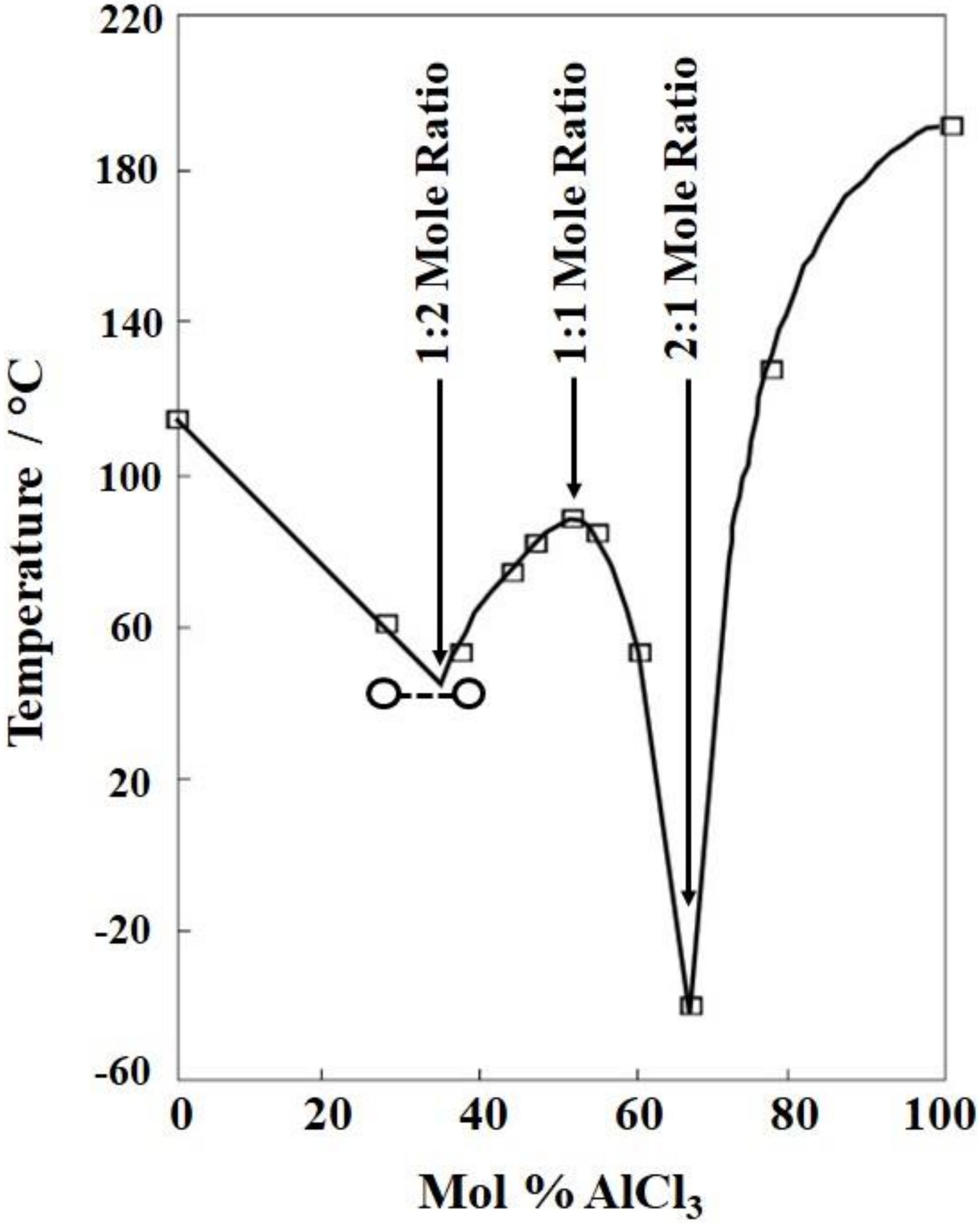


Figure 3.2 The phase diagram of the $[C_2py]Br + AlCl_3$ system; on the basis of the data published in [5].

Theoretical calculations in 1982 demonstrated, that [C_2mim]Cl, which is the chloride of the 1-ethyl-3-methylimidazolium cation (Figure 3.1) is stable in a broad potential range, and therefore it has redox properties superior to those of the similar pyridinium –based salts. In 1987, it was shown, that the [C_2mim]Cl + $AlCl_3$ mixtures are of low viscosity, but practical applications were severely hindered by the fact that $AlCl_3$ is sensitive to moisture.

In summary, up to the late 80’s in the last century, ionic liquids were sporadically studied and discovered, but were always disregarded, because of unfavourable features, like moisture sensitivity, oxidizability or toxicity.

3.2 Preparation and properties of ionic liquids

The cations and anions most often used are shown in Figure 3.3.

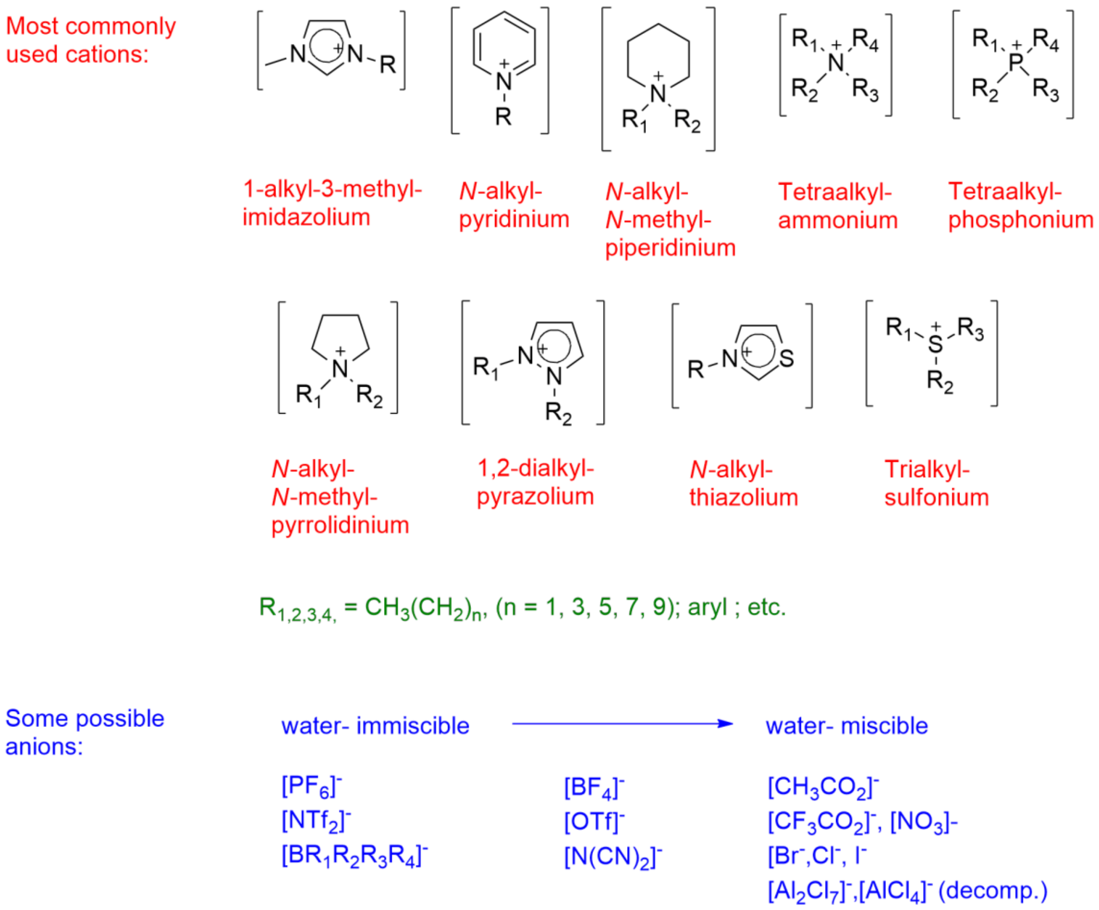
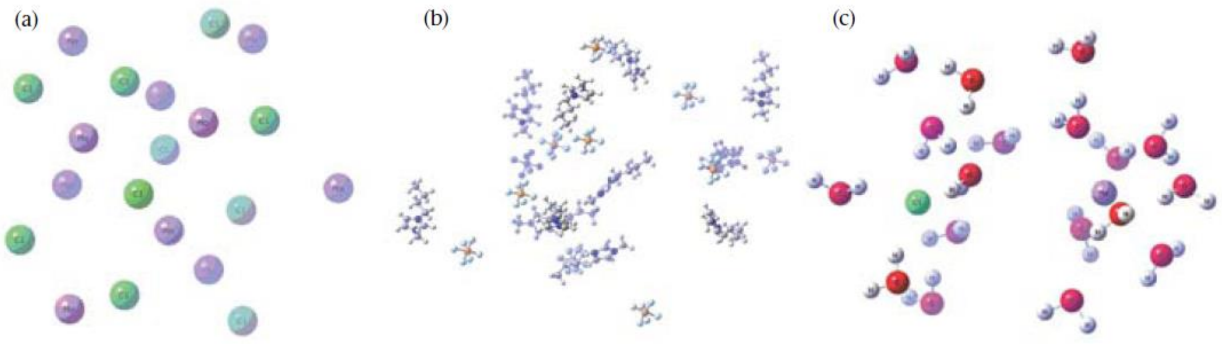


Figure 3.3 The most commonly used cations and anions for preparing ILs; on the basis of the data published in [5].

In 1992, Wilkes and Zaworotko reported, under the title of *“Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids”*, the preparation and characterization of a new range of ionic liquids that still contained the 1-ethyl-3-methylimidazolium cation, but now also contained a range of alternative anions, $[C_2mim]X$ (X^- = $[CH_3COO^-]$, $[NO_3^-]$ or $[BF_4^-]$).

Further useful anions in this sense are hexafluorophosphate, ethanoate, trifluoroethanoate, sulfate, hydrogensulfate, alkylsulfate, biscyanamide $[N(CN)_2]^-$, trifluoromethanesulfonate $[CF_3SO_3]^-$, *etc*. With the discovery of Wilkes and Zaworotko, ILs become instantaneously one of the most popular topics in contemporary chemistry: in 2017, on the WEB of Science database, 8422 documents were found, which contained the expression “ionic liquid”, 3480 of them are in the title.

The structure of the ILs is compared schematically with that of the molten salts and with that of the water in Figure 3.4.



molten NaCl $[C_4mim][PF_6]$ H_2O

Figure 3.4 The schematic structure of molten NaCl, $[C_4mim][PF_6]$ and H_2O; on the basis of the data published in [5].

The electrochemical windows of various commonly used ionic liquids are shown in Figure 3.5 (compare this with Figure 1.17). From this it is clear, that the ionic liquids have received extensive attention not only because of their low reactivity with water, but also because of their large electrochemical windows: the electrochemical window for water is 1.23 V, while for ionic liquids could be as large 5 – 6 V, meaning, that such solvents are suitable for being used as medium for oxidizing compounds that have very positive oxidation potential as well as reducing that have very negative reducing potential.

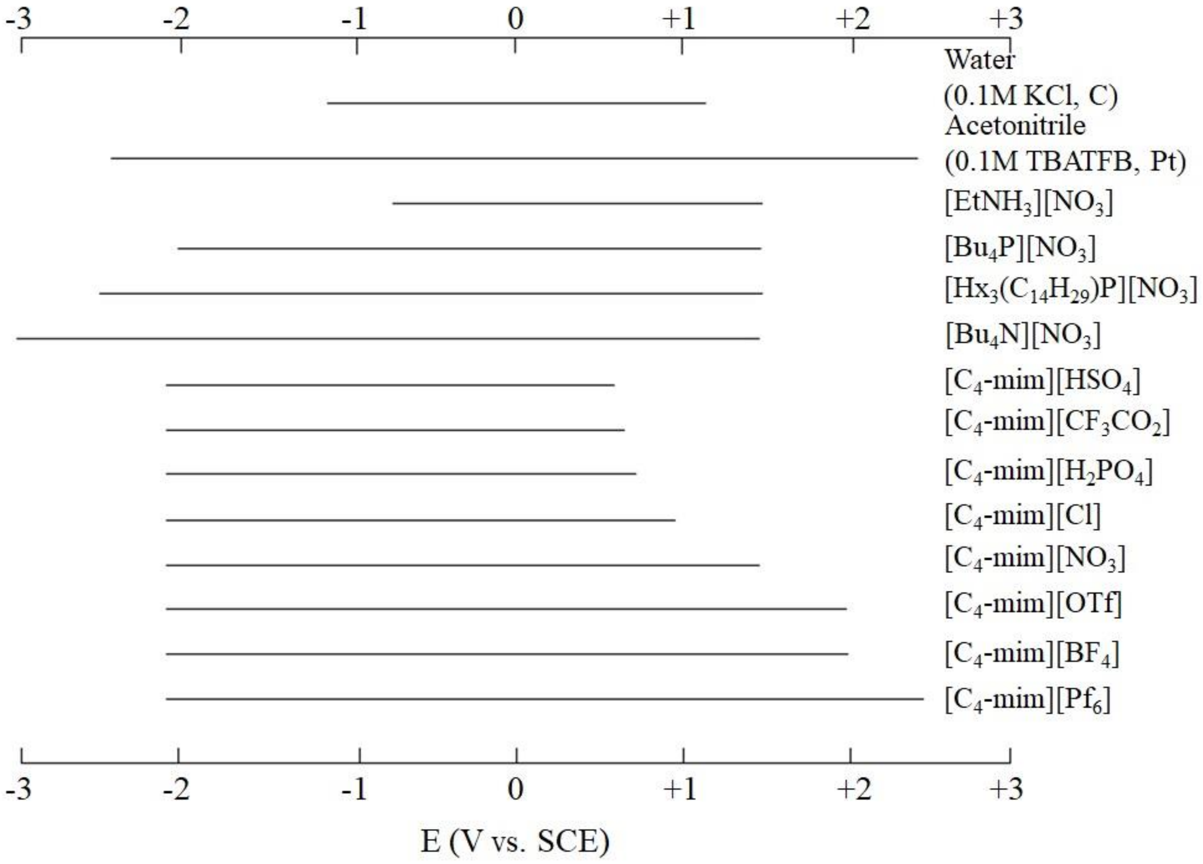


Figure 3.5 The electrochemical windows for some typical ionic liquids; on the basis of the data published in [5].

3.3 The melting point of ionic liquids

The melting point of ionic liquids is a very important issue. Factors that determine the melting point of an IL have been the subject of several studies. It was found, for example, that the more symmetric is the molecule, the larger is the melting point of the ionic liquid comprising of that molecule. For example, for $[FP(C_6H_{13})_3C_nH_{2n+1}][PF_6]$ salts, the largest melting point was found for the n = 6 case, that is, when the cation was the more symmetric, and it was the smallest for n = 3 and 12. Above n = 12, the melting point started to increase again showing, that the (as)symmetry is not the only parameter that prevails. This is also demonstrated by the melting points of the $[C_nmim][PF_6]$ series (Figure 3.6).

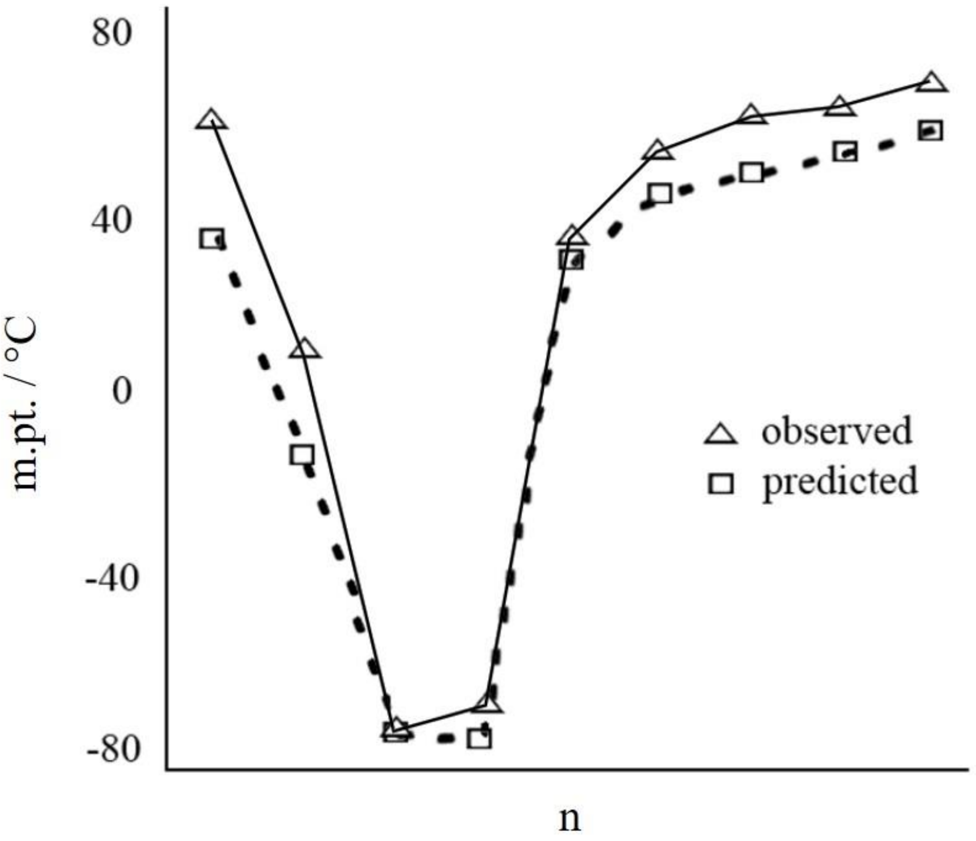


Figure 3.6 The melting point (observed and calculated) of ionic liquids $[C_nmim][PF_6]$ as a function of n; on the basis of the data published in [5].

Regarding the melting point variations, it can be generally stated, that if the size of the part of the molecule which causes asymmetry is *ca.* 5-12 Å long, – it will decrease the melting point as it breaks symmetry. However, if the size of the part of the molecule which causes asymmetry is larger than 12 Å, it will increase the melting point because of hydrophobic interactions.

Table 3.2 Comparison of the properties of ILs with common organic solvents; on the basis of the data published in [5]. [5].

Property	**Organic solvents**	**Ionic liquids**
Number of solvents	>1000	>1,000,000
Applicability	Single function	Multifunctional
Catalytic ability	Rare	Common and tuneable
Chirality	Rare	Common and tuneable
Vapour pressure	Obeys the Clausius-Capeyron equation	Negligible vapour pressure under normal conditions
Flammability	Usually flammable	Usually nonflammable
Solvation	Weakly solvating	Strongly solvating
Polarity	Conventional polarity concepst apply	Polarity concept questionable
Tuneability	Limited range of solvents available	Virtually unlimited range means „designer solvents”
Cost	Normally cheap	Typicallybetween 2 and 100 times the cost of organic solvents
Recyclability	Green imperative	Economic imperative
Viscosity/cP	0.2-100	22-40,000
Density/g cm^{-3}	0.6-1.7	0.8-3.3
Refractive index	1.3-1.6	1.5-2.2

3.4 Some applications of ionic liquids

Some properties of the ILs with those of common organic solvents are compared in Table 3.2. This compilation makes several interesting conclusions to be drawn. Perhaps the most important is, that of the 330 is commercially available ILs, it is (in principle) possible to make 10^{12} binary and 10^{18} ternary IL mixtures, resulting in designer solvents with tunable properties. The following landmark statements were made regarding this by Seddon in his famous work of *J. Chem. Technol. Biotechnol*., 1997, 68, p. 351.: *"The reactions we have observed represent the tip of an iceberg – all the indications are that room-temperature ionic liquids are the basis of a new industrial technology. They are truly designer solvents: either the cation or the anion can be changed, if not at will, then certainly with considerable ease, in order to optimize such phenomena as the relative solubilities of the reactants and products, the reaction kinetics, the liquid range of the solvent, the cost of the solvent, the intrinsic catalytic behavior of the media, and air-stability of the system. For the first time, it is possible to design a solvent to optimize a reaction (with control over both yield and selectivity), rather than to let the solvent dictate the course of the reaction. […] This, quite literally, revolutionizes the methodology of synthetic organic chemistry: it will never be the same again!"*

A large number of practical applications are known, which utilize successfully the ILs. Choosing the right solvent, the desired product can be selectively prepared with +99% yield in the reaction of toluene and nitric acid. The reaction medium is $[C_n\text{mim}][X]$. If X^- = halide, the product is a halide-substituted toluene, if $X^- = CF_3SO_3^-$, the product is nitro-toluene and if $X^- = CH_3SO_3^-$, the product is benzoic acid. Another example is the BASIL process (BASF). Here the solvent (C_0mim) acts not only as the medium, where the reaction takes place but it also binds the proton which is produced during the reaction (Figure 3.7)

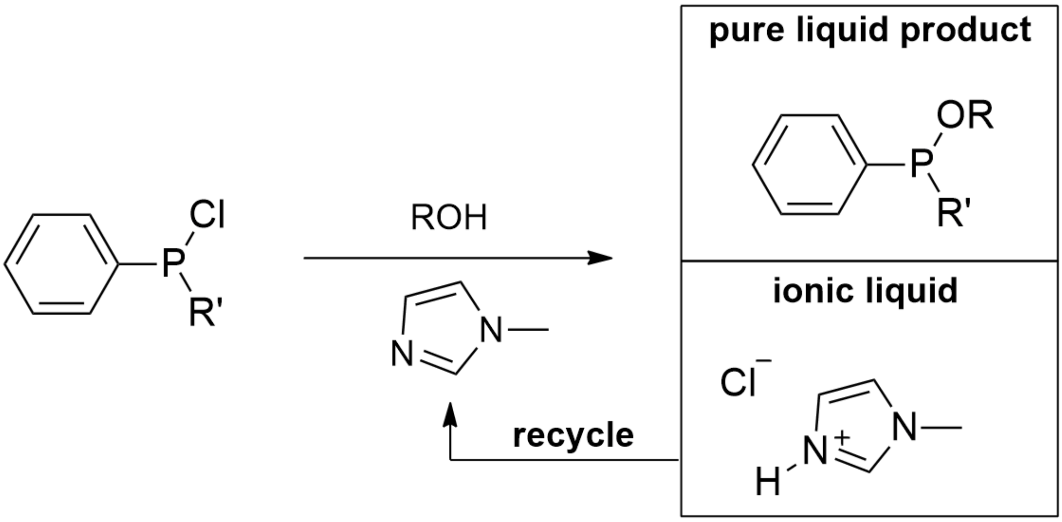


Figure 3.7 The Basil process; on the basis of the data published in [5].

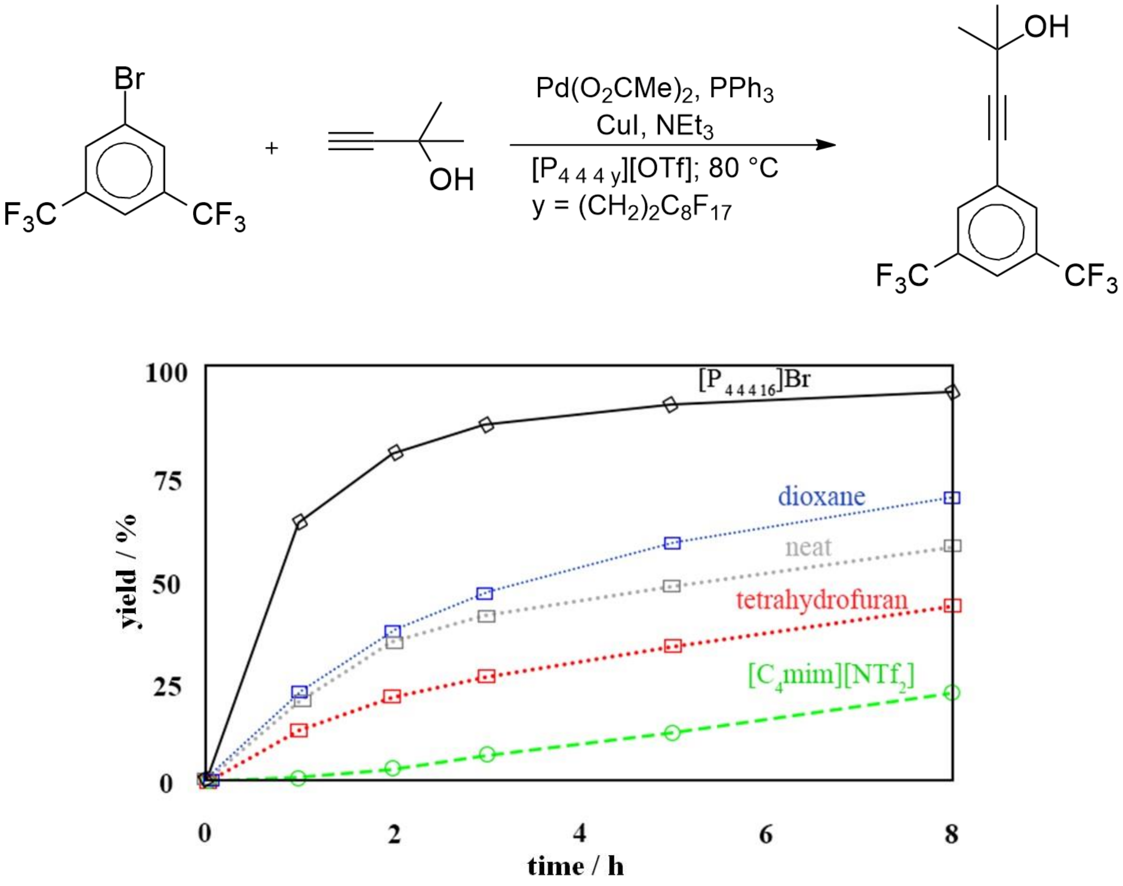


Figure 3.8 The Shonogashira reaction (top) and the conversion of the reaction in various solvents (bottom); on the basis of the data published in [5].

The preparation of 1,4-dichloro-butane from 1,4-butanediol requires the use of phosgene, $COCl_2$, which is very toxic. If the 1,4-dichloro-butane is transformed in HCl, multiplicity of products are obtained. However, *via* using IL, the desired product, 1,4-butanediol is obtained.

Finally, the example of the Shonogashira reaction (Scheme in Figure 3.8) will be presented. As it can be seen in Figure 3.8, in some IL, the reaction is slowed down, while in other, it was speeded up, relative to the use of common solvents or to the case, when no solvent at all was employed.

3.5 Questions and problems

1. What are the general physical and chemical properties of ionic liquids?
2. What type of ions are used for the preparation of ionic liquids?
3. What parameters determine the melting point of the ionic liquids?
4. Give a general comparison of the properties of regular (molecular) organic liquids and ionic liquids!
5. Select and analyse a practical application of an ionic liquid!

Chapter 4 Supercritical fluids

4.1 Definitions

A substance is supercritical when both its temperature and pressure are above the values at the critical point. Examples of critical temperature (T_c/ ^oC) and pressure (P_c/bar) data for some selected compounds are shown in Table 4.1.

Table 4.1 Critical temperature (T_c) and pressure (P_c) data for some selected elements and compounds

Compound		**T_c (^{o}C)**	**p_c(atm)**
Ammonia	NH_3	132.4	111.3
Bromine	Br_2	310.8	102.0
Caesium	Cs	1665	94.0
Ethanol	EtOH	241	62.18
Fluorine	F_2	−128.85	51.5
Helium	He	−267.96	2.24
Hydrogen	H_2	−239.95	12.8
Methane	CH_4	−82.3	45.79
Neon	Ne	−228.75	27.2
Nitrogen	N_2	−146.9	33.5
Oxygen	O_2	−118.6	49.8
Carbon-dioxide	CO_2	31.04	72.8
Sulphuric acid	H_2SO_4	654	45.4
Xenon	Xe	16.6	57.6
Mercury	Hg	1477	1720
Sulfur	S	1,041	207
Gold	Au	6977	5000
Water	H_2O	374	217.7

When for an element or a compound the relationships $T > T_c$ and $p > p_c$ are fulfilled, we say, that it is in a supercritical state (Figure 4.1), and is called supercritical fluid.

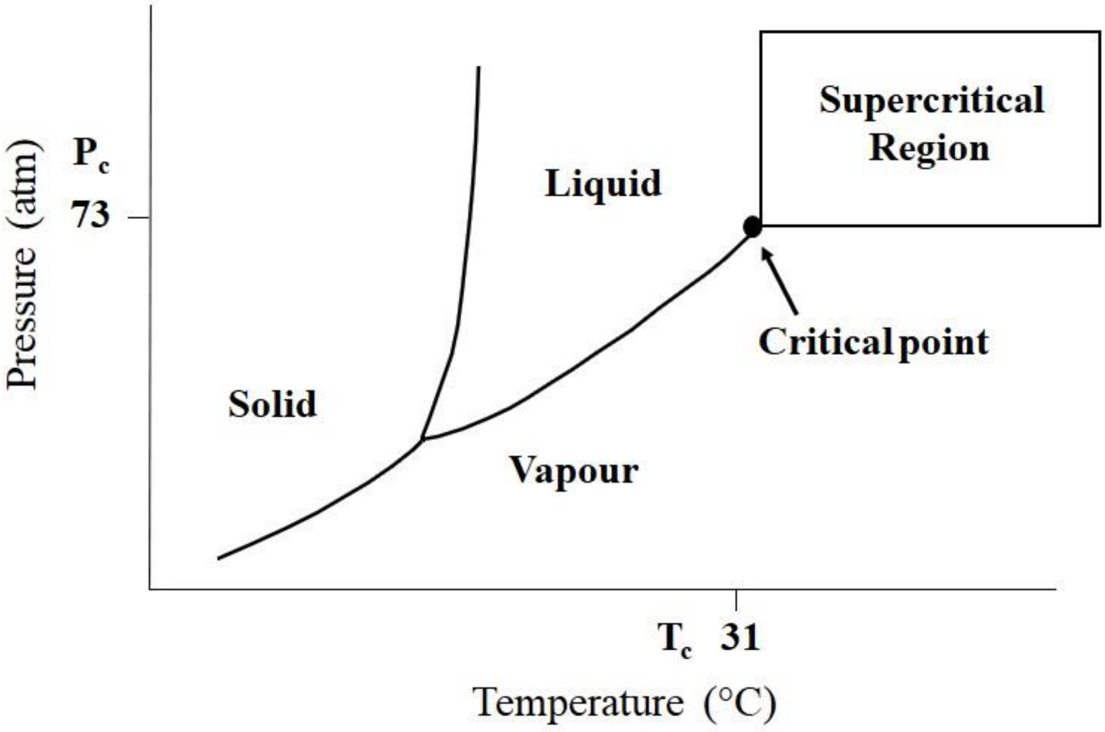


Figure 4.1 The phase diagram of CO_2

4.2 General properties of supercritical fluids

The characteristics of a fluid in supercritical state are significantly different from those of the gaseous and liquid states (Table 4.2). The density of a supercritical fluids is closer to that of liquids, however, their viscosity is similar to that of gases (this is in particular advantageous in terms of mass transfer.)

Table 4.2 Comparison of properties of supercritical fluids with those of gases and liquids; on the basis of the data published in [1].

State	Condition	Density g cm^{-3}	Viscosity g cm^{-1} s^{-1}	Diffusion coefficient cm^2 s^{-1}
Gas	1 atm, 25 °C	0.6- 2 x 10^{-3}	1- 3 x 10^{-4}	1- 4 x 10^{-1}
Liquid	1 atm, 25 °C	0.6- 2	0.2- 3 x 10^{-2}	0.2- 2 x 10^{-5}
Supercritical fluid	T_c, P_c	0.2- 0.5	1- 3 x 10^{-4}	0.5- 4 x 10^{-3}
	T_c, $4P_c$	0.4- 0.9	3- 9 x 10^{-4}	0.1- 1 x 10^{-3}

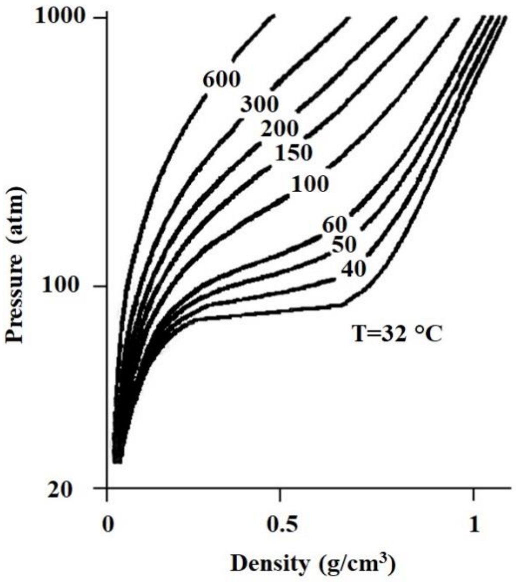


Figure 4.2 The variation of the density of supercritical CO_2 with the pressure at various temperatures; on the basis of the data published in [1].

The diffusion coefficient in a supercritical fluid is usually found between those of liquids and gases. Various properties, like density, of the supercritical fluids can be fine-tuned *via* changing the pressure and temperature (Figure 4.2). They are excellent solvents of certain compounds, and the solubility can also be fine-tuned *via* changing the operational parameters or *via* adding modifier compounds to the fluid.

4.3 The supercritical water and CO_2

From Table 4.1, the critical temperature and pressure of water is $T_c = 374\ ^oC$ and $p_c = 218$ atm. For example, in the nature, in deep-sea water regions (high p) during volcanic activities (high T) water may become supercritical. It has been shown that in super critical water, the efficiency of certain electrode reactions (the reaction rate of anodic oxidations) is enhanced relative to „normal" water. At the critical point, the permittivity of water significantly smaller than that of the "normal" water, under these conditions $\varepsilon_r = 5$. Therefore, water becomes apolar solvent as it approaches the supercritical state. As such, it becomes a good solvent of several apolar solutes, that is organic compounds. In presence of dissolved O_2 in SCW, various organic contaminants (*e.g.*, pesticide residues, chemical weapons, explosives, *etc.*) are rapidly and efficiently oxidized to harmless products (mineralization).

The critical parameters of water are somewhat outside of the "comfort zone" of everyday laboratory practice. This is not the case for CO_2 (Table 4.1), for which $T_c = 31\ ^oC$ and $p_c = 72.8$ atm. These are almost "ideal" critical values. Add to this, that the toxicity of CO_2 can be readily handled, it is non-flammable and environmentally friendly in the sense, that it is nowadays highly desirable to remove it (even if temporarily) from the environment. It is available in large quantities and in reasonable purity (*e.g.*, it can be obtained from the air and it can also be mined, like it is done in Répcelak, Hungary). It is somewhat a disadvantage, the supercritical CO_2 is apolar ($\varepsilon_r \approx 1.6$) in pure form, therefore it is good solvent of apolar solutes. With using polar modifiers (*e.g.*, water, MeOH, acetonitrile, *etc.*) the polarity can be enhanced and fine-tuned. The recovery of the dissolved compound is relatively easy, as the pressure of the fluid has to be lowered to $p < p_c$ and the solvent rapidly evaporates.

One of the most promising applications of the supercritical CO_2 is in the supercritical extraction. The schematic view of a supercritical extractor is shown in Figure 4.3. *Via* regulating p and T, from the sample placed in (6), the individual components can be selectively extracted. Advantages relative to traditional solvent extraction, that it is fast, the purification of the solvent is not necessary, the solvent is non-toxic, the properties of the solvent can be varied, the solute can be readily recovered and the solvent is easy to get rid of.

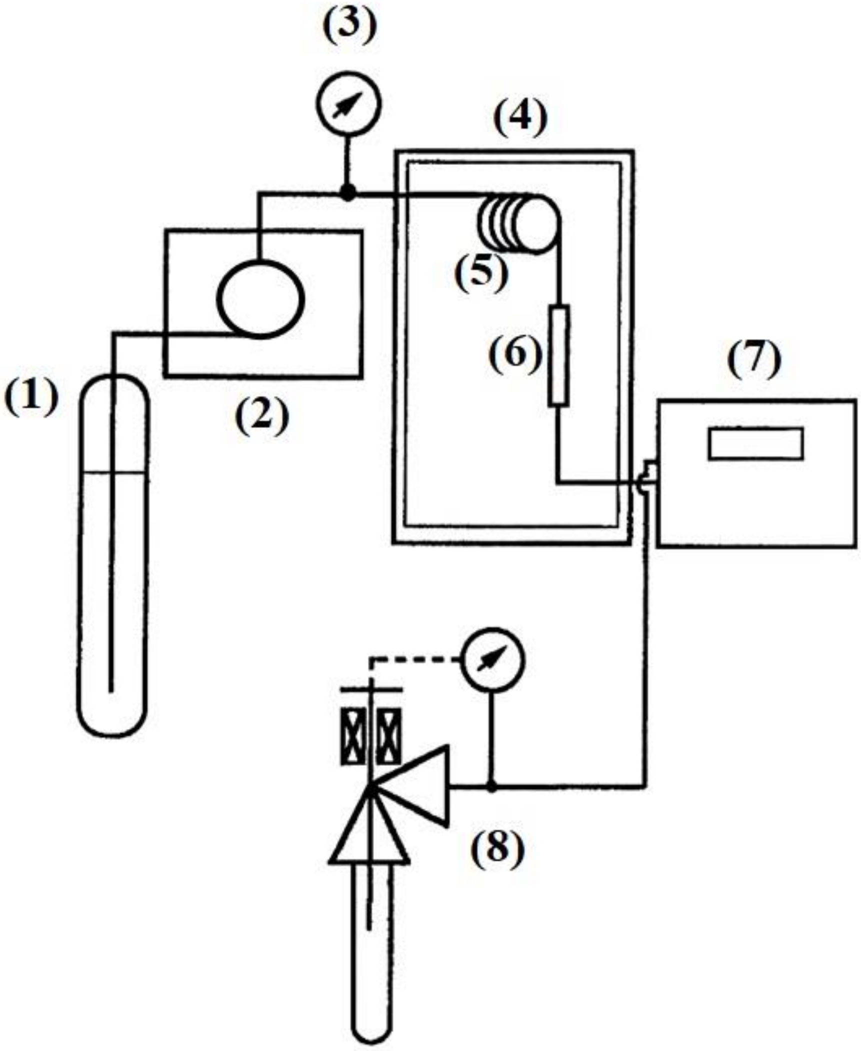


Figure 4.3 Schematic view of a supercritical extractor: 1. CO_2 cylinder; 2. pump; 3. pressure regulator; 4. oven; 5. volume buffer; 6. extraction cell; 7. spectrophotometer; 8. pressure equalizer

4.4 Problems and questions

1. What is the definition of the super-critical state? Demonstrate this with an example!
2. Compare the super critical state with the gaseous and liquid state!
3. Briefly describe the properties and use of super critical water!
4. Briefly describe the properties and use of super critical CO_2!
5. Explain the use of super critical CO_2 in a super critical extraction process!

Chapter 5 Extremely concentrated aqueous electrolyte solutions

Highly concentrated aqueous electrolyte solutions are common in our environment. Some examples:

1. During a variety of hydrometallurgical processes, highly concentrated process liquors are used, like during the production of alumina (highly alkaline aluminate solutions), production of non-ferrous metals (acid leaching of Cu, Ni, Co, *etc.*), gold production (cyanide leaching during the extraction of Au), *etc.*
2. Seawater is also a concentrated aqueous electrolyte solution, containing dissolved salts (mainly NaCl) in about 0.6 M concentrations;
3. During underground hydrothermal processes, often concentrated electrolytes are involved, leading to the formation of various large and spectacular single crystals;
4. In the chemical laboratory practice, for the study of solutions often highly concentrated background electrolytes are employed; their role is to maintain the activity coefficient of the solution constant during the chemical reactions that take place in the reaction mixture (according to the principle of the constant ionic environment);
5. In the analytical chemical practice, often concentrated stock solutions are used, these are diluted to the usual reagent concentrations which are most often in the range of 0.1 M – 0.01 M. One of the most concentrated common electrolyte in the laboratory practice is the saturated NaOH, the concentration of which is close to 20 M at room temperature; it is used for preparing NaOH titrant solutions that are free from Na_2CO_3, a compound which interferes with the end-point indication of acid base titrations.

During this course, the extremely concentrated solutions are by definition those for which the molar concentration of the solute is c > 1 M (*N.B.*, for dilute solutions the concentrations are usually not more than 0.1 M.) There are solutes, which are soluble in water to the extent that they may form extremely concentrated solutions, but are non-electrolytes (like certain sugars). Ployelectrolytes are also out of the scope of the present chapter: we will therefore deal with simple" electrolytes, the solubility of which are far larger than 1 M even at room temperature. The solubilities of some of them is collected in Table 5.1.

Some features of the concentrated aqueous electrolyte solutions:

- hydration of ions in them is incomplete (they are often called "water deficient" systems; *e.g.*, in several of them, in the saturated solution in Table 5.1, the number of water molecules is less than the amount necessary for the full hydration.)
- These solutions are "crowded", resulting in forced electrostatic interactions. It is easy to show, that the average distance of the neighbouring ions in a solution depends on the solute concentration. The average distance between the geometric center of the neighboring ions determines the average "space allowance" of the individual ions at various electrolyte concentrations.
- Under these conditions, ion-pair formation (interaction between ions of opposite charge) takes place even between ions which are not expected to form ion-pairs according to the Bjerrum-Fouss theory (see Section 1.5.6).
- In these "crowded" solutions, interaction between ions of the same charge may take place, resulting in the formation of di- and oligomeric species that are absent from less concentrated solutions.

Table 5.1 The solubility of some simple 1:1 and 2:1 electrolytes in water at 25 ºC.

	Solubility			
Electrolyte	**m/m%**	**mol kg^{-1}**	**$n_{H2O}/n_{electrolyte}$**	**Remark**
NH_4NO_3	68.2	26.5	2.08	
NH_4OOCCH_3	73.0	55.7	1.00	
NH_4NO_2	68.7	64.0	0.87	
LiBr	64.8	23.9	2.31	
$LiClO_3$	81.9	50.2	1.10	
$LiNO_2$	50.9	19.6	2.84	
$NaClO_4$	67.8	17.2	3.22	
NaOH	53.2	28.4	1.95	c = 20.2 M
$CsOOCCH_3$	91.3	54.7	1.01	
CsOH	76.6	21.8	2.34	c = 14.4 M
RbF	75.1	28.8	1.92	
$RbOOCCH_3$	89.3	57.8	0.96	
KNO_2	75.8	36.7	1.51	
KOH	52.0	19.4	2.87	c = 14.2 M
$CaCl_2$	77.6	31.2	1.80	t = 260 ºC
$Ca(ClO_3)_2$	66.1	7.89	7.03	
$Sr(ClO_4)_2$	75.6	10.8	5.14	

- The water deficiency may result in the inner sphere dehydration of the dissociated ions, therefore changing the structure of their primary hydration shell, relative to the diluted systems.
- In the crowded solutions, long range ordering can be observed; some properties are reminiscent to those of ionic melts.
- The lack of the full hydration results in an increase in chemical reactivity of the dissolved species, and in parallel to this, the mobility of the ions decreases.

5.1 The density and viscosity of concentrated electrolyte solutions

The density of a solution depends on the concentration of the solute. For a concentrated single electrolyte with a molar concentration of c, the Masson equation holds:

$$V_\phi = V_\phi^{\,0} + k_e \sqrt{c} \tag{5.1}$$

and

$$V_\phi = (M/\rho) - 10^3(\rho - \rho_0)/c\rho \tag{5.2}$$

where k_e is a constant, V_Φ and V_Φ^0 are the apparent molar volume and the molar volume at infinite dilution, respectively and

$$\rho = \rho_0 + \alpha c + \beta c^{3/2} \tag{5.3}$$

$$\alpha = 10^{-3}(\mathrm{M} - V_\phi^{\,0}\,\rho_0) \tag{5.4}$$

$$\beta = -k_e \rho_0 \tag{5.5}$$

ρ_0 and ρ are the density of the solvent and the solutions with a concentration of c, respectively and M is the molar mass. The statement of the Masson equation, that the apparent molar volume (therefore the density) is proportional to the square root of the concentration, is well demonstrated by Figure 5.1, where the densities of alkali-metal hydroxides are shown. It is apparent, that the density increases in the order of Li^+ → Cs^+, and the behavior of the $(CH_3)_4NOH$ is irregular.

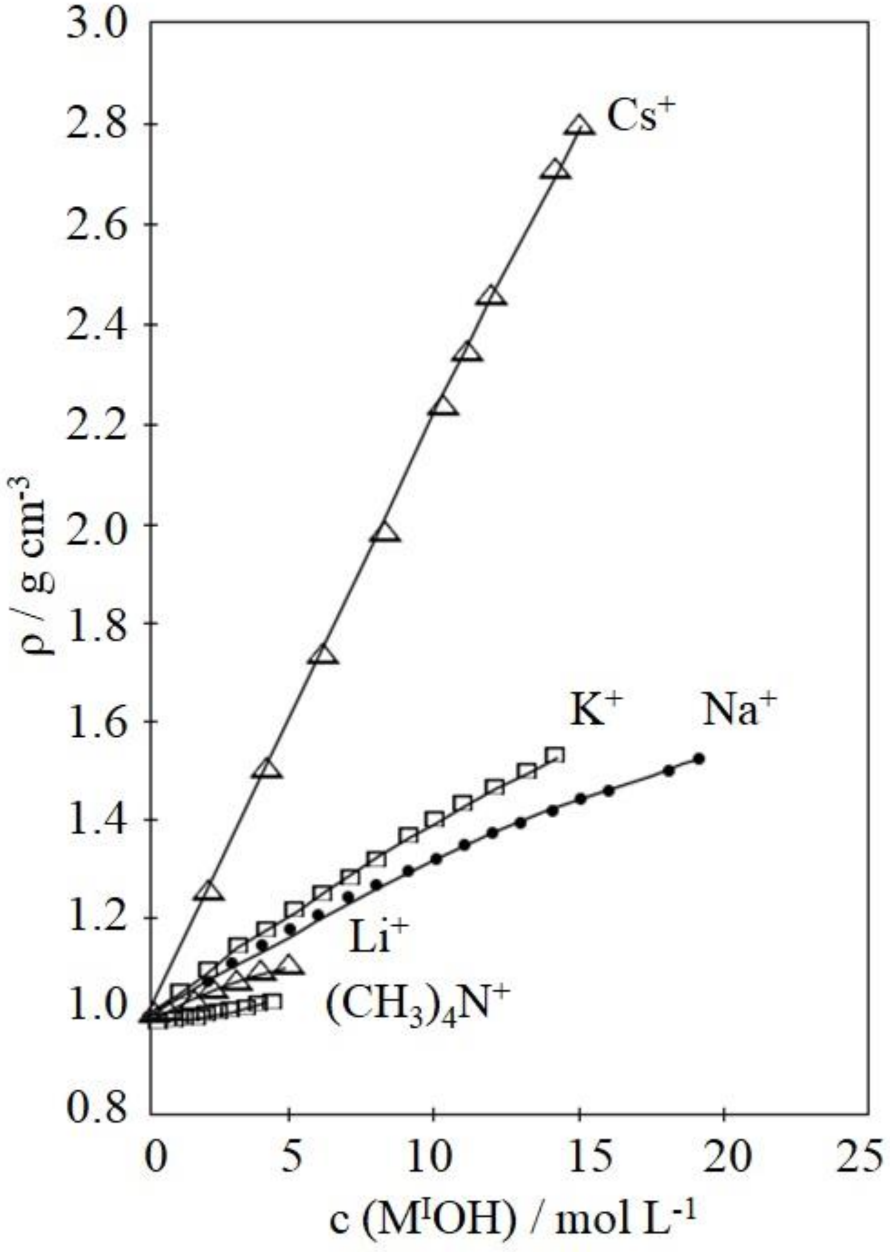


Figure 5.1 The densities of $(CH_3)_4NOH$, LiOH, NaOH, KOH and CsOH at 25 ^oC as a function of the molar concentration.

Very often, mixtures of concentrated electrolytes are used and it is desirable to have a handle on estimating their density. The Young's rule states, that the P_{x+y} property in a mixture of component X with concentration c_X and Y with concentration of c_Y, can be computed as the same property of the pure components at the same concentration, that is P_x and P_y at $c_T = c_X +$

c_Y are known. If this is the case, the property P changes *pro* rata with the concentration fraction of each component. Hence the Young's rule reads as

$$P_{x+y} = (\frac{c_x}{c_T})P_x + (\frac{c_y}{c_T})P_y \tag{5.6}$$

which reads for densities as

$$\rho_{x+y} = (\frac{c_x}{c_T})\rho_x + (\frac{c_y}{c_T})\rho_y \tag{5.7}$$

where ρ_x and ρ_y are the densities of the single component solutions containing X and Y in a concentration of c_T, while ρ_{x+y} is the density of a mixture containing X and Y in a concentration of c_x and c_Y, respectively. For non-1:1 electrolytes, the molar ionic strength, I, needs to be written in the place of c_x and c_y, where

$$I = \frac{1}{2}\Sigma c_i z_i^2 \tag{5.8}$$

where c_i is the concentration and z_i is the charge of the ion i. Based on this, the density of any mixture can be calculated, if the sum of the concentrations (or ionic strengths) and the density of the individual components are known.

The viscosity of a single concentrated electrolyte with concentration c can be described in terms of the Jones-Dole equation

$$\eta = \eta_0 + Ac^{1/2} + Bc + Dc^2 + Ec^{7/2} \tag{5.9}$$

where A, B, D and E are empirical constants. The Jones-Dole equation is suitable for describing alkali metal halide solutions, but that of alkali metal hydroxides are better described by a 5th order polynomial.

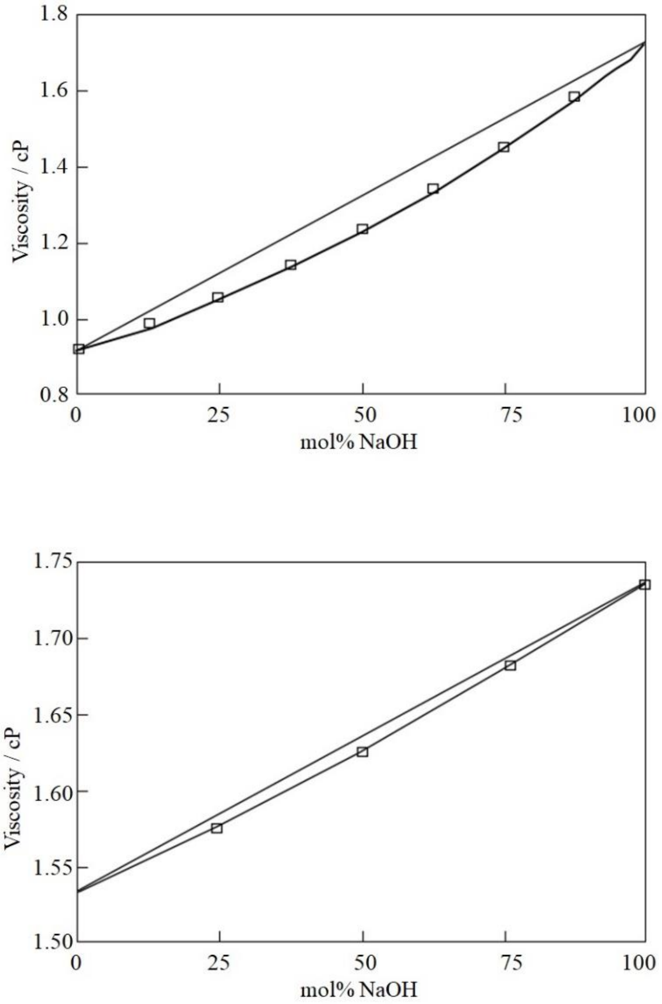


Figure 5.2 Viscosities of NaOH-Na_2CO_3 (top) and NaOH-KCl (bottom) mixtures as a function of the mol% of NaOH. Straight line represents behavior according to the Young’s rule.

Young’s-rule for viscosities reads as follows: the viscosity of the mixture of two electrolytes changes linearly with the mole fraction between the two viscosity extrema (one component solutions):

$$\eta_{x+y} = (\frac{c_x}{c_T})\eta_x + (\frac{c_y}{c_T})\eta_y \tag{5.10}$$

As it can be seen in Figure 5.2, the Young’s rule overestimates the viscosity of the mixtures. From Figure 5.2, it is also apparent, that the extent of the deviation (that is the difference between the predicted and calculated viscosities) is linearly proportional to the difference between the viscosities of the appropriate one-component systems. Hence, this correction can be scaled and taken into account during the calculations.

5.2 Experimental means for studying chemical equilibria in concentrated aqueous electrolytes

5.2.1 Determination of pH in extremely alkaline solutions *via* using potentiometry

Glass electrodes are routinely used in the chemical laboratories for the determination of the pH of aqueous solutions in the pH range of $2 < pH < 12$. In strongly alkaline (or hyperalkaline) solutions, the glass electrodes suffer from the so called alkaline error, which prevents from the accurate pH measurements in such systems. H_2/Pt electrodes are free from this alkaline error. They consist of a platinized Pt sheet, immersed in the solution to be studied. The electrode is in direct contact with H_2 gas bubbled through the system. The potential of this redox electrode is determined by the activity of the H^+ in the solution. If one constructs the cell

Ag/AgCl | 0.1 M NaCl, 7.9 M $NaClO_4$ || 8.0 M $NaClO_4$ || test solution | H_2/Pt (5.11)
salt bridge I = 8 M Na(ClO_4)

the electrode response follows the Nernst-equation up to $[OH^-] = 2$ M (Figure 5.3, uppermost curve); in a such solution, the pH is well over 14. It is important to note, that the potential variation at the liquid junction between the salt bridge and the test solution is practically zero. These features together make the system suitable for determining OH^- dependent chemical equilibria in these systems. For example, when a Na-aluminate solution is added to the background electrolyte (Figure 5.3, lower 4 curves), the OH^- binding or release of the various Al-containing species can be determined this way. It can be proven, that the linear shape of these titration curves is consistent with the presence of only one species, the $Al(OH)_4^-$ in the solutions; the curving up of the titration curves at higher NaOH concentrations stems from the ion-pairing of the aluminate ion with the background cation, Na^+.

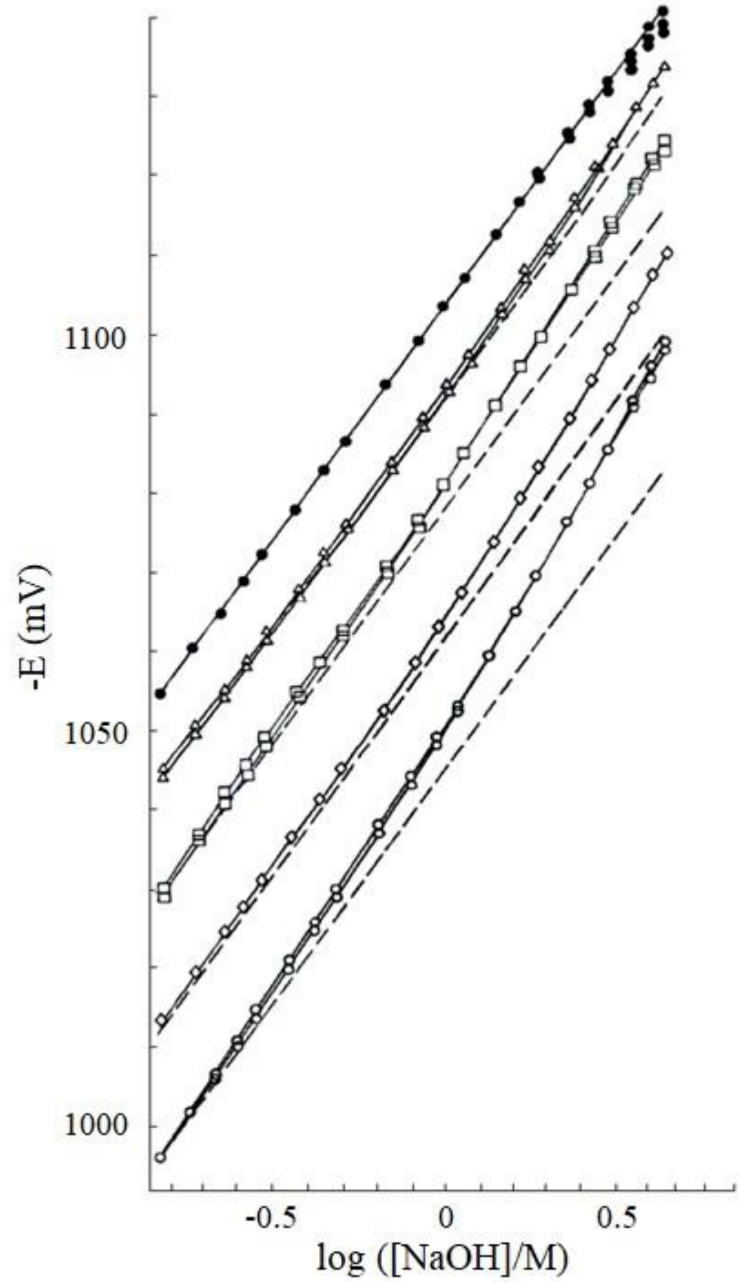


Figure 5.3 Cell potentials obtained for the cell (5.11) at various $[OH^-]_T/[Al(III)]_T$ ratios as a function of the $lg([NaOH]_T/M)$ at $I = 8$ M $Na(ClO_4)$. Calibration: •; $[OH^-]_T/[Al(III)]_T$ at the titrations in question: Δ: 6.92; □: 4.92; ◊: 4.52; ○: 4.30. The dashed line represents the cell potentials calculated for the $[Al(OH)_4^-] = [Al(III)]_T$ case.

5.2.2 The use of UV-Vis spectrophotometry for studying equilibria in hyperalkaline solutions

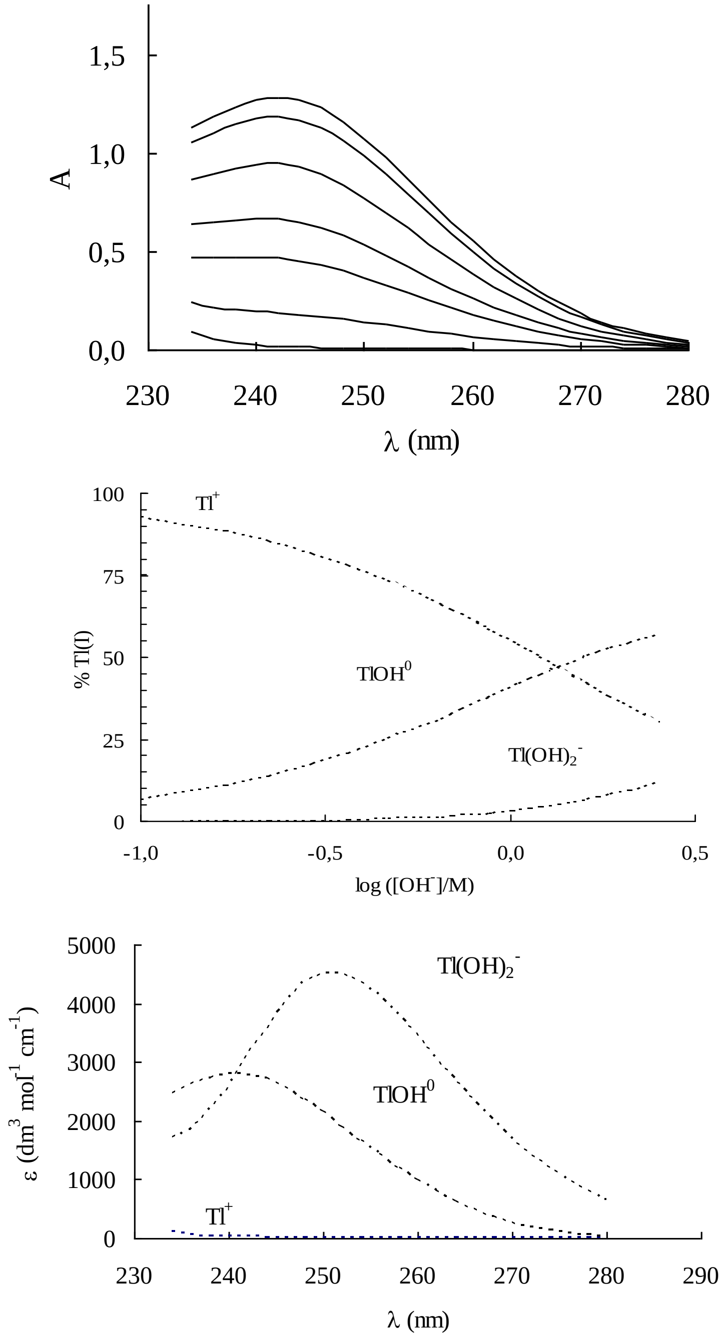


Figure 5.4 The UV-spectrum of Tl(I) in presence of increasing concentration of NaOH (from bottom to top, upper figure), the calculated species distribution diagrams (middle) and the individual spectra of the species obtained (bottom).

The use of UV-Vis spectrophotometry is inherently difficult for studying concentrated electrolytes, because the UV-active (UV-absorbing) contaminants may significantly contribute to the observed absorption, and in extreme cases it may completely ruin the experiment. This is why it is an imperative to use high purity components for the preparation of these solutions and to make the necessary corrections for contaminant effects.

Via using ultrapure components for the experiments, the UV-spectra of Tl(I) shown characteristic variations upon adding increasing amounts of NaOH to its solution (Figure 5.4, top). TlOH is a very strong base, but under these conditions, both the $TlOH^0$ and the $Tl(OH)_2^-$ complex are present in these systems in well detectable quantities (Figure 5.4, middle). With the increasing number of bound hydroxide ions, the spectrum is red shifted and its molar absorbance also increases.

5.2.3 The use of Raman spectroscopy for studying equilibria and for structure determination in concentrated electrolyte solutions

Raman spectroscopy is one of the most useful tools for studying equilibria and simultaneously for determining the structure of the species formed. For determining the Raman spectrum of a solution with a reasonably good signal-to-noise ratio, usually high concentrations of the solute are required. Fortunately, the Raman spectrum of aqueous solutions can readily be recorded, as the Raman spectrum of the solvent water is not too rich in bands (as opposed to that of the IR spectrum). Using careful experimental design and keeping the experimental parameters constant (*e.g.*, constant laser power), the Raman spectra can be used even for quantitative purposes. An example is shown in Figure 5.5, where the concentration of the added HCl increases (indicated with arrows) in a solution series containing a given amount (0.2 M, const.) of sulfate ion. On the Raman spectrum of the sulfate ion, at 982 cm^{-1} a sharp band can be observed, it corresponds to the symmetric stretching of the SO_4^{2-}. The intensity of this band decreases when the H^+ concentration is increased from 10^{-7} M to 0.4 M. This is due to the protonation of the sulfate ion, that is, formation of HSO_4^-. The band corresponding to the HSO_4^- emerges around 1055 cm^{-1}. As the peak area is proportional to the concentration of the corresponding species, from this spectral series, the acid dissociation constant of HSO_4^- can be determined.

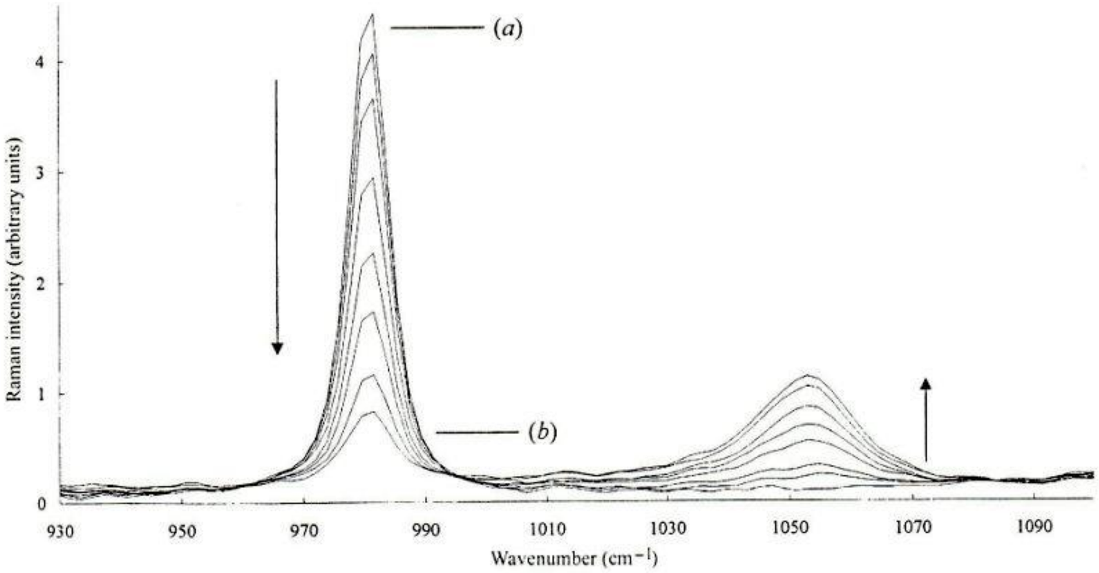


Figure 5.5 Raman spectra of sulfate (0.2 M) solutions as a function of added H^+ (from 10^{-7} M (a) to 0.4 M(b)).

Raman spectra can also be used for detecting contact ion pairs in aqueous solutions. In Figure 5.6, the variation of the position of the symmetric stretching of sulfate (at 982 cm^{-1}, right figure) and that of the carbonate (1066 cm^{-1}, left figure) is shown. It is clear, that the peak maximum is shifted upon addition of various alkali metal ions to the solution. The shift is due to the formation of contact ion-pairs between the anions and the alkali metal ions. It is interesting to note, that the cation, that is less hydrated (Cs^+ vs. Na^+) has stronger tendency to form contact ion-pairs, as the shift is the largest for Cs^+-containing solutions.

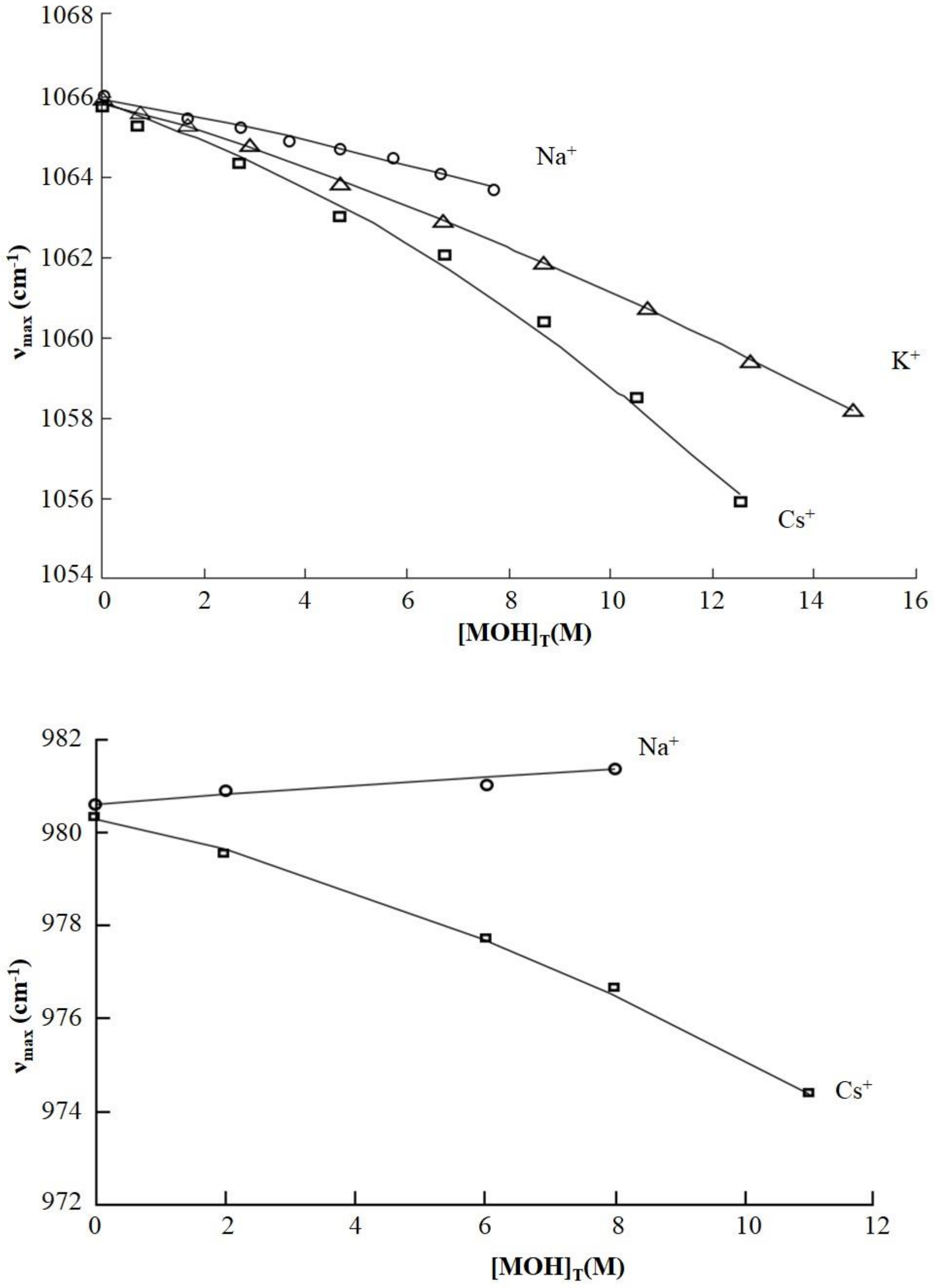


Figure 5.6 The position of the symmetric stretching vibration mode of the carbonate (left) and sulfate (right) ions as a function of the added alkali metal ion concentration (in form of its hydroxide).

Raman spectroscopy can also be used for the determination of the dimerization constant of the $Al(OH)_4^-$ ion (Figure 5.7). In a Na-aluminate solution, at relatively low concentration of aluminum (< 0.1 M), only one main peak is observed at *ca.* 620 cm^{-1}, which correspond to the symmetrical stretching vibration mode of the $Al(OH)_4^-$. When the concentration of the aluminum is increased, two peaks emerge at the two sides of the main peak, at *ca.* 500 cm^{-1} and at *ca.* 620 cm^{-1}.

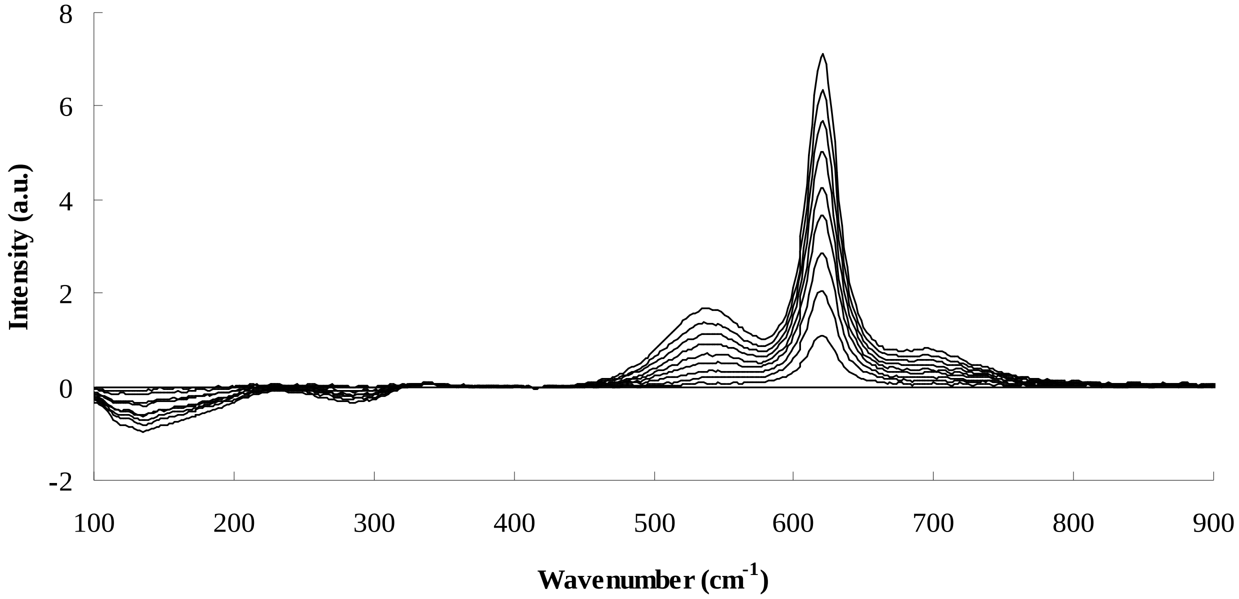


Figure 5.7 The background corrected Raman spectrum of Na-aluminate solutions, at Na$^+$-concentration of 8.2 M (const.) and at Al(III)-concentrations of 0.1- 4.2 M (from bottom to top); on the basis of the data published in [6].

The dimerization takes place according to

$$2\ Al(OH)_4^- \rightleftarrows [Al(OH)_3\text{–}O\text{–}Al(OH)_3]^{2-} + H_2O \qquad (5.12)$$

At high concentrations of Al(III) (*e.g.*, in solution used in the Bayer process to manufacture alumina from bauxites) the dimeric species is present in appreciable quantities. It has also been shown, that the dimerization is independent of the temperature. For the structure of the dimer, and oxo-bridged structure (Figure 5.8) was suggested, which was confirmed by single crystal XRD measurements (that is, the Raman spectrum of the solution and that of the single crystalline solid was found to be very similar.) Interestingly, this dimerization process can only be seen in alkaline Al(III)-solutions; such species is not detectable in analogous Ga(III) or B(III) containing, hyperalkaline solutions.

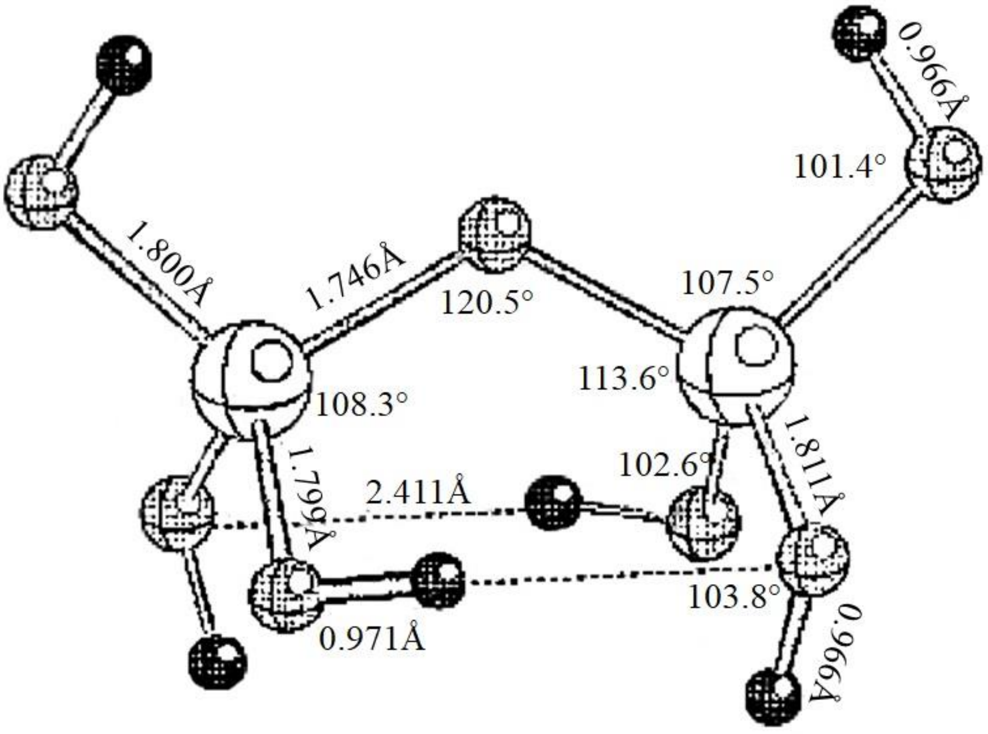


Figure 5.8 The structure of the $[Al(OH)_3–O–Al(OH)_3]^{2–}$ dimeric species in solution; on the basis of the data published in [6].

5.3 Application of extremely concentrated electrolytes in analytical chemistry

Extremely concentrated aqueous solutions are used for the removal of carbonate from MOH solutions, where M^+ = Li^+, Na^+, K^+, Cs^+ and $(CH_3)_4N^+$. It is well known, that Na_2CO_3 is practically insoluble in (that is, salted out from) saturated NaOH solutions, this is the basis for the so-called Sörensen method for carbonate removal from and preparation of NaOH titrant solutions. It has been shown, that significantly smaller NaOH concentrations (down to 8 M) can be made free of carbonate this way; the solubility of the Na_2CO_3 is sufficiently low under these conditions.

For MOH-s with M^+ = Li^+, K^+, Cs^+ and $(CH_3)_4N^+$ the salting-out method does not work. All these base solutions (except for CsOH) at any concentrations as well as NaOH solutions with concentrations less than 8 M can be made carbonate free, if CaO is added to the system and after intensive stirring, the solution is filtrated through a caustic resistant filter (such filtration systems are commercially available.) The basis of this method is, that CaO forms $CaCO_3$ precipitate with the carbonate ions, which can readily be removed from the slurry *via* filtration. Interestingly, CsOH solutions cannot be made carbonate free with using this method. For these solutions, the addition of $Ba(OH)_2 \cdot xH_2O$ proved to be the suitable means for carbonate removal. In this case, $BaCO_3$ precipitate is formed, which removes the carbonate content of the solution, practically quantitatively.

5.4 Questions and problems

1. Compare the physico-chemical properties of dilute and concentrated aqueous solutions!
2. How are density measurements performed for concentrated electrolyte solutions?
3. Describe the estimation of the density of aqueous electrolytes and their mixtures!
4. How are viscosity measurements performed for concentrated electrolyte solutions?
5. Describe the estimation of the viscosity of aqueous electrolytes and their mixtures!
6. How can one perform pH measurement in strongly alkaline solutions?
7. Give an example for the application of UV-Vis spectrophotometry in the study of extremely concentrated electrolyte solutions!
8. Give an example for the application of Raman spectroscopy in the study of extremely concentrated electrolyte solutions!
9. What is the role of extremely concentrated electrolyte solutions in the removal of carbonate from concentrated alkali-hydroxide solutions?

Literature

[1] K. Izutsu, Electrochemistry in Nonaqueous Solutions, Wiley-VCH 2002

[2] M. Guane-Escard: Molten salts: from Fundamentals to Applications, Kluwer, Dordrecht, 2001.

[3] V. Danek, Main Features of Molten Salt Systems, Physico-Chemical Analysis of Molten Electrolytes, Elsevier, Amsterdam, 2006.

[4] K. E. Johnson, What is an ionic liquid?, The Electrochemical Society Interface, Spring 2007

[5] N. V. Plechkova, K. R. Seddon, Application of Ionic Liquids in the Chemical Industry, Chemical Society Reviews, 2008, *37*, 128.

[6] P. Sipos, The structure of Al(III) in strongly alkaline aluminate solutions — A review, Journal of Molecular Liquids, 2009, *146*, 1.

Knowledge, skills, attitudes, responsibilities/autonomy

Upon absolving the course, the student

Knowledge	**Skills**	**Attitudes**	**Responsibilities/ autonomy**
understands the necessity of applying solvents other than water, the conditions of their possible use, and the underlying chemical reasons of the differences in their behavior	recognizes, that the application of non-aqueous solvents broadens the width of the “playground” in the chemical laboratory practice	looks at the application of non-aqueous solvents as a valuable intellectual asset that a chemist may have	builds in the chemistry in the non-aqueous solutions in his/her knowledge in a creative manner
has a clear understanding of the significance of the physical properties of molecular liquids	keeps the role of the physical properties in her/his mind in choosing the right solvent for a given process	upon designing the various experimental steps, takes into account the hazards associated with the use of non-aqueous solvents; makes efforts to pinpoint the optimal ensemble of solvent properties for the given chemical task	complies with the work- and safety regulations associated with the use of organic solvents; makes sure that these rules are observed by those who are supervised by her/him
possesses a thorough knowledge on the fundamentals, chemical reasons and trends of the chemical properties of non-aqueous solvents	has the ability of integrating the knowledge related to the chemistry of the non-aqueous solvents into her/his general-, physico-, inorganic-, organic- and analytical chemical skills	has a critical understanding on the criteria associated with the applicability of molecular liquids	
understands the structure and the acid-base, redox and coordination chemical properties of electrolytes and solutes dispersed in an organic solvent	has the skill of being able to predict the direction of the chemical reactions taking place in the solutions containing dissolved electrolytes or solutes	keeps the structure and the acid-base, redox and coordination chemical properties of electrolytes and solutes dispersed in an organic solvent in mind during reactor design	able to act independently in relation to the experimental application of organic solvents

understands the background of the physical and chemical properties of melts, in particular those of molten salts, their structure, the possible reactions taking place in them and their potential applications	able to analyze the chemical reactions taking place in the melts, understands the practical and technological relevance of them		complies with the work- and safety regulations associated with the use of molten salts and observes the special requirements of this area; makes sure that these rules are observed by those who are supervised by her/him
recognizes the technological and “green” relevance of ionic liquids and supercritical fluids	capable of applying her/his knowledge associated with ionic liquids and supercritical fluids in the design and development of chemical reactions and technologies	has a clear understanding on the environmental potential of ionic liquids and supercritical fluids, actively contributes to the dissemination of this in the public	upon decision making, takes responsibility in the professional soundness of introducing these novel concepts
recognizes the theoretical and practical relevance of extremely concentrated aqueous solutions, understands the theoretical and practical considerations associated with them; understands their structure, the way of their description and is aware of the complications associated with them	applies her/his knowledge related to extremely concentrated aqueous solutions in the everyday laboratory practice	ready to recognize the relevance of leaving the comfort zone of dilute solutions and the perspectives that their use opens	applies his/her knowledge in this field creatively

This teaching material has been made at the University of Szeged and supported by the European Union. Project identity number: EFOP-3.4.3-16-2016-00014