

ACID-BASE INTERACTIONS

10.1 GENERAL CONCEPT OF ACID-BASE INTERACTIONS

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Acid-base interactions have found numerous applications in research dealing with adsorption of molecules of liquids on the surfaces of solids. The main focus of this research is to estimate the thermodynamic work of adhesion, determine mechanism of interactions, analyze the morphology of interfaces and various surface coatings, develop surface modifiers, study the aggregation of macromolecular materials, explain the kinetics of swelling and drying, understand the absorption of low molecular weight compounds in polymeric matrices, and determine the properties of solid surfaces. In addition to these, there are many other applications.

Several techniques are used to determine and interpret acid-base interactions. These include: contact angle, inverse gas chromatography, IGC, Fourier transform infrared, FTIR, and X-ray photoelectron spectroscopy, XPS. These methods, as they are applied to solvents are discussed below.

Contact angle measurements have long been used because of common availability of instruments. In recent years, they have been developed from simple optical devices to the present day precise, sophisticated, computer-controlled instruments with sufficient precision. Van Oss and Good^{1,2} developed the basic theory for this method. Their expression for surface free energy is used in the following form:

$$\gamma = \gamma^{LW} + \gamma^{AB} = \gamma^{LW} + 2\sqrt{\gamma^+ \gamma^-} \quad [10.1.1]$$

where:

γ^{LW}	Lifshitz-van der Waals interaction
γ^{AB}	acid-base interaction
γ^+	Lewis acid parameter of surface free energy
γ^-	Lewis base parameter of surface free energy.

The following relationship is pertinent from the equation [10.1.1]:

$$\gamma^{AB} = 2\sqrt{\gamma^+ \gamma^-} \quad [10.1.2]$$

A three-liquid procedure was developed¹⁻³ which permits the determination of the acid-base interaction from three measurements of contact angle:

$$\begin{aligned}\gamma_{L1}(1 + \cos \theta_1) &= 2\left(\sqrt{\gamma_S^{LW} \gamma_{L1}^{LW}} + \sqrt{\gamma_S^+ \gamma_{L1}^-} + \sqrt{\gamma_S^- \gamma_{L1}^+}\right) \\ \gamma_{L2}(1 + \cos \theta_2) &= 2\left(\sqrt{\gamma_S^{LW} \gamma_{L2}^{LW}} + \sqrt{\gamma_S^+ \gamma_{L2}^-} + \sqrt{\gamma_S^- \gamma_{L2}^+}\right) \\ \gamma_{L3}(1 + \cos \theta_3) &= 2\left(\sqrt{\gamma_S^{LW} \gamma_{L3}^{LW}} + \sqrt{\gamma_S^+ \gamma_{L3}^-} + \sqrt{\gamma_S^- \gamma_{L3}^+}\right)\end{aligned}\quad [10.1.3]$$

Solving this set of equations permits the calculation of solid parameters from equation [10.1.1]. The work of adhesion, W_a , between a solid and a liquid can be calculated using the Helmholtz free energy change per unit area:

$$-\Delta G_{SL} = W a_{SL} = \gamma_S + \gamma_L - \gamma_{SL} = 2\left(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}\right) \quad [10.1.4]$$

Determination is simple. However, several measurements (usually 10) should be taken to obtain a reliable averages (error is due mostly to surface inhomogeneity). There is a choice between measuring the advancing or the receding contact angle. Advancing contact angles are more representative of equilibrium contact angles.³

Inverse gas chromatography data are interpreted based on Papirer's equation:^{4,5}

$$RT \ln V_N = 2N(\gamma_S^D)^{1/2} a(\gamma_L^D)^{1/2} + c \quad [10.1.5]$$

where:

R	gas constant
T	temperature
V_N	net retention volume
N	Avogadro's number
γ^D	dispersion component of surface energy
S, L	indices for solid and liquid, respectively
a	molecular area of adsorbed molecule
c	integration constant relative to a given column.

Several probes are used to obtain the relationship between $RT \ln V_N$ and $a\gamma_L^D$. From this relationship the reference retention volume, V_N^{REF} , is calculated and used to calculate the acid-base interaction's contribution to the free energy of desorption:

$$\Delta G_{AB} = RT \ln \frac{V_N}{V_N^{REF}} \quad [10.1.6]$$

If data from a suitable temperature range for ΔG_{AB} can be obtained, the acid-base enthalpy, ΔH_{AB} can be calculated using the following equation:

$$\Delta H_{AB} = K_a DN + K_b AN \quad [10.1.7]$$

where:

K_a	acid interaction constant
K_b	base interaction constant
DN	donor number
AN	acceptor number

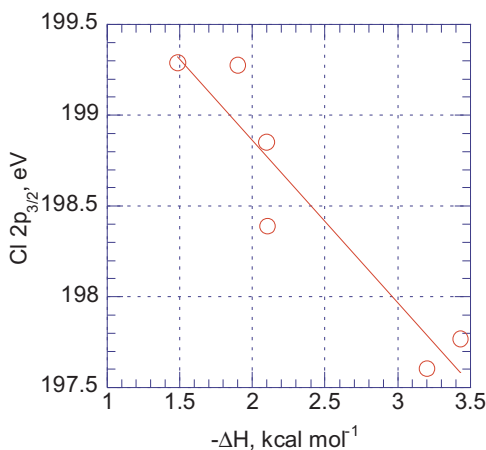


Figure 10.1.1. Correlation of binding energy and ΔH_{AB} for several polymers. [Adapted, by permission, from J F Watts, M M Chehimi, *International J. Adhesion Adhesives*, **15**, No.2, 91-4 (1995).]

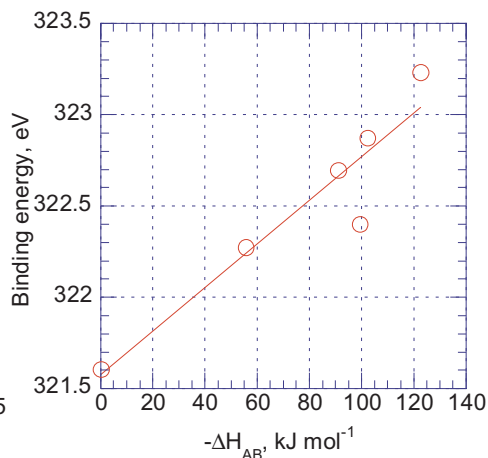


Figure 10.1.2. Correlation of binding energy and ΔH_{AB} for several solvents. [Adapted, by permission, from J F Watts, M M Chehimi, *International J. Adhesion Adhesives*, **15**, No.2, 91-4 (1995).]

Finally the plot of $\Delta H_{AB}/AN$ vs. DN/AN gives K_a and K_b . Further details of this method are described elsewhere.⁴⁻⁹ It can be seen that the procedure is complicated. The various conditions of experiments conducted in various laboratories were sufficiently different to prevent correlation of data between laboratories.¹⁰ To rectify this situation, a large body of data was obtained for 45 solvents and 19 polymers tested under uniform conditions.¹⁰

Fowkes¹¹ showed that the carbonyl stretching frequency shifts to lower values as the dispersion component of surface tension increases. The following empirical relationship was proposed:

$$\Delta H_{AB} = 0.236\Delta\nu^{AB} \quad [10.1.8]$$

where:

ΔH_{AB} the enthalpy change on acid-base adduct formation
 $\Delta\nu^{AB}$ projection of carbonyl stretching frequency on dispersive line.

It should be noted that, as Figure 7.1.16 shows, the change in frequency of carbonyl stretching mode is related to the process of crystallization.¹²

XPS is emerging as very precise method for evaluating acid-base interactions based on the works by Chehimi *et al.*⁶⁻⁹ There is very good correlation between XPS chemical shift and the change in exothermic enthalpy of acid-base interaction. Drago's equation is used for data interpretation:¹³

$$-\Delta H_{AB} = E_A E_B + C_A C_B \quad [10.1.9]$$

where:

A, B subscripts for acid and base, respectively
 E_A, E_B susceptibility of acid or base species to undergo an electrostatic interaction
 C_A, C_B susceptibility of acid or base species to undergo a covalent interaction.

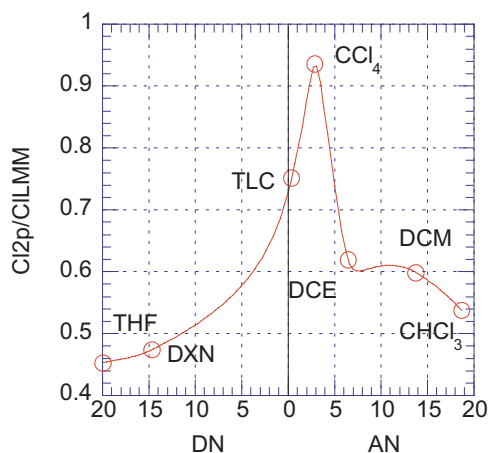


Figure 10.1.3. Intensity ratio vs DN and AN. [Adapted, by permission, from M L Abel, M M Chehimi, *Synthetic Metals*, **66**, No.3, 225-33 (1994).]

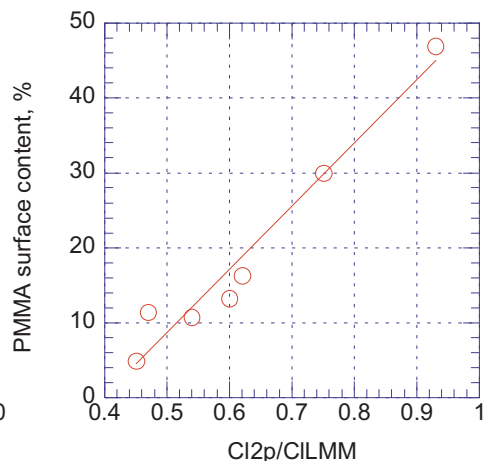


Figure 10.1.4. PMMA surface content vs. intensity ratio. [Data from M L Abel, M M Chehimi, *Synthetic Metals*, **66**, No.3, 225-33 (1994).]

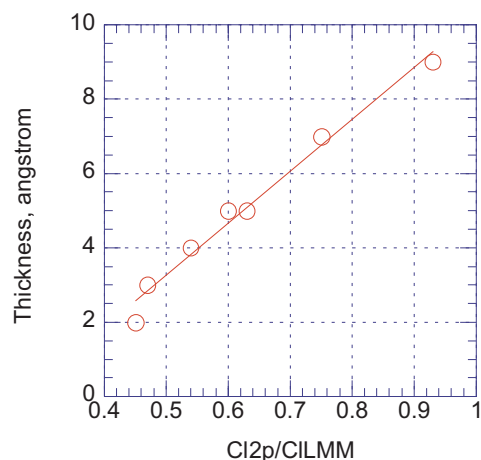


Figure 10.1.5. Thickness of PMMA overlayers vs. intensity ratio. [Data from M L Abel, M M Chehimi, *Synthetic Metals*, **66**, No.3, 225-33 (1994).]

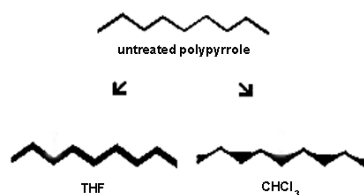


Figure 10.1.6. Schematic diagram of surface roughness of polypyrrole and deposition of PMMA from two different solvents. [Adapted, by permission, from M L Abel, J L Camalet, M M Chehimi, J F Watts, P A Zhdan, *Synthetic Metals*, **81**, No.1, 23-31 (1996).]

Figure 10.1.1. The enthalpy change caused by the acid-base adduct formation is obtained from a study of the same solid with different solvent probes (see Figure 10.1.2). Having this data, coefficients E and C can be calculated from the chemical shifts in any system.

Figure 10.1.3 shows that there is a correspondence between DN and AN values of different solvents and Cl(2p)/Cl(LMM) intensity ratios.⁷ Figure 10.1.4 shows that the type of solvent (measured by its Cl(2p)/Cl(LMM) intensity ratio) determines adsorption of basic PMMA on acidic polypyrrole. Figure 10.1.5 shows that also the thickness of PMMA overlayer corresponds to Cl(2p)/Cl(LMM) intensity ratio of solvent.

The determination of properties of unknown system requires that master curve be constructed. This master curve is determined by testing a series of different polymers exposed to a selected solvent. An example of such a relationship is given in

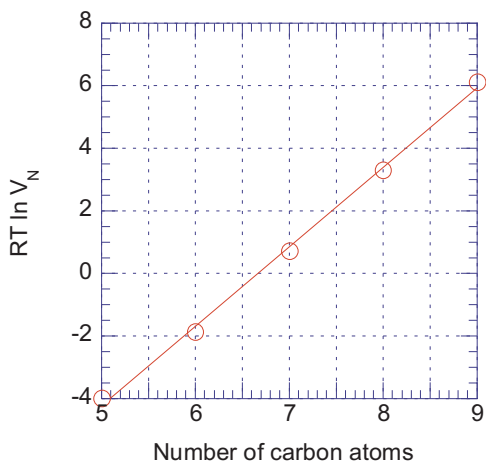


Figure 10.1.7. Relationship between $RT \ln V_N$ and number of carbon atoms in n-alkanes. [Adapted, by permission from M M Chehimi, E Pigois-Landureau, M Delamar, J F Watts, S N Jenkins, E M Gibson, *Bull. Soc. Chim. Fr.*, **9**(2) 137-44 (1992).]

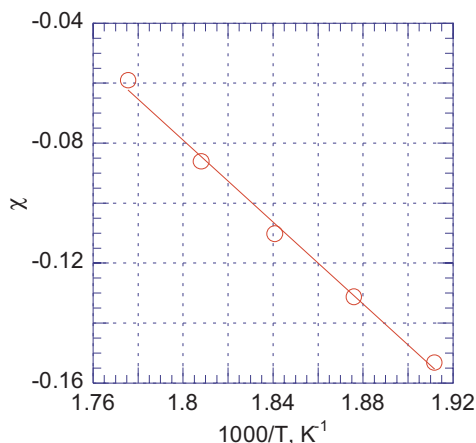


Figure 10.1.8. Flory interaction parameter vs. inverse temperature for polyamide. [Adapted, by permission, from L Bonifaci, G Cavalca, D Frezzotti, E Malaguti, G P Ravanetti, *Polymer*, **33**(20), 4343-6 (1992).]

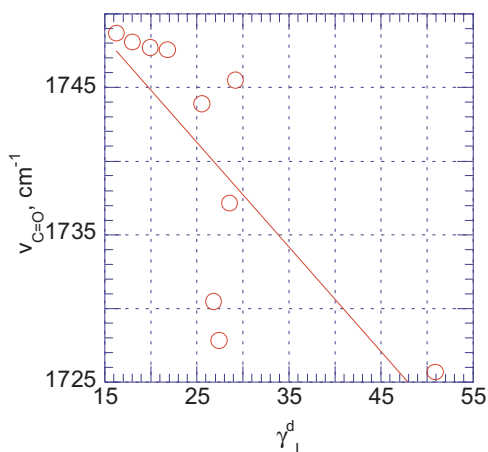


Figure 10.1.9. Carbonyl stretching frequency vs. dispersion contribution to surface tension of solvent. [Adapted, by permission from M M Chehimi, E Pigois-Landureau, M Delamar, J F Watts, S N Jenkins, E M Gibson, *Bull. Soc. Chim. Fr.*, **129**(2) 137-44 (1992).]

Such a correlation must be established to calculate the acid-base interaction's contribution to the free energy of desorption, ΔG_{AB} , as pointed out in discussion of equations [10.1.5] and [10.1.6]. Figure 10.1.8 shows that the Flory interaction parameter (measured by IGC) increases as the temperature increases.

XPS analysis combined with analysis by atomic force microscopy, AFM, determines differences in the surface distribution of deposited PMMA on the surface of polypyrrole depending on the type of solvent used (Figure 10.1.6).⁶ AFM, in this experiment, permitted the estimation of the surface roughness of polypyrrole. When PMMA was deposited from tetrahydrofuran, a poor solvent, it assumed a surface roughness equivalent to that of polypyrrole. Whereas PMMA, when deposited from a good solvent - CHCl_3 ,⁶ developed a smooth surface. The above examples show the importance of solvents in coating morphology.

Figure 10.1.7 shows the correlation between the number of carbon atoms in n-alkanes and the net retention volume of solvent using IGC measurements.⁸ Such a

Figure 10.1.9 shows a good correlation between carbonyl stretching frequency as determined by FTIR and the dispersion contribution of surface tension of the solvent.

The above shows a good correspondence between the data measured by different methods. This was also shown by a theoretical analysis of the effect of acid-base interactions on the aggregation of PMMA.¹⁴ But there is as yet no universal theory for the characterization of acid-base interaction.

The following Sections show specific applications of acid-base interactions and present data on solvents applied to various phenomena in which acid base interaction is important.

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10.2 EFFECT OF POLYMER/SOLVENT ACID-BASE INTERACTIONS: RELEVANCE TO THE AGGREGATION OF PMMA

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10.2.1 RECENT CONCEPTS IN ACID-BASE INTERACTIONS

Polymer solvent interactions determine several properties, such as, solubility, solvent retention, plasticizer action, wettability, adsorption and adhesion. The solubility parameter is an important criterion for the choice of solvents. However, acid-basic characters of both solvent and polymer are also determinant parameters, which can affect the solution and final film properties. This part, devoted to the influence of acid-base interactions on the aggregation of poly(methyl methacrylate) will first present some recent concepts in acid-base interactions, followed by two practical examples based on experimental results obtained for PMMA/solvent systems.

10.2.1.1 The nature of acid-base molecular interactions

10.2.1.1.1 *The original Lewis definitions*

The Lewis definitions of acid-base interactions are now over a half a century old. Nevertheless they are always useful and have broadened their meaning and applications, covering concepts such as bond-formation, central atom-ligand interactions, electrophilic-nucleophilic reagents, cationic-anionic reagents, charge transfer complex formation, donor-acceptor reactions, etc. In 1923 Lewis reviewed and extensively elaborated the theory of the electron-pair bond,¹ which he had first proposed in 1916.² In this small volume which had since become a classic, Lewis independently proposed both the proton and generalized solvent-system definitions of acids and bases. He wrote:

"An acid is a substance which gives off the cation or combines with the anion of the solvent; a base is a substance which gives off the anion or combines with the cation of the solvent".

The important point that Lewis revealed is that though the acid-base properties of species are obviously modified by the presence or absence of a given solvent, their ultimate cause should reside in the molecular structure of the acid or base itself, and in light of the electronic theory of matter, not in a common constituent such as H^+ or OH^- , but in an analogous electronic structure. He states that a basic substance is one which has a lone pair of electrons which may be used to complete the stable group of another atom (the acid) and that an acid substance is one which can employ a lone pair from another molecule (the base) in completing the stable group of one of its own atoms. Moreover by tying his definitions to the concept of chemical bond, Lewis linked their usefulness to contemporary views on the nature of the chemical bond itself. Hence, the shared electron-pair bond model explains the existence of both non-polar bond and polar link from the same premises. As the electrochemical natures of two atoms sharing an electron pair began to differ more and more, the pair should become more and more unequally shared, eventually becoming the sole property of the more electronegative atom and resulting in the formation of ions. Ionic and non-polar bonds appear as logical extremes of a continuum of intermediate bond type. Differences in the continuum are only attributable to variations in the electron-pair donation, i.e., in the way in which the charges are localized within the molecule. As a consequence the distinctions between salts, acids and bases, coordination compounds and organic compounds are not of fundamental nature.

10.2.1.1.2 *Molecular Orbital (MO) approach to acid-base reactions*

Translated into the idiom of molecular orbital theory,³ the acid-base definitions should be read as follows:

- A base is a species, which employs a doubly occupied orbital in initiating a reaction.
- An acid is a species, which employs an empty orbital in initiating a reaction.

The term species may mean a discrete molecule, a simple or complex ion or even a solid exhibiting non-molecularity in one or more dimensions (graphite as an example). Free atoms seldom act as Lewis acids and bases. They usually have one or more unpaired electrons and their reactions are more accurately classified as free radical. The donor orbital is usually the highest occupied molecular orbital HOMO, and the acceptor orbital is usually the lowest unoccupied molecular orbital or LUMO. The molecular orbital definitions have a number of important consequences:

First, it is not necessary that the donor and acceptor orbitals be localizable on a single atom or between two atoms, as implied by Lewis dot structures. That is, the orbitals may be multi-centered even in a relatively localized representation. Thus donor-acceptor interactions involving delocalized electron systems (π -ring)⁴⁻⁵ are naturally subsumed by the definitions.

Second, the HOMO or donor orbital on a base is likely to be either bonding or non-bonding in character, the latter always being the case for mono-atomic species. The LUMO or acceptor orbital on an acid is likely to be either anti-bonding or non-bonding in character, the latter always being the case for mono-atomic species.

Third, all degrees of electron donation are possible, ranging from essentially zero in the case of weak intermolecular forces and idealized ion associations to the complete transfer of one or more electrons from the donor to the acceptor. This continuity can be represented [10.2.1] by wave functions,⁶ where the degree of donation increases as the ratio (a/b).²

$$\Psi_{AB} = a\Psi_A + b\Psi_B \quad [10.2.1]$$

where:

Ψ_{AB}	wave function of the acid-base one-to-one adduct
Ψ_A	ground state wave function of the acid
Ψ_B	ground state wave function of the base
a, b	weighting coefficients

We have reported in Table 10.2.1 the possible adducts classified in terms of the bonding properties of the donor and acceptor orbitals of the acid and base. Complete description of the mechanisms involved during the following adducts formation can be found in Jensen⁷ complete review.

Table 10.2.1. Possible acid-base adducts in terms of orbitals properties

			Acceptor orbital of the acid		
			Non-bonding	Anti-bonding	
				n	σ^*
Donor orbital of the base	Non-bonding	n	n-n	n σ^*	n π^*
	Bonding	σ	σ n	$\sigma\sigma^*$	$\sigma\pi^*$
		π	π n	$\pi\sigma^*$	$\pi\pi^*$

Even if the nature of an acid or a base is highly relative, a brief classification based on bonds properties and orbitals symmetry can be proposed:

n donor:	Lewis bases, complex and simple anions, carbanions, amines, oxides, sulfurs, phosphines, sulfoxides, ketones, ethers, alcohols ...
π donor:	unsaturated and aromatic hydrocarbons having electron donor substituents.....
σ donor:	saturated hydrocarbons, CO, single links like C-C, C-H, polar links like NaCl, BaO, silanes....
n acceptor:	Lewis acids, simple cations....
π acceptor:	N ₂ , SO ₂ , CO ₂ , BF ₃ , dienic and unsaturated and aromatic hydrocarbons having electron acceptor substituents....

σ acceptor: Brönsted acids, boranes and alkanes having strong acceptor substituents, such as, CHCl_3 , halogens....

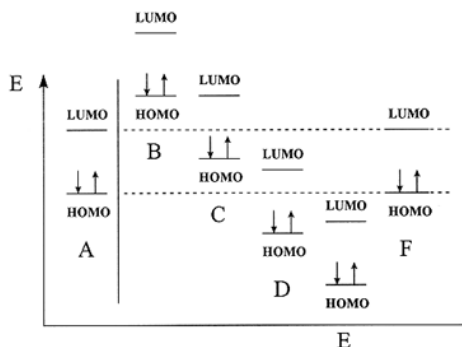


Figure 10.2.1. How do donor-acceptor molecular orbital interactions work?

To summarize how acid-base reactions do work on the basis of molecular orbitals perturbation theory, we have reported on Figure 10.2.1, the relative energies (as perturbed by the field of the other reactant) of the frontier orbitals HOMO and LUMO of a hypothetical species A and of the frontier orbitals of several hypothetical reaction partners B, C, D, E and F. This figure is intended to represent possible variations of donor-acceptor properties in the broadest possible context i.e. not only those species encountered in aqueous solution but also those stabilized by non-aqueous environments.

According to Figure 10.2.1, with respect to B, complete electron transfer from B to A will be favorable and A will act as an oxidizing agent. With respect to C, the A(LUMO) - C(HOMO) perturbation will be favorable and A will act as an acid. With respect to D, the A(HOMO) - D(LUMO) perturbation will be favorable and A will act as a base. Lastly, with respect to E, complete electron transfer from A to E will be favorable and A will act as a reducing agent. For F species, the frontiers orbitals are quite degenerated with those of A. Here neither species is clearly the donor nor acceptor and species may display both behavior simultaneously (case of multisite interactions encountered in concerted organic cycloaddition reactions).

10.2.1.1.3 The case of hydrogen bonding

In addition to the general discussion of Lewis acid-base interactions, hydrogen bonding represents a special case. According to Pauling, hydrogen bonding is partly covalent and partly ionic (polar). Nevertheless, it is obvious that electrostatic and charge transfer interactions are predominant for hydrogen bonds. In most cases the principal charge transfer contribution is derived from the proton acceptor - proton donor charge transfer complex through the σ -type interactions. Moreover hydrogen bonds complexes are linear and the angle between the H bond and the molecular axis of the proton acceptor are mainly 0° or 60° .

To conclude this first theoretical part, the chemical phenomena subsumed by the category of acid-base reaction, are the following:

- Systems defined by the Arrhenius description, solvent system, Lux-Flood and proton acid-base definitions
- Traditional coordination chemistry and “non-classical” complexes
- Solvation, solvolysis and ionic dissociation phenomena in both aqueous and non-aqueous solutions
- Electrophilic and nucleophilic reactions in organic and organometallic chemistry
- Charge transfer complexes, molecular addition compounds, weak intermolecular forces, hydrogen bonds
- Molten salt phenomena, salt formation

10.2.1.2 Quantitative determination of acid-base interaction strength

10.2.1.2.1 Perturbation theory

Hudson and Klopman⁸ proposed an equation to describe the effect of orbital perturbation of two molecules on chemical reactivity. Their hypothesis is that the initial perturbation determines the course of a reaction or an interaction. They applied quantum-mechanical method⁹ to treat the encounter of two interacting systems as reactivity. Their equation for interaction energy can be simplified by including only two terms [10.2.2]: the Coulombic interaction and the frontier orbital interaction between HOMO and LUMO.

$$\Delta E_{\text{int}} = -\frac{Q_N Q_E}{\epsilon R} + \frac{2(C_N C_E \beta)^2}{E_{\text{HOMO}} - E_{\text{LUMO}}} \quad [10.2.2]$$

where:

Q_N	total charges of nucleophile N
Q_E	total charges of electrophile E
C_N	coefficient of the atomic orbital N
C_E	coefficient of the atomic orbital E
β	resonance integral
ϵ	permittivity
R	interatomic distance
E_{HOMO}	energy level of the HOMO orbital
E_{LUMO}	energy level of the LUMO orbital

The relative magnitudes of the numerator and denominator of the second term determine the extent of perturbation and the type of reactivity. For electrostatic interactions, the first term dominates: this is the case of highly polar acceptors of low electron affinity and donors highly electronegative, while for electron donor - electron acceptor interaction, the second term dominates. Thus, a molecular interaction encompasses chiefly both acid-base and donor-acceptor interactions. On the other hand if the second frontier orbital term dominates, the extent of perturbation is large and the charge transfer is large, leading to a large gain in stability. The frontier orbital controlled processes are favored by the presence of weakly polar species lacking high charge density but possessing reactive atoms with large orbital radii. This second term is also benefitted by bases of low electronegativity and acids of high electron affinity.

10.2.1.2.2 Hard-Soft Acid-Base (HSAB) principle

The energy gap between HOMO and LUMO has been equated to the absolute hardness of the HSAB principle. This principle¹⁰ describes some basic rules about kinetics and equilibrium of the acid-base interactions in solutions. The HSAB principle will be described as it has evolved in recent years on the basis of the density-functional theory.¹¹ For organic interactions, the following statements were proposed:

- A hard acceptor has a high energy LUMO and usually a positive charge
- A soft acceptor has a low energy LUMO but does not necessarily have a positive charge
- A hard donor has a low energy HOMO and usually a negative charge
- A soft donor has a high energy HOMO but does not necessarily have a negative charge

The principle states that hard acid prefers to interact with a hard base, and vice versa, a soft acid with a soft base. A hard-hard interaction is fast because of large Coulombic attraction, a soft-soft interaction is fast because of large orbital overlap between HOMO and LUMO. However the problem is, what is the physical meaning of hardness?

10.2.1.2.3 Density functional theory

Parr and al.¹² gave in 1988 a theoretical support to the absolute hardness. In the density functional theory two basic parameters were introduced. Any chemical system can be characterized by its chemical potential, μ , and its absolute hardness, η . The chemical potential measures the escaping tendency of an electronic cloud, while absolute hardness determines the resistance of the species to lose electrons. The exact definitions of these quantities are:

$$\mu = \left(\frac{\partial E}{\partial N} \right)_v \quad \text{and} \quad \eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_v \quad [10.2.3]$$

where :

μ	chemical potential
η	absolute hardness
E	electronic energy
N	number of electrons
v	potential due to the nuclei plus any external potential.

However, according to frontier orbital method,¹³ the relationship between η and the HOMO and LUMO energies is reduced to:

$$\eta \approx -\frac{1}{2} (E_{HOMO} - E_{LUMO}) \quad [10.2.4]$$

where :

η	absolute hardness
E_{HOMO}	energy level of the HOMO orbital
E_{LUMO}	energy level of the LUMO orbital.

Of course the absolute softness is the reciprocal of the absolute hardness. The apparent success of the density-functional theory is to provide two parameters from which we can calculate the number of electrons transferred, resulting mainly from the charge transfer between two molecules, i.e., from electrons flow until chemical potential reaches an equilibrium. As a first approximation, the number of electron transferred is given¹⁴ by:

$$N_{trans} = \frac{\mu_B - \mu_A}{2(\eta_A - \eta_B)} \quad [10.2.5]$$

where:

N_{trans}	number of electrons transferred
μ_A	chemical potential of the acid
μ_B	chemical potential of the base
η_A	absolute hardness of the acid
η_B	absolute hardness of the base.

This number varies from 0 to 1 and it is in most cases a fractional number. As an example¹⁵ for the interaction between Cl_2 and substituted aromatic compounds, N_{trans} varies

from -0.013 to 0.20. Calculation for various solid polymers could be found in a paper of Lee.¹⁶

10.2.1.2.4 Effect of ionocity and covalency: Drago's concept

Similar to the perturbation theory, Drago and Wayland¹⁷ proposed a four-parameter equation for predicting reactions enthalpies between acid and base species. Both species are each characterized by two independent parameters: an E value which measures their ability to participate in electrostatic bonding, and a C value which measures their ability to participate in covalent bond. Both E and C values are derived empirically to give the best curve fit of calculated to experimental heats of formation for the largest possible number of adducts, leading to:

$$-\Delta H^{AB} = E_A E_B + C_A C_B \quad [10.2.6]$$

where:

ΔH^{AB}	enthalpy of acid-base adduct formation
E_A	ability of the acid to participate in electrostatic bonding
E_B	ability of the base to participate in electrostatic bonding
C_A	ability of the acid to participate in covalent bonding
C_B	ability of the base to participate in covalent bonding.

A self-consistent set of E and C values is now available¹⁸ for 33 acids and 48 bases, allowing ΔH prediction for over 1584 adducts. It is assumed that the conditions under which measurements are made (gas phase or poorly coordinating solvents) give rather constant entropy contribution and that most of adducts are of one-to-one stoichiometry. Table 10.2.2 gathers Drago's parameters, given in (kcal/mol)^{0.5} of some common solvents.

Table 10.2.2. Drago's parameters of some common solvents [after reference 18]

Acid	C_A	E_A	Base	C_B	E_B
Phenol	0.442	4.330	Acetone	2.330	0.987
Chloroform	0.159	3.020	Benzene	0.681	0.525
Water	2.450	0.330	Ethyl acetate	1.740	0.975
tert-Butyl alcohol	0.300	2.040	Pyridine	6.400	1.170
Iodine	1.000	1.000	Methylamine	5.880	1.300
Pyrrole	0.295	2.540	Tetrahydrofuran	4.270	0.978
Trifluoroethanol	0.451	3.88	Dimethylformamide	2.480	1.230

The major importance of the above four parameters is their relationship with the HSAB principle. Actually, through the plot of E_A versus C_A for several liquids on a solid, one can obtain indirectly the values of the chemical softness $1/\eta$ from the slope of C/E , as represented by the following equation :

$$E_A = -\frac{\Delta H^{AB}}{E_B} - C_A \frac{C_B}{E_B} \quad [10.2.7]$$

With the chemical hardness, η , and the electronegativity (or negative chemical potential), one can easily apply the HSAB principle to acid-base interaction and calculate the number of electron transferred.

10.2.1.2.5 Effect of amphotericity of acid-base interaction: Gutmann's numbers

Solvation, solvolysis and ionic dissociation phenomena, in both aqueous and nonaqueous solutions are subsumed by the Lewis definitions. In addition to the previous discussion of the dual polarity character of Lewis acids and bases, it should be noted that many of them are amphoteric, by definition. Donor number, DN, was developed¹⁹ in order to correlate the behavior of a solute in a variety of donor solvents with a given basicity or donicity. A relative measurement of the basicity of a solvent D is given by the enthalpy of its reaction with an arbitrarily chosen reference acid (SbCl_5 in the Gutmann's scale). Latter Mayer²⁰ introduced an acceptor number, AN, as the relative ³¹P NMR shift induced by triethylphosphine, and relative to acidic strength (AN=0 for hexane and 100 for SbCl_5). In 1989, Riddle and Fowkes²¹ modify these AN numbers, to express them, AN*, in correct enthalpic unit (kcal/mol). Table 10.2.3 gathers electron acceptor number AN and AN* and electron donor number DN for amphoteric solvents.

Table 10.2.3. Acceptor number, AN, and donor number, DN, for common solvents [After references 19, 21]

Amphoteric solvent	AN	AN*, kcal/mol	DN, kcal/mol
Acetone	12.5	2.5	17.0
Diethyl ether	3.9	1.4	19.2
Formamide	39.8	9.3	26.6
Tetrahydrofuran	8.0	0.5	20.0
Pyridine	14.2	0.14	33.1
Ethyl acetate		1.5	17.1
Benzonitrile	15.5	0.06	11.9
Nitromethane	20.5	4.3	2.7
Water	54.8	15.1	18.0

The most important assumption of Gutmann's approach is that the order of base strengths established remains constant for all other acids (solutes), the value of the enthalpy of formation of a given adduct is linearly related to the donor number of the base (solvent) through the equation [10.2.8]:

$$-\Delta H_{AB} = a_A DN_B + b_B \quad [10.2.8]$$

where:

ΔH_{AB}	enthalpy of acid-base adduct formation
DN_B	donor number of the base
a_A, b_A	constants characteristic of the acid

Graphically this means that a plot of the DN for a series of donor solvents versus $-\Delta H$ of their adducts formation with a given acid gives a straight line, allowing the determination of a_A and b_A . By experimentally measuring the enthalpy of formation of only two adducts for a given acid, one can predict, through the resulting a_A and b_A values, the enthalpy of adduct formation of this acid with any other donor solvent for which DN is known. Gutmann also proposes that the enthalpy of acid-base interaction could be approximated by a two-parameters equation of the form:

$$-\Delta H_{AB} = \frac{AN_A DN_B}{100} \quad [10.2.9]$$

where:

ΔH_{AB}	enthalpy of acid-base adduct formation
DN_B	donor number of the base
AN_A	acceptor number of the acid

The factor of 100 converts the AN value from a percentage of the $SbCl_5$ value to a decimal fraction. But one had to remind that on the 171 DN values reported in the literature²² only 50 were determined precisely, i.e., calorimetrically.

10.2.1.2.6 Spectroscopic measurements: Fowkes' approach

Fowkes²³ has proposed that for specific functional groups involved in acid-base interaction, the enthalpy of acid-base adduct formation is related to the infrared frequency shift, $\Delta\nu$, of its absorption band according to the following equation:

$$\Delta H_{AB} = k_{AB} \Delta\nu_{AB} \quad [10.2.10]$$

where:

ΔH_{AB}	enthalpy of acid-base adduct formation
$\Delta\nu_{AB}$	infrared frequency shift
k_{AB}	characteristic correlation constant between IR wavenumber shift and enthalpy

k_{AB} is a characteristic constant of the functional group determined on the basis of compared infrared and microcalorimetric results of adduct formation. As an example, the latter is equal to -0.99 kJ/mol/cm for the carbonyl group $C=O$. The stretching frequency of the $C=O$ vibration band is decreased by an amount $\Delta\nu_{AB}$ proportional to the enthalpy of acid-base bonding ΔH_{AB} according to k_{AB} . Such a methodology has recently been nicely confirmed not only for polymer-solvent adduction, but also for polymer/polymer²⁴ and polymer/metal²⁵ adduction.

10.2.2 EFFECT OF POLYMER/SOLVENT INTERACTIONS ON AGGREGATION OF STEREOREGULAR PMMA

10.2.2.1 Aggregation of stereoregular PMMA

PMMA chains are able to form aggregates in the presence of solvent²⁶ (in diluted solution, concentrated solution, gel or solid). Aggregation between isotactic and syndiotactic chains, after mixing in some solvents, leads to stereocomplexes, and self-aggregation corresponds to the aggregation of isotactic or syndiotactic chains together. These two kinds of aggregates result from the development of physical interactions between polymer chains. The formation of aggregates depends mainly on the PMMA degree of stereoregularity and on the nature of the solvent, but also on the temperature, the mixing time, and the isotactic/syndiotactic stoichiometric ratio for stereocomplexes.^{26,27} Complexing solvents fa-

vor the formation of aggregates and non-complexing solvents hinder the formation of aggregates. Table 10.2.4 presents the solvents classification as a function of complexing power for PMMA stereocomplexes formation.

Table 10.2.4. Solvents classification as a function of complexing power for PMMA stereocomplexes formation (after reference 26)

Strongly complexing solvents	CCl ₄ , acetonitrile, DMF, DMSO, THF, toluene, acetone
Weakly complexing solvents	benzene, o-dichlorobenzene, dioxane
Non-complexing solvents	chloroform, dichloromethane

Several works have shown that the aggregation of isotactic and syndiotactic chains leads to the formation of stereocomplexes for which the iso/syndio stoichiometry is found equal to 1/2,^{28,29} probably with a structure composed of a double-stranded helix of a 30/4 helicoidal isotactic chain surrounded by a 60/4 helicoidal syndiotactic chain.³⁰ Syndiotactic PMMA self-aggregates exhibit similar structures, with conformations close to extended chains.³¹ Experimental data indicate that, in self-aggregated syndiotactic PMMA in solution, some of the ester groups are close in contact, probably in a double helix structure³² with solvent molecules included in the cavities of inner- and inter-helices.³³ Isotactic PMMA self-aggregates also exhibit conformational helix structures.

These results prove that the presence of a complexing solvent leads to the formation of well-ordered structure made of paired PMMA chains.

A high degree of stereoregularity is needed to allow the formation of aggregates. Syndiotactic and isotactic sequences lengths have to be larger than a critical length in order to be involved in paired association. As the aggregation power of the solvent increases, the critical sequence length decreases.

Many authors explain aggregation as resulting from interactions between PMMA chains, probably through their ester functional groups.³⁴ The incidence of the nature of the solvent in the aggregate formation is not yet totally clarified in the literature. Apparently, there is no obvious relationship between the solvent polarity and the ability to induce aggregation of PMMA chains.

10.2.2.2 Relation between the complexing power of solvents and their acid-base properties

A tentative explanation of the effect of solvent has been proposed recently by using the Lewis acid-base concept.³⁵ The acid or basic character of a given solvent was studied simultaneously with its strength of complexation in order to establish a relationship between both parameters.

PMMA stereocomplexes and self-aggregates exhibit some similar aspects, particularly the complexing power of the solvent or the helical structure of paired chains.

PMMA is classified as a basic polymer (electron donor, according to the Lewis concept), due to the presence of ester functional groups, where the carbonyl oxygen atom is the basic site.³⁶ PMMA is therefore able to exchange strong acid-base interactions with an acidic solvent, such as, chloroform, which is also a non-complexing solvent. According to Fowkes works, PMMA and chloroform can form acid-base complexes, resulting from the

interaction between the ester basic group of PMMA and the hydrogen acid atom of chloroform.

According to Drago's classification, it appears therefore in Table 10.2.2 that chloroform exhibits an acid character.³⁷ PMMA presents a basic character, with $E_b=0.68$ and $C_b=0.96$.

The fact that an acidic solvent, such as, chloroform is able to exchange strong acid-base interactions with PMMA ester groups is able to explain its non-complexing behavior. Strong acid-base interactions between PMMA and chloroform molecules hinder the aggregation of PMMA chains, reflecting greater PMMA/solvent interactions compared to PMMA/PMMA interactions. In the presence of basic solvents, the lower PMMA/solvent acid-base interactions lead to inter-chains associations (and consequently aggregation), energetically favorable. Moreover, solvents, such as, acetone or THF possess a high degree of self-association (31%, 27% respectively) and Fowkes has shown that the contribution of solvent/solvent acid-base interactions to the heat of vaporization is proportional to the degree of self-association.³⁸ Acetone and THF are therefore strongly acid-base self-associated solvents. As a consequence, they would develop preferentially self-associations (between solvent molecules) rather than PMMA/solvent interactions. Hence the PMMA chains aggregation would be also favored.

Table 10.2.5. AN and DN numbers for complexing and non-complexing solvents (after reference 19)

	AN	DN, kcal/mol
DMF	16.0	26.6
Acetone	12.5	17.0
THF	8.0	20
DMSO	20.4	29.8
Benzene	8.2	0.1
Chloroform	23.1	0

Gutmann's numbers of complexing and non-complexing solvents are listed in Table 10.2.5. The results indicate also that chloroform is an acidic solvent, with a high Acceptor Number (acidic character), and a Donor Number (basic character) equal to zero. The advantage of Gutmann's approach is to consider the potential amphoteric character. As an example, benzene, which is classified as a basic solvent by Drago, exhibits an amphoteric character with a low AN, but also a DN close to zero. This result could explain that, in some cases, benzene (which is generally a complexing solvent) is described as a non-complexing solvent for syndiotactic PMMA.³¹ In this case, amphoteric character of benzene favors acid-base interactions with PMMA.

To resume this part, it is possible to correlate the complexing power of solvents towards stereoregular PMMA with their acid-base character. It appears that complexing solvents exhibit basic character, like PMMA. Moreover, some of them are strongly self-associated. Solvent/solvent and chain/chain interactions are consequently favored, leading to the formation of PMMA aggregates.

On the contrary, chloroform is an acidic solvent, and the development of acid-base interactions with PMMA ester groups helps to hinder the formation of chains aggregates. However, this original view on the relationship between complexing power and solvent acid-base character does not take into account the way of action of the solvent in terms of steric effect and macromolecular conformations of aggregates.

10.2.3 INFLUENCE OF THE NATURE OF THE SOLVENT ON THE α AND β -RELAXATIONS OF CONVENTIONAL PMMA

10.2.3.1 Introduction

Thin polymer films are generally obtained by solution casting, in many applications, such as paints, varnishes, or adhesives. The properties of polymer films obtained from a solution differ from the original bulk properties, and this effect can have some significant consequences on the expected behavior of the final film.

Recent studies have analyzed the influence of the nature of the solvent on the relaxation temperatures of conventional PMMA solid films.^{39,40} PMMA was dissolved in various solvents and the solid films (after solvent evaporation) were analyzed by dielectric spectroscopy. The purpose of the study was to investigate the influence of the nature of the solvent on the α and β -relaxations of PMMA solid films. The α -relaxation is related to the glass transition of PMMA and corresponds to the rotation of lateral groups around the main chain axis.⁴¹ The β -relaxation, which occurs at a lower temperature, is induced by the rotation of the acrylate groups around the C-C bonding which links them to the main chain. Different solutions of conventional (atactic) PMMA in good solvents (chloroform, acetone, toluene and tetrahydrofuran) are cast on a metallic substrate (aluminum). After solvent evaporation at room temperature, solid films of PMMA are analyzed by dielectric spectroscopy (DETA) at 100 Hz and 10 KHz from -40 to 135°C with a scanning temperature of 2°C/min. The variation of the loss factor $\tan \delta$ is studied as function of temperature. The temperatures of the $\tan \delta$ peaks are related to the relaxations temperatures of the polymer.⁴² The reference DETA spectrum is obtained by analyzing a bulk PMMA film obtained from heating press (without solvent).

At 10 KHz, only one peak is detectable (whatever the sample) which is attributed to the α -relaxation. However, the peak is not symmetrical, with a broadening towards the lower temperatures, due to the contribution of the β -relaxation. At 100 Hz, two peaks are present, the major at lower temperature, corresponding to the β -relaxation and the minor at higher temperature, attributed to the α -relaxation.

10.2.3.2 Dielectric spectroscopy results

Table 10.2.6 reports the temperatures of the α -relaxation (measured at 10 KHz) and the β -relaxation (measured at 100 Hz) for the reference sample (bulk PMMA) and the different solution-cast films.

Table 10.2.6. Temperature of α and β -relaxations of bulk PMMA and solution-cast films (after reference 40)

	PMMA bulk	PMMA/ chloroform	PMMA/ toluene	PMMA/ acetone	PMMA/ THF
T° of α peak, °C at 10KHz	108	75	96	85	82
T° of β peak, °C at 100 Hz	40	34	49	45	47

The results show that the temperature of the α -transition is significantly reduced for cast films compared to the bulk polymer, with a lower value for chloroform samples. The decrease of the α -transition temperature can be explained by the presence of residual solvent, inducing a plasticizing effect. On the contrary, an increase of the β -transition tempera-

ture is generally observed for the cast films, except for the 'chloroform' sample. An increase of the T_g -transition temperature indicates a lower mobility of the acrylate groups compared to the bulk polymer. However, for chloroform sample, this mobility is increased.

Two different effects appear and two groups of solvents can then be distinguished: the first group, with chloroform, which induces a higher mobility of both the main chain and the acrylate group (compared to the bulk polymer), and the second group, including acetone, toluene and THF which induce also an increase of the mobility of the main chain, but a decrease of the mobility of the lateral acrylate groups.

The influence of the nature of the solvent on the relaxation temperature can be explained by analyzing the acid-base properties of the polymer and the solvents. PMMA, which is a basic polymer can exchange strong acid-base interactions with an acidic solvent, such as, chloroform. In the solid cast films, acid-base interactions between acrylate groups and residual chloroform occur: some acrylate groups interact with chloroform molecules and PMMA/PMMA self-associations partially disappear, leading to a lower value of the T_g -transition temperature. The mobility of the lateral acrylate groups interacting with chloroform molecules is then higher than the mobility of acrylate groups interacting with other acrylate groups as in bulk PMMA.

Toluene, THF and acetone are described as basic solvents. The residual solvent molecules can therefore only weakly interact with the acrylate groups. Interactions between chains are then favored and self-associations between PMMA chains appear. The rotation of the acrylate groups becomes more difficult compared to the bulk PMMA, probably due to self-aggregation of some PMMA chains (even if the studied polymer is not stereoregular).

To resume, residual solvent molecules present in solid conventional PMMA films are able to significantly modify the polymer relaxation properties. The effect of residual solvent depends strongly on the nature of the solvent, specially its acid-base character.

10.2.4 CONCLUDING REMARKS

These works have shown that acid-basic character of solvent is able to have a major influence on polymer film properties. Acid-base interactions between stereoregular PMMA and some solvents can lead to the formation of aggregates, which modify the solution properties. Elsewhere, residual solvent molecules trapped in solid conventional PMMA films have an effect on the polymer chains mobility, depending on the acid-base character of the solvent. Both solvent effects, due to acid-base interactions, are able to modify the wetting and the adhesion properties of the films, but also the mechanical and the durability behavior of the final film. It is then necessary to take into account, in the choice of a solvent, its acid-base properties, in addition to its solubility parameter, especially for PMMA.

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10.3 SOLVENT EFFECTS BASED ON PURE SOLVENT SCALES

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INTRODUCTION

The solvent where a physico-chemical process takes place is a non-inert medium that plays prominent roles in chemistry. It is well-known¹ that, for example, a small change in the nature of the solvent can alter the rate of a reaction, shift the position of a chemical equilibrium, modify the energy and intensity of transitions induced by electromagnetic radiation or cause protein denaturation. As a result, the possibility of describing the properties of solvents in terms of accurate models has aroused the interest of chemists for a long time.

The interest of chemists in this topic originated in two findings reported more than a century ago that exposed the influence of solvents on the rate of esterification of acetic acid

by ethanol, established in 1862 by Berthelot and Saint-Gilles,² and on the rate of quaternization of tertiary amines by alkyl halides, discovered in 1890 by Menshutkin.³ In his study, Menshutkin found that even so-called “inert solvents” had strong effects on the reaction rate and that the rate increased by a factor about 700 from hexane to acetophenone. Subsequent kinetic studies have revealed even higher sensitivity of the reaction rate to the solvent. Thus, the solvolysis rate of tert-butyl chloride increases 340 000 times from pure ethanol to a 50:50 v/v mixture of this alcohol and water,^{4,5} and by a factor of 2.88×10^{14} from pentane to water.⁶ Also, the decarboxylation rate of 6-nitrobenzisoxazol 3-carboxylate increases by a factor of 9.5×10^7 from water to HMPT.⁷

10.3.1 THE SOLVENT EFFECT AND ITS DISSECTION INTO GENERAL AND SPECIFIC CONTRIBUTIONS

Rationalizing the behavior of a solvent in a global manner, i.e., in terms of a single empirical parameter derived from a single environmental probe, appears to be inappropriate because the magnitude of such a parameter would be so sensitive to the nature of the probe that the parameter would lack predictive ability. One must therefore avoid any descriptions based on a single term encompassing every potential interaction of the solvent, often concealed under a global concept called “solvent polarity”. One immediate way of dissecting the solvent effect is by splitting it into general (non-specific) interactions and specific interactions.

In relation to general interactions, the solvent is assumed to be a dielectric continuum. The earliest models for this type of interaction were developed by Kirkwood⁸ and Onsager,⁹ and were later modified with corrections for the effect of electrostatic saturation.^{10,11} The intrinsic difficulty of these models in accurately determining the dimensions of the cybotactic region (viz. the solvent region where solvent molecules are directly perturbed by the presence of solute molecule) that surrounds each solute molecule in the bulk solvent, have usually raised a need for empirical approximations to the determination of a parameter encompassing solvent polarity and polarizability. An alternative approach to the general effect was recently reported that was derived from liquid-state theories. One case in point is the recent paper by Matyushov et al.,¹² who performed a theoretical thermodynamic analysis of the solvent-induced shifts in the UV-Vis spectra for chromophores; specifically, they studied p-nitroanisole and the pyridinium-N-phenoxide betaine dye using molecular theories based on long-range solute-solvent interactions due to inductive, dispersive and dipole-dipole forces.

A number of general empirical solvent scales have been reported;^{1,13-15} according to Drago,¹⁴ their marked mutual divergences are good proof that they do not reflect general effects alone but also specific effects of variable nature depending on the particular probe used to construct each scale. In any case, there have been two attempts at establishing a pure solvent general scale over the last decade. Thus, in 1992, Drago¹⁴ developed the “unified solvent polarity scale”, also called the “S' scale” by using a least-squares minimization program¹⁶ to fit a series of physico-chemical properties (χ) for systems where specific interactions with the solvents were excluded to the equation $\Delta\chi = PS' + W$. In 1995, our group reported the solvent polarity-polarizability (SPP) scale, based on UV-Vis measurements of the 2-N,N-dimethyl-7-nitrofluorene/2-fluoro-7-nitrofluorene probe/homomorph pair.¹⁵

According to Drago,¹⁷ specific interactions can be described as localized donor-acceptor interactions involving specific orbitals in terms of two parameters, viz. E for electrostatic interactions and C for covalent interactions; according to Kamlet and Taft,^{18a} such interactions can be described in terms of hydrogen-bonding acid-base interactions. In fact,

ever since Lewis unified the acidity and basicity concepts in 1923,¹⁹ it has been a constant challenge for chemists to find a single quantifiable property of solvents that could serve as a general basicity indicator. Specially significant among the attempts at finding one are the donor number (DN) of Gutmann et al.,²⁰ the B(MeOD) parameter of Koppel and Palm,²¹ the pure base calorimetric data of Arnet et al.²² and parameter β of Kamlet and Taft.^{18b}

10.3.2 CHARACTERIZATION OF A MOLECULAR ENVIRONMENT WITH THE AID OF THE PROBE/HOMOMORPH MODEL

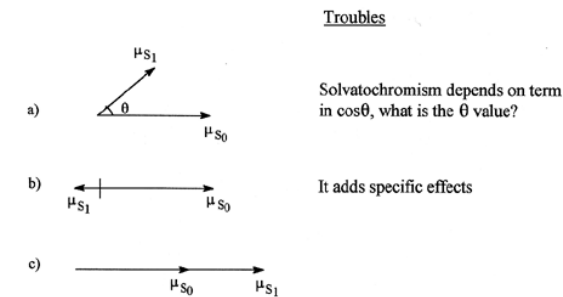
As a rule, a good solvent probe must possess two energy states such that the energy or intensity of the transition between them will be highly sensitive to the nature of the environment. The transition concerned must thus take place between two states affected in a different manner by the molecular environment within the measurement time scale so that the transition will be strongly modified by a change in the nature of the solvent. For easier quantification, the transition should not overlap with any others of the probe, nor should its spectral profile change over the solvent range of interest. Special care should also be exercised so that the probe chosen will be subject to no structural changes dependent on the nature of the solvent; otherwise, the transition will include this perturbation, which is external to the pure solvent effect to be quantified.

All probes that meet the previous requirements are not necessarily good solvent probes, however; in fact, the sensitivity of the probe may be the result of various types of interaction with the solvent and the results difficult to generalize as a consequence. A probe suitable for determining a solvent effect such as polarity, acidity or basicity should be highly sensitive to the interaction concerned but scarcely responsive to other interactions so that any unwanted contributions will be negligible. However, constructing a pure solvent scale also entails offsetting these side effects, which, as shown later on, raises the need to use a homomorph of the probe.

The use of a spectroscopic technique (specifically, UV-Vis absorption spectrophotometry) to quantify the solvent effect provides doubtless advantages. Thus, the solute is in its electronic ground state, in thermodynamic equilibrium with its environment, so the transition is vertical and the solvation sphere remains unchanged throughout. These advantages make designing a good environmental probe for any of the previous three effects quite easy.

A suitable probe for the general solvent effect must therefore be a polar compound. Around its dipole moment, the solvent molecules will arrange themselves as effectively as possible -in thermal equilibrium- and the interaction between the probe dipole and the solvent molecules that form the cybotactic region must be strongly altered by electronic excitation, which will result in an appropriate shift in charge; the charge will then create a new dipole moment enclosed by the same cybotactic cavity as in the initial state of the transition.

The change in the dipole moment of the probe will cause a shift in the electronic transition and reflect the sensitivity of the probe to the solvent polarity and polarizability. A high sensitivity in the solvent is thus usually associated with a large change in the dipole moment by effect of the electronic transition. However, the magnitude of the spectral shift depends not only on the modulus of the dipole moment but also on the potential orientation change. In fact, inappropriate orientation changes are among the sources of contamination of polarity probes with specific effects. For simplicity, orientation changes can be reduced to the following: (a) the dipole moment for the excited state is at a small angle to that for the ground state of the probe, so the orientation change induced by the electronic excitation can



Scheme I.

of the angle, which hinders its use in practice (see Scheme Ia). This difficulty vanishes at 0 and 180°, which are thus the preferred choices. A transition giving rise to an orientation change by 180° is usually one involving a molecule where charge is strongly localized at a given site and is discharged by delocalization upon electronic excitation; as a result, specific solvating effects in the initial state are strongly altered in the final state, so the transition concerned is strongly contaminated with specific interactions (see Scheme Ib). This situation is also inadvisable with a view to constructing a scale for the general solvent effect. The third possibility, where the transition causes no orientation change in the dipole moment, is the most suitable with a view to establishing the general effect of a solvent; the solvent box, which was the most suitable for solvating the probe, will continue to be so now with an increased dipole moment (see Scheme Ic). In summary, a suitable probe for estimating the general solvent effect must not only meet the above-described requirements but also be able to undergo a transition the dipole moment of which will increase markedly as a result while preserving its orientation.

A suitable basicity probe will be one possessing an acid group the acidity of which changes markedly with the electronic transition, so that the transition is affected mostly by solvent basicity. For its acidity to change to an appropriate extent upon excitation, the group concerned should resound with an appropriate electron acceptor and the resonance should increase during the transition by which the effect is probed. Obviously, the presence of this type of group endows the probe with a polar character; in addition, the charge transfer induced by the excitation also produces side effects that must be subtracted in order to obtain measurements contaminated with no extraneous effects such as those due to polarity changes or the acidity of the medium described above. Finding a non-polar probe with a site capable of inducing a specific orientation in the solvent appears to be a difficult task. The best choice in order to be able to subtract the above-mentioned effects appears to be an identical molecular structure exhibiting the same transition but having the acid group blocked. One interesting alternative in this context is the use of a pyrrole N-H group as probe and the corresponding N-Me derivative as homomorph.²³

The same approach can be used to design a suitable acidity probe. The previous comments on the basicity probe also apply here; however, there is the added difficulty that the basic site used to probe solvent basicity cannot be blocked so easily. The situation is made much more complex by the fact that, for example, if the basic site used is a ketone group or a pyridine-like nitrogen, then no homomorph can be obtained by blocking the site. The solu-

be neglected; (b) the two dipole moments are at an angle near 180° to each other; and (c) the two dipole moments form an angle in between the previous two.

Any transitions where the dipole moments for the states involved in the transition are at angles markedly different from 0 or 180° should be avoided as the spectral shift includes contributions that depend on the cosine of

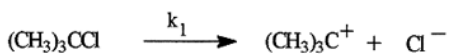
tion, as shown below, involves sterically hindering the solvent approach by protecting the basic site of the probe with bulky alkyl (e.g., tert-butyl) groups at adjacent positions.²⁴

One can therefore conclude that constructing an appropriate general or specific solvent scale entails finding a suitable molecular probe to preferentially assess the effect considered and a suitable homomorph to subtract any side effects extraneous to the interaction of interest. Any other type of semi-empirical evaluation will inevitably lead to scales contaminated with other solvent effects, as shown later on. Accordingly, one will hardly be able to provide a global description of solvent effects on the basis of a single-parameter scale.

10.3.3 SINGLE-PARAMETER SOLVENT SCALES: THE Y, G, E_T(30), P_v, Z, χ_R, Φ, AND S' SCALES

Below are briefly described the most widely used single-parameter solvent scales, with special emphasis on their foundation and use.

10.3.3.1 The solvent ionizing power scale or Y scale



Scheme II.

In 1948, Grunwald and Winstein²⁵ introduced the concept of “ionizing power of the solvent”, Y, based on the strong influence of the solvent on the solvolysis rate of alkyl halides in general and tert-butyl chloride in

particular (see Scheme II). Y is calculated from the following equation:

$$Y = \log k^{t\text{BuCl}} - \log k_0^{t\text{BuCl}} \quad [10.3.1]$$

where $k^{t\text{BuCl}}$ and $k_0^{t\text{BuCl}}$ are the solvolysis rate constants at 25°C for tert-butyl chloride in the solvent concerned and in an 80% v/v ethanol/water mixture - the latter constant is used as reference for the process.

The strong solvent dependence of the solvolysis rate of tert-butyl chloride was examined by Grunwald and Winstein^{25,26} in the light of the Brønsted equation. They found the logarithmic coefficient of activity for the reactant and transition state to vary linearly in a series of mixtures and the variation to be largely the result of changes in coefficient of activity for the reactant. By contrast, in the more poorly ionizing solvents, changes in k were found to be primarily due to changes in coefficient of activity for the transition state.

In a series of papers,²⁵⁻³² Grunwald and Winstein showed that the solvolysis rate constants for organic halides which exhibit values differing by more than 6 orders of magnitude in this parameter can generally be accurately described by the following equation:

$$\log k = mY + \log k_0 \quad [10.3.2]$$

where k and k_0 are the rate constants in the solvent concerned and in the 80:20 v/v ethanol/water mixture, and coefficient m denotes the ease of solvolysis of the halide concerned relative to tert-butyl chloride. By grouping logarithms in eq. [10.3.2], one obtains

$$\log(k / k_0) = mY \quad [10.3.3]$$

which is analogous to the Hammett equation:³³

$$\log(k / k_0) = \rho\sigma \quad [10.3.4]$$

There is thus correspondence between coefficient m and the Hammett reaction constant, ρ , and also between the ionizing power of the solvent, Y , and the Hammett substituent constant, σ .

In fact, the solvolysis of tert-butyl chloride is one of the cornerstones of physical organic chemistry.³⁴⁻³⁶ Thus, some quantitative approaches to the kinetics of spontaneous reactions in various solvents -and, more interesting, solvent mixtures- are based on linear free-energy relations such as that of Grunwald and Winstein²⁵ or its extensions.^{34,37-41} These equations allow one to interpolate or extrapolate rate constants that cannot be readily measured, and also to derive mechanistically significant information in the process.

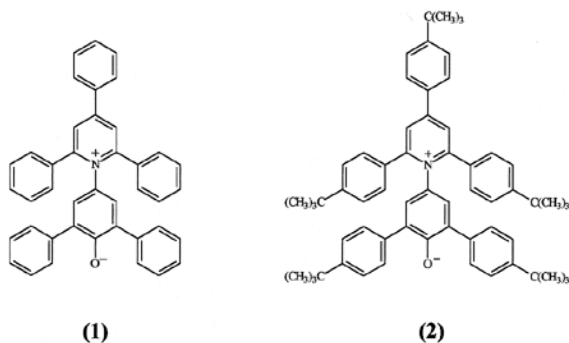
10.3.3.2 The G values of Allerhand and Schleyer

Allerhand and Schleyer⁴² found that a proportionality exists between the stretching frequencies of vibrators of the type $X=O$ (with $X = C, N, P$ or S) and the corresponding stretching frequencies in situations involving hydrogen bonds of the $X-H \cdots B$ type in a variety of solvents. They thought these results to be indicative that the solvents studied interacted in a non-specific manner with both types of vibrator, in contradiction with the specific interaction-only approach advocated by Bellamy et al.⁴³⁻⁴⁵ They used this information to construct a solvent polarity scale that they called "the G scale". Allerhand and Schleyer⁴² used an empirical linear free-energy equation to define G:

$$G = (v^0 - v^s) / av^0 \quad [10.3.5]$$

where v^0 and v^s are the corresponding stretching frequencies for one such vibrator in the gas phase and in solution, respectively; a is a function of the particular vibrator in a given probe and also a measure of its sensitivity to the solvent; and G is a function of the solvent alone. The scale was initially constructed from 21 solvents; zero was assigned to the gas phase and 100 to dichloromethane. Subsequently, other authors established the G values for additional solvents.^{46,47}

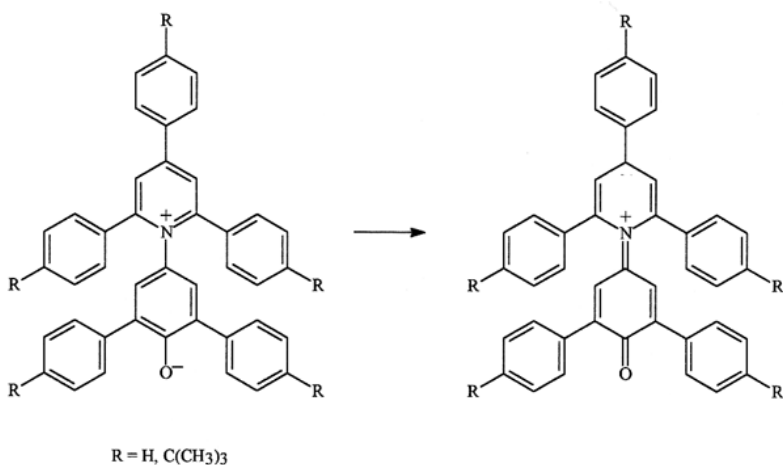
10.3.3.3 The $E_T(30)$ scale of Dimroth and Reichardt



The $E_T(30)$ scale⁴⁸ is based on the extremely solvatochromic character of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridophenoxy)phenoxide (1) and is defined by the position (in kcal mol^{-1}) of the maximum of the first absorption band for this dye, which has marked intramolecular charge-transfer connotations and gives rise to an excited electronic state that is much less dipolar than the ground state (see scheme III). This results in strong hypso-

chromism when increasing solvent polarity.

On this $E_T(30)$ scale, pure solvents take values from 30.7 kcal mol^{-1} for tetramethylsilane (TMS) to 63.1 kcal mol^{-1} for water. These data allow one to easily normal-



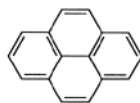
Scheme III.

ize the scale by assigning a zero value to tetramethylsilane and a unity value to water, using the following expression:

$$E_T^N = (E_T(\text{solvent}) - E_T(\text{TMS})) / (E_T(\text{water}) - E_T(\text{TMS})) = (E_T(\text{solvent}) - 30.7) / 32.4 \quad [10.3.6]$$

The corresponding E_T^N values (between 0 and 1) allow one to rank all solvents studied. This is no doubt the most comprehensive solvent scale (it encompasses more than 300 solvents) and also the most widely used at present.^{1,13} The probe (1) exhibits solubility problems in non-polar solvents that the authors have overcome by using a tert-butyl derivative (2). One serious hindrance to the use of this type of probe is its high basicity ($pK_a = 8.64^{49}$), which raises problems with acid solvents.

10.3.3.4 The P_y scale of Dong and Winnick

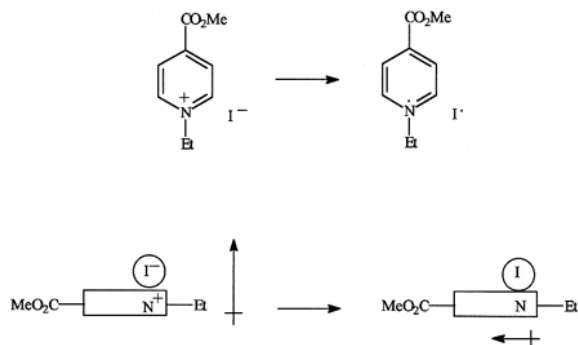


(3)

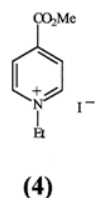
The P_y scale⁵⁰ is based on the ratio between the intensity of components (0,0) I_1 and (0,2) I_3 of the fluorescence of monomeric pyrene (3) in various solvents. It was initially established from 95 solvents⁵⁰ and spans values from 0.41 for the gas phase to 1.95 for DMSO. This scale is primarily used in biochemical studies, which usually involve fluorescent probes. However, it poses problems arising largely from the difficulty of obtaining precise values of the above-mentioned intensity ratio; this has resulted in divergences among P_y values determined by different laboratories.⁵¹ One further hindrance is that the mechanism via which low-polar solvents enhance the intensity of symmetry-forbidden vibronic transitions through a reduction in local symmetry is poorly understood.⁵²

10.3.3.5 The Z scale of Kosower

The Z scale^{53,54} is based on the strong solvatochromism of the 1-ethyl-4-(methoxycarbonyl)pyridinium iodide ion-pair (4) and defined by the position (in kcal mol⁻¹) of the maximum of its first absorption band, which has marked intermolecular charge-transfer connotations according to Scheme IV (the excited state of the chromophore is much less



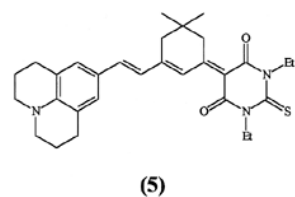
Scheme IV.



solvents by Marcus⁵⁶ and the original range extended to 55.3 kcal mol⁻¹ (for 2-methyltetrahydrofuran). Further expansion of this scale was precluded by the fact that high-polar solvents shift the charge-transfer band at the shortest wavelength to such an extent that it appears above the strong first $\pi \rightarrow \pi^*$ transition of the compound, thus hindering measurement; in addition, the probe (4) is scarcely soluble in non-polar solvents. One should also bear in mind that many solvents require using a high concentration of the probe in order to obtain a measurable charge-transfer band; as a result, the position of the band often depends on the probe concentration.

One other fact to be considered is that the interest initially aroused by this scale promoted attempts at overcoming the above-mentioned measurement problems by using correlations with other solvent-sensitive processes; as a result, many of the Z values currently in use are not actually measured values but extrapolated values derived from previously established ratios.

10.3.3.6 The χ_R scale of Brooker



In 1951, Brooker⁵⁷ suggested for the first time that solvatochromic dyes could be used to obtain measures of solvent polarity. This author⁵⁸ constructed the χ_R scale on the basis of the solvatochromism of the merocyanine dye (5), the electronic transition of which gives rise to a charge-transfer from the amine nitrogen to a carboxamide group at the other end of the molecule. Hence, the excited status is more dipolar than the ground state, and the resulting band is shifted

bathochromically as solvent polarity increases. χ_R values reflect the position of the maximum of the first band for the chromophore in kcal mol⁻¹.

The original scale encompassed 58 solvents spanning χ_R values from 33.6 kcal mol⁻¹ for *m*-cresol to 50.9 kcal mol⁻¹ for *n*-heptane.

10.3.3.7 The Φ scale of Dubois and Bienvenüe

Dubois and Bienvenüe⁵⁹ developed the Φ polarity solvent scale on the basis of the position of the $n \rightarrow \pi^*$ transition for eight selected aliphatic ketones that were studied in 23 solvents, using *n*-hexane as reference and the following equation for calculation:

dipolar). This transition undergoes a strong hypsochromic shift as solvent polarity increases, so much so that it occasionally overlaps with strong $\pi \rightarrow \pi^*$ bands and results in imprecise localization of the maximum of the charge-transfer band.

The Z values for the 20 solvents originally examined by Kosower⁵³ spanned the range from 64.2 for dichloromethane to 94.6 for water. The scale was subsequently expanded to an overall 61

$$\Delta\nu_H^S = \nu^S - \nu^H = \Phi(\nu^H - 32637) - 174 \quad [10.3.7]$$

where ν^S is the absorption wavenumber in solvent S and ν^H in n-hexane (the reference solvent). The absorption maxima of these ketones depend both on the solvent and on their own structure.

The Φ values spanned by the 23 solvents studied range from -0.01 for carbon tetrachloride to 0.65 for formic acid. The values for DMSO and water are 0.115 and 0.545, respectively.

10.3.3.8 The S' scale of Drago

Drago⁶⁰ developed a “universal polarity scale” (the S' scale) from more than three hundred spectral data (electronic transitions, ¹⁹F and ¹⁵N chemical shifts and RSE coupling constants) for 30 solutes in 31 non-protic solvents from cyclohexane to propylene carbonate. He used the equation

$$\Delta\chi = S'P + W \quad [10.3.8]$$

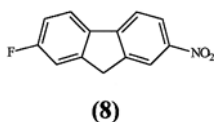
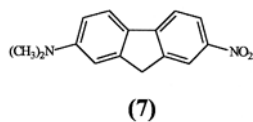
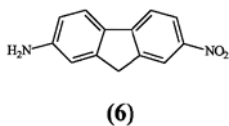
where $\Delta\chi$ is the measured physico-chemical property, S' the solvent polarity, P the solvating susceptibility of the solute and W the value of $\Delta\chi$ at S' = 0. Drago assigned an arbitrary value of 3.00 to DMSO in order to anchor the scale.

The S' scale was constructed from carefully selected data. Thus, it excluded data for (a) all systems involving any contribution from donor-acceptor specific interactions (donor molecules were only measured in donor solvents and data for π solutes were excluded); (b) concentrated solutions of polar molecules in non-polar solvents (which might result in clustering); and (c) polar solvents occurring as rotamers (each rotamer would be solvated in a different way).

In order to extend the S' scale to acid solvents, Drago⁶¹ devised an experiment involving separating general interactions from specific interactions using the E_T(30) scale. First, the probe [E_T(30)] was dissolved in a non-coordinating solvent of weakly basic character -so that it would not compete with the solute for the specific interaction- and slightly polar nature -so that the probe would not cluster at low concentrations of the acceptor solvent-; then, the acceptor solvent was added and the variation of the maximum on the absorption band for the E_T(30) probe was plotted as a function of the solvent concentration. By extrapolation to dilute solutions, the non-specific solvation component for the solvent was estimated. An interesting discussion of the solvent scales developed by Drago can be found in his book.⁶²

10.3.4 SOLVENT POLARITY: THE SPP SCALE¹⁵

As noted earlier, a suitable probe for assessing solvent polarity should meet various requirements including the following: (a) the modulus of its dipole moment should increase markedly but its orientation remain unaltered in response to electronic excitation; (b) it should undergo no structural changes by effect of electronic excitation or the nature of the solvent; (c) its basicity or acidity should change as little as possible upon electronic excitation so that any changes will be negligible compared to those caused by polarity; (d) the spectral envelope of the electronic transition band used should not change with the nature of the solvent; and (e) its molecular structure should facilitate the construction of a homomorph allowing



one to offset spurious contributions to the measurements arising from the causes cited in (b) to (d) above.

A comprehensive analysis of the literature on the choice of probes for constructing polarity scales led our group to consider the molecular structure of 2-amino-7-nitrofluorene (ANF) **(6)** for this purpose. This com-

compound had previously been used by Lippert⁶³ to define his well-known equation, which relates the Stokes shift of the chromophore with the change in its dipole moment on passing from the ground state to the excited state. He concluded that, in the first excited state, the dipole moment increased by 18 D on the 5.8 D value in the ground state. This data, together with the dipole moment for the first excited electronic state (23 D), which was obtained by Czekalla et al.⁶⁴ from electric dichroism measurements, allow one to conclude that the direction of the dipole moment changes very little upon electronic excitation of this chromophore. Baliah and Pillay⁶⁵ analyzed the dipole moments of a series of fluorene derivatives at positions 2 and 7, and concluded that both positions were strongly resonant and hence an electron-releasing substituent at one and an electron-withdrawing substituent at the other would adopt coplanar positions relative to the fluorene skeleton. In summary, a change by 18 D in dipole moment of a system of these structural features reflects a substantial charge transfer from the donor group at position 2 to the acceptor group at 7 upon electronic excitation.

Although ANF seemingly fulfills requirements (a) and (b) above, it appears not to meet requirement (c) (i.e., that its acidity and basicity should not change upon electronic excitation). In fact, electronic excitation will induce a charge transfer from the amino group, so the protons in it will increase in acidity and the transition will be contaminated with specific contributions arising from solvent basicity. In order to avoid this contribution, one may in principle replace the amino group with a dimethylamino group (DMANF, **7**), which will exhibit appropriate charge transfer with no significant change in its negligible acidity. The increase in basicity of the nitro group upon electronic excitation (a result of charge transfer from the N,N-dimethyl group), should result in little contamination as this group is scarcely basic and its basicity is bound to hardly change with the amount of charge transferred from the N,N-dimethylamino group at position 2 to the fluorene structure.

The analysis of the absorption spectra for DMANF in a broad range of solvents suggests that this probe possesses several interesting spectroscopic properties as regards its first absorption band, which is used to assess the polar properties of solvents. Thus,¹⁵ (a) its first absorption band is well resolved from the other electronic bands (an increase in solvent polarity results in no overlap with the other electronic bands in the UV-Vis spectrum for this probe); (b) the position of this band is highly sensitive to solvent polarity and is bathochromically shifted with increase in it (the bathochromic shift in the absorption maximum between perfluorohexane and DMSO is 4130 cm⁻¹); (c) in less polar solvents, where the band appears at lower wavelengths, it is observed at ca. 376 nm (i.e., shifted to the visible region to an extent ensuring that no problems derived from the cut-off of the solvent

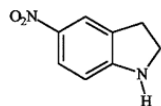
concerned will be encountered); and (d) its first band becomes structured in non-polar solvents (see Figure 1 in ref. 15).

In summary, DMANF is a firm candidate for use as a solvent dipolarity/polarizability probe since its absorption is extremely sensitive to changes in the nature of the solvent, largely as a result of the marked increase in its dipole moment on passing from the electronic ground state to the first excited state. In addition, the change does not affect the dipole moment direction, which is of great interest if the compound is to be used as a probe. Because it possesses a large, rigid aromatic structure, DMANF is highly polarizable; consequently, its first electronic transition occurs at energies where no appreciable interferences with the cut-offs of ordinary solvents are to be expected.

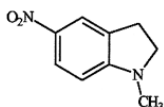
However, the change in structure of the first absorption band for DMANF in passing from non-polar solvents to polar solvents and the potential contaminating effect of solvent acidity on the position of this band entails introducing a homomorph for the probe in order to offset the detrimental effects of these factors on the estimation of solvent polarities.

The homomorph to be used should essentially possess the same structure as the probe, viz. a nitro group at position 7 ensuring the occurrence of the same type of interaction with the solvents and an electron-releasing group at position 2 ensuring similar, through weaker, interactions with the nitro function at 7 in order to obtain a lower dipole moment relative to

DMANF). The most suitable replacement for the $-NMe_2$ function in this context is a fluorine atom, which poses no structural problems and is inert to solvents. The homomorph chosen was thus 2-fluoro-7-nitrofluorene (FNF) (9). The analysis of the absorption spectra for FNF in a broad range of solvents clearly revealed that its first absorption band behaves identically



(9)



(10)

with that for DMANF (its structure changes in passing from non-polar solvents to polar ones). However, the bathochromic shift in this band with increase in solvent polarity is much smaller than that in DMANF (see Figure 1 in ref. 15).

Obviously, the difference between the solvatochromism of DMANF and FNF will cancel many of the spurious effects involved in measurements of solvent polarity. Because the envelopes of the first absorption bands for FNF and DMANF are identical (see Figure 1 in ref. 15), one of the most common sources of error in polarity scales is thus avoided. The polarity of a solvent on the SPP scale is given by the difference between the solvatochromism of the probe DMANF and its homomorph FNF [$\Delta\nu(\text{solvent}) = \nu_{\text{FNF}} - \nu_{\text{DMANF}}$] and can be evaluated on a fixed scale from 0 for the gas phase (i.e., the absence of solvent) to 1 for DMSO, using the following equation:

$$SPP(\text{solvent}) = [\Delta\nu(\text{solvent}) - \Delta\nu(\text{gas})] / [\Delta\nu(\text{DMSO}) - \Delta\nu(\text{gas})] \quad [10.3.9]$$

Table 10.3.1 gives the SPP values for a broad range of solvents, ranked in increasing order of polarity. Data were all obtained from measurements made at our laboratory and have largely been reported elsewhere^{15,66-70} -some, however, are published here for the first time.

Table 10.3.1. The property parameters of solvents: Polarity/Polarizability SPP, Basicity SB, Acidity SA

Solvents	SPP	SB	SA
gas phase	0	0	0 ^a
perfluoro-n-hexane	0.214	0.057	0 ^a
2-methylbutane	0.479	0.053	0 ^a
petroleum ether	0.493	0.043	0 ^a
n-pentane	0.507	0.073	0 ^a
n-hexane	0.519	0.056	0 ^a
n-heptane	0.526	0.083	0 ^a
isooctane	0.533	0.044	0 ^a
cyclopentane	0.535	0.063	0 ^a
n-octane	0.542	0.079	0 ^a
ethylcyclohexane	0.548	0.074	0 ^a
n-nonane	0.552	0.053	0 ^a
cyclohexane	0.557	0.073	0 ^a
n-decane	0.562	0.066	0 ^a
n-undecane	0.563	0.080	0 ^a
methylcyclohexane	0.563	0.078	0 ^a
butylcyclohexane	0.570	0.073	0 ^a
propylcyclohexane	0.571	0.074	0 ^a
n-dodecane	0.571	0.086	0 ^a
decahydronaphthalene	0.574	0.056	0 ^a
mesitylene	0.576	0.190	0 ^a
n-pentadecane	0.578	0.068	0 ^a
n-hexadecane	0.578	0.086	0 ^a
cycloheptane	0.582	0.069	0 ^a
tert-butylcyclohexane	0.585	0.074	0 ^a
cyclooctane	0.590	0.077	0 ^a
1,2,3,5-tetramethylbenzene	0.592	0.186	0 ^a
cis-decahydronaphthalene	0.601	0.056	0 ^a
tripropylamine	0.612	0.844	0 ^s
m-xylene	0.616	0.162	0 ^a
triethylamine	0.617	0.885	0 ^s

Solvents	SPP	SB	SA
p-xylene	0.617	0.160	0 ^a
1-methylpiperidine	0.622	0.836	0 ^s
tributylamine	0.624	0.854	0 ^s
1,4-dimethylpiperazine	0.627	0.832	0 ^s
hexafluorobenzene	0.629	0.119	0 ^a
trimethylacetic acid	0.630	0.130	0.471
dibutylamine	0.630	0.991	0 ^s
di-n-hexyl ether	0.630	0.618	0 ^a
1-methylpyrrolidine	0.631	0.918	0 ^s
tetrachloromethane	0.632	0.044	0 ^a
di-n-pentyl ether	0.636	0.629	0 ^a
butylbenzene	0.639	0.149	0 ^a
o-xylene	0.641	0.157	0 ^a
isobutyric acid	0.643	0.281	0.515
isovaleric acid	0.647	0.405	0.538
ethylbenzene	0.650	0.138	0 ^a
di-n-butyl ether	0.652	0.637	0 ^a
hexanoic acid	0.656	0.304	0.456
toluene	0.655	0.128	0 ^a
propylbenzene	0.655	0.144	0 ^a
tert-butylbenzene	0.657	0.171	0 ^a
N-methylbutylamine	0.661	0.960	0 ^s
heptanoic acid	0.662	0.328	0.445
di-isopropyl ether	0.663	0.657	0 ^a
N-methylcyclohexylamine	0.664	0.925	0 ^s
N,N-dimethylcyclohexylamine	0.667	0.998	0 ^s
benzene	0.667	0.124	0 ^a
1,2,3,4-tetrahydronaphthlene	0.668	0.180	0 ^a
ethylenediamine	0.674	0.843	0.047
di-n-propyl ether	0.676	0.666	0 ^a
propionic acid	0.690	0.377	0.608
tert-butyl methyl ether	0.687	0.567	0 ^a
diethyl ether	0.694	0.562	0 ^a

Solvents	SPP	SB	SA
2-methylbutyric acid	0.695	0.250	0.439
butyl methyl ether	0.695	0.505	0 ^a
pentafluoropyridine	0.697	0.144	0 ^a
1,4-dioxane	0.701	0.444	0.0
2-methyltetrahydrofuran	0.717	0.584	0.0
1-methylnaphthalene	0.726	0.156	0 ^a
butylamine	0.730	0.944	0.0
ethoxybenzene	0.739	0.295	0 ^a
piperidine	0.740	0.933	0.0
1-undecanol	0.748	0.909	0.257
isoamyl acetate	0.752	0.481	0.0
1-decanol	0.765	0.912	0.259
fluorobenzene	0.769	0.113	0 ^a
1-nonanol	0.770	0.906	0.270
tetrahydropyran	0.778	0.591	0.0
acetic acid	0.781	0.390	0.689
n-propyl acetate	0.782	0.548	0.0
n-butyl acetate	0.784	0.525	0.0
methyl acetate	0.785	0.527	0.0
1-octanol	0.785	0.923	0.299
chloroform	0.786	0.071	0.047
2-octanol	0.786	0.963	0.088
cyclohexylamine	0.787	0.959	0.0
trimethyl orthoformate	0.787	0.528	0.0
1,2-dimethoxyethane	0.788	0.636	0.0
pyrrolidine	0.794	0.990	0.0
ethyl acetate	0.795	0.542	0.0
1-heptanol	0.795	0.912	0.302
N,N,-dimethylaniline	0.797	0.308	0.0
methyl formate	0.804	0.422	0.0
2-butoxyethanol	0.807	0.714	0.292
1-hexanol	0.810	0.879	0.315
3-methyl-1-butanol	0.814	0.858	0.315

Solvents	SPP	SB	SA
propyl formate	0.815	0.549	0.0
1-pentanol	0.817	0.860	0.319
dibenzyl ether	0.819	0.330	0 ^a
methoxybenzene	0.823	0.299	0.084
chlorobenzene	0.824	0.182	0 ^a
bromobenzene	0.824	0.191	0 ^a
cyclooctanol	0.827	0.919	0.137
2,6-dimethylpyridine	0.829	0.708	0.0
2-methyl-2-propanol	0.829	0.928	0.145
2-pentanol	0.830	0.916	0.204
2-methyl-2-butanol	0.831	0.941	0.096
2-methyl-1-propanol	0.832	0.828	0.311
formamide	0.833	0.414	0.674
2,4,6-trimethylpyridine	0.833	0.748	0.0
3-hexanol	0.833	0.979	0.140
iodobenzene	0.835	0.158	0 ^a
ethyl benzoate	0.835	0.417	0.0
dibutyl oxalate	0.835	0.549	0.0
methyl benzoate	0.836	0.378	0.0
1-chlorobutane	0.837	0.138	0 ^a
1-butanol	0.837	0.809	0.341
2-methyl-1-butanol	0.838	0.900	0.289
tetrahydrofuran	0.838	0.591	0.0
pyrrole	0.838	0.179	0.387
cycloheptanol	0.841	0.911	0.183
2-butanol	0.842	0.888	0.221
1,3-dioxolane	0.843	0.398	0.0
3-methyl-2-butanol	0.843	0.893	0.196
2-hexanol	0.847	0.966	0.140
cyclohexanol	0.847	0.854	0.258
1-propanol	0.847	0.727	0.367
2-propanol	0.848	0.762	0.283
ethanol	0.853	0.658	0.400

Solvents	SPP	SB	SA
1,2-dimethoxybenzene	0.854	0.340	0.0
2-methoxyethyl ether	0.855	0.623	0.0
methanol	0.857	0.545	0.605
methyl methoxyacetate	0.858	0.484	0.0
3-pentanol	0.863	0.950	0.100
cyclopentanol	0.865	0.836	0.258
cyclohexanone	0.874	0.482	0.0
propionitrile	0.875	0.365	0.030
allyl alcohol	0.875	0.585	0.415
propiofenone	0.875	0.382	0 ^a
triacetin	0.875	0.416	0.023
dichloromethane	0.876	0.178	0.040
2-methylpyridine	0.880	0.629	0.0
2-butanone	0.881	0.520	0.0
acetone	0.881	0.475	0.0
2-methoxyethanol	0.882	0.560	0.355
3-pentanone	0.883	0.557	0.0
benzyl alcohol	0.886	0.461	0.409
4-methyl-2-pentanone	0.887	0.540	0.0
trimethyl phosphate	0.889	0.522	0.0
1-methylpyrrole	0.890	0.244	0.0
1,2-dichloroethane	0.890	0.126	0.030
2-phenylethanol	0.890	0.523	0.376
2-chloroethanol	0.893	0.377	0.563
nitroethane	0.894	0.234	0.0
acetonitrile	0.895	0.286	0.044
chloroacetonitrile	0.896	0.184	0.445
N-methylacetamide	0.897	0.735	0.328
1,2-butanediol	0.899	0.668	0.466
valeronitrile	0.900	0.408	0.0
N-methylaniline	0.902	0.212	0.073
2,3-butanediol	0.904	0.652	0.461
acetophenone	0.904	0.365	0.044

Solvents	SPP	SB	SA
nitromethane	0.907	0.236	0.078
cyclopentanone	0.908	0.465	0.0
triethyl phosphate	0.908	0.614	0.0
1,2-dichlorobenzene	0.911	0.144	0.033
tetrahydrothiophene	0.912	0.436	0 ^a
2,2,2-trifluoroethanol	0.912	0.107	0.893
butyronitrile	0.915	0.384	0.0
N-methylformamide	0.920	0.590	0.444
isobutyronitrile	0.920	0.430	0.0
pyridine	0.922	0.581	0.033
2-methyl-1,3-propanediol	0.924	0.615	0.451
1,2-propanediol	0.926	0.598	0.475
propylen carbonate	0.930	0.341	0.106
N,N-diethylacetamide	0.930	0.660	0.0
hexamethylphosphoric acid triamide	0.932	0.813	0 ^s
1,2-ethanediol	0.932	0.534	0.565
N,N-diethylformamide	0.939	0.614	0.0
1,3-butanediol	0.944	0.610	0.424
1,2,3-propanetriol	0.948	0.309	0.618
1-methylimidazole	0.950	0.668	0.069
1,4-butanediol	0.950	0.598	0.424
1,3-propanediol	0.951	0.514	0.486
tetramethylurea	0.952	0.624	0.0
N,N-dimethylformamide	0.954	0.613	0.031
2-pyrrolidinone	0.956	0.597	0.347
benzotrile	0.960	0.281	0.047
2,2,2-trichloroethanol	0.968	0.186	0.588
nitrobenzene	0.968	0.240	0.056
1-methyl-2-pyrrolidinone	0.970	0.613	0.024
N,N-dimethylacetamide	0.970	0.650	0.028
water	0.962	0.025	1.062
γ -butyrolactone	0.987	0.399	0.057
dimethyl sulfoxide	1.000	0.647	0.072

Solvents	SPP	SB	SA
sulfolane	1.003	0.365	0.052
m-cresol	1.000	0.192	0.697
1,1,1,3,3,3-hexafluoro-2-propanol	1.014	0.014	1.00
α α α -trifluoro-m-cresol	1.085	0.051	0.763

^aAssumed value because it is considered non acid solvent.

^aAssumed value because the first band of the TBSB spectra exhibits vibronic structure.

A brief analysis of these SPP data allows one to draw several interesting conclusions from structural effects on solvent polarity, namely:

- Cyclohexane is used as the non-polar reference in many scales. In the SPP scale, the polarity gap between cyclohexane and the gas phase (0.557 SPP units) is as wide as that between cyclohexane and the highest polarity (0.443 SPP units).
- Alkanes span a wide range of SPP values (e.g., 0.214 for perfluoro-n-hexane, 0.479 for 2-methylbutane and 0.601 for decalin).
- Unsaturation increases polarity in alcohols. Thus, the SPP values for n-propanol, allyl alcohol and propargyl alcohol are 0.847, 0.875 and 0.915, respectively.

10.3.5 SOLVENT BASICITY: THE SB SCALE⁷²

As stated above, for a probe of solvent basicity to be usable in UV-Vis spectroscopy, it should meet a series of requirements. One is that it should be acidic enough in its electronic ground state to allow characterization of the basicity of its environment. In addition, its acidity should increase upon electronic excitation such that its electronic transitions will be sensitive to the basicity of the medium. This behavior will result in a bathochromic shift in the absorption band the magnitude of which will increase with increasing basicity of the environment. The probe should also be free of potential conformational changes that might influence the electronic transition to be evaluated. Finally, its molecular structure should be readily converted into a homomorph lacking the acid site without any side effects that might affect the resulting solvent basicity.

5-Nitroindoline (NI, **9**) possesses the above-described electronic and structural features. It is an N-H acid with a single acid site borne by a donor group whose free rotation is hindered by an ethylene bridge on the ring. However, if charge transfer endows the compound with appropriate acid properties that increase with electronic excitation, the basicity of the acceptor (nitro) group will also increase and the polarity of the compound will be altered as a result. Both effects will influence the electronic transition of the probe that is to be used to evaluate basicity.

Replacement of the acid proton (N-H) by a methyl group in this molecular structure has the same side effects; as a result, the compound will be similarly sensitive to the polarity and acidity of the medium, but not to its basicity owing to the absence of an acid site. Consequently, 1-methyl-5-nitroindoline (MNI, **10**) possesses the required properties for use as a homomorph of 5-nitroindoline in order to construct our solvent basicity scale (SB). The suitability of this probe/homomorph couple is consistent with theoretical MP2/6-31G** data. Thus, both the probe and its homomorph exhibit the same sensitivity to solvent polarity/polarizability because of their similar dipole moments ($\mu_{\text{NI}} = 7.13$, $\mu_{\text{MNI}} = 7.31$ D) and

polarizabilities (20.38 and 22.78 $\alpha/J^{-1}C^2m^2$ for NI and MNI, respectively). Both also have the same sensitivity to solvent acidity as their surface electrostatic potential minima are virtually coincident [$V_{S,min}(NI) = -47.49 \text{ kcal mol}^{-1}$, $V_{S,min}(MNI) = -47.58 \text{ kcal mol}^{-1}$]; according to Politzer et al.,⁷¹ this means that they exhibit the same hydrogen-bonding basicity. In addition, the electrostatic potential surface in both molecules suggests that sole electrophilic sites are those on the oxygen atoms of the nitro group.

Obviously, the difference in solvatochromism between NI and MNI [$\Delta\nu(\text{solvent}) = \nu_{NI} - \nu_{MNI}$] will cancel many spurious effects accompanying the basicity effect of the solvent. In addition, NI and MNI possess several advantageous spectral features; thus, they exhibit a sharp first absorption band that overlaps with no higher-energy band in any solvent, and both have the same spectral envelope in such a band (see Figure 1 in ref. 72), which facilitates comparison between the two spectra and the precise establishment of the basicity parameter, SB. The basicity of a solvent (SB) on a scale encompassing values between zero for the gas phase -the absence of solvent- and unity for tetramethylguanidine (TMG) can be directly obtained from the following equation:

$$SB(\text{solvent}) = [\Delta\nu(\text{solvent}) - \Delta\nu(\text{gas})] / [\Delta\nu(\text{TMG}) - \Delta\nu(\text{gas})] \quad [10.3.10]$$

Table 10.3.1 lists the SB values for a wide range of solvents. All data were obtained from measurements made in our laboratory; most have been reported elsewhere^{70,72} but some are published here for the first time.

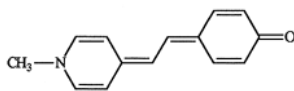
A brief analysis of these SB data allows one to draw several interesting conclusions as regards structural effects on solvent basicity. Thus:

- Appropriate substitution in compound families such as amines and alcohols allows the entire range of the solvent basicity scale to be spanned with substances from such families. Thus, perfluorotriethylamine can be considered non-basic (SB=0.082), whereas N,N-dimethylcyclohexylamine is at the top of the scale (SB=0.998). Similarly, hexafluoro-2-propanol is non-basic (SB=0.014), whereas 2-octanol is very near the top (SB=0.963).
- The basicity of n-alkanols increases significantly with increase in chain length and levels off beyond octanol.
- Cyclization hardly influences solvent basicity. Thus, there is little difference in basicity between n-pentane (SB=0.073) and cyclopentane (SB=0.063) or between n-pentanol (SB=0.869) and cyclopentanol (SB=0.836).
- Aromatization decreases solvent basicity by a factor of 3.5-5.5, as illustrated by the following couples: pyrrolidine/pyrrole (0.99/0.18), N-methylpyrrolidine/N-ethylpyrrole (0.92/0.22), tetrahydrofuran/furan (0.59/0.11), 2-methyltetrahydrofuran/2-methylfuran (0.56/0.16), cyclohexylamine/aniline (0.96/0.26), N-methylcyclohexylamine/N-methylaniline (0.92/0.21), N,N-dimethylcyclohexylamine/N,N-dimethylaniline (0.99/0.30) and a structurally less similar couple such as piperidine/pyridine (0.93/0.58).

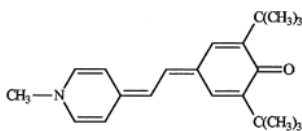
The potential family-dependence of our SB scale was examined and discarded elsewhere.⁷³

10.3.6 SOLVENT ACIDITY: THE SA SCALE⁷⁴

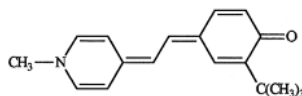
As stated above, a probe for solvent acidity should possess a number of features to be usable in UV-Vis spectroscopy. One is that it should be basic enough in its electronic ground state



(11)



(12)



(13)

to be able to characterize the acidity of its environment. In addition, its basicity should increase upon electronic excitation such that its electronic transitions will be sensitive to the acidity of the medium. This behavior will result in a bathochromic shift in the absorption band the magnitude of which will increase with increasing acidity of the environment. The probe should also be free of potential conformational changes that might influence the electronic transition to be evaluated. Finally, its molecular structure should be easily converted into a homomorph lacking the basic site without any side effects potentially affecting the resulting solvent acidity.

Our group has shown^{24,75} that the extremely strong negative solvatochromism of the chromophore stilbazolium betaine dye (**11**), about 6500 cm^{-1} , is not a result of a change in the non-specific effect of the solvent but rather of change in acidity. This was confirmed⁷⁵ by a study of the solvatochromic effect of a derivative of (**11**), o,o'-di-tert-butylstilbazolium betaine dye (DTBSB) (**12**) in the same series of solvents. In this compound, the basic site in the betaine dye (its oxygen atom) is protected on both sides by bulky tert-butyl groups; the specific effect of the solvent is hindered and the compound exhibits only a small solvatochromic effect that can be ascribed to non-specific solvent effects.⁷⁵

Since the carbonyl group of stilbazolium betaine possesses two lone pairs in the plane of the quinoid ring, one can have two (**11**), one (TBSB, **13**) or no channels (DTBSB) to approach hydrogen bond-donor solvents, depending on the number of o-tert-butyl groups present in the molecular structure of the (**11**) derivative concerned. Our group²⁴ has also shown that, for at least 20 alkanols, the wavenumber difference between the maximum of the first absorption bands for (**11**) and TBSB, and for TBSB and DTBSB, is virtually identical.

These results show that an oxygen lone pair in (**11**) is basic enough, as a result of hydrogen bonding, for (**11**) to be used as an acidity probe in UV-Vis spectroscopy; thus, the absorption maximum for TBSB shifts by about 1000 cm^{-1} from 1-decanol to ethanol,²⁴ whereas that for DTBSB shifts by only 300 cm^{-1} . This sensitivity to acidity, and the structural likeness of the probe and its homomorph -which must endow them with a similar sensitivity to solvent basicity and dipolarity/polarizability-, suggest that the two compounds make an appropriate probe-homomorph couple for developing a pure solvent acidity scale. For this purpose, the first visible absorption band for these compounds exhibits quite an in-

teresting spectroscopic behavior. Thus, in a non-HBD solvent (i.e., one that cannot interact directly with the oxygen lone pair), the band is structured; on the other hand, the band loses its structure upon interaction with an HBD solvent.⁷⁵

The SA acidity scale was established by comparing the solvatochromism of the probes TBSB and DTBSB using the method of Kamlet and Taft.^{18a} In this method, the solvatochromism of DTBSB in a solvent is used as the reference for zero acidity. Consequently, non-acidic solvents obey the equation

$$v_{TBSB} = 1.409v_{DTBSB} - 6288.7 \quad [10.3.11]$$

with $n = 50$, $r = 0.961$ and $sd = 43.34 \text{ cm}^{-1}$.

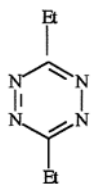
Based on eq. [10.3.11] for non-acidic solvents, the SA value for a given solvent can be obtained from the following expression, where a value of 0.4 is assigned to ethanol, the acid solvatochromic behavior of which is exhibited at 1299.8 cm^{-1} :

$$SA = [(v_{TBSB} - (1.409v_{DTBSB} - 6288.7)) / 1299.8]0.4 \quad [10.3.12]$$

Table 10.3.1 gives the SA values for a wide variety of C-H, N-H and O-H acid solvents. Data were all obtained from measurements made in our laboratory.⁷⁴ The homomorph was insoluble in some solvents, which therefore could not be measured, so they were assumed not to interact specifically and assigned a zero SA value if the probe exhibited a structured spectrum in them.

Evaluating the acidity of weakly acidic solvents entails using a probe basic enough to afford measurement of such an acidity; as a result, the probe is usually protonated by strongly acidic solvents and useless for the intended purpose. Stilbazolium betaines are subject to this constraint as they have pK_a values of about 10 (11) and DTBSB have a pK_a of 8.57^{76} and ca. 10,⁷⁷ respectively, which makes them unsuitable for the evaluation of solvents more acidic than methanol. This forced us to find a suitable probe with a view to expanding the SA scale to more acidic solvents. This problem is not exclusive to our scale; in fact, it affects all acidity scales, which usually provide little information about strongly acidic solvents.

The problem was solved thanks to the exceptional behavior of 3,6-diethyltetrazine⁷⁰ (DETZ, 14). This compound possesses two lone electron pairs located on opposite sites of its hexagonal ring; the strong interaction between the two pairs results in one antibonding n orbital in the compound lying at an anomalously high energy level; this, as shown below, has special spectroscopic implications. The π -electron system of DETZ is similar to that of benzene. Thus, the first $\pi \rightarrow \pi^*$ transition in the two systems appears at $\lambda_{max} = 252 \text{ nm}$ in DETZ and at 260 nm in benzene. On the other hand, the $\pi \rightarrow \pi^*$ transition in DETZ is strongly shifted to the visible region ($\lambda_{max} \approx 550 \text{ nm}$), which is the origin of its deep color. This unique feature makes this compound a firm candidate for use as an environmental probe as the wide energy gap between the two transitions excludes potential overlap. Problems such as protonation of the DETZ probe by acid solvents can be ruled out since, according to Mason,⁷⁸ this type of substance exhibits pK values below zero.



(14)

The sensitivity of the $n \rightarrow \pi^*$ transition in DETZ to the solvent is clearly reflected in its UV/Vis spectra in methylcyclohexane, methanol, trifluoromethanol,

hexafluoro-2-propanol, acetic acid and trifluoroacetic acid, with λ_{\max} values of 550, 536, 524, 517, 534 and 507 nm, respectively. In addition, the spectral envelope undergoes no significant change in the solvents studied, so a potential protonation of the probe -even a partial one- can be discarded.

The shift in the $n \rightarrow \pi^*$ band is largely caused by solvent acidity; however, an $n \rightarrow \pi^*$ transition is also obviously sensitive to the polarity of the medium, the contribution of which must be subtracted if acidity is to be accurately determined. To this end, our group used the solvatochromic method of Kamlet and Taft^{18a} to plot the frequency of the absorption maximum for the $n \rightarrow \pi^*$ transition against solvent polarity (the SPP value). As expected, non-acidic solvents exhibited a linear dependence [eq. (10.3.13)], whereas acidic solvents departed from this behavior -the more acidic the greater the divergence. This departure from the linear behavior described by eq. [10.3.13] is quantified by $\Delta\nu_{\text{DETZ}}$,

$$\nu_{\text{DETZ}} = 1.015\text{SPP} + 17.51 \quad [10.3.13]$$

with $n = 13$, $r = 0.983$ and $\text{sd} = 23 \text{ cm}^{-1}$.

The SA value of an acid solvent as determined using the DETZ probe is calculated using the expression established from the information provided by a series of solvents of increased acidity measurable by the TBSB/DTBSB probe/homomorph couple (viz. 1,2-butanediol, 1,3,-butanediol, ethanol, methanol and hexafluoro-2-propanol); this gives rise to eq. [10.3.14], which, in principle, should only be used to determine SA for solvents with $\Delta\nu_{\text{DETZ}}$ values above 100 cm^{-1} :

$$\text{SA} = 0.833\Delta\nu_{\text{DETZ}} + 0.339 \quad [10.3.14]$$

with $n = 6$ and $r = 0.987$.

Table 10.3.1 gives the SA values for a wide range of highly acidic solvents. Data were largely obtained from measurements made in our laboratory;⁷⁰ some, however, are reported here for the first time.

A brief analysis of these SA data allow one to draw several interesting conclusions from structural effects on solvent acidity. Thus:

- Substitution into alcoholic compounds allows the entire range of the solvent acidity scale to be spanned. Thus, 2-octanol can be considered to be scarcely HBD (SA=0.088) and ethylene glycol to be highly HBD (SA=0.717). Perfluoroalkanols are even more highly HBD.
- The acidity of 1-alkanols and carboxylic acids decreases significantly with increasing chain length but levels off beyond nonanol and octanoic acid, respectively.
- Cyclization decreases solvent acidity. Thus, SA decreases from 0.318 to 0.257 between 1-pentanol and cyclopentanol, and from 0.298 to 0.136 between 1-octanol and cyclooctanol.
- Aromatic rings make aniline (SA=0.131) and pyrrole (SA=0.386) more HBD than their saturated homologs: cyclohexylamine and pyrrolidine, respectively, both of which are non-HBD (SA=0).
- The acidity of alkanols decreases dramatically with increasing alkylation at the atom that bears the hydroxyl group [e.g., from 1-butanol (SA=0.340) to 2-butanol (SA=0.221) to tert-butyl alcohol (SA=0.146)].

10.3.7 APPLICATIONS OF THE PURE SPP, SA AND SB SCALES

The SPP general solvent scale, and the SA and SB specific solvent scales, are orthogonal to one another, as can be inferred from the small correlation coefficients obtained in mutual fittings involving the 200 solvents listed in Table 10.3.1 [$r^2(\text{SPP vs. SA}) = 0.13$, $r^2(\text{SPP vs. SB}) = 0.10$ and $r^2(\text{SA vs. SB}) = 0.01$]. These results support the use of these scales for the multi-parameter analysis of other solvent scales or data sets sensitive to the solvent effect on the basis of the following equation:

$$P = aSPP + bSA + cSB + P_0 \quad [10.3.15]$$

where P is the quantity to be described in a given solvent; SPP, SA and SB are the corresponding polarity/polarizability, acidity and basicity values for such a solvent; coefficients a , b and c denote the sensitivity of P to such effects; and P_0 is the P value in the absence of solvent (i.e., the gas phase, which is given a zero value in our scales).

Each of these scales (SPP, SB and SA) has previously been compared with other reported solvent scales and found to be pure scales for the respective effects. However, eq. [10.3.15] is used below to perform a multi-parameter analysis of various reported scales and experimental data sets of interest.

10.3.7.1 Other reported solvents scales

Reported scales for describing solvent polarity [$f(\epsilon, n)$,^{21,79} π^{*80} and S^{60}], basicity (DN^{20} and β^{18}) and acidity (AN^{81} and α^{18}) were previously analyzed against our SPP, SA and SB scales in the originating references, so no further comment is made here.

Rather, this section analyses the behavior of reported single-parameter scales developed to describe the global behavior of solvents [viz. the Z , χ_R , P_y , Φ , G and $E_T(30)$ scales] against the SPP, SB and SA scales on the basis of the 200 solvents listed in Table 10.3.1. The Y scale, established to describe the behavior of solvolysis-like kinetics, is dealt with in the section devoted to the description of kinetic data. The data used in this analysis were taken from the following sources: those for the Z scale from the recent review paper by Marcus;⁵⁶ those for the χ_R , Φ and G scales from the compilation in Table 7.2 of Reichardt's book;¹ those for parameter P_y from the paper by Dong and Winnik;⁵⁰ and those for $E_T(30)$ from the recent review by Reichardt¹³ or Table 7.3 in his book.¹

The Z value for the 51 solvents in Table 10.3.1 reported by Marcus allow one to establish the following equation:

$$Z = 22.37(\pm 4.85)SPP + 7.68(\pm 1.64)SB + 31.27(\pm 1.81)SA + 41.03(\pm 4.15) \quad [10.3.16]$$

with $r = 0.944$ and $sd = 3.03 \text{ kcal mol}^{-1}$.

This equation reveals that Z is largely the result of solvent acidity and polarity, and also, to a lesser extent, of solvent basicity. The strong delocalization of charge in the structure of the probe (**4**) upon electronic excitation, see scheme IV, accounts for the fact that the electronic transition of this probe is hypsochromically shifted by solvent polarity and acidity. The shift is a result of the increased stabilizing effect of the solvent -exerted via general and specific interactions- in the electronic ground state being partly lost upon electronic excitation through delocalization of the charge in the electronic excited state, which gives rise to decreased polarity and specific solvation. On the other hand, the small contribution of solvent basicity appears to have no immediate explanation.

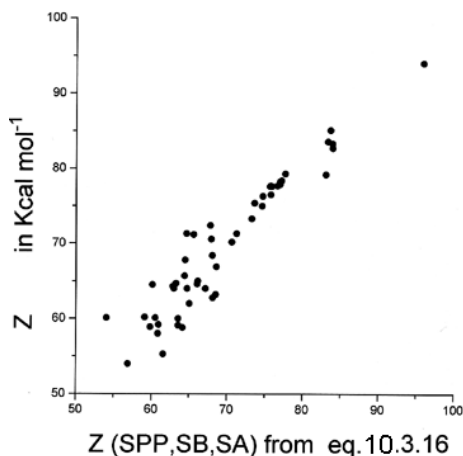


Figure 10.3.1. Plot of Kosower's Z values vs. the predicted Z values according to eq. [10.3.16].

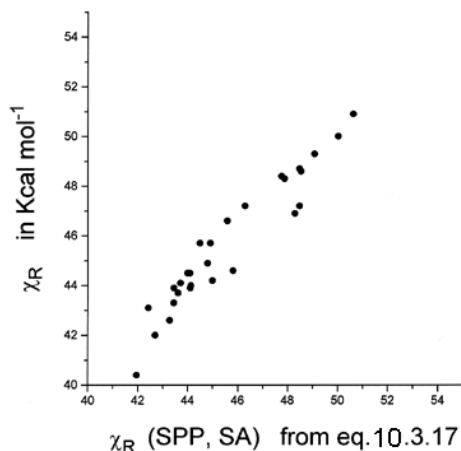


Figure 10.3.2. Plot of Brooker's χ_R values vs. the predicted χ_R values according to [eq. 10.3.17].



Scheme V.

It should be noted that the three solvent effects (polarity, acidity and basicity) increase Z ; also, as can be seen from Figure 10.3.1, the greatest imprecision in this parameter corresponds to solvents with Z values below 70 kcal mol^{-1} .

The 28 solvents in Table 10.3.1 with known values of χ_R reveal that this parameter reflects solvent polarity and, to a lesser extent, also solvent acidity:

$$\chi_R = -15.81(\pm 1.19)SPP - 4.74(\pm 0.90)SA + 58.84(\pm 0.94) \quad [10.3.17]$$

with $r = 0.958$ and $sd = 0.78 \text{ kcal mol}^{-1}$.

It should be noted that the two solvent effects involved (polarity and acidity) contribute to decreasing χ_R . As can be seen from Figure 10.3.2, the precision in χ_R is similarly good throughout the studied range. The structure of the probe used to construct this scale (**5**) reveals that its electron-donor site (an amino group) is not accessible for the solvent, so the charge transfer involved in the electronic excitation does not alter its solvation; rather, it increases its polarity and localization of the charge on the acceptor sites of the compound (carbonyl groups), see scheme V, so increasing solvent polarity and acidity will result in a bathochromically shifted electronic transition by effect of the increased stabilization of the excited state through general and specific interactions.

The results of the multi-parameter analysis of P_y suggests that its values are highly imprecise; even if the value for the gas phase is removed, this parameter only reflects -in an im-

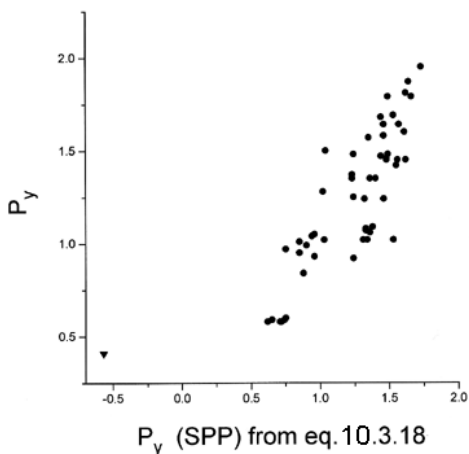


Figure 10.3.3. Plot of Dong and Winnick's P_y values vs. the predicted P_y values according to eq. [10.3.18] (Point for gas phase, ▼, is included in the plot, but not in the regression equation [10.3.18]).

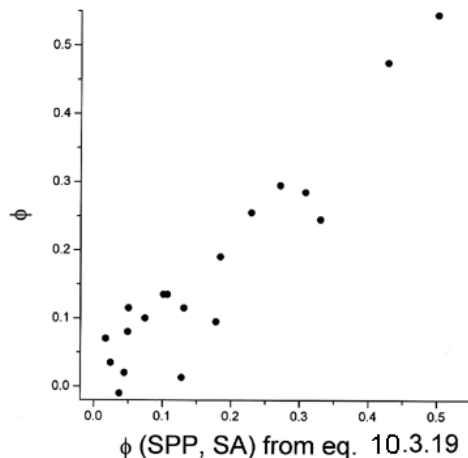


Figure 10.3.4. Plot of Dubois and Bienvenüe's Φ values vs. the predicted Φ values according to eq.[10.3.19].

precise manner- solvent polarity, as is clearly apparent from eq. [10.3.18] (see Figure 10.3.3):

$$P_y = 2.30(\pm 0.20)SPP - 0.57(\pm 0.16) \quad [10.3.18]$$

with $r = 0.839$ and $sd = 0.20$. The difficulty of understanding the performance of the probe precludes rationalizing its spectral behavior.

The 19 Φ values examined indicate that, based on eq. [10.3.19] and Figure 10.3.4, this parameter reflects mostly solvent acidity and, to a lesser extent, solvent polarity:

$$\Phi = 0.18(\pm 0.11)SPP + 0.38(\pm 0.04)SA - 0.07(\pm 0.08) \quad [10.3.19]$$

with $r = 0.941$ and $sd = 0.05$.

The Φ scale is based on the solvatochromic behavior of an $n \rightarrow \pi^*$ electronic transition, so it reflects a high hypsochromic sensitivity to solvent acidity (specific solvation between the lone pair involved in the electronic transition and solvent acidity is lost when one electron in the pair is electronically excited). An $n \rightarrow \pi^*$ electronic transition is also known to decrease the polarity of the chromophore concerned,⁸² so an increase in SPP for the solvent will cause a hypsochromic shift in the electronic transition.

Based on Figure 10.3.5 and the following equation, the values of G parameters are also dictated by solvent polarity and, to a lesser extent, solvent acidity:

$$G = 102.96(\pm 9.02)SPP + 78.20(\pm 27.78)SA - 0.35(\pm 6.28) \quad [10.3.20]$$

with $r = 0.965$ and $sd = 7.6$.

It should be noted that the independent term for the gas phase is very small and highly imprecise in both the G scale and the Φ scale.

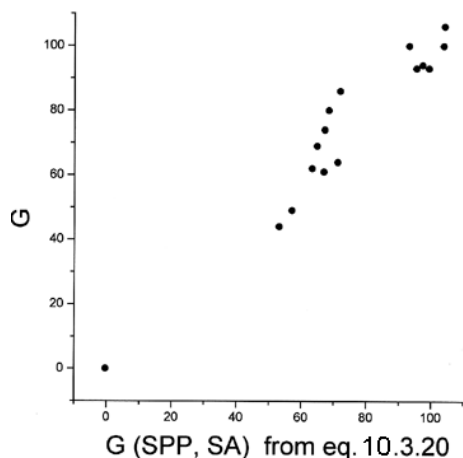


Figure 10.3.5. Plot of Allerhand and Schleyer's G values vs. the predicted G values according to eq. [10.3.20].

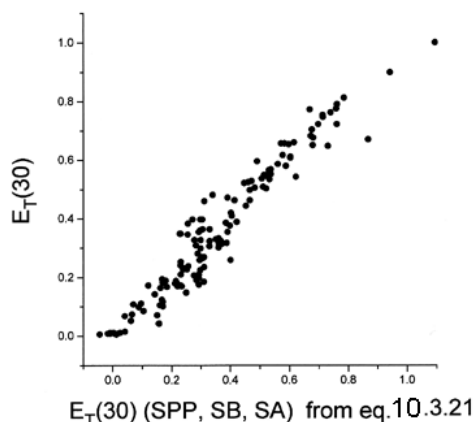


Figure 10.3.6. Plot of Reichardt's $E_T(30)$ values vs. the predicted $E_T(30)$ values according to eq. [10.3.21].

For the 138 solvents with a known $E_T(30)$ value listed in Table 10.3.1, this parameter reflects mostly solvent acidity and polarity, and, to a lesser degree, also solvent basicity (see Figure 10.3.6):

$$E_T(30) = 0.62(\pm 0.04)SPP + 0.12(\pm 0.02)SB + 0.77(\pm 0.02)SA - 0.31(\pm 0.03) \quad [10.3.21]$$

with $r = 0.965$ and $sd = 0.06$.

It should be noted that the three solvent effects (polarity, acidity and basicity) contribute to increasing $E_T(30)$, i.e., to a hypsochromic shift in the transition of the probe (see Figure 10.3.6).

The spectroscopic behavior of the probe used to construct this scale (**1**) is typical of a structure exhibiting highly localized charge on its carbonyl group in the electronic ground state, see scheme III, and hence strong stabilization by effect of increased solvent polarity and acidity. The electronic transition delocalizes the charge and results in an excited state that is much less markedly stabilized by increased polarity or acidity in the solvent. The decreased dipole moment associated to the electronic transition in this probe also contributes to the hypsochromic shift. The small contribution of solvent basicity to the transition of the probe (**1**) is not so clear, however.

10.3.7.2 Treatment of the solvent effect in:

10.3.7.2.1 Spectroscopy

Analyzing the SPP, SB and SA scales in the light of spectroscopic data that are sensitive to the nature of the solvent poses no special problem thanks to the vertical nature of the transitions, where the cybotactic region surrounding the chromophore is hardly altered. The papers where the SPP, SA and SB scales were reported discuss large sets of spectroscopic data in terms of the nature of the solvent. Some additional comments are made below.

Recently, Fawcett and Kloss,⁸³ analyzed the S=O stretching frequencies of dimethyl sulfoxide (DMSO) with a view to elucidating the behavior of 20 solvents and the gas phase.

They found the frequency of this vibration in DMSO to be shifted by more than 150 cm⁻¹ and to be correlated to the Gutmann acceptor number (AN) for the solvents. Based on our analysis, the frequency shift reflects the acidity and, to a lesser extent, the polarity of the solvent, according to the following equation:

$$\nu^{S=O} = 38.90(\pm 7.50)SPP - 89.67(\pm 4.60)SA + 1099.1 \quad [10.3.22]$$

with $n = 21$, $r = 0.979$ and $sd = 6.8 \text{ cm}^{-1}$.

This fit is very good, taking into account that it encompasses highly polar solvents such as DMSO itself, highly acidic solvents such as trifluoroacetic acid ($SPP=1.016$, $SA=1.307$), and highly non-polar and non-acidic solvents such as the gas phase.

Giam and Lyle⁸⁴ determined the solvent sensitivity of the ¹⁹F NMR shifts on 4-fluoropyridine relative to benzene as an internal reference in 31 of the solvents listed in Table 10.3.1. If DMF is excluded on the grounds of its odd value, the chemical shifts for the remaining 30 solvents are accurately described by the following function of solvent acidity and polarity:

$$\Delta^{4F} = -1.66(\pm 0.57)SPP - 6.84(\pm 0.36)SA - 6.50(\pm 0.45) \quad [10.3.23]$$

with $r = 0.971$ and $sd = 0.34 \text{ ppm}$.

Clearly, the acidity of the medium is the dominant factor in the chemical shift measured for this compound, which reveals the central role played by the lone electron pair in pyridine.

Both absorption and emission electronic transitions are acceptably described by our scales, as shown by a recent study⁸⁵ on the solvation of a series of probes containing an intramolecular hydrogen bond, so no further comment is made here other than the following: even if one is only interested in evaluating the change in dipole moment upon electronic excitation via solvatochromic analysis, a multi-parameter analysis must be conducted in order to isolate the shifts corresponding to the pure dipolar effect of the solvent.⁸⁵

Lagalante et al.⁸⁶ proposed the use of 4-nitropyridine N-oxide as a suitable solvatochromic indicator of solvent acidity. The hypsochromic shifts determined by these authors for 43 of the solvents in Table 10.3.1 are due largely to the acidity of solvent and, to a lesser extent, also to its basicity; based on the following equation, however, solvent polarity induces a bathochromic shift in the band:

$$\nu_{max} = -0.92(\pm 0.44)SPP + 0.68(\pm 0.17)SB + 3.63(\pm 0.23)SA + 29.10(\pm 0.31) \quad [10.3.24]$$

with $r = 0.943$ and $sd = 0.31 \text{ kK}$.

As can be seen from Figure 10.3.7, this probe classifies solvents in groups encompassing non-acidic solvents (below 29 kK), moderately acidic solvents (at about 30 kK) and highly acidic solvents (between 31 and 32 kK). Because the solvatochromism does not change gradually with increase in solvent acidity, the probe appears to be unsuitable for quantifying this effect.

Davis⁸⁷ determined the solvatochromism of a charge-transfer complex formed by tetra-n-hexylammonium iodide-nitrobenzene in 23 different solvents and, using the Z and E_T(30) scales, observed a bilinear behavior in scarcely polar and highly polar solvents. A

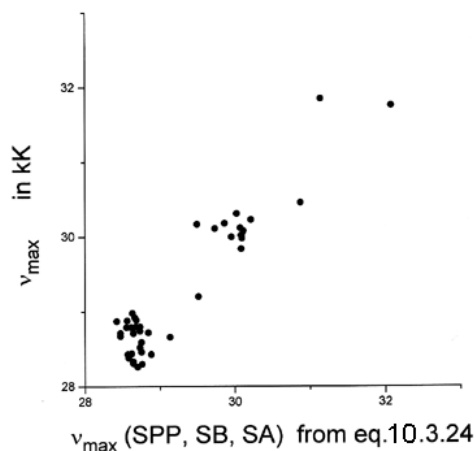


Figure 10.3.7. Plot of the experimental UV/Vis absorption maxima, v_{\max} , of 4-nitropyridine N-oxide vs. the predicted v_{\max} values according to eq. [10.3.24].

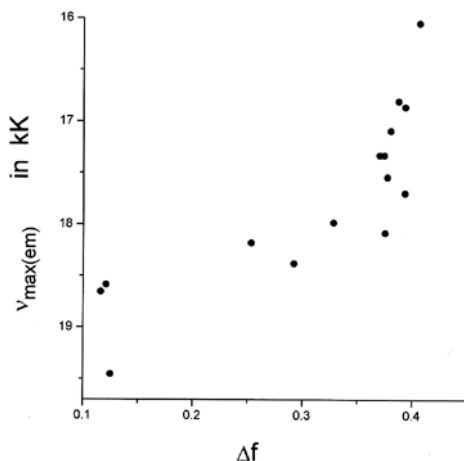


Figure 10.3.8. Plot of the fluorescence maxima, $v_{\max(\text{em})}$, for the Neutral Red in different solvents vs. the solvent polarity function Δf [$\Delta f = (\epsilon - 1)/(2\epsilon + 1) - (n^2 - 1)/(2n^2 + 1)$].

multi-parameter fit of the data for 22 of the solvents revealed that the solvatochromism is seemingly sensitive to solvent acidity only:

$$v_{c.t.} = 11.23(\pm 0.75)SA + 21.41(\pm 0.184) \quad [10.3.25]$$

with $n = 22$, $r = 0.959$ and $sd = 0.66$ kK.

An interesting situation is encountered in the analysis of electronic transitions that results from chromophores which, assisted by solvent polarity, can undergo a change in the electronic state responsible for the fluorescence emission; this is a frequent occurrence in systems involving a TICT mechanism.^{68,88-90} In this situation, a plot of Stokes shift against solvent polarity is a bilinear curve depending on whether the solvents are non-polar (where the fluorescence is emitted from the normal excited state of the chromophore) or polar enough for the transition to take place from the more polar state. Unless the solvents used are carefully selected, it is venturesome to assume that the electronic states will be inverted simply because the variation of solvatochromism with a function of solvent polarity is bilinear.

Recently, Sapre et al.⁹¹ showed that a plot of the maximum fluorescence of Neutral Red (NR) against the solvent polarity function Δf is clearly bilinear (see Figure 10.3.8). Accordingly, they concluded that, in solvents with $\Delta f > 0.37$, the emitting state changes to a much more polar, ICT state. The analysis of this spectroscopic data in the light of our scales reveals that, in fact, the solvatochromism of NR is normal, albeit dependent not only on the polarity of the solvent (SPP), but also on its acidity (SA) (see Figure 10.3.9):

$$v_{\max}^{NR} = -4.31(\pm 0.57)SPP - 1.78(\pm 0.19)SA + 21.72(\pm 0.47) \quad [10.3.26]$$

with $r = 0.974$ and $sd = 0.21$ kK.

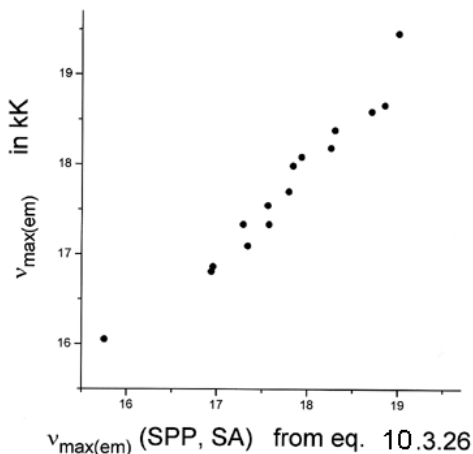


Figure 10.3.9. Plot of the fluorescence maxima, $v_{\max}(\text{em})$, for the Neutral Red in different solvents vs. the predicted, $v_{\max}(\text{em})$, values according to eq. [10.3.26].

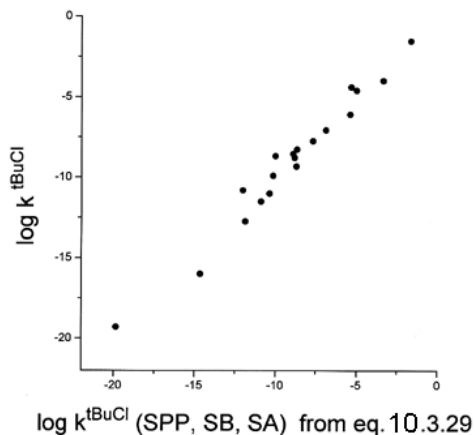


Figure 10.3.10. Plot of Grunwald and Wistein's $\log k^{\text{tBuCl}}$ values vs. the predicted $\log k^{\text{tBuCl}}$ values according to eq. [10.3.29].

10.3.7.2.2 Kinetics

Kinetics so closely related to the solvent effect as those of the Menshutkin reaction between triethylamine and ethyl iodide [eq. (10.3.27)], the solvolysis of tert-butyl chloride [eq. (10.3.28)] or the decarboxylation of 3-carboxybenzisoxazole [eq. (10.3.29)], are acceptably described by our scales.^{15,92,93}

The equation for the Menshutkin kinetics is

$$\log k_s/k_{\text{Hex}} = 8.84(\pm 0.66)SPP + 1.90(\pm 1.37)SA - 4.07(\pm 0.53) \quad [10.3.27]$$

with $n = 27$, $r = 0.947$ and $sd = 0.41$.

The rate of this reaction between triethylamine and ethyl iodide, which varies by five orders of magnitude from n-hexane ($1.35 \times 10^{-8} \text{ l mol}^{-1} \text{ s}^{-1}$) to DMSO ($8.78 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$), is accurately described by solvent polarity and acidity -the sensitivity to the latter is somewhat imprecise. The equation for the kinetics of solvolysis of tert-butyl chloride is:

$$\log k = 10.02(\pm 1.14)SPP + 1.84(\pm 0.99)SB + 8.03(\pm 0.69)SA - 19.85(\pm 0.70) \quad [10.3.28]$$

with $n = 19$, $r = 0.985$ and $sd = 0.80$.

Based on eq. [10.3.28], all solvent effects increase the rate of solvolysis. However, the strongest contribution is that of polarity and the weakest one that of acidity. Although much less significant, the contribution of solvent basicity is especially interesting as it confirms that nucleophilicity also assists in the solvolytic process. Taking into account that it encompasses data spanning 18 orders of magnitude (from $\log k = -1.54$ for water to $\log k = -19.3$ for the gas phase), the fit is very good (see Figure 10.3.10). The equation for the kinetics of decarboxylation of 3-carboxybenzisoxazole is:

$$\log k = 10.37(\pm 1.47)SPP + 2.59(\pm 0.74)SB - 5.93(\pm 0.58)SA - 9.74(\pm 1.17) \quad [10.3.29]$$

with $n = 24$, $r = 0.951$ and $sd = 0.73$.

Equation [10.3.29] reproduces acceptably well the sensitivity of the decarboxylation rate of 3-carboxybenzoxazole in pure solvents observed by Kemp and Paul.⁷ In addition, it clearly shows that such a rate increases dramatically with increasing polarity and, also, to a lesser degree, with solvent basicity. By contrast, it decreases markedly with increasing solvent acidity. This behavior is consistent with the accepted scheme for this decarboxylation reaction.⁹³

10.3.7.2.3 Electrochemistry

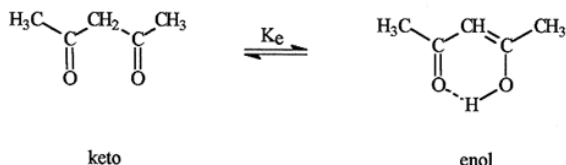
Gritzner⁹⁴ examined the solvent effect on half-wave potentials and found those of K^+ relative to bis(biphenyl)chromium(I)/(0), designated $E_{1/2(BCr)}K^+$, to be related to the Gutmann donor number (DN) for the solvents, so he concluded that K^+ behaves as a Lewis acid against basic solvents. Based on the following equation, the behavior of $E_{1/2(BCr)}K^+$ is dictated largely by the basicity of the solvent but it is also dependent, however weakly, on its acidity:

$$E_{1/2(BCr)}K^+ = -0.51(\pm 0.05)SB + 0.12(\pm 0.04)SA - 1.06(\pm 0.03) \quad [10.3.30]$$

with $n = 17$, $r = 0.941$ and $sd = 0.03$ V.

It should be noted that solvent basicity increases the half-wave potentials of K^+ whereas solvent acidity decreases it.

10.3.7.2.4 Thermodynamics



Scheme VI.

In order to compare the shifts of the conformational equilibrium position with solvent effects it is advisable to select species exhibiting negligible cavity effects on the equilibrium position. Two firm candidates in this respect are the conformational equilibria of 1,2,2-trichloroethane and the

equilibrium between the equatorial and axial forms of 2-chlorocyclohexanone; both are accurately described by our scales.¹⁵

Of special interest is also the equilibrium between the keto and enol tautomers of pentane-2,4-dione (see the scheme VI).

The ΔG values for this equilibrium in 21 solvents reported by Emsley and Freeman⁹⁵ are accurately reproduced by solvent polarity and acidity according to

$$\Delta G = 18.45(\pm 2.41)SPP + 4.22(\pm 0.86)SA - 18.67(\pm 1.96) \quad [10.3.31]$$

with $n = 21$, $r = 0.924$ and $sd = 1.34$ kJ mol⁻¹.

The equilibrium position is mainly dictated by solvent polarity; however, there is clearly a specific contribution of solvent acidity from the carbonyl groups of the dione.

10.3.7.3 Mixtures of solvents. Understanding the preferential solvation model

The solvation of a solute, whether ionic or neutral, in a mixture of solvents is even more complex than in a pure solvent.¹ This is assumed to be so largely because a solvent mixture

involves interactions not only between the solute and solvent but also among different molecules present in the mixture; the latter type of contribution also plays a central role in the solvation process. Among others, it results in significant deviations of the vapor pressure of a mixture with respect to the ideal behavior established by Raoult's law.

Solvation studies of solutes in mixed solvents have led to the conclusion that the above-mentioned divergences may arise from the fact that the proportion of solvent components may be significantly different around the solute and in the bulk solution. This would be the case if the solute were preferentially surrounded by one of the mixture components, which would lead to a more negative Gibbs energy of solvation.^{1,96} Consequently, the solvent shell around the solute would have a composition other than the macroscopic ratio. This phenomenon is known as "preferential solvation", a term that indicates that the solute induces a change with respect to the bulk solvent in its environment; however, such a change takes place via either non-specific solute-solvent interactions called "dielectric enrichment" or specific solute-solvent association (e.g. hydrogen bonding).

Preferential solvation has been studied in the light of various methods, most of which are based on conductance and transference measurements⁹⁶, NMR measurements of the chemical shift of a nucleus in the solute⁹⁷ or measurements of the solvatochromism of a solute in the IR⁹⁸ or UV-Vis spectral region.⁹⁹ Plots of the data obtained from such measurements against the composition of the bulk solvent (usually as a mole fraction) depart clearly from the ideal behavior and the deviation is ascribed to the presence of preferential solvation.

Several reported methods aim to quantify preferential solvation;⁹⁶⁻¹⁰⁰ none, however, provides an acceptable characterization facilitating a clear understanding of the phenomenon.

If preferential solvation is so strongly dictated by the polar or ionic character of the solute, then characterizing a mixture of solvents by using a molecular probe will be utterly impossible since any conclusions reached could only be extrapolated to solutes of identical nature as regards not only polarity and charge, but also molecular size and shape.

However, the experimental evidence presented below allows one to conclude that this is not the case and that solvent mixtures can in fact be characterized in as simple and precise terms as can a pure solvent.

In the light of the previous reasoning, describing the solvolysis of tert-butyl chloride or the decarboxylation kinetics of 3-carboxybenzoxazole in mixed solvents in terms of SPP, SB and SA for the mixtures appeared to be rather difficult owing to the differences between the processes concerned and the solvatochromism upon which the scales were constructed. However, the results are categorical as judged by the following facts:

(a) The solvolysis rate of tert-butyl chloride in 27 pure solvents and 120 binary mixtures of water with methanol (31 mixtures), ethanol (31), isopropyl alcohol (1), trifluoroethanol (8), dioxane (13), acetone (27) and acetic acid (9), in addition to the datum for the gas phase, all conform to the following equation:⁹²

$$\log k = 10.62(\pm 0.44)SPP + 1.71(\pm 0.22)SB + 7.89(\pm 0.17)SA - 20.07(\pm 0.34) \quad [10.3.32]$$

with $n = 148$, $r = 0.99$ and $sd = 0.40$.

(b) The decarboxylation rate of 3-carboxybenzoxazole in 24 pure solvents and 36 mixtures of DMSO with diglyme (4 mixtures), acetonitrile (4), benzene (7), dichloro-

methane (6), chloroform (6) and methanol (9) are accurately described by the following expression:

$$\log k = 10.03(\pm 1.05)SPP + 2.41(\pm 0.49)SB - 5.73(\pm 0.40)SA - 9.58(\pm 0.83) [10.3.33]$$

with $n = 60$, $r = 0.990$ and $sd = 0.60$.

Other evidence obtained in our laboratory using solvent mixtures and probes as disparate in size and properties as the cation Na^+ and Reichardt's $\text{E}_T(30)$, also confirm that solvent mixtures are no more difficult to characterize than pure solvents.

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10.4 ACID-BASE EQUILIBRIA IN IONIC SOLVENTS (IONIC MELTS)

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Ionic melts are widely used in the science and engineering as media for performing different processes such as electrolysis, electrochemical synthesis, single crystals growing, etc. Practically complete dissociation of ionic media to the constituent ions creates high current densities at electrolysis. The absence of oxidants, similar to H^+ , makes it possible to obtain products, which cannot be obtained from aqueous solvents (i.e., alkaline and alkaline earth metals, sub-ions, etc.). From the ecological standpoint, molten ionic media are especially available as technological solvents since their employment does not cause the accumulation of liquid wastes because cooling to the room temperature transforms ionic liquids into a solid state.

Processes taking place in ionic melt-solvents are considerably affected by impurities contained in the initial components of the melt or formed during preparation (mainly, melting) of solvents due to the high-temperature hydrolysis of melts or their interactions with container materials (Al_2O_3 , SiO_2 , etc.) or active components of atmosphere (O_2 , CO_2 , etc.). The list of these impurities is wide enough and includes multivalent cations of transition metals, different complex anions (oxo- or halide anions). The effect of the mentioned admixtures on the processes in ionic melts depends mainly on the degree of their donor-acceptor interactions with constituent parts of the melt.

10.4.1 ACID-BASE DEFINITIONS USED FOR THE DESCRIPTION OF DONOR-ACCEPTOR INTERACTIONS IN IONIC MEDIA

Donor-acceptor interactions in ionic media are often described as acid-base interactions according to Lewis¹ and Lux-Flood²⁻⁵ definitions. The classic variant of the former definition considers acids as acceptors of electron pairs and bases as their donors. In modern variant of this definition, acids are the electron pair (or anion) acceptors or cation (proton) donors, bases are the electron pair (anion) donors or cation (proton) acceptors.

Lux-Flood definition considers bases as donors of oxide-ion, O²⁻, its acceptors are Lux acids.

10.4.1.1 The Lewis definition

The Lewis acid-base process may be described by the following scheme:

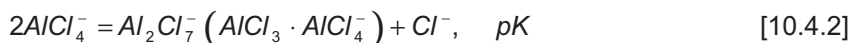


where:

- A an acid,
- B a base,
- K the equilibrium constant (used below $pK \equiv -\log K$).

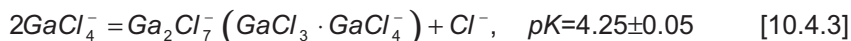
This definition can be used for the description of interactions in ionic melts, containing complex anions undergoing heterolytic dissociation. Processes reverse to [10.4.1], i.e., the acid-base dissociation of A:B adducts (ions) in some solvents are considered as acid-base equilibria of these solvents.

Alkaline chloroaluminate melts containing the excess of AlCl₃ vs. the stoichiometry are promising solvents for preparing sub-ions, e.g., Cd⁺(Cd₂²⁺), Bi⁺, Bi₅³⁺,^{6,7} the excess of acid (AlCl₃) favors their formation. Tremillon and Letisse,⁸ Torsi and Mamantov^{9,10} studied the acid-base properties of molten mixtures AlCl₃-MCl (M=Li, Na, K, Cs) with AlCl₃ concentration exceeding 50 mol% in the temperature range 175-400°C. Equilibrium molarities of Cl⁻ were determined by a potentiometric method with the use of a chloride-reversible electrode. The solvents undergo the acid-base dissociation according to the following equation:



In the melts, chloride-ion donors were bases and substances increasing AlCl₃ concentration were acids. The pK values decrease with the temperature (from 7.1 to 5.0 at temperatures 175 and 400°C, respectively, Na-based melt⁹) elevation and from Cs to Li (at 400°C pK were 3.8, 5.0, 5.8, 7.4 for Li-, Na-, K- and Cs-based melts, respectively¹⁰). The latter effect may be explained from the point of view of “hard” and “soft” acids and bases¹¹⁻¹³ - Li-Cl complexes should be more stable than Cs-Cl ones as formed by “hard” base (Cl⁻) and “more hard” acid (Li⁺).

Dioum, Vedel and Tremillon¹⁴ investigated molten KGaX₄ (X=Cl, I) as background for acid-base processes. The following acid-base equilibria exist in the pure solvents:



Wagner¹⁵ reported an electrochemical study of molten NaBF₄ at 420°C. The range of acid-base properties varying according to reaction:



has been estimated as ~2pF units. The acid-base ranges in ionic melts containing halide complexes are relatively narrow, it means that varying their halide basicity (i.e., equilibrium concentration of the halide ions) may be performed in 2-4 logarithmic units, although such changes are enough to obtain some unstable compounds with the intermediate oxidation degrees.^{6,7}

10.4.1.2 The Lux-Flood definition

Oxygen-containing impurities in molten salts are most usual, their effect on technological processes is mainly negative and consists of bonding acidic reagents with the formation of insoluble (suspensions) or slightly dissociated products. Similar reactions result in retarding the main processes caused by the decrease of the equilibrium concentrations of initial reagents, forming oxide inclusions in metals obtained by the electrolysis of melts, inclusions of insoluble particles in single crystals, considerable corrosion of container for crystal growth, etc. Therefore, quantitative studies of reactions with participation of oxide ions in ionic melts are of importance for scientific and engineering purposes.

Reactions with the transfer of oxide ions in ionic media are mainly considered as oxoacidity or acid-base equilibria by Lux-Flood:²⁻⁵



The addition of acids (bases) in a melt as it follows from [10.4.6] leads to changes of the oxide ion activity, for the characterization of melt acidities (basicities) Lux² proposed the oxygen index, or pO, which was similar to pOH (i.e., basicity index) in aqueous solutions:

$$pO \equiv -\log a_{O^{2-}} \quad (\equiv -\log m_{O^{2-}}) \quad [10.4.7]$$

where:

$a_{O^{2-}}$, $m_{O^{2-}}$ activity and molarity of oxide ions in the melt, respectively

The measurements of oxygen indices during various reactions in molten media define their thermodynamic characteristics - dissociation constants and solubility products. Most oxoacidity studies were made in nitrate melts, while there were much less communications dealing with the similar studies in higher-melting alkaline chlorides, molten bromides and iodides. There is a considerable scatter of obtained experimental results, which are often in conflict one with another. There were no serious attempts to generalize these data or consider them from the common point of view.

10.4.2 THE FEATURES OF IONIC MELTS AS MEDIA FOR ACID-BASE INTERACTIONS

Ionic melts as media for Lux-Flood acid-base reactions may be divided into two types on the base of constitutional (i.e., being a part of main components of the melt) oxygen ions: oxygen-less and oxygen-containing ones. Let us consider some features of acid-base interactions in the mentioned melts.¹⁶

10.4.2.1 Oxygen-less media

There are no oxide ions in the composition of these melts, therefore the pure melts cannot possess oxide-donor properties. Real oxygen-less melts contain small amounts of O^{2-} owing to inevitable ingress of oxygen-containing impurities into the melt, but oxide ion concentration in the “pure” melts is variable, depending on the concentration and acid-base character of impurities. For example, even considerable amounts of sulfates in melts do not create appreciable O^{2-} concentration, carbonate ion dissociation is substantially stronger, hydroxide ions may be referred to most strongly dissociated Lux bases. In “pure” oxygen-less melts oxygen index pO is usually in the range 3 to 4.5. The employment of strongest purifying agents (HCl, CCl_4 , etc.) does not allow to decrease this concentration essentially, the latter being in “an unavoidable harm” causing errors at the quantitative investigations, especially when small amounts of acid or bases are studied. But, in some cases, oxygen index for such a “pure” melt has been used as the internal standard for construction of acidity scales.¹⁷⁻²⁰

Quantitative studies of different Lux-Flood acids and bases in ionic melts were performed by two main ways: the construction of empirical acidity scales to estimate relative acidic strength of the substances and the determination of acid-base equilibria constants using potentiometric titration techniques. The first approach has been proposed in the classic work of Lux² who obtained the acidity scale for the equimolar mixture of potassium and sodium sulfates. Although this work was the basis for series of later studies, the results cannot be considered as undoubted ones. Addition of acids (bases) to the mentioned melt led to increasing (decreasing) e.m.f. of cell with the oxide-selective electrode vs. the corresponding magnitude in the neutral melt. Then, the e.m.f. value shifted progressively to that for the neutral melt because of SO_3 (Na_2O) evaporation from the acidic (basic) melt. Therefore, Lux extrapolated values of e.m.f. to the point of acid (base) addition to the melt. This resulted in the decrease of the data² accuracy.

The empirical acidity scales¹⁷⁻²⁰ give some information about strength of the acids and bases in melts studied. The principal error related to the term “acidity scale” in the case of oxygen-less melts is because it is not connected with the melt properties. Therefore, the values obtained could not be considered as the quantitative characteristics of the oxygen-less melts. The acidity scale length in a solvent is believed to be the interval (measured in acidity index units) between standard solutions of strong acid and base. If the solvent possesses its own acid-base autodissociation equilibrium then a substance creating unit concentration of acid (base) of solvent in the standard solution should be considered as the strongest acid (base). Addition of stronger acids (bases) should not result in extension of the acidity scale because of the known phenomenon of leveling acidic and basic properties by the solvent.²¹ Oxygen-less melts do not possess acid-base equilibrium, therefore, values of the basicity index, in the “pure” melts may have any reasonable value.

10.4.2.2 Oxygen-containing melts

Acid-base processes in oxygen-containing melts are more complex than those in oxygen-less ones, since they are accompanied by competitive equilibria of own acid-base autodissociation of the melt-solvent. The coexistence of acidity and basicity “carriers” into melt is the characteristic feature of oxygen-containing melts making them similar to low-temperature molecular solvents with own acid-base equilibrium.

But, there exist some principal features due to relatively high temperatures of the liquid state. Own acids of the melts are often unstable or volatile,^{2,22} therefore, acidic solutions,

as a rule, lose acids because of their evaporation² or decomposition,²² the oxygen index of such melts is shifted progressively to that of the neutral melt. Hence, in oxygen-containing melts it is possible to observe not only the leveling of acidic properties but also an upper limit of acidity.

CrO_3 and MoO_3 have been found²³ to breakdown the nitrate melt KNO_3 with the evaporation of NO_2 . It should be noted, that the temperature elevation leads to the efficient shrinkage of the acidic region in the melt. The interactions between the oxides and the melt have been assumed to result in the formation of nitrogen (V) oxide, N_2O_5 , and corresponding oxoanions. Since the acids studied (CrO_3 , MoO_3) may be referred to as very strong acids, it may be supposed that reaction:



should be completely shifted to the right and the strength of the acid is determined by acidic properties of nitronium cation, NO_2^+ . The stability of the latter is low and after achieving a certain concentration its reaction with the melt anions becomes intensive enough:

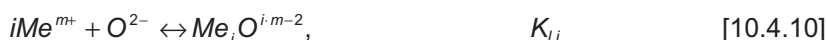


The so-called kinetic methods of melt acidity determination, which will be considered below, are based just on this reaction. The reaction [10.4.9] leads to the decrease of nitronium concentration and the rate of NO_2 emission decreases until essentially constant acid concentration is determined by a sequence of consecutive measurements. This concentration is the “upper limit” of acidity of the melt. The thermal dependence of upper limit of acidity²³ in nitrate melts can be easily explained on the basis of the increase of the melt temperature, which leads not only to the reduction of nitronium stability but also to the elevation of process [10.4.9] rate. Sulphate melts have the upper limit of acidity too, it seems connected with limited and low solubility of SO_3 at elevated temperatures, such assumption may be confirmed by results.²

10.4.2.3 The effect of the ionic solvent composition on acid-base equilibria

The equilibrium parameters of Lux acid-base reactions in ionic media (solubility products of oxides and acid-base equilibrium constants) are essentially affected by the acidic properties of the molten alkaline halide mixtures, i.e., they are dependent on the constituent cation acidities. Therefore, one should consider the reverse problem - the estimation of the basicity indices of ionic melts on the basis of the calculated equilibrium constants.

The default acid-base processes are actually a superimposed effect of interactions between oxide-ions formed and the most acidic cations of the melt:



where:

Me^{m+} the most acidic cation of the solvent

The increase of melt acidity ($K_{i,i}$) leads the shift of interactions [10.4.10] to the right. The distribution of oxide ions added to the melt between different complexes with the melt cations may be presented by the following equation (N is mole fraction, m - molarity):

$$N_{O^{2-}}^0 = N_{O^{2-}} \left(1 + \sum_{i=1}^n K_{i,i} N_{Me^+}^i \right) \quad [10.4.11]$$

It may be seen that the ratio “free oxide-ion/total oxide-ion” is the constant which may be designated as I_1 .²⁴

$$I_1 = N_{O^{2-}} / N_{O^{2-}}^0 = (m_{O^{2-}} / m_{O^{2-}}^0) = 1 / \left(1 + \sum_{i=1}^n K_{i,i} N_{Me^+}^i \right) \quad [10.4.12]$$

Now let us to estimate the equilibrium molarity of the constituent acidic cations in the melt, e.g., the eutectic KCl-LiCl melt (0.4:0.6) contains ~8.5 mole of Li^+ per 1 kg. Usually the ionic complexes in melts are characterized by the coordination number ~ 4-6.²¹ For the solution of O^{2-} of the 0.1 mole/kg concentration, the maximum possible quantity of fixed Li^+ concentration may be estimated as 0.4-0.6 mole/kg, i.e., efficiently lower than 8.5. In this case the change of actual Li^+ concentration is approximately equal to 5-7% and m_{Me^+} in this case may be suggested as constant. Therefore, for each melt the sum in the denominator of [10.4.12] is the constant reflecting its acidic properties. So, $pI_1 = -\log I_1$ is a measure of melt acidities and may be denoted as the “oxobasicity index” of the melt. Since the determination of the “absolute” concentration of free O^{2-} is practically impossible one should choose the “standard melt”, for which I_1 is conditionally equal to 1 and $pI_1=0$. It is reasonable to choose the equimolar mixture KCl-NaCl as the “standard melt”, since this melt is most frequently investigated. Further, one should choose “standard equilibria” and formulate the non-thermodynamic assumptions which usually postulate that the constant of the “standard equilibrium” calculated using “absolute” oxide ion concentrations remains the same for all other melts.

Now let us consider possible variants of such “standard equilibria” and conditions of their use.

One of the first attempts to define and estimate the oxoacidity parameters of ionic (chloride-based) melts was connected with the studies of the equilibrium



in different chloride mixtures.^{25,26} Here the partial pressures of H_2O and HCl are known and the oxide ion concentration is calculated on the base of the calibration data as $m_{O^{2-}}^0$ ($N_{O^{2-}}^0$). The equilibrium constant of [10.4.13] may be represented in terms of the “absolute” mole fractions of O^{2-} and I_1 by:

$$K_1 = \frac{p_{HCl}^2 (N_{O^{2-}} I_1^{-1})}{p_{H_2O} N_{Cl^-}^2} = K_{KCl-NaCl} I_1^{-1} \quad [10.4.14]$$

and, consequently:

$$pK_1 = pK_{KCl-NaCl} - pI_1 \quad [10.4.15]$$

Combes et al.²⁵ introduced the oxo-acidity function, Ω :

$$\Omega = 14 - pK_I + pO^{2-} \quad [10.4.16]$$

taking into account [10.4.15] eq. [10.4.16]

$$\Omega = (14 - pK_{KCl-NaCl}) + pI_I + pO^{2-} \quad [10.4.17]$$

where $(14 - pK_{KCl-NaCl})$ is the Ω value in KCl-NaCl standard solution ($pO=0$) and pO^{2-} is the instrumental pO in the solvent studied.

Therefore, the shift of pO scales vs. KCl-NaCl depends only on the I_I value. On the basis of [10.4.13] it has been estimated as +7-8 log units (Figure 3²⁵) for KCl-LiCl at 1000K.

Homogeneous Lux acid-base equilibria of type of [10.4.6] have not been earlier considered as available for estimations of oxoacidity indices. However, pK for these reactions may be written as

$$pK_1 = -\log \frac{N_B}{N_A (N_{O^{2-}} I_I^{-1})} = pK_{KCl-NaCl} + pI_I \quad [10.4.18]$$

For the use of this type of equilibrium it is necessary to make the following non-thermodynamic assumption:

$$\left(\frac{\gamma_B}{\gamma_A} \right)_I = \left(\frac{\gamma_B}{\gamma_A} \right)_{KCl-NaCl} \quad [10.4.19]$$

where:

γ corresponding activity coefficients of the acid and the base in solvent "I" and KCl-NaCl

The use of [10.4.16] where A and B are anion acid and base for estimations of the oxobasicity indices may be justified because the acid and the conjugated base are negatively charged (in the pair $Cr_2O_7^{2-}/CrO_4^{2-}$ they are of the same charge).

Finally, let us consider the usability of the oxide solubility data



for pI_I estimations. The solubility product value, P , may be presented as

$$P_{MeO,I} = N_{Me^{2+}} (N_{O^{2-}} I_I^{-1}) = P_{MeO,KCl-NaCl} I_I^{-1} \quad [10.4.21]$$

or

$$pP_{MeO,I} = pP_{MeO,KCl-NaCl} - pI_I \quad [10.4.22]$$

Metal cations in molten halides form halide complexes. The reaction [10.4.20] for chloride melts ($N_{Cl} = 1$) suggests that the distribution of Me^{2+} between different complexes $MeCl_n^{2-n}$ remains unchanged (similarly to eq. [10.4.10]-[10.4.12] for the oxide ion distribution). It is clear that the solubility data may be used for estimations of the oxoacidity indices only in melts with the same anion composition. The anion changes cause errors since Me^{2+} in eq. [10.4.21] is referred to essentially different acids, e.g., halide complexes $MeCl_4^{2-}$ and

MeBr_4^{2-} in the case of chloride and bromide melts. Therefore, regardless of the cation composition, the oxide solubilities are essentially affected by anion composition of a melt.²⁷

Equations [10.4.14], [10.4.18] and [10.4.22] estimate $pI_{\text{KCl-LiCl}}$ vs. KCl-NaCl as 7-8,²⁵ 3.7²⁴ and 3.4²⁴, respectively. This estimation is considerably larger than the estimation based on eq. [10.4.18] and [10.4.22]. For Ca^{2+} based chloride melts, the similar estimation made on the basis of [10.4.14] gave $pI \sim 10^{25}$ vs. ~ 4 determined on the basis of [10.4.22].²⁸ So, the oxobasicity indices calculated according to $\text{HCl}/\text{H}_2\text{O}$ equilibrium constant are essentially different from those obtained using reactions without reactive gas atmosphere.

Probably, this discrepancy may be explained by the features of the water behavior in aprotic ionic melts. It is known that, similar to basic properties, water possesses oxoacidic properties according to the reaction:



Such polynuclear complexes are stable according to spectral data²⁹ because of the H-bonds formation. Three acids ($\text{HCl} + \text{Me}^+ + \text{H}_2\text{O}$) exist in ionic melts saturated with water and HCl and consequently reaction [10.4.23] depends on the partial pressure of water. In Li- and Ca-based chloride melts, retention of water³⁰ and the solubility of H_2O is appreciably higher than in e.g. KCl-NaCl.

Apparently, even the simplest reaction [10.4.13] is actually complicated by additional interactions favoring the fixation of “free” oxide ions. Values of oxobasicity indices calculated from eq. [10.4.13] are thus somewhat overestimated.

The oxobasicity index for KCl-LiCl (0.4:0.6) compared with KCl-NaCl at 700°C lies within the range 3.4-3.7 log units.

10.4.3 METHODS FOR ESTIMATIONS OF ACIDITIES OF SOLUTIONS BASED ON IONIC MELTS

The literature data show that many methods were used for oxoacidity studies and estimation of the acidic properties of melts. One simplest method³¹ involves indicator. Acid-base indicators usually employed in aqueous solutions for protic acidity measurements have been used for acidity studies in molten $\text{KNO}_3\text{-LiNO}_3$ at 210°C and KSCN at 200°C. The color of indicator solution, relative to acidity, changes during titration of bases (sodium hydroxide or peroxide) by potassium pyrosulfate, $\text{K}_2\text{S}_2\text{O}_7$:



where:

HInd the protonized form of the acid-base indicator
Ind⁻ the anionic form of the said indicator

In molten nitrates such transition was observed only for phenolphthalein (yellow-purple), other indicators seemingly were oxidized by the melt (the conclusion made³¹ was “insoluble in the melt”). In molten KSCN not possessing oxidizing properties color transitions were observed for all indicators used (methyl red, thymolphthalein, etc.). The employment of indicators for acidity estimation is limited mainly by their thermal instability and tendency to oxidize at high temperatures. Since ionic melts, as a rule, have no constitutional water, the reverse transition of indicator into the protonized form [10.4.24] is hardly possible (the solution of phenolphthalein became yellow at the reverse transition “base-acid”³¹).

Therefore, the use of indicator method is possible only at low-temperatures (250°C) and in non-oxidizing ionic melts.

Spectral methods were also used for the melt basicity estimation.^{32,33} The scale of “optical” basicity for metallurgical slags with respect to CaO (standard) has been constructed.³² The “optical” basicity, Λ , was estimated from spectral line shifts (the transition $^1S_0 \rightarrow ^3P_1$) for Tl^+ , Pb^{2+} , Bi^{3+} cations in the basic medium. Ionic melts $Na_2O-B_2O_3-Al_2O_3$, $Na_2O-B_2O_3-SiO_2$, $Na_2O-SiO_2-Al_2O_3$ have been investigated by X-ray fluorescent spectroscopy,³² relative oxide acidities decrease in the sequence $B_2O_3 > SiO_2 > Al_2O_3$.

The use of spectral methods is based on studies of cooled (quenched) samples, such a routine may distort results because of inconsistency between the solution temperature and that of acidity estimations.

Data on the melt basicity estimations by the determination of acidic gases (SO_3 , CO_2 , H_2O) solubilities are presented elsewhere.^{34,35} Sulphur trioxide solubility in molten sodium phosphate was determined by thermogravimetric analysis,³⁴ the correlation between the melt basicity and the SO_3 solubility was found. The use of CO_2 and H_2O for basicity estimation was described elsewhere.³⁵ The similar methods may be used only for basic melts since acids displace the acidic gas from the melt. Furthermore, the interaction products of the acidic gas with the melt may be relatively stable, especially in basic solutions, and their formation leads to irreversible changes of the melt properties.

A “kinetic method” was used for Lux acidity studies in molten nitrates. The interaction between the nitrate melts KNO_3-NaNO_3 and potassium pyrosulfate was studied.^{36,37}



The formed nitronium cation, NO_2^+ , reacted with NO_3^- according to [10.4.9]. The latter stage is considerably slower than [10.4.25], hence, its rate allowed to estimate the melt acidity, which can be presented by the following sum: $T_A = [S_2O_7^{2-}] + [NO_2^+]$.³⁶

The acid-base interactions between $Cr_2O_7^{2-}$ and chlorate ions, ClO_3^- , in molten KNO_3-NaNO_3 are described by the following equations.^{38,39}



From two above processes, reaction [10.4.27] is the limiting stage, the rate of the chlorine evolution is proportional to the total acidity of the melt: $T_A = [Cr_2O_7^{2-}] + [ClO_2^+]$.

The reaction of bromate ions, BrO_3^- , with potassium dichromate in the nitrate melt has been studied.³⁸ Several studies³⁶⁻⁴⁰ gave estimate of relative acidities of the oxo-cations. The acidities increased in the sequence $BrO_2^+ < ClO_2^+ < NO_2^+$.

Slama^{41,42} used the kinetic method to investigate metal cation (Cu^{2+} , Co^{2+}) acidities in molten KNO_3-NaNO_3 in the temperature range 325-375°C. The cation acidities were estimated on the base of the NO_2 evolution rate [10.4.9]. Nitronium cation was formed as a product of the following reaction:



where:



Metal cation acidities are comparable with acidic properties of dichromate-ion and mentioned above³⁶⁻⁴⁰ cations.

A potentiometric method, or more accurately, method of e.m.f. measurements with liquid junction in cells with oxide-reversible electrodes was most advantageous in oxoacidity studies of various melts. The principal construction of electrochemical cells for oxoacidity studies may be presented by the following scheme:



In all known studies, the potential of liquid junction was zero. The known reference electrodes were metallic (i.e., metal immersed into the solution with the definite concentration of the corresponding cation) or gas oxygen electrodes immersed into solutions with definite oxide ion concentrations (concentration cells).

10.4.4 ON STUDIES OF THE HOMOGENEOUS ACID-BASE REACTIONS IN IONIC MELTS

10.4.4.1 Nitrate melts

Traditionally, nitrate melts are considered among most comprehensively studied ones. Relatively low melting temperatures both of individual nitrates and their mixtures allowed to use simpler experimental techniques. The potentiometric studies gave the acid-base equilibrium constants. Most studies were on oxoacidity reactions in molten KNO_3 at 350°C .^{23,43-67} Constants of acid-base reactions of Group V highest oxides (P_2O_5 , As_2O_5 , V_2O_5) with Lux bases were also investigated.⁴³⁻⁴⁸ All oxides breakdown the melt, the first stage is the formation of corresponding meta- acid salts and nitronium cation:



where:

R the designation of Group V element,

the second step is the redox interaction of NO_2^+ with NO_3^- according to [10.4.9], which is shifted to the right, NO_2 evolution took place until e.m.f. values reached down to ~ 0.5 V, this magnitude corresponded to the upper limit of oxo-acidity in molten KNO_3 . The oxygen index value for this limit can be estimated as $\sim 10^{-16}$.⁴³⁻⁴⁸ Addition of Na_2O_2 as a Lux base led to the following neutralization steps



The acidic properties of oxides increased in the sequence $\text{V}_2\text{O}_5 < \text{P}_2\text{O}_5 < \text{As}_2\text{O}_5$. Besides of reactions [10.4.30]-[10.4.32],⁴³⁻⁴⁵ the constants of the following assumed equilibria, with participation of hydroanions HPO_4^{2-} , H_2PO_4^- , HAsO_4^{2-} , $\text{H}_2\text{AsO}_4^{2-}$, were determined:

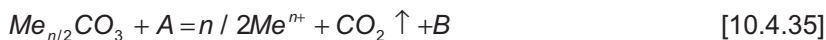


Since even the pure salts containing mentioned hydroanions undergo the decomposition at temperatures much lower than 350°C with the formation of corresponding meta- or pyro- salts,⁶⁸ equilibria [10.4.33] and [10.4.34] hardly take place in the absence of water vapor in atmosphere over the melt.

The acidic properties of highest oxides of VI Group elements (Cr, Mo, W) were investigated.^{23,48,49} Similarly to Group V oxides⁴³⁻⁴⁸ CrO_3 and MoO_3 destructed the nitrate melt with formation of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{Mo}_3\text{O}_{10}^{2-}$, respectively. After the complete evolution of NO_2 , e.m.f. values were close to 0.5 V, what was in a good agreement other studies.⁴³⁻⁴⁸ The potentiometric titration curves of the formed products contained only one drop of e.m.f. (or pO). Chromate and molybdate ions were the final products of the neutralization reactions. WO_3 was weaker acid and did not destruct the nitrate melt. Its titration was the one-stage process resulting in the tungstate formation. The acidities of oxides increased in the order: $\text{WO}_3 < \text{MoO}_3 < \text{CrO}_3$.

The equilibrium constants^{23,43-58} have incorrect values because calculated magnitudes had shift by order of a few pK units. Such phenomenon may take place either because of incorrect determination of reaction participants (stoichiometry) or slope changes of the calibration plot for the used oxygen electrode $\text{Pt}(\text{O}_2)$ in the acidic region.

Relative acidities of different metal cations in molten KNO_3 have been investigated⁵²⁻⁵⁴ using potentiometric titration of corresponding carbonates by dichromate⁵² and metaphosphate ions:⁵³



The cations studied were arranged in the following sequence: $\text{K} \sim \text{Na} > \text{Li} \sim \text{Ba} > \text{Sr} > \text{Ca} > \text{Pb}$ of basicity decrease. The cation sequence was in a good correlation with the electronegativity of metals. The proposed method of investigation had an essential problem since the acids used for titration fixed oxide ions with the simultaneous destruction of carbonate and formed insoluble chromates and phosphates with the majority of cations studied. As it has been shown,^{36,37} the addition of Ca^{2+} into nitrate melts leads to the shift of the interaction $\text{Cr}_2\text{O}_7^{2-} - \text{NO}_3^-$ to formation of nitronium cation and the melt decomposition although the solution without Ca^{2+} is stable. Such shift is explained by formation of slightly insoluble CaCrO_4 in nitrate melt and has no relation to Ca^{2+} acidity. It is referred to the barium position in the sequence that gives evidence of the said complexes or precipitates formation, since their acidic properties are substantially weaker than those of Li^+ . The formation of the BaCrO_4 precipitate leads to approaching of Ba^{2+} acidity to Li^+ acidity. Probably, the same reason effected arrangement of others alkaline earth metals in this sequence.

The relative strength of different Lux bases in nitrate melts was investigated.^{54,55} The bases studied were divided into two groups: the oxide ion group (OH^- , O^{2-} , O_2^{2-}) and the carbonate ion group (CO_3^{2-} , HCO_3^- , $(\text{COO})_2^{2-}$, CH_3COO^- , HCOO^-). The bases belonging to the first group have been assumed^{54,55} to be completely transformed into O^{2-} . The members of the first group of bases were weaker than the second group bases. From the thermal data it may be seen that at experimental temperature (350°C) all the second group bases are completely broken down to carbonate. The differences between single bases may be attributed to reduction properties - organic salts reduce nitrate ions to more basic nitrite ones and favor the accumulation of oxide and carbonate ions in the melt over the stoichiometric ratio.

Hence, the use of a majority of proposed bases for quantitative studies of oxoacidity is not possible, especially for acids having apparent oxidizing properties (chromates, vanadates, etc.).

Oxide ions in molten nitrates exist as the so-called pyronitrate ions $\text{N}_2\text{O}_7^{4-}$ which was a strong base with the basicity approximately equal to those for CO_3^{2-} .⁵⁵ The modern point of view excludes the existence of nitrogen compounds with the coordination number exceeding 3 by oxygen, hence pyronitrate was hardly existing in the mentioned conditions. Indeed, following oxoanion studies⁵¹ have demonstrated the absence of the mentioned ion in basic nitrate solutions. A possible way for the stabilization of O^{2-} in nitrate melts is the formation of silicates due to reactions with walls of the container (usually it is pyrex).

The anomalous behavior of the electrode $\text{Pt}(\text{O}_2)$ has been noted and explained by "peroxide" function of the gas oxygen electrodes (of the first type).^{57,58} On the contrary to gas electrodes, metal-oxide electrodes (of the second type) were reversible with the slope corresponding to the reaction:



The acid-base equilibria in complex solutions based on nitrates containing phosphates and molybdates were attributed^{59,60} to the formation of heteropolyacids in molten nitrates. This is confirmed by cryoscopic studies.⁶¹

Some features of potentiometric titration techniques in molten salts have been discussed.^{62,63} The automatic potentiometric titration described in details⁶² consists of the following. A rod, prepared as frozen $\text{K}_2\text{Cr}_2\text{O}_7$ solution in the melt, was immersed into the melt containing a base with the constant rate. e.m.f. data were recorded by the recording potentiometer. Such a routine may be used only for the detection of equivalence points in melts (with accuracy of $\sim 3.5\%$).

The effect of acidic oxides on the thermal stability of molten NaNO_3 has been investigated.⁶⁴ The increase of oxide acidity results in the decrease of the melt decomposition temperature. This is explained by the reduction of the activation energy of the decomposition owing to fixing oxide ions by acids. But there was also another explanation: decreasing temperature of melt decomposition is caused by the equilibrium shift towards the oxide-ions and nitrogen oxide formation under the action of the acid. Acidic properties of oxides decrease in the sequence $\text{SiO}_2 > \text{TiO}_2 > \text{ZrO}_2 > \text{Al}_2\text{O}_3 > \text{MgO}$.

Potentiometric method⁶⁵⁻⁶⁷ used metal-oxide electrodes ($\text{Nb}|\text{Nb}_2\text{O}_5$, $\text{Ta}|\text{Ta}_2\text{O}_5$, $\text{Zr}|\text{ZrO}_2$) for oxoacidity studies in the nitrate melt. The empirical acidity scale in molten potassium nitrate at 350°C was constructed: $\text{NH}_4\text{VO}_3 > \text{NaPO}_3 > \text{NaH}_2\text{PO}_4 > \text{K}_2\text{Cr}_2\text{O}_7 > \text{K}_2\text{HPO}_4 > \text{Na}_4\text{P}_2\text{O}_7 > \text{NaHASO}_4 > \text{K}_2\text{CO}_3 > \text{Na}_2\text{O}_2$. This sequence includes some acids seldom existing in molten salts. NH_4VO_3 at 350°C should be completely transformed into V_2O_5 with a partial reduction of the latter by ammonia. Acidic salts mentioned were decomposed to corresponding pyro- and meta-salts. Therefore the scale obtained contains a number of errors.

10.4.4.2 Sulphate melts

Sulphate melts are referred to melts with the own acid-base dissociation equilibrium:



There are rather few contributions devoted to the Lux acidity studies in the similar melts. This may be explained by relatively high melting points both of single sulfates and their eutectic mixtures. The weak stability of acidic solutions in sulphate melts can also be considered as a reason why these melts are studied insufficiently. Indeed, reaction [10.4.37] should result in SO_3 formation in the melt. Reference data,^{68,69} however, show that decomposition temperatures of pyrosulfates (i.e., complexes $\text{SO}_3(\text{SO}_4^{2-})$) do not exceed 460°C , in dissolved state stability of solvated SO_3 should be even lower. The absence of SO_3 partial pressure over the melt gives rise to removing SO_3 from the latter and, since the equilibrium state of [10.4.37] is not attained, SO_3 should be removed completely. Among sulphate melts the ternary eutectic mixture $\text{K}_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ (0.135:0.78:0.085) with the lowest melting point 512°C ⁷⁰ may be most promising for the acidity studies since it is possible to perform studies at the temperatures significantly lower than in the classic work of Lux.² Under these conditions stability of acidic and basic solutions increases.

Lux² reported the oxygen electrode reversibility investigation and construction of empirical acidity scale in the molten eutectic mixture $\text{K}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ at 800°C . The thermal stability of pyrosulfates has been shown by Flood³ to decrease with melt cation acidity increasing. Kaneko and Kojima^{71,72} investigated acid-base properties of different solutions in the molten $\text{K}_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ at 550°C ; the empirical acidity scale length was approximately 10 pO units between 0.01 mole/kg solutions of $\text{S}_2\text{O}_7^{2-}$ and O_2^{2-} ions. From the latter data, the acid-base interval of this solvent can be easily estimated as the length of acidity scale between standard solution - ~14 pO units. The pO range of VO^{2+} stability has been determined to be 8.5 to 10.6. To complete the consideration of investigations in sulphate melts the work⁷³ should be mentioned, it is concerned with potentiometric studies of the acidic properties of MoO_3 , $\text{Cr}_2\text{O}_7^{2-}$, PO_3^- , $\text{P}_2\text{O}_7^{4-}$, V_2O_5 in molten $\text{K}_2\text{SO}_4\text{-Li}_2\text{SO}_4\text{-Na}_2\text{SO}_4$ at 625°C . Acids mentioned were neutralized by sodium carbonate. The potential (pO) drop in equivalence points was observed at "acid-base" ratio 1:3 for vanadium oxide and 1:1 for all other Lux acids. Values of equilibrium constants were not presented.

10.4.4.3 Silicate melts

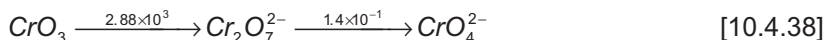
Studies performed in molten silicates are of importance for applied purposes, since systems under consideration are widely used in various industries (slugs, glasses, etc.). Flood et al.⁷⁴⁻⁷⁶ studied the acidity dependence of silicate melts upon their composition. A system PbO-SiO_2 have been studied in the range of SiO_2 concentrations of N_{SiO_2} from 0 to 0.6 at $1100\text{-}1200^\circ\text{C}$. The coexistence of $(\text{SiO}_3)_3^{6-}$ and $(\text{SiO}_{2.5})_6^{6-}$ polyanions together with the ordinary orthosilicate ions, SiO_4^{4-} has been shown. The basicities of molten glasses vs. $\text{Na}_2\text{O/SiO}_2$ ratios were studied⁷⁵ by the potentiometric method with the use of the gas oxygen electrode $\text{Ag}(\text{O}_2)$ in concentration cells. The decrease of the mentioned ratio has been stated to cause a reduction of the basicity, while magnesium oxide has been found to have no effect on the melt basicity. The gas oxygen electrode reversibility in molten PbO-SiO_2 , $\text{Na}_2\text{O-CaO-SiO}_2$, MeO-PbO-SiO_2 , where Me^{2+} - alkaline earth cation, has been investigated.⁷⁷ The electrode $\text{Pt}(\text{O}_2)$ has been shown to be reversible to O^{2-} .

The use of a membrane oxygen electrode $\text{Pt}(\text{O}_2)|\text{ZrO}_2$ for molten silicate acidity control during glass making has been described.⁷⁸ Studies of basicities in molten $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ using a potentiometric method⁷⁹ showed that the acidic properties of Al_2O_3 were weaker, than SiO_2 ones. Processes of glass corrosion in molten alkaline earth nitrates have been studied for glass compositions $\text{Na}_2\text{O}_x\text{Al}_2\text{O}_3\text{2SiO}_2$, where x was in the range from 0 to 0.4.⁸⁰ The degree of interaction between the melt and immersed glass in-

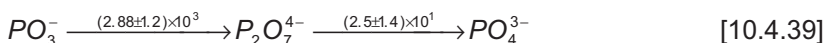
creased with the reduction of the alkaline earth cation radius. The effect of the cation charge and the radius on the basicity of lead meta-silicate melt at 800, 850, 900°C by additions of Tl_2O , PbO , CdO , ZnO and Bi_2O_3 has been studied by potentiometry.⁸¹

10.4.4.4 The equimolar mixture KCl-NaCl

This melt is the most investigated among chloride based melts. Some oxoacidity studies were performed by Shapoval et al.⁸²⁻⁸⁷ Main purposes of these works were to investigate oxygen electrode reversibility and to obtain equilibria constants for acid-base reactions including oxo-compounds of Cr^{VI} , Mo^{VI} and W^{VI} at 700°C. Equilibrium constants of acid-base interactions for CrO_3 and PO_3^- have been determined.⁸²⁻⁸⁴ The titration of the former substance proceeds in two stages:

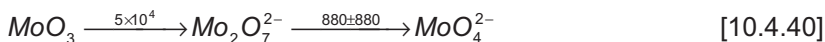


Sodium metaphosphate is two-basic acid too:

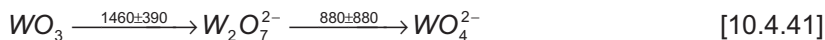


The excess of titrant, O^{2-} , has been found to cause the formation of basic phosphates with assumed composition $PO_3^- \cdot 2O^{2-}$. When Na_2CO_3 was used as titrant, there was no formation of the mentioned basic products. Ba^{2+} and Li^+ cations have been shown to possess appreciable acidic properties, corresponding constant values were estimated as 8.1×10^1 and 3.53×10^2 .

An investigation of acidic properties of MoO_3 was performed:⁸⁵



Acidic properties of oxo-compounds of W^{VI} have been studied.^{86,87} The titration of WO_3 in molten chlorides was a two-stage process:



Results formed the base for the following electrochemical studies of electroreduction processes of Group VI metals.⁸⁸⁻⁹⁰ These studies developed theoretical bases and principles to control electrochemical processes of metals and their compounds (carbides, borides, silicides) deposition from ionic melts.⁸¹

The acid-base equilibria in the scheelite ($CaWO_4$) solutions in the said chloride mixture at 1000K were investigated.⁹² CaO solubility in molten KCl-NaCl has been determined to be about 0.084 mol%, that of scheelite was $10^{-3.5}$ mole/kg. Equilibrium constants for acid-base reactions with WO_3 participation have been determined, too:



The reverse titration has been assumed by authors⁹² to result in the formation of polyanion $W_3O_{10}^{2-}$, $pK=12.7$. The titration curve was irreversible. This result can be easily explained taking into account that WO_3 is unstable in strong acidic chloride melts and removed from as WO_2Cl_2 . Therefore, additions of WO_3 into the acidic melt should lead to un-

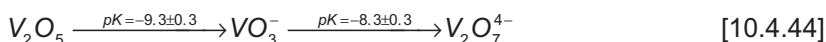
controlled titrant loss affecting experimental results. Ditto referred to all results obtained by the reverse titration by MoO_3 and CrO_3 as the equivalence point.

Acidic properties of P^{V} oxocompounds in the chloride melt at 700°C were investigated using a membrane oxygen electrode Ni,NiO|ZrO_2 .⁹³ Polyphosphates of compositions with $\text{Na}_2\text{O-P}_2\text{O}_5$ ratio from 1.67 to 3 formed in the acidic region:



The corresponding constants were estimated. Polyphosphate solubilities were determined by a cryoscopic method.

The titration of V_2O_5 proceed in two stages:⁹⁴



Some results of oxoacidity studies in molten KCl-NaCl were obtained in our works,⁹⁵⁻⁹⁹ they are presented in Table 10.4.1.

Table 10.4.1. The Lux acid-base equilibrium constants in molten KCl-NaCl and NaI (at the confidence level 0.95) [After references 95,96,98]

Equilibrium	-pK		
	m	N	mol%
KCl-NaCl			
$2\text{PO}_3^- + \text{O}^{2-} = \text{P}_2\text{O}_7^{4-}$	8.01±0.1	10.67	6.67
$\text{PO}_3^- + \text{O}^{2-} = \text{PO}_4^{3-}$	5.93±0.1	7.26	5.26
$\text{PO}_3^- + 2\text{O}^{2-} = [\text{PO}_4^{3-} \cdot \text{O}^{2-}]$	7.24±0.1	-	-
$\text{CrO}_3 + \text{O}^{2-} = \text{CrO}_4^{2-}$	8.41±0.1	9.77	7.77
$\text{Cr}_2\text{O}_7^{2-} + \text{O}^{2-} = 2\text{CrO}_4^{2-}$	7.18±0.1	7.18	7.18
$2\text{CrO}_4^{2-} + \text{O}^{2-} = [2\text{CrO}_4^{2-} \cdot \text{O}^{2-}]$	1.60±0.2	4.26	0.26
$\text{MoO}_3 + \text{O}^{2-} = \text{MoO}_4^{2-}$	8.32±0.2	9.65	7.65
$\text{MoO}_3 + 2\text{O}^{2-} = [\text{MoO}_4^{2-} \cdot \text{O}^{2-}]$	9.71±0.3	11.37	7.37
$\text{WO}_3 + \text{O}^{2-} = \text{WO}_4^{2-}$	9.31±0.2	10.64	8.64
$\text{WO}_3 + 2\text{O}^{2-} = [\text{WO}_4^{2-} \cdot \text{O}^{2-}]$	10.67±0.5	13.33	9.33
$\text{B}_4\text{O}_7^{2-} + \text{O}^{2-} = 4\text{BO}_2^-$	4.82±0.1	2.16	4.16
$\text{BO}_2^- + \text{O}^{2-} = \text{BO}_3^{3-}$	2.37±0.2	3.17	1.70
$\text{V}_2\text{O}_5 + \text{O}^{2-} = 2\text{VO}_3^-$	6.95±0.2	6.95	6.95
$\text{V}_2\text{O}_5 + 2\text{O}^{2-} = \text{V}_2\text{O}_7^{4-}$	12.23±0.1	14.89	10.89
$\text{V}_2\text{O}_5 + 3\text{O}^{2-} = 2\text{VO}_4^{3-}$	12.30±0.1	14.96	10.96
$\text{V}_2\text{O}_5 + 5\text{O}^{2-} = 2[\text{VO}_4^{3-} \cdot \text{O}^{2-}]$	13.88±0.5	19.20	11.20
$2\text{GeO}_2 + \text{O}^{2-} = \text{Ge}_2\text{O}_5^{2-}$	4.18±0.4	6.84	2.84

Equilibrium	-pK		
	m	N	mol%
NaI			
$2VO_3^- + O^{2-} = V_2O_7^{4-}$	5.40±0.3	7.10	4.10
$V_2O_7^{4-} + O^{2-} = 2VO_4^{3-}$	1.68±0.3	1.68	1.68
$B_4O_7^{2-} + O^{2-} = 4BO_2^-$	5.02±0.8	3.37	5.37

The results included in the Table 10.4.1 are in good agreement with the similar studies, performed using a membrane oxygen electrode Ni,NiO|ZrO₂. The use of the gas platinum-oxygen electrode resulted in significant underrating of constant values (of order of 3-4 pK units).

10.4.4.5 Other alkaline halide melts

Some studies of acid-base equilibria in molten alkaline halides have been performed by Rybkin et al.¹⁷⁻²⁰ The empirical acidity scales have been constructed on the base of potentiometric studies in molten KCl^{17,18} and CsI.¹⁹ The practical significance of the mentioned works consists in the proposition to use some buffer solutions - SO₄²⁻/S₂O₈²⁻, WO₄²⁻/W₂O₇²⁻, PO₄³⁻/P₂O₇⁴⁻ as reference standards for the indicator electrode calibration and determinations of pO in molten alkaline halides.

Rybkin and Banik²⁰ obtained the empirical acidity scale in molten NaI at 700°C. The basicities of CO₃²⁻ and OH⁻ were close which is incorrect since 0.01 mole/kg solutions were used for the scale constructing while equations



showed that these additions were not equivalent. CO₃²⁻ concentration recalculated to oxide ions was twice as high as OH concentration. Indeed, in the later work these authors^{100,101} showed that hydroxide ion was stronger base than carbonate ion.

We have performed a study of acidic properties of boron (III) and vanadium (V) oxo-compounds in molten NaI at 700°C⁹⁸ (see Table 10.4.1). A comparative study of strength of Lux bases OH⁻, CO₃²⁻, SO₄²⁻ was determined^{100,101} by potentiometric titration using sodium pyrophosphate as acid. Two moles of the first base may be neutralized by 1 mole of P₄O₇²⁻, while two other moles react with the acid in ratio 1:1. On the base of e.m.f. drop magnitude at the equivalence point, the bases have been arranged in sequence OH⁻>CO₃²⁻>SO₄²⁻ of basicity decrease. The equilibrium constants were not estimated.^{100,101}

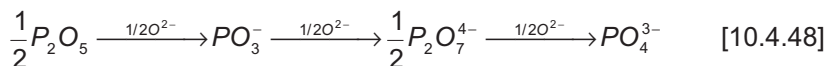
There is no correlation^{17,19} between substances entered into melt and those really existing in it. E.g., potassium nitrate and nitrite^{17,18} are decomposed to K₂O at temperatures considerably lower than the temperature of the experiment (700°C). Ditto^{17,18} referred to K₂S₂O₇ and Na₂S₂O₈ as acidic phosphates.¹⁹ In the latter work it has been found that pyrophosphate acidity is larger than that for metaphosphate. However, titration of phosphorus (V) oxo-compounds in melts runs according to the scheme [10.4.39]. The acidity decreases,

and, hence, pyrophosphate acidity should be lower, since in pair “metaphosphate-pyrophosphate” the latter is the conjugated base.

The absence of correlation between pH in aqueous solutions and pO in melts for the same substance is often noted, this conclusion is made mainly from data for oxocompounds of P^V. This fact is due to the following reason. The stages of phosphoric acid neutralisation in aqueous solutions are:



In melts, a similar sequence can be presented as



Hence, correlations should be found between the anion in aqueous solution and corresponding anhydro-acid in melt.

NaPO₃ and Na₄P₂O₇ may be easily obtained by the calcination of the corresponding acidic salts, but reverse processes do not take place in aqueous media and pyro- and metaphosphate exist in water as salts of stable acids. For arsenates which are more prone to hydrolysis similar correlation should take place. The absence of the correlation is caused mainly by kinetic limitations.

10.4.5 REACTIONS OF MELTS WITH GASEOUS ACIDS AND BASES

The gases present in the atmosphere over molten salts can react both with their principal components and with impurities. In reactions of the first kind, which include, in particular, hydrolysis, the gas (water) behaves as a Lux base since its action results in the increase of O²⁻ concentration. In reactions of the second type, which are usually employed for the purification of melts, the gas has acidic properties.

10.4.5.1 High-temperature hydrolysis of molten halides

These reactions were investigated mainly for alkaline halides and their mixtures. Hanf and Sole¹⁰² studied the hydrolysis of solid and molten NaCl in the temperature range 600-950°C by so-called “dynamic method” which consisted of passing inert gas (N₂) containing water vapor through a layer of solid or fused NaCl. The developed routine determined the equilibrium constant of the following reaction:

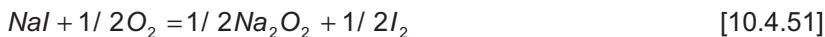


The values of the equilibrium constants (log K) of [10.4.49] for solid and liquid sodium chloride were in the ranges -8 to -6 (650-800°C) and -6 to -5 (800-900°C).

The hydrolysis of NaCl occurs to a slight extent, although the rate of HCl evolution exceeded the expected value because of dissolution of NaOH formed in NaCl.

An evident disadvantage of the above method¹⁰² is assumption that the partial pressure of HCl in the gas phase is equal to the equilibrium pressure. The same method was used to study the high-temperature hydrolysis and oxidation of sodium iodide.¹⁰³ According to the estimates, the heats of the reactions:





are 32.8 ± 2 and 13.9 ± 1 kJ/mole for solid NaI and 30.6 ± 2 and 9.3 ± 2 kJ/mole for liquid one. These values suggest that NaI has a greater tendency to oxidation than to hydrolysis. This conclusions cannot be adopted without stipulation, because it is based on values ΔH and not ΔG , although only the latter values determine the direction of a reversible reactions at constant p and T .

A simple but unquestionable method has been used to investigate high-temperature hydrolysis of molten KCl-NaCl.¹⁰⁴ A mixture of HCl and H₂O obtained by passing an inert gas through aqueous solutions at a definite concentration was passed into the melt. Measurements of the equilibrium O²⁻ concentration by potentiometric method allowed to calculate the equilibrium constants of [10.4.13] as $\text{pK} = 55.3 \times 10^3 T^{-1} - 40.2$. At 1000, $\text{pK} = 15.1$, it means that equilibrium [10.4.13] in molten KCl-NaCl is displaced to the left.

A similar method has been used to study the hydrolysis of the eutectic KCl-LiCl at 500°C ($\text{pK} = 9.77 \pm 0.4$).¹⁰⁵ The hydrolysis of the chloride melt is thermodynamically unfavorable and is completely suppressed in the presence of bases (even at a concentration of $\sim 10^{-3}$ mole/kg).

The potentiometric cells:



were used to investigate the hydrolysis of individual alkaline halide melts (with the exception of the lithium salts).¹⁰⁶

The e.m.f. of cell [10.4.52] is related to the concentration of the reactants by the expression:

$$E = E^0 + \frac{RT}{F} \ln \frac{P_{\text{H}_2}^{1/2} P_{\text{X}_2}^{1/2}}{P_{\text{H}_2\text{O}}} a_{\text{MeOH}} \quad [10.4.53]$$

where $P_{\text{H}_2}^{1/2}$ and $P_{\text{X}_2}^{1/2}$ are partial pressures of hydrogen and halogen over the melt, respectively.

The logarithms of the equilibrium constants

$$\ln K = \frac{F}{RT} E - \frac{\Delta G_{\text{HX}}^0}{RT} + \ln \frac{P_{\text{H}_2}^{1/2} P_{\text{X}_2}^{1/2}}{P_{\text{H}_2\text{O}}} a_{\text{MeOH}} \quad [10.4.54]$$

are negative for all the melts studied, which indicates that the hydrolysis of alkali metal halide melts is thermodynamically unfavorable. The trend towards hydrolysis of melts of individual alkaline halides diminishes with the increase in the radii of both cation and anion. According to the results of Smirnov et al.¹⁰⁶ the solutions of alkali metal hydroxides in the corresponding individual halides are close to ideality.

10.4.5.2 The processes of removal of oxide admixtures from melts

The studies of the elimination of oxygen containing impurities from ionic melts are of an applied character and are performed in melts having industrial applications. Various

halogenating agents, usually hydrogen halides or the halogens themselves, are used to eliminate the impurities:¹⁰⁷⁻¹¹¹



However, the water formed in reaction [10.4.55] exhibits the properties of Lux acid owing to process opposite to [10.4.45] and this retards the purification process. The cessation of the HX effect may lead to partial hydrolysis, because reactions of type of [10.4.55] are reversible. The shift of [10.4.55] to the left is also promoted by the thermal instability of HBr and HI.

The effectiveness of the purification of melts based on lithium salts by hydrogen halides is much lower. Water dissolves in the KCl-LiCl melt in appreciable amounts and is firmly retained at temperatures up to 400°C.³⁰ When dry HCl is passed for 1 h, removal of H₂O is incomplete.

The effectiveness of the purification by the halogens depends on their oxidation-reduction potentials and decreases from chlorine to iodine. In addition, the latter can disproportionate:



However, the addition of NH₄X is recommended only for the drying and heat treatment of the initial components and its use for industrial purification of fused salts is undesirable because it is much easier to ensure the continuous supply of the corresponding hydrogen halide in the melt being purified. An additional lack of this purifying agent results in evolution of gaseous ammonia as one of the finishing products.

It is believed that the most convenient method of the elimination of oxygen-containing impurities from alkali metal halide melts is carbohalogenation.¹¹²⁻¹¹⁸

The reduction of O²⁻ concentration under action of CCl₄, Cl₂, C (C is acetylene carbon black)+Cl₂ and COCl₂ may be explained by the occurrence of the following reactions:



Thermodynamic analysis of processes [10.4.58]-[10.4.60] showed that the effectiveness of the purification is in all cases approximately the same,¹¹³ but reaction [10.4.58] has the advantage that highly toxic reagents (Cl₂, COCl₂) are not used in it. For this reason, CCl₄ has been used in virtually all subsequent studies involving the carbochlorination of chloride melts.¹¹⁴⁻¹¹⁸

It has been suggested that CHBr₃, CBr₄, C₂H₅Br and CHI₃ may be used for the removal of oxygen-containing impurities from bromide and iodide melts.¹¹⁹ A significant advantage of carbohalogenation is that it leads to an appreciable decrease in the concentration of transition metal cations in the melt being purified. However, in the purification of melts by halo-

gen-substituted compounds with a relatively low halogen content, carbon (carbon black) accumulates in the melt and is displaced by the crystallization front when single crystals are grown.¹¹²

The presence of a suspension of carbon in alkali metal halide melts is not always desirable and this method cannot therefore be recognized as universal.

The carbohalogenation of melts results in formation of CO₂ as one of products of [10.4.58]-[10.4.60] processes, carbon dioxide reacts with remaining oxide ions and induces the accumulation of fairly stable carbonate-ions. The latter is the main form in which oxygen-containing impurities exist in melts purified in this way. The purification threshold of carbohalogenation is estimated as $1-2 \times 10^{-4}$ mole/kg of O²⁻.²⁴

The use of halo-derivatives of silicon for the purification of iodide melts¹²⁰ is based on the reaction:



the product of [10.4.61] is silicon dioxide, which is separated from the melt as a consequence of the difference between the densities. Thermodynamic analysis showed¹²¹ that the effectiveness of the purification of iodide melts diminishes in the sequence SiI₄>HI>I₂.

The use of silicon halides for the purification of the melts used in the growing single crystals does not lead to the appearance of additional impurities, because the processes are carried out in quartz (i.e., SiO₂) containers.

Although the methods of purification described are fairly effective in most cases, some kind of oxygen-containing and cationic impurities, characteristic of each method, always remains in the melt. The method of purification must therefore be selected depending on the aims of the subsequent application of the melt.

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