A REVIEW OF ELECTROCHEMISTRY IN NON-AQUEOUS SOLVENTS

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ABSTRACT

A review is given of the various extrathermodynamic assumptions made in the literature for the calculation of an ion distribution coefficient, for which the symbol $K_{s_2}^{s_1}$ ion is used in this paper. An example is given of the different values of $K_{AN}^{w}Ag^+$ (w = water, AN = acetonitrile) obtained on the basis of these assumptions. From ΔpK_{HA}^d between aprotic solvents the value of $K_{s_2}^{s_1}H^+$ can be found, but not from $\Delta K_{BH^+}^d$. Data on polarographic half-wave potentials published in the literature are critically discussed. The effect of small concentrations of hydrogen bond donors on the solvation of anions is best $K_{s_2}^{s_1}H^+$ can be found, but not from $\Delta K_{BH^+}^d$. Data on polarographic half-wave as a solvent of the effect of homoconjugation on conductometric and potentiometric titration curves, on the solubility of slightly soluble salts and of small concentrations of water (hydrogen bond donor) on the paH of a benzoate-benzoic acid mixture. Hydration constants of a number of cations and anions and of undissociated salts are presented in *Tables 8* and *9* respectively and hydration and alcoholation constants of the proton in AN in *Table 10*. Solvation in Lewis acid-base and complexation reactions and stability of free radicals are briefly discussed. Finally, a comprehensive review of the importance of non-aqueous electrochemistry in various provinces of chemistry is presented.†

ION DISTRIBUTION COEFFICIENTS

To every chemist working in non-aqueous electrochemistry the most interesting and important property is the ion distribution coefficient between different solvents. The concept is not new. It was introduced by the famous Danish chemist Niels Bjerrum[1], but there was a lapse of a quarter of a century before this distribution coefficient gradually became recognized as an important indicator of the extent of solvation of ions in different solvents, and before it allowed an interpretation of widely different kinetics of certain reactions in a variety of solvents[2]. The terminology for the distribution coefficient in the more recent literature varies; in Anglo-Saxon and Russian literature it is often referred to as the medium effect, the medium (solvent) activity coefficient or the degenerate activity coefficient, and in French literature more appropriately as 'coéfficient de solvation' or 'coéfficient de

† To give in a single lecture a complete review of non-aqueous electrochemistry is an impossibility. For this reason I confine myself to some of the fundamentals. Several effects are illustrated by results obtained with Dr Chantooni in our laboratory.

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transfert'. Also different symbols are used; in the English literature $^{\circ}\gamma_i^{s2}$ (o being reference solvent, s other solvent; i—ion) or $_m\gamma_i^3$, and in the French literature $^{\circ}\Gamma_i^{s\,4,\,5}$.

This Symposium is held under the auspices of I.U.P.A.C. and it has been suggested that Commissions I.3 of the Physical Chemistry and V.5 of the Analytical Chemistry Divisions propose a terminology and symbol which will be universally adopted. Since I.U.P.A.C. recommends for a distribution coefficient (which is an equilibrium constant) the symbol $K_\beta^\alpha B$, I will use in the present paper the symbol K_{s2}^{s1}Ion, anticipating that this will be proposed by I.U.P.A.C.†

In his original publication Bjerrum[1] measured the distribution coefficient of ions between water and ethanol, assuming that the liquid junction potential could be neglected. Some 30 years later he[6] published a theoretical paper in which he pointed out that it will forever be impossible to (accurately) determine partition coefficients of individual ions, because it is impossible to determine contact potentials. In order to approach values of ion distribution coefficients several extra thermodynamic proposals have been made. (For a review see[7,8].) Some 20 years after Bjerrum's publication Pleskov[9] proposed to consider the standard potential of the relatively big, slightly polarizable rubidium ion as a constant in all solvents. Strehlow[10,11] proposed small deviations from constancy of E_{Rb}° in four solvents. His major contribution is the proposal that the standard potentials of the ferrocene–ferricinium and cobaltocene–cobalticinium couples are practically constant in different solvents because of the large size of the ion and the fact that the electric charge is sandwiched between two layers. Much use of his proposal has been made during the last few years. Originally, Strehlow[10,11] also proposed that the Hammett acidity function might give a close approximation of the medium activity coefficient. However, in a more recent paper[12] the assumption that the free enthalpy of transfer for a Hammett indicator base is equal to that of the conjugate indicator acid IH^+ is rejected. Quite correctly it is stated that the proton attached to the indicator molecule is on the periphery of IH^+ so that specific effects of solvation are considerably different in different solvents. 'Therefore, this approach is a rather poor approximation, except possibly in solvents of high dielectric constant.' Below an example is given of the great difference in the proton distribution coefficient between water and dimethylsulphoxide derived from the Hammett acidity function approach and the constancy of the ferrocene–ferricinium potential. Also, in *Table 8* an example is given of the relatively strong hydration of the acid form of a Hammett indicator in acetonitrile upon addition of small concentrations of water, indicating that the solvation of the indicator cation is considerably greater in water than in acetonitrile (AN).

Another proposal for finding ion distribution coefficients is based on the validity of modifications of the Born equation. The method has been used particularly by Coetzee et al.[13,14] in deriving distribution coefficients of alkali ions between water on the one hand and acetonitrile and sulpholane on the other. The basic assumption is made that the interaction between the alkali metal ions and the above aprotic solvents and water is predominantly

† Note added in proof: Legitimate objections have been raised to the use of the symbol K_{s2}^{s1}.

electrostatic in nature and that the solvation energy differences of pairs of these ions in the aprotic solvents can be related to corresponding differences in water by appropriate empirical corrections for the crystallographic ionic radii in the Born equation. Alfenaar and de Ligny[15] took also into account the contribution by the non-electric part (in the case of alkali ions the noble gases). Izmailov[16] adopted a model in which the solvation energy of an infinitely large ion is zero. For a critical discussion of the above assumptions reference is made to Popovich[8] and Bates[3]. Quite a different and theoretically sound approach was made by Parsons et al.[17] who measured the surface potential difference between solvents which yield ΔG. The difficulty in this method is of an experimental nature. Finally, a proposal which has gained great popularity is the use of a 'reference electrolyte' composed of two large symmetrical ions of closely similar size and structure. Grunwald et al.[18], who first proposed this approach, recommended for this purpose tetraphenyl-phosphonium tetraphenylborate (Ph_4PPh_4B). Later, Popovich[19] recommended triisoamyl-n-butylammonium tetraphenylborate ($TABPh_4B$), while Parker et al.[20] based much of their extensive work on the use of tetraphenylarsonium tetraphenylborate (Ph_4AsPh_4B). Considering the uncertainty involved in the various assumptions it is not surprising that agreement between values of an ion distribution coefficient determined on the basis of one assumption may differ considerably from data obtained by using other assumptions. As an example, values of the log of the distribution coefficient of silver ion between water and acetonitrile (log $K_{AN}^w Ag^+$) are reported in Table 1.

Table 1. Values of log $K_{AN}^w Ag^+$ (molar) based on different assumptions

Method	log $K_{AN}^w Ag^+$	Author
$K_{AN}^w Ph_4As^+ = K_{AN}^w Ph_4B^-$	-5.5	Parker[20]
$K_{AN}^w Ph_4As^+ = K_{AN}^w Ph_4B^-$	$-4.1\,(-4.2^a)$	Popovich[7]
(a) $E^\circ_{ferrocene/ferricinium}: E^\circ$ in AN $= 0.34$	-6.7	Strehlow[10]
(b) $E^\circ_{ferrocene/ferricinium}: E^\circ$ in AN $= E^\circ$ in water $= 0.394$	-5.8	Kolthoff and Thomas[21]
Modified Born equation	$-2.65\,(-3.0^b)$	Coetzee[13, 14]
Extrapolation	-2.7	Izmailov[16]
Surface potential	-6.0	Parson et al.[17]

[a] From his value log $K_{AN}^w Cl^- = 7.4$ (molal), and $(pK_{AgCl}^{s,p})_{AN} = 13.1$ or 12.9 molal. Corrections were made for y (conventional activity coefficients).
[b] From their value log $K_{AN}^w Cl^- = 5.6$ ('rational' molal); and other data sub a.

Of course, if we knew $K_{s_1}^{s_1}$ of one ion with certainty, values of $K_{s_2}^{s_1}$ of all other ions could be obtained by thermodynamically sound methods. For example, for a slightly soluble salt AB the difference between the negative logarithm of solubility products in two solvents $p(K_{s_2}^{s_1})_{s.p.} = \log K_{s_2}^{s_1} A^+ + \log K_{s_2}^{s_1} B^-$ provided that the solid in the solvents is not solvated. The sum of the right hand side of the equation is then a thermodynamic constant. However, usually differences between values reported by various authors are found. An example is found in Table 2, the data of which are taken from a review by Popovich[8]. A critical review of reported data of solubility products, classical standard potentials in various solvents is desirable.

Table 2. $\log K_M^w Ag^+ + \log K_M^w Cl^-$ (w = water, M = methanol)
(rational molality)

Author	$\log K_M^w Ag^+$	$\log K_M^w Cl^-$	Sum
Pleskow[9]	-0.3	3.7	3.4
Izmailov[16]	3.5	1.0	4.5
Popovich[7] (TABPh$_4$B)	1.85	2.1	3.85
Parker[20] (Ph$_4$ASPh$_4$B)	1.2	2.2	3.4
Alfenaar and de Ligny[15]	-1.45	5.69	4.2
Andrews et al. (method of Feakins)[22]	-2.25	6.18	3.9

The ratio of distribution coefficients of anions or of cations also can be determined exactly. Consider the solubility products $K_{s.p.}$ of two salts $A_1 B$ and $A_2 B$ in s_1 and s_2. From equation 1 it is seen that:

$$\left(\Delta p K_{s_2}^{s_1}\right)_{s.p.\ A_1 B} - \left(\Delta p K_{s_2}^{s_1}\right)_{s.p.\ A_2 B} = \frac{\log K_{s_2}^{s_1} A_1^+}{\log K_{s_2}^{s_1} A_2^+} \tag{1}$$

A similar relation is found for two anions B_1^- and B_2^- from the $K_{s.p.}$ of salts AB_1 and AB_2.

It is of some interest to refer here to some unpublished results (with M. K. Chantooni, Jr.) on the relation between dissociation constants K_{HA}^d of a series of substituted benzoic acids HA and some phenols without intramolecular hydrogen bonding in acetonitrile (AN), dimethylformamide (DMF) and dimethylsulphoxide (DMSO)[23]. We find $(\Delta p K_{HA}^d)_{DMSO}^{AN}$ and $(\Delta p K_{HA}^d)_{DMF}^{AN}$ and $(\Delta p K_{HA}^d)_{DMSO}^{DMF}$ for a given pair of these three aprotic solvents is constant. This means that:

$$\log \frac{K_{s_2}^{s_1} A_1^-}{K_{s_2}^{s_1} A_2^-} = \log \frac{K_{s_2}^{s_1} HA_1}{K_{s_2}^{s_1} HA_2} \tag{2}$$

s_1 and s_2 referring to a given pair of the three aprotic solvents. We also have determined (by solubility or extraction methods) values of the distribution coefficients $K_{DMF}^{AN} HA$, and find in this way the distribution coefficient of A^- with reference to that of the unsubstituted benzoate ion. The ratio of the distribution coefficients of HA may be put equal to the non-electric contribution of the distribution coefficients of the ions. AN and DMF are isoelectric and it is reasonable to assume that the electric contribution is zero. Hence, we arrive at the conclusion that for substituted benzoic acids the following relation holds between AN and DMF (and probably other aprotic solvents which are about isodielectric)

$$\log K_{DMF}^{AN} A^- = \log K_{DMF}^{AN} HA$$

Values of $K_{s_2}^{s_1} A^-$ thus found will be checked with values obtained on the basis of other assumptions. If the last relation is correct, we also know $\log K_{DMF}^{AN} H^+$

$$\log K_{DMF}^{AN} H^+ = \Delta p K_{HA}^d$$

For substituted benzoic acids we[23] find $\log K_{DMF}^{AN}H^+ = -8.3$, and for the solvents AN and DMSO $\log KH^+ = -9.6$. Using Mme Courtot's[24] value of $\log K_{DMSO}^w H^+$ of -5.8 (her value is based on the Strehlow assumption of constancy of the ferrocene–ferricinium potential), we arrive at a value of $\log K_{AN}^w H^+$ of 3.8. Assuming that the $\Delta pK_{BH^+}^d$ of Hammett indicators would yield the proton distribution coefficient, $\log K_{AN}^w H^+$ would be equal to 5^{25}. As stated before, the difference between $K_{BH^+}^d$ of bases (B) is a poor indicator of $\Delta\log K_{s_2}^{s_1}H^+$. As an illustration we list in *Table 3* a representative group of bases of $\Delta pK_{BH^+}^d$ between water-AN and water-DMSO and AN-DMSO.

Table 3. $\Delta pK_{BH^+}^d$ of monoprotonated bases. w = water, D = DMSO, AN = acetonitrile

Base	ΔpK_{AN-w}^d	ΔpK_{D-w}^d	ΔpK_{AN-D}^d
Tetramethylguanidine	9.7	−0.4	10.1
Ethyl (or *n*-butyl)amine	7.7	0.5	7.3
Ammonia	7.3	1.3	6.0
Diethylamine	7.8	−0.5	8.3
Triethylamine	7.8	−1.7	9.5
Aniline	6.0	−1.0	7.0
Pyridine	7.1	−1.8	8.9
Dimethylaminoazobenzene	6.8	−2.6	9.4
Hammett indicator	5.0		
Largest differences	9.7 to 5.0	+1.3 to −2.6	10.1 to 6.0

Large differences in the degree of solvation of BH^+ and B in the various solvents must be responsible for the large differences in $\Delta pK_{BH^+}^d$ between different solvents. Whereas $(\Delta pK_{HA}^d)_{AN-D}$ for the groups of acids mentioned is constant, large variations are found in $(\Delta pK_{BH^+}^d)_{AN-D}$. Thus, we arrive at the conclusion that ΔpK_{HA}^d for aprotic solvents isodielectric (s_1, s_2) is a much better indicator for $K_{s_2}^{s_1}H^+$ than $K_{BH^+}^d$.

EXTENT OF SOLVATION DERIVED FROM POLAROGRAPHIC DATA

Knowledge of standard potentials of metal ion reductions to metal in non-aqueous solvents would yield the ratio of the distribution coefficients of the metal ion and the proton between solvents s_1 and s_2. For example, from data at 25° reported by Macfarlane and Hartley[25a] it is calculated that between methanol (M) or ethanol (E) and water

$$\frac{K_M^w H^+}{K_M^w Ag^+} = 4.0 \text{ and } \frac{K_E^w H^+}{K_E^w Ag^+} = 7.1,$$

indicating that the hydrogen ion in methanol and ethanol is less solvated than the silver ion as compared to the situation in water. Unfortunately, relatively few standard potentials are known in non-aqueous media. Several papers have been published in which polarographic half-wave potentials $E_{\frac{1}{2}}$ in non-aqueous media of metal ions are reported. Below we consider only $E_{\frac{1}{2}}$ values of systems yielding reversible reduction (with the exception of lithium

in. some solvents). As compared to straight potentiometry, the polarographic method has several disadvantages. In most studies the data are reported in 0.1 M supporting electrolyte, usually tetraethylammonium perchlorate, and correction is made for the iR drop. In media with a dielectric constant of the order of 40 (v.i.) metal salts (particularly salts of divalent ions) are incompletely dissociated into ions. Furthermore, in an intercomparison of $E_{\frac{1}{2}}$ it is tacitly assumed that the Debye–Hückel activity coefficient of the various ions is the same in the same (and sometimes different) supporting electrolytes. Most reported measurements have been carried out *versus* the saturated calomel electrode and in several studies it is tacitly assumed that the liquid junction potential is reproducible and the same when different supporting electrolytes are used. In their precise measurements in nitriles Coetzee *et al.*[26] observed reproducible $E_{1,j}$ *vs.* SCE, but different $E_{\frac{1}{2}}$ values were found when tetra-ethylammonium iodide instead of perchlorate was used. In *Table 4* we report values of $E_{\frac{1}{2}}$ in two protophobic and two protophylic solvents, all having a dielectric constant of the order of 40 with reference to potassium (taking $E_{\frac{1}{2}}$ of $K^+ = 0$). Values in DMSO are those reported by McMasters *et al.*[27]; their data check closely with those by Jones and Fritsche, Jr.[28]. For this reason the data by the latter are not listed in *Table 4*. Also, in DMF the McMaster's data are in close agreement with those reported by G. H. Brown and R. Urfali[29], and the values of the latter are not listed. Not knowing the distribution coefficient of potassium between water and any other solvent, no quantitative conclusions can be drawn from the data in *Table 4*. As compared to the potassium ion in water it appears that sodium is less solvated in aprotic protophobic solvents; while there is no difference in protophylic solvents. On the other hand, it is obvious that the lithium ion is less solvated in the protophobic and more solvated than potassium in protophylic solvents as compared to the situation in water. It is also clear that the relation between $E_{\frac{1}{2}}$ of potassium and thallium ions remains about the same in protophobic and protophylic solvents as it is in water. On the other hand, the divalent ions zinc, cadmium and lead appear to be less solvated in protophobic and more solvated in protophylic solvents than they are in water. Kumar and Pantony[30] also report $E_{\frac{1}{2}}$ values which are converted to the Strehlow scale (apparently assuming that $E_{\frac{1}{2}}$ of Rb^+ is constant in various solvents; but this is the Pleskov proposal). Gutmann and Schmid[31] presented in 1969 a summary of the results of their various papers and give a table in which the $E_{\frac{1}{2}}$ values are referred to that of bisdiphenylchromium(I)iodide, apparently considering $E_{\frac{1}{2}}$ of this ion constant in various solvents[32]. The chromium compound yields a one-electron reversible reduction wave:

$$(C_6H_5)_2Cr(C_6H_5)_2^+ + e \rightleftarrows (C_6H_5)_2Cr(C_6H_5)_2$$
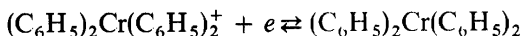
Its polarographic behaviour was first studied by Schröer and Vlček[32]; the current-potential curve is made complicated by the appearance of a prewave, attributed to the adsorption of the reduced form Cr(0). Schröer and Vlček state that in water the polarograms of the compound are greatly interfered with by maxima brought about by adsorption and insolubility of the reduced form. Rusina and Schröer[32a] and Gutmann and Heiling[33] report that in non-aqueous solvents the reduction of the compound is reversible. (It is a pity that Gutmann *et al.* did not use cobalticinium ion, which has been

Table 4. $E_{1/2}$ in various aprotic solvents and water with reference to $E_{1/2}$ of K^+ in 0.1 Et_4NClO_4

Ion	Water	Sulpholane		Acetonitrile			M[e]	DMSO		M[e]	DMF		Average	
		C[a]	P[b]	C[c]	P[b]	G[d]		G[d,f]	P[b]		G[f]	P[b]	Protophobic	Protophylic
K^+	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Na^+	+0.02	+0.10	+0.11	+0.11		+0.09	+0.015	+0.03	+0.01	+0.02	+0.02	+0.03	+0.10	+0.02
Li^+	−0.19	−0.01		−0.02		−0.02	−0.43[x]		−0.41[x]	−0.26		−0.33	−0.02	−0.30
Rb^+	+0.01	−0.01		−0.02				+0.03			+0.02	+0.04	−0.01	+0.03
Zn^{2+}	1.14		1.56	1.34	(1.18)	1.34	1.034	1.03	1.02	1.07	1.11	1.22	1.45	1.10
Cd^{2+}	1.56		1.88	1.70	(1.57)	1.70	1.40	1.42	1.39	1.46	1.51	1.50	1.80	1.45
Pb^{2+}	1.75		1.93		(1.51)		1.54		1.54	1.64		1.63	1.9	1.60
Tl^+	1.68			1.69		1.69	1.56	1.58		1.63	1.64		1.69	1.60

[x] Wave not quite reversible.

[a] J. F. Coetzee, J. M. Simon and R. J. Bertozzi, *Anal. Chem.* **41**, 766 (1969).

[b] G. P. Kumar and D. A. Pantony, *J. Polarographic Soc.* **14**, 84 (1968).

[c] J. F. Coetzee, D. K. McGuire and J. L. Hedrick, *J. Phys. Chem.* **67**, 1814 (1963).

[d] V. Gutmann, P. Heilmeier and G. Schoeber, *Monatsh.* **92**, 240 (1962).

[e] D. L. McMasters, R. B. Dunlap, J. Kuempel, L. W. Kreider and T. P. Shearer, *Anal. Chem.* **39**, 103 (1967).

[f] V. Gutmann and R. Schmid. *Monatsh.* **100**, 2113 (1969).

recommended by Strehlow as a reference ion. Using the assumptions used by Pantoni and by Gutmann it is possible to calculate from their data the ion distribution coefficients between water and the solvents listed in *Table 5*. It is seen from this table that the values based on Pantoni's data are in general 3 to 4 units greater than those derived from Gutmann's data. Considering that their values in *Table 4* (all referred to $E_{\frac{1}{2}}$ of K^+) are generally in good agreement, it must be concluded that the widely different values in *Table 5* are due, in part at least, to the difference in the validity of the assumptions

Table 5. Comparison of log K_s^w from data by Pantoni (a) and Gutmann (b). (c) refers to Parker's value for K^+

Ion	s = DMSO	DMF	AN	Sulpholane	Nitromethane
K^+	(a) -3.5	-4.0	$+5.8$	-1.5	—
	(b) 0	0	$+2.7$	—	—
	(c) -3.0	-2.2	-0.1	—	—
Tl^+	(a) —	—	—	—	—
	(b) -1.7	-0.5	$+3.0$	—	$+4.5$
Zn^{2+}	(a) -5.3	-2.5	$+6.7$	$+5.7$	—
	(b) -1.5	0	$+2.8$	—	$+13.0$
Cd^{2+}	(a) -6.0	-4.7	$+6.2$	$+4.2$	—
	(b) -1.7	0	$+5.8$	—	$+11.2$

on which the calculations are based. It is of interest to note that for potassium ion the values derived from Pantoni's data are in reasonable agreement with Parker's[20] values in DMSO and DMF, but differ by 5.9 units in AN. The value for potassium in sulpholane of -1.5 (Pantoni) must be wrong, it differs by 7.3 units from that in AN, whereas this difference is only 1 unit according to Coetzee et al.[14]. Schneider and Strehlow[33a] report some values of $E_{\frac{1}{2}}$ of thallium and cadmium in methanol and other alcohols, acetonitrile, acetone, DMSO, DMF, and a few other solvents. They refer $E_{\frac{1}{2}}$ to that of the cobaltici-nium ion. Based on their data we calculate log $K_s^w Tl^+$, $s = AN + 0.2$; $s = $ acetone -1.2, $s = $ DMSO -4.9, $s = $ DMF -4.5, for Cd^{2+} only values in the alcohols are reported. Schneider and Strehlow mention that the $E_{\frac{1}{2}}$ values vary with the concentration and kind of supporting electrolyte used. It is unfortunate that the measurements were made with a mercury pool as anode.

This section is concluded with the recommendation that in $E_{\frac{1}{2}}$ measurements of reversible electrode reactions in non-aqueous solvents a reference electrode, preferably composed of the system silver–silver perchlorate, be used. In order to keep $E_{1.j.}$ small and reproducible, the perchlorate ion concentrations in both half cells should be of the same order of magnitude and kept as small as feasable. A suitable perchlorate bridge in the same solvent should be used to connect the half cells. The concentration of the electroactive ion should be kept as small as feasible, in order to keep the iR correction small.

CLASSIFICATION OF SOLVENTS

Solvation of solutes by pure solvents depends on the characteristics of the

solvent. It is convenient to classify solvents in certain groups, even though no classification is perfect and there is some overlapping between one class and another. The following classification is convenient for practical purposes.

Amphiprotic solvents (1) and (2) good H-bond donors

  (1) Acid-base strength same order of magnitude as that of water but different dielectric constant (D.C.). Water, alcohols, glycols, phenols; (phenols are considerably stronger acids than water)

  (2) Protogenic: H_2SO_4, HF, HCOOH, CH_3COOH

  (3) Protophylic: Ethylenediamine, tetramethylguanidine, NH_3, $pK_s \sim 30$ (dimethylsulphoxide, $pK_s = 33$) These approach in their properties protophylic aprotic solvents.

Aprotic solvents (poor solvation of anions with localized charges)

  (1) Inert e.g. aliphatic hydrocarbons, CCl_4, $CHCl_3$; (low D.C. of the order of 2 and less than 10

  (2) Protophobic: acetonitrile (AN), $pK_s > 33$, ketones, (acetone, MEK, MIBK); sulpholane, nitromethane. (In general poor solvation of inorganic cations.)

  (3) Protophylic: dimethylformamide (DMF), DMSO[a], pyridine. (In general pronounced solvation of inorganic cations.)
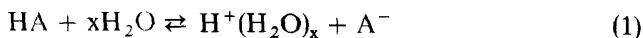
Inorganic Solvents (amphoteric, inert; e.g. for Lewis acid-base reactions; v.i.)

Fused Salts (see paper by Professor Trémillon)

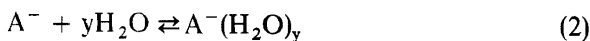[a] Note that dimethylsulphoxide is found in two groups. Its autoprotolysis constant $pK_s = 33^{34}$, and sodium and caesium lyates of the solvent are stable in DMSO. Since the acid properties of DMSO are very weak, it is also classified as a protophobic aprotic solvent.

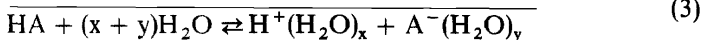## SOLVATION IN APROTIC SOLVENTS

Inert solvents have a low dielectric constant. Solubility of most salts is very small in these solvents, so is the dissociation into ions. In addition to ion pairs ion triplets and quadruplets are easily formed. Carboxylic and other acids dimerize or polymerize by intramolecular hydrogen bonding. Solvation studies in inert solvents are quite involved[35]. For such studies aprotic protophobic solvents of intermediate dielectric constant (*circa* 40) are particularly useful, especially for solvation studies by hydrogen bonding. Aprotic protophylic solvents, like dimethylsulphoxide (D.C. 44), DMF (D.C. 36) are relatively strong bases and association with acids by hydrogen bond formation is much more pronounced in the aprotic protophylic than in the protophobic solvents. Also, proton *transfer* from an acid to a weak base, like water or an alcohol (v.i.), is very much more pronounced in protophobic than protophylic solvents. We have studied in detail several effects of hydrogen bonding and also hydration and alcoholation of the proton in acetonitrile (AN). First, we consider the ionization of an acid in an amphiprotic solvent (hydrogen bond donor), e.g. water
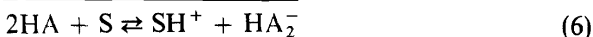
$$HA + xH_2O \rightleftarrows H^+(H_2O)_x + A^- \qquad (1)$$

$$\text{base}$$

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$$A^- + yH_2O \rightleftharpoons A^-(H_2O)_y \tag{2}$$

$$\frac{\text{H bond donor}}{HA + (x + y)H_2O \rightleftharpoons H^+(H_2O)_x + A^-(H_2O)_y} \tag{3}$$

When dealing in AN with an uncharged acid, the anion of which has a localized charge, such an anion is not stabilized by the solvent (denoted by S) but by the hydrogen bond donor HA:

$$HA + S \rightleftharpoons SH^+ + A^- \tag{4}$$

$$A^- + HA \rightleftharpoons HA_2^- \tag{5}$$

$$\overline{2HA + S \rightleftharpoons SH^+ + HA_2^-} \tag{6}$$

For simplicity we have written 1 S and 1 HA, but quite generally more molecules are involved. This 'complexation' (solvation) of A^- has been known for more than 20 years[36]; to distinguish it from other kinds of solvation we have proposed the notation 'homoconjugation' for reaction (5). If the solvation does not occur by the conjugate acid, but by another hydrogen bond donor, we speak of heteroconjugation. It is easily seen that:

$$K^d_{2(HA)} = \frac{aSH^+aHA_2^-}{[HA]^2} = K^f_{HA_2^-}K^d_{HA} \tag{7}$$

in which $K^f_{HA_2^-}$ is the formation constant of HA_2^-. This homoconjugation has a pronounced effect on the shape of conductometric titration curves[37, 38] with amines and on potentiometric titration curves[39]. First we consider the conductometric titration of a weak acid with an amine B, with the formation of the salt BHA (BH^+A^-). The ionic dissociation constant of BH^+A^- in acetonitrile is much smaller than that of the corresponding tetraalkyl-ammonium salt, because of the hydrogen bonding $BH^+\ldots A^-$. For example, K^d of triethylammonium 3,5-dinitrobenzoate is equal to 1.5×10^{-5}, while that of the tetraethylammonium salt is 6×10^{-2}[37]. Addition of HA (practically a non-electrolyte) to a solution of BH^+A^- greatly increases the conductance, because the dissociation equilibrium is displaced to the right by reaction (5). When the anions are practically completely transformed into the homoconjugate HA_2^- the dissociation constant of $BH^+HA_2^-$, ($B = Et_3N$; $HA = 3,5$ dinitrobenzoic acid) K^d is equal to 3.0×10^{-2}. Assuming that salt formation is quantitative in the titration of 3,5-dinitrobenzoic acid with triethylamine, a maximum in the conductance is found at about 50 per cent neutralization (see *Figure 1*). No such maximum occurs in the same titration when carried out in DMSO, because in this solvent the formation constant $K^f_{HA_2^-}$ is much smaller than in AN. Also, because of hydrogen bonding of Et_3NH^+ with DMSO the dissociation constant of Et_3NHA ($A^- = 3,5$-dinitrobenzoate) is some 650 times greater in DMSO than in AN. In the potentiometric titration in AN of an acid with a large homoconjugation constant with tetraalkylammonium hydroxide an inflection in the paH percentage neutralization curve is observed at 50 per cent neutralization. The shape of the neutralization curve depends on the magnitude of $K^f_{HA_2^-}$ and the concentration of the acid (see *Figure 2*). Since $K^f_{HA_2^-}$ is much smaller in the protophylic solvent DMSO than in AN, the neutralization curve of the
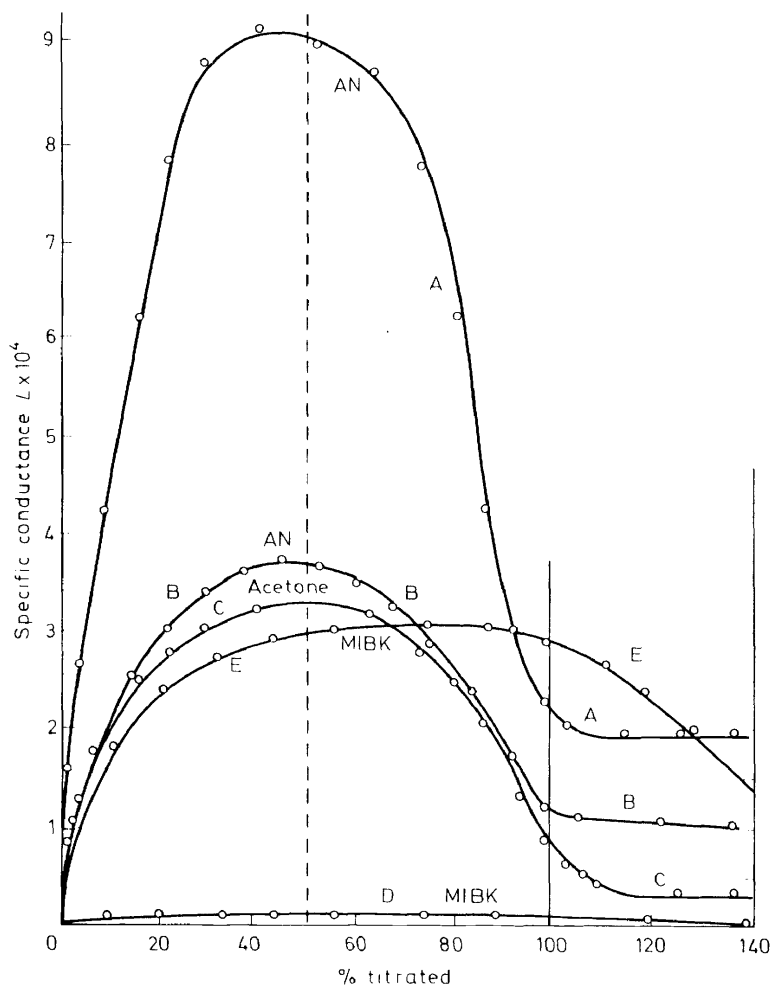
Figure 1. 3,5 Dinitrobenzoic acid (HDNB) with Et$_3$N in protophobic solvents. In AN (D = 38): A = 0.0619 M; B = 0.019 M. In acetone (D = 21): C = 0.0619 M. In MIBK (D = 13): D = 0.019 M; E = D, right-hand ordinate

above type of systems in DMSO more closely resembles that in water. When dealing with an acid, the anion of which has a delocalized charge, the homoconjugation constant is very small; for example $K^f_{HA_2^-}$ of the picrate ion in AN is only of the order of 2^{39}. Acids of this type yield no maximum in the conductometric titration curve in a protophobic aprotic solvent (AN) when titrated with an amine, and the potentiometric titration curves with tetraalkylammonium hydroxide do not exhibit an inflection at the half neutralization point.

Homoconjugation in a protophobic solvent not only causes an increase in the dissociation constant of a slightly dissociated salt BHA or BA but also
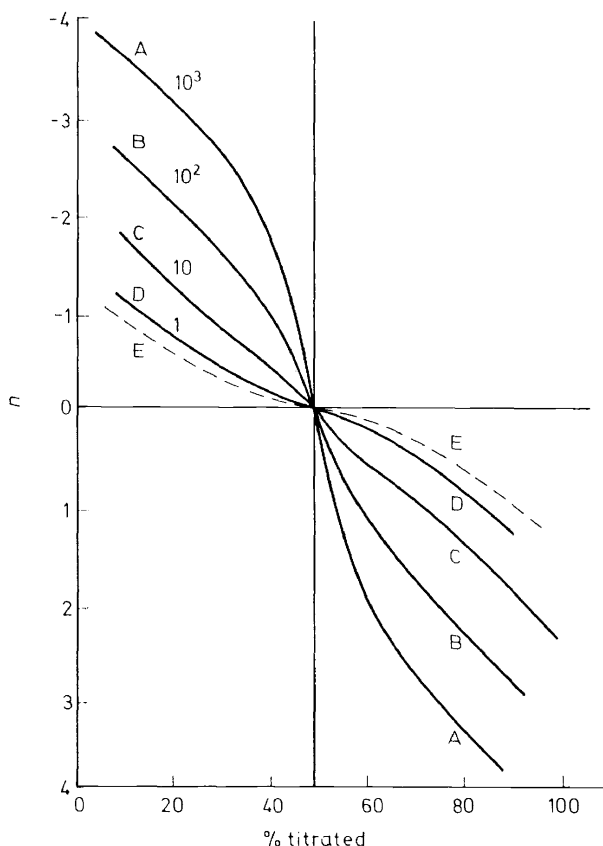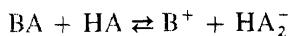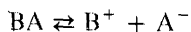
315

Figure 2. Changes of pH in mixtures of HA and Et_4NA, $c_a = \Sigma[HA_0]$; c_s = salt. $K^f_{HA^-}(c_a + c)$:
A, 10^3; B, 10^2; C, 10; D, 1; E, 0

increases the solubility of a slightly soluble salt:

$$BA \rightleftarrows B^+ + A^-$$

$$A^- + HA \rightleftarrows HA_2^-$$

$$\overline{BA + HA \rightleftarrows B^+ + HA_2^-}$$

An example is given in *Table 6*[37], which shows the great increase in AN of the solubility of potassium 3,5-dinitrobenzoate by addition of the free acid. As a matter of fact, from the increase the value of $K^f_{HA_2^-}$ can be found. Anions with a localized charge are not only stabilized by hydrogen bonding with its conjugate acid but also by any other hydrogen bond donor; this complexation is called heteroconjugation. Any Brønsted acid, including amphiprotic solvents like water, alcohols, phenols gives rise to hetero-

Table 6. Solubility in AN of potassium 3,5-dinitrobenzoate KA
in the presence of HA

c HA	*Solubility* $M \times 10^3$	$K^f_{HA_2^-}$ $\times 10^4$
0	0.314	—
0.003	1.8	—
0.006	2.45	2.1
0.0106	2.94	1.4
0.0190	4.52	1.5
0.0347	7.38	2.0
		Av. 1.7×10^4

conjugation. This heteroconjugation is dramatically demonstrated by adding traces of water or some alcohol to a solution of tetraethylammonium 3,5-dinitrophenolate in acetonitrile. The red colour of the anion then changes to a yellow colour of the heteroconjugate. As is to be expected, addition of the conjugate acid has the same effect. The change in absorption spectrum can be made use of in the spectrophotometric determination of homo-[40] and heteroconjugation constants. Analytical use of heteroconjugation is being made, for example, in the titration in acetonitrile of alkali carboxylates with a solution of perchloric acid in glacial acetic acid[41]. These carboxylates are insoluble in AN, but dissolve readily in glacial acetic acid; the presence of 20 per cent of this acid in the titration mixture hardly affects the sharpness of the potentiometric or visual end point.

As a result of heteroconjugation water, alcohols, phenols and other hydrogen bond donors greatly affect the paH of mixtures of acids and their tetraalkylammonium salts, the anions having a localized charge, like carboxylates. The effect is particularly large in mixtures containing an excess of salt over acid. If acid is in excess, the added hydrogen bonder HR must compete with the homoconjugate acid HA in heteroconjugating the anion A^-. When the salt is in excess, HR can combine with the excess, thus decreasing the paH of the mixture. The effect of water is illustrated in *Table 7*[42]. When the anion A^- has a delocalized charge, like in picrate, the effect of little water or alcohol on picric acid buffers in AN is negligible.

Table 7. Effect of water on paH of picrate and benzoate 'buffers.' Heteroconjugation of benzoate:
$$Bz^- + nH_2O \rightleftharpoons Bz^- \cdot nH_2O$$

Picrate buffers cHPi $= 4.75 \times 10^{-2}M$ cBu$_4$NPi $= 2.5 \times 10^{-3}M$		Benzoic acid-benzoate cHBz $= 8 \times 10^{-4}M$ cEt$_4$NBz $= 5.7 \times 10^{-3}M$	
$[\cdot H_2O]$ M	paH	H_2O M	paH
3×10^{-3}	9.56	3×10^{-3}	22.86
2×10^{-2}	9.58	5×10^{-2}	22.58
3.5×10^{-1}	9.56	9.1×10^{-2}	22.29
		2.2×10^{-1}	21.67
		3.4×10^{-1}	21.28

Addition of 1.1 M water to a mixture of 0.03 M Et_4NBz and 0.003 M HBz changes the paH from 23.6 to 20.6, or 3 units. Such an effect is not observed in picrate buffers. Alcohols have about the same effect as water. The effect of hydrogen bond donors in protophylic solvents is very much smaller than in the protophobic solvents, as the solvent base competes with A^- for the hydrogen bond donor. Also for this reason the aprotic protophylic solvents are much to be preferred over the protophobic solvents in the titration of acids.

Hydration and alcoholization in AN is observed with cations as well as anions. Equations have been derived which permit the calculation of hydration constants of cations and anions from the solubility product of slightly soluble salts and the total ionic solubility in the presence of various concentrations of water[43]. In this way the hydration constant(s) $K^f_{i_{xw}}$ (i = ion, w = water) of lithium, sodium, potassium, and caesium and of the monovalent anions, perchlorate, periodate, methanesulphonate, nitrate, 3,5-dinitrophenolate have been determined in AN at $25°$. For K^+, Cs^+, IO_4^-, ClO_4^- and picrate x = 1, for the other ions x = 1 and 2. Formation constants of the hydrates of some ions are given in *Table 8*. In the last three columns of the table are given in the presence of 1 M water the calculated ratios of the unhydrated or hydrated ions over the analytical concentrations of the ions. The hydration of the sodium ion is much greater than that of the potassium ion ($K^f_{K\dot{w}} = 1$). At a concentration of 1 M water in AN only 17 per cent of sodium ions is present in the unhydrated form, 33 per cent as monohydrate and 50 per cent as dihydrate. The hydration constants of the other cations in the *Table 8* have been determined in a later publication[44].

Table 8. Hydration of ions in AN containing 1M water

Ion	$K^f_{M\dot{w}}$ or $K^f_{A\bar{w}}$	$K^f_{M\bar{2}w}$ or $K^f_{A\bar{2}w}$	$\dfrac{[M^+]}{\Sigma[M^+]}$	$\dfrac{[M^+]_w}{\Sigma[M^+]}$	$\dfrac{[M^+]_{2w}}{\Sigma[M^+]}$
Cations					
Na^+	2.0	3.0	0.17	0.33	0.50
m-nitroanilinium	1.0	5.2	0.14	0.72	0.14
2-nitro-4,5-dimethylanilinium	0	1.2×10^1	0.08	0	0.92
Anilinium	0.8	1.8	0.22	0.50	0.28
p-naphtholbenzeinium	2.1	4.3	0.28	0.58	0.14
Anions			$\dfrac{[A^-]}{\Sigma[A^-]}$ or	$\dfrac{[A^-]_w}{\Sigma[A^-]}$	$\dfrac{[A^-]_{2w}}{\Sigma[A^-]}$
Cl^-	9	2.0×10^1	0.03	0.31	0.66
Methanesulphonate	3.6	8.0	0.08	0.28	0.64
Picrate	0.5				

It is particularly interesting to note that the protonated form of the Hammett indicator *m*-nitroaniline has large hydration constant. At a water concentration of 1M only 14 per cent of the indicator is present in the unhydrated form, while 72 per cent is present as monohydrate and 14 per cent as dihydrate. Protonated forms of other Hammett indicators undoubtedly are also strongly hydrated. It is fair to conclude that the Hammett indicator cations are much stronger solvated in water than in AN. Also for this reason the Hammett

acidity function does not yield a correct value for the distribution coefficient of the proton between water and acetonitrile. The two anions listed in *Table 8* are present almost completely in the hydrated forms in a solution 1 M in water in ·AN. On the other hand, the picrate ion is only slightly hydrated, it only forms a monohydrate: $K^f_{Pi_{1w}} = 0.5$. Solvation effects over a wide range of mixtures of solvents have been investigated by other workers (see e.g. papers by Professors Strehlow and Bates).

Most alkali salts in AN are incompletely dissociated into ions and it has been possible[45] to calculate ·from the total and ionic solubilities of various salts the hydration constants $K^f_{(MA)_w}$ and $K^f_{(MA)_{2w}}$ of dissolved undissociated mono- and dihydrated salts. Some results are summarized in *Table 9*.

Table 9. Hydration constants in AN of undissociated potassium salts. Fraction of salt present in unhydrated and hydrated form in presence of 1 M water

Potassium salt	$K^f_{(MA)_{1w}}$	$K^f_{(MA)_{2w}}$	$\dfrac{[MA]}{\Sigma[MA]}$ in 1 M water	$\dfrac{[MA.1w]}{\Sigma[MA]}$	$\dfrac{[MA.2w]}{\Sigma[MA]}$
Picrate	0	—	1	0	0
Salicylate	1.3	7.6	0.10	0.13	0.76
3,5-dinitrobenzoate	2.5	0	0.28	0.72	0
3,5-dinitrophenolate[a]	4	0	0.20	0.80	0

[a] At water concentrations greater than about 0.2 M the solid body is the monohydrate.

In solutions 1 M in water in AN undissociated potassium picrate appears to be present in the form of contact ion pairs, the other 3 salts are ion pairs in which at least the anions are hydrated. As far as pure solvents are concerned, in general one would expect more solvent separated ion pairs in protophylic than in protophobic aprotic solvents, considering that cations in general are much stronger solvated in the former than in the latter. Exceptions are found when there is specific interaction between solvent and cation, e.g. strong solvation of silver and copper (I) ions in AN. Excellent reviews of selective solvation of ions in mixed solvents are given by Schneider[46, 47], while properties of ion pairs are discussed in reviews by Ritchie[48] and by Garst[49].

PROTONATION IN ACETONITRILE OF WATER AND ALCOHOLS

The protonation of the weak bases (B) water and alcohols has been studied in AN by determining spectrophotometrically with Hammett indicators and dibromothymolbenzein their interaction with the proton H_s^+, s denoting the solvent[50]. In the 1968 publication it was assumed that the protonated forms of the indicators IH^+ are not being hydrated or alcoholated by the addition of water or alcohols. In a later publication[44] a special study was made of the hydration of IH^+ and the originally reported hydration constants of the proton were corrected for this effect. The corrections are relatively small and do not affect the overall conclusions. These corrected values are listed in *Table 10*. No study has been made of the alcoholation of IH^+. It is clear that acetonitrile is a very weak base as compared to water or

Table 10. $K_{B_nH^+}^f$ for water, alcohols, and ethyl ether in AN

B	$K_{BH^+}^f$	$K_{B_2H}^f$	$K_{B_3H^+}^f$	$K_{B_4H^+}^f$
Water [44]	1.6×10^2	8.0×10^3	6.0×10^4	2×10^5
Methanol	2.3×10^2	1.4×10^3	8.0×10^2	0
n-Butanol	1.4×10^2	4.2×10^3	2.1×10^3	0
t-Butanol	2.7×10^3	1.7×10^4	0	0
Diethylether	1.5	2.1×10^1	0	0

alcohols. In *Figure 3* are shown the calculated concentrations expressed as the fraction of total $[H^+]$ of H_s^+, $(H_2O)H^+$, $(H_2O)_2H^+$, $(H_2O)_3H^+$, and $(H_2O)_4H^+$. At a water concentration of $0.01\,M$ $[H_s^+]$ is only about 35 per cent of $\Sigma[H^+]$, when $[H_2O] = 0.1$ only $[H^+]_s$ is 2 per cent of $\Sigma[H^+]$. In solutions $1\,M$ in water the predominant species becomes $(H_2O)_4H^+$, which is also
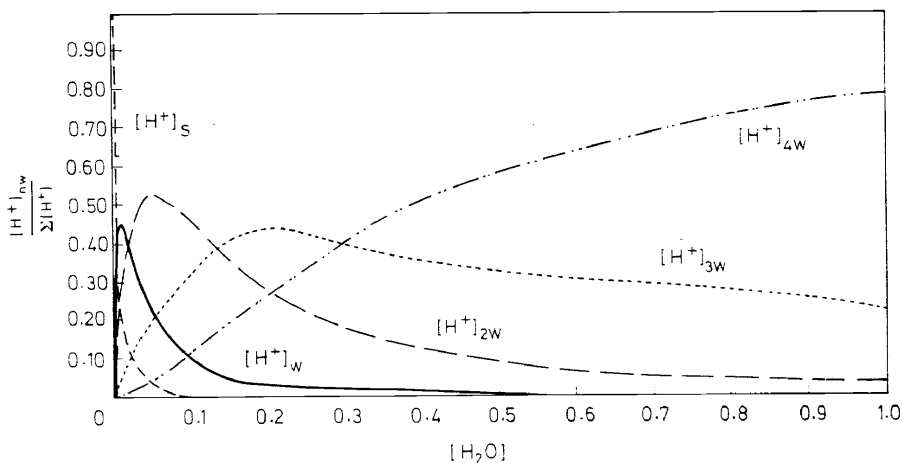

Figure 3. Plot of calculated values of $[H^+]_{nw}/\Sigma[H^+]$ *vs.* $[H_2O]$

considered to be the composition of the proton in water as a solvent. It is interesting to note that in methanol and n-butanol only mono-, di- and trialcoholated protons are formed, and in t-butanol and ether only the mono- and di-forms. Roughly, the overall basicity expressed in the terms of

$$\frac{[H^+]_s}{\Sigma[H^+]}$$

of the alcohols in AN is of the same order of magnitude as that of water; diethylether is very much weaker than are the alcohols or water.

SOLVATION IN LEWIS ACID-BASE AND COMPLEXATION REACTIONS

Most inorganic cations of charge greater than one are typical Lewis acids and they are much more strongly solvated in the more basic protophylic than in protophobic aprotic solvents. Also the alkali ions are much more

strongly solvated in the former than in the latter as is evident from several papers presented before this Symposium. Still there is considerable evidence that alkali ions are solvated in protophobic solvents. For example, from transference number and conductance determinations Della Monica et al.[51] find in the typical aprotic solvent sulpholane that at 30° λ_0 of potassium is 4.05, while λ of chloride is 9.30[52], indicating that the potassium (and other alkali ions) are considerably solvated (probably by ion–dipole interaction) whereas the chloride ion with a localized charge probably is not solvated.

Much work has been done on the interaction of uncharged Lewis acids compounds with organic and inorganic solvents.

Gutmann[53] distinguishes between donor and acceptor solvents. Ionization of Lewis acids is promoted in a donor solvent by solvation of cations and in acceptor solvents by solvation of anions. For example, AsI_3 is ionized in a donor solvent

$$AsI_3 + nD \rightleftarrows (AsI_2D_n)^+ + I^-$$
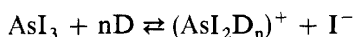
while in the acceptor solvent hydrochloric acid triphenylchloromethane is ionized:

$$(C_6H_5)_3CCl + HCl \rightleftarrows (C_6H_5)_3CH^+ + Cl^-$$
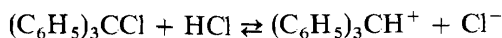
Caution must be observed in accepting published data on the ionic dissociation of Lewis acids in various solvents. For example, from conductance data in carefully purified solvent and compound Beattie et al.[54] conclude that in acetonitrile antimony pentachloride, tellurium tetrachloride and dichloro (dimethyl)silane in the presence of 2,2'-bipyridol are effective nonelectrolytes and that the relatively large conductances of such solutions given in the literature must be due to impurities in the solvent and/or solutes.

The negative enthalpy of coordination $-H$ of a donor molecule towards antimony(V)chloride has been suggested by Gutmann as a measure of its donor properties

$$D + SbCl_5 \rightleftharpoons DSbCl_5 \quad - H_{D.SbCl_5} \, (Table \ 11)$$
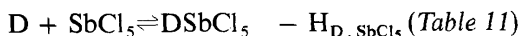
Gutmann lists the donor number of a host of solvents with dielectric constants varying between 90 and 4. A review of solvation of Lewis acids in inorganic and organic solvents and effect of this coordination upon stability of coordination compounds with other ligands is given by V. Gutmann[55]. Table 11 illustrates how the properties of a few solvents affect the ease of formation of CoX_4^{2-} upon adding a solution of X^- to $CoCl_2$. The notation DN refers to the 'donor number' with $SbCl_5$: $DN_{SbCl_5} = -\Delta H_{D-SbCl_5}$ (D = solvent). Note that the protophobic solvents NM and AN have a considerably smaller DN than the protophylic solvent DMSO and that

Table 11. Molar ratios required to give CoX_4^{2-} in 3 solvents

| Solvent	DN	$Co(N_3)_4^{2-}$	$Co(NCS)_4^{2-}$	$CoCl_4^{2-}$	$CoBr_4^{2-}$	CoI_4^{2-}
NM[a]	2.7	4	4	4	4	5
AN[b]	14.3	8	7	16	40	~
DMSO[z]	29.8	20	200	200	~	~

[a] nitromethane; [b] acetonitrile; [c] dimethylsulphoxide.

CoX_4^{2-} is considerably more stable in NM and AN than in DMSO. Probably, the reason is that the Co^{2+} ion is much more solvated in the latter solvent than in NM and AN.

FREE RADICAL FORMATION ON ELECTRO-OXIDATION OR -REDUCTION

In overall two-electron electro-oxidation or reduction in aprotic solvents free radicals are often formed which are much more stable than those formed in protic solvents. In the latter the free radicals are instantaneously protonated and further reduced (or oxidized) at the potential at which the radicals are produced. Reference is made to the classical papers of Hoijtink[56, 57], dealing with the polarographic reduction of hydrocarbons in dioxane rich water-dioxane mixtures. Since that time numerous electro-oxidation or reduction studies, often combined with e.s.r. measurements, have been carried out. Reference is made to the paper by A. J. Bard.

As far as inorganic compounds are concerned, the electroreduction of oxygen is of particular interest. As is well known, oxygen in aqueous medium yields two irreversible two-electron waves, the first one corresponding to the formation of (hydrogen)peroxide and the second one to the reduction of peroxide to hydroxyl ions. In aprotic solvents (in the absence of acid) oxygen yields two one-electron waves, the first one to superoxide ion and the second one to peroxide ion. The first electrochemical study of oxygen reduction was made in dimethylsulphoxide and dimethylformamide by Maricle and Hodgson[58]. Both at a platinum and a dropping mercury electrode oxygen is reduced by a one-electron reaction. At the dropping mercury electrode the first wave is quasi-reversible:

$$O_2 + e \rightleftarrows O_2^-$$
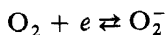
and with tetrabutylammonium hydroxide as supporting electrolyte the first half-wave potential was -0.73 v (vs. S.C.E.) and the second (reduction to O_2^{2-}) -2.40 v. By electrolytic reduction a solution of tetrabutylammonium superoxide was prepared. As was to be expected when dealing with reversible electrode reactions, a composite wave was observed in this solution in the presence of oxygen. The superoxide ion is a free radical ion which cannot be prepared in protic solvents as it is immediately protonated, the protonated product decomposing instantaneously to oxygen and hydrogen peroxide. Such a reaction also occurs in aprotic solvents in the presence of some proton donor like phenol or water or stronger acids. The first reduction wave then corresponds to an irreversible two-electron reduction to hydrogen peroxide. In the presence of alkali or other metal ions in aprotic solvents (free of a proton donor) insoluble superoxide salts are formed on reduction of oxygen. For further details on the electrochemistry of oxygen in aprotic solvents reference is made to the literature[59, 60, 61, 62].

IMPORTANCE OF NON-AQUEOUS ELECTROCHEMISTRY IN VARIOUS PROVINCES OF CHEMISTRY

Lecturers before this Symposium can be classified as organic-physical, physical, inorganic, and analytical chemists. Evidently the subject has

become important to workers in all the provinces of chemistry. Several references have been made in the present paper to studies which cover all provinces of chemistry. Without being exhaustive, we might conclude this review by listing topics which are of interest to all chemists and to those in specific fields of chemistry. Of course, there is no sharp demarcation line between the interest of those working in the specific fields.

General and physical chemistry. Ion distribution coefficients, solvation in pure and mixed solvents. Contact and solvent separated ion pairs. Acidity and basicity. Equilibrium constants, also with reference to dielectric constant. Walden's rule. Electrode, liquid junction and surface potentials. Hydrogen bonding. Polymerization in solvents. Solvent isotope effects on kinetics.

Inorganic chemistry. Complexation in organic and inorganic and mixtures of solvents, electrosynthesis in fused salts with formation of new compounds; ionic dissociation of group IV metals, stability of free radicals, stable and unstable valence states.

Organic chemistry. Kinetics of S_{N^2} (Parker)[63] and S_{N^1} reactions (see reference [48]), formation of free radicals, mechanism of reactions, electrochemistry of organometallic compounds.

Analytical chemistry. Electroanalysis. Resolution of acid and base strength, redox potentials, solubility products. Electrodes for H^+ useful in titrations (hydrogen, glass, platinum of various pretreatment, gold, antimony, bismuth, molybdenum, carbon–graphite in various forms, semiconductors, polarized electrodes). Electrometric titrations. Ion specific electrodes[64, 65]. Cathodic and anodic limitations of various electrodes, voltammetry, polarography. Separations, including exchange resins. Theory and practice of extraction analysis[66]. Purification and tests for purity of solvents.

Industrial chemistry. Fuel cells (non-aqueous), electrosynthesis (especially in fused salts as solvents).

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