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SOLVENT EFFECTS ON ION-PAIR EQUILIBRIA

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CONTENTS

A. INTRODUCTION

According to Fuoss and Accascina [1] two groups of electrolytes may be distinguished namely "ionogens" and "ionophores". The latter group comprises those electrolytes which form ionic lattices in the solid state.

The successful application of the elementary electrostatic theory to the calculation of activity coefficients by Debye and Hückel [2] and to the transport properties of ions by Debye and Hückel [3], and Onsager [4], led very early to the view that ion-pair formation in solutions of ionophores was a consequence of electrostatic interactions. Starting from this hypothesis Bjerrum [5] and Fuoss [6] derived their well-known equations which relate the ion-pair dissociation constants to the dielectric constants of the solvents. These equations have been widely used for the estimation of association constants.

During the last decade, however, many investigations have been carried out in non-aqueous solvents the results of which clearly show that the association behaviour of many ionophores in many solvent systems cannot be adequately represented by elementary electrostatic models.

Part of these investigations has been summarized in two recent review articles dealing with the results of various UV, IR and NMR measurements [7] and with the reactivity of organometallic compounds [8].

The present article is primarily concerned with the results of recent conductance studies. It is not intended to give an exhaustive literature survey but rather to present a selection of data which appear particularly suitable for comparing the applicability and limitations of the elementary electrostatic and the coordination chemical approach to ion-pair equilibria.

B. EMPIRICAL APPROACH TO SOLUTE—SOLVENT INTERACTIONS

The empirical approach to solute—solvent interactions rests on the view that in principle, each solvent is amphoteric, i.e. that it possesses both nucleophilic and electrophilic properties which may be described by means of suitable empirical parameters [9].

The function which is actually exercised by the solvent depends on whether the substrate acts as electrophile, nucleophile or as both at the same time [9].

A measure of the nucleophilic properties of the solvents is provided by the donicity or Donor Number, DN, which is defined as the negative ΔH-value for the 1 : 1 adduct formation between the reference acid $SbCl_5$ and the donor in the quasi-inert solvent 1,2-dichloroethane [10,11].

Unfortunately it is not possible to determine an analogous, experimentally directly accessible thermochemical quantity for characterizing the electrophilic properties of the solvents. Recently, the so-called Acceptor Number, AN has been introduced as an empirical measure of the solvent electrophilic properties, whose definition is based on the strong solvent dependence of the ^{31}P solution chemical shift of triethylphosphine oxide which serves as a reference base [12]. Owing to the unique solubility properties of this compound, Acceptor Numbers are accessible for all types of coordinating and non-coordinating solvents.

Alternatively, the free energies of solvation of the halide ions [13] or the half wave potentials for the redox couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ [14] may be used as a measure of the solvent electrophilic properties. The former values have been successfully used in thermodynamic calculations on the solvent dependence of coordination chemical equilibria and the kinetics of some substitution reactions [13], but are available only for a limited number of solvents.

In principle, two types of "ion-pairs" are distinguished in the literature. In the so-called "contact ion-pairs" the ions are in immediate contact with each other, whereas in "solvent separated ion-pairs" the ions are separated by one or several layers of solvent molecules. According to the coordination chemical approach [9] the formation of a "contact ion-pair" (eqn. 1) has to be considered as a substitution reaction in which solvent molecules are eliminated from both A^+ and B^- [7—9,15].

$$(A \cdot S_n)^+ + (B \cdot S_m)^- \rightleftharpoons [(A^+B^-) \cdot S_{n+m-x}]^0 + S_x \qquad (1)$$

Towards the acid A^+ the solvent acts as nucleophile (donor) whereas it behaves as electrophile (acceptor) towards the base B^-.

In a series of solvents with similar dielectric constants the ion associate will be more dissociated the stronger are the nucleophilic and (or) electrophilic properties of the solvents.

Usually, the formation of such a "contact ion-pair" involves coordinative interactions between the associated ions so that the "ion-pair" should more logically be considered as an un-ionized entity with a more or less strongly polarized bond [9].

If the bonds between the ions and the solvent molecules are very strong then the solvation shells of the ions may (at least in part) be retained on association so that solvent separated ion-pairs are formed (eqn. 2).

$$(A \cdot S_n)^+ + (B \cdot S_m)^- \rightleftharpoons [(A \cdot S_n)^+(B \cdot S_m)^-]^0 \qquad (2)$$

High nucleophilicity and (or) electrophilicity of the solvent apparently favours the formation of solvent separated ion-pairs instead of "contact ion-pairs".

In the following sections the applicability and efficiency of the elementary electrostatic, and the coordination chemical, approach will be compared and discussed for various groups of ionophores.

The most important parameters for characterizing solvent properties are compiled in Table 1.

C. TETRAALKYLAMMONIUM SALTS

In these electrolytes the cations are coordinately saturated so that the occurrence of strong specific solute—solvent interactions is restricted to interactions between the anion and the solvent molecules. Ion-pair association constants of various tetraalkylammonium halides in a number of hydroxylic and aprotic solvents are listed in Table 2. In the alcohols the association constants generally decrease in the order I > Br > Cl, contrary to what would be expected from elementary electrostatic considerations. Just the reverse trends are found in the aprotic solvents where the association constants increase in the series I < Br < Cl.

It might be argued, that the decrease in the association constants with decreasing atomic number of the halide ions as observed in the alcohols is a consequence of the (numerically) increasing Born solvation energies of the halide ions. Whereas the Born solvation energies are certainly increasing in this series, this argument cannot explain the trend observed in the alcohols since the same trend should then also be found in those aprotic solvents which have higher dielectric constants than the alcohols such as AN, NB or DMF. Obviously this is not the case; the stability order in AN, NB or DMF is the reverse of that observed in the alcohols.

Likewise the assumption of increasing ion—dipole interactions in the series $I^- < Br^- < Cl^-$ does not provide a satisfactory explanation for the trend observed in the alcohols, since the same behaviour should then be found in the

TABLE 1

Solvent parameters. DN = Donor Number [10,11], AN = Acceptor Number [12], $\Delta\Delta G_{sv}(Cl^-) = \Delta G_{sv}^{S}(Cl^-) - \Delta G_{sv}^{AN}(Cl^-)$ = difference of the free energies of solvation of the chloride ion in the solvent (S) and the reference solvent acetonitrile (AN) [13,16,17], $E_{1/2}$ = half wave potential for the redox couple $[Fe(CN)_6]^{3-}/[Fe(GN)_6]^{4-}$ in 0.1 molar solution of NBu_4ClO_4 referred to bisbiphenylchromium(I)iodide [14], ϵ = dielectric constant, μ = dipole moment. All values at 25° C

Solvent	DN	AN *	$\Delta\Delta G_{sv}(Cl^-)$ (Kcal)	$E_{1/2}$ (V)	ϵ	μ (Debye)
Hexane	0.0	0.0	—	—	1.9	0.0
Carbon tetrachloride	0.0	8.6	—	—	2.2	0.0
1,2-Dichloroethane (DCE)	0.0	16.7	—	−0.31	10.1	1.75
Sulfuryl chloride	0.1	—	—	—	10.0	1.81
Benzene	0.1	8.2	—	—	2.3	0.0
Thionyl chloride	0.4	—	—	—	9.2	1.45
Acetyl chloride	0.7	—	—	—	15.8	2.71
Tetrachloroethylene carbonate	0.8	—	—	—	9.2	—
Dichloromethane	—	20.4	—	—	8.9	1.5
Chloroform	—	23.1	—	—	4.7	1.1
Benzoyl fluoride	2.0	—	—	—	22.7	—
Benzoyl chloride	2.3	—	—	—	23.0	3.26
Nitromethane (NM)	2.7	20.5	−3.13	−0.14	36.67	3.57
Dichloroethylene carbonate	3.2	—	—	—	31.6	3.47
Nitrobenzene (NB)	4.4	14.8	—	—	34.69	4.03
Acetic anhydride	10.5	—	—	—	20.7	3.15
Phosphorus oxychloride	11.7	—	—	—	14.0	2.41
Benzonitrile (BN)	11.9	15.5	—	—	25.2	3.9
Selenium oxychloride	12.2	—	—	—	46.0	2.64
Acetonitrile (AN)	14.1	18.9	0.00	−0.42	36.02	3.96
Sulfolane (TMS)	14.8	—	0.14	—	43.3	4.81
Propanediol-1,2-carbonate (PDC)	15.1	18.3	−0.14	−0.20	65.0	4.98
Benzyl cyanide	15.1	—	—	—	18.4	3.50
Ethylene sulphite	15.3	—	—	—	41.0	3.68
iso-Butyronitrile	15.4	—	—	—	20.4	3.61
Propionitrile	16.1	—	—	—	27.7	4.03
Ethylene carbonate	16.4	—	—	—	89.1	4.51
Phenylphosphonic difluoride	16.4	—	—	—	27.9	—
Methylacetate	16.5	—	—	—	6.7	1.69
n-Butyronitrile	16.6	—	—	—	20.3	4.07
Acetone (AC)	17.0	12.5	3.54	—	20.70	2.86
Ethyl acetate	17.1	—	—	—	6.0	1.85
Water	18.0	54.8	−8.71	—	78.5	1.8
Phenylphosphonic dichloride	18.5	—	—	—	26.0	—
Methanol	19.0	41.3	−5.98	0.38	32.62	1.70
Ethanol	—	37.1	−4.76	0.24	24.33	1.70
iso-Propanol	—	33.5	—	—	18.3	1.70
Ethylene glycol dimethyl ether (glyme)	—	10.2	—	—	7.0	—

TABLE 1 (continued)

Solvent	DN	AN *	$\Delta\Delta G_{sv}(Cl^-)$ (Kcal)	$E_{1/2}$ (V)	ϵ	μ (Debye)
Diethylene glycol dimethyl ether (diglyme)	—	9.9	—	—	—	—
Dioxane	—	10.8	—	—	2.2	0.4
Diethyl ether	19.2	3.9	—	—	4.2	1.25
Tetrahydrofuran (THF)	20.0	8.0	—	—	7.4	1.7
Formamide	—	39.8	−6.39	—	109.5	3.4
Diphenylphosphonic chloride	22.4	—	—	—	—	—
Trimethyl phosphate (TMP)	23.0	—	—	—	20.6	3.02
Tributyl phosphate (TBP)	23.7	—	—	—	6.8	3.07
N-Methylformamide (NMF)	—	32.1	—	—	182.4	3.8
N,N-Dimethylformamide (DMF)	26.6	16.0	1.22	−0.61	36.71	3.86
N,N-Dimethylthioformamide (DMTF)	—	18.8	—	−0.36	47.5	4.37
N-Methyl-ε-caprolactame	27.1	—	—	—	—	—
N-Methyl-2-pyrrolidinone (NMP)	27.3	13.3	2.04	−0.63	33.0	4.1
N,N-Dimethylacetamide (DMA)	27.8	13.6	2.45	—	37.78	3.81
Dimethyl sulphoxide (DMSO)	29.8	19.3	0.00	−0.39	46.68	3.90
N,N-Diethylformamide	30.9	—	—	—	—	—
N,N-Diethylacetamide	32.2	—	—	—	—	3.75
Pyridine	33.1	14.2	—	—	12.3	2.2
Hexamethylphosphoric-triamide (HMPA)	38.8	10.6	4.08	—	29.6	4.48

* AN = Acceptor Number; not to be confused with the abbreviation AN for the solvent acetonitrile.

aprotic solvents which generally have higher dipole moments.

The only reasonable explanation is that in the alcohols, in addition to the electrostatic interactions between the halide ions and the solvent there are hydrogen bond interactions, which strongly increase in the series $I^- < Br^- < Cl^-$, i.e. with increasing donor strength of the halide ions [29].

Based on these considerations, it is possible to rationalize the variations in the association constants as a function of the cation radius observed in protic and aprotic media (Table 2).

In the alcohols, the association constants of the halide salts with a given cation become increasingly differentiated with increasing radius of the cation. In MeOH, for example, the association constants for Me_4NBr and Me_4NI differ by a factor of about 1.3, for Pr_4NBr and Pr_4NI by about 3 and for the corresponding butyl salts by more than 5. The same behaviour is observed in

TABLE 2

Ion-pair association constants of tetraalkylammonium halides in solvents of different properties at 25°C

Solvent	MeOH [18]	EtOH [19]	Prop. [19]	AN [20]	DMF [23]	NB	AC	MEK [28]
ϵ	32.62	24.33	20.45	36.02	36.71	34.69	20.70	18.01
μ	1.70	1.70	1.66	3.96	3.86	4.03	2.86	2.76
AN *	41.3	37.1	—	18.9	16.0	14.8	12.5	—
Me_4NCl	7	122	456	56 [21]				
Me_4NBr	14	146	638	46	37			4544
Me_4NJ	18			19	14			969
Et_4NCl						80 [24]		
Et_4NBr	10	99	373		16	62 [24]		958
Et_4NJ		133	466	8 [22]	12	29 [22]		434
Pr_4NCl								
Pr_4NBr	6	78	270	4	12			940
Pr_4NJ	17	120	391	5	8		162 [26]	442
Bu_4NCl		39	149				435 [26]	
Bu_4NBr	3	75	266	2		56 [24]	264 [27]	787
Bu_4NJ	16	123	415	3	8	27 [25]	143 [27]	382

* See footnote to Table 1.

the other alcohols, for example, in EtOH the association constants of Me_4NCl and Me_4NBr differ by a factor of 1.2 whereas a factor of 2 is found for the corresponding butyl salts.

Exactly the reverse trend is found in the aprotic solvents. In methylethylketone (MEK), for example, Me_4NBr is 5 times more associated than the iodide, whereas the constants of the corresponding butyl salts differ by a factor of only 2. Similarly, in AN, Me_4NBr is definitely more strongly associated than the iodide, whereas the corresponding propyl (or butyl) salts have nearly the same constants.

This can be explained in the following way. In the gas phase the stability of the ion-pairs (with a given cation) generally increases in the series $I < Br < Cl$. Since the interaction energy for a given halide ion decreases with increasing radius of the cation, the differences in the free energies of association in a series of halides with a given cation become smaller with increasing cation radius. On the other hand, the free energies of solvation of the halide ions increase (numerically) in the order $I^- < Br^- < Cl^-$ both in hydroxylic and aprotic solvents. This increase in the solvation energies, however, is much more pronounced in the hydroxylic solvents, since the increase in the Born solvation energies is dramatically enhanced by the influence of hydrogen bond solvation. As a consequence, the stability order as observed in the gas phase is reversed in hydroxylic solvents even for halides with small tetraalkylammonium cations. Naturally, this influence of hydrogen bonding will become the more pronounced the smaller the differences in the corresponding gas phase association constants, that means the larger the radius of the cation.

In aprotic solvents the free energies of solvation of the halide ions also increase (numerically) in the order $I^- < Br^- < Cl^-$ but to a much lesser degree than in hydroxylic solvents owing to the lack of hydrogen bond interactions. As a consequence, the gas phase stability order is retained in aprotic solvents, at least for those salts which contain small tetraalkylammonium cations. For salts with large counter cations the differences in the gas phase association constants of the halides (with given cation) become smaller and are therefore more easily compensated by the variation in the free energies of solvation of the halide ions. Consequently, and contrary to the situation in hydroxylic solvents, one has to expect a levelling of the association constants or even a reversal in stability order with increasing cation radius. This is indeed observed experimentally; in acetonitrile, for example, the tetramethylammonium salts differ considerably in their association constants, whereas the propyl and butyl salts, respectively, show nearly the same constants.

It is easily understood that the predicted levelling effect, or even reversal, in stability order will become increasingly visible with increasing electrophilicity, i.e. anion solvating power of the solvent. In DMF, for example, the levelling effect is obviously less pronounced than in acetonitrile, which agrees with the fact that DMF is a weaker electrophile (Table 1) than acetonitrile. In DMF, the association constants of Me_4NBr and Me_4NI differ by a factor of about 2.5, and by a factor of 1.5 for the corresponding propyl salts.

A levelling effect clearly exists also in MEK. The fact that the association constants in this solvent are well differentiated even for the larger tetraalkylammonium salts, results from the very weak electrophilic properties of the solvent molecules and the low dielectric constant of the medium (Table 1).

Additional information concerning the relative influence of electrostatic and hydrogen bond contributions may be obtained by comparing the association constants in pairs of hydroxylic and aprotic solvents with similar dielectric constants.

In propanol, for example, tetrabutylammonium chloride is less associated than in acetone although the latter definitely has a higher dipole moment and the same dielectric constant. This is most probably due to the specific solvation of the chloride ions in propanol by hydrogen bonding which makes up for the stronger ion—dipole forces expected in acetone. The iodide on the other hand is more strongly associated in propanol than acetone. The iodide ion is a much weaker donor than the chloride ion so that in propanol the hydrogen bond interaction makes a comparatively weak contribution as compared to the ion—dipole interactions. Both effects obviously cancel each other in case of the bromide, for which essentially the same constants are obtained in both solvents.

The influence of hydrogen bonding is expected to be more pronounced in the solvent methanol, which is a stronger acceptor than propanol (Table 1).

In fact, both Me_4NCl and Me_4NBr are less associated in MeOH than in acetonitrile, although acetonitrile has a higher dielectric constant and a much higher dipole moment. The association constants of the iodide are nearly equal, indicating a compensation of hydrogen bond and ion—dipole contributions *.

Differences in molecular size may also be important. For example, the salts are more strongly associated in MEK than in acetone although the dielectric constants and dipole moments of the two solvents are nearly equal. Obviously, stabilization of ions by ion—dipole interactions is less effective in MEK than in acetone owing to the larger steric requirement of the methylethylketone molecules.

The influence of the electrophilic properties of the solvents on ion association equilibria has recently been demonstrated [30] by measuring the half wave potentials for the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple in 0.1 molar NBu_4ClO_4 and NEt_4ClO_4 solution, respectively (Table 3). On the whole the differences, $\Delta E_{1/2}$, in the half wave potentials decrease (numerically) with increasing Acceptor Numbers or decreasing $\Delta\Delta G_{sv}(Cl^-)$ values, i.e. with increasing electrophilic properties of the solvents. This shows that the extent of the as-

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* For the higher tetraalkylammonium halides the situation becomes more complicated since specific differences are also to be expected in the solvation energies of the cations, owing to the fact that methanol is a highly structured liquid.

TABLE 3

Half wave potentials $E_{1/2}$ for the redox couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ in 0.1 molar solution of tetrabutylammonium perchlorate (TBAP) and tetraethylammonium perchlorate (TEAP) as supporting electrolyte in solvents of different properties at 25°C [30]

Solvent	$E_{1/2}$ (V)		$\Delta E_{1/2}$ (V)	$\Delta\Delta G_{sv}(Cl^-)$ (kcal)	AN	ϵ	μ (Debye)
	TEAP	TBAP					
DMF	−0.31	−0.61	−0.30	1.22	16.0	36.71	3.86
AN	−0.28	−0.42	−0.14	0.00	18.9	36.02	3.96
DMSO	−0.27	−0.39	−0.12	0.00	19.3	46.68	3.90
PDC	−0.17	−0.20	−0.03	−0.14	18.3	65.00	4.98
NM	−0.07	−0.14	−0.07	−3.13	20.5	36.67	3.57
EtOH	+0.30	+0.24	−0.06	−4.76	37.1	24.33	1.70
MeOH	+0.47	+0.38	−0.09	−5.98	41.3	32.62	1.70

sociation between the tetraalkylammonium ions and the complex anions decreases with the increasing acceptor properties of the solvents as a consequence of the increasing outer-sphere solvation of the highly basic complex anions [14,15,31]. This effect is necessarily more pronounced for the tetraethylammonium salts (which are strongly associated) than for the corresponding butyl salts, and this explains the decrease in $|\Delta E|$ with increasing solvent acceptor properties. The numerically small ΔE value found for PDC must be ascribed to the high dielectric constant of this solvent which, in addition to the influence of outer-sphere coordination, favours the dissociation of the ion associates.

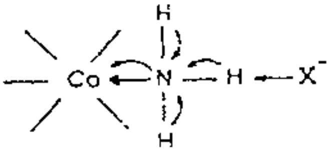
No general relationship exists between $\Delta E_{1/2}$ and the dielectric constants or dipole moments of the solvents.

D. IONOPHORES CONTAINING ACIDIC HYDROGEN ATOMS

The association behaviour of transition metal aquo and amine complexes provides many indications for ion-pairing via hydrogen bonding.

Linhard, for example, investigated the UV-spectra of Co^{III}- and Cr^{III}-hexamine and trisethylenediamine halides and found that these salts are strongly associated even in dilute aqeous solutions [32]. These results were supported later by various conductometric, spectrophotometric and polarographic investigations [33—38]. Similar effects were detected for related compounds by Taube, Pearson, Tobe and others in kinetic studies on substitution reactions of transition metal amine and aquo complexes [39—41]. This subject was reviewed some years ago by Beck [42].

As pointed out previously [7,31] the reason for these strong "outer sphere" interactions is to be sought in the fact that the acidity of the NH hydrogens of the amine ligands is considerably increased by coordination to the transition metal ion which acts as a strong Lewis acid.



These acidic hydrogens may undergo hydrogen bond interactions either with solvent molecules or with sufficiently basic counterions. The same applies to coordinated water molecules with the distinction that the water molecules are more susceptible to deprotonation so that the situation might be complicated by the formation of hydroxo species.

Among the very few systematic studies the work of Watts should be mentioned. He studied the "ion-pair" formation between the cis-dichlorobisethylenediamine Co(III)-cation and chloride ion in several solvents [43,44] (Table 4). The association constants are considerably larger than one would expect from elementary electrostatic considerations in view of the high dielectric constants and dipole moments of the solvents.

According to the coordination chemical approach the formation of the "ion-pair" has to be considered as a substitution reaction in which a solvent molecule coordinated to an acidic hydrogen atom is replaced by a chloride ion, with the formation of a hydrogen bonded outer-sphere complex. The increase of the association constants in the order DMSO, DMF and DMA, reflects primarily the decreasing electrophilic properties of these solvents which have similar donor strengths. In case of DMSO a somewhat higher contribution from the Born - free energy of solvation must be taken into account, as evidenced by the big jump in the association constants observed in going from DMSO to DMF.

The large value for the association constant in TMS results from the superposition of two opposing effects: TMS is a stronger electrophile than both DMF and DMA but a much weaker donor, so that the nucleophilic influence is prevailing.

TABLE 4

Formation constants for the one-to-one outer sphere complex between $[Co(en)_2Cl_2]^+$ and Cl^- in solvents of different properties at 25° C [43,44].

Solvent	K_{form} $(mol^{-1} \cdot l^{1})$	DN	AN *	$\Delta\Delta G_{sv}(Cl^-)$ (kcal)	ϵ	μ (Debye)
DMSO	400	29.8	19.3	0.00	46.68	3.90
DMF	8000	26.6	16.0	1.22	36.71	3.86
DMA	20000	27.8	13.6	2.45	37.78	3.81
TMS	42000	14.8	—	0.14	43.3	4.81

* See footnote to Table 1.

The large association constant found in TMS cannot be explained by the elementary electrostatic approach since TMS has the highest dipole moment of the solvents investigated and a dielectric constant which is only slightly lower than that for DMSO.

Direct evidence for the acidic nature of the NH-hydrogens in transition metal amine complexes is provided by the results obtained for the polarographic reduction of $Co(en)_3^{3+}$ to $Co(en)_3^{2+}$ [45]. With increasing donicity of the solvents the half wave potentials are shifted to more negative values. This is due to the fact that the Co^{III}-complex is a stronger Lewis acid than the Co^{II}-complex so that the former is increasingly stabilized as compared to the latter, with increasing donor strength of the solvents.

The results of these studies suggested that hydrogen atoms directly bonded to the nitrogen atom in ammonium cations might also be capable of forming hydrogen bonds with neutral or charged bases. In order to test this, the association behaviour of quinuclidinium chloride and *n*-butylammonium chloride was recently studied in various nonaqueous solvents [46]. The cage amine quinuclidine was chosen in order to minimize the possible influence of variable entropy contributions resulting from different conformations of the alkyl groups in the free ammonium ion and the "ion-pair", respectively. The results are listed in Table 5.

Let us first consider the data for quinuclidinium chloride.

The variation in the dissociation constant in DMSO, DMA and DMF follows the trend expected from elementary electrostatic considerations: QHCl is more strongly dissociated in DMSO ($\epsilon \approx 47$) than in DMA or DMF ($\epsilon \approx 37$).

In acetonitrile and NM, however, the dissociation constants are much lower than in DMA or DMF although these solvents have similar dielectric constants. A comparison of the dipole moments does not provide a satisfac-

TABLE 5

"Ion-pair" dissociation constants K_{diss} of quinuclidinium chloride (QHCl) and *n*-butylammonium chloride ($BuNH_3Cl$) in solvents of different properties at 25° C [46,47]

Solvent	K_{diss} ($mole^1 \cdot l^{-1}$)		DN	$\Delta\Delta G_{sv}$ (Cl^-) (kcal)	ϵ	μ (Debye)
	QHCl	$BuNH_3Cl$				
DMSO	$1.20 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	29.8	0.00	46.68	3.90
DMA	$1.80 \cdot 10^{-4}$	$3.17 \cdot 10^{-4}$	27.8	2.45	37.78	3.81
DMF	$4.09 \cdot 10^{-4}$	$6.57 \cdot 10^{-4}$	26.6	1.22	36.71	3.86
PDC	$2.74 \cdot 10^{-4}$	$2.85 \cdot 10^{-4}$	15.1	−0.14	65.00	4.98
AN	$6.03 \cdot 10^{-5}$	$5.29 \cdot 10^{-5}$	14.1	0.00	36.02	3.96
NM	$3.74 \cdot 10^{-5}$	$2.19 \cdot 10^{-5}$	2.7	−3.13	36.67	3.57
NB	$\approx 10^{-6}$		4.4	1.8 *	34.69	4.03

* See footnote on page 170.

tory explanation either since acetonitrile has a higher dipole moment than DMA or DMF.

In PDC, QHCl is as equally strongly dissociated as in DMF or DMA and much less dissociated than in DMSO, although PDC has a much higher dielectric constant and dipole moment.

Likewise, the behaviour in nitrobenzene cannot be explained by elementary electrostatic models. In NB the dissociation constant is lower than in DMA or DMF by more than two powers of ten, and lower than in acetonitrile or NM by more than one power of ten, although nitrobenzene has a higher dipole moment and nearly the same dielectric constant.

In contrast to the elementary electrostatic theory, the observed trends can be understood from the coordination chemical point of view assuming that the NH-hydrogens are sufficiently acidic to form hydrogen bonds with solvent molecules or chloride ions.

$$R_3N^+{-}H \leftarrow S + Cl^- \rightleftharpoons [R_3N^+{-}H \leftarrow Cl^-]^0$$

The ion-association equilibrium is considered as a competitive reaction in which solvent molecules coordinated to the NH-hydrogens of the cation are replaced by chloride ions with formation of a neutral hydrogen bonded complex.

In a series of solvents with similar dielectric constants, the position of the equilibrium depends on the specific nucleophilic and electrophilic properties of the solvent molecules. With increasing nucleophilicity of the solvent molecules, the latter will be less easily replaced by chloride ions so that the equilibrium is shifted to the left hand side.

The influence of the electrophilic properties of the solvents results from the solvation of the chloride ions. The latter are more strongly solvated in the free state than in the complex, so that the equilibrium is shifted to the left hand side with increasing electrophilicity of the solvent molecules.

The observed trends in the dissociation constants can now easily be explained by taking into account the different nucleophilic and electrophilic properties of the solvents (Table 5) *. The largest dissociation constant is observed in DMSO, which is a strong donor and a fairly strong electrophile. The much lower dissociation constant observed in DMA reflects the weaker electrophilic properties of this solvent whose donor number is also somewhat lower. The fact that the dissociation constant in DMF is somewhat higher than in DMA despite a somewhat lower dielectric constant, is now readily understood; both solvents have nearly the same donor properties but DMF

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* Since the subsequent discussion refers to the association behaviour of chlorides it seems appropriate to use the $\Delta\Delta G_{sv}(Cl^-)$-value instead of the Acceptor Number as a measure of the solvent electrophilic properties. In general, there exists a good functional relationship between these two quantities [12], which has been used to estimate the $\Delta\Delta G$-value of NB given in Table 5.

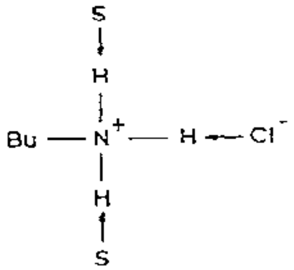
acts as a stronger electrophile. The dissociation constant in acetonitrile is considerably lower than in DMF: acetonitrile is a stronger electrophile than DMF but a much weaker donor so that the influence of the nucleophilic effect is dominating.

The dissociation constant in NM is similar to that in acetonitrile. Nitromethane is a much weaker donor than acetonitrile but a much more powerful electrophile (in fact the strongest electrophile of the solvents investigated), so that the nucleophilic and electrophilic contributions largely compensate each other. The fact that the constants in NM are somewhat lower for both salts as compared to acetonitrile shows that the nucleophilic effect prevails slightly. The low dissociation constant observed in NB fits perfectly into this pattern; nitrobenzene is both a weak donor and a weak electrophile so that the hydrogen bonded complex is most stable in this solvent despite the high dielectric constant and dipole moment.

An additional effect on the position of the equilibria is to be expected if the dielectric constants of the solvents to be compared are very different. For example, both salts show higher dissociation constants in PDC than in acetonitrile although these solvents have essentially the same nucleophilic and electrophilic properties. Clearly, this must be ascribed to the higher Born solvation energy contribution in PDC which has a considerably higher dielectric constant. To a lesser degree the same effect must be taken into account if the dissociation constants in DMSO ($\epsilon \approx 47$) are compared to those in DMF or DMA ($\epsilon \approx 37$). Exactly the same trends as observed for quinuclidinium chloride are found for the butyl salt so that these data need not be discussed in detail. It is, however, interesting to compare the dissociation constants of the two electrolytes in a given solvent.

Consideration of the relative gas phase basicities of quinuclidine and *n*-butylamine suggests that the NH-hydrogens in the butylammonium ion are more acidic than in the quinuclidinium ion so that generally lower dissociation constants might be expected for the butyl compound. Actually, the experimental values are very similar and are even lower for quinuclidinium chloride in the case of DMA and DMF.

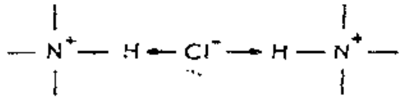
Again this can be explained by the coordination chemical model



In the hydrogen bonded complex formed by the butylammonium ion only one of the three acidic hydrogen atoms is coordinated to a chloride ion, the remaining hydrogens being occupied by solvent molecules. This means that the acceptor strength of the butylammonium ion towards the coordinated chloride ion, in solution depends on the donor strength of the coordinated solvent molecules. If, in particular, the electron donating effect of the coordinated solvent molecules exceeds the inductive effect exerted by an alkyl group (such as in quinuclidine) — a situation that may well occur in strong donor solvents — then the butylammonium ion will actually behave as a weaker acceptor than the quinuclidinium ion, contrary to what may be expected from the gas phase basicities of the parent amines. In weak donor solvents, on the other hand, the relative acceptor strengths of the two ions should approximate the situation that exists in the gas phase. This situation (with the exception of DMSO) is indeed confirmed by the experimental values; the dissociation constants of butylammonium chloride are higher than for quinuclidinium chloride in DMF and DMA which are strong donors, are nearly equal in acetonitrile and PDC which show medium donor strengths, and are lower in weakly basic media such as NM.

An interesting observation, which further supports the coordination chemical model, was made in the analysis of the conductance data. Despite the fact that only data below the critical concentration were used in the calculations, the Fuoss functions deviated from linearity when the range of the measurements was extended to the more concentrated region. Characteristically, this effect does not depend on the dielectric constant of the solvent but becomes increasingly visible with decreasing nucleophilicity and electrophilicity of the solvents, being most pronounced in nitrobenzene.

Apparently, higher ionic aggregates are present even in comparatively dilute solutions.

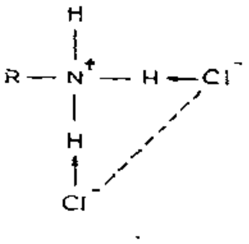


$$-\overset{|}{\underset{|}{N^+}}-H\leftarrow Cl^-\rightarrow H-\overset{|}{\underset{|}{N^+}}-$$

(a)

$[Cl^-(R_3\overset{+}{N}H)Cl^-]^-$

(b)



(c)

Coordination chemical considerations suggest that these aggregates are probably triple cations (a) in which a chloride ion acts as a bridging ligand between two ammonium ions.

The formation of triple anions of reasonable stability can fairly safely be ruled out for quinuclidinium chloride (b) on the basis of simple electrostatic considerations, and appears highly unlikely for butylammonium chloride (c)

TABLE 6

Comparison of calculated and experimental values for the dissociation constants of QHCl and $BuNH_3Cl$ in different solvents at 25°C [46,47]

Solvent	K_{diss} (mole^1 · l^{-1})		
	QHCl	$BuNH_3Cl$	Fuoss Eqn. a = 311 pm
DMSO	$1.20 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$	$2.78 \cdot 10^{-1}$
DMA	$1.80 \cdot 10^{-4}$	$3.17 \cdot 10^{-4}$	$1.12 \cdot 10^{-1}$
DMF	$4.09 \cdot 10^{-4}$	$6.57 \cdot 10^{-4}$	$9.70 \cdot 10^{-2}$
PDC	$2.74 \cdot 10^{-4}$	$2.85 \cdot 10^{-4}$	$8.24 \cdot 10^{-1}$
AN	$6.03 \cdot 10^{-5}$	$5.29 \cdot 10^{-5}$	$8.90 \cdot 10^{-2}$
NM	$3.74 \cdot 10^{-5}$	$2.16 \cdot 10^{-5}$	$9.70 \cdot 10^{-2}$
NB	$\approx 10^{-6}$		$7.32 \cdot 10^{-2}$

since coordination of two chloride ions to adjacent hydrogens would lead to repulsive forces. The assumption of triple cation formation is supported by the preliminary results of attempts to fit the conductance curves in the higher concentration region by allowing for an additional triple cation equilibrium, as well as by the results of cryoscopic measurements carried out in acetonitrile.

If triple ion formation was a consequence of purely electrostatic interactions such effects could never be observed, in view of the high dielectric constants of the solvents investigated.

A further indication for the existence of strong coordination chemical interactions is finally provided by the magnitude of the dissociation constants which, in fact, appear surprisingly low from the electrostatic point of view.

In Table 6 the experimental dissociation constants are compared with those calculated from the Fuoss-equation [6]. Similar values are obtained if the Bjerrum-equation [5] is used. The center to center distance, (311 pm) equals the sum of the ionic radii of the ammonium and the chloride ion. It is seen that the calculated values are generally too high, the observed differences ranging from about one power of ten for DMSO to nearly five powers of ten for NB. Even if one admits that the calculated values are only rough approximations, these large differences show that the elementary electrostatic approach apparently fails in these systems.

E. ALKALI METAL SALTS

In the case when "contact ion-pairs" are formed, the situation is entirely analogous to that discussed for the ammonium salts in Sect. D.

Stabilization of the ions A^+ and B^- not only results from the dielectric polarization of the medium but also from specific interactions with the solvent molecules which act as nucleophiles towards A^+ and as electrophiles towards B^-.

$$(A \cdot S_n)^+ + (B \cdot S_m)^- \rightleftharpoons [(A^+B^-)S_x]^0$$

Association constants of various alkali metal salts are listed in Table 7.

In order to avoid the situation becoming too complicated, a series of solvents has been chosen which show very similar electrophilic properties so that the influence of specific ion—solvent interactions is confined to the interactions between the cations and the solvent molecules.

An instructive example is provided by the association behaviour of the lithium halides. Lithium bromide and chloride are much more strongly associated in PDC and TMS than in DMSO. Obviously this cannot be explained by the elementary electrostatic theory: PDC and TMS have higher dipole moments than DMSO; the dielectric constant of PDC is considerably higher, and that of TMS only slightly lower, than that of DMSO. The association constants of LiBr and LiCl in PDC and TMS are much higher than would be predicted from the elementary electrostatic theory (Table 8).

These results can readily be interpreted from the coordination chemical point of view. PDC and TMS are weak donors as compared to DMSO, so that solvent molecules of the solvation shell of the lithium ion can be much more easily replaced by counterions in PDC or TMS than in DMSO. The high values of the association constants of LiBr and LiCl in PDC and TMS clearly show that covalent interactions must be involved in the formation of the "contact ion-pairs" which, as in the case of quinuclidinium or butylammonium chloride, should more realistically be considered as un-ionized spe-

TABLE 7

Experimental "Ion-pair" association constants of several alkali metal salts in solvents of different properties at 25° C

Solvent	PDC [48,49]	TMS [50]	DMSO [52]	AN [54]
ϵ	65.00	43.30	46.68	36.02
μ	4.98	4.81	3.90	3.96
DN	15.1	14.8	29.8	14.1
$\Delta\Delta G_{sv}(Cl^-)$	−0.14	0.14	0.00	0.00
LiCl	557	13900	50 [53]	
LiBr	19	278	0	
LiI	0	6	0	
$LiClO_4$	0	6	0	4 [55]
$NaClO_4$	0	7	0	10
$KClO_4$	0	8	0	14
$RbClO_4$	0	9	0	19
NaSCN		46 [51]	0	87 [56]

TABLE 8

Ion-pair association constants of alkali metal salts in various solvents at 25°C calculated (this work) from the Bjerrum equation, assuming formation of contact ion-pairs

Salt	Solvent			
	PDC	TMS	DMSO	AN
LiCl	2.22	14.28	10.04	34.40
LiBr	2.01	12.97	9.24	30.77
LiI	1.72	11.51	8.21	26.95
$LiClO_4$	1.36	9.88	7.01	22.73
$NaClO_4$	0.96	8.33	5.86	19.19
$KClO_4$	0.55	6.95	4.80	16.29
$RbClO_4$	0.39	6.46	4.44	15.43

cies. This is also supported by the dramatic increase in the association constants in the series LiI < LiBr < LiCl observed in PDC and TMS, which corresponds to the increasing donor strength of the halide ions. If ion association was a consequence of electrostatic forces only, then the association constants should be much less differentiated, as shown in Table 8.

In DMSO, LiI and LiBr are fully dissociated whereas LiCl is weakly associated. This agrees with the results obtained some years ago for the relative donor strengths of various neutral and anionic bases which indicate that iodide and bromide ions in solution are weaker donors than DMSO, whereas the donor strength of the chloride ion and DMSO are comparable [57] *.

Contrary to the behaviour in PDC and TMS, LiBr and LiCl are fully dissociated in HMPA [58], although HMPA has a lower dipole moment and a much lower dielectric constant (Table 1). This is explained by the formation of tightly solvated lithium ions in HMPA as a consequence of the extraordinarily high Donor Number of this solvent. Apparently the elementary electrostatic theory is not able to predict the formation of such tightly solvated ions.

Alkali metal perchlorates are generally strongly dissociated (Table 7) owing to the low ionic potential and the weak basic properties of the perchlorate ion, which therefore acts as a weak competitive ligand for the solvent molecules.

The association constants in acetonitrile and TMS (Table 7) are of the same order of magnitude as those calculated from the Bjerrum equation

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* These measurements have been carried out in the solvent acetonitrile using vanadyl(IV)-acetylacetonate as reference acid [57]. In this study it has been pointed out that the effective donor strength of the anions depends strongly on the acceptor properties of the solvent. Fortunately, the electrophilic properties of acetonitrile are very similar to those of DMSO, PDC and TMS (Table 1) so that essentially the same order of relative donor strengths of the halide ions should exist in these solvents.

(Table 8) indicating that the cation—anion interaction is essentially electrostatic in nature. On the other hand, the association constants both in acetonitrile and TMS decrease with decreasing radius of the cation, contrary to the stability order in the gas phase. From the elementary electrostatic point of view, this trend might be explained by the (numerical) increase of the Born free energies of solvation in the series $Rb^+ < K^+ < Na^+ < Li^+$, or by a corresponding increase in the ion—dipole interactions.

From the coordination chemical point of view, this trend most probably results from additional covalent interactions between the cations and the solvent molecules which increase in the series $Rb^+ < K^+ < Na^+ < Li^+$, i.e. with increasing acceptor strength of the cations. In this context must be pointed out the remarkable relationship found by Popov [59] between the ^{23}Na chemical shifts of the sodium ion in solution and the Donor Numbers of the solvents, which shows that even in the solvation of alkali metal ions there exist small but significant contributions from covalent bonding.

In order to clarify the situation, measurements are now in progress on the association behaviour of alkali metal salts (including the perchlorates) in solvents with low donor strength, such as NB, NM and DMTF. In particular, NB and NM have similar dipolar and dielectric properties as acetonitrile, but are very poor donors (Table 1). Hence, if the solvation of the alkali metal ions was purely electrostatic in nature then the perchlorate salts should exhibit the same behaviour in NM and NB as in acetonitrile.

If, on the other hand, the stability order found in acetonitrile (or TMS) is a consequence of additional covalent interactions between the cations and the solvent molecules, then the reverse stability order should most probably be found in NM, NB or DMTF, owing to their very low donor strengths *. Qualitative measurements carried out in NM by Hartley and co-workers [62], do in fact strongly support the latter interpretation, $LiClO_4$ showing a much stronger deviation from Onsager's limiting law than $NaClO_4$.

In DMSO, the perchlorates are fully dissociated, but are associated in TMS. From the coordination chemical point of view, this is a consequence of the higher donor strength of DMSO since similar association constants would have been expected from the Bjerrum equation (Table 8). Likewise, sodium thiocyanate is associated in TMS but fully dissociated in DMSO.

The weakness of the elementary electrostatic model also follows from the association behaviour of the silver halides in DMTF (Table 9) [63]. Despite the high dielectric constant and dipole moment of this solvent (Table 1) the halides are strongly associated. The association constants increase in the series AgCl < AgBr < AgI, corresponding to the stability order expected for soft acids [64]. The experimental association constants are much higher than the calculated values apart from the reversal in stability order. Silver—

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* DMTF, which is a "soft" base, acts as a poor donor towards "hard" acids such as alkali metal ions, whereas it behaves as a very strong donor towards "soft" acids such as Ag^+ [60,61].

TABLE 9

Experimental [63] and calculated (this work) "ion pair" association constants of silver halides in dimethylthioformamide (DMTF) at 25°C. R = silver—halogen bond distances obtained from the X-ray analysis [65] of the solid adducts AgCl · $(DMTF)_2$, AgBr · $(DMTF)_2$ and AgI · DMTF; r^+ and r^- = ionic radii.

Salt	K_{ass}(exp) (mole^{1} · litre^{-1})	K_{ass}(calc) * (mole^{1} · litre^{-1})	R (pm)	$r^+ + r^-$ (pm)
AgCl	147	6.41	254	307
AgBr	194	5.96	266	321
AgI	735	5.34	280	342

* Calculated assuming contact ion-pair formation.

halogen bond distances, recently determined from an X-ray analysis of the solid adducts AgCl · $(DMTF)_2$, AgBr · $(DMTF)_2$ and AgI · DMTF [65], are considerably smaller than the sum of the crystallographic radii, indicating the occurrence of strong donor—acceptor interactions.

The influence of the dielectric constant on the position of the ion association equilibria can be deduced from Table 7 by comparing solvents with similar Donor and Acceptor Numbers. For example, the lithium halides are more strongly associated in TMS than in PDC owing to the higher dielectric constant of PDC. Likewise the association constants of the perchlorates decrease in the series acetonitrile > TMS > PDC, corresponding to the increase in the dielectric constants and dipole moments.

F. SUMMARY AND CONCLUSION

It has been shown that the association behaviour of many ionophores in nonaqueous solvents cannot usually be rationalized by purely electrostatic models. A satisfactory interpretation is possible on the basis of coordination chemical considerations by taking into account the specific nucleophilic and electrophilic properties of the solvents, which are characterized by means of empirical quantities such as the Donor Number, Acceptor Number or related parameters.

In solvents with different dielectric constants, differences in the stabilization of the ions by Born solvation must additionally be taken into account.

Attempts are now being made to arrive at a semiquantitative, or perhaps nearly quantitative, description of ion association equilibria by considering the combined influence of the donor, acceptor and dielectric properties of the solvents.

Purely electrostatic models may be successfully applied only in the case when the ions are either coordinatively saturated, such as tetraalkylammonium or tetraalkylboride ions, or exhibit only poorly developed donor or acceptor properties, such as the perchlorate ion or the higher alkali metal ions.

The results of this study support the view [9] that coordinative interactions are frequently involved in the formation of so-called "contact ion-pairs" which should therefore more logically be considered as un-ionized entities.

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