Infrared Studies of Water–Ion Interactions in Aprotic Solvents

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Abstract: The infrared and NMR spectra of HDO and MeOH at low concentration in acetonitrile (MeCN), propylene carbonate (PC), 1,1,3,3-tetramethylurea (TMU), and *N,N*-dimethylformamide (DMF) containing various salts were studied at 35 ± 2°. As many as four OH stretching bands for MeOH or HDO can be detected. Typical values for the OH frequencies are 3535, 3440, 3315, 3200 cm^{-1} in the MeOH–LiBr system, suggesting the presence of solvent-bonded, cation-bonded, anion-bonded, and solvent-shared/or solvent-separated ion complexes. Dependence of infrared spectra on the water and salt concentrations is also reported. Association constants of water and MeOH with individual ions have been estimated to ±25%; typical values are 6.5, 3.5, 1.6, for Li^+–HDO complexes and 3.4, 1.5, 1.2 for Li^+–MeOH complexes in MeCN, PC, and TMU, respectively.

The properties of electrolyte solutions are exceedingly sensitive to solvent. Electrostatic theory[1,2] predicts that the dielectric constant of the solvent has the most direct influence.[3,4] Ionic conductivity, for example, is an exponential function of the solvent dielectric constant. Recently, there has been increasing interest in a molecular approach to electrolyte solutions.[5-10] A substantial number of papers have appeared that suggest specific ion–solvent complexation plays an important role in the electrical and spectroscopic properties of ions in solution.[5-8,11-16] We might anticipate from earlier studies[5-8,12,13] that protic molecules, being potential proton donors as well as potential proton acceptors, are very likely to exhibit a strong propensity for ionic solvation. Protic solvents are usually better solvents for electrolytes than one would predict from their dielectric properties alone,[3] suggesting that they provide some level of specific interaction with ionic species.

We have used infrared spectroscopy to examine protic molecule solutes in a number of nonpolar aprotic electrolyte solutions.[7,8] We used water, methanol, and phenol as protic solutes. Infrared spectroscopy is well suited to a study of these compounds because of its sensitivity to the molecular environment of the hydroxyl group. The infrared spectra of water in organic solvents have been carefully studied.[17-21] Further, a detailed review of the infrared and Raman spectra of aqueous electrolyte solutions is also available.[22] This paper extends our studies to polar aprotic solvents and a much wider range of salts. We report direct evidence for both anionic and cationic solvation by the protic solutes. There are indications of solvent-shared and/or solvent-separated ion aggregates as well.

Methods

HDO. Falk and others[23-25] have suggested the use of HDO as a probe molecule because it produces a simpler infrared spectrum than either H_2O or D_2O. The reason for this is that the two fundamental OH or OD stretching frequencies for the isolated H_2O or D_2O molecules are close together (typical separations of ca. 100 cm^{-1}).[26] Two bands are retained when H_2O or D_2O are dissolved in most organic solvents.[17,18,20] The HDO molecule replaces the closely spaced symmetric and antisymmetric vibrations with two well-separated bands corresponding to the uncoupled OH and OD stretching frequencies: 3300–3600 cm^{-1} and 2200–2600 cm^{-1}, respectively. Another advantage of HDO is that the isotopic ratio and hence the ir absorption can be adjusted without changing the total water concentration. This permits reasonably high water concentrations and, at the same time, manageably long cell path lengths. Typical values for our experiments were: total water concentrations of 0.1 to 5 *M;* H/D ratios of 0.005 to 0.15; and cell path lengths of 0.05 to 1 mm. Isotopic dilution and path length were adjusted to produce an absorbance of 0.1 to 1 at the OH maximum. Some supplemental observations have been made using MeOH and *t*-BuOH as protic solutes. Typical concentrations were 0.1 *M*, and cell path lengths were 0.1 mm.

Salts and Solvents. Commercial reagent grade salts were used. The salts were dried exhaustively in vacuo and assayed for residual moisture by examining the OH stretching region in concentrated solutions to which no water was added. Solvents, reagent or spectroquality grade, were distilled from drying agents. All solutions were prepared in a drybox. Residual water from either solvent or salt was never more than 1% of the water used in the experimental solutions.

The presence of sharp *solvent* absorption bands in the 3300–3700 cm^{-1} required a somewhat novel compensation technique. We observed that salt and/or water influenced the position of the solvent bands. Thus the normal procedure of using HDO, salt, and solvent in the sample beam and solvent alone or salt and solvent in the reference beam produced additional bands in the difference spectrum. Instead we used salt, solvent, *and* D_2O in the reference beam. Omitting either the salt or the D_2O caused sufficient shifts of the solvent bands that good difference spectra could not be obtained. The reference solutions for MeOH or *t*-BuOH experiments were aprotic solvent plus salt.

All of the experiments were performed on a Beckman IR-9 with a variable scale expansion accessory. Wider than normal slit widths were used (ca. 1 mm) to increase the signal/noise ratio. Experiments at smaller slit widths and slow scanning speeds confirmed that the wide slits did not distort the broad OH stretching bands (half-widths ca. 50–300 cm^{-1}). Beer's law was obeyed up to about 0.5 *M* water. Above this concentration water line widths increased, presumably because of water dimer formation.[20,21] In most experiments, one fixed and one variable path length cell were used, each with CaF_2 windows. The cells were not thermostated. The ambient temperature of the cells was 35 ± 2°.

Data Analysis. In most cases the spectra to be discussed contained two or more overlapping absorption bands. While many systems showed readily apparent maxima for these bands, even a preliminary analysis requires some form of band resolution technique. We used two: a Du Pont Model 310 curve resolver and an interactive digital computer curve

Table I. Aprotic Solvent Properties and Solvent-Sensitive OH Stretching Absorption (Band I)

			OH stretching bands[c]					
			HDO			MeOH		
	Dielectric constant	Donicity[b]	ν, cm^{-1}	w, cm^{-1}	ϵ, l. mol^{-1} cm^{-1}	ν, cm^{-1}	w, cm^{-1}	ϵ, l. mol^{-1} cm^{-1}
MeCN[a]	36	14.1	3570	110	75	3540	90	125
PC[a]	69	15.1	3570	110	75	3540	110	110
Acetone	20.	17	3560			3510		
Dioxane	2.		3540	135	135			
THF[a]	7.6	20	3524	145	85	3475	120	125
TMU[a]	26		3515	105	90	3430	135	145
DMF[a]	36.7	26.6	3515	140	150	3435	155	105
HMPA[a]			3415	115	155	3337	120	180
Pyridine	12.3	33.1	3410	200	95	3313	180	105
D_2O	81	18	3400	260				

[a] Abbreviations: MeCN, acetonitrile; PC, propylene carbonate; THF, tetrahydrofuran; TMU, tetramethylurea; DMF, dimethylformamide; HMPA, hexamethylphosphoric triamide. [b] Reference 28. [c] ν is the peak frequency, w is the width at half-height, ϵ is the molar extinction coefficient, uncertainties are ±5 cm^{-1}, ±15 cm^{-1}, and ±10%, respectively.

Table II. Stretching Frequencies of Anion-Sensitive OH Band (Band III) for HDO in Aprotic Solvents[a]

	ν, cm^{-1} [b]			
	MeCN	PC	TMU	DMF
(ClO_4)[c]	(3570)[c]	(3570)[c]	(3515)[c]	(3515)[c]
Bu_4NNO_3	3440	3440		
Bu_4NI	3445	3440		
NaI	3430			
LiI	3550			
$Ba(I)_2$	3350			
$Fe(I)_2$	3340			
$Al(I)_3$	3335			
Bu_4NBr	3380	3370	3405	3405
LiBr	3330	3335	3340	3350 ± 10
Bu_4NCl	3330	3325	3330	3335

[a] Approximate concentrations were 0.2 *M* for HDO, 0.5 *M* for salts. [b] Uncertainties ±5 cm^{-1}. [c] $ClO_4^-\cdots$ water band not resolved for any cation (Bu_4N^+, Li^+, Na^+, Sr^{2+}) in these solvents, see text.

Table III. Stretching Frequencies of Cation-Sensitive OH Band (Band II) for HDO in Aprotic Solvents[a]

		ν, cm^{-1} [b]			
	Z/R[c]	MeCN	PC	TMU	DMF
Bu_4N^+[d]	0.2	(3570)[d]	(3570)[d]	(3515)[d]	(3515)[d]
$NaClO_4$	1.03	3525			
NaI	1.03	3525			
LiCl	1.47	3495	3490	3425	
LiI	1.47	3495			
LiBr	1.47	3495	3495	3435	3445
$Ba(I)_2$	1.49	3485			
$Sr(ClO_4)_2$	1.79	3480	3485		3320 ± 20
$Ca(SCN)_2$	2.02	3445			
$Mg(ClO_4)_2$	3.03	3400			
$Co(SCN)_2$	2.78	3390			
FeI_3	4.69	3315			
AlI_3	3.88	3270			

[a] Approximate concentrations: 0.2 *M* for HDO, 0.5 *M* for salts. [b] ±5 cm^{-1} unless shown. [c] *Z*, ionic charge; *R*, ionic radii in Å. [d] $Bu_4N^+\cdots$ water band not resolved for any anion (e.g., ClO_4^-, NO_3^-, I^-, Br^-, Cl^-), see text.

resolving program (using a NOVA 1220, Data General Corp.) patterned after the Du Pont instrument. Both methods used Lorentzian line shapes that are only first approximations to the true line shape.[23] The resolved bands were used to calculate equilibrium quotients as described previously.[6] There are, of course, significant uncertainties in both the band resolution and curve fitting routine for estimating equilibrium quotients. For these reasons we view the results below as semiquantitative (uncertainties ~±25% for equilibrium quotients), but we feel that the trends to be discussed are well established even if the absolute values of the equilibrium quotients may be modified at a later stage.

Results

Band Assignment. We found that a number of aprotic solvents useful for ir studies will dissolve a variety of inorganic salts (e.g., LiBr, $Ca(SCN)_2$) to the level of several tenths molar (see ref 3). These solvents include acetonitrile (MeCN), propylene carbonate (PC), dimethylformamide (DMF), and tetramethylurea (TMU). Most previous work on the ir spectra of hydroxylic solutes in aprotic electrolyte solutions was limited to a narrow range of organic cations because of solubility considerations. These early studies reported only two resolved OH absorption bands in the OH stretching region. The higher frequency band was assigned to OH···solvent interactions[17,20,21,27] because it is present in the absence of salt and its intensity decreases as the salt concentration increases. The OH stretching frequency of this band is strongly solvent dependent (Table I). In later discussion we will call this absorption band I.[43] The second band has been assigned to OH···anion hydrogen bonding.[6,8,24,27] The band is not present in the absence of salt. Its intensity increases with increasing salt concentration. Its band frequency is a strong function of anion, somewhat dependent on cation, and is weakly independent on solvent (Table II). We shall refer to this absorption as band III.[43] We note that some anions (e.g., ClO_4^-) perturb the water so slightly that a separate OH···anion band cannot be detected in the solvents used here (i.e., bands I and III are degenerate), although it can be resolved in more nonpolar solvents such as CCl_4 and $CHCl_3$.[6,8]

In addition to the two OH absorptions just discussed, most *inorganic* salt solutions show a third band (Figure 1). It is clearly due to OH absorption since its intensity is proportional to the H_2O/D_2O ratio. It is also detected when the water is replaced with MeOH, phenol, or *t*-BuOH. The band is not present in the absence of salt or hydroxylic solute. Its frequency is determined by the cation and is essentially independent of the anion. The band frequency decreases markedly as the charge/radius ratio of the cation increases (Table III). We will refer to this band as band II.[43] The band frequency is solvent dependent, with the frequency roughly parallel to that for the OH···solvent absorption (band I). Taking all these observations into account, we tentatively assign this peak to one or more water molecules in the coordination sphere of the cation. These water molecules are presumably oriented with the oxygen atoms pointed in toward the cation, so that the hydrogens are still available for hydrogen bonding to the solvent or nearby anions.

In analogy to the observations for some anions, large, univalent cations (e.g., Bu_4N^+, K^+) do not show this water

Table IV. Stretching Frequencies (cm^{-1}) of OH Bands for MeOH in Different Solvents[a,b]

	MeCN				PC				TMU			
	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4	ν_1	ν_2	ν_3	ν_4
Bu_4NI	3535	*c*	3380	*c*	3540	*c*	3375	*c*				
Bu_4NBr	3535	*c*	3325	*c*	3540	*c*	3310	*c*	3430	*c*	3290	*c*
Bu_4NCl									3430	*c*	3215	*c*
$LiClO_4$	3535	3440	*c*	*c*	3540	3455	*c*	*c*	3430	3350	*c*	*c*
$Sr(ClO_4)_2$	3535	3440	*c*	*c*	3540	3452	*c*	*c*				
LiBr	3535	3440	3315	3200	3540	3450	3315	3200	3430	3340	3272	3136
$Ca(SCN)_2$	3535	3415	*c*	*c*	3540	3420	*c*	*c*	3430	3330 ± 20	*c*	*c*

[a] Approximate MeOH concentration 0.1 *M*, salt concentration 0.4 *M*. [b] ν_1, band I assigned to MeOH-solvent; ν_2, band II assigned to MeOH-cation; ν_3, band III assigned to MeOH-anion; ν_4, band IV tentatively assigned to MeOH in solvent-shared ion pair: see text for assignments. [c] Separate bands not resolved.

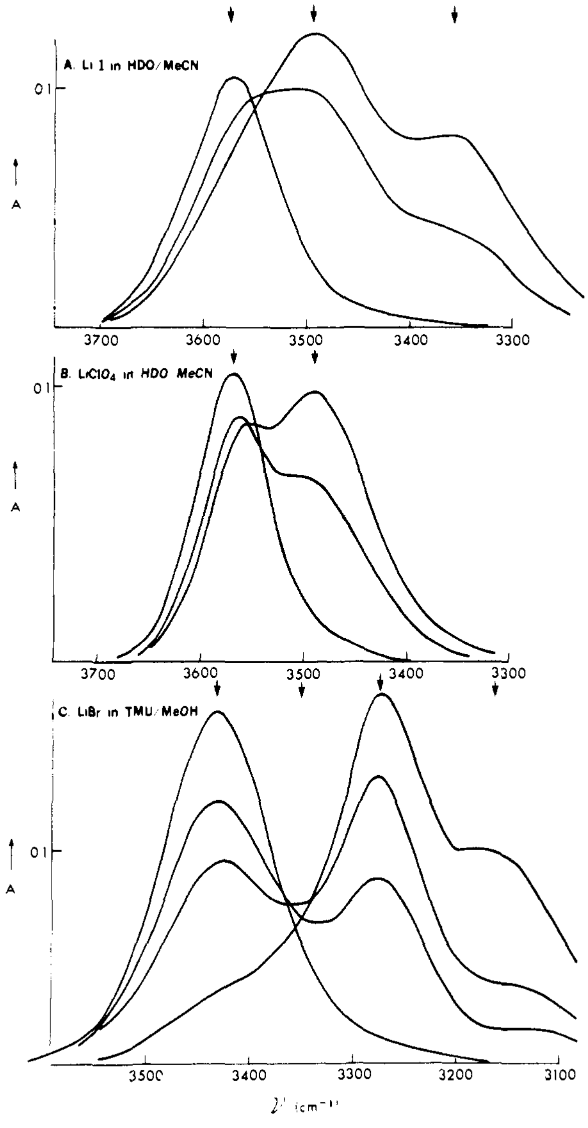

Figure 1. Ir spectra of the OH stretching region for protic solute and solvent as shown in the figure and for salts as given below. (A) LiI concentration 0, 0.09, and 0.33 *M*, HDO (0.2 *M*), H/D ratio 0.15, cell path length 0.25 mm. (B) $LiClO_4$ concentration 0, 0.07, and 0.15 *M*, HDO (0.2 *M*), H/D ratio 0.15, cell path length 0.25 mm. (C) LiBr concentration 0 (0.1), 0.18, and 1 *M*, MeOH (0.1 *M*), cell path length 0.1 mm bands assignment, see text, temperature 35 ± 2°.

band, presumably because they do not alter the OH frequency sufficiently to permit its resolution. This is apparently true for organic cations even in very nonpolar solvents.[6,8]

For some salts that were quite soluble (concentrations 0.5-1 *M*), a fourth OH peak (band IV) appeared to the low frequency side of the OH···anion signal (band III). The frequency of band IV is both anion and cation dependent and may reflect the presence of ion aggregates in which the protic solute is directly involved as in "solvent-shared" ion pairs.[29] This band is better resolved using MeOH instead of HDO as the protic solute. MeOH results for all bands are collected in Table IV.

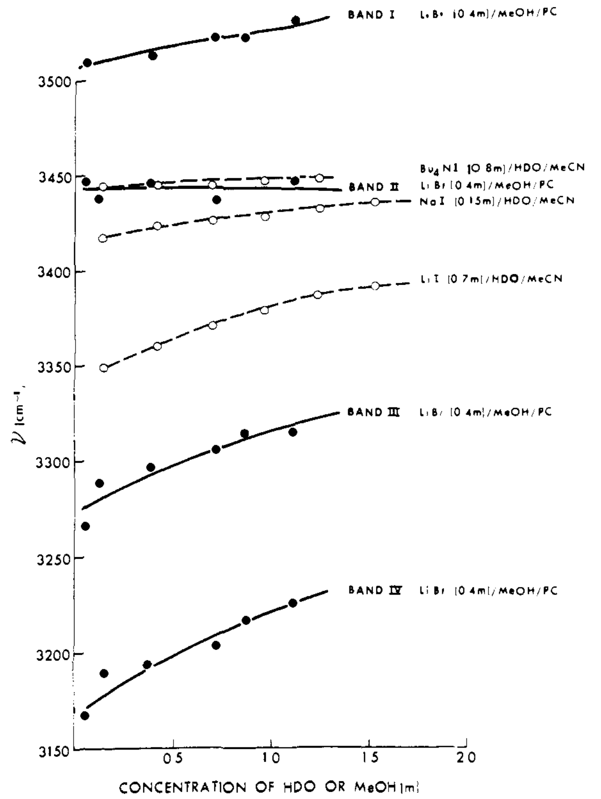

Figure 2. Frequency dependence of OH stretching bands as functions of HDO (or MeOH) concentration. Salts concentrations as shown (bands assignment, see text), temperature 35 ± 2°.

Water and Salt Concentration Effects on Band Frequencies. Of the four OH absorptions described above, only those assigned to the OH···anion interactions (bands III and IV) showed significant frequency shifts as a function of water concentration. Representative data are assembled in Table V and Figure 2. Some dependence of band frequency on cation type is also apparent. A small dependence on salt concentration, particularly at high water contents, can be noted. To summarize the data: low water concentrations, high salt concentrations, and strongly polarizing cations favor a low frequency for the OH···anion bands, while high water concentrations (ca. 1-3 *M*) and weakly polarizing cations favor a high frequency. These effects are most likely to be manifestations of ion association. Similar results were obtained using MeOH as the protic solute. We emphasize

Table V. Water Concentration Effects on the Stretching Frequencies of the Anion-Sensitive OH Band (Band III) of HDO in MeCN (see Figure 2)

	Salt concn, *M*	HDO concn, *M*							
		0.278	0.833	1.39	1.94	2.5	3.06	3.61	4.17
Bu_4NI	0.2	3446	3446	3455	3463				
Bu_4NI	0.8	3444		3446	3449	3450			
NaI	0.15	3418	3425	3428	3430	3434	3438		
LiI	0.7	3550	3361	3372	3380	3388	3393		
Bu_4NBr	0.6	3389	3401	3410		3416	3416		
LiBr	0.14	3340	3351	3380	3393	3406		3402	3406
LiBr	0.55	3345	3358	3364	3380	3386	3399	3396	3399

that the salt concentration effects are small over the concentration range accessible to us.

The *intensities* of all bands were dependent on salt, water, and solvent. The changes in band intensities were used to calculate equilibria quotients as described later.

Aprotic Solvent Effects on Band Frequencies. Most of the above experiments were performed using MeCN as the bulk solvent. Three other solvents have been explored in a preliminary way. Propylene carbonate (PC) yields quite similar results to those found for MeCN with respect to OH frequencies. All four bands described above were also found in PC under appropriate conditions of salt and water or MeOH concentration. TMU and DMF cause major shifts of the OH stretching frequencies for absorption bands assigned to the water-solvent (band I) and cation-water-solvent (band II) interactions. There is a rough equivalence in the shifts of the two sets of bands in the latter solvents, the shifts being to lower frequencies compared with MeCN and PC. Bands III and IV are not as sensitive to changing solvent.

Apparent Equilibrium Quotients. The fast intrinsic time scale associated with ir permits the detection of equilibrium species with lifetimes longer than ca. 10^{-11} sec. This is in contrast to magnetic resonance where lifetimes longer than ca. 10^{-3} sec are required for the detection of separate bands. Equilibria among short-lived complexes can thus be monitored directly by ir band intensities if the molecular environments are sufficiently distinct as to give rise to resolvable absorption bands. There are three main difficulties in the calculation of equilibrium constants. First, a precise relationship between chemical species and ir absorption bands must be determined. Second, some estimate of activity coefficients is required. Third, species concentrations must be calculated using experimentally determined extinction coefficients. Let us consider these problems in order. Identification of chemical species is not easy. Even if we limit our attention to species containing only unitary representation of water, cations, or anions, and neglect next nearest neighbor interactions, there remain a substantial number of complexes that differ in the composition of the primary coordination shell for each water molecule. For example, one can imagine the water molecule completely surrounded by aprotic solvent, by a single cation plus aprotic solvent, by a single anion plus aprotic solvent, or by ion aggregates of various types. At the present time we will restrict our analysis to the simplest formulation of the chemical equations

$$C + W \overset{K_c}{=} CW$$
$$A + W \overset{K_a}{=} AW$$

where C, A, and W are the cation, anion, and water molecules and CW and AW are monohydrated ions. We assume all species are solvated by the aprotic solvents. Hydrated ion pairs of all types are here treated as the appropriate hydrated ion. We will ignore, at this point, all activity corrections and turn to estimates of extinction coefficients for the OH absorption band. It is straightforward to obtain the overall interaction of water (or an alcohol) with a salt by monitoring the decrease in the "free water" concentration (band I). The loss of water from this band into the cation and anion hydrate bands can be followed since the extinction coefficient of the "free" peak can be determined directly in the absence of salt. This simple experiment does not determine either K_a or K_c directly. Instead such an experiment measures an equilibrium quotient, K_s, for the hydration of the *salt*

$$S + W \overset{K_s}{=} SW$$

where [S] and [SW] represent the concentrations of solvated salt and solvated salt monohydrate. The resulting equilibrium quotient, K_s, represents, to a first approximation, the sum of the two equilibrium quotients for the separate ions: K_a, K_c.[44] For those salt solutions where both the solvated cation and solvated anion bands could be resolved from the water-solvent absorption, the determination of K_s can be accomplished as described in our earlier papers[6,8] by replacing the anion concentration with the salt concentration. However, for some cations (Bu_4N^+, K^+) or anions (ClO_4^-, SCN^-), we now think that the water-solvent band is a composite containing both the "free" water and one of the hydrated ion absorptions. How does this affect the determination of *K* for the resolved ion-water interaction? If we use the loss of the water-solvent band, as before, we clearly introduce an error as some of the water signal at this frequency arises from the unresolved absorption. If one assumes that the water-solvent band and the unresolved water-ion band have equal extinction coefficients[45] our usual data analysis will provide a *K'* that is less than or equal to the proper K_a or K_c. The approximate relationship (see Appendix) between these two quantities is

$$K_r' = K_r/(1 + K_u U_0)$$

where K_r is the equilibrium quotient for the resolved species, K_r' is the *apparent* equilibrium quotient obtained using the methods of ref 6, K_u is the equilibrium quotient for the unresolved species, and U_0 is the total concentration of the unresolved species. K_u's are thought to be small,[12,30] 1 l./mol or less. U_0's are of the order of 0.1-1 *M* so that K_r' is in the range $K_r/2$ to K_r.

To summarize, even very simple formulations of the chemical species present lead to complex algebraic relationships. If we measure the *loss* of the water-solvent peak for salts with resolved ion-water bands, we can derive an equilibrium quotient for the hydrated salt, K_s, that is approximately the sum of the independent ion quotients for univalent ions. For those salts where only one ion-water band can be resolved, the *apparent* equilibrium quotient is smaller than the "correct" quotient by a factor of order 2.

The spectra (e.g., Figure 1) were decomposed using the curve resolver and/or the curve resolving programs as described. The extinction coefficients of the "free water" were measured directly (Table I); the extinction coefficients of the unresolved hydrated ion bands were taken as equal to

Table VI. Equilibrium Quotients K_r' or $(K_S)^a$ of Salt–HDO and Salt–MeOH Complexes in Different Solvents

	MeCN		PC		TMU	DMF
	K(ir)	K(NMR)	K(ir)	K(NMR)	K(ir)	K(ir)
			Salt–HDO			
Bu_4NNO_3	2		0.5			
Bu_4NI	1.5		0.9			
Bu_4NBr	7.5		4.5		1.7	0.9
Bu_4NCl	16		14			1.6
$NaClO_4$	1.15			1		
$LiClO_4$	5	7	2	4	2	
LiI	9^a	10				
LiBr	25^a	16	8^a	10	3.2^a	1.4^a
$Sr(ClO_4)_2$	25		10	12		
$Ca(SCN)_2$	85	75	22		0.5	
$Co(SCN)_2$	0.5					
			Salt–MeOH			
Bu_4NI	1.6					
Bu_4NBr	4.5		4		2.9	
$LiClO_4$	2		1		1	
$Sr(ClO_4)_2$	4.5		1.5			
LiBr	12^a		8.5^a		7.5^a	
$Ca(SCN)_2$	25		2.0			

[a] K_S, all others K_r' (see text).

those of the "free water". Water concentrations were calculated and the methods of ref 6 were used to determine the equilibrium quotients K_s and K_r' (Table VI). A small number of parallel NMR experiments were performed, where the chemical shift of the proton donor was monitored. The salt concentration dependence of the chemical shift can be used to give equilibrium quotients,[6,30] and these values are included in the table. We also made some attempts at estimating independent ion equilibrium quotients. Table VII gives these results, along with the various assumptions employed.

It is difficult to assess the overall uncertainties in the reported equilibrium quotients. Experimental limitations suggest errors of order ±25%. The various assumptions used in data analysis could lead to *systematic* errors of about a factor of 2.

The general results are straightforward. Equilibrium quotients in any given solvent increase with increasing charge density of the cation and "basicity" of the anion. Increasing the electron donor ability of the aprotic solvent acts to decrease the apparent equilibrium quotients. These effects can be large. The only salt that stands out as unusual in terms of the above summary is $Co(SCN)_2$. Its K_r' in MeCN (0.5 l./mol) is much smaller than expected from the other divalent cations (e.g., $Ca(SCN)_2$). Overall, MeOH appears to give similar results to HDO with somewhat stronger anion interactions and weaker cation solvation.

We should emphasize, at this point, that we do not distinguish between the hydration of "free" ions and the hydration of ion pairs. The apparent equilibrium quotients are not very dependent on salt concentration in the range available to us (ca. 0.1-1 *M*), so there is no simple way to determine the extent or importance of ion pairing effects from the ir data alone (see below).

Discussion

We first consider what conclusions can be drawn from the infrared work. We then turn our attention to the relationship between these results and other studies of ionic solutions.

The molecular environment of hydroxylic solutes in aprotic electrolyte solutions is clearly complex. We feel that there is substantial evidence for four types of OH hydrogen bonds in such solutions. We tentatively assign these species as:

Band I: OH···solvent
Band II: cation···OH···solvent
Band III: OH···anion
Band IV: cation···OH···anion

We note that there can be overlapping bands, particularly for the "weak" cations and anions. Thus, for example, bands I and II and bands III and IV for salts containing Bu_4N^+ cannot be resolved. Similarly, we think bands I and III and II and IV are degenerate for anions such as ClO_4^-. We discuss each band in detail below.

Band I. The basic behavior of the protic solute in the *absence* of salt fits a reasonable pattern. OH frequencies, band widths, and extinction coefficients are determined by the proton acceptor ability of the aprotic solvent. Our observations are in good agreement with previous workers in this regard.[17,18,20] The aprotic solvents can be ranked in the order of increasing proton acceptor ability: $CCl_4 < CH_2Cl_2 < CHCl_3 <$ MeCN < PC < dioxane < TMU < DMF < pyridine. Solvent dielectric constant, alone, is not a good indicator of proton acceptor ability, and it does not correlate well with the hydroxyl stretching frequencies. Gutman's donicity values[28] do somewhat better.

Of more concern to us is the direct binding of water (or MeOH) by the aprotic solvent. Some data are available (Table VIII). To a first approximation, the fraction of HDO "bound" to the solvent in binary complexes is given by $KS_0/(1 + KS_0)$ where K is the binary equilibrium constant and S_0 is the solvent molarity.[6] If we assume that PC is about the same as ethyl acetate, and that the equilibrium constants for HDO/TMU are the same as those for HDO/DMF, we find that the "free" water concentration decreases about twofold going from PC to DMF. With similar assumptions, the free MeOH concentration would change about fourfold. This reduction in "free" protic solute would act to decrease all the equilibrium quotients in Tables VI and VII by a two-fourfold factor. Thus simple competition between the aprotic solvent and the salt for the protic solute can explain most, but perhaps not all, of the solvent effects on the OH···ion interactions discussed here (see also ref 6).

Band II. We next consider the bands assigned to water–cation interactions. These absorptions have been reported previously in MeCN,[33] and some recent work suggests cation perturbation of H_2O stretching frequencies in aqueous solutions of highly charged cations.[22] The only detailed discussion of cation effects on OH stretching frequencies of which we are aware is the work of Zundel on polyanionic films.[34]

A reasonable model for our results is that these bands are due to the hydroxylic solute in the primary solvation shell of the cation, coordinated via the oxygen atom. The electric field of the cation would be expected to lower the OH vibrational frequency both by polarization of the OH bond[34] and because the polarized bond, being a better donor, interacts more strongly with the solvent.[35] The observations that OH stretching frequencies are lowered in proportion to cation electric field (Table III) and that the apparent water-cation equilibrium quotients increase in the same way (Table VI) support this simple picture. Additional support is that band II frequencies depend on the aprotic solvent in the same way as OH···solvent absorption signals (band I). We think the actual species being detected is

cation···OH···solvent

We should stress that band II is quite independent of anion (e.g., all the lithium salts we have studied in MeCN

Table VII. Equilibrium Quotients K of Separate Ion–Protic Solute Complexes in Different Solvents

Ion	MeCN/HDO				PC/HDO			TMU/HDO		
Bu_4N^+	(0.7)^a				(0.3)^a			(0.3)^a		
Na^+		1.3^a	1.35^b							
Li^{+d}	13^b	6.5^b	5.5^a	6.5^b	2.3^a	3.5^b	3.5^b	2.3^a	1.6^b	1.6^b
Sr^{2+}		33^a	30^b		11.5^a					
Ca^{2+}		115^c	90^b		33^c	30^b				
ClO_4^-	(0.7)^a				(0.3)^a			(0.3)^a		
NO_3^-	2.7^a									
I^-	2,^{a} 3^b				1^a	1.8^b				
Br^{-d}	10^a	8.5^b	10^b		5.2^a	4.4^b	7.5^b	2^a	1.2^b	2^b
Cl^-	22^a	19^b			16^a	10^b				

Ion	MeCN/MeOH	PC/MeOH	TMU/MeOH
Bu_4N^+	(0.35)^e		
Li^+	3.4^c	1.5^c	1.2^c
Sr^{2+}	4.5^c		
Ca^{2+}	19		
ClO_4	(0.3)		
I^-	1.5^c	1.3^c	
Br^-	6^c	4^c	5^c

[a] Calculated from K_C for Bu_4N^+ of 0.7 (ref 12) in MeCN, 0.3 in PC (ref. 30) and TMU (assumed as 0.3). $K_a$from $ClO_4^-$of 0.7 in MeCN (ref 12) and 0.3 in PC (ref. 30) and TMU (assumed as 0.3). [b] Calculated for increase in band II (or band III); extinction coefficients for band II (or band III) of Ca^{2+}, Sr^{2+}, Li^+, Br^-, Cl^-, I^-, Na^+ are 1.4, 1.4, 1.45, 1.2, 1, 1 times band I, respectively, as measured by the slope of the loss of band I vs. gain of band II or III. [c] Calculation from K_a for SCN^- of 0.7 l./mol. [d] Multiple values from different salts. [e] Taken as 0.5 of HDO value of ref 12 (see ref 38).

Table VIII. Equilibrium Quotients (l./mol) for Protic Solute–Aprotic Solvent Interactions

Proton donor	Proton acceptor					
	MeCN	EtAc	Dioxane	Acetone	Pyridine	DMF
H_2O^b			1.3	2.4	2.6	2.2^a
$MeOH^c$		1.4	1.5	1.8	3.0	5.5
Phenol^d	4.8	7.2	13.5	11.9	79	107

[a] 25°, CCl_4 is reference solvent, except for H_2O–DMF where 1,2-dichloroethane is used. See ref 21 for discussion of the role of the reference solvent. [b] From ref 21. [c] From ref 31. [d] From ref 32.

show a band at 3495 ± 5 cm^{-1}). Nor is this band sensitive to salt or water concentration. It remains at 3495 cm^{-1}, for example, as the LiBr concentration varies from 0.14 to 0.55 M and the water concentration varies from 0.3 to 4 M. By way of comparison, the water-anion band (band III) shifts from 3345 to 3420 cm^{-1} under the same conditions.[46]

Band III. The absorption signals we and others have assigned to OH···anion hydrogen bonding present a more complicated picture. The (decreasing) OH frequency (increasing) OH band width, and (increasing) equilibrium quotients can be used to rank the anion···protic solute interactions in analogy to the usual hydrogen bonding.[36] The familiar lyotropic series emerges.[8,37]

$$ClO_4^- < SCN^- < I^- < NO_3^- < Br^- < Cl^-$$

We have noted that the OH stretching *frequency* associated with the OH···anion complex is not particularly sensitive to solvent (Table II) but it is responsive to water concentration (Figure 2) and to cation type (Table II). The OH stretching frequency for a particular water-anion band approaches a limiting high frequency at low salt concentration (0.1 M) and high water concentration (above 1 M), and with weakly polarizing cations such as Na^+ or Bu_4N^+. Conversely, increasing salt concentrations, decreasing water concentrations, and strongly polarizing cations cause substantial low frequcy shifts. As an example, the extreme values observed for water-iodide are 3460 cm^{-1} (0.2 M $Bu_4N^+I^-$ in 2 M water/MeCN) and 3330 cm^{-1} (1 M LiI in 0.1 M water/MeCN). While the high frequencies appear to approach some limiting value for each anion type, it is not clear that a low frequency limit has been reached at the lowest water concentrations we have studied. The dependence of the band III frequencies on cation type and protic solute concentrations have not been stressed in earlier work,[6,8,27] because of the much more limited range of cations and concentrations studied.

Taken together, these findings suggest that the water-anion band cannot represent a single well-defined complex; it must include contributions from ion aggregate species as well. The complicated behavior of this band may reflect the presence of multiple hydration of anions and/or solvent separated ion pairs: (cation···solvent···OH···anion).

Band IV. The fourth OH band is usually quite broad and often cannot be directly resolved from band III. It is most easily detected using MeOH as the protic solute. Band IV increases linearly with salt concentration. It definitely grows at the expense of the "free" solute peak and may grow at the expense of band II. Its frequency depends more strongly on anion than does band III and more strongly on cation than does band II. Its solvent dependence is similar to that of band III. This general behavior is consistent with ion aggregates of the "solvent-shared" type:[29,47] cation···OH···anion. Considerably more work is required on the properties of band IV.

Comparison with Other Techniques. The ir results can be compared with a number of other studies using NMR and conductiometric techniques. Direct and indirect estimates of water-ion interactions are compiled in Table IX. The overall agreement with the results of Table VII is generally good, considering the differing assumptions and the complexity of the systems. Conductivity studies have been primarily concerned with ion association phenomena. However, some details of ionic solvation can be derived from the limiting conductances of individual ions in the aprotic solvents of interest to us. The limiting conductances of small, highly charged cations are usually found to be lower than those of anions of equivalent crystal radius.[40] In terms of Stokes radii, the anionic radii are roughly comparable in solutions and in crystals, while the cationic radii are much larger in solution.[5,40] These results suggest that the cations are strongly solvated by aprotic solvents, while the anions are not. Some evidence for anion solvation is found in MeOH and other protic solvents. A detailed study of the

Table IX. Literature Values for Equilibrium Quotients (l./mol) of Ion–Solute Complexes in Different Solvents

Ions	$MeCN/H_2O$	MeOH/MeOH	PC/H_2O	CCl/ MeOH	$CDCl_3$/ H_2O
Et_4N^+			0.3 ± 0.1[c]		
ClO_4^-	0.7[a]		0.3 ± 0.2[c]		4[e]
I^-				42[d]	
Br^-				46[d]	11[e]
Cl^-	9[a]		7	55[d]	25[e]
K^+	1[a]		0.4 ± 0.1[c]		
Na^+	2,[a] 2.3[b]	1.5[b]	1.4 ± 0.1[c]		
Li^+	14[b]	5.6 ± 0.1[b]	6.5 ± 0.3[c]		
Ba^{2+}	16[b]	8.3 ± 0.8[b]			
Sr^{2+}	45 ± 10[b]	16 ± 2[b]			
Ca^{2+}	151 ± 69[b]	37 ± 10[b]			

[a] Reference 12, conductivity method. [b] Reference 38, NMR. [c] Reference 30, unit, kg/mol, NMR. [d] Reference 39, ir. [e] Reference 8, ir.

role of protic and aprotic solvation is available through the work of Evans.[5]

The available conductivity[5,40,41] data indicate a marked degree of ion association would be expected in the solutions we have used (association constants are of order 10-100 in the *absence* of protic solute) except for propylene carbonate[42] where association is reduced. While neither the conductivity nor the ir experiments can unambiguously determine the types of nonconducting species that are present, a reasonable speculation that fits both sets of data is that the bulk of the ions are in the form of solvent-separated or solvent-shared ion pairs. As suggested above, we tentatively identify the anion sensitive ir bands as arising from water (or MeOH) in solvent-separated ion pairs for the high frequency absorption (band III) and solvent-shared ion pairs for the lower frequency band (band IV). The cation···OH···solvent peak (band II) might come as well from the solvent-separated ion pairs or might arise from a population of "free" solvated cations.[48]

In conclusion, the molecular environment of hydroxylic solutes in aprotic electrolyte solutions is clearly quite heterogeneous. The ir results suggest at least two different types of ion association are occurring, and that cation and anion hydration can be monitored independently. The decrease in water-ion interactions as the coordinating power of the aprotic solvent is increased is not surprising. Our results suggest that small but significant differences in water-ion interactions should persist in aqueous electrolyte solutions and in aqueous solutions of biological macromolecules.

Finally, we should stress that our interpretation of the infrared results has been heavily guided by the conductivity literature. It is possible that the molecular details revealed by infrared studies will require modification of our concepts of the molecular complexes that are important in the solutions we have studied.

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Appendix

Equilibrium quotients for water-salt interaction with one unresolved water-ion band. Let U and R be solvated ions and Y and X represent their monohydrated form. Assume that the water molecule associated with Y has the same infrared spectrum as that for a water-solvent complex ("free" water). We use K_u and K_r to represent the equilibrium quotients for the reactions

$$\mathrm{U} + \mathrm{W} \overset{K_u}{\rightleftharpoons} \mathrm{Y}$$

$$K_u = [\mathrm{Y}]/[\mathrm{U}][\mathrm{W}] = [\mathrm{Y}]/(U_0 - [\mathrm{Y}])[\mathrm{W}] \qquad (1)$$

$$\mathrm{R} + \mathrm{W} \overset{K_r}{\rightleftharpoons} \mathrm{X}$$

$$K_r = [\mathrm{X}]/[\mathrm{R}][\mathrm{W}] = [\mathrm{X}]/(R_0 - [\mathrm{X}])[\mathrm{W}] \qquad (2)$$

The apparent "free" water concentration, W_{app}, and the total water concentration, W_0, are related to X and Y as

$$W_{app} = W + Y, \; W_0 = X + Y + W, \; W_0 = X + W_{app}$$

The apparent degree of hydration, $\bar{n}_{app}$ is given by the following from (2)

$$n_{app} = (K_r R_0 W)/R_0(1 + K_r W) = \frac{K_r R_0 W_{app}}{(1 + K_r R_0(W_{app} - Y))R_0} - \frac{K_r R_0 Y}{(1 + K_r(W_{app} - Y))R_0}$$

Consider the limit as $W_{app} \rightarrow 0$

$$Y \cong \frac{(K_u U_0 W_{app})}{(1 + K_u U_0)}$$

and

$$\bar{n}_{app} = (K_r R_0 W_{app})/R_0 - K_r(K_u U_0)/(1 + K_u U_0)W_{app}$$

$$(K_r')_{app} = \frac{\partial \bar{n}_{app}}{\partial W_{app}} = K_r - K_r(K_u U_0)/(1 + K_u U_0)$$

or

$$K_r' = K_r/(1 + K_u U_0)$$

References and Notes

(1) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Interscience, New York, N.Y., 1959.
(2) N. Bjerrum, *K. Dan. Vidensk. Selsk., Mat. Fys. Medd.*, 7 (1926).
(3) J. Padova, "Water and Aqueous Solutions", R. A. Horne, Ed., Wiley-Interscience, New York, N.Y., 1972, p 109.
(4) S. Petrucci, "Ionic Interactions", S. Petrucci, Ed., Academic Press, New York, N.Y., 1971, p 118.
(5) D. F. Evans and M. A. Matesich, *J. Solution Chem.*, **2**, 193 (1973).
(6) R. P. Taylor and I. D. Kuntz, *J. Phys. Chem.*, **74**, 4573 (1970).
(7) R. P. Taylor and I. D. Kuntz, *J. Am. Chem. Soc.*, **92**, 4813 (1970).
(8) R. P. Taylor and I. D. Kuntz, *J. Am. Chem. Soc.*, **94**, 7963 (1972).
(9) M. Swarcz, "Carbanion's Living Polymers, and Electron Transfer Processes", Interscience, New York, N.Y., 1968.
(10) M. L. Friedman, ref 3, p 723.
(11) M. K. Wong, W. J. McKinney, and A. I. Popov, *J. Phys. Chem.*, **75**, 55 (1971).
(12) M. K. Chantooni and I. M. Kolthoff, *J. Am. Chem. Soc.*, **89**, 1582 (1967).
(13) R. D. Green and J. S. Martin, *J. Am. Chem. Soc.*, **90**, 3669 (1968).
(14) J. F. Coetzee and J. J. Campion, *J. Am. Chem. Soc.*, **89**, 2513 (1967).
(15) G. J. Janz, M. J. Tait, and J. Meier, *J. Phys. Chem.*, **71**, 963 (1967).
(16) D. E. Irish, *J. Chem. Phys.*, **46**, 378 (1967, *Ibid.*, **50**, 2262 (1969).
(17) D. N. Glew and N. S. Rath, *Can. J. Chem.*, **49**, 837 (1971).
(18) S. C. Mohr, W. D. Wilk, and G. M. Barrow, *J. Am. Chem. Soc.*, **87**, 3048 (1965).
(19) E. T. P. Jwili and T. A. Ford, *Adv. Mol. Relaxation Processes*, **5**, 75 (1973).
(20) D. R. Cogley, M. Falk, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **77**, 2407 (1973).
(21) S. D. Christian, A. A. Taha, and B. W. Gash, *Q. Rev., Chem. Soc.*, **24**, 20 (1970).
(22) R. E. Verrall, "Water—A Comprehensive Treatise", Vol. 3, F. Franks, Ed., Plenum Press, New York, N.Y. 1972, p 211.
(23) M. Falk and T. A. Ford, *Can. J. Chem.*, **44**, 1699 (1969).
(24) G. Brink and M. Falk, *Can. J. Chem.*, **48**, 3019 (1970).
(25) K. A. Hartman, *J. Phys. Chem.*, **70**, 270 (1966).
(26) D. Eisenberg and W. Kauzmann, "The Structure Properties of Water", Oxford University Press, London, 1969.
(27) A. Allerhand and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1223 (1963).
(28) U. Mayer and V. Gutman, *Struct. Bonding* (*Berlin*), **12**, 113 (1972).
(29) T. R. Griffiths and C. R. Symoms, *Mol. Phys.*, **3**, 90 (1960).
(30) D. R. Cogley, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **75**, 1477 (1971).
(31) E. D. Becker, *Spectrochim. Acta.*, **17**, 436 (1961).
(32) T. D. Epley and R. S. Drago, *J. Am. Chem. Soc.*, **89**, 5770 (1967).
(33) A. Z. Gadzhiev, *Zh. Prikl. Spektrosk.*, **10**, 534 (1969); A. Z. Gadzhiev and I. S. Pominov, *Tepl. Dvizhenie Mol. Mezhmol. Vzaimodeistvie Zhidk. Rastvorakh, Mater. Mezhvuz. Nauchn. Konf., 2nd, 1966*, 129 (1969).
(34) G. Zundel, "Hydration and Intramolecular Interactions", Academic Press, New York, N.Y., 1969.
(35) P. A. Kollman and I. D. Kuntz, *J. Am. Chem. Soc.*, **94**, 9236 (1972).
(36) G. Pimentel and A. L. McClellan, *Annu. Rev. Phys. Chem.*, **22**, 347 (1971).
(37) P. H. von Hippel and T. Schleich, "Structure and Stability of Biological Macromolecules", S. N. Timasheff and G. D. Fasman, Ed., Marcel Dekker, New York, N.Y., 1969, p 417.
(38) G. W. Stockton and J. S. Martin, *J. Am. Chem. Soc.*, **94**, 6921 (1972).

(39) P. C. Dmivedi and C. N. Rao, *Spectrochim. Acta, Part A*, **28**, 1535 (1970).

(40) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1962).

(41) P.G. Sears, E. D. Wilhoit, and L. R. Dawson, *J. Phys. Chem.*, **59**, 373 (1955); E. G. Taylor and C. A. Kraus, *J. Am. Chem. Soc.*, **69**, 1731 (1947); M. J. McDowell and C. A. Kraus, *J. Phys. Chem.*, **60**, 129 (1956).

(42) M. L. Jansen and H. L. Yeager, *J. Phys. Chem.*, **77**, 3081 (1973).

(43) Absorption bands have been numbered from high to low frequency. In a few cases, there are sufficiently large frequency shifts so that some band positions are out of normal order. These occasions will be noted as they arise.

(44) Writing out explicit expressions for K_s: $K_s = [SW]/[S][W]$; $[SW] = [CW] + [AW]$; $[CW] = K_c[C][W]$; $[AW] = K_a[A][W]$. Substituting these quantities into the expression for K_s, we find $K_s = K_cC_0/[S] + K_aA_0/[S]$, where C_0 and A_0 are the stoichiometric concentrations of the ions. Consider the limiting case of a small degree of hydration of the salt. Then $[S] \rightarrow S_0$, the stoichiometric salt concentration, and $K_s = nK_c + mK_a$, where n and m are the moles of cations and anions per mole of salt. Thus, under the special conditions of low water concentration (e.g., only monohydrate formation) and low salt concentration, we expected K_s to be the weighted sum of the independent ion equilibrium quotients.

(45) This assumption is not unreasonable for weakly perturbed systems.[17]

(46) One can rationalize the difference in sensitivity to counter-ion since anions, in general, are much more polarizable than are cations. The OH stretching frequency is presumably responsive to the (small) changes in electron distribution induced via such polarization effects.

(47) In our experiment, these species would be more correctly designated "solute shared".

(48) We note in passing that these bands move to lower frequency as the cation polarizing ability increases. Bands arising from water molecules associated with anions in *contact ion pairs* would be expected to show an increasing frequency because the cations would remove electron density from the vicinity of the protons of the water/methanol molecules. This behavior has not been observed in our experiments. Nor is the concentration of contact ion pairs expected to be significant in the aprotic solvents we used.

Equilibrium Studies by Electron Spin Resonance. XII. The Relationship between Charge Density and Ion Pair Dissociation Determined by the Use of *g* Values

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Abstract: The addition of salt (KI) to solutions of the free anion radical of 2,6-di-*tert*-butylbenzoquinone, anthraquinone, or naphthaquinone results in a decrease in the observed *g* value due to the formation of ion pairs. The observed *g* value for the anion radical in solution containing a given amount of KI has been found to be a weighted average between that for the ion pair and that for the free ion in pure hexamethylphosphoramide. The equilibrium constant for the dissociation of the ion pair to form the free anion radical has been algebraically related to the observed *g* value leading to the first determination of ion pair dissociation constants by the use of *g* values. Further, the enthalpy of ion pair dissociation has been related to the rate of change of the *g* value with respect to temperature (dg/dT). To use the time averaged *g* values the rate of ion pair dissociation and formation must be fast on the ESR time scale. This has been found for semiquinones, for which the INDO calculated electron density on the oxygen atoms available for ion pair formation is less than 6.459. When the oxygen electron density is larger than this value the free ion and ion pair are observed simultaneously. Not only are the kinetics of ion pair dissociation affected by the INDO calculated charge densities, but the K_{eq} decreases with increasing charge density. However, the anthrasemiquinone system yields a K_{eq} that is too small according to this trend. This suggests a greater polarizability of this system.

The thermodynamic parameters controlling the dissociation of ion pairs have been determined by the use of three basically different ESR techniques. These include methods based upon ESR coupling constants,[2] line widths (relaxation times),[3] and line intensities (spin concentrations).[4,5] Here we describe a new technique that can be used for the determination of the thermodynamic parameters controlling the dissociation of ion pair (β) to form free ion (α) and the solvated cation, eq 1. This technique is based upon the use of *g* values.

$$\beta \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \alpha + M^+ \qquad (1)$$

Since the first accurate measurements of *g* values for organic anion radicals in solution, several workers have noticed changes in *g* values with temperature.[6-8] Recently it has been reported that the *g* value dependence upon temperature is at least partially due to ion pairing.[9] The *g* values for the ion pair and free ion of durosemiquinone in dimethoxyethane have been accurately determined for a series of counterions, and for all cases the *g* value for the free ion is larger than that for the ion pair.[4]

It has been shown for a series of substituted nitrobenzene anion radicals[3,5a] and for benzosemiquinones[5b,2c] that the free ions exist simultaneously with the ion pairs in hexamethylphosphoramide (HMPA) containing a small amount of alkali metal salt. Further, the equilibrium between the ion pair and the free ion can be described by the two-site model expressed in eq 1. In the absence of the alkali metal salt many of these anion radicals are free of ion pairing in HMPA.[2c,3,5,10] For the substituted nitrobenzene systems the equilibrium constant for eq 1 increases with the σ value of the para substituent.[5a] This indicates that the ability of the ion pair to dissociate is inversely proportional to the charge density on the NO_2 group. For the semiquinone anion radicals ion pairing takes place at the site of the oxygen atoms.[2c,5b,7,11] Here we wish to report upon the relationship between the charge density on the oxygen atoms determined by INDO open shell calculations and the thermodynamic parameters of ion pair dissociation. This work should allow new insight as to the importance of coulombic attraction between the anion radical and the cation in ion pairing. Other factors, such as solvation and polarization of the anion, will also be discussed.