# Hydration of Ions in Dipolar Aprotic Solvents

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**Abstract:** Interactions between water at low concentrations and 1:1 electrolytes have been studied in four dipolar aprotic solvents of increasing basicity: sulfolane (TMS) < acetonitrile (AN) < propylene carbonate (PC) ≪ dimethyl sulfoxide (DMSO). The experimental methods used involved solubility, proton nmr, vapor pressure, and calorimetric determinations. Results are interpreted in terms of hydration constants $K_1$ and enthalpies $\Delta H_1$ for the 1:1 complexes with $Cl^-$, $NO_3^-$, $H^+$, $Li^+$, $Na^+$, and $Ag^+$ ions in most of the cited solvents. The $K_1$ values are somewhat insensitive to the nature of the ion, except for $H^+$, but sensitive to the nature of the solvent. For DMSO all $K_1$ values are particularly low, thus accounting for this solvent retaining its dipolar aprotic character in the presence of some water. The values of $K_1(Cl^-)$ are directly proportional to Henry's law constants for water in each solvent. The enthalpy changes $\Delta H_1$ are low and nearly equal for the replacement of one AN or PC molecule by one water molecule in the solvation shells of $Cl^-$ and $Li^+$. It follows that the strong solvation of $Cl^-$ by bulk water is due to cooperative effects. Comparison of the $\Delta H_1$ values with gas-phase ionic hydration enthalpies shows contrasting behavior for negative and positive ions. The calculated values of the solvation enthalpies of the hydrated ions are discussed. Some comments are made regarding the acidity of $H_3O^+$ in solvents.

The comparison of rates or equilibrium constants of ionic reactions in water with those in dipolar aprotic (DPA) solvents has received a great deal of attention.[1] The observed solvent effects have been discussed in terms of changes in ionic solvation energies.[1,2] Relatedly, the behavior of binary mixtures of water–DPA solvents offers further interest; a first step in understanding ionic solvation in these complex media is to study water-poor binary mixtures. A knowledge of ionic hydration in such aqueous media also throws light on the role of water as a solvent, since the self-association of water in DPA solvents may be reduced or eliminated according to its concentration and the basicity of the solvent.[3] It can then be advanced that ionic hydration in aqueous DPA solvents bears some relation to the now well-documented hydration of ions in the gas phase.[4]

The present work was undertaken to study the interactions between water at low concentrations and 1:1 electrolytes, mainly perchlorates and tetraethylammonium salts, in four DPA solvents, in order to provide thermodynamic data for a comparison of the hydration of $Cl^-$, $NO_3^-$, $H^+$, $Li^+$, $Na^+$, and $Ag^+$ in these aqueous media. The ions $NO_3^-$, $Li^+$, $Na^+$, and $Ag^+$ were selected to afford an eventual comparison with hydration in molten nitrates and concentrated nitrate aqueous solutions. The DPA solvents chosen, sulfolane (TMS), acetonitrile (AN), propylene carbonate (PC), and dimethyl sulfoxide (DMSO) have different donor groups and increasing basicities in the order TMS < AN < PC ≪ DMSO. The experimental methods used to obtain the 1:1 ionic hydration constants or to redetermine previously reported ones,[5-8] involved solubility, proton nmr, and water vapor pressure measurements to test the validity of the interpretations. In addition, calorimetric determinations were carried out to yield some of the corresponding ionic hydration enthalpies and to establish some relation with ionic gas-phase hydration data.[4]

## Experimental Section

**Materials.** The purification method for sulfolane from Shell was given earlier.[9] Fisher reagent DMSO was treated according to a method reported previously.[10] Purification of PC from Eastman Kodak is described elsewhere.[3] Eastman Kodak AN, low in residual water, was further treated with 4A molecular sieves. Water contents of the resulting solvents as determined by Karl Fischer titration were $4.7 \times 10^{-3}$, $1.0 \times 10^{-2}$, $3.9 \times 10^{-3}$ and $1.0 \times 10^{-3}$ M, respectively. Tetraethylammonium perchlorate, tetraethylammonium chloride, and perchlorates of lithium, sodium, and silver were from Eastman Kodak, Baker, and Smith, respectively. These salts were dried in vacuum desiccators over phosphorus pentoxide. Sodium and potassium chlorides used were Fisher certified reagents. Tetraethylammonium nitrate was prepared by a method adapted from Kraus[11] and twice recrystallized from pure ethanol. Trifluoromethanesulfonic acid from 3M Co. had a purity of 99.5%. Tetraphenylarsonium chloride (Koch-Light) was purified by neutralization and extraction to give a product assaying 8.38% chloride (calcd 8.47%).

**Solubility Measurements.** Measurements at 25° were made on NaCl and KCl in DMSO solutions containing variable amounts of water determined by the Karl Fischer method. Solubilities were obtained by potentiometric titration. The composition of the saturating salt was also analyzed and no solvates were found after 2 weeks of equilibration, although the existence of KCl 0.66 DMSO has been reported.[12]

**Proton Magnetic Resonance.** Nmr measurements were carried out with 60 MHz and 100 MHz JEOL spectrometers, at 22 and

24°, respectively, as determined by the method of Van Geet.[13] Solutions of 0.1 $M$ water with electrolyte concentrations between 0 and 0.7 $M$ were prepared by mixing electrolyte–DPA solvent and aqueous DPA solutions of known concentrations. Resonance signals of hydroxyl protons, measured with reference to those of DMSO and AN methyl protons, to the center of PC methyl doublet, and to those of TMS $\beta$-methylene protons, are reported in parts per million relative to internal tetramethylsilane.

**Vapor Pressures.** The apparatus and procedure for vapor pressure experiments at 25° are similar to those given before,[3] except that concentrations of water after measurement were checked by Karl Fischer titrations. Slight discoloration of silver perchlorate solutions was observed in PC as was also noted by Yeager;[14] this salt interfered in the Karl Fischer titration so that concentrations were obtained from the weights. Test solutions were 0.5 $M$ electrolytes with variable concentrations of water mostly below 1 $M$; a series of 1 $M$ sodium perchlorate PC solutions was also studied.

**Calorimetry.** The calorimetric procedure and apparatus have been previously described.[15] The heats of mixing known weights of water with 27 ml of 0.5 $M$ electrolytes–PC, AN, and TMS and 0.7 $M$ electrolytes–DMSO (including $HCF_3SO_3$ a strong acid[10]) were determined for concentrations of water less than 0.15 $M$ (0.5 $M$ for electrolytes–DMSO). From 3 to 8 determinations were made for each electrolyte at 25°.

## Results and Discussion

**Solubility.** The total solubilities of NaCl and KCl in aqueous DMSO are given below as a function of water concentration.

| Water concentration ($M$) | 0.000 | 0.010 | 0.34 | 0.67 | 1.01 |
|---|---|---|---|---|---|
| NaCl solubility ($\times 10^2\ M$) | 8.4 | 8.5 | 9.6 | 10.5 | 11.5 |
| KCl solubility ($\times 10^2\ M$) | 2.48 | 2.49 | 2.76 | 3.06 | 3.38 |

These data were treated by a simple method based on that used by Kolthoff[5] and Pawlak.[16] It is assumed on the basis of stronger solvation by bulk water[2] that $Cl^-$ first hydration constant $K_1$ is larger than those of $Na^+$ and $K^+$; the following equation holds at low water concentrations

$$f^2 S^2 = K_{sp}[1 + K_1(H_2O)] \tag{1}$$

where $f$ is the mean ionic activity coefficient, $S$ the ionic solubility, $K_{sp}$ the solubility product in dry DMSO, and $(H_2O)$, the free water concentration which can be approximated to that of total water. The values obtained for $K_1 \sim 0.7$ (NaCl) and $\sim 0.6$ (KCl) are in good agreement and suggest $K_1 \leq 0.1$ for $Na^+$ and essentially complete dissociation. Butler's data[17] on solubility of AgCl in aqueous DMSO when similarly treated give $K_1 \sim 0.5$, neglecting $Ag^+$ hydration.

Our use of the solubility method to study ionic hydration was limited as there are few suitable sparingly soluble salts which are strong electrolytes. Although data can be treated when dissociation is incomplete by the use of conductivity measurements,[5] the method may become somewhat cumbersome as evidenced by our study of the solubility of alkali nitrates in aqueous PC.[18] Attempts to measure LiF and NaF solubilities in aqueous DMSO and PC proved unsuccessful: solubilities are very low ($\sim 2.7 \times 10^{-4}\ M$ for NaF in dry DMSO), the salts appear incompletely dissociated and some solutions are unstable.

**Nmr.** Hydroxyl proton nmr was used[6–8] to study ionic association with water in DPA solvents. Assuming fast exchange between unbound and water bound to an $I^{\pm}$ ion, the proton average signal $\delta$ is given by

$$\delta = \delta_0 \frac{[H_2O]}{C_{H_2O}} + \delta_1 \frac{[I^{\pm}H_2O]}{C_{H_2O}} \tag{2}$$

where $C_{H_2O}$ is the total water concentration and $\delta_0$ and $\delta_1$ the chemical shifts respectively of unbound water and bound water in the 1:1 hydrate. This equation combined with the mass balance relations allows the calculation of $K_1 = [I^{\pm}H_2O]/[I^{\pm}][H_2O]$ and $\delta_1$. The experimental results giving $\delta - \delta_0$ against the salt concentration $C_{I^{\pm}}$ for $C_{H_2O} \sim 0.1\ M$ are plotted in Figure 1 for $Cl^-$, $NO_3^-$, and $Ag^+$ in AN and for $Cl^-$ and $Li^+$ in DMSO. Analysis of such data by an extrapolation method[6,7] was later criticized.[8] The treatment adopted here was that preferred by Martin[8] and is based on the Scott–Benesi–Hildebrand equation

$$\frac{[I^{\pm}]}{\delta - \delta_0} = \frac{[I^{\pm}]}{\delta_1 - \delta_0} + \frac{1}{K_1(\delta_1 - \delta_0)} \tag{3}$$

which is solved by iteration. The hydration constants $K_1$ and $\delta_1 - \delta_0$ for $Cl^-$ and $NO_3^-$ in AN are given in Table I,

**Table I.** Hydration Constants (1. $mol^{-1}$) and ($\delta_1 - \delta_0$) (ppm) from Nmr at Room Temperature

| | TMS ($\delta_0 = 2.57^a$ ppm) | | AN ($\delta_0 \approx 2.20^a$ ppm) | | PC ($\delta_0 = 2.38^a$ ppm) | | DMSO ($\delta_0 = 3.35^b$ ppm) | |
|---|---|---|---|---|---|---|---|---|
| | $K_1$ | $\delta_1 - \delta_0$ | $K_1$ | $\delta_1 - \delta_0$ | $K_1$ | $\delta_1 - \delta_0$ | $K_1$ | $\delta_1 - \delta_0$ |
| $Cl^-$ | 7.5 | 1.08 | $8^a$ | $1.28^a$ | $5.4^d$ $8^{a,i}$ | $1.96^e$ $1.3^{a,i}$ | $0.6^h$ | 0.4 |
| $NO_3^-$ | | | $0.9^a$ | $1.30^a$ | $1.2^a$ | $1.2^a$ | | |
| $Li^+$ | 7 | 1.52 | $16^c$ | $1.48^b$ | $9.5^d$ | $1.49^e$ | $\sim 0.2^{a,f}$ | 1.49 |
| $Na^+$ | | | $2.5^c$ | $0.89^b$ | $1.8^d$ | $0.94^e$ | | |
| $Ag^+$ | | | $\sim 0.1^g$ | 1.72 | $4.8^a$ | 1.72 | | |

$^a$ This work. $^b$ Reference 8 (35°). $^c$ Converted into values at 25° from ref 8 using our hydration enthalpies. $^d$ Recalculated from ref 6 using eq 3, density of solvent, and our hydration enthalpies. $^e$ Recalculated from ref 6 (36°) using eq 3. $^f$ Calculated on the assumption that $\delta_1 - \delta_0 = 1.49$ ppm. $^g$ Calculated on the assumption that $\delta_1 - \delta_0 = 1.72$ ppm. $^h$ From the solubility method. $^i$ Using tetraphenylarsonium chloride instead of $NEt_4Cl$ (ref 6) to give more easily interpreted nmr spectra.

as well as those for $Cl^-$, $Li^+$, and $Na^+$ in PC, recalculated from previous results[6] or obtained from new data. For $Cl^-$ and $Li^+$ in DMSO and $Ag^+$ in AN, the nearly linear variation of $\delta$ with $C_{I^{\pm}}$ does not allow the simultaneous calculation of $K_1$ and $\delta_1 - \delta_0$. However, since according to Martin,[8] $\delta_1 - \delta_0$ values for a cation hydrate

$$M^+ \cdots O \overset{H}{\underset{H}{\diagdown}}$$
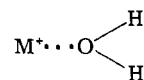
should be independent of the solvent, $K_1$ therefore could be calculated for $Li^+$ and $Ag^+$ using $\delta_1 - \delta_0$ values obtained for another solvent. Conversely for $Cl^-$, taking $K_1 = 0.6$ from the stability method led to $\delta_1 - \delta_0 = 0.4$ ppm, i.e., $\delta_1 = 3.7$ ppm. Martin[8] has asserted that $\delta_1$, the proton chemical shift of an anion-hydroxylic molecule complex, should be independent of the solvent. Our $\delta_1$ values obtained for

$$Cl^- \cdots H - O \overset{}{\underset{H}{\diagdown}}$$
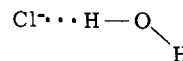
(3.5 ppm (AN), 3.7 ppm (PC), 3.7 ppm (DMSO), and 3.6 ppm (TMS)) support Martin's assertion.

As pointed out by a referee, there is in our interpretation an assumption that the role of an $I^{\pm}$ ion in altering the water proton chemical shift $\delta_0$ arises only when $H_2O$ is in contact with $I^{\pm}$. This assumption indeed is also implicit in previous work.[6–8] The fact that $\delta - \delta_0$ is less than 0.05 ppm in 0.7 $M$ solutions of $NEt_4ClO_4$ and of some other electrolytes[7] in the four DPA solvents lends some support to our assumption which is further strengthened by the results of the vapor pressure method.
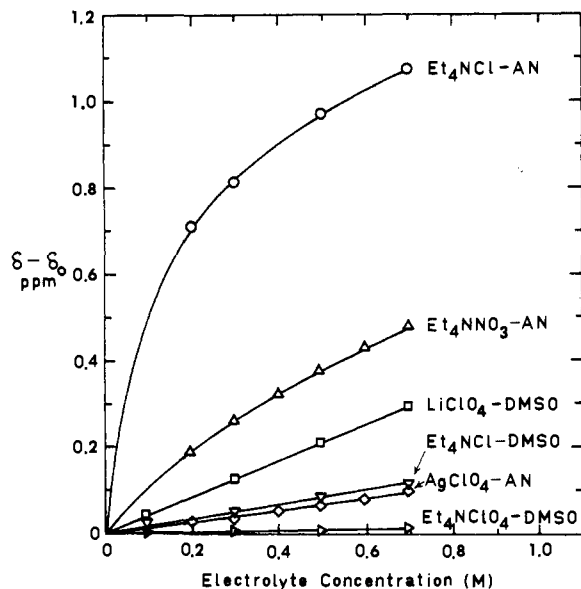
**Figure 1.** Chemical shifts of 0.1 $M$ water in aqueous electrolyte-AN or -DMSO solutions as a function of electrolyte concentration.

**Vapor Pressures.** Extensive determinations of water vapor pressure were made on $H_2O$-electrolyte-PC systems in order to provide an independent method of study. The partial vapor pressures of water were obtained by substracting the very small vapor pressure of pure PC (0.05 mm) from the measured total pressure at 25°. These pressures $p_{H_2O}$ are given in Figure 2 as a function of $C_{H_2O}$, the total water concentration, for pressures below 8 mm. Assuming that the lowering of water vapor pressure observed for each electrolyte results from hydration of the smaller ion, then for a given pressure, free and bound water concentrations were calculated. From these values, $\bar{n}$, the average number of water molecules bound to one central ion was computed. Finally the stepwise hydration constants $K_1$ and $K_2$ were calculated by using a treatment described in the text of Rossotti.[19]

The obtained $K_1$ and $K_2$ values are summarized in Table II. In this analysis of the data, it is tacitly assumed that the

**Table II.** Ionic Hydration Constants (1. mol⁻¹) in PC and TMS Calculated from Water Vapor Pressures at 25°

| $M$ | $I^{\pm}$ | $K_1$ | $K_2$ |
|-----|-----|-----|-----|
| | PC | | |
| 0.5 | Na⁺ | 2.1 | 1.7 |
| 1.0 | Na⁺ | 2.6 | 1.3 |
| 0.5-1.0 | Na⁺ | 2.1ᵃ | 1.2ᵃ |
| 0.5 | Li⁺ | 6.5 | 4.6 |
| 0.5 | Ag⁺ | 5.0 | 1.4 |
| 0.5 | Cl⁻ | 11.5 | 3.2 |
| 0.5 | NO₃⁻ | 2.1 | 1.2 |
| 0.5 | ClO₄⁻ | 0.2 | |
| | TMS | | |
| 0.5 | Li⁺ | 4.5 | 3.1 |
| 0.5 | Cl⁻ | 8.2 | 2.8 |

ᵃ Calculated on the assumption that $\log f_{H_2O} = -0.04 C_{NaClO_4}$.

water activity coefficient $f_{H_2O}$ has the value 1, *i.e.*, that there is no salting effect on water. There are unfortunately very few literature data on salting effects on nonpolar or polar molecules by electrolytes in nonaqueous solvents. A reference[20] indicates that $O_2$ solubility in PC is unchanged by 1 $M$ LiClO₄ but the accuracy of the data is low. Although the lowering of $p_{H_2O}$ over 0.5 $M$ NEt₄ClO₄ solu-
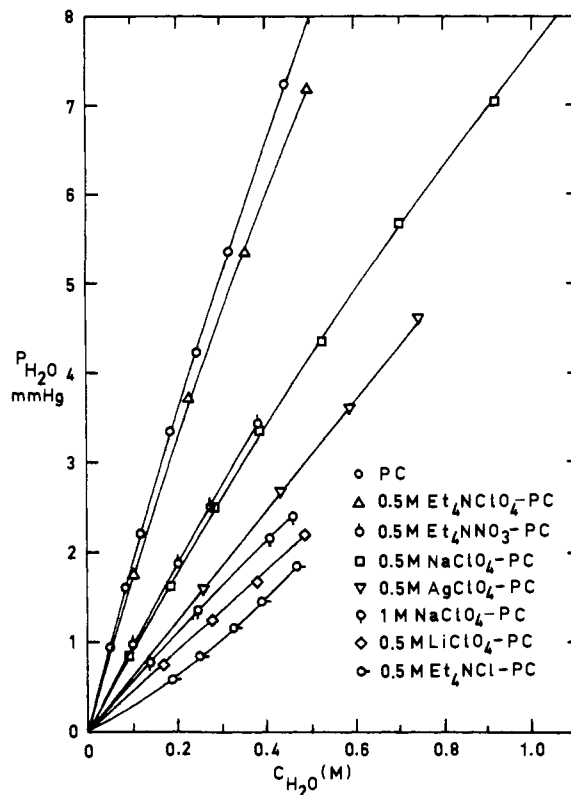


**Figure 2.** Vapor pressures of water for aqueous electrolyte-PC solutions as a function of water concentration at 25°.

tions may be interpreted in terms of weak hydration of $ClO_4^-$, with $K_1 \sim 0.2$, in fair agreement with nmr results,[6] it could alternatively be explained by a salting effect on water with a calculated 0.08 salting-in coefficient. Likewise, the difference between both sets of $K_1$ and $K_2$ values listed in Table II for 0.5 and 1.0 $M$ NaClO₄ solutions disappears by assuming a salting-in coefficient and taking log $f_{H_2O} = -0.04 C_{NaClO_4}$. At this point it is not possible to. favor either weak ionic hydration or salting-in of water, so that the discussion which follows will be limited to that of $K_1$ values, and the lowest values are to be considered only approximate. It must be pointed out that in the interpretation of the nmr data, it is also tacitly assumed that $f_{H_2O}$ as well as $K_1$ do not change when the salt concentration is varied from 0.1 to 0.7 $M$. The vapor pressure method would thus appear preferable over the nmr method as data are obtained at constant salt concentration. The relatively small influence of NEt₄ClO₄ on $p_{H_2O}$ brings some justification in the use of perchlorate and tetraethylammonium salts to study hydration of small cations and anions respectively as was done by other workers.[6-8]

Some vapor pressure measurements were made on the systems $H_2O$-salt-DMSO with 0.7 $M$ Et₄NCl, Et₄NClO₄, LiClO₄, KClO₄, and Ca(ClO₄)₂, but the total pressures were comparable to the vapor pressure of pure DMSO, so that no accurate water partial pressures could be calculated by difference. The $K_1$ and $K_2$ values for Cl⁻ and Li⁺ obtained from measurements on the systems $H_2O$-0.5 $M$ NEt₄Cl (and LiClO₄)-TMS are included in Table II. We note that the experimental ratios $K_1/K_2$ deduced from data in Table II appear to be somewhat lower for Li⁺ and higher for Cl⁻ than the statistical ratios 2.7 and 2.4 corresponding to coordination numbers 4 and 6, respectively.

The hydration constants $K_1$, as obtained by the various methods, in the four DPA solvents are summarized in Table III for relevant ions. The water vapor partial pressures

Table III. Hydration Constants (1. mol⁻¹) and Water Vapor Partial Pressures (mm) of 1 $M$ H₂O Solutions at 25°

| I±: | TMS^a | | AN | | PC | | DMSO |
|---|---|---|---|---|---|---|---|
| H+: | ~10^{6.0 e} | | ----106^f---- | | Slow^h | | 0.5^d |
| | Vp^a | Nmr^a | Nmr | Solub^c | Vp^a | Nmr | |
| Li+ | 4.5 | 7 | 16^b | ~3 (?) | 6.5 | 9.5^b | ~0.2^a (nmr) |
| Na+ | | | 2.5^b | 2 | 2.1 | 1.8^b | ≤0.1^a (solub) |
| Ag+ | | | ~0.1^b | | 5.0 | 4.8^a | |
| Cl- | 8.2 | 7.5 | 8^a | 9 | 11.5 | 8^a | 0.6^a (solub) |
| NO₃⁻ | | | 0.9^a | 2 | 2.1 | 1.2^a | |
| pH₂O | 11.5^a | | 10.9^a | | 18.5^a | | 0.53^a |

^a This work. ^b From data in Table I. ^c Reference 5. ^d Reference 7. ^e P. Pichet, Ph.D. Dissertation, Université de Montreal, 1973. ^f Reference 31. ^g At 30°. ^h Slow hydrolysis of solvent.

$p_{H_2O}$ linearly extrapolated from dilute aqueous solutions to a 1 $M$ water concentration are also given. Considering the weak hydration, the values of the equilibrium constants $K_1$ obtained by the three different methods are in fair agreement. Two methods were used to yield $K_1$ for each ion in TMS, AN, and PC. The vapor pressure and nmr methods used for TMS and PC involved measurements on 0.5 $M$ and 0–0.7 $M$ electrolyte solutions, respectively. The agreement of the results supports the previously stated assumptions inherent to each method and also suggests that if there is ion pairing in these perchlorate and tetraethylammonium salt solutions it is limited. This latter point is strengthened by the results of the solubility method for AN involving low electrolyte concentrations, results which compare favorably with the nmr ones. Furthermore, our recent conductivity and solubility study of hydration of alkali nitrates in PC,[18] made at low concentrations and with due regard here to extensive ion-pair formation, gave the following global hydration constants: NO₃⁻ + Li⁺ (8.9); NO₃⁻ + Na⁺ (4.9); and NO₃⁻ + K⁺ (2.9). These values compare favorably with the individual hydration constants obtained from the vapor pressure method: NO₃⁻ (2.1), Li⁺ (6.5), Na⁺ (2.1). It therefore appears that ion-pair formation between ClO₄⁻–Li⁺, -Na⁺, -Ag⁺ and NEt₄⁺-Cl⁻, -NO₃⁻ plays no important part in the four DPA solvents studied. In this respect, results of current spectroscopic studies[21] (mainly ³⁵Cl⁻, ²³Na⁺, and ⁷Li⁺ nmr) of possible ion pairing should prove of great interest particularly with the salts and solvents we studied, LiClO₄ and NaClO₄, and TMS, AN, PC, where ion pairing is likely to be higher. In AN it would seem that contact ion-pair formation in 0.2–1.0 $M$ solutions is negligible for NaClO₄, small for LiClO₄, but strong for Mg(ClO₄)₂.[21b]

Our $K_1$ values for the hydration of the anions Cl⁻ and NO₃⁻ listed in Table III are seen to increase in the order DMSO < AN ~ TMS < PC, $i.e.$, the order of increasing water activity or water vapor pressure in the solvents. The influence of water activity on Cl⁻ solvation in binary water–AN and water–DMSO mixtures has already been remarked upon.[22] Actually the fairly close proportionality between $K_1$ and $p_{H_2O}$ means that $\Delta G$ (solv) for the reaction Cl⁻ (solv) + H₂O(g) = Cl⁻H₂O(solv) is independent of the solvent, $i.e.$, that $\delta\Delta G_{tr}$, the difference between the free energies of transfer of Cl⁻ and Cl⁻H₂O between a pair of DPA solvents, is nearly constant. Similar results have been obtained for other anion pairs Cl⁻–AgCl₂⁻ [23] and I⁻–I₃⁻.[24] The low values of the hydration constants in DMSO for H⁺, Cl⁻, and presumably larger anions explains why the presence of water in this solvent has little influence on the dissociation of acids[10] and brings some justification to the use of 1 $M$ H₂O–DMSO as a nearly aprotic medium to carry out some anion–molecule reactions.[25] Turning to the influence of the solvent on the hydration constants $K_1$ for the cations listed

in Table III, it is apparent that strong specific interactions between cation and solvent, such as those of Ag⁺ with AN, and those for Li⁺ with solvents other than AN, preclude a close relationship between $K_1$ and $p_{H_2O}$ such as that for the anions which do not interact specifically with the solvent. Nevertheless, when expressed in kilocalories per mole, the $\delta\Delta G_{tr}$ of I⁺ and I⁺H₂O between two DPA solvents for the cations studied are still relatively low, less than 2.5 kcal mol⁻¹. In the case of H⁺, the trend of the hydration constants $K_1$ reflects in some measure the basicity order of the solvents, deduced from estimated values[26] of the solvation enthalpy of the gaseous proton: TMS (−245) < AN (−247) < PC (−252) ≪ DMSO (−268 kcal mol⁻¹).

**Calorimetry.** The heats of mixing water with TMS, PC, AN, and DMSO were found to be 1.63 ± 0.02 (30°), 1.93 ± 0.02, 1.98 ± 0.02, and −1.29 ± 0.01 kcal/mol of water, respectively, at infinite dilution. When the solvents contain Et₄NClO₄, the heat of mixing of water is unchanged for PC (1.96) and AN (1.98) but is slightly less exothermic for DMSO (−1.20). This latter change may reflect variations of the salting-in coefficient of water with temperature. For the other electrolytes, the enthalpy change on mixing water with the electrolyte–DPA solvent was taken as the sum of two contributions: the enthalpy of mixing water with the DPA solvent (or NEt₄ClO₄–DMSO) and the hydration enthalpy of the smaller ion. From our values of the hydration constants, $K_1$, the concentrations of bound water were estimated and the corresponding ionic hydration enthalpies $\Delta H_1$ calculated. Results are given in Table IV together

Table IV. Ionic Hydration Enthalpies (kcal mol⁻¹) at 25°

| | H⁺ | Li⁺ | Na⁺ | Ag⁺ | Cl⁻ | NO₃⁻ |
|---|---|---|---|---|---|---|
| | H₂O(solv) + I±(solv) = I±H₂O(solv) (ΔH₁) | | | | | |
| TMS | −11.4^a | −3.0 | | | −2.6 | |
| AN | | | −2.4 | −1.6 | ~0.4 | −2.1 | −1.8 |
| PC | | | −2.4 | −1.2 | −2.2 | −2.7 | −1.4 |
| DMSO | {−1.2^b / −1.5^c | ~−0.8^b / ~−1.6^c | | | −0.1^b / −0.5^c | |
| | H₂O(g) + I±(solv) = I±H₂O(solv)^d (ΔH(solv)) | | | | | |
| TMS | −20.3^a | −11.9 | | | −11.5 | |
| AN | | | −10.9 | −10.1 | ~−8.1 | −10.6 | −10.3 |
| PC | | | −11.0 | −9.8 | −10.8 | −11.3 | −10.0 |
| DMSO | {−13.0^b / −13.3^c | ~−12.6^b / ~−13.3^b | | | −11.9^b / −12.2^c | |
| | H₂O(g) + I⁻(g) = I±H₂O(g)^e (ΔH(g)) | | | | | |
| | −165 | ~−34 | −24.0 | | −13.1 | −12.4 |
| | H₂O(l) + I±(g) = I±(w)^f (ΔH_w) | | | | | |
| | −261 | −124 | −97 | | −113 | −87 |

^a Unpublished results of J. Charbonneau at 30° using HSbCl₆ as strong acid. ^b Calculated on the basis of enthalpy of mixing water with DMSO, −1.29 kcal mol⁻¹. ^c Calculated on the basis of enthalpy of mixing water with 0.7 $M$ NEt₄ClO₄–DMSO, −1.20 kcal mol⁻¹. ^d Heat of vaporization of water taken as 10.5 kcal mol⁻¹ at 25°. ^e Reference 4. ^f Reference 27.

with the enthalpy values $\Delta H$(solv) for the related hydration reactions H₂O(g) + I±(solv) = I±H₂O(solv), the gasphase hydration enthalpies $\Delta H$(g) as reported by Kebarle,[4] and the ionic solvation enthalpies in bulk water $\Delta H_w$.[27]

Looking first at the influence of the solvent, we find that for any ion other than H⁺ and Ag⁺, the $\Delta H$(solv) values vary but little, although for Cl⁻ the change of $\Delta H$(solv) is larger than that of the corresponding $\Delta G$(solv), indicating some compensating entropy contribution. Next we see that in AN or PC the hydration enthalpies $\Delta H$(solv) depend little on the ion I± except for Ag⁺. Thus the enthalpy changes are nearly the same for the replacement of one solvent molecule by one water in the solvation shell of Cl⁻ and Li⁺, al-

though Cl⁻ is more strongly solvated by bulk water than by DPA solvents while Li⁺ does not appear to prefer water.[2] The strong solvation of Cl⁻ by bulk water is therefore due to cooperative effects absent in dilute aqueous DPA solvents. Interestingly, the data of Kebarle[28] on gas phase solvation of Cl⁻ by water and AN also suggest that preference of water over AN only takes place for a large number of solvating molecules. In the media studied, preferential hydration, *i.e.*, formation of a strong bond to water, is limited to that of H⁺ in the weakly basic solvent TMS where binding of one water gives some $-10$ kcal mol⁻¹ which can be compared to $-16$ kcal mol⁻¹ for the heat of transfer of H⁺ from TMS to bulk water.

We now turn to a comparison of the enthalpy values $\Delta H(\text{solv})$ and $\Delta H(g)$ for a given ion I±. It is apparent from the data in Table IV that when I is an anion, $\Delta H(g)$ is only slightly more exothermic than $\Delta H(\text{solv})$ whereas when I is a cation $\Delta H(g)$ is much higher than $\Delta H(\text{solv})$. Actually, the difference $\Delta H(g) - \Delta H(\text{solv})$ is equal to $\Delta H_s(\text{I}±) - \Delta H_s(\text{I}±\text{H}_2\text{O})$, *i.e.*, the difference in solvation enthalpy of I± and I±H₂O in the solvent S. We can therefore calculate the solvation enthalpy $\Delta H_s$ of I±H₂O from our results and $\Delta H_s$ values for I±. These latter values are deduced from the corresponding ionic solvation enthalpy in bulk water $\Delta H_w$, and the transfer enthalpy from water to solvent,[2] this transfer being based on an extrathermodynamic assumption.

For the various solvents, the solvation enthalpy of Cl⁻H₂O is only 1 to 2.5 kcal mol⁻¹ less than that of Cl⁻. On account of ion sizes alone, this difference appears low compared to the estimated 10 kcal mol⁻¹ difference between the solvation enthalpies of ClHCl⁻ and Cl⁻ in TMS.[15] Assuming that related Cl⁻HOH and ClHCl⁻ are not too different in size, it could then be suggested that the stronger solvation (9 to 8 kcal mol⁻¹) of Cl⁻HOH over that of ClHCl⁻ is due, at least in part, to H bonding of Cl⁻HOH with the dipolar aprotic solvent. We can also attempt to compare the enthalpy of solvation of Cl⁻H₂O in a DPA solvent such as DMSO and bulk water. Taking the solvation enthalpy of Cl⁻ as $-82$ and $-87$ kcal mol⁻¹ in DMSO and water[2] respectively, we calculate for Cl⁻H₂O from the data in Table IV the corresponding values $-81$ and $-84$[29] kcal mol⁻¹. The hydrated chloride ion would then interact less favorably with DMSO than with bulk water. This argument was advanced by Stengle[22] to explain ³⁵Cl⁻ nmr results which indicated the lack of strong preference of Cl⁻ for water in water–DMSO mixtures.

In contrast to the small differences between the solvation enthalpies $\Delta H_s$ of Cl⁻ and Cl⁻H₂O, the differences between $\Delta H_s$ of I⁺ and I⁺H₂O, as deduced from the data in Table IV, are large and decrease from H⁺ to Li⁺ and Na⁺. We consider first the case of H⁺ and H₃O⁺. Taking $-261$, $-268$, and $-245$ kcal mol⁻¹ for the solvation enthalpy of the gaseous proton in water, DMSO,[26] and TMS,[26] respectively, we calculate for the solvation enthalpy of H₃O⁺, $-106$, $-116$, and $-100$ kcal mol⁻¹ in water, DMSO, and TMS, respectively. These results imply that H₃O⁺ is more strongly solvated by DMSO than it would be by water. The solvation enthalpies of K⁺, an ion whose size is close to that of H₃O⁺, are $-85$ and $-83$ kcal mol⁻¹ in DMSO and TMS,[2] respectively, compared with the above $-116$ and $-100$ kcal mol⁻¹ for H₃O⁺. These large differences suggest that H₃O⁺ is strongly H bonded to basic solvent molecules and would help to explain why H₃O⁺ is a relatively weak acid in DPA solvents, and also in bulk water, in spite of the very low proton affinity (basicity) of gaseous water molecules ($-165$ kcal mol⁻¹). We can comment further on the acidity of H₃O⁺ and H⁺ in DPA solvents by considering AN, whose gas-phase proton affinity is known,[32] $-186$ kcal

mol⁻¹. We estimate the solvation enthalpy of H₃O⁺ in AN as $-102$ kcal mol⁻¹ by taking $-247$ kcal mol⁻¹ for the solvation enthalpy of H⁺ in AN[26] and assuming $\Delta H(\text{solv}) = -20$ kcal mol⁻¹ for H₂O(g) + H⁺(AN) = H₃O⁺(AN) on the basis of the corresponding TMS value. In contrast, the hypothetical solvation enthalpy of protonated AN and HAN⁺ would be calculated as $-69$ kcal mol⁻¹, using $-8$ kcal mol⁻¹ for the heat of vaporization of AN. Thus, even though H₃O⁺ is a stronger acid than HAN⁺ in the gas phase, the order is reversed in bulk AN, and this reversal would be accounted for by a much stronger solvation of H₃O⁺ than of HAN⁺ by AN. Although the calculation of the enthalpies of solvation of HS⁺ in the bulk solvent S is somewhat arbitrary, the fact remains that the difference between the heat of protonation of S in the gas phase and the heat of solvation of the gaseous proton in the bulk solvent S is large for water ($-165$ and $-261$ kcal mol⁻¹) and small for AN ($-186$ and $-247$ kcal mol⁻¹) implying much stronger stabilization of the solvated proton in water than in AN. It is not without significance that Kebarle[33] has recently shown that the heat of binding successive water molecules to H⁺ in the gas phase, in accordance with the *ab initio* calculations made by Newton,[34] decreases fairly continuously, while for dimethyl ether Me₂O there is a dramatic drop in $\Delta H$ after binding the first two molecules to H⁺. This has been attributed to blocking of H bonding past the structure H(Me₂O)₂⁺. A similar pattern could be expected for the binding of AN to H⁺ and then would support our views.

Returning to Table IV, we cannot expect, in view of the part played by H bonding, the solvation enthalpies of other cations to relate to those of H⁺ and H₃O⁺. For instance, while K⁺ follows H⁺ in binding AN more strongly than water in the gas phase,[28] the solvation enthalpy of K⁺ in bulk AN is presumed to be larger than in bulk water while we have seen that the reverse holds for H⁺. Our data give the following solvation enthalpy values $\Delta H_s$ (kcal mol⁻¹) in PC, 101 (Li⁺H₂O), 83 (Na⁺H₂O), and an estimated 75 (K⁺H₂O). Were the gas-phase hydration enthalpy of Ag⁺ available, it would be of interest to calculate $\Delta H_s$ for Ag⁺H₂O in view of the large solvation enthalpy of Ag⁺, the high value of the chemical shift difference $\delta_1 - \delta_0$ found in PC, and the unusual effect of Ag⁺ on the water proton nmr resonance in bulk water.[35] Finally, it is to be noted that while K⁺ is better solvated than its isoelectronic ion Cl⁻ in PC ($-83$ against $-80$ kcal mol⁻¹) the opposite is true of K⁺H₂O and Cl⁻H₂O ($\sim-75$ against $-78$ kcal mol⁻¹).

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# Exciplexes and Electron Donor–Acceptor Complexes in the 9,10-Dicyanoanthracene and Alkylnaphthalene Systems

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**Abstract:** The fluorescence and absorption spectra of electron donor–acceptor complexes between 9,10-dicyanoanthracene and alkyl-substituted naphthalenes in a nonpolar solvent were observed below about 125°K, while the exciplex fluorescence was observed from room temperature to about 160°K. The fluorescence maxima and lifetimes of both exciplex (room temperature) and EDA complex (77°K) and the dipole moments in the fluorescent state of the exciplex markedly increase with decreasing ionization potential of the electron donor. The fluorescence and excitation spectra of the EDA complexes at 77°K indicate that CT absorption bands lie in the same wavelength region as the $^1L_a$ band of the electron acceptor. Fluorescent states of the exciplex and the EDA complex previously proposed to be identical are discussed.

Electron donor–acceptor (abbreviated to EDA) systems are classified as EDA complexes (stable in the ground state) and exciplexes (stable only in the excited state).[1,2] Recent laser photolysis demonstrates that the transient absorption spectra of the exciplex and the EDA complex are essentially identical with the absorption spectra of the anion radical of the electron acceptor molecule in the EDA system.[3] Numerous experimental results and theoretical considerations have led to the conclusion that the fluorescent state of the exciplex may be identical with that of the corresponding EDA comlex, while their Franck–Condon excited states should be different from each other. However, few cases of exciplex and EDA complex fluorescence in the same EDA system have been reported,[4] and no direct comparison of the exciplex and the EDA complex has been made.

The previous paper of this series reported the fluorescence and absorption spectra of the EDA complex at low temperature in nonpolar solutions such as 3-methylpentane (MP) of 9,10-dicyanoanthracene (DCA) and 2-methylnaphthalene (2-MN), which showed the exciplex fluorescence at room temperature, and discussed the experimental evidence for an identical fluorescent state of the exciplex and the EDA complex.[5] On the other hand, two different fluorescent states were suggested for the intramolecular interaction in the (9,10-dicyanoanthracene)-(CH₂)₃-(naphthalene) systems (DCAN) in the nonpolar solvent from temperature dependences of their lifetimes and quantum yields.[6,7] The electronic interaction producing the difference in the fluorescent states of the exciplex and the EDA complex was ascribed to the forbidden internal or geometrical conversion from the Franck–Condon excited states to an

identical fluorescent state by a steric factor concerned with trimethylene.

This paper describes the further investigation of the fluorescent states of the exciplex and the EDA complex between DCA and various alkyl-substituted naphthalenes. The fluorescence maxima ($\lambda_{max}$) and lifetimes ($\tau$) of both exciplex and EDA complex and the dipole moments in the fluorescent state of the exciplex show parallel increases with decreasing ionization potential (IP) of the electron donor. Continuous changes of $\lambda_{max}$ and $\tau$ from room temperature to 77°K were observed in the exciplex and EDA complex of the DCA and acenaphthene (AcN) system. Furthermore, the determination of the fluorescence and excitation polarizations and the absorption spectra at 77°K demonstrated that the charge-transfer (CT) band in the DCA–AcN system lies at longer wavelengths than that of the $^1L_a$ band of DCA and in the EDA complexes with other alkylnaphthalenes in almost the same region as that of DCA. On the basis of the observation of these distinct CT absorption bands and the behavior of the fluorescent states of the exciplex and the EDA complex reported here, the fluorescent states of the exciplex and the EDA complex are discussed.

## Experimental Section

Purifications of materials and solvents were described in previous papers.[5-7] Commercial zone refined samples of naphthalene (Tokyo Kasei) were used after recrystallization (two times) from ethanol. Acenaphthene, 1,5-dimethylnaphthalene, and 2,3,5-trimethylnaphthalene were purified by chromatography (silica: benzene–hexane) and recrystallized six or seven times from ethanol. Determinations of the fluorescence and absorption spectra and fluorescence lifetimes have been described previously. For determination of the fluorescence (excitation) polarization, two polarizers