

also served to measure the probe temperature, these shifts previously having been calibrated against the methanol nmr thermometry data of Van Geet.²⁵ Where necessary all data were related to $t = +38^\circ$. For the gas shifts of the reference materials, these were mixed with some ethane and measured internally; the possible error due to different van der Waals shifts of gaseous reference and ethane is estimated to be less than -0.1 Hz at the low pressures employed. All reference compound solutions were measured at four concentrations (2 to 10%) and graphically extrapolated to zero concentration. A Varian A-60A spectrometer was used throughout. Audio side-band techniques were used to ensure accurate line positions (usually ± 0.1 Hz, but somewhat larger for some of the steroid methyl groups which showed unresolved long-range coupling). Molecular susceptibilities of $\chi_M = -54.85 \times$

10^{-6} and $\chi_M = -59.30 \times 10^{-6}$ for benzene and chloroform, respectively, were used.²⁶ Densities²⁷ were calculated for the temperature prevailing at each experiment. It was assumed that the volume susceptibilities of CDCl_3 and CHCl_3 are the same, which is corroborated by the density data of CDCl_3 .²⁸

Acknowledgment. The financial assistance of the National Research Council and of the Province of Saskatchewan for a Summer Temporary Employment grant (R. K.) is gratefully acknowledged.

(26) Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. 2, Part 10, 6th ed, Springer Verlag, Berlin, 1967.

(27) "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928.

(28) M. H. Earing and J. B. Clarke, *J. Amer. Chem. Soc.*, **73**, 769 (1951).

(25) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

Proton Nuclear Magnetic Resonance Study of Diamagnetic Cation Association with Hydroxylic Substrates. Interpretation of Ionic Molal Shifts in Methanol and Water

Gerald W. Stockton and John S. Martin*

Contribution from the Department of Chemistry, The University of Alberta, Edmonton, Alberta, Canada T6G 2G2. Received March 2, 1972

Abstract: Association constants and hydroxyl proton nmr shifts have been measured for one-to-one complexes in acetonitrile of six diamagnetic cations with six hydroxylic substrates, including water and methanol. Their values follow the trend appropriate to a simple electrostatic association of the cation with the oxygen of the substrate. Molal shifts, Δ_m , of small cations in methanol and water may be adequately accounted for by a model which takes explicit account of nearest-neighbor interactions only. It leads to an equation of the form $\Delta_m = (nM/1000)(\Delta_c + \Delta_h)$, where n is the solvation number, M the molecular weight of the solvent, Δ_c the cation complex shift, and Δ_h a desolvation shift characteristic of the solvent. n appears to have a value near six for small and/or polyvalent cations. Δ_h has a value of about 1.5 ppm for cations in methanol at -69° and water at $+25^\circ$. It decreases with increasing temperature, and presumably reflects the amount of hydrogen bonding in the solvent. Deviations from the predicted behavior by Rb^+ and Cs^+ , and the molal shifts of the larger halide ions, are most plausibly interpreted in terms of a disordered primary solvation shell, so that the effective solvation numbers of these ions are less than the number of nearest-neighbor solvent molecules. It may be possible to interpret the desolvation shift in terms of structure making by small cations and structure breaking by large anions.

Hydroxylic solvents, in particular water and the alcohols, are the principal media of ionic chemistry. Thus their mechanisms of ionic solvation are of great significance. Nuclear magnetic resonance can follow a hydroxylic molecule through the solvation process, since the shielding of the hydroxyl proton is extremely sensitive to the associations which distinguish the isolated, bulk liquid, and solvated states. It has been observed that, when an ionic salt is added to water or methanol, at most temperatures only a single time-averaged OH signal is observed, which shifts with concentration.¹ In the limit of low concentration, the molal shifts have been shown to be additive in the ions.¹⁻³

It is reasonable to postulate that when ions are added to a hydroxylic solvent, those solvent molecules which interact with the ions undergo a change of state characterized by at least two effects: partial desolvation

(that is, separation from one or more nearest-neighbor molecules) and polarization by the ion. It would be desirable to separate the net time-averaged shielding change caused by the ion into two corresponding terms. If these could be evaluated, then it would be possible to investigate secondary effects. For example, it has been postulated that structure-making and structure-breaking phenomena must be invoked to account for the molal shifts of ions in methanol³ and water,⁴ though the significance of these effects has been questioned.⁵

It is possible to observe 1:1 association of ions with hydroxylic substrates in an inert solvent.⁶⁻⁸ If the desolvation effect is small, or if it can be evaluated, then the direct ion-molecule polarization shift is accessible to experimental observation. Ormondroyd, *et al.*,⁷

(4) J. C. Hindman, *J. Chem. Phys.*, **36**, 1000 (1962).

(5) J. Davies, S. Ormondroyd, and M. C. R. Symons, *Trans. Faraday Soc.*, **67**, 3465 (1971).

(6) R. D. Green, J. S. Martin, W. B. Cassie, and J. B. Hyne, *Can. J. Chem.*, **47**, 1639 (1969).

(7) S. Ormondroyd, E. A. Phillipott, and M. C. R. Symons, *Trans. Faraday Soc.*, **67**, 1253 (1971).

(8) D. R. Cogley, J. N. Butler, and E. Grunwald, *J. Phys. Chem.*, **75**, 1477 (1971).

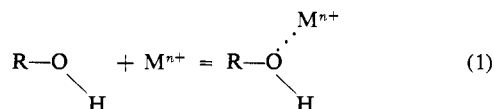
(1) J. N. Shoolery and B. J. Alder, *J. Chem. Phys.*, **23**, 805 (1955).

(2) H. G. Hertz and W. Spalthoff, *Z. Elektrochem., Ber. Bunsenges. Phys. Chem.*, **63**, 1096 (1959).

(3) R. M. Hammaker and R. M. Clegg, *J. Mol. Spectrosc.*, **22**, 109 (1967).

have related the polarization shifts in halide ion-methanol complexes to the corresponding molal anion shifts in bulk methanol. We have applied the method to the study of association of group I and II cations with water and alcohols in perdeuterioacetonitrile.

The experiment is performed as follows. To solutions containing tracer quantities (*ca.* 0.1 *M*) of the substrate, increasing amounts of a suitable salt of the cation are added. These conditions are chosen to favor 1:1 association.



It is found that only the substrate hydroxyl proton signal is significantly affected by the added salt. It shifts to lower shielding, but remains sharp, thus indicating rapid equilibration of free and complexed substrate. Analysis of the dependence of substrate shielding on salt concentration yields an association constant and a shielding shift on complex formation.

Perchlorate salts were used to minimize anion effects. Acetonitrile was the "inert" solvent. It is available in perdeuterated form, which does not obscure the spectral region of interest. It is chemically inert to these systems; if well-purified materials were used, there was no evidence of reaction or decomposition over a period of several months. It is known to solvate hydroxyl protons,⁹ thus reducing self-association of the substrate. It dissolves adequate amounts (to *ca.* 1 *M*) of the salts but solvates cations relatively weakly.¹⁰ (Dimethyl sulfoxide, on the other hand, solvates cations so strongly that no substrate shifts were perceptible on addition of the salts.)

Nitriles are known to cause significant shielding shifts of solutes, arising from specific interactions.^{11,12} These arise partly from magnetic anisotropy. The possibility thus arises that a substantial desolvation shift may accompany the replacement of acetonitrile by an ion, which is implicit in eq 1. We shall present evidence that this effect is insignificantly small in the case of cation complexes, though it contributes substantially to anion complex shifts. Thus the observed one-to-one cation complex shifts in acetonitrile may be taken as representative of the cation-substrate direct interaction.

Experimental Section

Materials. Stohler Isotopic Chemicals perdeuterioacetonitrile (99% ²H) was distilled from freshly opened P₂O₅, collecting the middle 90% over 4A molecular sieve. Tetramethylsilane (TMS) was added before sample preparation to serve as an nmr internal reference.

Nmr Specialties tetramethylsilane was refrigerated over 4A molecular sieve before use.

Baker reagent grade acetonitrile was distilled twice from P₂O₅ and then from CaH₂, collecting the middle 80% each time and finally storing over 4A molecular sieve.

Reagent grade alcohols were soxhlet extracted with 4A molecular sieve for 24 hr, the middle 60% being collected and stored over 4A molecular sieve.

(9) S. C. Mohr, W. D. Wilk, and G. M. Barrow, *J. Amer. Chem. Soc.*, **87**, 3048 (1965).

(10) R. G. Bates in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N. Y., 1969, pp 89-93.

(11) P. J. Berkeley and M. W. Hanna, *J. Phys. Chem.*, **67**, 846 (1963).

(12) P. J. Berkeley and M. W. Hanna, *J. Amer. Chem. Soc.*, **86**, 2990 (1964).

The sample of purified water was supplied by Dr. H. B. Dunford. It had been passed over cation- and anion-exchange resins, distilled three times from alkaline permanganate, and finally distilled straight.

The calcium and strontium perchlorates were hexahydrates, and the barium salt was the trihydrate; they were dehydrated by heating at 100° on the vacuum rack, gradually increasing to 200° over several days. The lithium, sodium, and magnesium salts were obtained labeled "anhydrous." They were dried by heating at 200° on the vacuum rack.

All of the perchlorate salts were then dissolved in a minimum of acetonitrile. The heat of solution in most cases caused the solvent to boil and the hot solutions were filtered through previously dried Whatman's No. 1 papers to remove slight residues. The solutions were cooled and the crystals separated by filtration. Occluded solvent was removed by pumping the salts on the rack, and they were finally dried by heating at 200° for several days.

All materials were stored in the drybox; 100-MHz nmr spectra of the solvents and concentrated acetonitrile solutions of the salts were used to confirm the absence of significant residual water. The salts contained no chloride detectable by the silver nitrate test.

Preparation of Samples for Nmr. All materials except water were handled in a specially equipped glove box. The nitrogen atmosphere was constantly exposed to fresh P₂O₅ and was cycled using a small gas pump, which bubbled the nitrogen through H₂SO₄ and over NaOH pellets. The glove box was kept slightly above atmospheric pressure.

All weighings were done inside the glove box on a Cahn DTL millibalance. Solids were weighed directly in 1-ml volumetric tubes. Solvent was added to dissolve the solids and the liquids were added from 10-μl syringes. Solvent was then added to make the solutions up to the calibrated volume. The solutions were mixed and transferred to 5-mm o.d. medium wall nmr tubes fitted with auxiliary stopcocks to exclude air. The tubes were connected to the vacuum rack, the solutions degassed by freezing and pumping, and the tubes sealed.

Nmr Spectra. Most were obtained on a Varian HA-100 spectrometer; the rest on a HA-60. All spectra were at ambient probe temperature, 35 ± 1°. Line widths were <1 Hz at salt concentrations below 0.5 *M*, and <2 Hz in all cases. The fully coupled OH proton spectrum appeared in all cases, demonstrating that intermolecular OH proton exchange was slow, and thus that the samples were free of significant acidic or basic impurities.

Line positions were measured to 0.1 Hz by setting the frequency sweep at resonance, adjusting the radiofrequency field to avoid saturation, and measuring the frequency difference between the sweep and lock oscillators. All chemical shifts are reported as shieldings; that is, a positive shift is upfield and represents increased nuclear shielding. In some cases, overlap of strongly coupled multiplets required computer simulation in order to obtain accurate chemical shifts.

Observations

Analysis of Ion-Molecule Association. In the case of rapid exchange of a substrate molecule between the free form S and the complex C with an ion I, the observed population averaged shielding σ will be given by

$$\sigma = \frac{[S]}{C_S} \sigma_S + \frac{[C]}{C_S} \sigma_C \quad (2)$$

C_S is the made-up substrate concentration. The 1:1 molar association constant, K , is defined as

$$K = [C]/[S][I] \quad (3)$$

We define the shift, Δ , and the complex shift, Δ_c , as

$$\Delta = \sigma - \sigma_S \quad (4)$$

$$\Delta_c = \sigma_C - \sigma_S \quad (5)$$

and note that

$$C_S = [S] + [C] \quad (6)$$

$$C_I = [I] + [C] \quad (7)$$

where C_I is the made-up salt concentration. Equations

Table I. Equilibrium Constants (l. mol⁻¹) of Cation-Substrate Complexes, with the Substrate at 0.1 M in Acetonitrile at 35 ± 1°

Substrate	Na ⁺	Li ⁺	Ba ²⁺	Sr ²⁺	Ca ²⁺	Mg ²⁺
H ₂ O	2.3 ± 0.1	14 ± 1	16 ± 2	45 ± 16	151 ± 69	Large
MeOH	1.5 ± 0.2	5.6 ± 0.1	8.3 ± 0.8	16 ± 2	37 ± 10	300 ± 100
EtOH	1.5 ± 0.1	5.7 ± 0.3	5.7 ± 0.4	10 ± 2	19 ± 4	140 ± 80
<i>n</i> -BuOH	1.6 ± 0.2	5.2 ± 0.6	4.2 ± 0.2	7.3 ± 0.6	22 ± 6	150 ± 70
<i>i</i> -PrOH	1.1 ± 0.2	4.2 ± 0.2	2.8 ± 0.1	3.8 ± 0.2	8.2 ± 0.7	66 ± 30
<i>t</i> -BuOH	0.7 ± 0.1	3.2 ± 0.2	1.2 ± 0.1	1.0 ± 0.1	1.7 ± 0.1	2.8 ± 0.2

2 to 7 yield the Scott-Benesi-Hildebrand equation¹³

$$\frac{[I]}{\Delta} = \frac{[I]}{\Delta_c} + \frac{1}{K\Delta_c} \quad (8)$$

Figure 1 shows computer simulations of several possible graphs of σ vs. C_I at constant C_S . The complex shift is the same for all curves. It is evident that for large association constants ($K > 100$) the shielding should become independent of salt concentration when the salt is in excess, and the complex shift may be observed directly. This was observed in several cases. In these cases, the observed shielding approached the stoichiometric line (line a in Figure 1), thus supporting the assumption that only 1:1 association is significant.

In cases of smaller association constants, Δ_c and K were evaluated by a linear least-squares fit of $[I]/\Delta$ to $[I]$, according to eq 8. Deranleau¹⁴ has shown that, to confirm 1:1 association and to obtain reliable values of K and Δ_c , it is necessary to observe at least 75% of the curve defined in terms of the saturation fraction, $S = [C]/C_S$. Our studies, which were limited primarily by the solubilities of the salts, satisfied this criterion in all cases except complexes of all ions with *tert*-butyl alcohol and complexes of sodium with all substrates. For complexes with water and methanol, a range of at least 0.8 was observed, except in the case of sodium (0.66 with water; 0.62 with methanol).

Our error analysis is consistent with Deranleau's criteria: somewhat larger relative errors are given for cases of restricted saturation range. The computer program used for this analysis weights points inversely as the squares of their estimated error.¹⁵ Points at high salt concentration have the largest $[I]$ and Δ , and thus least error. It is these points, for which multiple substrate-ion complexing is least likely (see curve e, Figure 1), which have greatest weight in the analysis. Consequently, even though multiple substrate complexes are not explicitly treated, the analysis suppresses their effect on the deduced parameters. Further evidence that multiple equilibria are not significant is the fact that no significant curvature was observed in any linear regression according to eq 8.

The actual free ion concentration, $[I]$, used in eq 8 is unknown. It is related to the salt concentration, C_I , by eq 7. Since the substrate concentration is small, $[I]$ is initially approximated by C_I . It is then recalculated using deduced values of K and Δ_s . The n th iteration value of $[I]$ is calculated as

$$[I]_n = C_I - C_S \frac{\Delta}{\Delta_{c,n-1}} \quad (9)$$

In all cases, the calculation was iterated until the deduced values of K and Δ_c did not change.

(13) R. L. Scott, *Recl. Trav. Chim. Pays-Bas.*, **75**, 787 (1956).

(14) D. A. Deranleau, *J. Amer. Chem. Soc.*, **91**, 4044, 4050 (1969).

(15) R. D. Green and J. S. Martin, *ibid.*, **90**, 3659 (1968).

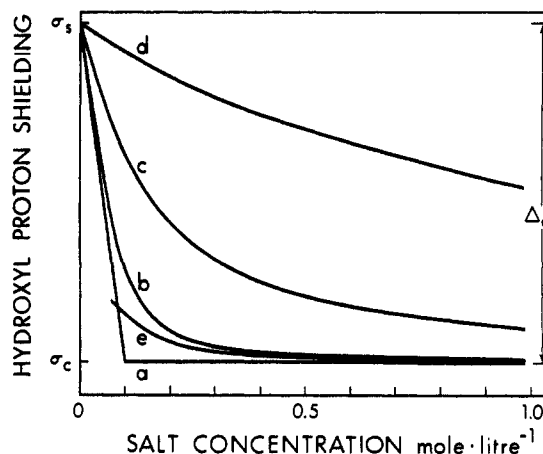


Figure 1. Simulations of the dependence of the hydroxyl proton shielding on the concentration of added salt for various equilibrium constants K , at a fixed substrate concentration (0.1 M) and complex shift Δ_c : (a) $K = \infty$, (b) $K = 100$, (c) $K = 10$, (d) $K = 1$. Curve e illustrates the occurrence of multiple equilibria at low salt concentrations.

The apparent equilibrium constant, K , appearing in eq 8 can be shown to be $K = (\gamma_s \gamma_I / \gamma_C) K_{th}$, where K_{th} is the thermodynamic equilibrium constant, and the γ 's are appropriate activity coefficients. Analysis according to eq 8 will yield the correct value of Δ_c provided that the value of K is independent of the salt concentration, $[I]$. Debye-Hückel theory predicts that γ_s will be independent of ionic strength; γ_C and γ_I will both vary as the square root of ionic strength, which is proportional to the total salt concentration. Consequently, the quotient $\gamma_s \gamma_I / \gamma_C$ will be independent of salt concentration, to a first approximation. Thus, our analysis should yield the correct value of Δ_c and an apparent equilibrium constant K which is not the thermodynamic equilibrium constant K_{th} , but is related to it by a factor significantly smaller than a typical ionic activity coefficient.

Association Constants. Table I gives the deduced substrate-cation molar association constants, in acetonitrile at 35°, of all systems studied. The value for the water-magnesium complex is listed as "large" since it cannot be precisely determined from the concentration dependence of the shift. It is probably of the order of several thousand. Some of the magnesium systems showed evidence of multiple substrate-ion association at low salt concentration, as in curve e of Figure 1. However, we consider that the values reported, based on the points at high salt concentration, are representative of the 1:1 complexes.

The error estimates are standard deviations and include both the estimated error in the experimental points and the standard deviation of fit to the Scott equation.

Table II. Limiting Shifts, Δ_c (ppm), of Cation-Substrate Complexes in Acetonitrile at $35 \pm 1^\circ$

Substrate	Na ⁺	Li ⁺	Ba ²⁺	Sr ²⁺	Ca ²⁺	Mg ²⁺
H ₂ O	-0.89 ± 0.03	-1.48 ± 0.02	-1.54 ± 0.03	-1.75 ± 0.03	-2.17 ± 0.02	-2.98 ± 0.02
MeOH	-0.78 ± 0.05	-1.57 ± 0.02	-1.45 ± 0.03	-1.65 ± 0.03	-2.09 ± 0.03	-2.99 ± 0.03
EtOH	-0.70 ± 0.03	-1.51 ± 0.02	-1.31 ± 0.04	-1.47 ± 0.06	-1.98 ± 0.03	-2.75 ± 0.04
<i>n</i> -BuOH	-0.63 ± 0.05	-1.47 ± 0.06	-1.36 ± 0.03	-1.53 ± 0.03	-1.94 ± 0.05	-2.70 ± 0.05
<i>i</i> -PrOH	-0.7 ± 0.1	-1.48 ± 0.02	-1.17 ± 0.03	-1.35 ± 0.03	-1.79 ± 0.03	-2.45 ± 0.03
<i>t</i> -BuOH	-0.85 ± 0.12	-1.52 ± 0.04	-1.34 ± 0.06	-1.66 ± 0.02	-2.08 ± 0.07	-2.36 ± 0.07

Complex Shifts. Table II gives the deduced complex shifts, Δ_c , of all the systems studied. Where the association constant was large, the deduced shift was close to that observed at high salt concentrations. The shielding in the complex may be deduced by adding the complex shift to that of the substrate in 0.1 *M* acetonitrile solution, given in Table III.

Table III. Shieldings (ppm) *vs.* TMS of Substrates, 0.1 *M* in Acetonitrile, at $35 \pm 1^\circ$

Substrate	Shielding (±0.01)	Substrate	Shielding (±0.01)
H ₂ O	-2.10	<i>n</i> -BuOH	-2.38
MeOH	-2.10	<i>i</i> -PrOH	-2.44
EtOH	-2.41	<i>t</i> -BuOH	-2.31

Effect of Temperature. The cation-methanol experiments were repeated at lower temperatures, using the sodium, lithium, and magnesium perchlorates. These salts span the range of observed shifts and association constants, and thus should represent the temperature dependence of the cation-substrate association.

Over the range $+35$ to -21° , the cation-methanol association constants increased with decreasing temperature, by a factor of 2 or 3. As shown in Table IV,

Table IV. Temperature Dependence of Shifts and Shieldings of Methanol Cation Complexes^a

Temp, °C	Complex shifts, ppm			Shielding of methanol
	Na ⁺	Li ⁺	Mg ²⁺	
35.0	-0.75	-1.54	-2.99	-2.10
21.5	-0.76	-1.52	-2.98	-2.17
10.0	-0.73	-1.52	-2.96	-2.23
0.5	-0.71	-1.51	-2.95	-2.28
-10.5	-0.68	-1.49	-2.92	-2.33
-21.0	-0.66	-1.44	-2.91	-2.38

^a The methanol shielding is for 0.1 *M* methanol in acetonitrile; it is in ppm *vs.* internal TMS. Standard errors: in temperature, 1° ; in complex shifts (Li⁺ and Na⁺) 0.06 ppm, (Mg²⁺) 0.03 ppm; in methanol shielding, 0.01 ppm.

the complex shifts changed only by amounts comparable to their standard errors. The substrate shielding, and thus the complex shieldings, decreased significantly as the temperature decreased.

At the two lowest temperatures, where the shifts appear to show significant change, limited solubility restricted the range of salt concentrations used; thus the probable errors at these temperatures may be larger than those quoted in the table.

It appears that, to within experimental error, the shieldings of free and complexed methanol both decrease with decreasing temperature, but their differences (the complex shifts) do not.

Molal Shift of Barium. Molal shifts in methanol of all our cations have been published, with the exception of barium. We determined the molal shift of barium perchlorate by the method of Butler and Symons.¹⁶ The time-averaged hydroxyl proton shift, *vs.* the methyl peak, was measured as a function of salt concentration, over the range 0.03 to 1 *M*. The molal shift of Ba(ClO₄)₂ in methanol at -69° , evaluated as the slope at zero concentration, was determined to be $+0.28 \pm 0.02$ ppm kg mol⁻¹.

Discussion

Association Constants. It is apparent from Table I that, for a given ion, the variation with substrate is in the order, H₂O > (CH₃OH, C₂H₅OH, *n*-C₄H₉OH) > *i*-C₃H₇OH > *t*-C₄H₉OH. This differs from the trend found for anion complexes of alcohols.⁶ The anion association constants reflect the inductive properties of substituents on the α -carbon atom; the cation constants do not.

It is possible that the small cation association constants of *tert*-butyl alcohol and iso-propyl alcohol are related to the crowding of methyl groups about the oxygen atom. Formation of the complex with such alcohols may require an exceptional amount of desolvation of the ion. This is not observed in the case of anions, since they associate with the more accessible hydrogen, and because anions in carbon tetrachloride are less strongly solvated than cations in acetonitrile.

The cation association constants of water are larger than those of any alcohol. Since acetonitrile is a basic solvent, it will preferentially solvate the hydrogen of a hydroxyl group. Thus, alcohols will be singly, and water doubly hydrogen bonded to the solvent. The charge shift accompanying hydrogen bonding should enhance the nucleophilicity of the water oxygen, and thus the association constant, relative to those of the alcohols.^{17,18}

For all substrates except isopropyl and *tert*-butyl alcohols, there is a regular variation of equilibrium constant across the rows of Table I. The substrates are more strongly bound to ions of high surface potential. This was previously observed in the case of anion complexes. Isopropyl and *tert*-butyl alcohols show a less regular variation, more closely related to the ionic size than to the ionic charge. It is possible that association with these substrates is sterically controlled.

We have calculated cation-molecule association potential energies, U_e , for the various ions with methanol, using a model previously applied to anion-molecule association.¹⁵ The ion is regarded as interacting with

(16) R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, **65**, 2559 (1969).

(17) P. A. Kollman and L. C. Allen, *J. Amer. Chem. Soc.*, **93**, 4991 (1971).

(18) R. U. Lemieux and A. A. Pavia, *Can. J. Chem.*, **47**, 4441 (1969).

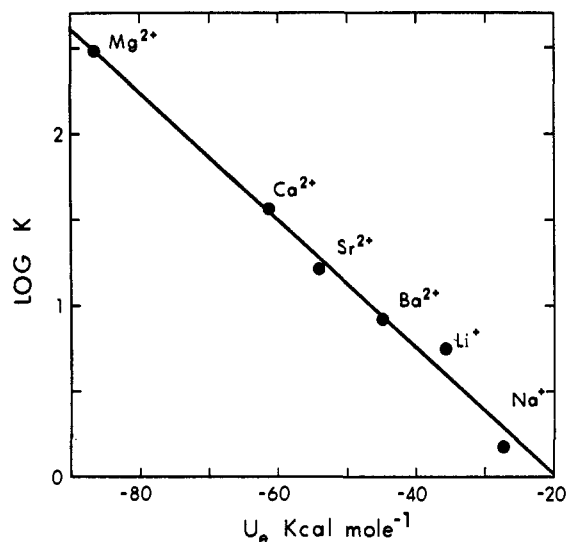


Figure 2. Relationship between the observed cation-methanol association constant and the calculated electrostatic association energy.

the permanent and induced bond dipoles of the molecules.

$$U_e = -\sum_i (\mathbf{u}_i \mathbf{E}_i + \mathbf{E}_i \alpha_i \mathbf{E}_i) \quad (10)$$

In the sum over bonds i , \mathbf{u}_i is the permanent bond dipole, α_i is the bond polarizability tensor, and \mathbf{E}_i is the ion's field at the bond.

The calculations were made using standard values of bond polarizabilities, bond lengths, bond angles, and ionic and van der Waals radii.^{19,20} The bond moments of Groves and Sugden²¹ were used.

Examination of energies calculated with the ion in contact with the envelope of the atomic van der Waals surfaces showed, as one would expect, a minimum energy of association at the oxygen atom. The minimum was broad, so the energy is not critically dependent on the assumed geometry of the complex. The values presented are for a planar complex in which the cation is on the bisector of the oxygen bond angle.

For complexes of similar structure, one would expect the computed electrostatic potential energy to predict the gross trends in the enthalpy of association. If, as is usually found,²² the entropy changes and desolvation contributions are either constant or proportional to the enthalpy changes, then $\log(K)$ should be linear in U_e . Figure 2 shows that such a relationship does obtain. It appears that the dependence of the energy on the cation may be accounted for electrostatically.

Complex Shifts. The values in Table II show a large regular variation* with ionic surface potential. The variation with substrate is smaller and irregular. For a given cation, all substrates show the same complex shift, with a relative standard deviation of 10% or less. This suggests that in all cases the ion complexes have the same structure, which is primarily determined by the properties of the hydroxyl group.

(19) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

(20) "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Co., Cleveland, Ohio, 1967.

(21) L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937).

(22) G. C. Pimentel and A. L. McClellan, *Annu. Rev. Phys. Chem.*, **22**, 347 (1971).

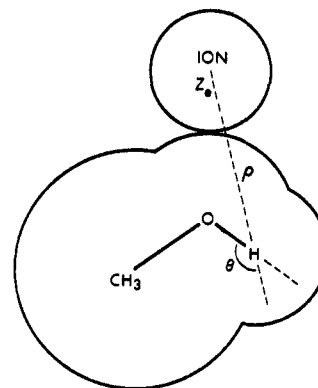


Figure 3. Structure of a planar cation-alcohol complex.

The strong dependence of the shifts on cation surface potential suggests that they are related to the electrostatic field of the ion. Buckingham²³ and Musher²⁴ have described the shielding change of a proton in a covalent X-H bond in terms of the electric field, E , at the bond where the z axis is directed from X to H. The

$$\Delta\sigma_e = A \times 10^{-12} E_z - B \times 10^{-18} E^2 \quad (11)$$

coefficient B is usually taken to have the atomic hydrogen value²⁵ 0.74 esu^{-2} . A , the coefficient of the linear term, has been evaluated theoretically²⁴ and experimentally^{6, 15, 26} for various bonds to first-row atoms and is of the order of $2\text{--}16 \text{ esu}^{-1}$.

Assuming, for simplicity, that the cation complex is planar, then the geometry specified in Figure 3 leads to the equation

$$\Delta_e = 4.80AZ \cos \theta r^{-2} - 23.1BZ^2 r^{-4} \quad (12)$$

where Z is the ionic charge number. It turns out that in this system the term $\cos \theta r^{-2}$ is insensitive to the position of the ion on the oxygen, within reasonable limits. Thus one can, without making specific assumptions about the geometry of the complex, evaluate A by a linear fit of $y = \Delta_e + 23.1BZ^2 r^{-4}$ to $x = 4.80Z \cos \theta r^{-2}$. Assuming van der Waals contact between oxygen and ion, the shifts for water, methanol, ethanol, and all the ions were so fitted and yielded $A = 1.6 \pm 0.3 \text{ esu}^{-1}$.

This A coefficient is substantially smaller than the value of 5.5 previously inferred⁶ from the shifts of anion-alcohol complexes. This discrepancy is greatly in excess of experimental error, and we believe that it cannot be resolved in terms of the simple electrostatic model.

The counterion, perchlorate, may contribute to the field at the proton, but its effect is much less than that of the cation. We studied the effect of added tetra-*n*-butylammonium perchlorate on the substrate hydroxyl shieldings. The salt-induced shift was to lower shielding and did not exceed 0.2 ppm up to 1 *M* salt concentration. This sets an upper limit on the perchlorate ion effect. Cogley, *et al.*,⁸ reported that salt-induced shifts of water in propylene carbonate were identical for perchlorate, tetrafluoroborate, and tetraphenylborate salts. Thus it is reasonable to propose that the counterion contribution to the salt association shifts is negligible.

(23) A. D. Buckingham, *Can. J. Chem.*, **38**, 300 (1960).

(24) J. I. Musher, *J. Chem. Phys.*, **37**, 34 (1962).

(25) T. W. Marshall and J. A. Pople, *Mol. Phys.*, **1**, 199 (1958).

(26) W. T. Raynes and B. P. Chadburn, *ibid.*, **17**, 543 (1969).

The electrostatic model we have used takes no account of dielectric polarization of solvent and substrate. There is no obvious way to evaluate this effect; however, there appears to be no reason why it should differentiate strongly between cation and anion association.

The discrepancy between the two A values does not arise from saturation of the hydroxyl charge shift by large electric fields. The fields arising from the cations studied can be calculated; they span the range of the anions' electrostatic fields.

It is of interest to evaluate the hydroxyl shift arising from solvating acetonitrile. Using the model of Berkeley and Hanna,¹² and their value of the nitrile anisotropy, the shift arising from a collinear O-H...NCCH₃ complex in van der Waals' contact was calculated to be -0.2 ppm if $A = 1.6$, and -2.1 ppm if $A = 5.5$. The observed shielding of dilute monomeric methanol is about 2 ppm less in acetonitrile than in hydrocarbon solvents.²⁷ If the difference arises entirely from acetonitrile association with the hydroxyl proton, then it is more in accord with the calculation using $A = 5.5$, as in the case of anion association.

At this point it appears that the most reasonable way to reconcile the two values of A is to postulate that the value 1.6 esu^{-1} , derived from cation association at a point remote from the hydrogen, is representative of purely electrostatic deshielding. The larger effects observed when an ion or molecule associates directly with the proton involve an additional mechanism, possibly a covalent contribution to the hydrogen bond.

Molal Shifts in Water and Methanol

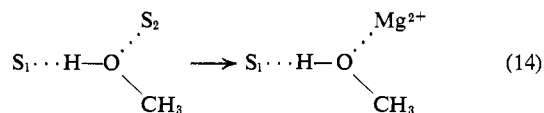
The molal shift of a salt is defined as

$$\Delta_m = \lim(m \rightarrow 0) \frac{d\sigma}{dm} \quad (13)$$

where σ is the solvent shielding and m is the molal salt concentration. The salt shifts are additive in ionic contributions, and scales of absolute ionic molal shifts have recently been proposed in methanol¹⁶ and water.²⁸

In order to relate the complex shifts observed in acetonitrile to the molal shifts in pure hydroxylic solvents, it is necessary to consider carefully the changes in state involved in the two processes. This is done in the following three sections.

Cation Solvation in Acetonitrile. Using the methanol-magnesium complex as an example, the change of state relevant to the hydroxyl proton shielding, on formation of the complex, may be represented as



S represents a solvating acetonitrile molecule. The solvation of the proton by S_1 is significant. In the previous section, the effect of acetonitrile solvation was estimated as *ca.* -2 ppm. We assert that solvation at the hydrogen (S_1) contributes to the deshielding, but solvation at the oxygen (S_2) does not, and thus that the cation-substrate shifts contain no desolvation contributions.

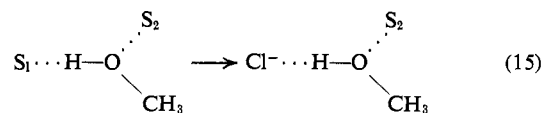
(27) W. B. Dixon, *J. Phys. Chem.*, **74**, 1396 (1970).

(28) J. Davies, S. Ormondroyd, and M. C. R. Symons, *Chem. Commun.*, 1426 (1970).

This is supported by the work of Cogley, *et al.*,⁸ who studied complexes of water with lithium and sodium in propylene carbonate solution. If their data are analyzed by the Scott method,²⁹ complex shifts of -1.49 ppm for lithium and -0.96 for sodium are deduced. Thus, the cation-water complex shifts are the same in both solvents, even though the shieldings of both substrate and complex differ between the two solvents. Apparently the solvent effect on the hydroxyl proton shielding is unaffected by formation of the complex, in accord with our model.

The absence of temperature effects on the complex shifts is also consistent with the assertion that all significant substrate-solvent interactions, which presumably give rise to the temperature effect, occur at a site other than that at which the complex forms.

Anion Solvation in Acetonitrile. Similar studies of anion complexes support the postulates made in the previous section. In accord with that model, the significant change of state on formation of a methanol-chloride complex is



One would expect that, since the important solvation is removed on formation of the complex, the complex shift would be solvent dependent, but that the shielding of the complexed substrate would be insensitive to the solvent.

Ormondroyd, *et al.*,⁷ have shown that the methanol-chloride complex has the same hydroxyl proton shielding in acetonitrile and carbon tetrachloride. In these solvents, dilute methanol has widely different shieldings. Thus, the anion complex shift is solvent dependent, while the complex shielding is not.

The cation and anion complex shifts thus indicate that the largest contribution to the solvent-induced shielding of hydroxyl protons in dilute solution arises from solvation of the hydrogen, and that solvation at the oxygen does not produce a significant effect. Thus cation-induced shifts are dominated by the direct ion-substrate interaction.

Solvation in Hydroxylic Solvents. Molal shifts determined in water and methanol have been interpreted¹⁻⁵ in terms of three simultaneous effects.

1. A direct effect of the ion on solvent molecules in the primary solvation shell. It is generally assumed that this term should be negative for both cations and anions. Cations associate with the negative (oxygen) end of the hydroxyl group, anions with the positive (hydrogen) end. In both cases, the ionic field produces a shift of electrons away from the proton and results in deshielding. In this and previous work⁶ we have confirmed that this is the case for all cations and anions studied.

2. An effect representing the disruption of the hydrogen-bonded structure of the solvent when a molecule is removed from the bulk liquid into the solvation shell. Since it represents the breaking of hydrogen

(29) Cogley, *et al.*,⁸ analyzed their shift *vs.* concentration curves by an uniterated Benesi-Hildebrand method in which the equilibrium ion concentration is assumed to be the total ion concentration. For reasons stated previously, we consider our iterated analysis to be more self-consistent. The values of complex shifts quoted above were obtained from Cogley's data by our method of analysis.

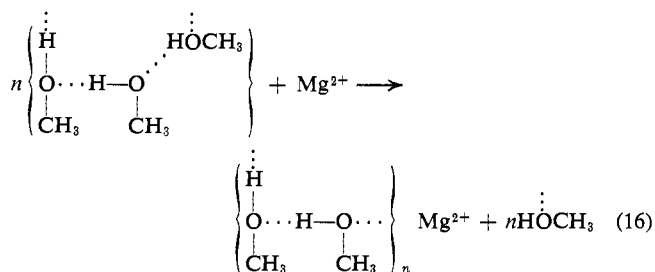
bonds, it is positive. Observed molal shifts are both negative and positive in sign; consequently there must exist some such positive effect to counteract the universally negative direct interaction.

3. Secondary effects, operating on molecules outside the primary solvation sphere. While it is unlikely that the direct ion-molecule interaction extends beyond the nearest-neighbor molecules, there is considerable evidence³⁰ that the structure of water is altered in the neighborhood of ions.

It appears that large monovalent cations and most anions are "structure breaking;" that is, they induce a decrease in the order of the hydrogen-bonded structure, relative to that of pure water. Small ions, and polyvalent ions, are "structure making."

Previous discussions of molal shifts have been rather contradictory,³¹ since the ionic shifts depended on various rather arbitrary separations of cation and anion effects, and since there was no way unambiguously to distinguish the three effects above in a single set of measurements. Now that reasonably consistent sets of ionic molal shifts have been proposed in both solvents,^{5,16} and we have measured directly the ion-molecule interaction shift, it is appropriate to reevaluate the processes involved in the molal shifts.

A Model of the Molal Shift Mechanism. The simplest conceivable model of solvation is that used by Butler and Symons.³² Again using magnesium ion in methanol as an example, the change of state on solvation of an ion may be described as shown in eq 16. This model



takes explicit account of nearest-neighbor interactions only. It predicts that the change of shielding, Δ_s , of a solvent molecule on entering an ion's primary solvation shell, is

$$\Delta_s = \Delta_c + \Delta_h \quad (17)$$

Δ_c is the direct ion-molecule interaction shift. If molecules in the solvation sphere do not significantly affect each other's shielding, Δ_c is adequately measured as the 1:1 complex shift in acetonitrile. Δ_h represents the average shift resulting from disruption and rearrangement of the solvent (effects 2 and 3 described above) per solvent molecule entering the solvation shell.

If a solvent, of $b = 1000/M$ mol kg⁻¹, contains cations of molality m mol kg⁻¹ and solvation number n , its concentration averaged shielding, σ , will thus be

$$\sigma = \sigma_b + (nm/b)\Delta_s \quad (18)$$

where σ_b is the shielding of bulk solvent. Using eq 13

(30) H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, 24, 133 (1957).

(31) J. F. Hinton and E. S. Amis, *Chem. Rev.*, 67, 367 (1967); see pp 368-374.

(32) R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 65, 945 (1969).

and 17, we predict the molal shift

$$\Delta_m = (n/b)(\Delta_c + \Delta_h) \quad (19)$$

In the absence of secondary effects, Δ_h , as well as b , should be characteristic of the solvent alone. Δ_c and n are characteristic of the ion in the solvent. The solvation number, n , appearing here is the time-average statistical excess of nearest-neighbor solvent molecules which are polarized in the same orientation as that of the 1:1 complex in an inert solvent. If the ion's field is sufficient to orient completely the inner shell, then n will be determined primarily by close packing requirements. For ions of radius about 1 Å in methanol and water, the number of nearest-neighbor solvent molecules is of the order of six. An incompletely oriented inner shell would show an effective solvation number n , less than the number of nearest-neighbor molecules.

Molal Shifts in Methanol. Butler and Symons¹⁶ have proposed a scale of absolute ionic molal shifts in methanol at -69° . At this low temperature, the primary solvation shells of Mg²⁺, Zn²⁺, and Al³⁺ give separate hydroxyl signals.³² The average shielding of the rest of the solvent appears to be linear in perchlorate ion concentration; if no secondary cation effects occur, the latter effect implies a perchlorate molal shift of $+0.125$ ppm kg mol⁻¹.

At -69° , at infinite dilution in methanol, the hydroxyl proton in the solvation shell appears at -1.69 ppm relative to bulk methanol. If there are no secondary cation effects, this shift may be identified as $\Delta_s = \Delta_c + \Delta_h$ (eq 17). From this a value of the magnesium molal shift may be calculated as $(n/b)\Delta_s$ (eq 19). Butler and Symons' value of -0.30 ppm kg mol⁻¹ was calculated using their determination of the magnesium solvation number: 5.5 ± 0.5 . Since several recent determinations^{33,34} indicate that the solvation number is 6, we have recalculated the magnesium molal shift using this value and obtain $\Delta_m(\text{Mg}^{2+}) = -0.324$ ppm kg mol⁻¹. We shall use this as the "observed" value.

The experimental value of Δ_s for magnesium may be used to evaluate Δ_h as $\Delta_s - \Delta_c$. If we assume that our observed values of Δ_c are substantially independent of temperature, we deduce that $\Delta_h = -1.69 - (-2.99) = +1.30$ ppm. Table V shows the values of Δ_m pre-

Table V. Prediction of Cation Molal Shifts in Methanol at -69°

Ion	Δ_c , ppm	n	Δ_m , ppm kg mol ⁻¹		
			Obsd	Calcd ^a	Calcd ^b
Na ⁺	-0.78	6	+0.17 ^c	+0.10	+0.17
Li ⁺	-1.57	4	-0.06 ^c	-0.04	-0.01
	-1.57	6	-0.06 ^c	-0.05	
Ba ²⁺	-1.45	6	+0.03 ^d	-0.03	+0.02
Sr ²⁺	-1.65	6	+0.03 ^e	-0.07	-0.02
Ca ²⁺	-2.09	6	-0.13 ^e	-0.15	-0.12
Mg ²⁺	-2.99	6	-0.32 ^f	-0.32	-0.32

^a Calculated using $\Delta_h = 1.30$ ppm and n shown in column 3.

^b Calculated using least-squares values: $\Delta_h = 1.54$ ppm, $n = 6.9$.

^c Reference 5. ^d Calculated from our molal shift of Ba(ClO₄)₂,

using perchlorate molal shift $+0.125$ (ref 5). ^e Estimated from Figure 1 of ref 28. ^f Recalculated from data of ref 32, using a solvation number of 6.

(33) S. Nakamura and S. Meiboom, *J. Amer. Chem. Soc.*, 89, 1765 (1967).

(34) J. F. Hinton and E. S. Amis, *Chem. Rev.*, 71, 627 (1971).

Table VI. Prediction of Cation Complex Shifts and Molal Shifts

Ion	Radius, Å	Complex shift, ppm	Molal shifts, ppm kg mol ⁻¹			
			Methanol, -69°		Water, +25°	
			Calcd	Obsd ^a	Calcd	Obsd ^b
Zn ²⁺	0.74	-2.63	-0.24	-0.32	-0.115	
K ⁺	1.33	-0.64	+0.20	+0.15	+0.068	+0.050
Rb ⁺	1.48	-0.57	+0.22	+0.17	+0.074	+0.037
Cs ⁺	1.69	-0.50	+0.23	+0.14	+0.081	+0.025

^a Reference 16. ^b Reference 5.

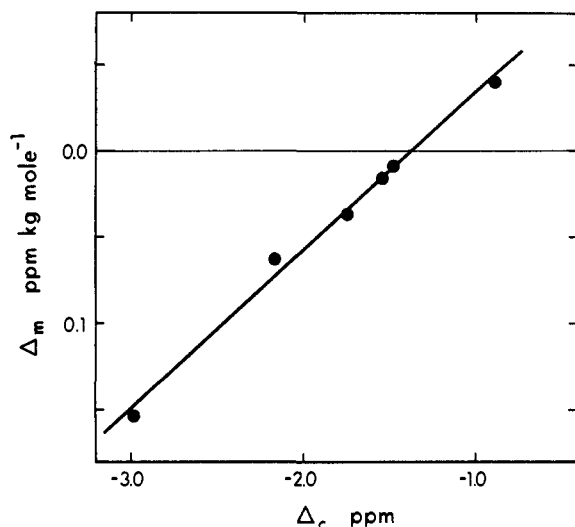


Figure 4. Correlation of Δ_m , the molal cation shift, in water at 25°, with Δ_c , the water-cation complex shift in acetonitrile.

dicted by eq 19 using this value of Δ_h and commonly accepted solvation numbers.³⁴ The root-mean-square deviation of observed and calculated molal shifts is 0.05 ppm kg mol⁻¹.

Note that a lithium solvation number of 4 does not significantly improve the agreement with observation. Thus it appears that the solvation number of all of these ions may be about 6. If n is the same for all ions, eq 19 becomes a linear relationship between Δ_m and Δ_c , with n and Δ_h as adjustable parameters. A least-squares fit of Δ_m to Δ_c yields an average solvation number $n = 6.9 \pm 0.7$ and $\Delta_h = 1.5 \pm 0.3$ ppm. The rms deviation is 0.03, and the standard deviation of fit is 0.04 ppm kg mol⁻¹.

Thus the model represented by eq 19 fits the observed data to within the probable error of the measured values. The rms deviation is comparable to that observed in similar correlations, for example, that with ionic radii.²⁸ Note that the molal shifts change sign at the point where Δ_c is comparable in magnitude to Δ_h .

Molal Shifts in Water. Equation 19 may be applied to molal shifts in water at 25°. Figure 4 shows that our complex shifts, Δ_c , and the molal shifts,⁵ Δ_m , are linearly related. A least-squares fit yields an average solvation number, $n = 5.1 \pm 0.2$, and $\Delta_h = 1.38 \pm 0.11$ in water at 25°. The standard deviation of fit is 0.007 ppm kg mol⁻¹. The average hydration number is reasonably close to the value 6, commonly observed for these ions.³⁴ Thus it appears that solvation of these ions by water is remarkably similar to that by methanol, when the solvents are both about 25° above the melting point.

Limitations of the Model. We have shown that the molal shifts of six small cations may be interpreted in terms of a primary solvation shell of about six completely oriented molecules. This is not surprising, since these ions, which have high surface potentials, should be strongly solvated. In fact, it is for this reason that their 1:1 complex shifts could be determined. Only the perchlorates of small cations are soluble in acetonitrile; KClO₄, RbClO₄, and CsClO₄ are insoluble, and thus their cation complex shifts are not accessible to direct measurement.

Since complex shifts may be adequately calculated by the electrostatic model, it is of interest to use the ionic radii to predict complex shifts by eq 12, use eq 19 to predict molal shifts, and compare the results to experimental values. This has been done for four cations, in methanol at -69° and water at 25°, using the least-squares values of n and Δ_h . The predicted and observed values are given in Table VI.

Considering that the predicted values arise from application of two semiempirical models, using only the ionic radius, the molal shifts of zinc and potassium are adequately represented. On the other hand, the trend to less positive molal shifts with increasing radius in the series K⁺, Rb⁺, and Cs⁺ (a reversal of the normal sequence) is not predicted by the model. The model unambiguously predicts an increasingly positive Δ_m as $|\Delta_c|$ decreases, in the order K⁺ > Rb⁺ > Cs⁺; on the other hand, all determinations of molal shifts^{5,16,31} clearly show an inversion of this normal sequence, beginning at K⁺ or Rb⁺.

Other properties, such as entropy, related to the structures of aqueous and methanolic solutions, also show anomalies in the case of large cations.³⁵ These have been explained in terms of exceptionally great structure breaking in the secondary solvation region, beyond a normal primary solvation shell. We believe that this explanation is inadequate to account for the molal shifts. If the very large cations, Rb⁺ and Cs⁺, differed from the smaller ones only by the presence of exceptional secondary structure breaking, one would expect a positive contribution to Δ_h , reflecting decreased hydrogen bonding in the solvent. This would produce an anomalously large positive molal shift; what is observed is an anomalously small one.

Structure of the Primary Solvation Shell. We propose, as an explanation of the anomalously small molal shifts of the large cations, a phenomenon discussed by Hindman⁴ and Butler and Symons,¹⁶ and first suggested by Bernal and Fowler.³⁶ If the ion-molecule interaction energy exceeds a certain value, of the order of the solvent intermolecular energy, then solvation shell

(35) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).

(36) J. D. Bernal and R. H. Fowler, *ibid.*, **1**, 515 (1933).

molecules will be completely oriented during their residence time, as in Figure 5a. The solvation number will be the number of nearest-neighbor molecules, and Δ_c will have the value appropriate to the minimum energy complex. These assumptions are implicit in our model and appear to be valid for the small cations.

Bernal and Fowler suggest that when the ion-molecule interaction falls below a critical value, which they estimate to occur at ionic radius *ca.* 1.5 Å (that of rubidium), the ion cannot maintain order in its primary solvation shell. The situation is illustrated in Figure 5b. The nearest-neighbor molecules differ from those in bulk solvent by a statistical bias in favor of the oriented arrangement, oxygen toward the ion. The onset of a disordered primary solvation shell will be manifest in all of the parameters of eq 19, but it is most simply envisioned in terms of a decrease in the effective solvation number, *n*. This will result in a decrease in the absolute value of the molal shift, as the primary shell becomes less ordered, in the series $K^+ > Rb^+ > Cs^+$, as observed.

Anions also appear to have disordered primary solvation shells, of low effective solvation number.³⁴ This is reflected in their small molal shifts in methanol,¹⁶ even though their complex shifts with methanol are known to be negative and very large.⁷ If one does a formal analysis of the molal shifts according to eq 19, using the observed complex shifts of methanol in CCl_4 ,⁷ one obtains effective solvation numbers of *ca.* 2 and Δ_h *ca.* +6 ppm. These values have little physical significance, but they do suggest that the idea of a partially polarized, disordered primary solvation shell is consistent with the observed molal shifts of both anions and large cations.

Structure of the Solvent. The quantity Δ_h is a measure of the disruption of the hydrogen bonding of the solvent when the molecule enters the solvation shell. Equation 16 suggests that if the bulk solvent contains *h* moles of hydrogen bonds per mole, then *h* hydrogen bonds are broken per molecule entering the solvation shell. This would imply that Δ_h should be of the order of the bulk liquid to monomer shift, which is about 5 ppm for both water³⁷ at 25° and methanol^{27,38} at -69°. The much smaller observed values, about 1.5 ppm, suggest that the solvent molecules displaced by a cation become hydrogen bonded into the remaining bulk solvent, which consequently becomes more highly structured than pure solvent at the same temperature. Thus the small values of Δ_h for cations could be interpreted as evidence that these ions are structure making outside the primary solvation shell, in both water and methanol. The large Δ_h deduced for anions is consistent with the structure-breaking property of these ions.

Our model suggests that the temperature dependence of the molal shifts arises primarily in Δ_h . If the cation shifts in water⁵ at 0, 25, and 40° are analyzed according to eq 19, there is no significant temperature dependence of the average solvation number. Δ_h changes monotonously with temperature: 1.60 ± 0.32 at 0°, 1.38 ± 0.11 at 25°, 1.32 ± 0.19 at 40°. The decrease in Δ_h with temperature is expected, if Δ_h is related to the proportion of hydrogen bonding in the liquid.³⁹

(37) W. G. Schneider, H. J. Bernstein, and J. A. Pople, *J. Chem. Phys.*, **28**, 601 (1958).

(38) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

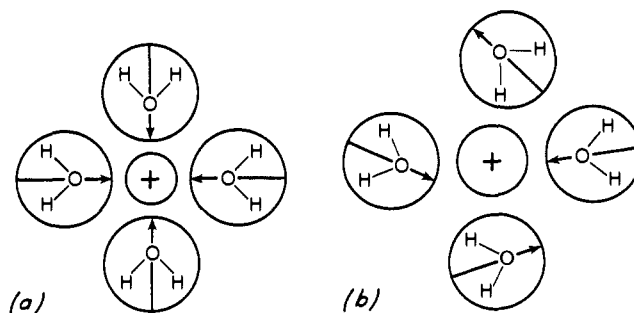


Figure 5. Primary cation solvation shells: (a) ordered, (b) disordered.

Conclusions

Cation Complexes in Acetonitrile. The association constants and hydroxyl proton complex shifts of 1:1 cation complexes with water and several alcohols all show the dependence on ionic charge and radius to be expected of an electrostatic interaction. The shifts are negative, consistent with cation association in the neighborhood of the oxygen lone pairs. Their values suggest a Buckingham-Musher *A* coefficient of 1.6 esu⁻¹ for the OH bond, in contrast to the value of 5.5 found in anion complexes with hydroxyl protons. It also appears that solvation effects at the oxygen may be reasonably accounted for using *A* = 1.6 esu⁻¹, whereas hydrogen bonding produces shifts of the hydrogen involved which are consistent with the larger value of *A*. Thus it appears that one of the interactions (most probably the direct hydrogen bond) cannot be accounted for adequately by the electrostatic model.

Molal Shifts. The molal shifts of cations in methanol at -69° and water at +25° may be related to the 1:1 complex shifts, Δ_c , by a simple model involving only nearest-neighbor interactions. The implications of the model are best explained in terms of the parameters used.

The direct ion-molecule interaction shift is assumed to be Δ_c , the complex shift measured in acetonitrile. It is the quantity which characterizes individual ions; it may be estimated reasonably accurately by an electrostatic model. It is, to within experimental error, independent of temperature; this is reasonable for an interaction of energy in excess of 15 kcal/mol of solvate.⁴⁰

The solvation number determined by this correlation is to be regarded as a measure of the average number of oriented nearest-neighbor solvent molecules. For small and/or highly charged cations this number is about 6, which is a reasonable value for the total number of nearest neighbors. These ions, therefore, have completely oriented solvation shells, consistent with their large negative contributions to the entropy of solution.³⁵ Large monovalent cations and anions appear to have small effective solvation numbers. This suggests that they do not have oriented solvation shells, but rather a slight statistical excess of nearest neighbors in the lower energy orientation. The absence of a structured solvation shell is consistent with the anomalously high entropies of solutions of these ions.³⁵

(39) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Oxford University Press, London, 1969, p 178.

(40) N. Muller and R. C. Reiter, *J. Chem. Phys.*, **42**, 3265 (1965).

The quantity Δ_h , which evaluates the net disruption of the solvent per solvating molecule, is related to the amount of hydrogen bonding in the solvent. It decreases with increasing temperature, as expected. It is the only quantity sensitive to secondary solvation effects. Since the nearest-neighbor interaction model suggests that Δ_h should be about 5 ppm for all ions, the observed values might be interpreted as representing some structure making near cations and some structure breaking near anions. This is quite speculative and contradicts the usual picture of secondary cation solvation.³⁰ There is no necessity that the degree of ordering correspond precisely to the proportion of hydrogen bonding.

All measured characteristics of the solvation process are essentially equal in water at +25° and methanol at

−69°, that is, about 25° above the freezing point in each case. As a consequence of this, the molal shifts of cations in the two solvents are observed to be in the ratio of the solvent molecular weights.

Now that it is possible to evaluate separately the direct ion-molecule shift, the solvent shielding in ionic solutions may be used as a probe to evaluate more subtle effects of hydrogen bonding and liquid structure.

Acknowledgments. We wish to thank Mr. F. Fujiwara and Dr. B. Kratochvil for valuable discussions about some aspects of this work, and Jack Pannekoek and Mon Pon (our summer research assistants) for their help in the preparation of nearly 1000 nmr samples. This research was supported in part by National Research Council of Canada Grant No. A-2051.

Endor-Detected Nuclear Magnetic Resonance Studies of Small Ring Systems. I. $(\text{CH}_2)_3\text{C}(\text{COOD})_2$ ^{1a}

Larry R. Dalton^{1b} and Alvin L. Kwiram*^{1c}

Contribution from the Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138. Received March 2, 1972

Abstract: A technique for observing enhanced proton and deuteron magnetic resonance in single crystals of $(\text{CH}_2)_3\text{C}(\text{COOD})_2$ is described. From an investigation of the proton dipolar and deuteron quadrupolar interactions, the conformation of the $(\text{CH}_2)_3\text{C}(\text{COOD})_2$ molecules and the relationship of the molecules to the external morphology of the crystal are established. Molecules of 1,1-cyclobutanedicarboxylic acid at 4.2°K were found to be bound together by hydrogen-bonded carboxylic acid bridges which zigzag along the crystallographic *c* axis. The normal to the plane of the slightly puckered four-membered ring also lies approximately along the *c* axis with the C-C bonds of the ring oriented approximately along the *a* and *b* axes. The spatial separation between geminal protons is found to be 1.895 Å. The proton ednmr data are best described by a dihedral angle of 165°, a C-H distance of 1.10 Å, and an H-C-H angle of 116°.

It has been known for some time that structural information can be gained by investigating the nuclear magnetic resonance (nmr) of oriented single crystals;²⁻⁹ however, studies involving the conventional wide-line nmr technique are often fraught with difficulties. Sensitivity is a serious problem particularly for nuclei with small magnetic moments or those present in low concentration. Moreover, radiofrequency saturation is a problem particularly at low temperatures (less than 10°K) but often even at ambient temperatures. The investigation of malonic acid by Derbyshire, *et al.*,⁹ provides an example of the difficulty of applying the wide-line nmr technique to the study of organic single crystals. Even at ambient tem-

peratures, 5-hr scans were required to avoid saturating the deuteron magnetic resonance of perdeuteriomalonic acid crystals. Minor over-modulation and radio-frequency saturation resulting in some line-shape distortion were necessary to produce signals above the noise level.

Hahn and coworkers¹⁰⁻¹⁷ have developed a pulsed multiple resonance technique for significantly enhancing the resonance signals of nuclei present in small concentrations by monitoring changes in the resonance signal of a more abundant species of nuclei. Inherent to the success of such experiments is the criterion that two species of nuclei be effectively coupled by nuclear spin diffusion and that this spin diffusion be fast relative to spin-lattice relaxation times. The technique of Hahn and coworkers has proved to be eminently successful; the following species have been detected in natural abundance: ⁴¹K (7%), ⁴⁰K (0.012%), ⁴³Ca (0.13%), ¹³C (1.1%), and ²H (0.016%).

(1) (a) This work was supported by National Science Foundation Grants GP-4612 and GP-7428. (b) National Institutes of Health Pre-doctoral Fellow, 1966-1970; (c) Alfred P. Sloan Fellow; author to whom correspondence should be addressed at Department of Chemistry, University of Washington, Seattle, Wash. 98105.

(2) (a) G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948); (b) S. Ketudat and R. V. Pound, *ibid.*, **26**, 708 (1957).

(3) T. Chiba, *ibid.*, **39**, 947 (1963).

(4) T. Chiba, *ibid.*, **41**, 1352 (1964).

(5) B. Pedersen, *Acta Crystallogr.*, **20**, 412 (1966).

(6) M. Weissman, *J. Chem. Phys.*, **44**, 422 (1966).

(7) R. Blinc and D. Hadzi, *Nature (London)*, **212**, 1307 (1966).

(8) B. Pedersen, *Acta Chem. Scand.*, **22**, 453 (1968).

(9) W. Derbyshire, T. C. Gorvin, and D. Warner, *Mol. Phys.*, **17**, 401 (1969).

(10) S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, **128**, 2042 (1962).

(11) R. E. Slusher and E. L. Hahn, *Phys. Rev. Lett.*, **12**, 246 (1964); *Phys. Rev.*, **166**, 332 (1968).

(12) E. L. Hahn, *Proc. Colloq. AMPERE*, **13**, 42 (1964).

(13) C. J. Gabriel, Thesis, University of California, Berkeley, 1964.

(14) D. McArthur, Thesis, University of California, Berkeley, 1967.

(15) M. Schwab, Thesis, University of California, Berkeley, 1968.

(16) M. Schwab and E. L. Hahn, *J. Chem. Phys.*, **52**, 3152 (1970).

(17) E. P. Jones and S. R. Hartmann, *Phys. Rev. Lett.*, **22**, 867 (1969).