The Association of Water with Bases and Anions in an Inert Solvent[1]

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Infrared spectra of water–base and water–alkylamine halide systems in carbon tetrachloride solutions in the 3-μ region show absorptions that allow the species formed in these systems to be identified. In all oxygen- and nitrogen-containing bases studied, some of which contain two nearby basic sites, a one-to-one complex involving one hydrogen bond occurs at low base concentrations. At higher base concentrations, complexes involving one water and two base molecules are formed. Similarly, the ion-pair systems reveal that hydration of halide ions involves a single hydrogen bond at low salt concentrations. There is, however, indication of two salt to one water species at higher salt concentrations and, for the fluoride ion, a two water to one salt species at higher water concentrations.

Introduction

Although some spectroscopic studies of liquid systems involving water and various bases or anions have been reported and although the interaction between water molecules and such molecules or ions must be expected to occur in many chemical systems, only recently have attempts been made to determine the nature of the species formed in such systems.

Early infrared and near-infrared spectral studies have been made on systems involving water in pure bases by Errera, Gaspart, and Sock[4] and by Greinacher, Luttke, and Mecke.[5] In the first of these studies it was assumed that the species present was a one-to-one association complex between a water molecule and a base molecule. The second study was concerned primarily with the pattern of overtone bands and the association species present were not investigated.

Recently Linnell[6] has made arguments regarding the association of water to pyridazine based on ultraviolet spectral shifts while Arnett and Wu[7] have used measurements of base strengths to deduce a possible association complex formed between dioxane and water. The Raman spectra of water–methanol complexes in carbon tetrachloride have been obtained by Kecki[8] and the nature of the association has been discussed.

The association of water molecules themselves, a similar but more complex phenomenon than the water–base and water–ion association to be dealt with here has been the subject of spectral investigations by Van Thiel, Becker, and Pimentel,[9] and Buijs and Choppin.[10]

The nature of the hydration of ions has been approached by many means, and recently spectral studies of water–anion complexes in aqueous solution have been reported by Hindman[11] and Walrafen.[12] In similar studies the nature of the species formed in concentrated aqueous solutions of electrolytes have been investigated by Waldron,[13] using the infrared region and by Choppin and Buijs[14] by means of near-infrared absorptions.

In view of the general importance of solvation by water molecules and the possibilities of solvation of a single base molecule, or anion, by a water molecule so as to form two hydrogen bonds, as suggested in some of the work referred to, it is of interest to investigate further the nature of water–base and water–anion complexes. Studies of these complexes in an inert solvent offer, as will be shown, more detailed spectral data bearing on the nature of the complexes than do studies of solutions in which water serves as the solvent as well as a participant in hydrogen bonding to the base or anion. Measurements of the absorption bands in the 3-μ OH stretching region of carbon tetrachloride solutions containing small amounts of water and various concentrations of different bases and anions, in the form of substituted amine halides, are here reported. The spectral features adequately reveal the nature of the association species formed in many water–base and water–anion association complexes.

Experimental

All spectral measurements were made with a Beckman IR-7 prism-grating spectrometer. Both single beam operation and double beam operation with matched sets of quartz and sodium chloride cells ranging from 1 cm. to 0.1 mm. were used. For double beam operation, solutions for the sample and reference beam cells were prepared from the same stock solution of base in carbon tetrachloride. Micropipet quantities, to bring the excess water concentration up to the range of hundredths molar, were then added to the solution to be used in the sample beam. Since no equilibrium constant values were deduced from the spectra, it was not necessary to know the exact water concentration of the solutions. In most cases, however, the water concentration was about 0.01 M. In a few special experiments at high base concentrations, water concentration of up to about 0.3 M were used to investigate the possibility of water–water association.

For the study of anion–water association in carbon tetrachloride, Eastman tetrabutylammonium bromide,

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(2) N.S.F. Summer Undergraduate Research Participant, 1961.

(3) N.S.F. Summer Undergraduate Research Participant, 1963.

(4) J. Errera, R. Gaspart, and H. Sock, J. Chem. Phys., 8, 63 (1940).

(5) E. Greinacher, W. Luttke, and R. Mecke, Z. Elektrochem., 59, 23 (1955).

(6) R. H. Linnell, J. Chem. Phys., 34, 698 (1961).

(7) E. M. Arnett and C. Y. Wu, J. Am. Chem. Soc., 84, 1684 (1962).

(8) Z. Kecki, Spectrochim. Acta, 18, 1155 (1962).

(9) M. Van Thiel, E. O. Becker, and G. Pimentel, J. Chem. Phys., 27, 486 (1957).

(10) K. Buijs and G. R. Choppin, ibid., 39, 2035 (1963).

(11) J. C. Hindman, ibid., 36, 1000 (1962).

(12) G. E. Walrafen, ibid., 36, 1035 (1962).

(13) R. D. Waldron, ibid., 26, 809 (1957).

(14) G. R. Choppin and K. Buijs, ibid., 39, 2042 (1963).

dibutylammonium chloride, and tetraheptylammonium iodide were used without further purification. The preparation of tetrabutylammonium fluoride followed the procedure given by Fowler and Krause[15] for tetramethylammonium fluoride. An aqueous solution of the bromide salt is allowed to react with freshly precipitated silver oxide, and the resulting silver bromide is removed by filtration. Neutralization of the hydroxide with hydrofluoric acid produces the desired salt which may be crystallized from solution. The tetrabutylammonium fluoride obtained by this method was crystalline but even on drying could not be obtained entirely free of infrared-detectable amounts of water.

Tetrabutylammonium chloride was prepared according to the procedure of Baay and Gutmann[16] in which tetrabutylammonium iodide in absolute ethanol is refluxed in the presence of excess silver chloride. The resulting crude product was recrystallized from carbon tetrachloride-ether solutions.

Tributylammonium fluoride, chloride, and bromide were obtained by the addition of the appropriate hydrogen halide gas to the parent amine. Added ether then removed the excess amine and forced crystallization of the desired salt.

The spectra between about 3100 and 3800 cm.$^{-1}$ of the water-base association species were obtained with the solvent carbon tetrachloride and various base concentrations up to the limit of pure base. For the salts, solubilities limited the range and systems were studies with salt concentrations of 0.033 mole/l.

Results

A. *Hydration of Base Molecules.* Spectra were obtained for water-carbon tetrachloride solutions containing various amounts of the bases listed in Table I.

For all bases, but at various base concentrations, generally around 0.2 M, a species is formed as a result

Table I. The Frequencies (cm. $^{-1}$) of the OH Stretching Mode Absorption Bands of the Association Complexes Formed between Water and Various Bases in Carbon Tetrachloride Solution[a]

| | 1:1 complex | | 2:1 complex | |
	$\bar{\nu}$(free)	$\bar{\nu}$(bonded)	$\bar{\nu}$(antisym.)	$\bar{\nu}$(sym.)
Nitromethane	3700	3610	3670	3580
Nitrobenzene	3700	3585	3675	3590
Trioxane	3695	3580		
Dimethyl phthalate	3695	3575	3650	3565
3,4-Dimethoxybenzaldehyde	3690	3560		
Acetonitrile	3690	3555	3640	3545
Butyrolactone	3690	3550		
Ethyl acetate	3690	3545	3640	3550
Methylal	3690	3525	3650——3570	
Acetone	3690	3525	3610——3530	
Dioxane	3690	3520	3585	3525
t-Butyl peroxide	3690	3500		
Ethyl ether	3687	3490	3600	3525
N,N-Dimethylformamide	3688	3490	3550——3490	
Pyridazine	3682	3430	3400	
Pyridine	3682	3390	3400	
4-Picoline N-oxide	3680	3350		

[a] Data are not available for the 2:1 complex for those bases that absorb in this spectral region and therefore interfere at high concentrations.

(15) D. L. Fowler and C. A. Krause, *J. Am. Chem. Soc.*, **62**, 1143 (1940).
(16) M. Baay and V. Gutmann, *Monatsh. Chem.*, **90**, 256 (1959).

of water-base association that is characterized by two absorption bands in the OH stretching region. The higher frequency band is narrow and lies slightly shifted from the position of the antisymmetric ν_3 stretching mode of free water which, in CCl$_4$, occurs at 3706 cm.$^{-1}$. The lower frequency band that characterizes this association species is broad and considerably displaced to frequencies lower than the range of free OH stretching modes. Spectra, for this spectral region, are shown in Figure 1 for a base of intermediate strength and in Figure 2 for a representative strong base. Very weak bases, such as nitromethane, lead to such small spectral shifts that the higher frequency band does not come in as a distinguishable new feature but rather causes a shift in the position of the band from that of the ν_3 band of free water. The lower frequency band enters to produce a shoulder and then a broadened band.

For all the bases studied, further additions of base led to the disappearance of the sharp high-frequency band. For the weaker bases two broad bands in the lower-frequency region were then observed. For the stronger bases a single, very broad band suggesting some structure is obtained. These features are recognized in Figures 1 and 2, which are typical of the spectra obtained for the many bases studied. The appearance of these spectra is, moreover, retained for increased base concentrations up to the limit of pure base. Furthermore, the spectra of these solutions with high base concentrations agree with those reported by Greinacher, Luttke, and Mecke.[5]

Increasing the water concentration in these base-rich solutions produces no spectral changes up to water concentrations of about 0.2 M for bases like ether. At higher water concentrations, a broadening and intensification of the low frequency side of the absorption region does occur.

The frequencies of the principal bands in the OH stretching region for the systems studied are given in Table I. The tabulation is given there in terms of the one water molecule to one base molecule species which, as the discussion below will indicate, is the species formed at low base concentrations and the one water to two base species that is suggested to be the species at higher base concentrations. For these latter species, the bands overlap for the stronger bases, and this spectral feature is indicated by a line connecting the frequencies of the discernible maxima. The breadth of the bands in the last three columns limits the accuracy with which the band maxima can be located to about ±10 cm.$^{-1}$.

B. *Hydration of Anions.* The spectra obtained in the OH stretching region of the infrared for water-quaternary ammonium halide systems in carbon tetrachloride are shown in Figure 3. The use of the tetraheptyl compound for the iodide is dictated by solubilities but the evidence of Allerhand and Schleyer[17] on hydrogen bonding to halide ions suggests that no appreciable frequency changes are to be expected in going from the tetrabutyl to the tetraheptyl compound. The relatively low salt concentration used for the spectra in Figure 3 results in the presence, except for the fluoride, of appreciable free water bands, but otherwise the spectral features are similar to those of water-base

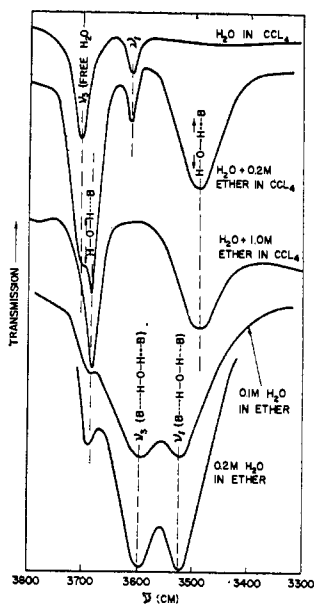(17) A. Allerhand and P. von R. Schleyer, *J. Am. Chem. Soc.*, **85**, 1233 (1963).

Figure 1. The infrared absorption spectra in the OH stretching region of carbon tetrachloride solutions progressively richer in ethyl ether. The first three spectra were obtained with a 1-cm. cell and a water concentration near the saturation value of 0.008 M for pure CCl_4. The cell length for the lower two spectra was 0.5 mm.

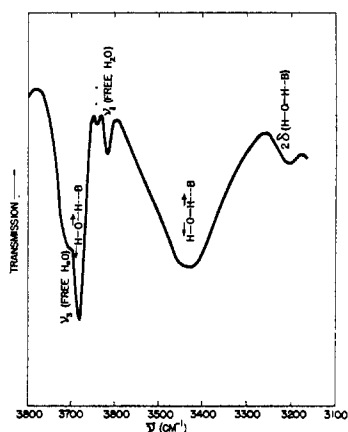Figure 2. The OH stretching region for a carbon tetrachloride solution containing 0.14 M pyridazine and about 0.01 M water in a cell of length 1 cm.

systems at relatively low base concentration. As the data of Table II show, the nature of the cation does, however, strongly affect the frequency shifts of the water absorption bands if the degree of alkyl substitution in the nitrogen atom is changed.

Table II. Hydrogen-Bonding Shifts for Association to Halides of Ion Pairs

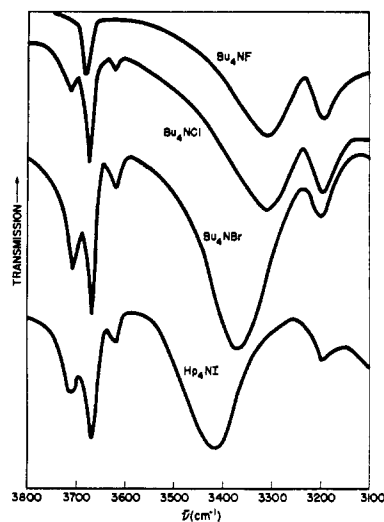|	$\bar{\nu}$(free)	$\bar{\nu}$(bonded)	Δ(free-bonded)
Bu₄NF	3679	3307	372
Bu₄NCl	3678	3308	370
Bu₄NBr	3676	3376	300
Hp₄NI	3677	3422	255
Bu₃NHF	3682	3405	277
Bu₃NH	3679	3405	274
Bu₂NH₂Cl	3678	3447	231
Bu₃NHBr	3678	3429	249

Figure 3. The infrared spectra in the OH stretching region of quaternary ammonium halide–water systems in carbon tetrachloride. For the fluoride, the salt concentration was 0.35 M, no water was added, and the cell length of 1.6 mm. was used. The other salts were at a concentration of 0.033 M, the water concentration was about 0.01 M, and a 1-cm. cell was used.

The virtual absence of free water shown by the spectrum of the tetrabutylammonium fluoride in CCl_4 in Figure 3 suggests that additional water can be added without the separation of a water layer as occurs with the solutions of the other salts. A series of spectra showing the OH stretching region of tetrabutylammonium fluoride–carbon tetrachloride solutions as a function of the water concentration is shown in Figure 4. At the higher water concentrations, free water does show up and, furthermore, the bound water is characterized under these conditions by a very broad shifted band and an almost absent high frequency component at 3678 cm.⁻¹.

Discussion

The spectral changes for all the bases and the salts studied, except for tetrabutylammonium fluoride in solution with relatively high water concentrations, can be interpreted in terms of two types of water–base associated species. Discussion of the association with the base molecules can be done in terms of a representative system and that involving ether, for which some of the spectral results have been presented in Figure 1, will be used.

The base-free water in carbon tetrachloride spectrum in the OH stretching regions shows two bands, at 3706 and 3615 cm.⁻¹, which can be identified as ν_3, the antisymmetric, and ν_1, the symmetric OH stretching modes.

The two bands that take over for small base additions show the characteristics expected for a one water to one base molecule species of the type

$$\begin{array}{c} O-H\cdots B \\ / \\ H \end{array}$$
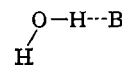
The sharp, high-frequency band can be attributed to stretching of the free OH bond, while the broad low-frequency band is to be associated with the hydrogen-bonded OH group. It is interesting that this descrip-
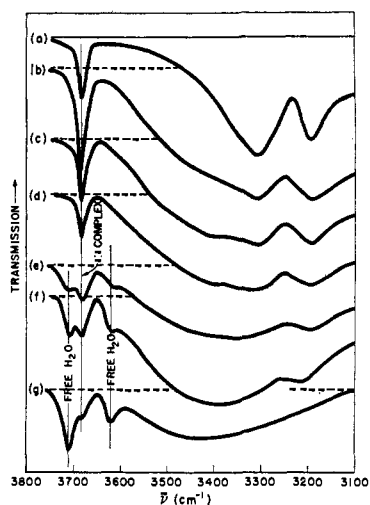
Figure 4. The infrared spectra of the OH stretching region of tetrabutylammonium fluoride–water solutions in CCl₄ for various concentrations of salt and water: (a) salt at 0.35 M, no water added, cell length 1.6 mm.; (b–f) salt at 0.01 M, cell length 1 cm., water concentration increments of about 0.0025 M; (g) salt at 0.005 M, cell length 1 cm., and water 0.004 M greater than in (f). The total water concentration in (g) is about 0.03 M.

tion, rather than one based on somewhat perturbed symmetric and antisymmetric vibrations, with approximately equal band breadths, seems called for in view of the marked difference observed in the breadth of the two bands.

A third band at about 3200 cm.⁻¹ is also observed in some of the spectra of solutions containing this one-to-one species. This band, of intermediate breadth, can be attributed to the overtone of the bending vibration. The increase in the intensity of this band, over that observed for the free water molecule, can be explained on the same basis as used by Thompson and Pimentel[18] for the intensity of the overtone of the $Cl_3{\equiv}C{-}H$ bending mode of hydrogen-bonded chloroform and on the basis of Fermi resonance with the nearby fundamental.

The change in the spectra to two broad relatively low frequency bands observed in the ether series of Figure 1 suggest the formation of a 1:2 species of the form

$$\begin{array}{c} O \\ H \quad\quad H \\ B \quad\quad B \end{array}$$
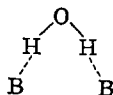
Now the symmetry of the system is regained, and symmetric and antisymmetric modes of the two bonded OH groups give rise to the two equally broad bands. Apparently, as recognized by Greinacher, Luttke, and Mecke, with strong bases these two vibrations approach the same frequency and the two bands are not resolved.

The changes that set in at high water concentrations indicate the formation of water–water association species similar to those that occur in liquid water and give rise to Raman shifts reported by Busing and Hornig[19] at 3225 and 3450 cm.⁻¹.

(18) W. E. Thompson and G. C. Pimentel, Z. Elektrochem., **64**, 748 (1960).
(19) W. R. Busing and D. F. Hornig, J. Phys. Chem., **65**, 284 (1961).
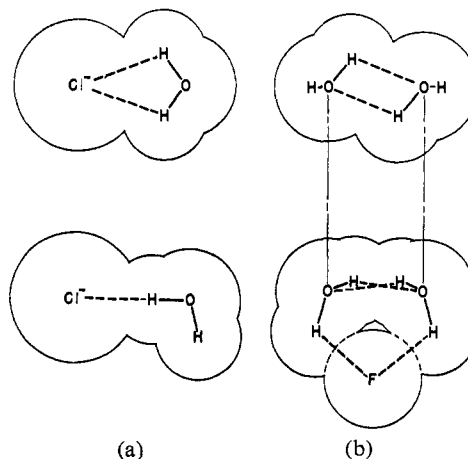
(a)   (b)

Figure 5. (a) The possible structures for the solvation of a halide ion. The spectral evidence indicates that the single bonded structure is formed. (b) A water dimer structure and the association of such a dimer to a fluoride ion as is suggested for the solvation of tetrabutylammonium fluoride in CCl₄.

Of special interest is the fact that with all the bases listed in Table I, the 1:1 species is associated through a hydrogen bond involving one of the OH bonds of the water molecule, the other bond remaining free. Furthermore, in all cases studied, this species gives way at higher base concentrations to one involving two base molecules attached to each water molecule. The early spectral measurements of water in pure base solvents by Errera, Gaspart, and Sock,[4] which were interpreted in terms of species of the type

$$\begin{array}{c} CH_3 \\ {\diagdown} \\ {\diagup} \quad C=O \cdots \overset{\diagup H}{\underset{\diagdown H}{\diagup}} O \\ CH_3 \end{array}$$
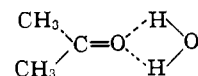
must be recognized as due to species containing more than one base molecule associated with each water molecule.

The nature deduced for the first species formed holds also for the molecules with two base sites, such as pyridazine and dioxane. For both these compounds, the narrow OH band, at 3682 cm.⁻¹ for the 1:1 pyridazine species, as shown in Figure 2, and at 3690 cm.⁻¹ for the 1:1 dioxane, is observed. One must conclude, therefore, that contrary to the suggestions of Linnell[6] and of Arnett and Wu,[7] a water molecule in the system and at the temperature used here does not attach itself to a pyridazine or to a dioxane molecule by two hydrogen bonds. (Preliminary experiments indicate, however, that association through two hydrogen bonds may occur in 1,10-phenanthroline as suggested by Linnell. Further work will be done to clarify the factors which operate to determine the nature of the association in such molecules.)

The similarity of the amine halide solution spectra to those of the water–base systems that contain the one-to-one species indicated that similar hydrogen bond association exists; i.e., the association, or hydration, is through one hydrogen bond as shown in Figure 5a.

This type of association is that favored by Bernal and Fowler[20] and more recently by Verwey[21] and by Harris and O'Konski.[22] It is, furthermore, to be expected on the basis of the acute angle required for the

(20) J. D. Bernal and R. H. Fowler, J. Chem. Phys., **1**, 515 (1933).
(21) E. J. W. Verwey, Rec. trav. chim., **61**, 127 (1942).
(22) F. E. Harris and C. T. O'Konski, J. Phys. Chem., **61**, 310 (1957).

hydrogen bonds if two bonds were to form. On the other hand, inclusion of van der Waals radii in diagrams such as those of Figure 5 make the double hydrogen-bonded structure less unreasonable, particularly for larger ions. This structure, furthermore, lines up the dipole of the water molecule with the electric field imposed by the ion and, on this basis, this more symmetric structure has been favored by Buckingham[23] for the first hydration layer of anions in aqueous solution. However, anions of ion pairs in carbon tetrachloride should provide the most favorable circumstances for this double-bonded association. The absence of this association in such systems indicates that in aqueous systems, where solvent molecules are available to associate with the OH bond, which in carbon tetrachloride is free, the single-bonded structures are to be expected. Furthermore, the spectral results for bases with two base sites, which indicate the tendency of a single water molecule not to be held to both sites, suggest that even with ions such as SO_4^{2-}, where the geometry might be more favorable for a chelate-type hydration, such hydration will still not be important.

Although the species to which the water molecules are attached in this study are ion pairs, there is no evidence that there is any direct interaction between the oxygen of the water and the cation. If the water molecules were to enter the ion pair between the anion and cation, in structures like those suggested for aqueous systems by Choppin and Buijs[14] and by Waldron,[13] some spectral changes might reasonably be expected. The spectra, however, all suggest hydrogen bonding to the halide ion in essentially the same way as found for bonding to oxygen and nitrogen bases.

The spectra in Figure 4 show the unique behavior of the fluoride system with additional water. With low water concentrations these spectra reveal the formation of a one-to-one hydrogen-bonded species, as with the other halides, while at higher water concentrations the low frequency band broadens considerably. The intensity of the sharp high frequency band, due to the free OH of the bound water, decreases. The dependence on water concentration requires these spectral features to be assigned to a species involving two or more molecules. A possible structure, which is based on the structure favored for water dimers as a result

(23) A. D. Buckingham, *Discussions Faraday Soc.*, 151 (1957).

of the work of Van Thiel, Becker, and Pimentel,[9] is shown in Figure 5b. Some distortion of the cyclic water dimer is necessary to form such a structure but this distortion is not large. Furthermore, the spectral features, the absence of a free OH due to the bound water, and a very broad shifted band, which could well result from the overlapping of several hydrogen-bonded OH groups, are nicely implied by such a structure.

The frequency shifts shown in Table II for ionic halides increase in the order $I^- < Br^- < Cl^- \cong F^-$ in contrast to the order found by West, *et al.*,[24] for the covalently bound halides. The frequency shift for bonding to the ionic halides for a similar system employing methanol was found by Allerhand and Schleyer[17] to increase in the order $I^- < Br^- < F^- < Cl^-$ with the fluoride showing an appreciably smaller shift than the chloride. Although it is not clear why the OH band of alcohol and water should behave differently in this regard, the comparison is perhaps upset by the Fermi resonance between the OH stretching and the overtone of the H_2O bending in the water system. The strengthening of this overtone band, which occurs at about 3200 cm.$^{-1}$, in the top two spectra of Figure 3 seems likely to be a consequence of Fermi resonance. The frequencies of the involved bands will therefore also be affected. (Unfortunately the location of the band due to the fundamental bending mode cannot be found because of solvent interference.)

A rather striking dependence of the frequency shift on the number of alkyl groups on the nitrogen is shown by the results listed in Table II. Such behavior is in line with the results of Allerhand and Schleyer on the much smaller shifts shown by tetrasubstituted nitrogen and arsenic cations with alkyl groups of varying size. The decreasing frequency shifts shown in Table II can be attributed to a greater withdrawing of electrons from the site on the anion at which the water hydrogen bonds when the ion pair is such that the two ions can more closely approach one another. The exposed portion of the anion is then less capable of forming a hydrogen bond that would show a large frequency shift. A similar sensitivity of anion solvation to the presence of nearby cations in aqueous solutions must also be expected.

(24) R. West, D. L. Powel, L. S. Whately, M. K. T. Lee, and P. von R. Schleyer, *J. Am. Chem. Soc.*, 84, 3221 (1962).