

Water Structure and Reactivity

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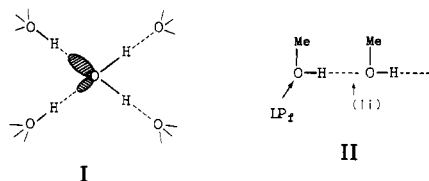
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There is an enormous literature relating to the structure of water, aqueous solutions, and rates of reactions therein, and I hesitate to add to it! However, any concept that can shed light on some of the complexity of these systems may be welcome. Most discussions on water focus attention on bulk thermodynamic properties, and on radial distribution functions revealed by scattering studies. Sometimes specific models, such as the "flickering cluster" model of Frank and Wen,¹ are used in conjunction with statistical mechanics^{2,3} in attempts to reproduce these properties. Recently the computer-based Monte Carlo⁴ and molecular dynamics⁵ techniques have been used in similar attempts, which are, indeed, quite successful.

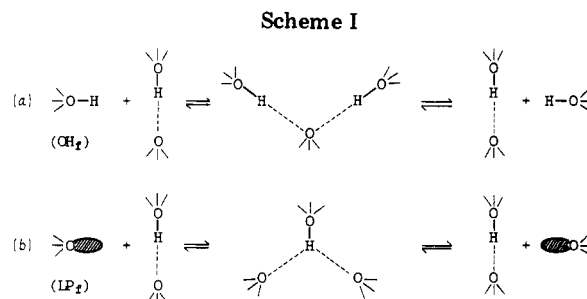
Less attention has been given to spectroscopic studies of water and its solutions, possibly because the results seem to be somewhat intractable. Thus infrared and Raman spectroscopic features are almost devoid of significant structure and are not greatly modified in the presence of a range of solutes.⁶ Proton resonance spectra comprise a single resonance which exhibits complex shifts when solutes are added, but exchange processes are generally too rapid for the detection of separate species even at low temperatures. (We have, however, recently resolved the OH proton resonances of alcohols and sugars in aqueous solution⁷.)

Water structure, although complex, is what one would expect in view of the three-dimensional nature of its hydrogen-bonded structure and the strongly directional character of its near-tetrahedral bonding (I). I envisage



water as a three-dimensional network involving such units fortuitously linked together, with four, five, six, and seven ring systems distinguishable but not of any particular significance because they must be quite haphazardly strung together.⁸ In contrast with some other scientists, I do not envisage ordered, icelike regions in the liquid. In view of the continuous rapid motion of these molecules, hydrogen bonds (H bonds) are subject to constant strain. Thus they bend, stretch, and occasionally break. When they break, the "ends" move away and become uncorrelated. Their ability to move is enhanced by exchange processes involving bifurcated H bonds, as shown in Scheme I. In (a) two OH groups share one lone pair, and in (b) two lone pairs

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share an OH group. These interactions are weak, and in the continuously moving system the bifurcated units have very short lifetimes. Such structures do contribute in a permanent sense in certain salt hydrates and especially in crystalline sugars.

Overtone Infrared Studies

It has long been realized that relatively narrow features detected in O-H stretching overtones of water must relate to free or weakly bound OH groups. One of the best features to study is in the $2\nu_{OH}$ region for HOD in D_2O .⁹ Figure 1 shows this feature, which clearly links the $2\nu_{OH}$ for HOD monomers in the gas phase. Conceptual difficulties have been voiced because of the apparent absence of any such unique feature in the fundamental OH stretching region of the infrared spectrum of water. It now seems to be accepted that this is fortuitous: in the fundamental region, the oscillator strengths for strongly H-bonded O-H groups are greater than those for weakly bonded groups, but in the 2ν region the reverse is true.

Because of the close link between this narrow feature at ca. 7050 cm^{-1} and the gas-phase monomer band, it was originally assumed that this band should be assigned to monomers. This assignment supported the "flickering cluster" model¹ which requires the presence of many monomers. However, in view of the scavenging ability of polymeric water, I concluded that monomeric molecules must have undetectably low concentrations

- (1) H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, **24**, 133 (1957).
- (2) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382 (1962).
- (3) G. Nemethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3401 (1962).
- (4) See, for example: G. C. Lie and E. Clementi, *J. Chem. Phys.*, **62**, 2195 (1975); J. C. Owicki and H. A. Scheraga, *J. Phys. Chem.*, **82**, 1257 (1978); S. Swaminathan and D. L. Beveridge, *J. Am. Chem. Soc.*, **99**, 8392 (1977).
- (5) See, for example: A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, **55**, 3336 (1971); A. Rahman, F. H. Stillinger, and H. L. Lemberg, *ibid.*, **63**, 5223 (1975).
- (6) W. A. Senior and R. E. Verrall, *J. Phys. Chem.*, **73**, 4242 (1969); T. T. Wall and D. F. Horning, *J. Chem. Phys.*, **47**, 784 (1967).
- (7) J. M. Harvey, S. E. Jackson and M. C. R. Symons, *Chem. Phys. Lett.*, **47**, 440 (1977); J. M. Harvey and M. C. R. Symons, *J. Solution Chem.*, **7**, 571 (1978).
- (8) M. C. R. Symons, *Philos. Trans. R. Soc. London, Ser. B*, **272**, 13 (1975).
- (9) (a) J. D. Worley and I. M. Klotz, *J. Chem. Phys.*, **45**, 2868 (1969); (b) W. A. P. Luck and W. Ditter, *Ber. Bunsenges. Phys. Chem.*, **70**, 1113 (1966); *Z. Naturforsch., B: Anorg. Chem., Org. Chem.*, **24B**, 482 (1969).

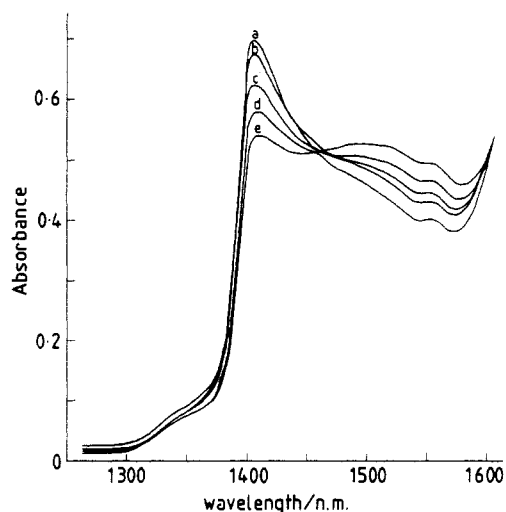
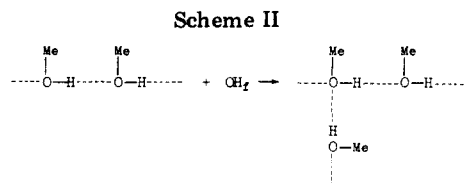


Figure 1. Absorption spectrum in the $2\nu_{\text{OH}}$ region for HOD in D_2O as a function of temperature. The narrow band at ca. 1418 nm (7050 cm^{-1}) is assigned to OH groups: (a) 64.6°C , (b) 54.7°C , (c) 44.7°C , (d) 34.8°C , (e) 24.7°C .

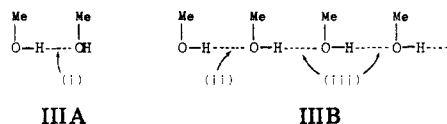
at ambient temperatures,⁸ and a careful study of the H_2O spectrum in this region strongly supported this contention.¹⁰ This feature, as we have stressed,^{8,10} is surely due to O-H groups that are not H bonded, but that belong to molecules still forming three H bonds. As a result, several workers have considered the importance of such OH groups (OH_{free} or OH_f in our nomenclature). However, a consequence of this reassignment has, until recently, been overlooked, namely, that if OH_f groups are present, there must be an equal number of nonbonded lone pairs (designated LP_f).⁸

Unfortunately, we have not yet devised a method for directly detecting LP_f groups. Perhaps the most direct would be by photoelectron spectroscopy since molecules containing such groups should be photoionized more readily than fully H-bonded molecules. So far, this technique cannot be applied to liquid water. In principle, infrared spectroscopy should help, and indeed, for liquid methanol, we think we have succeeded in characterizing LP_f groups both in the fundamental and the $2\nu_{\text{OH}}$ overtone regions.^{11,12} The structure of liquid methanol is simpler than that of water, and we have therefore studied methanolic solutions in the expectation that any gain in our understanding of methanol would help in the study of water.

One difference between methanol and water is the almost complete absence of an OH_f band in the $2\nu_{\text{OH}}$ region for methanol. (The increase in $[\text{OH}_f]$ on heating is greater for methanol, and this situation is reversed at ca. 180°C .^{9b}) I have suggested that this occurs, not because methanol-methanol H bonds are stronger, but because methanol is 1 + 2 functional, and while it normally utilizes only one of its two lone pairs for bonding, any OH_f group will immediately form a weak H bond to one of these excess lone-pair units, as in Scheme II. For clarity, I confine the symbol LP_f to terminal methanol molecules, as in II, since such methanol molecules are unique. The basis for our de-

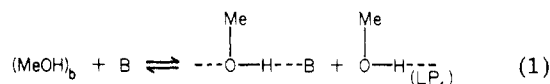


tection of such terminal molecules lies in the fact that the H bonds that they form (ii in II) are expected to be weaker than the normal H bonds within the polymer chains. This is a crucial aspect of methanol and water structure⁸ which, although obvious, is frequently ignored. These important cooperative effects on H-bond strengths are illustrated in III. Bonds i, ii, and iii are



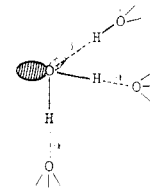
progressively stronger, with iii approximately equal to the "bulk" bond. The strength of i in the dimer is approximately half of that of iii, as judged by infrared shifts.

Thus ii is a unique type of bond, and terminal methanol molecules should be detectable by infrared spectroscopy. No well-defined features are detectable in the room temperature spectra of pure methanol, but when basic cosolvents are added, OH groups are scavenged, and hence the $[\text{LP}_f]$ increases:

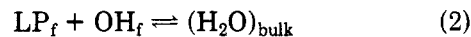


[(MeOH)_b represents bulk methanol.] If B is entirely bonded as a monobase, the $[\text{LP}_f]$ will approximately equal [B]. Our results show that a well-defined band at ca. 3440 cm^{-1} in the O-H fundamental region and ca. 6790 cm^{-1} in the $2\nu_{\text{OH}}$ region grows in, independently of the nature of B. Since this band falls between the OH_f and OH_{bound} regions, we assign it to LP_f .¹⁰

For water, the situation is more complicated, and no well-defined single band has been detected for LP_f groups. Considering structure IV for these groups, I



expect bonds α to be slightly weaker than usual and β to be stronger. Since the bound O-H features for water are always broad, all this is likely to do at room temperature is to add an extra width increment. This is unfortunate, but if we assume that the law of mass action applies to equilibrium 2 between bound and free



groups, we can estimate the $[\text{LP}_f]$ groups from the measured $[\text{OH}_f]$ groups. There is some uncertainty here also, since the OH_f peak in the $2\nu_{\text{OH}}$ region, especially at low temperatures and in the presence of bases, can only be separated from the absorption due to bound water molecules in a somewhat arbitrary way. Furthermore, most calculations assume that the absorbance for OH_f oscillators is equal to that for HOD in the

(10) L. M. Kleiss, H. A. Strobel, and M. C. R. Symons, *Spectrochim. Acta, Part A*, **29A**, 829 (1973).

(11) M. C. R. Symons, N. J. Fletcher, and V. K. Thompson, *Chem. Phys. Lett.* **60**, 323 (1979).

(12) M. C. R. Symons, N. J. Fletcher, and V. K. Thomas, *J. Chem. Soc., Faraday Trans. 1*, in press.

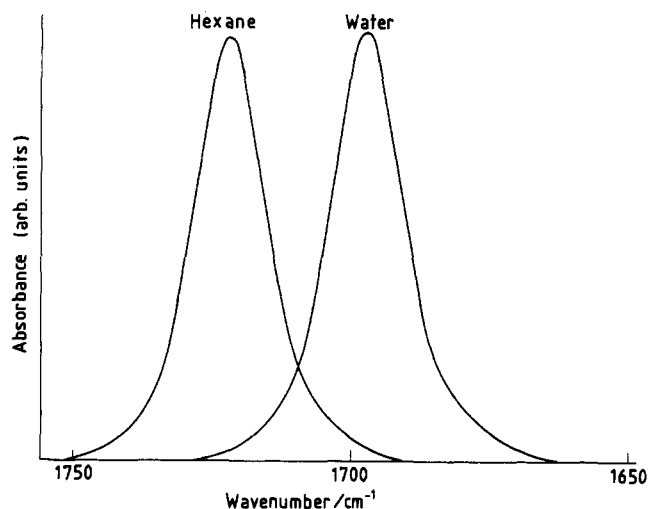


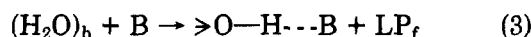
Figure 2. Fundamental C=O stretching band for dilute solutions of acetone (i) in hexane and (ii) in water.¹⁴

monomeric state. This ignores any effect that the three H bonds present in OH_f molecules may have on the oscillator strength. Thus there are inherent errors in our attempts to quantify $[\text{OH}_f]$, which we have not yet been able to circumvent. Nevertheless, approximate values can certainly be obtained, and it is worth considering some of the consequences of the presence of OH_f and LP_f groups on the chemistry of liquid water.

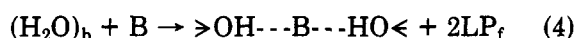
If OH_f and LP_f groups really are present at about 10% at normal temperatures, their presence must contribute to many of the physical properties of water, especially those that depend on rates of libration, rotation, migration, etc. Luck has recently taken up my concept of an equilibrium involving these groups in an interesting attempt to explain several such thermodynamic properties, with some success.¹³ Space does not permit a review of these ideas herein.

Effect of Added Aprotic Bases

Most polar aprotic solvents are bases. Water will normally only accept high concentrations of cosolvents if it forms hydrogen bonds therewith, since strongly structured water opposes the insertion of noninteracting molecules. Our infrared studies of a wide range of basic cosolvents strongly support this contention,^{14,15} characteristic bands for the bases being relatively narrow singlets well shifted from the "free" oscillator bands (Figure 2). Thus, in strongly aqueous region (1.0–0.8 mol fraction water) we can write for a monobasic cosolvent



or for a dibasic cosolvent



Our infrared studies^{14,15} suggest that weak bases behave as monobases (e.g., MeCN) and strong bases generally behave as dibases (e.g., Me_2SO); for the former, as the concentration of base increases, features characteristic of the "free" base grow in, while for the latter, spectra due to singly hydrogen-bonded bases grow in before free base oscillators are detected. Although qualitatively we

(13) W. A. P. Luck, *Angew. Chem.*, 19, 28 (1980).

(14) M. C. R. Symons, G. Eaton, T. A. Shippey, and J. M. Harvey, *Chem. Phys. Lett.*, 69, 344 (1980).

(15) M. C. R. Symons and G. Eaton, unpublished results.

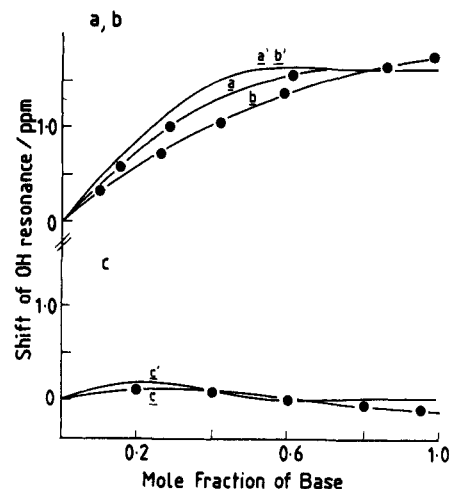


Figure 3. Some examples of the ^1H resonance shifts for OH protons of methanol on the addition of basic aprotic solvents (a, b, c), together with our predicted trends (a', b', c').^{10,11} Key: (a,a') Me_2SO , (b,b') DMF, (c,c') HMPA.

can assess these changes, it is difficult to obtain quantitative estimates of the concentrations of these species because oscillator strengths are unknown. Hence most of the discussion that follows is, at best, only semi-quantitative.

When basic cosolvents are added to methanol there is rapid growth in the LP_f band, and OH groups hydrogen bonded to the base can also usually be detected in the ν_{OH} or $2\nu_{\text{OH}}$ spectral region. Bases such as MeCN, Me_2CO , Me_2SO , Me_3PO can be studied directly (in the C–N, C–O, S–O, and P–O stretching regions) and a rough estimate of H bonded and "free" molecules obtained. Using these results, we have been able to reproduce the OH proton resonance for methanol through the complete mole fraction range for a range of binary mixtures with fair success, as indicated in Figure 3.¹¹

For binary aqueous systems involving basic cosolvents the most outstanding result is the rapid fall in $[\text{OH}_f]$ groups indicated by the overtone infrared spectra (Figure 1). We originally interpreted this fall in terms of the concept that most solvents act as monobases,¹⁶ but our new infrared results¹¹ suggest that many strong bases scavenge two OH_f groups per molecule. This is satisfactory since on the monobase concept, we obtained a good fit only by invoking an initial concentration of ca. 4% for OH_f ¹⁶ (Figure 4). On the dibase assumption that is increased to ca. 8%, a value in better accord with general expectation.¹³ Besides detecting this loss of OH_f groups in the 1.0–0.8 mol fraction water region, we can also follow changes in the bonding to base molecules. These results have again enabled us to explain ^1H resonance shifts in water in binary systems. The NMR results (Figure 5) differ remarkably from those for methanol–base systems (Figure 3) in that for the stronger bases there is a plateau region in the shift–mole fraction plot or even a slight shift to low field before the expected upfield trend sets in. This region is nicely accommodated by use of our data for OH_f groups. These groups make an upfield contribution to the ^1H resonance shift of pure water, and as they are scavenged by the basic cosolvent, this contribution is lost, thereby giving an apparent downfield increment.

(16) M. C. R. Symons, J. M. Harvey, and S. E. Jackson, *J. Chem. Soc., Faraday Trans. 1*, 76, 256 (1980).

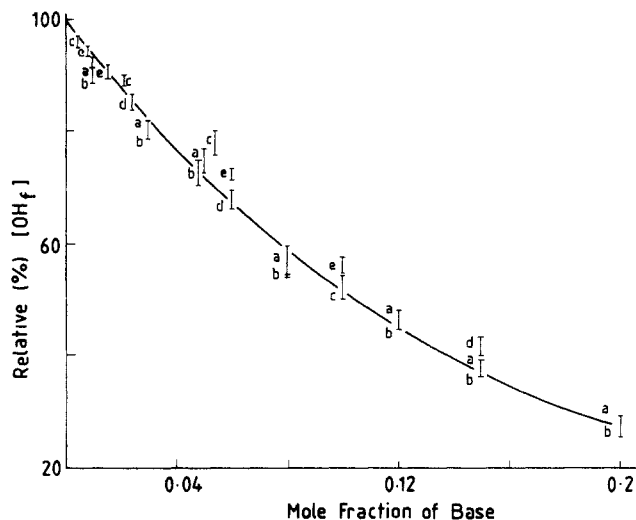


Figure 4. Fall in $[\text{OH}_f]$ groups estimated from the $2\nu_{\text{OH}}$ overtone band, as a function of the mole fraction of added base: (a) Me_2SO , (b) HCONMe_2 , (c) tetrahydrofuran (THF), (d) Et_3N , (e) MeCONMe_2 .

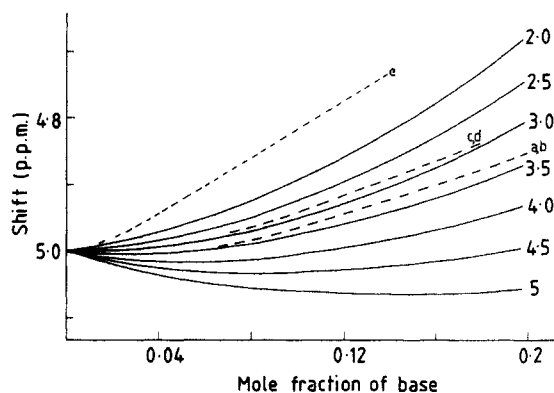
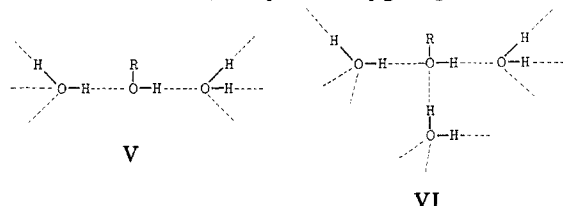


Figure 5. Proton shift for water as a function of the mole fraction of added base. Dashed curves (a) Me_2SO , (b) HCONMe_2 , (c) THF, (d) Me_2CO , (e) MeCN . Full curves are estimated as described in ref 16.

Cosolvents such as alcohols and amides are amphoteric, and form bonds to their basic and acidic functions. I had therefore anticipated that alcohols would cause little change in the $2\nu_{\text{OH}}$ OH_f absorption, whereas in fact there is a marked reduction in this band. Had the only units formed been V, OH_f and LP_f groups would have



been equally taken up, and the net change in $[\text{OH}_f]$ would have been only a minor decrease. In order to explain the marked fall detected, I propose that methanol acts as a dibase, forming units such as VI.

Effect of Added Salts

When a typical metallic salt, M^+X^- , dissolves in water, the cations interact with LP_f groups and the anions interact with OH_f groups, effectively by hydrogen bonding. Given that cation and anion solvation numbers are about the same and that other water-water bonds remain intact, there should be only a small loss in both OH_f and LP_f groups. In fact, for many 1:1

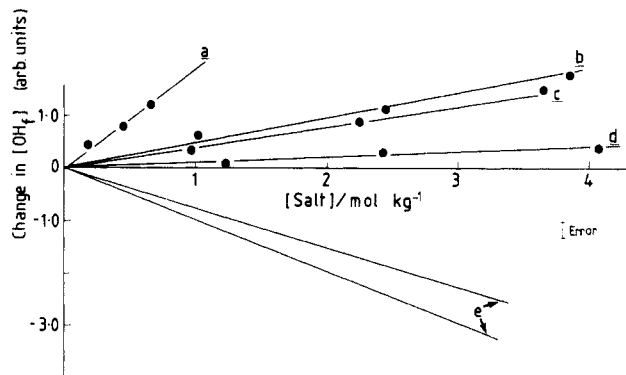
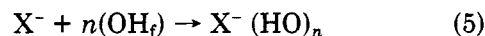


Figure 6. Change in $[\text{OH}_f]$ groups estimated from the $2\nu_{\text{OH}}$ overtone band, as a function of the concentration of added salts: (a) NaBPh_4 , (b) KBr , (c) KCl , (d) KF , (e) R_4Nhal (various).

electrolytes, changes are indeed small.¹⁷ Minor differences probably reflect differences in solvation numbers. In contrast, tetraalkylammonium (R_4N^+) salts cause a rapid fall in the OH_f band.^{17,18} This has been interpreted in terms of a "structure-making" effect of the R_4N^+ ions.¹⁸ However, in our view, loss of OH_f is almost entirely due to scavenging by the anions uncompensated by cation solvation:



Certainly R_4N^+ ions have an effect on water structure which may well result in a small loss of both OH_f and LP_f groups, but this must be a secondary effect. Indeed, if we ignore R_4N^+ ions and accept a solvation number for Cl^- of nearly 6,¹⁹ we expect that the rate of loss of OH_f groups would be nearly 3 times that for a typical dibasic cosolvent. This is approximately true.

If this is correct, then we can predict that salts with inert anions, that is, anions with little or no propensity to form H bonds, will show the reverse trend, namely a gain in the OH_f band. This is indeed true for $\text{Na}^+\text{-BPh}_4^-$ (Figure 6). Our interpretation is that Na^+ ions scavenge LP_f groups, thus tipping equilibrium 2 to favor OH_f groups. From these results for Na^+ and Cl^- ions we are in a position to derive single ion values for all ions. This has been done, but errors are large and we hope to refine the results before publishing them. Nevertheless, our present results lead to estimates of solvation numbers that are quite reasonable.

One aspect of our studies deserves special comment. By working at low temperatures we have been able to resolve ν_{OH} into two or more features for certain salts.²⁰ The data establish what may seem to be a surprising result, namely, that ν_{OH} for the halide ion solvation shell occurs at frequencies between those for the OH_f band and that for bulk solvent (HOD or MeOH). Thus solvent-solvent interaction is apparently stronger than solvent-anion interaction. The reason for this is simply the fact that there are ca. six H bonds to each halide ion. This result is in accord with our single ion ^1H resonance shift parameters for salts in water²¹ and

(17) S. E. Jackson and M. C. R. Symons, *Chem. Phys. Lett.*, **37**, 551 (1976).

(18) See, for example: O. D. Bonner and C. F. Jumper, *Infrared Phys.*, **13**, 233 (1973); P. R. Philip and C. Jolicoeur, *J. Phys. Chem.*, **77**, 3071 (1973).

(19) A. K. Soper, G. W. Neilson, J. E. Enderby, and R. A. Howe, *J. Phys. Chem.*, **10**, 1793 (1977).

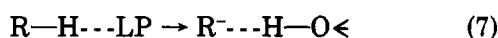
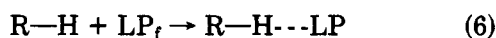
(20) I. M. Strauss and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 1*, **73**, 1796 (1977); **74**, 2146 (1978); **74**, 2518 (1978).

methanol.²² We have interpreted the shifts to high fields induced by ions such as Na⁺ or Cl⁻ simply in terms of H bonds that are slightly weaker than those formed by bulk water or methanol.

Kinetic Consequences: Carbon Acids

In seeking to understand the role of OH_f and LP_f groups in the chemistry of water, I make the following assumptions. Fully bound water molecules are treated as being inert. Reactions which involve attack by OH groups are treated as involving OH_f groups, and those requiring attack by LP groups are treated as involving LP_f groups. Since there are ca. 10% of each in pure water at 25 °C and since the effective mobility of these groups must be high, I consider that reactions could involve two groups at a time. Obviously, attention must be confined to reactions involving water rather than its ions.

A simple reaction requiring LP_f groups is proton removal. Many carbon acids have been studied extensively, good examples being the detritation of malononitrile (pK_A = 11.19) and of *tert*-butylmalononitrile (pK_A = 13.10).²³ The Brønsted coefficient β (0.98) for these reactions suggests that the transition state closely resembles the ion pair, in which the proton is almost completely transferred to water. The simplest scheme involving LP_f would be

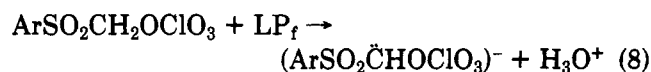


The extent to which H bonding as in (6) may be important is unknown, but (7) is clearly rate determining. If this scheme is correct, then we can write

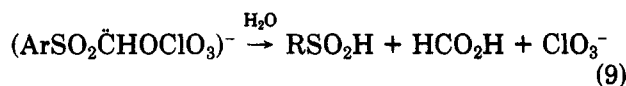
$$\text{rate} = k_2[\text{LP}_f][\text{RH}] \quad (\text{A1})$$

These reactions are generally treated either as pseudo first order, in which case the measured k_1 values can be set equal to $k_2[\text{LP}_f]$, or as second order, with all the water molecules being envisaged as potentially involved.

Another reaction that has been even more thoroughly studied is the water-catalyzed decomposition of various covalent arylsulfonylmethyl perchlorates: ArSO₂CH₂OCIO₃.²⁴ The rate-determining step is again loss of a C-H proton:



followed by rapid decomposition



In this case the Brønsted β coefficient is ca. 0.5, which suggests that the transition state is reached some time before the proton is fully transferred. This makes the mechanistic arguments somewhat easier to apply since

(21) J. Davies, S. Ormondroyd, and M. C. R. Symons, *Chem. Commun.*, 1426 (1970); *Trans. Faraday Soc.*, 3465 (1971).

(22) R. N. Butler and M. C. R. Symons, *Trans. Faraday Soc.*, 65, 945, 2559 (1969).

(23) F. Hibbert and E. A. Long, *J. Am. Chem. Soc.*, 94, 7637 (1972).

(24) (a) L. Menninga and J. B. F. N. Engberts, *Tetrahedron Lett.*, 617 (1972); (b) *J. Phys. Chem.*, 77, 1271 (1973); (c) L. Menninga, W. D. Steenge, and J. B. F. N. Engberts, *J. Org. Chem.*, 40, 3292 (1975); (d) L. Menninga and J. B. F. N. Engberts, *ibid.*, 41, 3101 (1976); (e) L. Menninga and J. B. F. N. Engberts, *ibid.*, 42, 2694 (1977).

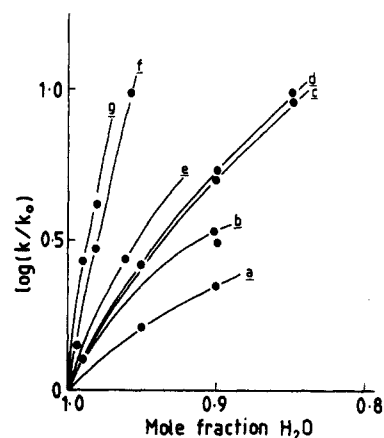
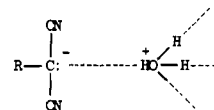


Figure 7. Some rate trends [$\log(k/k_0)$ where k_0 is the rate in pure water at 25 °C] reported by Engberts and co-workers for various organic perchlorates, together with my predicted trends based on the LP_f concept. I have used an initial [LP_f] of 0.1 mol fraction. Similar sets of curves are obtained when this is varied. (a) Theoretical trend for a dibase, first order in LP_f. The trend for a monobase, second order in LP_f, is close to this curve. (b) Aqueous dioxane. (c) Theoretical trend for a dibase, second order in LP_f. (d) Aqueous Me₂SO. (e) Aqueous Me₄N⁺Cl⁻. (f) Theoretical trend for a hexasolvated anion. (g) Aqueous Bu₄N⁺Br⁻; results for HMPA lie close to this line.

back-reaction of the ion pairs will not be so important. (I stress that these are not ordinary ion pairs, since the H-bond between anion and cation, as in VII, must be



VII

strong, even though the lone pair of electrons on carbon are considerably delocalized.)

For both sets of compounds, the initial effect of added basic aprotic cosolvents is a rapid increase in rate (Figure 7). At mole fractions governed by the base and the substrate, there is a maximum in rate which then falls, often to values less than that for pure water. Similar trends were observed for alcohol + aprotic solvent systems. Salt effects on these organic perchlorates were varied, with tetraalkylammonium salts giving large rate enhancements and alkali metal perchlorates slowing down the reactions.²⁵

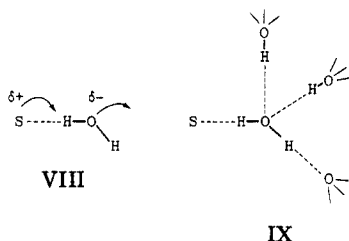
It seems that the initial rate enhancements came as some surprise, and various explanations have been offered. A term "kinetic basicity" is widely used in discussing the results.²⁶ The rate maxima are said to be unexpected in view of the low kinetic basicity of the cosolvents and the decreasing polarity of the media. Long et al. explain their results in terms of water structure, the suggestion being that the cosolvents enhance water structure and this leads to enhanced hydrogen-bonding stabilization of the transition state.²³ I know of no evidence that cosolvents such as Me₂SO enhance water structure, nor can I understand why they should do so. Anyway, insofar as enhancing water structure is equivalent to a cooling effect, I fail to see why this should lead to enhanced "kinetic basicity".

Engberts and his co-workers²⁶ favor a somewhat different explanation. They suggest that the basicity

(25) L. Menninga and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, 98, 7652 (1976).

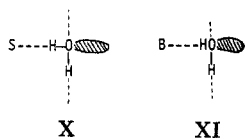
(26) J. B. F. N. Engberts, *Water, Compr. Treatise*, 6 (1979).

of water is enhanced by hydrogen bonding to the cosolvent, the process being depicted as in VIII. They



quote gas-phase basicities to support this concept, pointing out that the proton affinity of MeCN, for example ($186 \text{ kcal mol}^{-1}$), is greater than that for water.

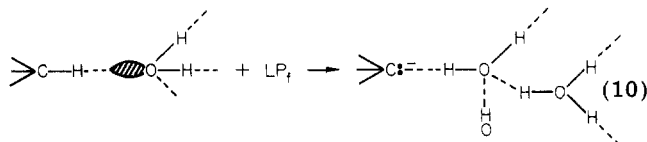
While I agree that such bonding must affect the situation (see below), I do not believe that it can explain the rate maxima under consideration. It is important to realize that the basicity of LP_f groups in bulk water is very much greater than that of monomeric H_2O , and is certainly greater than that of MeCN. Evidence for this statement comes directly from infrared and NMR studies.^{11,16} Clearly, structure VIII taken alone is misleading. In fact, the normal unit will be IX rather than VIII, which, like bulk water, will be relatively inert. What really matters is the difference in basicity (kinetic or otherwise) between lone pairs of units of type X and normal LP_f units. This will lead to slightly reduced



or enhanced basicity depending on the relative basicity of S.

If my hypothesis is correct, addition of a cosolvent than can scavenge OH_f groups must cause a rate enhancement. Initially, as the cosolvent is added, the major reagent will be normal LP_f . Strong bases such as Me_2SO generate two LP_f groups per molecule. The very strong base hexamethylphosphoramide (HMPA) probably generates at least three LP_f per molecule initially.¹¹ Qualitatively, these considerations explain the behavior indicated in Fig. 7, the enhancements being $\text{HMPA} > \text{DMSO} > \text{dioxane}$, for example. However, two extra factors need to be considered. One is the participation of LP_f units of type XI (B-LP_f). The probability of such units being formed will increase with [B], and they must ultimately be of major significance. For very strong bases this will lead to a further rate enhancement, but for weakly basic cosolvents there will be a fall in rate.

The other factor that needs to be considered is that as $[\text{LP}_f]$ increases, the possibility of processes bimolecular in LP_f must increase. A second LP_f group will facilitate reaction in the following way:



This reaction is more favorable than (9) for two reasons. One is that the resulting H_3O^+ ion is ideally solvated by three hydrogen bonds, whereas unit VII has an unwanted bond formed by its remaining LP group. The second is that the proton is removed from the anion. To what extent Engberts' reaction might profit by this

second LP_f group is not clear, but the possibility surely needs to be considered.

I have calculated the rate enhancements expected for mono-, di-, and tribasic cosolvents in the 1.0–0.8 mol fraction region on the simple assumptions that only LP_f groups are involved and that the reactions are first order in $[\text{LP}]$ (Figure 7).

The increases predicted are of the correct form, but are uniformly too small. However, if two LP_f groups are required, prediction and experiment are in better agreement. The dibase curve is almost identical with that for Me_2SO , a typical strong dibasic solvent. Dioxane falls off from the predicted curve, as expected for a relatively weak base. Results for HMPA are clearly anomalous since the rate enhancement is comparable with that for $\text{Bu}_4\text{N}^+\text{Br}^-$. As can be seen from Figure 7, the plot for an additive with a basicity of 6 falls reasonably close to the results for $\text{Bu}_4\text{N}^+\text{Br}^-$. I cannot explain the remarkable results for HMPA except to say that it is in line with our preliminary results on the OH_f $2\nu_{\text{OH}}$ band, since HMPA causes a loss close to those for $\text{Bu}_4\text{N}^+\text{hal}^-$ salts.

Thus the predicted curves fit reasonably well, provided it is accepted that two LP_f groups are required in the transition state. If only one is required, then the predicted rates are too small although the trends are correct.

Qualitatively, the subsequent trends reported by Engberts and his co-workers are in accord with expectation. We expect a relatively rapid reduction in rate to set in for weakly basic cosolvents and a less rapid reduction to appear at a later stage for strongly basic cosolvents. In the mole fraction region ≤ 0.7 (H_2O) two other factors need to be considered. One is that the $[\text{LP}_f]$ will fall as the total $[\text{H}_2\text{O}]$ falls. The other is that the concentration of the strongly basic three H-bonded LP_f unit will fall rapidly in this region, giving way via two and one H-bonded units ultimately to single H_2O units, whose reactivity will be less than LP_f units, but greater than that of monomer water since the limiting structure is $\text{B} \cdots \text{HOH} \cdots \text{B}$. At this stage, if B is a strong base it will react directly, since there is plenty of "free" base in the system. If it is a weak base and unable to react directly, the $\text{B} \cdots \text{HOH} \cdots \text{B}$ units may react, but they will be far less reactive than LP_f units. Hence in both cases, the rate should fall, and in the latter case it will tend toward zero. For di- or tribasic cosolvents, as $[\text{H}_2\text{O}]$ falls, so the trend $\text{B}(\text{s})_3 \rightarrow \text{B}(\text{s})_2 \rightarrow \text{B}(\text{s})_1 \rightarrow \text{B}$ will be superimposed on those considered above. The rate of increase will fall, as the effective basicity falls. We hope, eventually, to be able to make numerical predictions in the whole binary solvent range. The present qualitative agreement makes us optimistic.²⁷

My simple theory also predicts salt effects accurately. Thus $\text{R}_4\text{N}^+\text{hal}^-$ salts produce large rate enhancements,²⁴ the initial increases being about that expected for halide ion solvation numbers of ca. 6. Most salts have only minor effects, the trends being very similar to their effect on the OH_f band. Perchlorates have a clear retarding effect, in accord with the weak solvation of perchlorate ions, so that cation solvation dominates. We cannot estimate the extent to which salts like NaClO_4 scavenge LP_f groups because the OH_f band and

(27) M. C. R. Symons, *J. Chem. Res., Synop.*, 140 (1978); *J. Chem. Soc., Chem. Commun.*, 418 (1978).

Table I
Reported ΔH^\ddagger Values ($\Delta H^\ddagger_{\text{exptl}}$) for the Hydrolysis of
 $p\text{-NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{OCIO}_3$ in Water and the System 0.9
 $\text{H}_2\text{O} + 0.1$ Dioxane^{24d} Together with Values ($\Delta H^\ddagger_{\text{cor}}$)
for the Influence of LP_f Groups

| [base] | $[\text{LP}_f]/$ 25 °C | $[\text{LP}_f]/$ 50 °C | $\Delta H^\ddagger_{\text{exptl}}/$ kcal | $\Delta H^\ddagger_{\text{cor}}/$ kcal ^a | $\Delta H^\ddagger_{\text{cor}}/$ kcal ^b |
|--------|---------------------------|---------------------------|---|--|--|
| 0.0 | 0.10 | 0.13 | 18.4 | 16.38 | 14.38 |
| 0.1 | 0.225 | 0.24 | 15.6 | 15.38 | 15.15 |

^a Assuming first order in LP_f . ^b Assuming second order in LP_f .

that due to OH groups H-bonded to ClO_4^- ions overlap too strongly, but it is clear that there must be considerable generation of OH_f groups.

Before leaving the work of Engberts and co-workers, I should mention their data for binary mixtures containing ethanol. As stressed above, the pure solvent is already rich in weakly basic LP_f groups and hence cannot be thought of as inert in the sense that 4-bonded water molecules are inert. Nevertheless, generation of the more basic LP_f groups by addition of basic cosolvents should give an initial rate enhancement, and this is indeed observed for $\text{EtOH} + \text{Me}_2\text{SO}$ and $\text{R}_4\text{N}^+\text{hal}^-$ systems.²⁴ For ethanol + dioxane systems there is a small increase or plateau region before the normal decrease sets in. We are not able to estimate the extent to which dioxane forms hydrogen bonds in ethanol, but acetone, which is of comparable base strength, is only partially H-bonded, whereas Me_2SO remains fully H-bonded in the 1.0–0.4 mol fraction range. Hence, I would expect that the effect of Me_2SO would be far larger than that of dioxane, as observed. It seems probable that, because of the presence of weakly basic lone pairs on every alcohol molecule, the extra catalytic effect of LP_f groups is less pronounced than for aqueous systems.

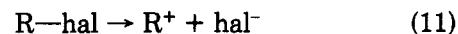
In accord with usual practice, values for ΔH^\ddagger and ΔS^\ddagger are quoted for a number of these reactions, and great weight is placed on their mechanistic significance. I hesitate to comment on the arguments put forward since I remain unsure about the real significance of these quantities, especially when mixed solvents are used. Solvents change quite drastically with temperature and so do equilibrium constants, so great care is needed when giving direct thermodynamic significance to such values. The present reaction is a case in point. When water is heated, there is a steady increase in $[\text{OH}_f]$ and $[\text{LP}_f]$. This means that the concentration of one of the reagents is changing, and surely allowance must be made for this?

In the mole fraction range 1.0–0.8 (H_2O) there is a dramatic increase in ΔH^\ddagger followed by a return to a more normal trend such as might be expected in a mixed solvent system. Qualitatively, such anomalous trends can be explained by the effect of temperature on the $[\text{LP}_f]$ groups and the effect of an added base thereon. This can be seen from the results of a simple calculation based on the law of mass action and on the assumption that on going from 25 to 50 °C the $[\text{LP}_f]$ groups increase from ca. 0.10 to 0.13 for pure water (Table I). When these results are included in the rate equations, the unusually rapid increase in ΔH^\ddagger is seen to arise largely as a result of changes in $[\text{LP}_f]$ groups. This factor diminishes and is ultimately lost in the 0.8–0.7 mole fraction (H_2O) region. Thus the "anomalous" behavior

is to be expected for aqueous systems.

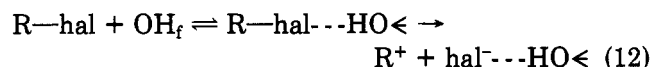
Kinetic Consequences: $\text{S}_{\text{N}}1$ Reactions

There is on-going controversy regarding the proper description of reactions traditionally viewed as $\text{S}_{\text{N}}1$ processes. Much of this centers on kinetic differences between "free" systems such as $\text{Me}_3\text{C}-\text{Cl}$ and constrained systems such as 1-adamantyl halides.^{28,29} Since the latter cannot react via direct nucleophilic attack on carbon, differences are associated with "nucleophilic solvent assistance" for the former, though the current literature does not make this phase very explicit. Unfortunately, space does not permit a critical discussion of the arguments involved. For present purposes I will assume that the rate-determining step in " $\text{S}_{\text{N}}1$ type" solvolysis is simple ionization:

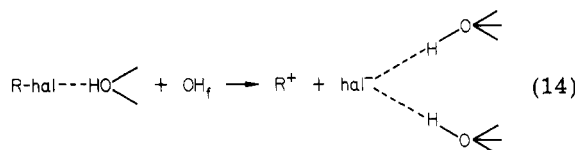
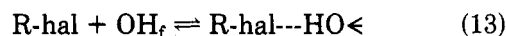


and the following discussion lends some support to this formulation.

Clearly, if nucleophilic attack on carbon is ruled out, then reaction 11 can only proceed if the halide ion is already partially solvated in the transition state. This means that OH_f groups are required. Two reasonable alternatives are:



and



Alkyl halides are sparingly soluble in water, and the extent of hydrogen bonding is not clear. I make the assumption that this is sufficiently extensive to justify consideration of reaction 14 as a reasonable process, especially when $[\text{OH}_f]$ is high. Reaction 13 is strongly supported by our recent infrared studies of related systems. I also stress that the preequilibrium of eq 13 should be taken into consideration in any analysis of rates. Its effect could well help to explain the marked curvature of Arrhenius plots for $\text{S}_{\text{N}}1$ processes.

Some qualitative predictions follow directly. Addition of basic cosolvents results in a loss of OH_f groups and hence should cause the rate of these reactions to fall. The predicted rate of decrease is too slow if reaction 12 is assumed, but if 14 is the rate-determining step, then the predicted initial decrease is in the correct range (Figure 8). Indeed, the second-order lines (in OH_f) for mono- and dibases embrace all the data with the exception of tetrahydrofuran (THF), which causes an anomalously rapid fall in rate. Since simple 1:1 electrolytes, M^+X^- do not change $[\text{OH}_f]$ extensively, their effect on the rates should be relatively small, and this is again observed. Similar considerations lead to the prediction that R_4N^+ salts should be strongly retarding, whereas NaBPh_4 and alkali metal perchlorates should give rise to rate enhancements. Preliminary results

(28) T. W. Bentley and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 2542 (1976).

(29) T. W. Bentley, C. T. Bowen, W. Parker, and C. I. F. Watt, *J. Am. Chem. Soc.*, **101**, 2486 (1979).

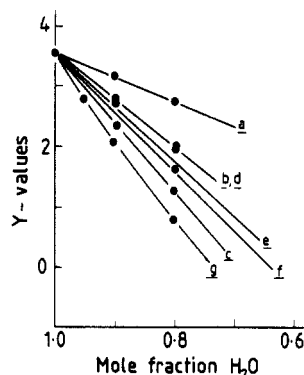


Figure 8. Plot of Y value against mole fraction (H_2O) for various H_2O + aprotic solvent systems together with my calculated values. (a) Theoretical trend for a monobase, first order in OH_f . (b) Theoretical trend for a monobase, second order in OH_f . The trend for a dibase, first order in OH_f , is close to this curve. (c) Theoretical trend for a dibase, second order in OH_f . (d) Aqueous MeCN. (e) Aqueous Me_2CO . (f) Aqueous Me_2SO . (g) Aqueous THF.

using aqueous $\text{Me}_3\text{C-I}$ containing ca. 0.1 mol fraction aprotic base to retard the reaction appear to confirm these predictions.³⁰ Indeed, the retarding effect of the tetraalkylammonium salts is about equal to that expected for halide ion solvation numbers of 5–6. So, in this case also, there are large salt effects when cations are inert which are readily explained by the OH_f/LP_f theory.

Many studies of $\text{S}_{\text{N}}1$ solvolyses are concerned with analysis of ΔH^\ddagger , ΔS^\ddagger , and ΔC_p^\ddagger . As with reactions 8 and 9, ΔH^\ddagger falls rapidly in the 1.0 to 0.9 mol fraction (H_2O) region, reaches a minimum, and then rises again. Whatever may be the true total explanation of these anomalies, there can be no doubt that the effect of temperature on the relative $[\text{OH}_f]$ in this composition range makes an important contribution to the apparent ΔH^\ddagger (and hence ΔS^\ddagger) values, of exactly the type observed.

Kinetic Consequences: $\text{S}_{\text{N}}2$ Solvolyses

In most $\text{S}_{\text{N}}2$ solvolyses there is a nucleophilic attack which for water on my theory involves LP_f groups, but there must also be solvation of the leaving anion which requires OH_f groups. Thus both types of water defect are required. Additives that reduce $[\text{OH}_f]$ normally increase $[\text{LP}_f]$, and vice versa. This will give concurrent rate gain and rate loss contributions, and hence aqueous $\text{S}_{\text{N}}2$ solvolyses should be far less sensitive to such additives. This is the case for well established $\text{S}_{\text{N}}2$ processes.

Hydrophobic Contributions and Structure Making/Breaking Effects

Some of the phenomena discussed above have been interpreted by others in terms of "structure making" or "structure breaking". Since water has such a close-knit three-dimensional structure, it might be expected that this can be modified by additives, as indeed it is by temperature and pressure changes. Urea is often taken to be a typical structure breaker, while *tert*-butyl alcohol, triethylamine, and R_4N^+ ions are taken to be structure makers. Our unpublished spectroscopic studies on urea give no evidence for any breakup of

water structure in the presence of urea. However, I think that the clathrate-cage concept is quite well established for certain solutes, and this *could* be taken as a "structure-making" effect. The cage concept is taken from our knowledge of solid-state clathrates, in which each water molecule forms its normal set of four H bonds but in such a way as to define large voids which house guest molecules of suitable sizes.³¹ Just as ice organization is lost on melting, but less defined structure is maintained, so clathrate structure must be lost on melting though some echo thereof may be retained, especially at low temperatures. Thus, one important criterion of cage formation in the liquid phase should be a rapid loss of observable phenomena associated with cages on warming.³²

One contribution to this field has been our observation of a strongly temperature-dependent downfield shift of the water proton resonance in the 1.0–0.9 mol fraction (H_2O) region for Me_3COH and R_4N^+ salts.^{33,34} For Me_3COH we have studied H_2O and ROH protons separately,⁶ and only the former show this effect. It is far in excess of the effect ascribed to loss of OH_f groups, discussed above. This suggests a general strengthening of water–water bonds, but it is not accompanied by a major extra loss of OH_f or LP_f groups, as judged by overtone infrared spectra.

It seems that large, nearly spherical molecules have the greatest propensity to encourage cage formation in liquid water. It certainly cannot be concluded that molecules which give solid-state water clathrates will give significant liquid-phase cages. A nice example is that of acetone. This gives a well-defined solid clathrate,³⁵ and some have inferred that there is a tendency toward cage formation in the liquid state. In fact, the two systems are quite different.³⁶ In liquid water, the $\text{C}=\text{O}$ stretching band for acetone is strongly shifted, indicative of two hydrogen bonds to the oxygen lone pairs (Figure 2). There is no contribution from monosolvates or from molecules not hydrogen bonded ("free"). In marked contrast, the $\text{C}=\text{O}$ frequency for the solid clathrate is equal to that for solutions in hexane, there being no contribution from hydrogen-bonded molecules.

Gain or loss of the overtone OH_f peaks for water have often been taken to indicate structure breaking (an increase in structural temperature) or structure making (a decrease in structural temperature). The discussion given herein shows how misleading this can be: in most systems, had the $[\text{LP}_f]$ groups been monitored instead of $[\text{OH}_f]$ groups, the inferences about structural temperature would have been exactly the reverse!

It is probable, therefore, that clathrate effects will be manifested by aqueous systems containing such species as R_4N^+ ions or *tert*-butyl alcohol. If this affects rates, there should be large temperature effects on the rates since these cage phenomena are rapidly lost on heating. The unusual ΔH^\ddagger and ΔS^\ddagger results for systems contain-

(31) D. W. Davidson, *Water, Compr. Treatise*, 2 (1973).

(32) M. J. Blandamer and M. C. R. Symons in "Hydrogen Bonded Solvent Systems", A. K. Covington and P. Jones, Eds., Taylor & Francis, London, 1968.

(33) B. Kingston and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 69, 978 (1973).

(34) J. Davies, S. Ormondroyd, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 68, 686 (1972).

(35) A. S. Quist and H. S. Frank, *J. Phys. Chem.*, 65, 560 (1961); G. J. Wilson and D. W. Davidson, *Can. J. Chem.*, 41, 264 (1963).

(36) G. Eaton and M. C. R. Symons, unpublished.

(30) M. J. Blandamer, N. G. Pay, and M. C. R. Symons, unpublished.

ing Bu_4N^+ ions reported by Engberts and co-workers may well reflect such changes.²⁴

Conclusion

Liquid water is an important chemical, as a solvent, as a reagent, and in the support of life in all its forms. Understanding its structure is, therefore, of significance to chemists, physicists, and biologists. Despite wide-ranging studies, both experimental and theoretical, one important aspect of its structure has been largely neglected, namely the presence of "free" groups in an otherwise fully hydrogen-bonded network. I have attempted to show that several aspects of the varied role

that water plays in chemistry are illuminated by a consideration of these groups.

I have sorely neglected the theories of others, in order to make room for my own. Some of these theories are highly sophisticated, utilizing the latest concepts in physical chemistry, and my ideas look elementary in contrast. My only justification is to say that no amount of algebra will help if the initial premise is incorrect.

I very much hope that with the help of my collaborators, currently Dr. M. J. Blandamer, N. G. Pay, G. Eaton, and N. J. Fletcher, and G. Smith, these ideas can be placed on a more quantitative footing. I thank V. Orson-Wright and C. A. Crane for help in the preparation of this text.