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NEAR-INFRARED STUDIES OF THE STRUCTURE OF WATER

I. PURE WATER
II. IONIC SOLUTIONS

by

K. BUIJS (EURATOM) G.R. CHOPPIN (C.E.N.)

1964

Work performed under EURATOM/C.E.N.
contract No. 002-61-2 TPU B

Reprinted from
THE JOURNAL OF CHEMICAL PHYSICS
Vol. 39, No. 8 - 1963

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cations : order-producing : $La^{3+} > Mg^{2+} > H^+ > Ca^{2+}$,
order-destroying : $K^+ > Na^+ > Li^+ > Cs^+ = Ag^+$;
anions : order-producing : $OH^- > F^-$,
order-destroying : $ClO_4^- > I^- > Br^- > NO_3^- > Cl^- > SCN^-$.

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Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 39, No. 8, 2035–2041, 15 October 1963
Printed in U. S. A.

Near-Infrared Studies of the Structure of Water. I. Pure Water*

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(Received 27 May 1963)

The absorption bands of water in the 1.1-to-1.3-μ region have been measured. From the extinction coefficients, concentrations of water species involving 2,1, and 0 hydrogen bonds per molecule were calculated. The temperature dependence of these concentrations yielded a value of 3.7–4.5 kcal for the energy involved in breaking one mole of hydrogen bonds in water. On melting, 46% of the hydrogen bonds originally present in ice are broken; by 72°C the percentage broken has increased to 61. Further, the results were used in conjunction with the flickering cluster model of Frank and Wen to obtain an upper limit for the average size of the water polymers of 90 molecules of H_2O at 20°C.

INTRODUCTION

THE role of water as "the universal solvent" has caused it to be the object of many investigations. Many of the unique properties of water as a liquid were interpreted over 40 years ago to indicate that water exists as an associated liquid due to strong intermolecular attractions. Hydrogen bonding was considered to be responsible for the greatest part of this intermolecular attraction.[1]

In 1933 Bernal and Fowler suggested that water has a broken-down ice structure which still maintains most of the hydrogen bonds. Each H_2O molecule has a tetrahedral configuration in which four hydrogen bonds are involved. As the temperature increases, hydrogen bonds are broken and the liquid structure becomes more closely packed. In the 30 years that have elapsed, the weight of evidence from studies of water and aqueous solutions by infrared, Raman, x-ray, dielectric relaxation, and other techniques have tended to substantiate the general concepts of Bernal and Fowler, i.e., the existence of regions of extensive hydrogen bonding and the gradual decrease in hydrogen bonding with increasing temperature. Much of the important work since the introduction of these ideas by Bernal and Fowler has been reviewed recently by Nemethy and Sheraga.[2]

Recently, we became interested in a possible study by infrared techniques of the species of water in concentrated electrolyte solutions. Quite definite effects were observed for absorption bands in the 1.1–1.3-μ region, which correlated with the general order–disorder effects of ions postulated by Gurney.[3]

As our studies continued, it came to our attention that these absorption bands had been investigated some time ago by Suhrmann and Breyer.[4,5] Although their interpretation of their results remains in general quite acceptable, neither their instrumental resolution nor the state of the theory of aqueous solutions was sufficient in 1933 to permit full exploitation of the spectral effects in this wavelength region.

In this paper we describe the resolution into three bands of the absorption band of water between 1.1–1.3 μ, the spectral assignments and the extinction coefficients of each band. The concentration of each of the three absorbing species is calculated as a function of water temperature and a model is proposed for liquid water which involves three species. Using this model and the concentration of each species a number of the properties of water are calculated. In the following paper[6] the results are presented of a study of the same absorption bands in ionic solutions.

EXPERIMENTAL

The spectra were recorded using a Cary 14 spectrophotometer. All measurements were made in fused silica cells with 1-cm optical pathlength unless stated otherwise. Temperature control was achieved by equilibrating the sample cells in a water bath at a fixed temperature. Experiments were run in which careful checks were made on the decrease in temperature during the time the spectra were recorded. In this way, the listed temperatures are believed to be correct to within 2°C.

ASSIGNMENTS

In Fig. 1 are shown the near-infrared spectra of water at 21° and 72°C. Figure 2 shows the spectrum of ice at 0°C. It is readily seen from Fig. 1 that at least two close-lying bands change their relative intensities when the temperature of the water is varied. The position of the maxima of two bands can be taken as 1.16 μ

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* Research carried out in the framework of the Euratom Transplutonium Program under contract 002/61/2 TPU B.

† On leave from the Department of Chemistry, Florida State University, Tallahassee, Florida.

[1] H. M. Chadwell, Chem. Rev. **4**, 375 (1927).

[2] G. Nemethy and H. A. Sheraga, J. Chem. Phys. **36**, 3382 (1962).

[3] R. W. Gurney, *Ionic Processes in Solution* (McGraw-Hill Book Company, Inc., New York, 1953).

[4] R. Suhrmann and F. Breyer, Z. Physik. Chem. **B20**, 17 (1933).

[5] R. Suhrmann and F. Breyer, Z. Physik. Chem. **B20**, 193 (1934).

[6] G. R. Choppin and K. Buijs, J. Chem. Phys. **39**, 2042 (1963) (following paper).

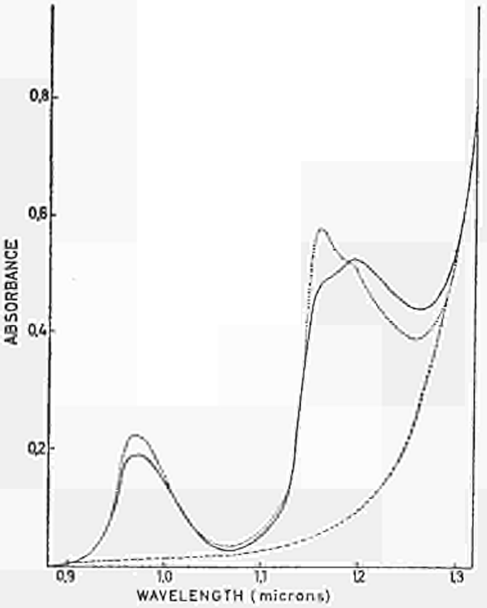

FIG. 1. Near-infrared spectra of liquid water between 0.9 and 1.3 μ. The solid curve is the spectrum at 21°C, the dotted curve that at 72°C. The lower dashed curve is the calculated base line.

(8620 K) and 1.20 μ (8330 K). The measured value for the maximum of the 1.16-μ band is more accurate than that of the 1.20-μ band. From the behavior of the absorption minimum around 1.25 μ in a number of spectra of pure water and of solutions it was concluded that a band in this wavelength region also plays a role. This band was identified as the band found for ice at approximately 1.25 μ (8000 K) as shown in Fig. 2.

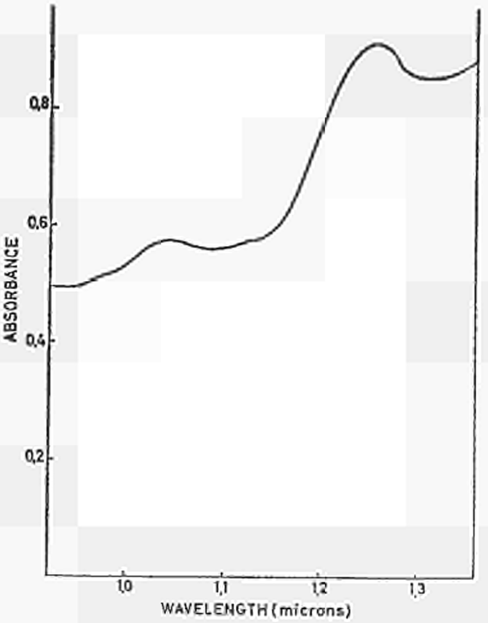

FIG. 2. Near-infrared spectrum of ice at 0°C.

A ready explanation for these bands is found in their assignment to water molecules having different degrees of polymerisation. This approach is supported by the findings of Van Thiel, Becker, and Pimentel,[7] who studied the spectrum of water by the matrix isolation technique and found peaks at different fixed frequencies for various polymeric species. Weston[8] and Schultz and Hornig[9] in their Raman studies of water report intensity changes and frequency shifts with varying temperature. Our view point is not necessarily in conflict with their observations for if the bands due to the various species are not resolved in the fundamental region, relative intensity changes in these separate bands would appear as frequency shifts and intensity changes of the observed broad band. A more detailed description of the polymeric species involved depends on the assignment of the bands to the appropriate sum, or multiple of fundamental vibration bands. The fundamental vibrations are ν_1 (symmetric stretching), ν_2 (bending), and ν_3 (asymmetric stretching). A comparison of the spectra of the condensed phases with the vapor spectrum[10] shows that the bands in the 1.2-μ region can be assigned to the $\nu_1+\nu_2+\nu_3$ vibration, which in the vapor phase gives rise to the most intense band in this region and occurs at 1.135 μ (8807 K). More evidence for this assignment in the case of the 1.16-μ band is described

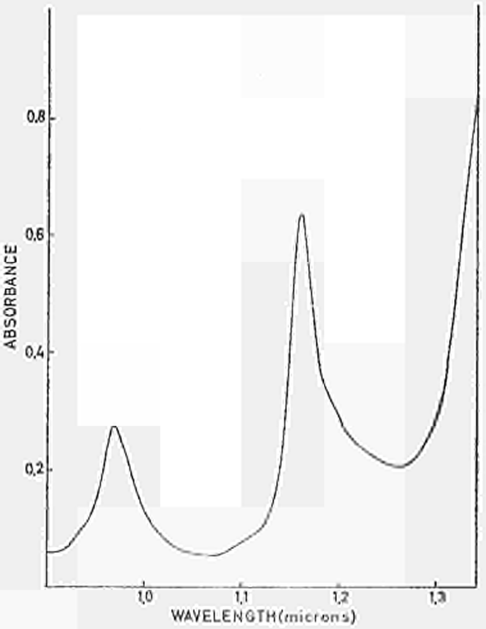

FIG. 3. Near-infrared spectrum of a 13m solution of $NaClO_4$ at 21°C.

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[7] M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. **27**, 486 (1957).

[8] R. E. Weston, Spectrochim. Acta **18**, 1257 (1962).

[9] J. W. Schultz and D. F. Hornig, J. Phys. Chem. **65**, 2131 (1961).

[10] H. H. Landolt and R. Börnstein, *Zahlenwerte und Funktionen* (Springer-Verlag, Berlin, 1951), Band I, Teil 2, S. 333.

later. If the vibrational transition of the bands is accepted as being $\nu_1+\nu_2+\nu_3$, the following assignment would seem to be logical:

1.16 μ (8620 K)—water molecules with neither OH group bonded (S_0);
1.20 μ (8330 K)—water molecules with 1 OH group bonded (S_1);
1.25 μ (8000 K)—water molecules with 2 OH groups bonded (S_2).

As the combination vibration contains both stretching vibrations (ν_1 and ν_3) an equal number of times, only one band can be expected for each of the above-mentioned species of water molecules. The situation becomes somewhat more complicated by the possibility of proton acceptance by the O atom, which has some effect on the vibrational frequencies. This effect must, however, be smaller by an order of magnitude than the direct effect of the proton being bonded as the binding electrons of the proton are only affected indirectly. The rather contradictory observations on this effect are discussed by Van Thiel, Becker and Pimentel.[11] The increased broadness of the bands going from 1.16 to 1.25 μ is further substantiation of our assignments since hydrogen bonding increases bandwidths.

The polymeric species of water to which we ascribe an absorption band identical to the band found for ice, is often referred to in the literature as being "icelike."[12] There is no reason, however, to assume that the long-range structure of this species is identical with any of the known modifications of the structure of ice. Hornig *et al.*[13] could not detect any significant spectroscopic difference between the hexagonal form of ice on the one hand and either the cubic or the glass form on the other. As a result we feel justified in using the spectroscopic data for ice in the case of the S_2 species, without identifying this species with an actual ice structure.

TABLE I. The frequencies of overtone and combination bands of unbonded water molecules in the liquid phase and in the vapor phase.

Band	Frequency (K) in liquid	Frequency (K) in vapor[a]	Liquid system studied
I	5 226	5 332 ($\nu_2+\nu_3$)	$NaClO_4$ solution
II	7 040	7 252 ($\nu_1+\nu_3$)	$NaClO_4$ solution
III	8 620	8 807 ($\nu_1+\nu_2+\nu_3$)	$NaClO_4$ solution and H_2O
IV	10 340	10 613 ($2\nu_1+\nu_3$)	H_2O
V	11 900	12 151 ($2\nu_1+\nu_2+\nu_3$)	H_2O
VI	13 500	13 831 ($3\nu_1+\nu_3$)	H_2O

[a] See Ref. 10.

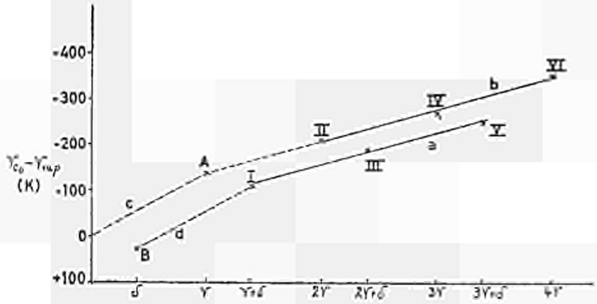

FIG. 4. Plot of the infrared absorption frequency shifts for various combination bands of nonhydrogen-bonded water molecules for the transition vapor→liquid.

Assignment of the 1.16-μ Band

The band at 1.16 μ (8620 K) is very pronounced in the spectrum of a 13*m* $NaClO_4$ solution (Fig. 3). The frequency of this band does not change with dilution nor is its intensity very different from that in pure water. Consequently we could use $NaClO_4$ solutions in thin layers to study the more intense bands of water in the overtone region to obtain data on other overtone and combination bands due to unbonded water molecules. This approach is supported also by the fact that the peaks at 0.97 μ coincide for hot water and $NaClO_4$ solution. In Table I the frequencies of the observed bands are listed, together with the strongest vapor bands occurring nearby.

In Fig. 4 the frequency differences between vapor and liquid phase are plotted versus the number of times a stretching vibration occurs in the combination or multiple. In fact, the graph has two independent abscissas, one for $n\cdot\nu$ and the other for $\delta+n\cdot\nu$. Both sets of three points lie on straight lines which is in agreement with the general principles of vibration frequency shifts due to intermolecular interaction. It has been derived theoretically by Buckingham[14] and found experimentally for HCl in several solvents by West and Edwards[15] and for polyatomic ions in alkali-halide lattices by Price *et al.*[16] that $\Delta(\nu_n+\nu_m)=\Delta\nu_n+\Delta\nu_m$. The slopes of our lines thus give the frequency shift for a stretching vibration in the transition from vapor to unbonded liquid.

The frequency shifts for ν_2 and ν_3 are obtained from the broken lines. These were constructed by continuing the straight line to point A. This point gives the fre-

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[11] M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. **27,** 95 (1957).
[12] H. S. Frank, Proc. Roy. Soc. (London) **A247,** 481 (1958).
[13] D. F. Hornig, H. F. White, and F. P. Reding, Spectrochim. Acta **12,** 338 (1958).
[14] A. D. Buckingham, Proc. Roy. Soc. (London) **A255,** 32 (1960).
[15] W. West and R. T. Edwards, J. Chem. Phys. **5,** 14 (1937).
[16] W. C. Price, W. F. Sherman, and G. R. Wilkinson, Proc. Roy. Soc. (London) **A255,** 15 (1960).

TABLE II. The molar absorption coefficients at 1.16, 1.20, and 1.25 μ for water at various temperatures.

T (°C)	$E_{1.16}$ (10^{-3} liter mole^{-1} cm^{-1})	$E_{1.20}$ (10^{-3} liter mole^{-1} cm^{-1})	$E_{1.25}$ (10^{-3} liter mole^{-1} cm^{-1})
6	6.85	7.52	4.23
21	7.56	7.58	4.17
34	7.95	7.50	3.93
47	8.37	7.23	3.61
61	8.80	7.11	3.30
72	9.09	6.94	2.99

quency shift for ν_3 (about -150 K). Line c connects A to the origin; through Point I the Line d has been drawn parallel to c. Point B on Line d then gives the frequency shift for ν_2 (about $+30$ K). A check on the validity of this procedure is given by inspection of the fundamental vibration frequencies of liquid water. The absorption spectrum of the liquid in the 3-μ region is rather complex, so that no quantitative check on the results can be made. In any case, the frequencies observed for water and ionic solutions are lower than those of water vapor. The bending frequency, according to our plot, must show a positive shift and from the vapor frequency of 1595 K we predict a frequency of about 1625 K for water molecules which have no hydrogen bonds in the liquid state. In the Raman studies of solutions a value of 1630 K has been found for a 6M KI solution, a solution for which we find a strong 1.16-μ peak.[7] We believe that the very satisfactory agreement for the bending mode justifies our treatment of the frequency shifts.

The following conclusions can be drawn from Fig. 4:

(1) The fundamental frequency shifts for water molecules going from the vapor to the unbonded state in the liquid are -60 K for ν_1, $+30$ K for ν_2, and -150 K for ν_3.

(2) The strong bands below 2.5 μ in the spectrum of liquid water are combination bands, not overtones, with the same assignments as the nearby vapor bands. This implies that the bands in the 1.2-μ region must be assigned to $\nu_1+\nu_2+\nu_3$.

EVALUATION OF THE RESULTS

The intensities of the three bands can be used to give information on the concentrations of the various species in water. In order to get quantitative results a baseline has to be constructed to subtract the contribution of the strong band at 1.447 μ (6910 K). This baseline was calculated using a least squares method and was forced through the portions of the spectral curves which are below 1.060 μ (neglecting the band at 0.98 μ) and between 1.30 and 1.36 μ. Two types of functions were tried, a sum of exponentials $A=A_1e^{d_1(\lambda-\lambda_0)}+A_2e^{d_2(\lambda-\lambda_0)}$ and a Lorentz function $A=a/[(\nu-\nu_0)^2+b^2]$, which seems more justified theoretically. The validity of the functions was checked by performing the same calculation on a spectrum of 98% H_2SO_4. Concentrated H_2SO_4 has only a very weak band in the 1.2-μ region, which can be easily accounted for by visual inspection. In this case the sum of exponentials proved to be superior to the Lorentz function and consequently this type of function was used for the water spectra. The calculated baseline is shown in Fig. 1. For the spectrum of ice another baseline had to be used. For this case and for the spectra of aqueous solutions[6] a series of curves were constructed by multiplying the ordinate of the water baseline curve with a series of factors, varying between 0.25 and 8. One curve out of this series always fitted in a given spectrum and could be used to obtain a baseline. The inaccuracies which might result from this procedure were minimized by using only the optical densities at 1.16 and 1.20 μ for quantitative evaluation, the region with the steepest slope thus being avoided. The optical density at 1.25 μ was only used to perform checks on the calculations.

The observed molar absorption coefficients at the wavelengths of three bands for water at various temperatures are listed in Table II.

The relative amounts of the various species of water molecules were calculated from the following set of four equations:

$$\mathcal{E}_{1.16}{}^0C_0+\mathcal{E}_{1.16}{}^1C_1+\mathcal{E}_{1.16}{}^2C_2=E_{1.16}, \tag{1}$$

$$\mathcal{E}_{1.20}{}^0C_0+\mathcal{E}_{1.20}{}^1C_1+\mathcal{E}_{1.20}{}^2C_2=E_{1.20}, \tag{2}$$

$$\mathcal{E}_{1.25}{}^0C_0+\mathcal{E}_{1.25}{}^1C_1+\mathcal{E}_{1.25}{}^2C_2=E_{1.25}, \tag{3}$$

$$C_0+C_1+C_2=1, \tag{4}$$

where C_0, C_1, and C_2 are the relative concentrations of nonbonded, singly bonded, and doubly bonded molecules and $\mathcal{E}_{1.16}{}^0$ designates the molar absorption coefficient of the nonbonded species at 1.16 μ, etc. If the nine coefficients are known, the four equations have only three unknowns, allowing use of Eq. (3) only as a check. In this way, the uncertainty involved in the handling of the absorption at 1.25 μ is minimized. The $\mathcal{E}_\lambda{}^i$'s have to be treated as if they were independent of temperature, a procedure which certainly introduces some inaccuracy into the results. This inaccuracy is kept at a minimum by putting equal weight on the data obtained at 6° and 72°C in calculating the $\mathcal{E}_\lambda{}^i$'s. Another assumption is that the presence of an ionic solute effects all coefficients in a similar systematic way. Similar treatment of the spectra of aqueous solutions then provided a number of additional systems to give information on the values of the $\mathcal{E}_\lambda{}^i$'s. The molar absorption coefficients for the doubly bonded species ($\mathcal{E}_\lambda{}^2$) were taken from the spectrum of ice. The coefficient $\mathcal{E}_{1.25}{}^0$ is zero as a consequence of the sharpness of the band at 1.16 μ;

furthermore, the peak centered at 1.20 μ is assumed to be approximately symmetric which leads to $\mathcal{E}_{1.16}^{1}=\mathcal{E}_{1.25}^{1}$. So only four absorption coefficients were left to be determined, viz., $\mathcal{E}_{1.16}^{0}$, $\mathcal{E}_{1.16}^{1}$, $\mathcal{E}_{1.20}^{0}$, and $\mathcal{E}_{1.20}^{1}$. Of these, $\mathcal{E}_{1.20}^{0}$ is small compared to the others, because the 1.16-μ band is sharp. The set of coefficients obtained by considering the spectra of water and a number of aqueous solutions resulted in sets of concentrations for all systems studied, which satisfied Eq. (3) to within a few percent. The set of molar absorption coefficients in 10^{-3} liter mole^{-1} cm^{-1} obtained for water is

$$\mathcal{E}_{1.16}^{0}=17.5 \qquad \mathcal{E}_{1.16}^{1}=4.5 \qquad \mathcal{E}_{1.16}^{2}=0.8$$

$$\mathcal{E}_{1.20}^{0}=0.7 \qquad \mathcal{E}_{1.20}^{1}=14.0 \qquad \mathcal{E}_{1.20}^{2}=4.6$$

$$\mathcal{E}_{1.25}^{0}=0.0 \qquad \mathcal{E}_{1.25}^{1}=4.5 \qquad \mathcal{E}_{1.25}^{2}=7.5.$$

In Table III the calculated values of C_0, C_1, and C_2 for pure water at various temperatures are listed.

DISCUSSION

Number of Hydrogen Bonds in Water

The quantities listed in Table III give direct information on the number of hydrogen bonds present in water. Since the maximum number of hydrogen bonds is present in ice (100%), the number present at a certain temperature is $100-C_0-0.5C_1$. Thus, we find that in the range 6° to 72°C the percentage hydrogen bonding decreases from 52% to 39%. The extrapolated C_i values for 0°C are: $C_0=0.26$, $C_1=0.41$, $C_2=0.33$. This results in a value of 54% for the hydrogen bonds present in water at 0°C. The values derived from earlier experiments by other workers vary between about 50% (Cross *et al.*[17]) and nearly 100% (Pople[18]). However, our values agree very closely with recent statistical mechanical calculations.[2]

TABLE III. Relative concentrations of nonbonded (C_0), singly bonded (C_1), and doubly bonded (C_2) water molecules in pure water at various temperatures.

Temp (°C)	C_0	C_1	C_2
6	0.27	0.42	0.31
21	0.31	0.42	0.27
34	0.33	0.44	0.23
47	0.36	0.43	0.21
61	0.38	0.43	0.19
72	0.40	0.42	0.18

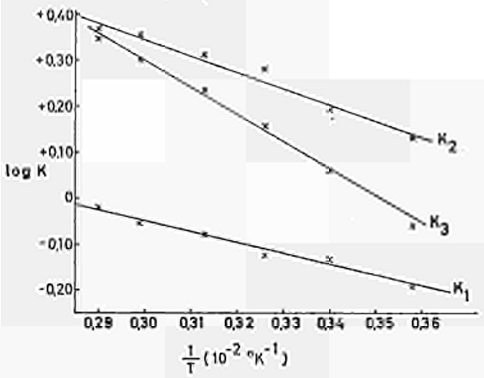

FIG. 5. Plots of logk_i vs $1/T$ for the equilibria between the three species of water molecules in liquid water.

Energy of Hydrogen Bonding

Another important quantity about which the results listed in Table III can give some information is the energy change associated with the hydrogen bonding. A wide variety of values is reported in the literature,[19] the disagreements stemming at least in part from the different chemical processes for which the values are calculated. If it is assumed that the following equilibria exist

$$S_1 \rightleftarrows S_0; k_1=C_0/C_1,$$

$$S_2 \rightleftarrows S_1; k_2=C_1/C_2 \quad \text{and} \quad k_3=k_1k_2=C_0/C_2,$$

it is possible to obtain values for the heats of reaction from plots of log k_i vs $1/T$ (Fig. 5). The method of least squares was used to construct the straight lines in these plots. The enthalpy values obtained in this fashion are

$$E_H^1=1.1 \text{ kcal/mole } (S_1 \leftrightarrows S_0),$$

$$E_H^2=1.6 \text{ kcal/mole } (S_2 \leftrightarrows S_1),$$

$$E_H^3=2.7 \text{ kcal/mole } (S_2 \leftrightarrows S_0).$$

These energies are *not* the energy associated with hydrogen bonding. When a water molecule in the liquid breaks one or both hydrogen bonds, it assumes a more closely packed configuration. This results in an increase in van der Waals energy. Thus the E_H^1 values are the sum of the energy of hydrogen bond rupture and the change in van der Waals energy. Grjotheim and Krogh-Moe[20] have used the temperature dependence of the molar volume of water to calculate a value of 2.6 kcal/mole for the process corresponding to $S_0 \leftrightarrows S_2$. Nemethy and Sheraga[2] have used the flickering cluster model of water suggested by Frank and Wen[21] to calculate a value of 2.64 kcal/mole. A value of 9.45

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[17] P. C. Cross, J. Burnham, and P. A. Leighton, J. Am. Chem. Soc. **59**, 1134 (1957).

[18] J. A. Pople, Proc. Roy. Soc. (London) **A205**, 163 (1951).

[19] G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (W. H. Freeman and Company, San Francisco, 1960), p. 214.

[20] K. Grjotheim and J. Krogh-Moe, Acta Chem. Scand. **8**, 1193 (1954).

[21] H. S. Frank and W-Y Wen, Discussions Faraday Soc. **24**, 133 (1957).

kcal/mole for the heat of vaporization of the hypothetical close-packed liquid at 0°C is calculated from the value of 2.7 kcal/mole and the heat of sublimation of ice (12.15 kcal/mole). This may be compared to 10.7 kcal/mole, the heat of vaporization of water at 0°C. The higher experimental value reflects the extra effect of the hydrogen bonding in the water polymers. The energy associated with the breakage of hydrogen bonds can be calculated from our results only if the number of nearest neighbors for a molecule in the close-packed liquid structure is known. A value of 8 for the coordination number has been deduced from radial distribution curves and molar volume calculations.[2] For solid H_2S, however, a compound, which is expected to show relationship to H_2O, a number of 12 nearest neighbors is quoted.[22] Taking 8 and 12 as lower and upper limits for the number of nearest neighbors, the change in van der Waals energy in the transition ice-structure$\leftrightarrows$close-packed liquid falls within the range 4.7–6.3 kcal/mole. The energy associated with the breakage of both hydrogen bonds is therefore 7.4–9.0 kcal/mole, which yields a value for one mole of hydrogen bonds between 3.7 and 4.5 kcal.

Heat of Fusion

The value for E_H^3 of 2.7 kcal/mole as a measure of the hydrogen bond energy is dependent on the model chosen for the structure of water only in so far as the assignment of the band at 1.16 μ to unbonded water molecules is correct. In this sense the value of E_H^3 can be regarded with more confidence than the values of E_H^1 and E_H^2, although we did not attempt to put an exact limit of accuracy into it. More definite evidence for the reliability of the values, however, can be obtained from calculation of thermodynamic properties of water such as the heat of fusion.

As mentioned previously, a short-range extrapolation provides values of concentrations of the three species at 0°C of $C_0=0.26$, $C_1=0.41$, and $C_2=0.33$. The heat of fusion can be calculated, using these values, from $\Delta H^f=C_0E_H^3+C_1E_H^2$. The value calculated in this way is 1.36 kcal/mole, compared with the experimental value of 1.44 kcal/mole. This agreement between the observed value and the value calculated by us points to two things: (1) not only the value of E_H^3, obtained from the temperature variance of the C_i's but also the values of the C_i's themselves are reasonable; (2) the agreement for ΔH^f is better using the value of $E_H^2=1{,}1$ kcal/mole rather than a value for E_H^2 which is half the value of E_H^3 (which gives a ΔH^f of 1.25 kcal/mole). This suggests that the difference between the observed E_H^1 and E_H^2 is to some extent real and is not only a result of experimental uncertainty. A second supporting fact for this conclusion is presented in the next section.

Structural Model for Liquid Water

The calculations in the foregoing paragraphs were not dependent on the detailed features of a model describing the structure of water. Now we wish to consider a more explicit model which agrees with the observed relative concentrations of water molecules showing successive steps of hydrogen bonding. From the observations described in this paper no direct information about the sizes and shapes of the water "polymers" can be obtained. In his papers on the structure of water, Frank[12,21] argues that hydrogen bond formation is a cooperative phenomenon, where a number of hydrogen bonds are formed simultaneously between a group of water molecules. It is pointed out that the slight covalency of the hydrogen bond brings about a certain amount of charge separation, which would favor the formation of new hydrogen bonds by molecules already bonded. As a consequence water molecules will cluster together in such a way that the number of hydrogen bonds in the cluster is a maximum. This phenomenon leads to clusters with a high volume-to-surface ratio (e.g. spheres) in which the stabilization per hydrogen bond for molecules in the interior of the cluster is greater than for those at the surface. Such a theory is in accordance with our finding that E_H^2 (1.6 kcal/mole) seems to be greater than E_H^1 (1.1 kcal/mole). However, as E_H^1 and E_H^2 do not represent simply the hydrogen bond energies, but rather the hydrogen bond energies minus the increase in van der Waals energy, a difference between E_H^1 and E_H^2 might be due to different values of the van der Waals interaction energy for the S_1 and S_2 species. Such an effect also would be most prominent in the case of compact clusters in which the possibility for closer packing of S_1 molecules (surface molecules) would be smaller than would be the case for chain polymers for instance.

From dielectric relaxation data, Frank argues that the average lifetime of the clusters should be of the order of $10^{-11}-10^{-10}$ sec. This time is sufficiently long compared to the period of a molecular vibration that there would be no perturbation of the spectroscopic characteristics of the clusters. Referring to the short lifetime of the clusters, the model is called the flickering-cluster model.

Average Cluster Size

There seems to be nothing in the flickering cluster model of Frank which is incompatible with our observations. It is therefore worthwhile to try and obtain from our results some information about an interesting parameter, viz., the average size of the clusters.

X-ray diffraction studies[23,24] of liquid water have provided evidence for tetrahedral structure in the water polymers. Rectangular blocks consisting of water molecules arranged in the tridymite structure thus provide a simplified geometric model for the clusters. In a first approximation the molecules on the surface have either an unbonded lone pair on the oxygen atom (Type I) or an unbonded proton (Type II). These two types are equal in number. Type I molecules would belong to our species S_2, Type II molecules to S_1. Type I molecules according to Frank's theory have a strong tendency to form a hydrogen bond with a new molecule which we then designate as Type III. Type III molecules would belong to our species S_1. Another possibility is the attachment of a new molecule to the proton of a Type II molecule. This new molecule (Type IV) would belong to species S_0. The original Type I and II molecules would become interior molecules by these processes. We have calculated the ratios of the numbers of interior and surface molecules for various cluster sizes, assuming that only Types II and III occur on the surface. As both Type II and Type III molecules belong to species S_1, it follows that the ratios of interior to surface molecules can be expressed as C_2/C_1. A plot of C_2/C_1 versus cluster size is shown in Fig. 6. The smooth curve is drawn through the points corresponding to the most compact clusters. Obviously substitution of Type III by Type I and of Type II by Type IV would decrease the percentage of species S_1 molecules on the surface, thus increasing C_2/C_1 for a given cluster size (i.e., decreasing the cluster size for a given C_2/C_1 ratio). Consequently the cluster sizes at various temperatures which we obtain from our observed C_2/C_1 ratios constitute upper limits of the actual cluster sizes. For water at 72°C the clusters contain an average of 60 molecules. At 20°C the average cluster size is about 90 molecules whereas at 0°C it becomes 130.

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[22] R. Stevenson, J. Chem. Phys. **27**, 147 (1957).

[23] J. Morgan and B. E. Warren, J. Chem. Phys. **6**, 666 (1938).

[24] G. W. Brady and W. J. Romanov, J. Chem. Phys. **32**, 306 (1960).

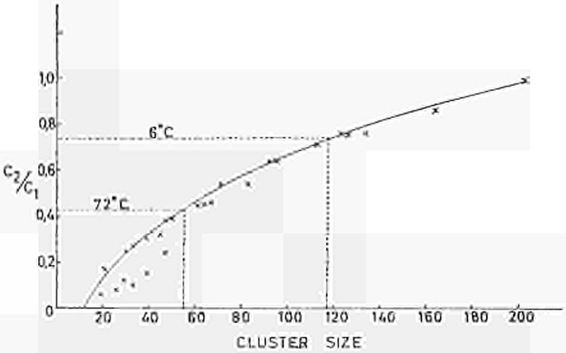

FIG. 6. Variation of calculated cluster size of water polymers as a function of the ratio of doubly to singly hydrogen-bonded water molecules (C_2/C_1).

These values of cluster size, which are upper limits, are larger than those calculated by Nemethy and Sheraga for the same model. Our calculations depend on experimental concentrations of 3 species, whereas they use a statistical mechanical calculation with 5 species. Considering this and, also, that our value is an upper limit, the disagreement is not unsatisfactory. In fact, the general agreement may add substantial weight to the flickering cluster model.

ACKNOWLEDGMENT

One of us (G.R.C.) wishes to express his gratitude to the Centre d'Etude de l'Energie Nucléaire for the invitation to spend an academic year at the Centre. Further, the interest and encouragement of Dr. J. Kooi is gratefully acknowledged.

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 39, No. 8, 2042–2050, 15 October 1963
Printed in U. S. A.

Near-Infrared Studies of the Structure of Water. II. Ionic Solutions*

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(Received 27 May 1963)

The infrared absorption bands of water in the 1.1- to 1.3-μ region have been studied. Variations in intensities of three bands have been used to calculate for ionic solutions the mole fractions of water molecules in which zero, one, and two of the hydrogens are involved in hydrogen bonding. The average sizes of water clusters in HCl, HBr, HNO_3, $HClO_4$, H_2O_2, NaOH, KOH, $NaNO_3$, and $NaClO_4$ solutions were calculated. From this and from qualitative evaluations for other solution systems, it was possible to assign the following effect on the water structure to the ions:

cations: order-producing: $La^{3+} > Mg^{2+} > H^+ > Ca^{2+}$,

order-destroying: $K^+ > Na^+ > Li^+ > Cs^+ = Ag^+$;

anions: order-producing: $OH^- > F^-$,

order-destroying: $ClO_4^- > I^- > Br^- > NO_3^- > Cl^- > SCN^-$.

INTRODUCTION

In our first paper[1] we described the results of a study of the infrared absorption bands of water in the region between 1.1 and 1.3 μ. The three overlapping absorption bands observed in this region were associated with water molecules which have zero, one, and two hydrogen bonds formed by the hydrogen atoms. The mole fractions of these three species of water molecules were calculated from the observed absorption intensities. These same absorption bands have been measured in a variety of ionic solutions in order to gain some knowledge about the structure of water in such solutions.

Bernal and Fowler[2] as well as Cox and Wolfenden[3] interpreted the lower viscosity of some electrolyte solutions relative to that of pure water in terms of a decrease in the short-range tetrahedral structure of liquid water. This short-range structure results from hydrogen bonding. Suhrmann and Breyer[4] interpreted changes in the infrared spectrum of water upon formation of ionic solutions as due to changes in the degree of polymerization of the liquid water. Much of the research on ionic solutions between 1933 and 1957 was reviewed and discussed at a meeting of the Faraday Society in 1957.[5] More recent studies have utilized Raman,[6,7] nuclear magnetic resonance,[8,9] and x-ray diffraction techniques.[10]

Frank and Evans,[11] from an analysis of the solution entropies of ionic solutes, have suggested a model for ionic solutions involving three concentric zones of water about each solute particle. In the inner, first zone are the water molecules which have been oriented by ionic attraction. These ordered arrangements of water molecules about the ion are spoken of as "frozen icebergs." The outermost zone, in which the ionic influence is simply one of dielectric polarization, has the structure of normal water which is due to interaction between water molecules. Between the inner and the outer regions is a "thawed" region in which the influences of the other two regions are mutually canceling to produce less order than in pure water. The influence of ions in increasing or decreasing the net amount of ordering in water depends on the relative sizes of the inner and of the middle zones. The structural entropies calculated by Frank and Evans indicated that all the alkali and halide ions except Li^+ and F^- have a net structure-breaking effect. Frank and Wen[12] have discussed these concepts in terms of a "flickering cluster" model for the structure of water. In our first paper[1] we have shown that this model is compatible with our observations for

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* Research carried out in the framework of the Euratom Transplutonium Program under contract 002/61/2 TPU B.

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[1] K. Buijs and G. R. Choppin, J. Chem. Phys. **39**, 2035 (1963).

[2] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).

[3] W. M. Cox and J. H. Wolfenden, Proc. Roy. Soc. (London) **A145**, 475 (1934).

[4] (a) R. Suhrmann and F. Breyer, Z. Physik. Chem. **B20**, 17 (1933); (b) **B23**, 193 (1933).

[5] A general discussion on interactions in ionic solutions, Discussions Faraday Soc. **24**, (1957).

[6] (a) W. R. Busing and D. F. Hornig, J. Phys. Chem. **65**, 284 (1961). (b) J. W. Schultz and D. F. Hornig, *ibid.* **65**, 2131 (1961).

[7] R. E. Weston, Spectrochim. Acta **18**, 1257 (1962).

[8] J. N. Schoolery and B. J. Alder, J. Chem. Phys. **23**, 805 (1955).

[9] J. C. Hindman, J. Chem. Phys. **36**, 1000 (1962).

[10] (a) G. W. Brady and J. T. Krause, J. Chem. Phys. **27**, 304 (1957); (b) G. W. Brady, *ibid.* **28**, 464 (1958); (c) **29**, 1371 (1958); (d) **33**, 1079 (1960).

[11] H. S. Frank and M. Evans, J. Chem. Phys. **13**, 507 (1945).

[12] H. S. Frank and W-Y Wen, Discussions Faraday Soc. **24**, 133 (1957).

pure water. In this model, ions which have an inner region consisting of no more than a single layer of water molecules would serve as disturbing centers and would inhibit cluster formation as well as increase cluster disintegration to produce a net structure-breaking effect. Opposite in effect would be ions which have an inner region extending beyond the first ion–water layer. In these cases, which occur with small and highly charged ions, the charge separation in the outer molecules of the inner region would cause these ions, with their inner regions, to serve as seed nuclei for cluster growth. The net effect is an increase in the degree of ordering.

Gurney[13] has suggested a slightly simpler but basically similar model to that of Frank and Evans. The major difference is that Gurney allows the complete elimination of the inner zone by the more random thawed zone in the cases of univalent ions which are larger than a water molecule. Nevertheless, Gurney agrees qualitatively with Frank and Evans on the relative ordering or disordering behavior of cations and anions.

EXPERIMENTAL

The spectra were taken on a Cary 14 spectrophotometer in exactly the same way as described in our first paper.[1] All chemicals used were Analytical Reagent quality. The densities of the solutions were either taken from the *Handbook of Chemistry and Physics*[14] or measured by weighing a known volume of solution.

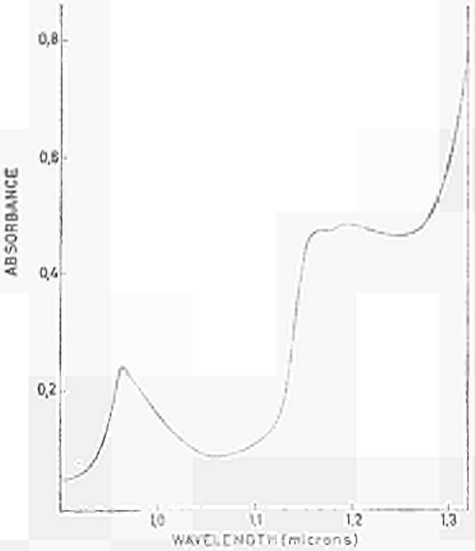

FIG. 1. Near-infrared spectrum of 4.6m KOH solution at 21°C.

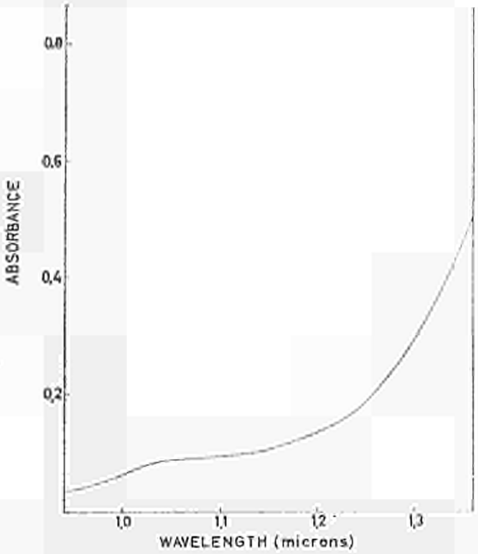

FIG. 2. Near-infrared spectrum of 98% sulfuric acid at 21°C.

ASSIGNMENTS

In Fig. 1 of this paper and Fig. 3 of the preceding paper the spectra in the 1.2-μ region of aqueous solutions of KOH and $NaClO_4$, respectively, both containing 1 mole of salt per 12 moles of water are shown. These spectra, and the others taken indicate that the differentiation into the three bands at 1.16, 1.20, and 1.25 μ, which are found in the spectrum of pure water, seems also justified for these solutions. For most solutions no frequency shifts were observed. Nor does the presence of the solutes seem to effect the intensities of the bands to any significant extent. In fact when intensity changes and frequency shifts are observed, they often occurred together, especially in the cases of very concentrated solutions.

The water bands in the 1.2-μ region due to the $\nu_1+\nu_2+\nu_3$ combination vibration of the water molecules are not perturbed by the presence of a solute containing OH groups, as isolated OH groups do not absorb in this region. This is illustrated in Fig. 2 by the spectrum of 98% H_2SO_4 where only a weak absorption due to water is found.

EVALUATION OF THE RESULTS

Molar absorption coefficients E_λ were determined using the method of base-line drawing described in the first paper.

The determination of the $\epsilon_\lambda{}^i$'s, the molar absorption coefficients for the nonhydrogen-, monohydrogen-, and dihydrogen-bonded species at the wavelengths studied was complicated by the fact that for most solutions only the spectrum at room temperature was measured. A series of spectra, one of which is shown as Fig. 3 of the preceding paper, at varying temperatures were recorded for a solution of $NaClO_4$ in water with a 1:12

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[13] R. W. Gurney, *Ionic Processes in Solution* (McGraw-Hill Book Co., Inc., New York, 1953).

[14] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1958), pp. 1955–2083.

TABLE I. The molar absorption coefficients $\epsilon_\lambda{}^i$ used to calculate the C_i values of the solutions.

	Solution (1:12)	Value of $10.9\ E_{1.16}+E_{1.20}$ $+22.3\ E_{1.25}$	$\epsilon_{1.16}{}^0$ $(\times 10^3)$	$\epsilon_{1.20}{}^0$ $(\times 10^3)$	$\epsilon_{1.16}{}^1=\epsilon_{1.25}{}^1$ $(\times 10^3)$	$\epsilon_{1.20}{}^1$ $(\times 10^3)$	$\epsilon_{1.16}{}^2$ $(\times 10^3)$	$\epsilon_{1.20}{}^2$ $(\times 10^3)$	$\epsilon_{1.25}{}^2$ $(\times 10^3)$
I	$NaClO_4$	0.197	18.0	0.7	5.5	14.5	0.9	5.0	8.2
II	KBr	0.190	17.8	0.7	5.2	14.3	0.9	4.9	8.0
III	$MgCl_2$	0.185	17.7	0.7	5.1	14.2	0.8	4.8	7.9
IV	KI	0.182	17.7	0.7	5.0	14.2	0.8	4.8	7.8
V	KSCN	0.180	17.7	0.7	4.8	14.1	0.8	4.8	7.7
VI	H_2O	0.176	17.5	0.7	4.5	14.0	0.8	4.6	7.5
VII	KOH[a]	0.172	17.0	0.7	4.3	13.5	0.7	4.3	7.2
VIII	NaOH	0.158	17.0	0.7	3.5	13.4	0.7	4.2	6.8

[a] The coefficients for the 1:12 KOH solution were determined independently.

mole ratio. The $\epsilon_\lambda{}^i$ values for this system were evaluated in the same way as described for water in the first paper; they were found to be the following: $\epsilon_{1.16}{}^0=18.0$, $\epsilon_{1.20}{}^0=0.7$, $\epsilon_{1.25}{}^0=0.0$; $\epsilon_{1.16}{}^1=\epsilon_{1.25}{}^1=5.5$, $\epsilon_{1.20}{}^1=14.5$; $\epsilon_{1.16}{}^2=0.9$, $\epsilon_{1.20}{}^2=5.0$, $\epsilon_{1.25}{}^2=8.0$ (all values in 10^{-3} mole^{-1} liter cm^{-1}). When the $\epsilon_\lambda{}^i$ values are known it is possible to eliminate the c_i's from the set of four equations

$$\epsilon_{1.16}{}^0c_0+\epsilon_{1.16}{}^1c_1+\epsilon_{1.16}{}^2c_2=E_{1.16}, \qquad (1)$$

$$\epsilon_{1.20}{}^0c_0+\epsilon_{1.20}{}^1c_1+\epsilon_{1.20}{}^2c_2=E_{1.20}, \qquad (2)$$

$$\epsilon_{1.25}{}^0c_0+\epsilon_{1.25}{}^1c_1+\epsilon_{1.25}{}^2c_2=E_{1.25}, \qquad (3)$$

$$c_0+c_1+c_2=1. \qquad (4)$$

The result of this calculation for the $NaClO_4$ solution is

$$10.9E_{1.16}+E_{1.20}+22.3E_{1.25}=0.197. \qquad (5)$$

If now the $\epsilon_\lambda{}^i$ values are not affected by a change in solute, this same Eq. (5) must hold for all solutions. Unfortunately this was not the case. The fact that the set of numerical coefficients of Eq. (5) is obtained from the spectrum of the $NaClO_4$ solution does not cause the discrepancy, as similar results are obtained using the data from other spectra. However, the deviations from the value of 0.197 are not large. For a 1:12 KOH solution, the spectrum of which is shown in Fig. 1, the corresponding value is 0.172 notwithstanding the fact that this spectrum is completely different in appearance from that of the $NaClO_4$ solution. Indeed, it was found that for 90% of the systems studied, including pure water and the solutions of the alkali halides, the sum $(10.9E_{1.16}+E_{1.20}+22.3E_{1.25})$ fell within the range 0.158–0.197. This result was taken to indicate that the evaluation of the c_i's for various solutions is not precluded by the effect of the solute on the molar absorption coefficients. For a few systems the sums were so low that we did not consider it justified to do any further calculations on them (e.g., NaOH solutions with a mole ratio of water to solute of 1.9:1 and of 5:1; H_2SO_4 of 1.4:1, and $NaClO_4$ of 4.3:1).

The $\epsilon_\lambda{}^i$ value used to calculate the c_i's for the various solutions were evaluated by interpolation and extrapolation from the values of E_λ using the values of pure water and $NaClO_5$ solution (12:1) as references. The values of KOH solution (12:1) were evaluated independently to compare with those of pure water as a check on this method. The resulting $\epsilon_\lambda{}^i$ values are listed in Table I.

As described in the preceding paper for the case of pure water, the c_i values were calculated using Eqs. (1), (2), and (4). Equation (3) was used only as a check on the results. For the systems to which the sets of Eqs. I–VIII apply, Eq. (3) was satisfied to within 5%.

The relative concentrations C_0, C_1, and C_2 calculated in this way for a number of solutions are listed in Tables II and III.

DISCUSSION

In our first paper we used a model of liquid water in which the three observed absorption bands corresponded to vibrations of water molecules with no hydrogen bonds (C_0), one hydrogen bond (C_1) and two hydrogen bonds (C_2). Only hydrogen bonds involving the hydrogens of the H_2O molecule under consideration affected the spectra. Molecules in which the hydrogen bonding involved only the oxygen would also fall under the C_0 species as this seems to have little effect on the O–H frequency under observation. Assuming that these latter hydrogen bonded species are relatively few, it was possible to calculate average sizes of the clusters of H_2O molecules in liquid water as a function of temperature.

In this paper we use the same model for the solvent water with some modification due to the water molecules in the hydration spheres of solute ions. Any H_2O–H_2O bonding (e.g., between primary and secondary hydration layers) falls into one of our three species above. However, the primary hydration layer is different as it involves ion–H_2O interaction. From a careful

TABLE II. Molar absorption coefficients and relative concentrations of water species at different concentrations.

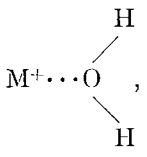
System	Mole ratio (H_2O: solute)	Molar absorption coefficients (10^{-3} mole^{-1} liter cm^{-1}) $E_{1.16}$	$E_{1.20}$	$E_{1.25}$	Relative concentrations of water species C_0	C_1	C_2
H_2SO_4	1.4:1	2.55	2.55	1.65	...	...	...
	5.6:1	6.60	6.35	4.68	0.28	0.28	0.44
	17:1	7.22	6.68	4.10	0.30	0.33	0.37
	110:1	7.62	7.33	4.09	0.30	0.40	0.30
HCl	3.5:1	4.67	6.26	5.36	0.17	0.25	0.58
	4.7:1	5.20	6.38	4.91	0.20	0.27	0.53
	8.2:1	6.27	6.86	4.53	0.25	0.34	0.41
	22:1	7.24	7.56	4.61	0.27	0.41	0.32
	56:1	7.27	7.53	4.51	0.28	0.40	0.32
HBr	4.8:1[a]	5.98	7.71	5.79	0.20	0.37	0.43
	7.9:1	6.23	7.28	4.57	0.20	0.40	0.40
	11.1:1	7.12	7.59	4.52	0.27	0.42	0.31
	17.3:1	7.02	7.31	4.08	0.29	0.44	0.27
	29.8:1	7.06	7.11	3.79	0.30	0.42	0.28
	42.3:1	7.16	7.18	3.96	0.30	0.43	0.27
	61:1	7.11	7.07	3.85	0.30	0.42	0.28
HNO_3	1.9:1[a]	11.19	6.59	3.70	0.49	0.36	0.15
	4:1[a]	8.55	6.21	2.63	0.41	0.38	0.21
	8:1	8.00	6.63	4.02	0.34	0.34	0.32
	14:1	7.90	6.86	3.98	0.33	0.34	0.31
	26:1	7.89	7.09	3.83	0.33	0.39	0.28
	50:1	7.89	7.28	3.89	0.32	0.41	0.27
	74:1	7.65	7.27	3.82	0.31	0.40	0.29
$HClO_4$	2.4:1	7.11	7.07	4.61	0.28	0.35	0.37
	3.4:1	9.73	6.79	3.82	0.42	0.37	0.21
	4.4:1	10.47	6.88	3.51	0.45	0.40	0.15
	7:1	10.55	6.48	3.35	0.47	0.36	0.17
	9:1	10.30	6.39	3.30	0.46	0.35	0.19
	11.6:1	9.96	6.76	3.48	0.43	0.38	0.19
	21:1	8.84	6.66	3.62	0.38	0.37	0.25
	48:1	8.43	7.13	3.72	0.35	0.40	0.25
	75:1	8.35	7.20	3.69	0.34	0.41	0.25
H_2O_2	4.4:1	9.64	7.91	5.14	0.34	0.40	0.26
	12:1	8.54	7.78	4.48	0.31	0.49	0.20
NaOH	1.9:1	2.08	1.65	0.93	...	...	...
	5:1	3.71	3.29	2.14	...	...	...
	10:1	6.15	5.80	3.82	0.29	0.28	0.43
	15:1	6.95	6.55	4.07	0.31	0.36	0.33
	25:1	7.20	6.89	4.04	0.30	0.37	0.33
	50:1	7.39	7.04	3.93	0.30	0.39	0.31
$NaNO_3$	5:1	10.33	8.15	3.38	0.44	0.52	0.04
	7.5:1	10.15	7.89	3.11	0.42	0.50	0.08
	10:1	9.81	7.66	3.06	0.40	0.48	0.12
	15:1	9.44	7.36	3.50	0.39	0.44	0.17
	50:1	8.38	7.59	3.98	0.34	0.43	0.23
$NaClO_4$	4.3:1	17.21	5.91	1.79	...	...	...
	9:1	13.07	6.93	2.60	0.57	0.43	0.00
	10.7:1	11.68	6.47	2.49	0.53	0.41	0.06
	12:1	11.39	7.04	2.93	0.50	0.43	0.07
	22:1	10.16	7.04	3.08	0.45	0.43	0.12
	33:1	9.50	7.37	3.37	0.40	0.45	0.15
	50:1	8.75	7.17	3.51	0.37	0.41	0.22
	75:1	8.44	7.37	3.85	0.35	0.42	0.23
LiCl	12:1	7.88	8.08	3.92	0.30	0.47	0.23
NaCl	12:1	8.75	8.35	3.78	0.34	0.52	0.14

TABLE II (*Continued*)

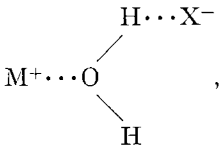
System	Mole ratio (H_2O: solute)	Molar absorption coefficients (10^{-3} mole^{-1} liter 1 cm^{-1})			Relative concentrations of water species		
		$E_{1.16}$	$E_{1.20}$	$E_{1.25}$	C_0	C_1	C_2
KCl	12:1	8.82	8.29	3.76	0.34	0.52	0.14
CsCl	12:1	7.72	8.02	3.91	0.29	0.47	0.24
$MgCl_2$	12:1	5.78	7.82	5.12	0.20	0.40	0.40
$CaCl_2$	10.4:1[a]	6.32	7.44	3.45	0.27	0.45	0.28
$LaCl_3$	12:1	5.00	9.30	5.88	0.11	0.49	0.40
$LiNO_3$	12:1[a]	7.52	6.00	2.24	0.39	0.38	0.23
KNO_3	12:1	9.05	7.23	2.92	0.41	0.48	0.11
$AgNO_3$	12:1	7.58	7.14	3.56	0.32	0.44	0.24
$Ca(NO_3)_2$	9:1[a]	7.76	5.50	2.31	0.41	0.33	0.26
$Na_2S_2O_3$	15:1[a]	8.30	9.00	4.86	0.28	0.51	0.21
NaI	12:1	8.90	8.35	3.19	0.36	0.55	0.09
$AgClO_4$	11.7:1[a]	8.11	4.53	2.00	0.47	0.24	0.29
KF	12:1	7.51	7.51	4.58	0.29	0.41	0.30
KBr	12:1	9.27	8.67	3.58	0.36	0.54	0.10
KI	12:1	9.61	8.57	3.09	0.38	0.57	0.05
KOH	12:1	7.06	6.57	3.94	0.31	0.36	0.33
KSCN	12:1	9.08	7.60	3.29	0.38	0.47	0.15
K_2CrO_7	124:1	8.23	7.83	4.25	0.32	0.44	0.24
H_2O	pure, 20°C	7.56	7.58	4.17	0.31	0.42	0.27

[a] For these systems the sum values for Eq. (5) were outside the range 0.158–0.197 and, hence, the calculated concentration values are less reliable.

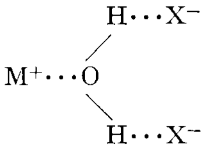
qualitative assessment of the results of the absorption intensities and frequencies in the solutions studied, it seems logical to make the following assignments:



C_0



C_1



C_2

As in the case of C_0, interaction of the metal ion and oxygen causes no apparent change in the H_2O frequency from that of a molecule not bonded to a metal ion. This can be seen from the constancy of position of the 1.16-μ peak in the solutions. These "free" molecules are close-packed, and experience van der Waals interactions, so they are not in the same state as gaseous H_2O molecules. It is more difficult experimentally to be certain that the C_1 and C_2 species do not show slight frequency shifts. Indeed, in some few cases of very concentrated solutions (e.g., $ZnCl_2$ in a 2:1 mole ratio) there seemed to be shifts. Careful resolution of other solution absorption curves into three bands provided no evidence of shifts from the frequencies observed in pure water. Attempts to resolve the curves into more than three bands between 1.16 and 1.25 μ were unsuccessful.

The question of anion hydration is the subject of some

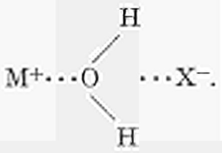
TABLE III. Molar absorption coefficients and relative concentrations of water species at different temperatures.

System	Mole ratio (H_2O: solute)	Temperature (°C)	Molar absorption coefficients (10^{-2} mole^{-1} liter cm^{-1}) $E_{1.16}$	$E_{1.20}$	$E_{1.25}$	Relative concentrations of water species C_0	C_1	C_2
LiCl	2.8:1[a]	21	7.51	9.62	4.05	0.24	0.60	0.16
		34	7.62	9.49	3.95	0.25	0.59	0.16
		47	8.41	9.59	4.82	0.28	0.63	0.09
		61	8.49	9.36	4.54	0.29	0.61	0.10
		72	8.87	9.10	4.33	0.32	0.59	0.09
LiCl	12:1	21	7.49	7.86	3.90	0.30	0.47	0.23
		34	7.71	7.76	3.78	0.31	0.46	0.23
		47	8.00	7.56	3.51	0.33	0.45	0.22
		61	8.35	7.59	3.33	0.35	0.46	0.19
		72	8.86	7.37	3.22	0.38	0.45	0.17
KOH	12:1	21	7.00	6.55	4.04	0.31	0.36	0.33
		34	7.23	6.51	3.94	0.32	0.36	0.32
		47	7.49	6.47	3.77	0.33	0.37	0.30
		61	7.81	6.49	3.74	0.35	0.38	0.27
		72	8.04	6.26	3.42	0.37	0.36	0.27
$NaClO_4$	5.1:1[a]	27	14.50	5.98	2.15	0.63	0.37	0.00
		42	15.05	6.08	2.15	0.63	0.37	0.00
		53	15.28	5.78	1.88	0.65	0.35	0.00
		75	15.63	5.35	1.60	0.68	0.32	0.00
$NaClO_4$	12:1	21	11.39	7.04	2.93	0.50	0.43	0.07
		34	11.91	7.04	2.78	0.53	0.44	0.03
		47	12.24	6.72	2.50	0.55	0.42	0.03
		61	12.59	6.59	2.37	0.57	0.42	0.01
		72	12.93	6.33	1.96	0.60	0.40	0.00

[a] See footnote to Table II.

debate. Both Brady[10c] and Hindman[9] interpret their results to indicate that the anions are not hydrated in the same sense as the cations. To the extent that anion hydration occurs, these species would be expected to be found in C_1 and C_2.

An additional complication to any rigorous interpretation of the solution results is the relatively high molalities studied. It was necessary to study concentrations whose spectra were sufficiently different from that of water to allow reasonable certainty in the differences calculated in the C_0, C_1, and C_2 values. A water-to-solute mole ratio of 12:1 seemed to be a reasonable compromise between spectral differences and concentrations. In addition, some solutions were studied over a concentration range. It is realized that in the 12:1 solutions, the zones of influence of the ions cannot be considered as isolated, but rather must overlap considerably. Furthermore, for some solutes there must be a considerable degree of ion-pair formation. Depending on the ions involved, such ion pairs could be of the type $M^+\cdots X^-$, or of the type

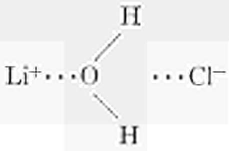


The possible concurrence of the phenomena of cluster disruption or promotion, of hydration and of ion-pair formation allows only a qualitative interpretation of results in all but a few systems.

Temperature Effects

We consider first the temperature data in Table III. To aid in interpretation, values of X_0, X_1, X_2 have been plotted in Fig. 3, where $X_i = C_i$ (solution)/C_i (pure H_2O). Both c_i (solution) and c_i (pure H_2O) are taken at the same temperature in an attempt to correct for the effects of changes in C_0, C_1, and C_2 due to disruption of the water structure with temperature increase.

In the 12:1 solution of LiCl, the values testify to a close resemblance to pure water. The high charge-to-volume ratio for the lithium ion would be expected to promote a relatively large frozen zone about the cation while the chloride anion has no marked structure-breaking effect.[13] The consequence is a waterlike solution. Although the particular concentration values for the 2.8:1 solution of LiCl are somewhat suspect, the high values of C_1 are evidence for a large degree of



ordering.

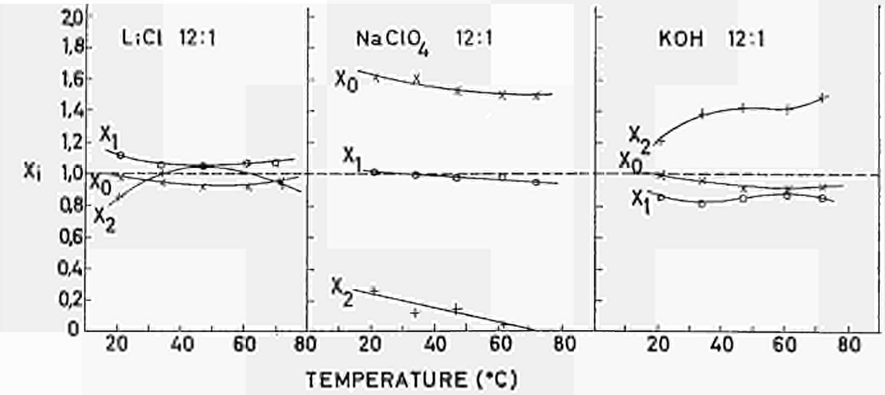


FIG. 3. The temperature dependent variation of C_0, C_1, and C_2 relative to pure water at the same temperature [$X_i = C_i$ (solution)/C_i (pure H_2O)].

In both the 12:1 and 5:1 solutions of $NaClO_4$, the very high values of C_0 and very low values of C_2 are striking. Likely conclusions are that: (1) the frozen zone about the sodium ion is not as large as about the lithium ion; (2) the amount of anion hydration and of ion-pair formation is not very large; (3) the perchlorate ion has a very large order-destroying effect on the water clusters. The second conclusion is substantiated by the higher values of C_0 in the 5:1 solution relative to the 12:1 solutions. These conclusions are in agreement with the expected behavior of Na^+ and ClO_4^- anions. If contributions to the magnitude of C_1 by hydration and ion-pairing are assumed to be negligible, it is possible to estimate that the average size of the water clusters involving only H_2O molecules at 20°C in the 12:1 solution of $NaClO_4$ is only 20–25 molecules compared to the estimated value of 90 molecules for pure water at the same temperature.[1]

In Fig. 3, the high value of X_2 for the KOH solution must be indicative of the ability of hydroxide ion to promote cluster formation.[15] Busing and Hornig[6] interpret the Raman spectra of KOH solutions as indicating that hydroxide ions are not strongly hydrogen bonded via their hydrogens but do interact with at least one H_2O molecule in a strong hydrogen bond. In contradiction, Brady and Krause,[10] from a consideration of the radial distribution functions for KOH solutions, state that the hydration number of OH^- must be either 4 or 6. There is evidence, then, that OH^- might fit into the tetrahedral structure of the water clusters, and, by reason of its charge, even promote increase in the average cluster size. Potassium ion, as a result of its close resemblance to water molecules in size and of its low hydration number, should have small effect on the water structure. An estimate of the cluster size in 12:1 solutions of KOH gives a value of 175 molecules at 20°C. Moreover, the positive temperature coefficient for X_2/X_1, indicates that the decrease in cluster size is smaller than in pure water with increase in temperature. At 72°C, the calculated average cluster size is 120 molecules compared to a value for pure water of only 55 molecules. If we apply the concept of structural temperature suggested by Bernal and Fowler[2] (i.e., the temperature at which pure water has the same cluster size), a 12:1 solution of KOH at 72°C would have a structural temperature of 5°C. The 12:1 solution of $NaClO_4$ even at 20°C would have a structural temperature well above 100°C. For LiCl, hydration effects make any attempt to calculate cluster sizes too uncertain. Qualitatively, from Fig. 3 we can see that LiCl solutions should be rather similar to pure water in structural temperature. The relative magnitudes of X_0, X_1, and X_2 in Fig. 3, also, are in agreement with our assignments of the absorbing species for the three absorption bands (both for the H_2O–H_2O and ion–H_2O species).

Concentration Effects

Since all the water molecules in the solution contribute to the three absorption bands, it is not surprising that the values of C_0, C_1, and C_2 approach those of pure water rather rapidly with dilution. The net effect of the solute is relatively small already in 1m solutions. Furthermore, the trends observed in C_0, C_1, and C_2 in Table II are regular with dilution at least from 12:1 to more dilute solutions. This indicates that the study of 12:1 solutions dictated by practical considerations,

TABLE IV. Average cluster size in solutions (20°C).

Solute	1m	2m	3m	4.6m
HCl	130	135	150	175
HBr	95	95	95	100
HNO_3	100	100	115	135
$HClO_4$	90	95	90	80
H_2O_2	...	...	...	55
NaOH	135	160	160	150
$NaNO_3$	70	70	60	40
$NaClO_4$	40	45	30	25
H_2O (pure)	95			

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[15] Th. Ackermann, Discussions Faraday Soc. **24,** 180 (1957).

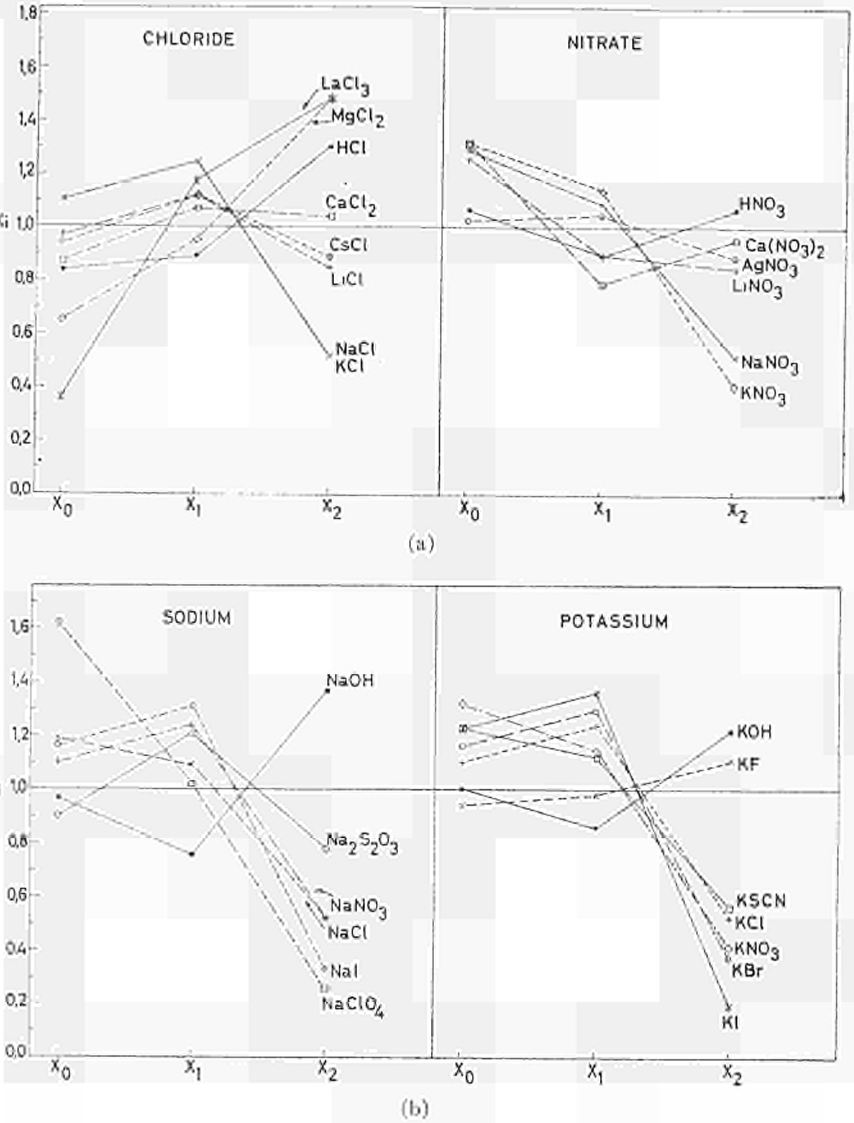

Fig. 4. (a) The variation in values of X_i for 4.6*m* solutions of chloride and nitrate salts. (b) The variation in values of X_i for 4.6*m* solutions of sodium and potassium salts.

should yield results directly related to the situation in more dilute solutions.

It is common to speak of the order-producing and order-destroying effects of ions.[13] However, it must be kept in mind that ions such as Li^+ or Mg^{2+} which are considered as order-producing cause ordering about themselves which is not identical to the "ice structure" of pure water. On the other hand, hydrogen ions and hydroxide ions presumably are capable of direct incorporation into the "icelike" water clusters. Their order-producing effect, then, is different in kind from that of other ions.

For a series of strong mineral acids the hydrogen ions would tend to increase cluster size. The differences, then, in calculated cluster sizes should reflect the relative effect of anions on the water structure. Calculation of cluster sizes for salt solutions is less justified due to the problem of water species in hydration layers contributing to C_0, C_1, and C_2. For NaOH, $NaNO_3$, and $NaClO_4$, if the extent of ion-pair formation via the hydrated sodium ion is small, the hydration species should contribute predominantly to C_0. Since only the ratio C_2/C_1 is used to estimate cluster size, these estimates may not be very greatly in error, particularly at 1–2*m*. The results of some cluster size estimates are listed in Table IV.

The values in Table IV are in agreement with Gurney's list of order-destroying power for these anions, i.e., $ClO_4^- > Br^- > NO_3^- > Cl^-$.

Both hydrogen and hydroxide ions promote cluster formation and the data for HBr indicate that the order-producing tendency of H^+ is approximately equal to the order-destroying tendency of Br^-. The cluster size in hydrogen peroxide is probably due to the structural strain imposed on clusters in which H_2O_2 is incorporated.

Solutions of 12:1 Mole Ratio (4.6*m*)

The values of X_0, X_1, and X_2 for the 12:1 solutions are shown in Fig. 4. Some qualitative interpretations and correlations of these curves are possible.

In the chloride systems, the high values of X_2 and low values of X_0 for La^{3+} and Mg^{2+} suggest that the relatively large charge-to-volume ratios for these ions produce large frozen and small thawed zones about each cation. In addition, at this concentration, there can be a substantial degree of ion-pair formation of hydrated cations. This is more prevalent for $CaCl_2$ and $LaCl_3$[10,16] than for $MgCl_2$ which may account for the larger values of X_1 for the former two solutes. The relative behavior of Li^+ and Na^+ is in line with the expectation of their relative effects on the magnitudes of the frozen and the thawed zones. The tendency to ion-pair formation would be $Cs^+ > K^+ > Na^+ > Li^+$. The somewhat surprising behavior of CsCl is possibly due to ion-pair formation at this high concentration.

In the nitrate systems the corresponding values of X_0 are larger and those of X_2 lower. This is interpreted to be indicative of the greater disordering action of NO_3^- relative to Cl^-. Otherwise, except for $Ca(NO_3)_2$ the trends are in line with the considerations for the chloride systems. There are several possible explanations for the $Ca(NO_3)_2$ data. First, this is one of the systems which were outside of the range of the sum values (see footnote, Table II). Second, for $Ca(NO_3)_2$, which has a higher degree of ion pairing,[17] the waters in the hydrated ion pairs may have a rather large probability of both hydrogen atoms being hydrogen bonded by two oxygens of a nitrate ion. This would increase the value of C_2 relative to C_1. $CaCl_2$ would show much less of this since only one hydrogen can be bonded per chloride ion, and the amount of ion-pair formation is much less than in $Ca(NO_3)_2$.[17] Although the result must be considered with some hesitation due to the uncertainty of the role that hydration plays in the C_2 values, we would interpret our results to indicate the following cation effects in 4.6*m* solutions:

Order producing	Order destroying
$La > Mg > H > Ca$,	$K > Na > Li > Cs = Ag$.

For the K^+ and Na^+ systems, the same general considerations used above seem to explain the data. The order of anion effect is:

Order producing	Order destroying
$OH > F$,	$ClO_4 > I > Br > NO_3 > Cl > SCN$.

SUMMARY

From the infrared absorption at 1.15–1.25 μ, it is possible to study the effects of ionic solutes on the structure of liquid water. In some cases such as solutions of the strong mineral acids and of hydroxides, it is possible to estimate the effect on the average size of the water clusters. For the salts, it can be seen that the effects on the water structure are in agreement with the ionic sequences proposed by Gurney and others.

ACKNOWLEDGMENTS

One of us (G.R.C.) wishes to express his gratitude to CEN for the invitation to spend an academic year at the center. Further the interest and encouragement of Dr. J. Kooi is gratefully acknowledged.

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[16] G. R. Choppin and P. Unrein, J. Inorg. Nucl. Chem. (to be published).

[17] C. W. Davies, *Ion Association* (Butterworths Scientific Publications Ltd., London, 1962), p. 170.

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