pulse radiolysis in cyclohexane containing as little as 4% methanol.[18b] The yield of electrons is six times greater than that expected from the mole fraction of methanol. This strongly suggests efficient trapping by alcohol aggregates. In these systems then, the alcohol, present in concentrations sufficient for spur penetration, would serve to stabilize the electron, preserving it for reaction with $I_2$. Alternatively, the alcohol could be suppressing recombination by undergoing reaction with the parent hydrocarbon ion in a proton-transfer reaction. These reactions would lead to species $ROH_2^+$ and $I_3^-$ which should be quite stable in the systems under investigation.

In some preliminary experiments in which $n$-amyl alcohol was used, the limiting yield of $I_3^-$ was not reached until somewhat higher concentrations of alcohol were employed than those used in the ethanol experiments. In fact, at very low concentration of amyl alcohol the yield of $I_3^-$ was reduced from the zero alcohol value. Spectroscopic studies and an nmr inves-

tigation show that amyl alcohol is considerably less hydrogen bonded at low concentration than is ethanol in the same solvents. Furthermore, in ternary solutions containing iodine the iodine is not fully complexed until significantly higher concentrations of alcohol are reached compared to those which produce total complexing in the ethanol case. These observations suggest that both the polar aggregate of alcohol molecules and the iodine–alcohol complex play a role in these ternary systems. These effects are under continued investigation.

(18) (a) Unpublished results, this laboratory. (b) T. J. Kemp, C. A. Salmon, and P. Wardman in "Pulse Radiolysis," M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Ed., Academic Press, London 1965, p 247.

# The Influence of the Alkaline Earth Chlorides

# on the Structure of Water[1]

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Entropies of transfer between heavy and normal water for $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ have been determined from combination of free energies of transfer obtained from cell measurements with heats of transfer obtained from calorimetric measurements. The free energy and heat values indicated a spontaneous and exothermic transfer of the salts from $D_2O$ to $H_2O$. Solvent-structure influence, established from the sign and magnitude of the entropy, indicated that the alkaline earth chlorides behave as structure-breaking salts. The order of structure-breaking influence for the cations was found to be $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$ with $Mg^{2+}$ behaving as a structure maker. The structure influence of the cations has been attributed to their long-range interaction with the bulk solvent.

## Introduction

Recent studies of the nature of the structure of water and aqueous solutions have been carried out by investigating differences in the properties of heavy and normal water solutions.[2-7] For example, measurements of Walden products for solutions of quaternary alkyl ammonium halides in each of the solvents have yielded the structure-making sequence of these salts.[4] We,[2,3] among others,[5,6] have taken a different approach by determining entropies of transfer for various species passing between $H_2O$ and $D_2O$ and attributing

the sign and magnitude of the entropy values to structure influence. The entropy values were obtained by

(1) This research was supported by the Research Division of the Office of Saline Water, U. S. Department of the Interior, under Contract No. 14-01-0001-1701.

(2) J. Greyson, *J. Phys. Chem.*, 66, 2218 (1962).

(3) J. Greyson, *ibid.*, 71, 2210 (1967).

(4) R. L. Kay and D. F. Evans, *ibid.*, 69, 4216 (1965).

(5) Y. C. Wu and H. L. Friedman, *ibid.*, 70, 166 (1966).

(6) R. E. Kerwin, Ph.D. Thesis, University of Pittsburgh, Pittsburgh, Pa., 1964.

combining free energies of transfer derived from cell measurements with heats of transfer derived from calorimetric heats of solution. Based on this approach, a structure-influencing sequence for the ions of the alkali halides was established.[3] In this paper, we report the details of similar measurements for $H_2O$ and $D_2O$ solutions of the alkaline earth chlorides and compare the resulting structure-influencing sequence for the alkaline earth cations with the previously reported sequence for the alkali and halide ions.

## Experimental Section

*Materials.* Heavy water (99.75% D) was obtained from the U. S. Atomic Energy Commission, Savannah River Operations Office, Aiken, South Carolina. It was used without further purification. All normal water solutions and heat measurements were made with conductivity water ($3.6 \times 10^{-7}$ ohm$^{-1}$ cm$^{-1}$ at 25°). All starting salts were reagent grade and were used without further purification. For measurements with KCl, the salt was oven dried to constant weight at 150°. Anhydrous alkaline earth chlorides were prepared from the hydrates. The anhydrous $SrCl_2$ and $BaCl_2$ were prepared by grinding the hydrates in a mortar and heating at 150° to constant weight. Gravimetric chloride analyses showed these anhydrous salts to be 99.9% pure.

High-purity $MgCl_2$ and $CaCl_2$ cannot be prepared simply by heating the hydrates because of their tendency to form the oxides. Thus, these anhydrous salts were prepared in a fashion similar to a method developed for anhydrous $MgCl_2$ by Richards and Parker.[8] Starting with the appropriate mixed salt of the hydrated alkaline earth chloride and ammonium chloride,[9] dehydration and decomposition were carried out in a stream of dry HCl.

The preparation procedure involved the formation of the mixed salt by recrystallization from a hot, saturated, aqueous solution containing approximately equimolar quantities of the hydrate and $NH_4Cl$. The crystals were then separated by filtration and heated in a vacuum oven at 80°. This served to partially dehydrate the mixed salt hydrate and substantially reduced the quantity of HCl consumed in preparing the anhydrous salt.

Final dehydration and decomposition were carried out in a quartz tube furnace. Electronic grade (99.99%) HCl and high-purity (99.9%) $N_2$ gases, fed through the tube, were purified by passing them through a bed of finely divided alumina, heated with a Meker burner to aid in the removal of hydrocarbon impurities,[10] and a trap containing 4A molecular sieve, maintained at Dry Ice temperatures, to remove traces of moisture. Approximately 3 g of the partially dehydrated mixed salt could be processed at one time yielding about 1 g of anhydrous salt.

Temperature programming in the tube furnace was

as follows: with HCl flowing, the temperature was raised to about 200° over a period of about 1 hr to complete dehydration of the mixed salt. The temperature was then increased to 400° over a 2 to 3-hr period to liberate the $NH_4Cl$ which was collected downstream. The anhydrous salt was then heated at 600° for about 0.5 hr to assure removal of the $NH_4Cl$. The HCl gas stream was replaced by $N_2$ and heating was continued for an additional 0.5 hr at 600° after which the product was furnace cooled under nitrogen. After preparation, the salt was stored over $P_2O_5$. All transfer operations were carried out in a glove box under dry nitrogen. The resulting anhydrous salts were found to contain less than 0.013 mol % $NH_4Cl$ by micro-Kjeldahl analyses. Gravimetric chloride assays showed them to be 99.9% pure.

*Heat of Solution Measurements.* Heat of solution measurements were made with an LKB-Produkter AB (Stockholm, Sweden) Model 8700-1 precision calorimetry system. The system is essentially a calorimeter of the nonisothermal, constant-temperature environment type with associated thermostat, temperature sensing, and calibration apparatus. The calorimeter is based on a design described by Sunner and Wadso.[11] Detailed specifications of the system are available from the U. S. distributor.[12] The calorimeter consists of a chromium-plated brass submarine and a 100-ml Pyrex reaction vessel containing a 2000-ohm thermistor temperature sensor, a 50-ohm manganin wire heater, and a combined sample holder–stirrer made of 18K gold. The sample holder supports a glass ampoule approximately 1 cc in volume. Sample ampoules for these measurements were filled under dry nitrogen and sealed by melting off an attached filling tube.

The overall temperature sensitivity of the calorimeter was found to be about 0.1 millidegree, and heat effects could be measured with precision of approximately 0.3%. Heat effects resulting from ampoule breaking in the reaction vessel were found to be negligible.

For the measurements reported here for KCl and $SrCl_2$, the calorimeter stirrer was operated at 150 rpm. At that speed, the KCl and $SrCl_2$ dissolved in less than

(7) E. M. Arnett and D. R. McKelvey, "Solvent Interactions," J. Coeffee and C. D. Ritchie, Ed., Interscience Publications, New York, N. Y., in press.

(8) T. W. Richards and H. G. Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 53 (1896).

(9) For magnesium chloride, a double salt, $NH_4Cl \cdot MgCl_2 \cdot 6H_2O$ is formed.

(10) In some initial experiments, the $MgCl_2$ was contaminated with an impurity which turned visibly grey as the temperature approached about 400°. Investigation revealed a hydrocarbon impurity in the HCl. A mass spectrographic analysis of the gas indicated that it contained 0.4% $C_7$ hydrocarbons, 1.1% $SO_2$, and possibly 0.8% HCN. The problem was resolved by using the electronic grade HCl and the heated alumina.

(11) S. Sunner and I. Wadso, *Acta Chem. Scand.*, **13**, 97 (1959).

(12) LKB Instruments, Inc., Rockville, Md.

4 min. However, the low solubility rate of $BaCl_2$ precluded accurate measurements at 150 rpm. Reaction times in water with $BaCl_2$ were 35 min, 12 min, and 1 min, at stirring speeds of 150, 300, and 600 rpm, respectively. Therefore, a stirring speed of 600 rpm was used for the $BaCl_2$, $CaCl_2$, and $MgCl_2$ measurements. For the last two, reaction times at 600 rpm were less than 1 min.

Heat calculations were based on the Dickinson technique[13] with extrapolations carried out to the time for half the temperature rise for the electrical calibration measurements and to the time for 0.6 of the temperature change for the heat of solution measurements. The extrapolation correction to the temperature changes never exceeded 10% of the entire change.

Calorimeter constants were measured before and after each experiment and a weighted mean value was calculated for the mean temperature of the dissolution reaction.

To test the overall performance of the calorimeter, the integral heat of solution of KCl (crystal) in water was measured. The results are shown in Table I.

**Table I:** Integral Heats of Solution of KCl(c) in Water

| $\Delta H$, kcal/mol | Temp, °C | Final aquamolality | $\Delta H°_\infty$, kcal/mol |
|---|---|---|---|
| 4.143 | 25.31 | 0.01396 | 4.106 |
| 4.176 | 24.97 | 0.08162 | 4.098 |
| 4.173 | 25.00 | 0.07986 | 4.096 |
| | | | $\overline{\Delta H°_\infty}$ 4.100 |

The mean enthalpy of solution at infinite dilution, obtained by applying heat of dilution values as tabulated in NBS Circular 500,[14] is seen to be 4100 cal/mol. This is in good agreement with the many values reported in the literature and with Parker's[15] selection of the "best" value of $\Delta H°_\infty$ (4115 ± 10 cal/mol).

*Emf—Transfer Free Energy Measurements.* The experimental apparatus and general procedure for obtaining transfer free energies from heavy–normal water cells has been described in detail elsewhere.[2] For this work, potential measurements were made with a Leeds and Northrup volt potentiometer and a Hewlett-Packard 425A dc microvolt ammeter serving as the null detector. The high input impedance of the null detector is such that negligible current flowed through the cell even at large offsets from null. A Varian Associates Model G-11 recorder was used to monitor the output of the null detector. Measurements were carried out at 25.0 ± 0.2°.

Measurements were made in cells of the type

$$Ag|AgCl|MCl_2(a_H)|{}^+|MCl_2(a_D)|AgCl|Ag \qquad (I)$$

where the symbol $|{}^+|$ represents a cation exchange membrane and the $a$'s are the activities of the salts

($MCl_2$) in their respective solutions. The emf's of such cells have been shown[16] to be related to the free-energy change for the process of transfer of an equivalent of salt from $D_2O$ at activity $a_D$ to $H_2O$ at activity $a_H$.

Measured potentials were plotted vs. the logarithm of the activity ratios ($a_D/a_H$). The intercept at unit ratio is the cell potential with equal activities in each half-cell and, corrected for the nonideality of the membrane, represents the standard emf for the cell.

The activity ratios were calculated from the compositions with the aid of activity coefficients due to Stokes.[17] It was assumed that the tabulated aqueous activity coefficients were applicable to heavy water solutions. The sign of the emf was defined such that positive values indicated a spontaneous transfer of salt from heavy to normal water.

At 25°, a tenfold change in activity ratio in cell I yields an emf change of 88.5 $t^+$ mV, where $t^+$ is the cation transport number and is a measure of the permselective efficiency of the membrane. Thus, the slope of the graph of measured emf vs. log $a_D/a_H$ yields the correction to $E°$ for membrane nonideality.

Solutions used for the cell measurements were about 0.11 ± 0.01 aquamolal, i.e., moles of salt/55.5 moles of solvent. They were prepared by weight from the same homogenous samples of salt as were used for the calorimetric measurements. The membranes used as the cell junctions were the same as those reported previously.[16]

**Results**

The integral heats of solution of $MgCl_2$, $CaCl_2$, $SrCl_2$ and $BaCl_2$ in $H_2O$ and $D_2O$ are given in Table II. Final concentrations ranged from 0.005 to 0.08 aquamolal. Values in $H_2O$ compared to NBS tabulated[14] values to 2% or better for all the salts. The heats were corrected to 0.015 aquamolal by reference to data tabulated in NBS Circular 500.[14] For each salt, the tabulated data were plotted according to the equation

$$\Delta H_s = \Delta H_s° + k\left(\frac{I^{1/2}}{1 + I^{1/2}}\right)$$

(where $I$ is the ionic strength of the solution) and the slope, $k$, of the resulting line, was determined. It was then assumed that the line drawn through each experimental data point with slope equal to that obtained

(13) H. C. Dickinson, U. S. National Bureau of Standards, Bulletin No. 11, U. S. Government Printing Office, Washington, D. C., 1915, p 189.

(14) F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffee, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Circular 500, U. S. Government Printing Office, Washington, D. C., 1952.

(15) V. B. Parker, "Thermal Properties of Aqueous Uni-univalent Electrolytes," National Standard Reference Data Series, National Bureau of Standards 2, U. S. Government Printing Office, Washington, D. C., April 1965.

(16) J. Greyson, J. Phys. Chem., 71, 259 (1967).

(17) R. H. Stokes, Trans. Faraday Soc., 44, 295 (1948).

**Table II:** Integral Heats of Solution of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ in $H_2O$ and $D_2O$ at 25.0°

| Salt | Solvent | Temp, °C | Final concentration, aquamolality, $m$ | $\Delta H$, kcal/mol[a] | |
|---|---|---|---|---|---|
| | | | | Measd | Cor to 0.015 $m$ |
| $MgCl_2$ | $H_2O$ | 25.00 | 0.007883 | −37.10 | −37.04 |
| | | 24.99 | 0.01036 | −37.04 | −37.01 |
| | | 25.03 | 0.01187 | −37.00 | −36.98 |
| | | 25.02 | 0.02047 | −37.05 | −37.08 |
| | | 25.02 | 0.02355 | −37.00 | −37.05 |
| | | | | $\overline{\Delta H} = -37.03 \pm 0.04$ | |
| | $D_2O$ | 25.00 | 0.01285 | −36.18 | −36.16 |
| | | 25.03 | 0.01305 | −36.04 | −36.03 |
| | | 25.03 | 0.01348 | −36.19 | −36.18 |
| | | 25.03 | 0.02007 | −36.13 | −36.16 |
| | | 25.02 | 0.02159 | −36.22 | −36.26 |
| | | | | $\overline{\Delta H} = -36.16 \pm 0.08$ | |
| $CaCl_2$ | $H_2O$ | 25.00 | 0.007594 | −19.31 | −19.25 |
| | | 25.00 | 0.008280 | −19.22 | −19.16 |
| | | 25.00 | 0.01134 | −19.27 | −19.24 |
| | | 25.00 | 0.01313 | −19.28 | −19.27 |
| | | 25.00 | 0.02094 | −19.20 | −19.24 |
| | | | | $\overline{\Delta H} = -19.23 \pm 0.04$ | |
| | $D_2O$ | 25.00 | 0.005694 | −18.10 | −18.02 |
| | | 25.00 | 0.006279 | −18.22 | −18.14 |
| | | 25.01 | 0.008138 | −18.00 | −17.94 |
| | | 25.01 | 0.009888 | −18.07 | −18.03 |
| | | | | $\overline{\Delta H} = -18.03 \pm 0.08$ | |
| $SrCl_2$ | $H_2O$ | 25.00 | 0.007172 | −12.04 | −11.99 |
| | | 24.98 | 0.009045 | −12.05 | −12.02 |
| | | 25.00 | 0.01848 | −11.93 | −11.95 |
| | | 24.99 | 0.01873 | −11.98 | −12.00 |
| | | 25.00 | 0.03286 | −11.94 | −12.00 |
| | | | | $\overline{\Delta H} = -11.99 \pm 0.03$ | |
| | $D_2O$ | 25.00 | 0.009814 | −10.74 | −10.71 |
| | | 24.98 | 0.01626 | −10.77 | −10.78 |
| | | 24.99 | 0.01644 | −10.72 | −10.73 |
| | | 24.98 | 0.02523 | −10.66 | −10.70 |
| | | 25.00 | 0.03541 | −10.60 | −10.67 |
| | | | | $\overline{\Delta H} = -10.72 \pm 0.04$ | |
| $BaCl_2$ | $H_2O$ | 25.00 | 0.01560 | −2.937 | −2.94 |
| | | 25.00 | 0.01811 | −2.976 | −2.99 |
| | | 25.00 | 0.03083 | −2.889 | −2.94 |
| | | 25.00 | 0.03234 | −2.901 | −2.96 |
| | | 25.00 | 0.05918 | −2.852 | −2.97 |
| | | | | $\overline{\Delta H} = -2.96 \pm 0.02$ | |
| | $D_2O$ | 25.00 | 0.01091 | −1.652 | −1.63 |
| | | 25.00 | 0.03257 | −1.500 | −1.56 |
| | | 25.00 | 0.04285 | −1.524 | −1.60 |
| | | 25.00 | 0.05513 | −1.544 | −1.65 |
| | | 25.01 | 0.06165 | −1.467 | −1.59 |
| | | 25.00 | 0.07824 | −1.441 | −1.58 |
| | | | | $\overline{\Delta H} = -1.60 \pm 0.03$ | |

[a] The mean values (corrected to 0.015 $m$) and the root mean square deviations are also listed.

with the NBS data represented the correct heat-concentration dependence.

For $D_2O$ solutions, the same values for $K$ were used. Justification for doing so derives from Debye–Hückel theory which predicts that in dilute solutions (ionic strengths below 0.1), the limiting slope for the concen-tration dependence of the heat of solution depends only upon the temperature coefficients of the dielectric constants of the solvents. These are almost identical for $H_2O$ and $D_2O$ at 25°.[18] Equal slopes for the concen-

(18) C. H. Collie, J. B. Hasted, and D. M. Pitson, *Proc. Roy. Soc.*, **A 60**, 145 (1948).

tration dependence of dilution heats in $H_2O$ and $D_2O$ solutions were also observed by Wu and Friedman[5] for dilute solutions (below 0.1 aquamolal) of several alkali halides.

The mean values of the corrected heats and the root mean square deviations are included in Table II.

The heat of transfer, $\Delta H_t$, for these salts between heavy and normal water is defined as the difference between the values of the standard heats of solution, i.e., $[\Delta H°(H_2O) - \Delta H°(D_2O)]$. Thus, in principle, it is necessary to extrapolate the data to infinite dilution to obtain values of $\Delta H_t°$. Extrapolations can be carried out for these salts by assuming, as above, equal slopes for both the heavy and normal water data. This is equivalent to assuming that the heat of transfer at 0.015 aquamolal is equal to that at infinite dilution. Heats of transfer from $D_2O$ to $H_2O$ calculated on the basis of this assumption are listed in Table III.

**Table III:** Heats of Solution and Heats of Transfer for $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ at 25.0°

| Salt | Solvent | $\Delta H$, kcal/mol | $\Delta H_t(H_2O - D_2O)$, cal/mol |
|------|---------|------|------|
| $MgCl_2$ | $H_2O$ | $-37.03$ | |
| | $D_2O$ | $-36.16$ | $-870$ |
| $CaCl_2$ | $H_2O$ | $-19.23$ | |
| | $D_2O$ | $-18.03$ | $-1200$ |
| $SrCl_2$ | $H_2O$ | $-11.99$ | |
| | $D_2O$ | $-10.72$ | $-1270$ |
| $BaCl_2$ | $H_2O$ | $-2.96$ | |
| | $D_2O$ | $-1.60$ | $-1360$ |

The results of the cell measurements are shown graphically in Figure 1, which is a deviation plot of the function $(E_{measd} - 88.5t^+ \log a_D/a_H)$ vs. $\log a_D/a_H$. Values of $t^+$, as calculated from the slope of a graph of $E_{measd}$ vs. $\log a_D/a_H$, are also shown in Figure 1 along with values of $E°$ after correction for the nonideality of the membrane. Figure 1 illustrates that the precision of the emf measurements was approximately $\pm 0.2$ mv.

The calorimetric and cell data are summarized in Table IV along with calculations of the associated free energy and entropy changes for the transfer process.

It should be pointed out that the calculated free energies shown in Table IV probably contain errors

**Table IV:** Emf, Free Energy, Heat, and Entropy of Transfer of Alkaline Earth Chlorides from $D_2O$ to $H_2O$

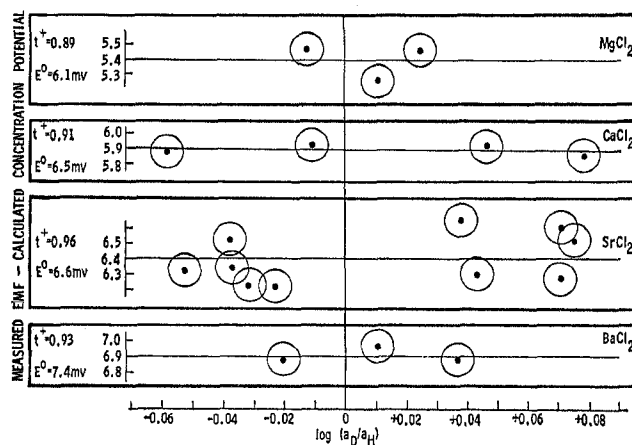| Salt | Emf, mv | $-\Delta F_t$, cal/mol | $-\Delta H_t$, cal/mol | $-\Delta S_t$, cal/mol deg |
|------|---------|--------|--------|--------|
| $MgCl_2$ | 6.1 | 280 | 870 | 2.0 |
| $CaCl_2$ | 6.5 | 300 | 1200 | 3.0 |
| $SrCl_2$ | 6.6 | 300 | 1270 | 3.2 |
| $BaCl_2$ | 7.4 | 340 | 1360 | 3.4 |

Figure 1. Deviation plot of the quantity $[E_{measd} - 88.5t^+ \log (a_D/a_H)]$ vs. $\log (a_D/a_H)$ for the alkaline earth chlorides.

from contributions to the measured emf values resulting from solvent transport through the cell membrane.[16] However, as has been noted previously for the alkali halides, and as can be seen for these salts also, the value of the entropy of transfer is dominated by the heat of transfer. Thus, relatively large errors can be tolerated in the free energy values before significant effects are reflected in the entropies. Furthermore, as has been discussed before,[16] the solvent emf contributions which appear in ion-exchange membrane cells have the property of enhancing the apparent spontaneity of the transfer of salt from $D_2O$ to $H_2O$; i.e., they make the free energy values appear too negative. Corrections for solvent transfer, therefore, might result in somewhat more negative entropy values than those in Table IV, but they would not be expected to change the sequence of the values or their signs.

**Discussion**

It is significant that the sign of the free energy values shown in Table IV indicates spontaneous transfer of salt from $D_2O$ to $H_2O$, and the decreasing entropies indicate *increased* ordering in the transfer process. Entropy decreases in the transfer of salt from heavy to normal water have been interpreted[2,3,5-7] as being indicative of the structure-*breaking influence* of the transferring salts. The argument presented has been that the higher concentration of structure in heavy water, compared to normal water, is more effectively disrupted by structure-breaking species, leading to a decrease in entropy in passing from $D_2O$ to $H_2O$.

It is convenient to represent the data in Table IV in a fashion similar to that suggested by Arnett and McKelvey.[7] These authors assigned zero values to lithium for the entropy and enthalpy of transfer from $H_2O$ to $D_2O$ and thence calculated entropies and enthalpies for other ions. By plotting the resulting ionic enthalpies vs. entropies, they obtained a straight line with structure-breaking ions in the upper right quadrant and structure makers tending toward the

lower left. The physical significance of the graph is obscure. It does, however, provide an interesting presentation of the sequence in structure-influencing properties of the ions. Such a graph is shown in Figure 2. It includes enthalpy and entropy data for the alkali and halide[3] ions as well as the alkaline earth ions. For consistency with Arnett and McKelvey, the data are presented for the process of transfer from normal to heavy water; i.e., the signs have been reversed from those in Table IV. In contrast to Arnett and McKelvey, however, sodium has been selected as the zero reference. Sodium was selected because doing so yielded a $\Delta H_t$ vs. $\Delta S_t$ graph with considerably less data scatter than that obtained by using lithium as the reference ion. Furthermore, based on Kaminsky's[19] discussion of the temperature dependence of its viscosity $B$ coefficient (and heat capacity), sodium ion seems the more natural choice; i.e., it seems to have the least net effect on solvent structure.

As can be seen by examination of the data of Table IV and the sequence in Figure 2, not only do the salts of the alkaline earths appear to be structure breakers on this scale; the individual cations, with the exception of magnesium, also are structure breakers. In fact, the larger ions appear to be somewhat more structure breaking than their group Ia counterparts while magnesium appears to be a stronger structure maker than lithium. These relationships are dependent to some extent upon the choice of reference ion. However, selection of sodium as reference yields the same sequence as does selection of lithium.

To attribute structure-breaking behavior to the larger alkaline earth cations appears, at least superficially, to be in conflict with conclusions drawn from other measurements. Viscosity $B$ coefficients for these ions are positive. One, therefore, would have expected them to behave as structure makers. However, in terms of structural influences, the entropy relationships illustrated in Figure 2 do not necessarily parallel viscosity effects. As will be seen, the transfer entropies probably result primarily from long-range ion–solvent interactions while solution viscosity variations probably result from a balance of both short- and long-range interactions.

Division of the influence of dissolved ions on solvent structure into long- and short-range ordering has been discussed at length by Kaminsky,[19] who proposed that viscosity effects resulted from a combination of the influence of the ions on the bulk structure of the solvent as well as on primary solvation. Thus, high charge density and strongly solvating species like magnesium or lithium also orient water at a distance and are strong structure makers while weakly hydrating potassium or chloride ions compete for water molecules with the structured components of the bulk solvent and in so doing cause structure disruption. Kaminsky also attributed viscosity changes with temperature to
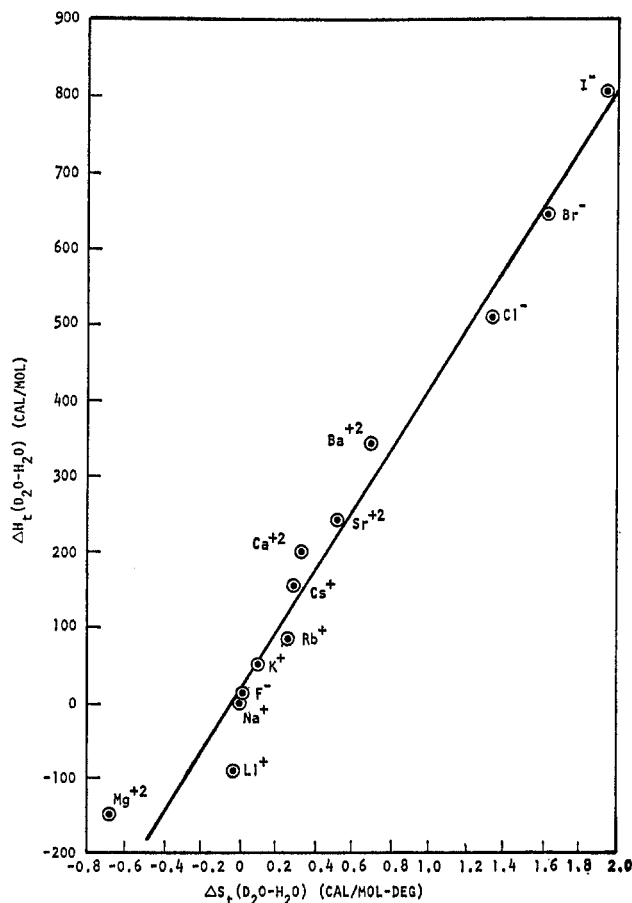


Figure 2. Water structure influencing sequence for ionic species.

changes in the net effects of the short- and long-range interactions. Thus, an increase in temperature can disrupt the long-range orientation influence of magnesium and lithium ions leading to a decrease in viscosity relative to the pure solvent. On the other hand, increasing the temperature of solutions of structure breakers tends to disrupt still more bulk structure. More water molecules are then available for further solvation and a net increase in viscosity relative to pure solvent is obtained. Where these effects balance, as with sodium ion, no temperature dependence is observed.

Applying Kaminsky's argument to the data obtained in this study, one must consider that some of these proposed interactions can be equivalent in isotopic solvents and cancel one another in a difference measurement. For example, that primary solvation is the same in heavy and normal water can be concluded from the value of the enthalpy of transfer. If a solvent molecule were shed or gained in the transfer process, one would expect a heat effect of the same order of magnitude as the heat of vaporization of the solvent, i.e., about 10 kcal/mol. However, as can be seen in Table IV, the transfer enthalpies which have been measured are of

(19) M. Kaminsky, Discussions Faraday Soc., 24, 171 (1957).

the order of 1 kcal/mol. One concludes therefore that that short-range orientation in both solvents is about the same and that entropy contributions resulting from it cancel in the transfer process. Thus, the observed transfer entropies are attributable to the relative extent to which the ions can impose either long-range orientation or disruption on the isotopic solvents. Ions like $Ba^{2+}$, $Sr^{2+}$, or $Ca^{2+}$ apparently can assert a disrupting influence on the bulk solvent structure despite the net increase in viscosity which results from strong primary solvation.

Other experimental evidence is available which leads to the conclusion that long-range interactions can determine structure influence. Combination of Wu and Friedman's entropy of dilution data in heavy and normal water[5] with entropies of transfer at infinite dilution[3] leads to the concentration dependence for the transfer of salts between the isotopic solvents. It is noteworthy that for the several alkali halides for which data are available, the transfer entropies decrease in absolute value as concentration increases, consistent with the conclusion that short-range interactions are about equivalent in both solvents.

Interestingly, Gurney[20] points out a similar phenomenon based on measurements of equivalent conductivity. Sodium and potassium acetates appear to be more "lively" in heavy water than would be expected by consideration of the relative viscosities of normal and heavy water. However, acetate ion is referred to as a strong structure maker by Kavenau[21] and would be expected to increase the viscosity of heavy water

and suffer a diminishment in its "liveliness" relative to normal water. That the opposite is observed, as for the alkaline earth cations, also implies that long-range effects may be involved.

The nature of these long-range disruption processes is not clear. Perhaps the solvated ions are point sources of energy which, in their movement through the solvent, serve as the fluctuations which make and break the "flickering clusters" of Frank and Wen.[22] Or, as suggested by Kaminsky, the larger solvated ions may compete with solvent clusters for water molecules and cause a net disruption effect. Whatever the processes, it seems clear from the entropy sequence shown in Figure 2 that unless the ions have sufficiently high charge density to give rise to significant long-range ordering as with magnesium or lithium, some solvent structure breaking occurs which is unrelated to the short-range orientation associated with ion solvation.

Perhaps one of the more important conclusions to be drawn from the data is that considerable caution must be used in relating structural implications derived from measurements in concentrated salt solutions where short-range interactions predominate to those derived from dilute solutions where long-range interactions may become significant.

(20) R. W. Gurney, "Ionic Processes in Solution," Dover Publications, Inc., New York, N. Y., 1953, p 79.

(21) J. L. Kavanau, "Water and Solute–Water Interactions," Holden-Day, Inc., San Francisco, Calif., 1964, p 58.

(22) H. S. Frank and W. Y. Wen, Discussions Faraday Soc., 24, 133 (1957).