Stable Isotope Geochemistry: A Tribute to Samuel Epstein
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Editors: H. P. Taylor, Jr., J. R. O'Neil and I. R. Kaplan

Oxygen isotope fractionation studies of solute-water interactions

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Abstract—Equilibrium oxygen isotope fractionations were measured between CO_2 and concentrated aqueous solutions and compared to those between CO_2 and pure H_2O at 0, 25, and 38.5°C. Inferences from these data are that (1) the direction and relative magnitudes of the measured fractionations at any temperature are well correlated with the structure-making and structure-breaking capacity of the solute, (2) concentrated aqueous solutions of structure-making salts assume at least two thermodynamically distinct structural states that depend on critical concentrations of di- and trivalent cationic charge equivalents, (3) the same structural state of solutions of structure-breaking salts can be attained with organic solutes, (4) Mg^{2+} and Al^{3+} ions are completely solvated in their respective sulfate ion-pairs, and (5) after a critical concentration of about 50 volume % dioxane, additional dioxane breaks hydrogen bonds between water molecules causing the liquid water in the solution to have isotopic properties more like those of water vapor. The simple CO_2-equilibration technique has provided insights into important aspects of aqueous chemistry in the past and continues to hold great promise for future investigations of fundamental interactions between solutes and water.

INTRODUCTION

THE STUDIES reported in this paper are a direct outgrowth of the work of TAUBE (1954) who first applied the CO_2-equilibration technique to the study of aqueous solutions. The technique consists of equilibrating the oxygen isotopes of CO_2 with pure water and with aqueous solutions at constant temperature. Taube found that the $^{18}O/^{16}O$ ratio of CO_2 equilibrated with pure water at 25°C decreased upon the addition of $MgCl_2$, $AlCl_3$, HCl, and LiCl; remained essentially unchanged for NaCl, NaI, and $NaClO_4$; and increased when $CaCl_2$ was added to the water. The changes in $^{18}O/^{16}O$ ratio are roughly linear with the molality of the solute (our data are shown in Fig. 1) and this is normally taken to indicate a constant coordination number of the cation for water in the first hydration sphere with no effect attributed to hydration of the anion. Taube attributed such isotopic effects to differences between the isotopic properties of water in the hydration sheath of the cation and the remaining "bulk" water. These oxygen isotope fractionations are described in terms of the vibrational frequencies (and frequency shifts on isotopic substitution) associated with the bonding in the two types of water and consequently bear on fundamental thermodynamic properties of water and aqueous solutions.

Using this oxygen isotope technique, SOFER and GAT (1972, 1975) studied a series of solutions of geochemical interest. They called attention to the difference between the activity of $H_2{}^{18}O$ (the quantity actually measured by this technique) and the concentration of $H_2{}^{18}O$ and also pointed out the importance of correcting for salt effects when analyzing natural brines for their ^{18}O content by the CO_2-equilibration method. The questions of variation in oxygen isotope activity of aqueous solutions with temperature and the importance of making corrections to natural and experimental data has been examined several times (TRUESDELL, 1974; KENDALL *et al.*, 1983; KASAHAYA, 1986; COLE and WESOLOWSKI, 1989; LIGANG *et al.*, 1989) but these issues remain effectively unresolved. O'NEIL and ADAMI (1969) used the CO_2-equilibration technique to measure the oxygen isotope partition function ratios of liquid water at frequent intervals from 2 to 85°C and discussed the temperature dependence of this property in relation to its compatibility with theories of the structure of water. The results of their study provide a reference for the solution data taken at the relatively low temperatures employed in the present work.

The topics covered in this report include: (1) the temperature dependence of the fractionation of oxygen isotopes between concentrated aqueous solutions and pure water, (2) the variation of water structure with the nature and concentration of added solutes, (3) the correlation of oxygen isotope effects with the structure-making and structure-breaking properties of various solutes, with separation of the effects into those caused by cations and anions, (4) the nature of sulfate ion pairs of Mg^{+2} and Al^{+3} and the 1:1 fluoride complex of Al^{+3}, and (5) the nature of the interactions between water and organic solutes.

EXPERIMENTAL PROCEDURES

The CO_2-equilibration technique used is a modification of the technique first described by COHN and UREY (1938)

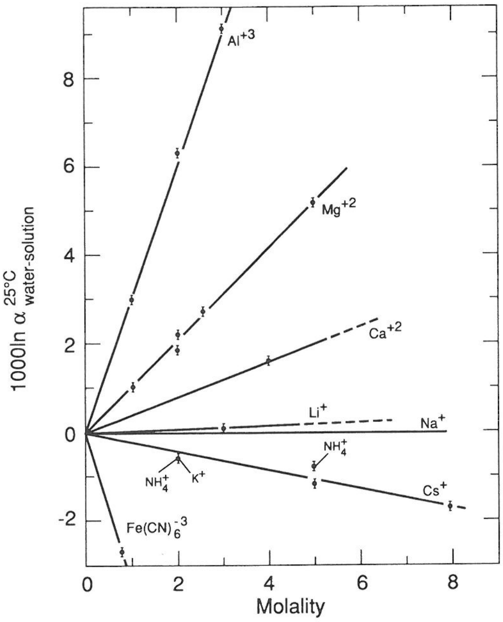

FIG. 1. Oxygen isotope per mil fractionations between pure water and solutions of various ions. Positive values are associated with structure-making electrolytes and negative values with structure-breaking electrolytes and organic solutes (see text).

and employed by EPSTEIN and MAYEDA (1953) in their seminal publication on the variations in the ^{18}O contents of natural waters. Approximately 150 μmoles of dried CO_2 were transferred to vessels containing 5 ml of degassed water or solution. These large amounts of CO_2 and H_2O were used in order to be able to take several aliquots of CO_2 during the equilibration as a check on rates of isotopic exchange and to use the same preparations for runs at different temperatures. The vessels were placed in a constant temperature bath regulated to ±0.1°C and shaken several times a day. Isotopic equilibration was assumed to be complete when the isotopic composition of the CO_2 ceased to change with time (normally 1–2 days depending on the degree of shaking and the nature and concentration of the solution). For the very viscous and acidic $AlCl_3$ solutions, isotopic equilibrium was demonstrated in this work by approaching the equilibrium value from opposite sides of the equilibrium distribution. An aliquot of the CO_2 was removed at the equilibration temperature and its $\delta^{18}O$ value measured on an isotope ratio mass spectrometer. This value is the relative difference, in parts per thousand (per mil), between the $^{18}O/^{16}O$ ratio of the sample and that of the working standard of the mass spectrometer and can be determined with a precision of better than ±0.1 per mil.

Many of the salts used in these studies are hygroscopic and extensive precautions were taken to avoid contamination by extraneous water. Commercial anhydrous salts were heated on a vacuum line to remove traces of water and then weighed into the equilibration vessel in a dry box. In some cases, hydrated salts were weighed into the equilibration vessels and dehydrated by vacuum distillation at 100°C. Water of known isotopic composition was then distilled into the vessel on the vacuum line. After equilibration, conventional chemical analyses were made of the solutions as a check on concentration. In the case of $AlCl_3$, chemical analyses of the solutions indicated that hydrolysis and loss of HCl during the dehydration of the salt was negligible. No solution that was chemically analyzed differed by more than 0.1–0.2 in molality from that expected from the weights of salt and water used in the preparation. Equilibrations were made on three separate 1.0 molal solutions of $AlCl_3$ as a check on the reproducibility of the method as the $AlCl_3$ solutions proved to be the most intractable in the laboratory. The results given in Table 1 indicate that the reproducibility of the method for this solution, and by inference for all the other solutions, is typically about 0.1 per mil or better.

MODELS OF ION HYDRATION AND ORIGIN OF ISOTOPIC EFFECTS

FRANK and WEN (1957) proposed that water associated with ions in solution exists in several forms. In the inner hydration sheathes of ions of high ionic potential (F^-, polyvalent cations, alkali cations other than Rb^+ and Cs^+), water is dense, immobilized and structured with its dipoles oriented radially to the ion. Water in the outer hydration sheathes of cations and probably all water associated with anions (other than F^-) and large, singly-charged cations is unstructured and mobile though still more dense than normal water. For cations, this unstructured water results from the discontinuity between the structure of normal water and the structure of inner-sphere, tightly-bound water. In anions it results from disruption due to the physical presence of the ion.

This model can be successfully applied to the isotopic effects of salts through an equation that relates the concentration of ions, their hydration number, and the fractionation factor between bulk water and water of hydration (TAUBE, 1954). This equation is here extended to include water in the several distinct hydration spheres postulated by Frank and Wen. The derivation of the equation is not exact because the $^{18}O/^{16}O$ ratio is taken as the mole fraction of ^{18}O. For ordinary water, however, these quantities differ by very little. The extended equation is

$$10^3 \ln \alpha = \frac{\sum m_i \sum n_{ij}(K_{ij} - 1)}{55.51}$$

where m_i is the molality of the ion, n_{ij} is the number of water molecules in the jth hydration shell of each ith ion, and K_{ij} is the oxygen isotope fractionation factor between water in the jth hydration shell of the ith ion and bulk water defined as

$$K_{ij} = \frac{(^{18}O/^{16}O)_{ij\ \text{hydrate water}}}{(^{18}O/^{16}O)_{\text{bulk water}}}.$$

Using this equation the total isotopic effect can in theory be divided into the individual effects due to the inner and outer hydration spheres, to the cation, and to the hydration sphere of the anion.

Before attempting to correlate the observed isotopic effects with properties of aqueous solutions, it is useful to consider the possible origins of these effects. Taube chose to explain them in terms of a separation of the available water into at least two different species: water bound in coordination spheres of the solutes and remaining "bulk" water—the latter behaving isotopically like pure water. That is, when the three oxygen-containing species in the system (CO_2, bound water, and bulk water) are all in oxygen isotope equilibrium, and when the bound water concentrates ^{18}O relative to the bulk water, the CO_2 becomes isotopically lighter on addition of the solute to pure water. Another point of view considers the effects to be a consequence of the different fractionation factors between CO_2 and the various solutions treated as homogeneous substances. That is, if the solute alters the water structure, the resultant changes in the vibrational frequencies of the water will change the CO_2-H_2O fractionation factor with a corresponding change in the isotopic composition of the CO_2.

The second hypothesis above is not readily amenable to quantitative treatment but is an important consideration in this paper. It is instructive, however, to point out that there is a problem in relating the absolute magnitude of the isotopic effects observed to thermodynamic properties of the solution. There is little doubt that ions in aqueous solutions are solvated and that the bonds between water molecules and the solute ions are different from the bonds between water molecules themselves. So, indeed, there are different species of H_2O in an aqueous solution and each species has its unique isotopic properties. O'Neil and Adami (1969) demonstrated that thermodynamic differences between the various molecular varieties of H_2O should be detectable by the isotopic fractionation technique. Bulk water in a concentrated solution, then, should have isotopic properties that are different from those of pure water. Thus, the lack of knowledge of the fractionation factors between CO_2 and bulk waters places constraints on the application of the CO_2-equilibration technique to quantitative thermodynamic problems of aqueous solutions. The observed isotopic effects undoubtedly arise from *both* a separation of the water into two or more H_2O species *and* to changes in the structure of water upon the addition of solute. Experiments to delineate these effects were performed and are discussed below.

RESULTS

The per mil fractionations between pure water and the solutions at various concentrations and temperatures are given in Tables 1, 2, and 3. The lack of data in certain columns arises from either a failed experiment (typically a leaky stopcock during the equilibration) or simply that the experiment was made only at 25°C. The fractionation factor between pure water and the solution, $\alpha(H_2O\text{-soln})$, is given by the following expression:

$$\alpha(H_2O\text{-soln}) = \frac{(^{18}O/^{16}O)_{\text{water}}}{(^{18}O/^{16}O)_{\text{soln}}} = \frac{1000 + \delta(CO_2\text{-}H_2O)}{1000 + \delta(CO_2\text{-soln})}$$

where $\delta(CO_2\text{-}H_2O)$ means the $\delta^{18}O$ value of CO_2 which was equilibrated with pure water. Water of the same isotopic composition was used in all the experiments. Values of $10^3\ln\alpha$ rather than of α are tabulated because of the greater simplicity of the numbers and because the logarithmic function has theoretical significance (Urey, 1947; Bigeleisen and Mayer, 1947). It is this function which is normally used in relating the variation of α with temperature. In Table 1, the first entry at 0°C means that at 0°C, CO_2 in isotopic equilibrium with pure water is enriched in ^{18}O by 1.25 per mil relative to CO_2 in equilibrium with a 1.0 molal solution of $MgSO_4$. A negative value means that CO_2 in equi-

Table 1. Experimental determinations of the per mil fractionations, $10^3 \ln \alpha$, between pure water and solutions of structure-making electrolytes at different temperatures

Solution	0.0°C	25.0°C	38.5°C
6.0 m NaCl	—	0.00	—
1.0 m LiCl	—	0.10	—
1.0 m $MgSO_4$	1.25	1.05	0.79
2.0 m $MgSO_4$	2.42	1.82	1.70
2.0 m $MgCl_2$	2.22	1.80	1.63
3.0 m $MgCl_2$	3.60	3.00	2.80
3.5 m $MgCl_2$	4.30	3.65	3.32
4.0 m $MgCl_2$	6.30	4.50	3.70
5.0 m $MgCl_2$	7.35	5.20	4.35
1.0 m $AlCl_3$	3.55	3.00	2.85
1.0 m $AlCl_3$	3.65	3.04	2.78
1.0 m $AlCl_3$	3.60	2.98	2.70
2.0 m $AlCl_3$	7.05	6.30	5.85
1.0 m $Al_2(SO_4)_3$	—	6.19	5.66
3.0 m $AlCl_3$	11.25	9.05	8.05
1.0 m $AlCl_3$ + 1 m NaF	—	2.46	—
4.0 m $CaCl_2$	1.91	1.63	—
4.0 m $CdCl_2$	—	1.10	—

Table 2. Experimental determinations of the per mil fractionations, $10^3 \ln \alpha$, between pure water and solutions of structure-breaking electrolytes at different temperatures

Solution	0.0°C	25.0°C	38.5°C
2.0 m KCl	—	−0.56	—
6.0 m NaI	−1.10	−0.77	−0.60
11.7 m NaI	−1.11	−0.83	−0.62
2.0 m NH_4Cl	—	−0.50	—
5.0 m NH_4Cl	—	−0.77	—
6.0 m NH_4I	—	−0.78	—
5.0 m CsCl	−1.41	−1.13	−1.22
8.0 m CsCl	−1.97	−1.62	—
0.8 m $Na_3Fe(CN)_6$	—	−2.83	−0.64

librium with pure water is depleted in ^{18}O by that amount relative to CO_2 in equilibrium with the solution. As discussed above, this technique is extremely reproducible and for that reason the fractionations are reported to the nearest ±0.01 per mil although a figure of ±0.05 is more realistic. Errors in solution preparation or hydrolysis reactions for certain solutes will introduce additional errors outside the small analytical error of isotopic measurement and explain some of the scatter observed.

The measured fractionations range from −3.71 for a concentrated solution of dioxane to 11.25 for a 3.0 molal solution of $AlCl_3$, so the effects of added solutes to the isotopic properties of water are indeed very large and meaningful.

STRUCTURE-MAKING AND STRUCTURE-BREAKING SOLUTES

It is readily apparent from the data in Tables 1 and 2 that electrolytes normally considered structure makers (*e.g.*, Mg^{+2}, Al^{+3}) yield positive values of $10^3 \ln\alpha$ and that the structure breakers (*e.g.*, Cs^+) yield negative values. FRANK and WEN (1957) were the first to discuss the structure-making and structure-breaking effects of electrolytes on water, and others have since couched these discussions in other terms, like "flickering clusters." We choose not to use terms germane to only one theory of the structure of water and solutions but merely to use the operational definition implied above: structure makers yield positive isotopic fractionations and structure breakers yield negative isotopic fractionations. This definition is not arbitrary because the isotopic fractionation between ice and liquid water is positive (O'NEIL, 1968) and the fractionation between vapor and liquid is negative (MAJOUB, 1971). That is, any solute that results in a positive value of $10^3 \ln\alpha$ is one that causes the solution to be more structured or ice-like.

Equilibrations were made with alkali chloride solutions and the results indicate the following structure-breaking order: $Cs^+ > K^+ > Na^+ > Li^+$ with Li^+ just at the experimentally detectable limit (0.1 per mil) of being a structure maker. Inasmuch as the net isotopic effect caused by both cations and anions is measured, it is probable that Li^+ is a *bona fide* structure maker by isotopic criteria, and runs made with sodium salts indicate that I^- is a greater structure breaker than Cl^-. Another sequence examined in this work is the following group of structure makers: $Al^{+3} > Mg^{+2} > Ca^{+2}$ (Table 1). Cs^+, NH_4^+ salts, urea, and dioxane all yield negative isotopic fractionations (Table 2) and are thus classified as structure breakers. The results of other techniques are in agreement with these classifications and sequences in some cases and not in others. No attempt will be made to compare results considering the vast literature on this subject.

Structure makers

Several experiments were made in an attempt to assess the relative importance of ionic size, mass, and electronic configuration of cations to their structure-making properties. In general, ions with large ionic potentials are the greatest structure makers. There is little doubt that the development of hydration sheathes around small, highly charged positive ions is chiefly responsible for the increased order observed in their solutions. The vibrational frequencies of water bonded to cations are different from those of water bonded to other water molecules and thus an isotopic fractionation between bound and bulk water is expected. In the case of Al^{+3} solutions, the isotopic fractionation between bound and bulk water is 25.6 per mil at 25°C. This value is calculated from the measured 3.1 per mil fractionation between pure water and 1.0 molal $AlCl_3$ solution, and assuming a coordination number of 6 for Al^{+3}, complete dissociation, and equal values for the fractionation factors between CO_2-bulk water and CO_2-pure water. This fractionation of 25.6 per mil is on the order of those measured between crystalline silicates and water and between solid carbonates and water (*e.g.*, FRIEDMAN and O'NEIL, 1977). On this basis the fractionations between bound and bulk waters measured in these experiments seem too large, although this cannot be rigorously proved. In accordance with the model used, 32% of the water in a 3.0 molal solution of $AlCl_3$ is bonded to Al^{+3} in the first coordination sphere. Given this high percentage of bound water, the remaining bulk water should not have the properties of pure water. At higher concentrations this problem becomes acute. In the 5 molal $MgCl_2$ solution studied, 54% of the water is bound water. The assumption that the fractionation factor between CO_2 and bulk water is identical to that between CO_2 and pure water is clearly weak in these cases of very concentrated solutions. Nonetheless, it is safe to say that for those solutions with a positive value of $10^3\ln\alpha$, the bound water is indeed enriched in ^{18}O relative to the bulk water. This is tantamount to saying that the cation-H_2O bonds are stronger than the H_2O-H_2O bonds in these solutions.

In light of the above discussion, it is interesting to compare the results of equilibrations of CO_2 with solutions of $CdCl_2$ and of $CaCl_2$. It was mentioned above that Ca^{+2} is a structure maker on isotopic grounds, a 1.0 molal solution yielding $10^3\ln\alpha$ equal to +0.40. Cd^{+2} is almost identical in ionic radius to Ca^{+2} and therefore any difference in the isotopic behavior of these two solutions must be attributed to differences in mass and/or electronic configuration of the ions. The value of $10^3\ln\alpha$ for a 1.0 molal solution of $CdCl_2$ is +0.25. Assuming equal coordination numbers for the two cations and similar isotopic properties for the bulk waters, the data are interpreted to reflect an enrichment of ^{18}O in the water sheath of Ca^{+2} relative to Cd^{+2}. The effect is principally one of mass, the higher vibrational frequencies (of the bonds between cation and water) and tendency to concentrate ^{18}O being correlated with the lighter Ca^{+2} ion (*e.g.*, O'NEIL, 1986). A similar correlation was observed in the case of oxygen isotope fractionation between H_2O and the carbonates $CaCO_3$ and $CdCO_3$ (O'NEIL *et al.*, 1969).

Structure breakers

A size comparison can also be made for structure breakers using, for example, salts of NH_4^+ and K^+ whose ionic radii are very similar. With the notable exception of $Fe(CN)_6^{-3}$, however, *all ionic structure breakers investigated yield approximately the same negative value of $10^3\ln\alpha$.* For these solutions one might say that the cation-H_2O bonds are weaker than the H_2O-H_2O bonds, but if this were the nature of the isotopic effect, there should be a variety of fractionations for the various solutions. From the similarity of the results, we suggest that the addition of these structure-breaking cations results in a uniform alteration of the water structure with a concomitant change in the CO_2-H_2O fractionation factor. Implied here is little or no isotopic fractionation between bound and free water.

NaCl is an unique salt in its failure to cause an appreciable isotopic effect. On comparing the results of TAUBE (1954), SOFER and GAT (1972), and this work, it is clear that at low temperatures Na^+ is nearly equal and opposite in its properties to Cl^- even at very high concentrations. If anything, Na^+ acts as a mild structure breaker. NH_4Cl, on the other hand, acts as a distinct structure breaker. Inasmuch as the Cl^- ion is common to both NaCl and NH_4Cl, it is reasonable to assume that NH_4^+ is the dominant structure breaker. Similarly NaI is a distinct structure breaker and I^- is reasonably assumed to be the cause. If each structure breaker altered the water structure in an unique way, then combinations of structure breakers, for example, the salt NH_4I, should produce an isotopic effect greater than that of either ion alone or as much as the sum of the effects of each ion. From Table 2 it is seen that 5.0 molal NH_4Cl, 6.0 molal NaI, and 6.0 molal NH_4I yield values of $10^3\ln\alpha$ of −0.77, −0.83, and −0.78, respectively, which are identical within the limits of analytical error. This is further evidence that the average-size, structure-breaking ion, *regardless of sign,* alters the structural state of the water in an unique and common way.

The importance of ionic size in disrupting water structure can be tested by using an extremely large ion. Unfortunately, most salts of the large ions used in other studies are not soluble enough to produce a measurable isotopic effect. The salt $Na_3Fe(CN)_6$ was chosen because of its fairly high solubility (0.8 molal at 25°C). The equilibration vessel was covered with aluminum foil to prevent any photochemical reactions that might occur during the equilibration time. The measured isotopic fractionation of −2.8 per mil is as large a negative fractionation on a 1.0 molal basis as is found for Al^{+3} in the other direction (Fig. 1). This ion is particularly susceptible to a variety of chemical reactions in solution so that the magnitude of this isotopic effect should be viewed with reservation. Cyanide hydrolysis was proved to be insignificant by analyzing the $^{13}C/^{12}C$ ratio of the CO_2. This ratio did not change during the equilibration. The result was reproducible and it is tentatively concluded that the size of anionic structure breakers can be extremely important in determining the nature of water-structure alteration.

Considering the similarity of the isotopic fractionations among solutions of structure breakers that are not too different in size and the unusual result for the very large ferricyanide ion, it may be that there is a critical size of the ion above which a profound alteration in water structure is necessary in order to provide accommodation sites for the large ion. The change of over 2.0 permil in the value of $10^3\ln\alpha$ on going from Cs^+ or I^- to $Fe(CN)_6^{-3}$ is indeed a very large isotopic effect and cannot be explained by differences in the "relatively weak" bonding between anions and water. Rather it must have something to do with a fundamental change in the structure of the water.

Non-electrolytes

The influence of non-electrolytes on the isotopic properties of water was investigated by equilibrating CO_2 with a solution of urea and with a series of dioxane-water mixtures. The measured fractionations for all these experiments are given in Table 3 and shown graphically in Fig. 3. Similar experiments with a different approach and somewhat different goals were conducted with pyridine by BETTS *et al.* (1977) and with urea by KAKIUCHI and MATSUO (1985). The fractionations for the one (5.0 molal) solution of urea analyzed and the relatively dilute dioxane solutions are all about −0.55 per mil. This is a value similar to those of the solutions of structure-breaking electrolytes except for those of highly concentrated solutions of CsCl and the solution of $Na_3Fe(CN)_6$ which are significantly larger. The important implication is that water may be assuming the same structural state for all these solutions regardless of whether ionic species are present. Apparently, for each non-electrolyte there is a critical concentration above which water assumes a different and more disordered structural state.

If the dioxane does nothing more than break hydrogen bonds to accommodate itself into the water structure, it would tend to make the water behave isotopically more like water vapor. This is indeed the direction of the change (Fig. 2). With increasing dioxane/water ratio, however, a limiting fractionation of about 4.0 per mil is reached. Liquid water is enriched in ^{18}O by 9.0 per mil relative to water vapor at 25°C (MAJOUB, 1971). This difference of five per mil presumably reflects the restrictions placed on the motions of the separated water molecules in this condensed state.

Table 3. Experimental determinations of the per mil fractionations, $10^3 \ln \alpha$, between pure water and solutions of organic solutes at different temperatures

Solution	0.0°C	25.0°C	38.5°C
5.0 m urea	—	−0.56	—
20% dioxane	−0.35	−0.49	—
30% dioxane	−0.50	−0.58	—
50% dioxane	−1.19	−1.48	−1.75
80% dioxane	−3.07	−2.66	−2.59
90% dioxane	−3.71	−3.39	−3.11
0.01 mole $MgSO_4$ in 10 ml 50–50 mixture	—	0.77	—
0.01 mole $MgCl_2$ in 10 ml 50–50 mixture	—	0.86	−1.90

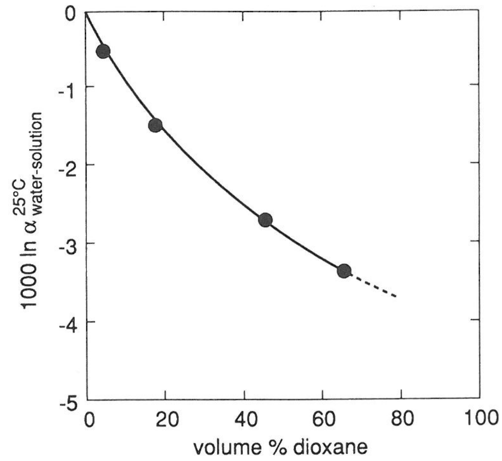

FIG. 2. Oxygen isotope per mil fractionations between pure water and solutions of dioxane. With increasing dioxane content more hydrogen bonds in water are broken and the water becomes isotopically more like water vapor.

Equilibrations were carried out with solutions of 0.01 mole of $MgCl_2$ or $MgSO_4$ in 10 ml of 50–50 mixtures of dioxane and water. The preliminary results presented in Table 3 are from a series of experiments designed to elucidate the effect of changes in dielectric constant of the solvent on the solute-solvent interactions. Changing the dielectric constant of the solution by temperature alone presents certain technical difficulties and, in addition, the sensitivity of the technique is lowered at high temperatures because isotopic fractionations decrease with increasing temperature. The addition of dioxane to water permits the equilibrations to be done at low temperatures in solutions of reduced dielectric constant. The data are most easily interpreted by separating the interaction of the magnesium salt and water from that of dioxane and water. The isotopic effects for $MgSO_4$ and $MgCl_2$ solutions at 25°C are close to being the sum of the ion-water effect and the dioxane-water effect. At 38.5°C, however, the fractionation is nearly identical to that of the 50–50 dioxane-water mixture alone. It is tentatively concluded that under these conditions of temperature and dielectric constant, the Mg^{+2}-H_2O interactions are drastically reduced or eliminated.

ION-PAIRING IN CONCENTRATED SULFATE SOLUTIONS

The largest isotopic effects observed in the earlier and present work are for the magnesium and aluminum chloride solutions. Of interest, then is the magnitude of the effects when magnesium and aluminum ions are extensively associated as in their

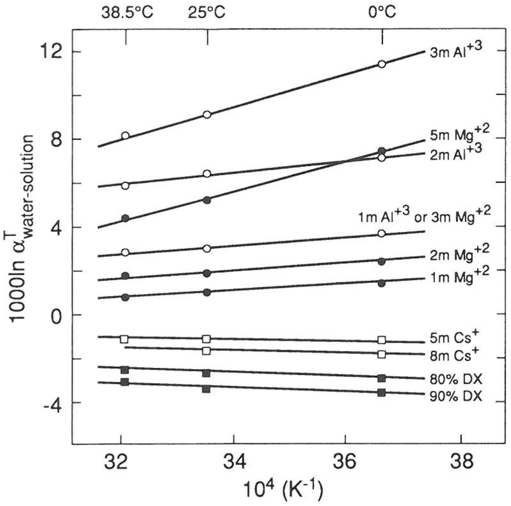

FIG. 3. Temperature dependence of the per mil fractionations between pure water and various solutions. Note the similarity in slopes of structure makers and structure breakers and that the curves for 1 m Al^{+3} and 3 m Mg^{+2} are identical. At certain critical concentrations of Al^{+3} and Mg^{+2}, the slope of the curves change, signalling a transition to another structural state of the solution.

concentrated sulfate solutions. The dissociation constants for $MgSO_4^0$ and $Al(SO_4)^+$ at 25°C are $10^{-2.3}$ and $10^{-3.2}$, respectively. That is, the predominant solute species at the concentrations studied are the ion-pairs. It was expected that the formation of stable ion-pairs would decrease the magnitude and extent of the cation-water interaction such that the measured isotopic effect would approach that characteristic of pure water. As seen in Table 1, however, the fractionation factors are about the same for the $MgCl_2$ and $MgSO_4$ solutions and for the $AlCl_3$ and $Al_2(SO_4)_3$ solutions. On a 1.0 molal cation basis, at 25°C, the values of $10^3 \ln\alpha$ are approximately 3.0 for the aluminum solutions and 1.0 for the magnesium solutions. These data show unambiguously that the cations are solvated in the sulfate ion-pairs to the same extent that they are solvated in the unassociated chloride solutions. In addition, the presence of SO_4^{-2} in the vicinity of the solvated Mg^{+2} or Al^{+3} ions does not appear to alter the isotopic behavior of the aqueous solutions. This is a very surprising result.

The common characterization of magnesium and aluminum sulfate ion-pairs as "outer-sphere" complexes is of some concern in light of current usage of aqueous complex ions as kinetic entities. FRENKEL *et al.* (1967) concluded from NMR experiments with $MnSO_4$ solutions that the predominant species at high concentrations is the contact ion-pair, the SO_4^{-2} ion acting as a bidentate ligand. But it is clear from the isotopic measurements that at least one water molecule separates the Mg^{+2} and Al^{+3} ions from SO_4^{-2}. This conclusion is in agreement with the findings of ATKINSON and PETRUCCI (1966) who deduced from ultrasonic absorption experiments that ten Angstroms, or the distance of two water molecules, separates the Mg^{+2} and SO_4^{-2} ions in the ion-pair. In addition, HESTER and PLANE (1964) reported Raman spectral evidence for the existence of bonds between magnesium and water-oxygen in concentrated $MgSO_4$ solutions. According to the results of ultrasonic absorption experiments, there are at least three ion-pair species present in a 2:2 electrolyte (ATKINSON and KOR, 1965). These species differ in their degree of solvation and are in equilibrium. The isotopic effects measured in these systems are the averages of the effects due to all species present. In the case of the concentrated sulfate solutions examined here, the isotopic data indicate that the predominant magnesium and aluminum species are those that are extensively hydrated.

TEMPERATURE DEPENDENCE OF $10^3 \ln\alpha$(WATER-SOLUTION)

CO_2 equilibrations were carried out at 0, 25, and 38.5°C and values of $10^3 \ln\alpha$(water-soln) are plotted against $1/T$ in Fig. 3. At low temperatures, a straight-line relation between $10^3 \ln\alpha$ and $1/T$ is justified by theoretical arguments of UREY (1947) and BIGELEISEN and MAYER (1947). There are several points of interest in Fig. 3:

(1) The isotopic properties of water and the solutions vary smoothly from 0 to 40°C, in contrast to reports of profound and abrupt changes (kinks) in thermodynamic properties of water over this same range.

(2) The slopes of related families of straight lines (fractionation curves) are identical indicating that the *^{18}O fractionation between hydration water and bulk water is temperature independent.*

(3) At a critical concentration which varies for each salt (between 3.5 and 4.0 m for $MgCl_2$), the slope of the lines changes to a steeper one that is constant for very concentrated solutions of magnesium and aluminum chloride.

(4) The fractionation curves for 1 m $AlCl_3$ and 3 m $MgCl_2$ are identical.

(5) The slopes of the fractionation curves of structure breakers are negative and equal, regardless of whether the solute is an electrolyte (Cs^+) or nonelectrolyte (dioxane).

The lack of a measurable temperature dependence for the fractionation factors between the postulated bound and unbound waters is a most unexpected and important result. While $d\alpha/dT$ may indeed be zero for these fractionations, it would not be in keeping with the isotopic behavior of other substances. As mentioned above, fractionation factors between hydration water and bulk water, calculated assuming a separation of available water into these two types and a coordination number of six, are relatively large and very different for the various cations (25.6 per mil for Al^{+3} versus 8.3 per mil for Mg^{+2} at 25°C). In comparison to other ^{18}O fractionations this large, temperature coefficients of around 0.1–0.2 per mil/degree might be expected for the fractionations between the various hydration waters and bulk water, corresponding to changes of 4–8 per mil over the 40° range of temperature studied. Such changes would be reflected by different slopes of the fractionation curves for each solute and easily detected by the techniques used. It is strongly suggested from these results that the conventional interpretation of isotopic effects associated with solute additions to water is either too simplistic or incorrect.

The solutions behave isotopically as if the addition of a solute does nothing more than change the isotopic properties of the water in the solution as a whole. If the solute were to alter the structure of water (by breaking a specific number of hydrogen bonds, changing the relative positions and bonding characteristics of discrete clusters of water molecules, or whatever), the overall changes in the vibrational frequencies of the water would be reflected by changes in $\alpha(CO_2\text{-}H_2O)$. With this interpretation, concentrated aqueous solutions are viewed as existing in a number of thermodynamically distinct states (two for structure makers and at least one for structure breakers, by isotopic criteria).

There is abundant spectroscopic evidence that cations, particularly those of high ionic potential, are solvated in aqueous solution. In fact one of our experiments (Table 1) supports the traditional view that Al^{+3} is strongly bonded to six water molecules in its first coordination sphere: the $10^3\ln\alpha$ value of 2.46 for a solution that is 1.0 m in both NaF and $AlCl_3$ is $\frac{5}{6}$ the value of 3.00 measured for $AlCl_3$ alone demonstrating that the strong F^- ligand has taken up the position of one of the six water molecules in the first hydration sphere of Al^{+3}. The evidence for strong bonding between cations and water molecules must be reconciled with the lack of temperature dependence of the fractionation factor between bound and bulk water.

The fractionation curves for 1 m $AlCl_3$ and 3 m $MgCl_2$ are indistinguishable, and there is an abrupt change in slope that occurs at some critical concentration for solutions of both $MgCl_2$ and $AlCl_3$. These results suggest that it is a property of the solution, probably involving critical concentrations of cationic charge equivalents, and not the chemical nature of the cations, that is dominant in controlling the isotopic effects. At some critical concentration of solute, the structure of bulk water may change in some significant way that would be reflected in $\alpha(CO_2\text{-}H_2O)$. Consider the properties of bulk water in a 3 m solution of $AlCl_3$ where 32% of the water is bound in the first coordination sphere of Al^{+3}. Unbound waters in such concentrated solutions cannot have the properties of pure water.

Oxygen isotope effects attendant on addition of solutes to water are best explained as a combination of the effects of partitioning of ^{18}O between bound and bulk water and the establishment of discrete structural states of aqueous solutions that have unique isotopic properties. Kinetics may be playing a role in these observations. That is, during the times of the experiments, isotopic equilibrium may be established between CO_2 and bulk water but not between hydration waters and bulk waters. If, however, the rates of isotopic exchange between bound and free waters are indeed fast, the structural changes dominate the observed isotope effects and we are overestimating the magnitude of the incorporation of ^{18}O in hydration sheathes.

CONCLUSIONS

The oxygen isotope CO_2-equilibration technique has been used in this and previous studies in an attempt to elucidate details of solute-water interactions. The conventional interpretation of the equilibrium partitioning of oxygen isotopes between hydration water and bulk water to explain the often large isotopic effects attendant on addition of solutes to water is shown to be inadequate. Such partitioning should and probably does occur, but there is strong isotopic evidence in the data reported here that solutions can assume thermodynamically distinct structural forms with characteristic oxygen isotope properties. In most cases this structural effect supersedes the isotopic distinction between bulk water and hydration water. For structure-making electrolytes, different structural states were identified by a change in the temperature coefficient of the oxygen isotope fractionation between pure water and the solution. The abruptness of the change at what appears to be a critical concentration of charge equivalents signals a first order transition. In the case of structure-breaking solutes, solutions of both relatively low concentrations of certain electrolytes and non-electrolytes have similar oxygen isotope properties (roughly the same value of $10^3 \ln\alpha$ at T and the same temperature coefficient of α). This implies a common structural state of disordered water. At higher concentrations of some structure breakers, the matter becomes more complex.

The concepts of solvation numbers and contact ion-pairs have been brought into question numerous times over the years. Our data on the 1:1 Al-F complex ion support the traditional view that six molecules of water are strongly bonded to aluminum ion in the first coordination sphere. Our data on the sulfate ion pairs of magnesium and aluminum, however, do not support the idea of contact ion pairs. There is little or no difference in the isotopic effects of adding chlorides (highly dissociated) or sulfates (highly associated) to water demonstrating that the cations in both environments are solvated to about the same extent. This simple technique so useful to the isotope geochemist is very well suited to the investigation of these and other details of solute-water interactions.

Acknowledgements—The authors thank Lanford Adami for his help in the laboratory. Financial support for this research was provided partially by NSF Grant EAR-9005717.

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