Oxygen Isotope Fractionation and the Structure of Aqueous Alkali Halide Solutions

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The oxygen isotope effects between H_2O and D_2O solutions of various alkali-halides and the respective pure solvents have been measured by means of the CO_2 equilibration technique. In general, the effects for H_2O are smaller than those for D_2O. With "hydration numbers" estimated from the angular distributions of the water dipoles around the ions obtained from MD-simulations and with the plausible assumption that in highly concentrated LiCl solutions the effect is purely cationic, the measured effects are separated into effects between the hydration shells of the individual ionic species (Li, Na, K, Cs, Cl, Br, I) and bulk water. The cationic effects thus obtained are compared with the corresponding effects between free water-cation-pairs and bulk water calculated on the basis of the energy surfaces published by Kistenmacher et al. It is found that, in general, the trends coincide but the former effects are smaller than the latter ones.

Introduction

The fractionation of the oxygen isotopes in aqueous electrolytes was first investigated by Taube[1] with the CO_2 equilibration technique. In the limits of error of his measurements he found essentially that the fractionation factor between CO_2 equilibrated with an aqueous solution and with pure water of the same isotopic composition depends linearly on the salt concentration and is independent of the anion; indicating a constant separation factor α between the hydration water of the cations and free water, and no corresponding effect for the anions. Sofer and Gat[2] extended these measurements to other salt solutions, which are of special interest in geochemistry. They found a linear relation between α and the ratio of charge q over Pauling radius R of the cations. In connection with investigations on oxygen isotope effects in $CuSO_4 \cdot 5\,H_2O$, aqueous solutions of $CuCl_2$ and $CuSO_4$ were studied and, contrary to the findings of Taube, an influence of the anion was found[3]. Subsequent investigations of potassium halide solutions confirmed the anion dependence[4]. In addition it was shown that the effect changes significantly when H_2O is replaced by D_2O as solvent.

The multidimensional energy surfaces of single water molecules in the fields of alkali ions as calculated by Clementi et al.[5–7] provided the basis for calculations of gas phase separation factors of the oxygen isotopes between water molecules hydrated to an ion and free water molecules[8]. By applying some approximations, the gas phase results could be employed for the understanding of the effects in aqueous solutions and lead to at least qualitative agreement with the available measurements. The large temperature effects found by Truesdell[9] for various aqueous electrolytes cannot be explained on the basis of these approximate calculations.

In this paper a more quantitative understanding of the oxygen isotope fractionation is attempted. Recent experimental and theoretical data on the structure of aqeous alkali halide solutions will be used to deduce oxygen isotope fractionation factors for individual ions from the measured concentration dependences. The values so obtained are compared with the ones calculated previously[8], and it is checked how the results fit into existing models for the structure of alkali halide solutions.

Experimental Procedure and Results

The solutions were prepared from carefully dried salts (reagent grade, Merck) in a closed vessel in order to prevent isotope fractionation by vaporization of water. The D_2O used was better than 99.9% (Rohstoff Import). The ^{18}O content of the D_2O used was of almost natural abundance.

The oxygen isotope fractionation in the solutions was determined by the CO_2 equilibration technique[10]. In this technique, the $^{18}O/^{16}O$-ratios $R^{*}_{CO_2}$ of CO_2 gas equilibrated with solution water (SW) and R_{CO_2} of CO_2 gas equilibrated with pure

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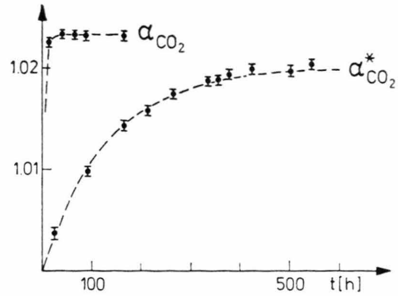

Fig. 1. The time dependence of the equilibration process for pure H_2O and a 14.5 molal LiCl solution in H_2O at an equilibration temperature of 10 °C.

water (PW), where $R_{SW} = R_{PW}$, are measured with respect to the $^{18}O/^{16}O$-ratio R'_{CO_2} of unequilibrated (standard) CO_2 gas:

$$\alpha^*_{CO_2} = R^*_{CO_2}/R'_{CO_2}, \quad \alpha_{CO_2} = R_{CO_2}/R'_{CO_2}.$$

$\alpha^*_{CO_2}/\alpha_{CO_2}$ equals to the value of R_{SW}/R_{PW} which would result if the solution would have been equilibrated with pure water.

As solutions at temperatures as low as 10 °C and concentrations up to 15 molal were investigated, the time necessary to reach equilibrium had to be checked. As an example, Fig. 1 shows the different times necessary to reach isotopic equilibrium for pure H_2O and a 14.5 molal LiCl solution at 10 °C. As expected, the curves show an exponential time dependence. The observed time constants range from a few hours for pure H_2O at 25 °C to about 4 weeks for a 12.5 molal LiCl solution in D_2O at 10 °C.

The equilibrium isotope fractionations between solutions water and pure water are given in terms of

$$\delta = (1 - \alpha^*_{CO_2}/\alpha_{CO_2}) \cdot 10^3 .$$

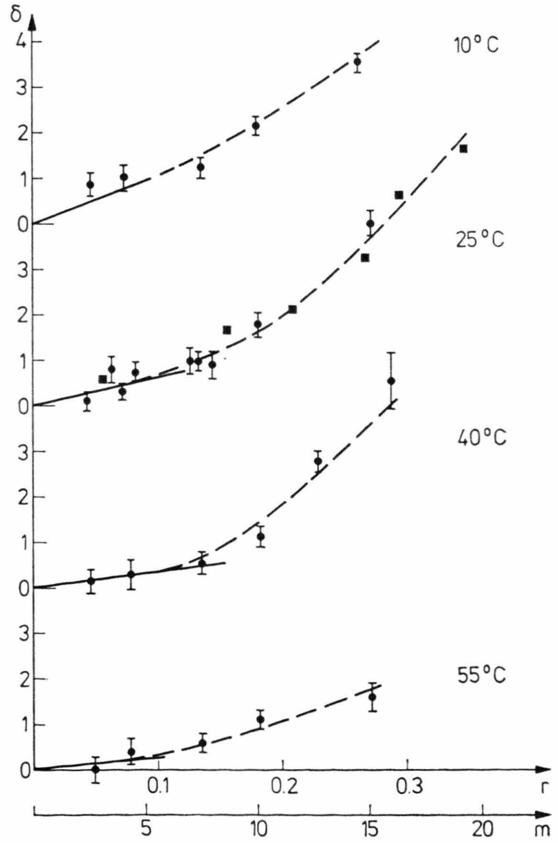

Fig. 2. The concentration dependence of the measured δ-values for LiCl solutions in H_2O for four different temperatures of equilibration. The squares in the plot for 25 °C were taken from[1]. *m* is the molality and *r* the number of moles of salt per mole of water.

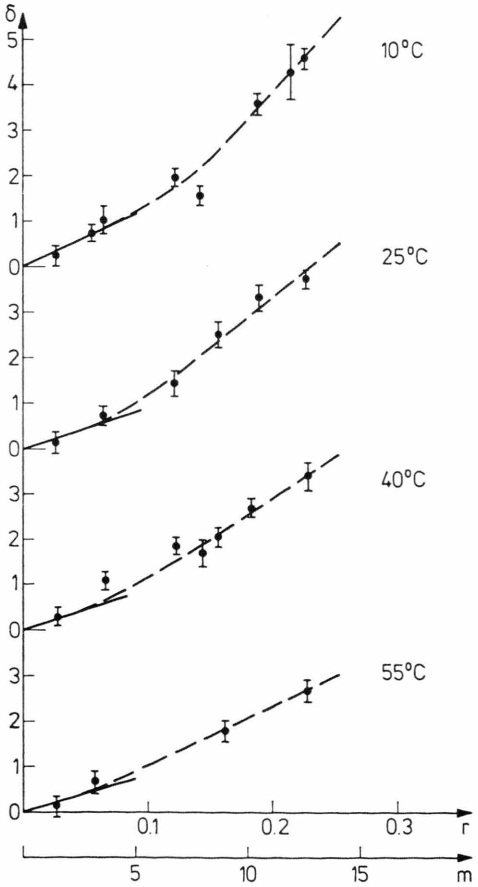

Fig. 3. The concentration dependence of the measured δ-values for LiCl solutions in D_2O for four different temperatures of equilibration.

The concentration dependence of such δ values for LiCl solutions at four different temperatures are plotted in Fig. 2 for H_2O and in Fig. 3 for D_2O as solvent. An average of four equilibrations was performed for any concentration and temperature. The error bars are the cumulated mass spectroscopical and other errors, due for instance to possible small leaks during the very long equilibration time. Linear functions were fitted to the measured values in the low concentration range, the slopes δ/r of which are reported in Table 1. Such slopes were also obtained for solutions of LiJ, NaJ and CsCl and are also reported in Table 1 together with values obtained from the literature.

Discussion

On the basis of earlier measurements[3] it has been shown that the conclusion reached by Taube[1] that the anion effect is negligible can no longer be considered valid. In a previous paper[4] the influence of the anions on the water which is not hydration water of the cations has been described in terms of their structure breaking effect. New information on the structure of aqueous solutions obtained from molecular dynamics (MD) simulations let it appear more appropriate to describe the anion effect on the measured oxygen isotope fractionation by an additional term of similar structure as the term already introduced[4] to describe the influence of the cations. The measured quantity δ can then be written as:

$$\delta = r \cdot (n_C\, \delta_C + n_A\, \delta_A)\,, \qquad (1)$$

where r is the concentration in moles of salt per mole of water, n_C and n_A are the hydration numbers of cation and anion, respectively and δ_C and δ_A the oxygen isotope fractionation factors between a water molecule hydrated to a cation or an anion and a water molecule in pure water.

At low concentrations the above equation yields a linear relation between δ and r. It has already been experimentally observed by Taube[1], though not taken into consideration in interpreting the data, that for the salts with the highest solubilities (LiCl and $AgClO_4$) a marked deviation from linearity occurs at higher concentrations. The measurements reported in this paper have ascertained this nonlinearity in the case of LiCl (compare Figs. 2 and 3).

It is obvious that the hydration numbers become concentration dependent at high concentrations. Assuming hydration numbers of about 5 for cation and anion yields a limit for the linear part of Eq. (1) for $r = 0.1$ (5.5 molal). At higher concentrations, the hydration layers of cations and anions will merge.

X-ray and neutron diffraction measurements[12] have shown the coordination number of Li^+ to be constant and equal to 4 up to very high concentrations. At a concentration of $r = 0.25$ all water can therefore be considered coordinated to Li^+ ions, and it might be expected that these $Li^+ \cdot 4\,H_2O$ groups do not share water molecules with each other. The influence of neighbouring $Li^+ \cdot 4\,H_2O$ groups and of the Cl^- ions on the oxygen isotope effect of the group can be estimated equal to the influence of neighbouring water molecules in a more dilute solution. This estimation is supported by calculations analogous to those performed in [8], which yield an only slightly higher enrichment of ^{18}O in a Cl^--H_2O-Li^+ group than in a H_2O-Li^+ group, and by investigations of Langer and Hertz[11] and Narten et al.[12] who have shown that the Li-O distance varies only little or even shows a slight increase with increasing concentration. Thus, for LiCl solutions

$$\delta(r = 0{,}25) \approx \delta_{Li}\,.$$

This approximation, ascribing the total effect at high concentration to the cation and thus yielding a decrease of the influence of the anion with increasing concentration, is also in keeping with IR absorption measurements by Hartmann[13]. For LiCl the IR measurements show a maximum of the frequency shift at a concentration of about 6 molal ($r = 0.11$) followed by a decrease up to the highest measured concentration of 15 molal; thus a decrease of the anionic influence with increasing concentration.

The values δ_{Li} obtained under these assumptions from an inter- and extrapolation procedure of the measured values are listed for various temperatures in Table 2. The error connected with this procedure is estimated to be ± 0.2. In order to deduce equivalent δ_{Cl} values from the measured δ/r values at low concentration reported in Table 1, values for n_{Li} and n_{Cl} have to be inserted in Eq. (1).

A set of consistent hydration numbers has been obtained from MD simulations by Heinzinger and Vogel[14,15] and has been compared with experimental values in a subsequent paper[16]. This comparison shows that the hydration numbers obtained from the simulations by integration of the

Table 1. Experimental slopes δ/r for $r < 0.1$ for various alkali-halide solutions in H_2O and D_2O from this work and from the literature. r is the number of moles of salt per mole of water.

	T (°C)	H_2O	D_2O	Ref.
LiCl	10	10.6 ± 1.5	13.0 ± 0.9	this work
	25	6.4 ± 0.5	9.4 ± 0.7	this work and 1
	40	3.7 ± 0.5	8.6 ± 1.5	this work
	55	2.5 ± 0.8	8.1 ± 0.8	this work
LiI	25	5.4 ± 0.9	6.7 ± 0.9	this work
NaCl	25	0.0	0.0 ± 1.5	1, 4
NaI	25	-4.7 ± 0.5	12.2 ± 2.0	this work
	25	-1.5		1
KCl	25	-7.7 ± 0.3	14.2 ± 2.8	2, 4
KBr	25	-9.5 ± 0.8	6.3 ± 0.7	4
KI	25	-11.3 ± 0.8	-5.0 ± 0.9	4
CsCl	4	-13.3		1
	25	-11.9 ± 1.0	-6.9 ± 0.5	this work
	25		-7.4 ± 0.7	4

Table 2. Oxygen isotope fractionation factors for Li^+ from $\delta(r = 0.25)$ and for Cl^- from the slopes at low concentrations measured in LiCl solutions in H_2O and D_2O at four different temperatures.

T	H_2O		D_2O	
	δ_{Li}	δ_{Cl}	δ_{Li}	δ_{Cl}
10 °C	3.5 ± 0.2	-0.5 ± 0.5	5.5 ± 0.2	-1.3 ± 0.3
25 °C	3.1 ± 0.2	-0.9 ± 0.2	4.5 ± 0.2	-1.2 ± 0.2
40 °C	2.9 ± 0.2	-1.1 ± 0.2	3.8 ± 0.2	-0.9 ± 0.2
55 °C	1.7 ± 0.2	-0.6 ± 0.3	3.0 ± 0.2	-0.6 ± 0.3

ion oxygen radial pair correlation function up to its first minimum are usually larger than the numbers obtained from experimental methods. This is due to the fact that, especially for the larger ions, water molecules quite disoriented relatively to the ion, though located in its vicinity, are counted as hydrated water molecules by this method. This can be seen from the distributions of water molecule orientations around cations, which also have been obtained from MD simulations[17].

An inspection of the Li-water pair potential given by Clementi and Popkie[5] shows for instance that the ion oxygen force constant decreases with increasing deviation from 180° of the angle Θ between the water dipole moment and the vector pointing from the oxygen to the centre of the ion; that is with increasing disorientation of the water molecules relatively to the ion. This will also be the case for the other cations. Furthermore, it may be expected that the less a water molecule is oriented by the ion, the more it will be a part of the water hydrogen bond network. Therefore a strong decrease of the fractionation with increasing disorientation of the water molecule is to be expected, and so it does not seem sensible to ascribe the measured effect to the total number of water molecules in the hydration shell.

As there is also no clear indication which of the numerous (and discrepant) experimental values should be used to describe this situation, we have chosen to integrate the unnormalized angular distribution functions corresponding to those given in [17] in the range from $\cos\Theta = -1$ to $\cos\Theta = -0.6$. That is, we take into account for the interpretation of the isotope effect only water molecules which have their dipole moments within a cone with a conical angle of about 110°, corresponding to all orientation between the "lone pair" orientation and the "dipole moment" orientation. Figure 4 shows these two extreme orientations.

Within the limits of error, the result of these integrations is about 4 for Li^+, Na^+ and Cs^+, thus an n_C value of 4 has been used for all cations. Additionally, the more common value of 6 was also used for the evaluation of the results for CsCl. In this approximation all counterion-, concentration or eventual solvent isotope effects on the hydration numbers have to be neglected. These assumptions are also consistent with the model used for the evaluation of δ_{Li}: the most strongly oriented water molecules will also be those residing nearest to the ion and will be counted as coordinated water molecules in the first neighbour model used by Narten et al.[12].

In the case of the anions, no obvious dependence of the relevant force constant on the water molecule

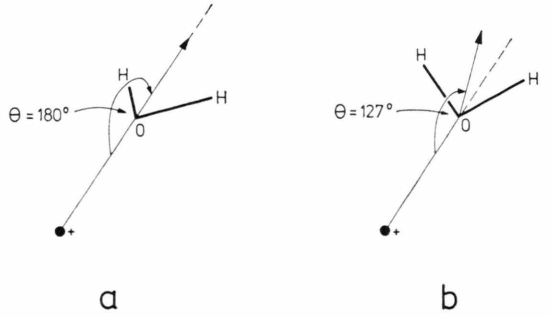

Fig. 4. The "dipole moment" orientation (called a in [8]) and the "lone pair" orientation (called b in [8]) of a water molecule in the vicinity of a cation. (All geometries which can be generated by a rotation around the dipole moment are considered equivalent in this context.)

orientation is to be seen. Therefore we had no other choice than averaging the measured effect over the total number of water molecules in the hydration layer. Neglecting again the counterion- and concentration dependences we chose $n_A = 7$, the average of the values obtained from MD in 2.2 molal LiCl and NaCl solutions. Using these hydration numbers and the δ/r values from Table 1, δ_{Cl} as well as δ_C and δ_A for all other ions can be determined. The results obtained for ions solvated in H_2O at an equilibration temperature of 25 °C are shown in Table 3. In the two last columns of this table, the calculated values of $n_C \delta_C + n_A \delta_A$ and the measured δ/r values are given. Table 4 is an analogue to Table 3 for ions solvated in D_2O. The errors of δ_C and δ_A given in these tables were obtained from the uncertainties of the measured slopes and of the δ_{Li} values at 25 °C, neglecting errors in the n_C and n_A which can hardly be estimated. They must therefore be considered lower limits.

Table 3. Oxygen isotope fractionation factors determined from the measured slopes reported in Table 1 and the assumed hydration numbers $n_C = 4$ and $n_A = 7$ for solutions in H_2O at an equilibration temperature of 25°C. (*: $n_{Cs} = 6$).

	δ_C	δ_A	$n_C \cdot \delta_C + n_A \cdot \delta_A$	δ/r
LiCl	3.1 ± 0.2	−0.9 ± 0.2	6.1	6.4
LiI	3.1 ± 0.2	−1.3 ± 0.2	3.3	5.4
NaCl	1.6 ± 0.2	−0.9 ± 0.2	0.1	0.0
NaI	1.6 ± 0.2	−1.3 ± 0.2	− 2.7	− 3.1
KCl	−0.4 ± 0.2	−0.9 ± 0.2	− 7.9	− 7.7
KBr	−0.4 ± 0.2	−1.1 ± 0.2	− 9.3	− 9.5
KI	−0.4 ± 0.2	−1.3 ± 0.2	−10.7	−11.3
CsCl	−1.4 ± 0.2	−0.9 ± 0.2	−11.9	−11.9
CsCl *	-0.9_3 ± 0.2	−0.9 ± 0.2	−11.9	−11.9

Table 4. Oxygen isotope fractionation factors determined from the measured slopes reported in Table 1 and the assumed hydration numbers $n_C = 4$ and $n_A = 7$ for solutions in D_2O at an equilibration temperature of 25 °C (*: $n_{Cs} = 6$).

	δ_C	δ_A	$n_C \cdot \delta_C + n_A \cdot \delta_A$	δ/r
LiCl	4.5 ± 0.2	−1.2 ± 0.2	9.6	9.4
LiI	4.5 ± 0.2	−1.6 ± 0.2	6.8	6.7
NaCl	2.1 ± 0.2	−1.2 ± 0.2	0.0	0.0
NaI	2.1 ± 0.2	−1.6 ± 0.2	−2.8	12.2
KCl	1.6 ± 0.2	−1.2 ± 0.2	−2.0	14.2
KBr	1.6 ± 0.2	−1.4 ± 0.2	−3.4	6.3
KI	1.6 ± 0.2	−1.6 ± 0.2	−4.8	−5.0
CsCl	0.3 ± 0.2	−1.2 ± 0.2	−7.2	−7.2
CsCl *	0.2 ± 0.2	−1.2 ± 0.2	−7.2	−7.2

The δ_C and δ_A values reported in Table 3 show the expected decrease with increasing ionic radii. A comparison of the two last columns of this table shows that for all salts the measured δ/r values are very well approximated by the constant δ_C and δ_A values (δ_C and δ_A independent of the anion and cation, respectively).

In the case of D_2O (Table 4) no agreement with the measured δ/r values could be reached with universal δ_C and δ_A values. While the values obtained for δ_{Na} from NaCl and δ_K from KI seem to be within the range of what could be expected, this is not the case for the values obtained from the other salts of these cations. Assuming the values δ_{Cl} and δ_I from LiCl and LiI, which lead to acceptable values for δ_{Na} in NaCl, δ_K in KI and δ_{Cs} in CsCl, and assuming that $\delta_{Cl} \geqq \delta_{Br} \geqq \delta_I$ leads to a δ_{Na} value of about 5 in NaI and a δ_K of 3−4 in KCl and KBr. This is contrary to the expectation that $\delta_{Li} \geqq \delta_{Na} \geqq \delta_K \geqq \delta_{Cs}$. As the values of $\delta_{Na} = 2.1$ and $\delta_K = 1.6$ seem basically correct, they will be assumed in the subsequent discussion.

A comparison of the Tables 3 and 4 shows that the δ_C values are higher in D_2O than in H_2O while the δ_A values are slightly lower in D_2O than in H_2O. This result is in agreement with theoretical calculations for the cations. Figures 5 and 6 show the calculated[8] (squares) and measured (circles) δ_C and δ_A values for ions solvated in H_2O and D_2O in dependence of the Pauling ionic radii. The error connected with the calculated δ values was estimated to be at the most 1.5% for the Li^+ ion and smaller for the other ions[8].

For Li^+ two different geometries were considered for the isotope effect calculations, named a and b in [8], a corresponding to the orientation of the dipole moments of the water molecules toward the ion and b to the orientation of a lone pair orbital of the water molecules toward the ion. The ^{18}O enrichment was smaller for the geometry b than for the geometry a. In both solvents H_2O and D_2O, the experimentally determined δ_{Li} are markedly lower than the values calculated for the geometry a and slightly lower than those for geometry b. This is in agreement with the reported[17] angular distribution, which shows that this orientation is predominant. For Na^+ the measured and calculated values are in good agreement in both solvents. The experimentally determined δ_K value is positive in D_2O and

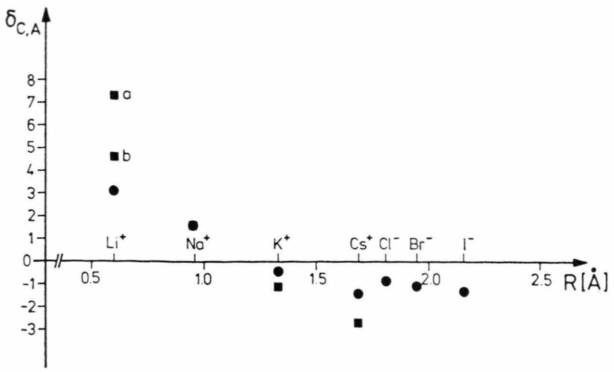

Fig. 5. Experimentally (circles) and theoretically[8] (squares) obtained oxygen isotope fractionations for cations and anions in H_2O versus the Pauling ionic radii, a and b refer to the two geometries considered in[8] and illustrated in Figure 4.

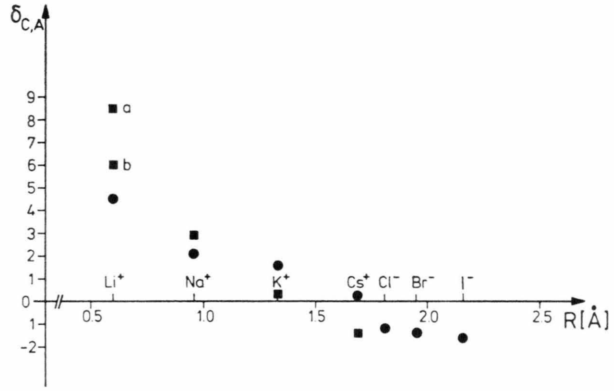

Fig. 6. Experimentally (circles) and theoretically[8] (squares) obtained oxygen isotope fractionations for cations and anions in D_2O.

negative in H_2O, which is in agreement with the calculations. Because of the uncertainty connected with their determination, only a qualitative character can be ascribed to the δ_{Na} and δ_K values in D_2O. A positive value in D_2O and a negative value in H_2O is also observed for Cs^+, though here the calculations yield a depletion of ^{18}O in the hydration layer of this ion in both solvents. With the exception of K^+ in D_2O, it can be stated that in general the measured effects are of smaller absolute magnitude than the calculated effects.

In the case of H_2O this corresponds to an attenuation of the isotope enrichment or depletion in the hydration layer of the cations compared to the values obtained in the gas phase and transfered into the liquid phase by multiplying the gas phase effect with the vapour pressure ratio. This must be understood as an effect of the surrounding structure.

For the anions, theoretical gas phase calculations analogous to those performed for the cations are not appropriate to approximate the behavior of these ions in a solution: because of their geometrical orientation[17], the oxygen atoms of water molecules hydrated to anions will be affected in a direct way by any change occuring in the surroundings of hydration complex and not mostly through the hydrogens as in the case of cationic hydration. As could be expected from the preceding paper[4] the measured effects are negative, their magnitude increasing slightly with increasing ionic radius.

A further observation relating the measured and calculated oxygen isotope fractionations to other properties of solvated ions can be made: while the δ_C values for Li^+ and Na^+ in H_2O are positive, they are negative for all other ions measured. This is in agreement with the evidence from a large number of studies [compare Ref. [19]] that Li^+ and Na^+ are positively hydrated at room temperature while K^+ and Cs^+ and the anions Cl^-, Br^- and I^- are found negatively hydrated. The ionic radius at which the transition from negative to positive hydration occurs can be determined from a linear interpolation between the values for Na^+ and K^+ in H_2O. This yields a radius of 1.25 Å if the interpolation is done for the experimental values, and 1.18 Å from the calculated values, in agreement with the value of approximately 1.1 Å given by Samoilov[20] for the slightly lower temperature of 21.5 °C.

In this context some qualitative remarks on the temperature dependence of the isotopic enrichment determined by Truesdell[9] can be made. It has been observed (compare Ref. [19] and references therein) that the above mentioned radius at which the transition from negative to positive hydration occurs increases with increasing temperature. This means that ions which are negatively hydrated at room temperature (e.g. K^+) will be positively hydrated at higher temperatures. This could explain the behaviour observed by Truesdell for NaCl and KCl in the temperature range up to 100–130 °C (it might be noted that Δ in Truesdell's notation is $-\delta$ in our notation).

The results obtained for D_2O (Fig. 5) show similar general features as the results for H_2O. For the cations, both calculated and measured separation factors are higher than in H_2O. Theoretically, this result was obtained by multiplying the calculated gas phase separation factors, which are almost equal for H_2O and D_2O, with the vapour pressure ratio, which is markedly higher for H_2O than for D_2O[21, 22]. These results are not in agreement with the usually accepted model that D_2O is more structured than H_2O, and that consequently the hydration should have a more negative character in heavy water. Though it has been reported[23] that this change in structure breaking effect might be strongly temperature dependent, no clear explanation for this phenomenon could be found.

For the anions, the δ_A values are about 30—40% lower than in H_2O, in agreement with the concept that D_2O is more structured than H_2O. Like in H_2O a slight decrease of δ_A with increasing ionic radius is observed. This different behaviour of anions and cations when the solvent H_2O is replaced by D_2O is a further indication that the solvations of anion and cation involve different interaction mechanisms, as could be expected from the different arrangement of the water molecules around cation and anion.

The temperature dependence of the measured separation factors is summarized in Table 2 and Figure 7. As expected, the absolute magnitude of the separation factors decreases with increasing temperature for anions and cations in both solvents. For the cations in H_2O, the observed decrease agrees very well with the calculated behaviour, while it is markedly stronger for D_2O. This may be seen as a hint that the solvation in D_2O is somewhat different than the solvation in H_2O, as has already been pointed out in the literature [compare Ref. [19]]. In general it can be said that a description of the behaviour of an aqueous solution over a large temperature range cannot be expected from a model which does not take account of the changes in the hydration layer brought about by higher temperatures.

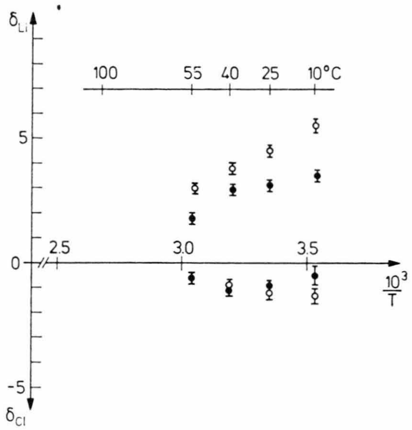

Fig. 7. Mesured δ_{Li} and δ_{Cl} for four different temperatures in H_2O (full points) and D_2O (circles).

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