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Reorientational relaxation of water molecules in LiCl solution studied by depolarised Rayleigh scattering

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Abstract. Brillouin scattering and depolarised Rayleigh scattering have been used to study the reorientational motion of the water molecules in the LiCl primary hydration shell. The relaxation time is found to be dependent on the LiCl concentration, varying from 0.7×10^{-11} s at 9 mol% to 1.8×10^{-11} s at 36 mol%. The relaxation times at 26 mol% and 36 mol% follow a simple Arrhenius relation with activation energies of $5.5 \text{ kcal mol}^{-1}$ and $6.3 \text{ kcal mol}^{-1}$ respectively. The results are consistent with NMR studies, but not with dielectric measurements. Both the measured refractive index and the scattering intensity indicate that the electronic polarisability of the hydration shell also is dependent on ion concentration. The concentration dependence of the adiabatic compressibility indicates a possible structural transition at about 20 mol%.

1. Introduction

Ionic hydration has been an important subject in physics and chemistry for a long time (Conway 1981; Enderby and Neilson 1981). It plays important roles not only in electrochemical processes, but also in biochemical and biophysical processes. For example, hydrated counter ions are regarded as an integral part of the fundamental molecule of life, DNA (Soumpasis *et al* 1987). The dynamics of DNA are very important in the frequencies from a few GHz to a few hundred GHz (Lindsay *et al* 1985), so the study of the dynamics of ionic hydration shells at these frequencies is essential for a full understanding of DNA dynamics.

Ionic solutions are also important in their own right. They exhibit interesting glass transitions at low temperature (Angell and Sare 1970). Study of the dynamics of these ionic solutions may provide insight into glass transitions. We chose LiCl solution to study because its research literature is richer compared to that of other electrolyte solutions.

Water molecules surrounding a charged ion are usually described in terms of a primary (A zone) and a secondary (B zone) hydration shell (Frank and Wen 1957). The primary hydration shell contains those water molecules whose structure is dominated by the ion, and which remain bound to it for times long compared with characteristic correlation times for motions of the bulk water. The secondary hydration shell consists of the water molecules that are weakly influenced by the ion. Since the water molecules in the secondary hydration shell are similar to bulk water, direct experimental study is difficult. Rather detailed structural features of the primary hydration shell of LiCl have

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been revealed by neutron scattering (Enderby *et al* 1973, Enderby and Neilson 1980), x-ray diffraction (e.g. Magini 1983), and molecular dynamic simulations (e.g. Clementi *et al* 1976). A recent Raman study (Green *et al* 1987) of the water O–H stretching bands in LiCl solution was used to probe the structure of the water molecules in LiCl solutions in terms of their tetrahedrally hydrogen bonded network.

Dynamic properties of the hydration shell of LiCl, such as the residence time, reorientational relaxation time and self-diffusion coefficient of the water molecules in the ionic hydration shell have been studied by NMR (with the assistance of some structural models (Hertz 1973)). Dielectric relaxation measurements have been pursued (Pottel 1973), but the results have been difficult to interpret. Recently, quasi-elastic neutron scattering has been able to measure not only the self-diffusion constants of the water molecules in the primary hydration shell, but also that of molecules in the *secondary* hydration shell (Hewish *et al* 1982, 1983, Salmon 1987). The dynamics of the LiCl hydration shell has also been studied by Brillouin scattering, and it has been found that the acoustic wave in the solutions couples strongly with a relaxational process of the hydration shell (Tao and Lindsay 1988). In this paper, we report measurements of the reorientational relaxation of the water molecules in the primary hydration shell as studied by depolarised Rayleigh scattering.

Reorientational relaxation of many molecular liquids has been studied by depolarised Rayleigh scattering (Pinnow *et al* 1968). Investigation of Rayleigh scattering in ionic solutions (Hsich *et al* 1972) has appeared, but a study of the dynamics of the hydration shell has not been reported. Presumably, this is because depolarised Rayleigh scattering from the water molecules is very weak and it is difficult to resolve the spectrum with conventional Brillouin spectrometers. Recent development of the tandem multi-pass Fabry–Perot (Sandercock 1978, Lindsay *et al* 1981) makes it easier to study the weak depolarised spectra of ionic solutions, and it also allows us to study the full Brillouin spectral shape (Tao and Lindsay 1988).

The theory of depolarised light scattering by the molecules in liquids has been worked out for some years (Berne and Pecora 1976). The reorientational motions of water molecules in the liquid state have been studied by molecular dynamics simulations (Impey *et al* 1982). It has been found that $D_x \approx D_z$ (D_i , $i = x, y, z$, are the elements of the rotational diffusion coefficients along the principal axes), and D_y is about 30% smaller than D_x or D_z , so water molecules can be treated approximately as symmetric diffusors (the x axis is normal to the plane of a water molecule and the z axis bisects the bond angle in the plane). For symmetric diffusors, the depolarised Rayleigh scattering is given by (Berne and Pecora 1976)

$$I_{\text{VH}}(\omega, \mathbf{q}) = N \frac{1}{10} \left(|\alpha_0^{(2)}|^2 \frac{6D_x}{\omega^2 + 6D_x^2} + |\alpha_2^{(2)}|^2 \frac{6D_x + 4(D_x - D_y)}{\omega^2 + [6D_x + 4(D_x - D_y)]^2} \right) \quad (1)$$

where N is the number of molecules per unit volume, $\alpha_0^{(2)} = 1/(6)^{1/2}[3\alpha_{zz} - (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})] \equiv \Delta\alpha$, $\alpha_2^{(2)} = (1/2)(\alpha_{xx} - \alpha_{yy})$. Using the polarisability components of water molecules in the vapour phase, and considering that D_x is 30% larger than D_y , we see that the second term of equation (1) describes a Lorentzian with an intensity of only 20% of the first one, and a width which is 20% broader. This means the depolarised light scattering of water molecules is dominated by the first Lorentzian in equation (1). In fact, the measured spectrum of the depolarised Rayleigh light scattering of the reorientational relaxation of water molecules is well described by single Lorentzians (Montrose *et al* 1974; Alitta *et al* 1986). As we will see, the single Lorentzian approximation works also for the depolarised light scattering of the water molecules in LiCl

solution. Equation (1) holds only for low particle concentration. This is because cross terms enter into the expression for the square of the polarisability fluctuations (Berne and Pecora 1976). When the correlations between scattering particles are significant (as may be the case at high ion concentrations here) $\alpha_{\delta}^{(2)}$ in equation (1) ($\equiv \Delta\alpha$) must be replaced with

$$\Delta\alpha' = \Delta\alpha[1 + Nf] \quad (2)$$

where f is a measure of the static correlation (relative to α) of a pair of particles (Berne and Pecora 1976). An effective diffusion constant is given by

$$D'_x = D_x(1 + Ng)/(1 + Nf) \quad (3)$$

where g is a measure of the dynamic correlation between pairs of particles (Berne and Pecora 1976). Values for diffusion constants (or relaxation times) may be quite different from those determined by probes of single particle dynamics (such as NMR) at high concentrations.

Of course, the reorientational relaxation of water molecules is not the only possible source of Rayleigh scattering in LiCl solutions. For example, ion diffusion and entropy fluctuations can also give rise to Rayleigh scattering. However, for the reasons given below, these processes do not contribute to the spectra we observe.

2. Experiments

VH depolarised Rayleigh spectra were taken on a nine-pass tandem Fabry–Perot interferometer (Lindsay *et al* 1981) using about 150 mW of the 5145 Å line of a Spectra Physics 2020 argon-ion laser. VH means that the incident light is vertically polarised, while the scattered light is collected in horizontal polarisation. LiCl was purchased from JT Baker Chemical Co (purer than 99% by weight), and solutions were sealed in glass vials. The experiments were performed as a function of LiCl concentration, scattering angle and temperature in both H₂O and D₂O LiCl solutions. The temperature was varied from 0°C to about 95°C, and it was controlled to better than 0.5°C. A residue of the instrumental response function is seen in the centre of our spectra. This corresponds to the tails of the response to elastic light. The full width at half height is much narrower, not exceeding 500 MHz in this work, so we made no corrections for instrumental broadening.

3. Results

The depolarised Rayleigh spectra of 36 mol% LiCl solution (36 mol LiCl per hundred mol water molecules) taken in 90° (bottom) and 25° (top) scattering geometries are compared in figure 1. The former spectrum was fitted by a single central Lorentzian, while the latter shows not only a broad central mode, but also a longitudinal mode (marked by arrows) due to leaked vv component. By fitting the leaked scattering using the actual vv spectrum with an appropriate weighting, we were able to extract the broad central mode, which we then fitted with a single central Lorentzian. We found that the central Lorentzians in both scattering geometries have the same width (within the experimental uncertainty of about 10%). The width is about 9 GHz, corresponding to a relaxation time of 1.8×10^{-11} s. It is well known that for a translational diffusion

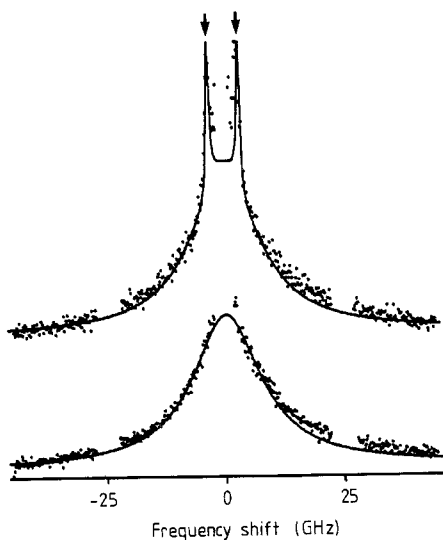


Figure 1. Depolarised (vH) Rayleigh spectra of 36 mol% LiCl solution in 25° (top) and 90° (bottom) scattering geometries. The leaked longitudinal acoustic mode component is indicated by arrows. The dots are experimental spectra and the full curves are calculated spectra (as described in the text).

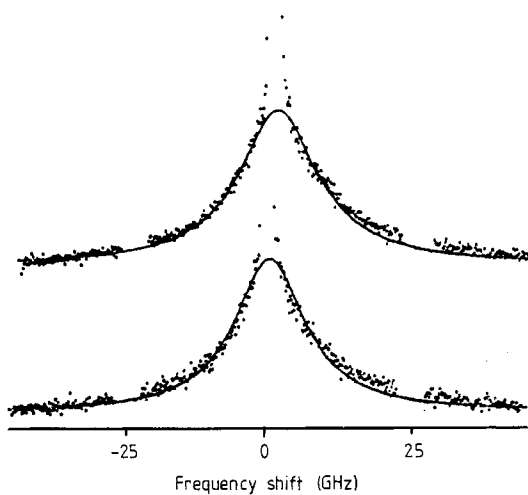


Figure 2. Depolarised (vH) Rayleigh spectra of 36 mol% LiCl H₂O (top) and D₂O (bottom) solutions in a 90° scattering geometry. The dots are experimental spectra, and the full curves are single Lorentzian fits.

process, the spectral width is proportional to q^2 , where $q = (4\pi n/\lambda)\sin(\theta/2)$; n is the refractive index of the solution, λ is the wavelength of incident light and θ is the scattering angle. Thus the independence of the central Lorentzian width on the scattering angle means that the scattering is not due to a thermal or other simple translational diffusion processes.

Relative diffusion between anions and cations can give a q -vector-independent line width at small q (Berne and Pecora 1976). However, the ions are optically isotropic, so this process cannot give depolarised light scattering. We have found that the spectral line width decreases as the LiCl concentration increases, which is another piece of evidence that the scattering is unlikely to be due to relative ion diffusion; the theory (Berne and Pecora 1976) predicts an *increase* in width as ion concentration increases (D_i decreases more slowly than a linear function of the ion concentration). Therefore we believe that the scattering is due to a reorientational relaxation of the water molecules in the hydration shell.

A spectrum of LiCl 36 mol% D₂O solution was also taken in 90° scattering geometry, and it is compared with that of the H₂O solution at same concentration in figure 2. The width of the spectrum of the D₂O LiCl solution is somewhat narrower than that of the H₂O LiCl solution. Fitting the spectra with single Lorentzians, we find the width of the peak for the LiCl D₂O solution is about 30% narrower, so the relaxation time is about 30% slower. The Debye relaxation time of D₂O is about 30% slower than that of H₂O (Hasted 1971). This result further indicates that the scattering comes from the reorientational relaxation of the water molecules in the LiCl hydration shell.

Figure 3 shows the vH spectra of the LiCl solution in a 90° scattering geometry as a function of LiCl concentration. We found that the linewidth decreases as the concentration increases, corresponding to an increase in the reorientational relaxation time

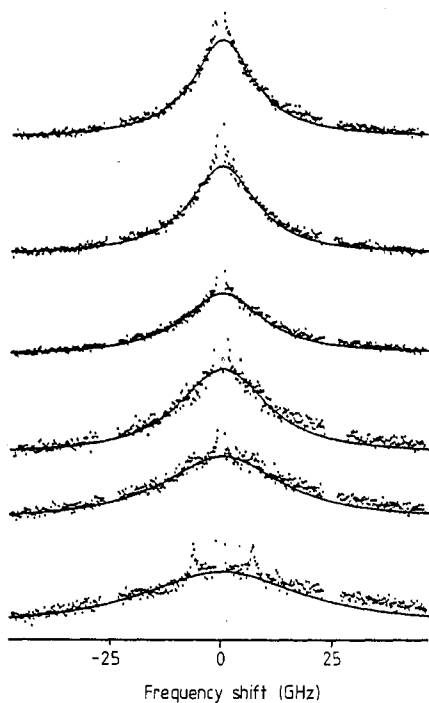


Figure 3. Depolarised (vH) Rayleigh spectra of LiCl solutions of 36, 34, 30, 26, 20 and 14 mol% (from top to bottom) in 90° scattering geometry. The dots are experimental spectra, and the full curves are single Lorentzian fits. There is some vv leakage at low frequencies.

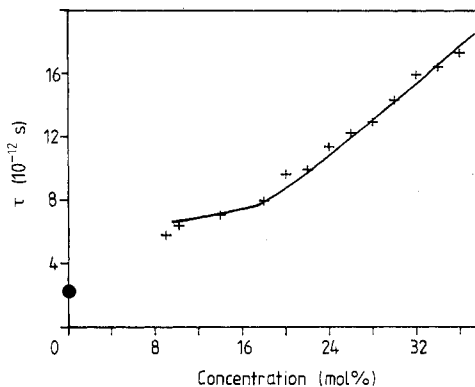


Figure 4. Reorientational relaxation time (+) of the water molecules in the LiCl primary hydration shell as a function of LiCl concentration. The dot represents the reorientational relaxation time of pure water (Montrose *et al* 1974, Alitta *et al* 1986). The full curve is a guide for the eye.

from 0.7×10^{-11} s at 9 mol% to about 1.8×10^{-11} s at 36 mol%. The reorientational relaxation time τ_0 is plotted as a function of LiCl concentration in figure 4 (the reorientational relaxation time of bulk water at room temperature, $\tau_0 \approx 0.2 \times 10^{-11}$ s, is also shown as a full circle). As the solution is diluted from 36 to about 20 mol%, τ decreases quite fast, then it approaches about 0.7×10^{-11} s at 0 mol%. This may result from correlation effects in the light scattering, or it may be a consequence of modification of the ionic hydration shells as the ions interact. The asymptotic value, 0.7×10^{-11} s, appears to be the relaxation time of an isolated ionic hydration shell. A molecular dynamics simulation at 26 mol% LiCl solution found that the rotational diffusion coefficient, D_x , of the water molecules was about $1.1 \times 10^{10} \text{ s}^{-1}$ (Okada *et al* 1983). Using the relation, $\tau = 1/6D_x$, the corresponding reorientational relaxation time is 1.4×10^{-11} s. This is remarkably close to 1.5×10^{-11} s measured by this work at the same concentration. The reorientational relaxation time of water molecules in the LiCl primary hydration shell was also estimated from NMR data by Hertz *et al* (1973) and from theoretical considerations by Bockris and Saluja (1972). Both methods gave about 1.5×10^{-11} s. However, the relaxation time has not been reported as a function of concentration, so the value of 1.5×10^{-11} s is presumably for an isolated hydration shell. This value is as twice large as our result of about 0.7×10^{-11} s.

vH Rayleigh spectra of 26 and 36 mol% LiCl solutions were taken as a function of temperature (figure 5). As we may expect, the width of the spectrum broadens as a result of increasing relaxation rate as temperature increases. Plotting $\ln(\tau)$ obtained

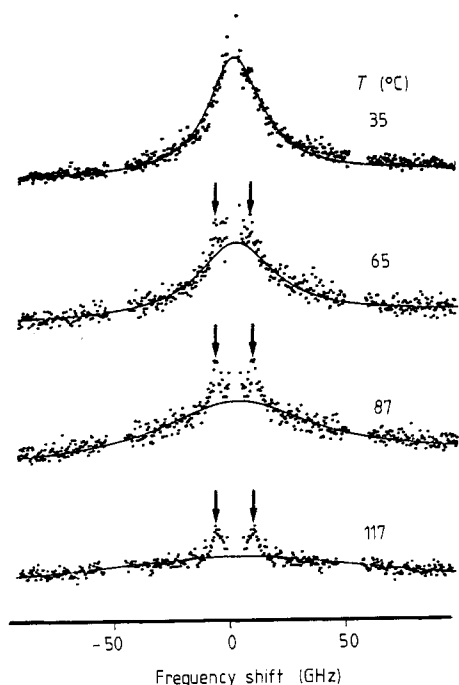


Figure 5. Depolarised (vH) Rayleigh spectra of 36 mol% LiCl solution at various temperatures as indicated. The spectra were obtained in 90° scattering geometry. The dots are experimental data, and the full curves are single Lorentzian fits. Leaked vv components are marked by arrows.

from these spectra as a function of $1/T$ in figure 6, we find that our data follow straight lines (open circles for the 26 mol% solution, and full circles for the 36 mol% solution), obeying the simple Arrhenius relation, $\tau = \tau_0 \exp(\Delta E/k_B T)$, where τ_0 is a constant, ΔE is the activation energy and k_B is the Boltzmann constant. The activation energies for the two solutions are 5.5 and 6.3 kcal mol⁻¹ respectively, more than twice the value for pure water (2.3 kcal mol⁻¹, Montrose *et al* 1974). This indicates a significant difference between the structure of the water molecules in the ionic hydration shell and pure water. The activation energy of the reorientational relaxation process was estimated as 4.7 kcal mol⁻¹ using proton magnetic relaxation measurements (Hertz 1973), a value comparable with our results.

We have also obtained the adiabatic compressibility from Brillouin shifts, densities and refractive indexes at various concentrations.

4. Discussion

Below about 20 mol%, some of the water molecules are in the secondary hydration shell, thus one may expect that the water molecules in both states will contribute to the depolarised Rayleigh spectra. However, only a single Lorentzian is observed at all salt concentrations. This is probably due to the fact that the scattering from the secondary hydration shell is much weaker than that from the primary hydration shell. The water molecules in the secondary hydration shell are similar to bulk water, and it has been found that, in depolarised scattering, the scattering from reorientational relaxation of pure water is indeed very weak at room temperature (Montrose *et al* 1974, Alitta *et al* 1986). We noticed that the signals from pure water are ~ 100 times lower than the scattering from 36 mol% solution. Besides, water molecules (in bulk water) are expected

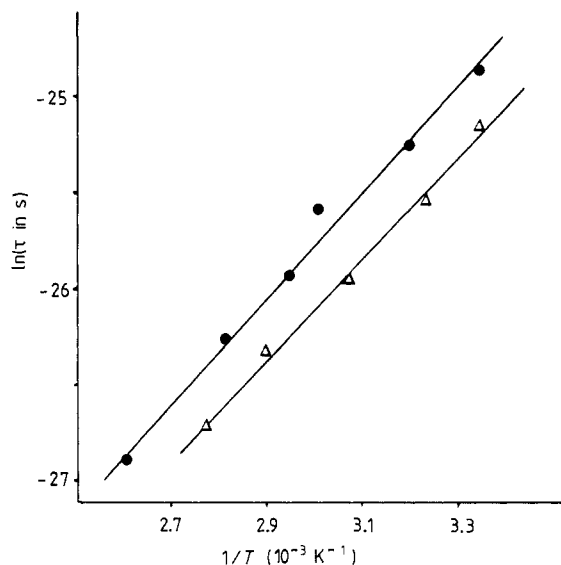


Figure 6. Arrhenius plots of the reorientational relaxation for 36 (full circles) and 26 mol% (open triangles) LiCl solutions.

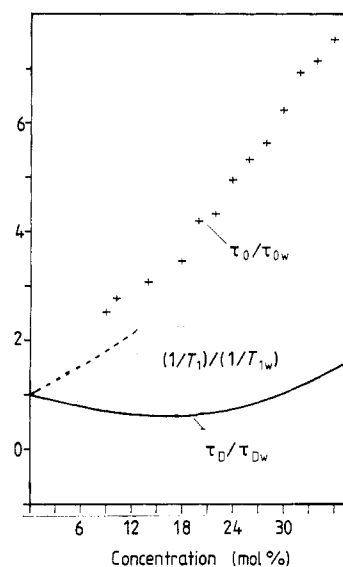


Figure 7. Ratios of relaxation time in solution to that in water for this work (τ_0/τ_w , marked as +); for the intramolecular proton magnetic relaxation rate ($(1/T_1)/(1/T_{1w})$, broken curve) and dielectric relaxation time (τ_D/τ_{Dw} , full curve) as a function of LiCl concentration (Pottel 1973).

to relax at a much higher rate than those in the primary hydration shell, giving a much broader linewidth, (not distinguishable from the background). We should point out that the reorientational relaxation time of the secondary hydration shell is even faster (Pottel 1973) than for pure water. In very dilute solutions (e.g. below 4 mol%), a depolarised Rayleigh spectrum might have to be decomposed into several components corresponding to the water molecules from different hydration shells and free water states.

Dielectric (Pottel 1973) and NMR (Hertz 1973) measurements have also been performed in LiCl aqueous solution at various LiCl concentrations. The dielectric relaxation time, τ_D , and the proton magnetic relaxation rate, $1/T_1$, are plotted with the reorientational relaxation time, τ_0 , measured by this work in figure 7. Note that all the relaxation times are normalised by the values for pure water. First of all, we notice that τ_D depends on the concentration in a very different way from τ_0 . As the concentration of LiCl increases, τ_D decreases quite rapidly and reaches a minimum of $0.75\tau_D(\text{H}_2\text{O})$, and then rises to a value of $1.25\tau_D(\text{H}_2\text{O})$ at the saturation concentration (~ 36 mol%). Both τ_D and τ_0 characterise the rotational correlation time of the molecules. According to Debye's model, $\tau_D = 3\tau_0$ (Debye 1929). A more general model gives $\tau_0 \leq \tau_D \leq 3\tau_0$ (Ivanov 1964). For pure water, τ_D is roughly 3τ (Hasted 1971), the value obtained from the depolarised light scattering. The significant discrepancy between the dielectric relaxation time and the reorientational relaxation time in LiCl solutions indicates that the two experiments measure different processes.

To compare our depolarised Rayleigh scattering with the proton magnetic relaxation measurement directly, it is necessary to have a relation between $1/T_1$ and the reorientational relaxation time. Such a relation was discussed by Hertz (1973), and it depends on the structural model used for interpreting the data. However, he argued that the reorientational relaxation time increases as concentration increases. These results are in qualitative agreement with our light scattering results.

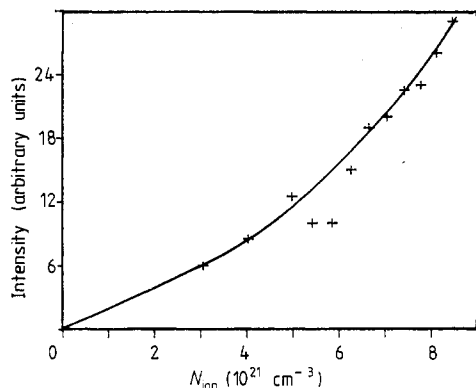


Figure 8. Integrated intensity of the depolarised Rayleigh scattering as a function of the number of LiCl ion pairs per unit volume.

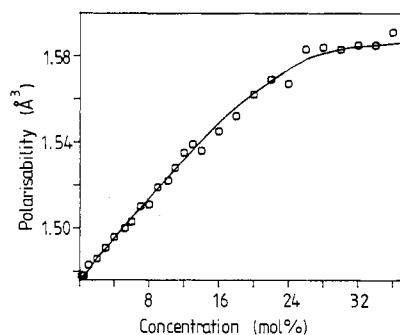


Figure 9. Optical polarisability of a water molecule in LiCl solution as a function of LiCl concentration (see text for the calculation). The open squares are the calculated points, and the full curve is to guide the eye.

The mechanism behind the discrepancy between the measurements of the dielectric relaxation time and the proton magnetic relaxation time has been a subject of debate (Pottel 1973, Frank and Wen 1957). Since our light scattering results agree qualitatively with proton magnetic relaxation experiments, these discussions are probably also valid for the discrepancy between the dielectric measurements and our light scattering studies, although, as we have pointed out, discrepancies may arise because of correlation effects in the light scattering (equation (3)). Frank and Wen (1957) interpreted the small dielectric relaxation time as a result of structural mismatch between the inner hydration sphere and the unperturbed water. The water molecules in this region have faster reorientational relaxation time as a consequence of the disruption of the hydrogen bonds. The mismatched region is regarded as the secondary hydration shell of the ions. Assuming the water molecules in the primary hydration shell do not contribute to the dielectric reorientational polarisation, a decrease of τ_D with increasing LiCl concentration is to be expected. In contrast, both light scattering and proton magnetic relaxation measurements involve the water molecules in the hydration shell, leading to the opposite effect. However, such a picture has a difficulty for highly concentrated solutions, where the secondary hydration shell does not exist. In this case, other effects, such as ion pairs (Pottel 1973) may be involved. We note that Pottel's data have been reinterpreted because of the large contribution of conduction losses in highly concentrated solutions (Angell 1983). More extensive data have just been published by Sridhar and Taborek (1988). The original interpretation of dielectric data (Pottel 1973) may not give reliable values for the structural relaxation time.

The integrated intensity of the VH spectrum at 90° scattering angle is plotted in figure 8 as a function of LiCl concentration. The intensity increases more rapidly than a linear function of the ion concentration. According to equation (1), the integrated intensity is proportional to $N(\Delta\alpha)^2$, where N is the average number of water molecules in the hydration shell per unit volume, and $\Delta\alpha$ is the anisotropy of the optical polarisability of the water molecules. Assuming there are n_h water molecules in a primary hydration shell, and N_{ion} ion pairs per unit volume, then $N = n_h N_{\text{ion}}$. Roughly, $(\Delta\alpha)^2$ is proportional to the slope of the intensity-concentration plot, which is clearly concentration dependent. Thus we conclude that $\Delta\alpha$ is a function of the ion concentration. This effect may

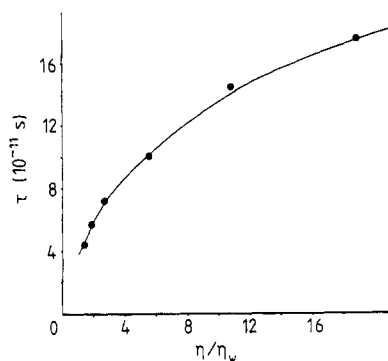


Figure 10. Plot of reorientational relaxation time as function of shear viscosity, η .

be attributed to the pair correlation effect as shown in equation (2). However, neutron scattering (Newsome *et al* 1980) and other experiments indicate that the structure of the water molecules in the hydration shell is a strong function of ion concentration, so $\Delta\alpha$ might well change. This explanation is supported by the refractive index data as discussed below.

We have measured the refractive index of the solutions as a function of concentration using an Abbe refractometer. According to the Lorentz–Lorenz relation (Lorentz 1880, Lorenz 1880)

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)(N_w\alpha_w + N_{\text{ion}}\alpha_{\text{ion}}) \quad (4)$$

where n is the refractive index, N_w and N_{ion} are numbers of water molecules and ions per unit volume respectively, α_w and α_{ion} are the polarisabilities of a water molecule and an ion pair. Taking the polarisability of crystalline LiCl for α_{ion} , and using the density given by Washburn (Washburn 1929), we have calculated α_w from the measured refractive index according to equation (2). α_w is plotted as a function of LiCl concentration in figure 9. It increases from 1.47 \AA^3 (the value for pure water) to 1.59 \AA^3 at 36 mol%. Of course, the change in the calculated α_w may not come just from the polarisability change of the water molecules; it is likely that both α_w and α_{ion} are LiCl concentration dependent. But such a calculation of α_w does tell us that the electronic structures of the ions and water molecules are influenced by the interionic interactions, a conclusion consistent with the intensity changes of the depolarised Rayleigh scattering.

Debye's model (Debye 1929) gives

$$\tau_0 = 4\pi r^3 \eta / 3k_B T \quad (5)$$

where r is the radius of the molecules. A general relation (Bauer *et al* 1974) is

$$\tau_0 = C\eta + \tau^0 \quad (6)$$

where τ^0 corresponds to the reorientational time of a free molecule, and C is a constant that depends on boundary conditions.

τ_0 is plotted as a function of η (Washburn 1929) in figure 10. The non-linear behaviour suggests that these simple relations do not hold in LiCl solution. This is probably due to the frequency dependence of η as indicated by the Brillouin scattering (Tao *et al* 1988). τ_0 was measured at GHz frequencies while the data for η were measured at zero frequency. Relations (3) and (4) may be correct if the relaxation time of η is much faster than τ_0 .

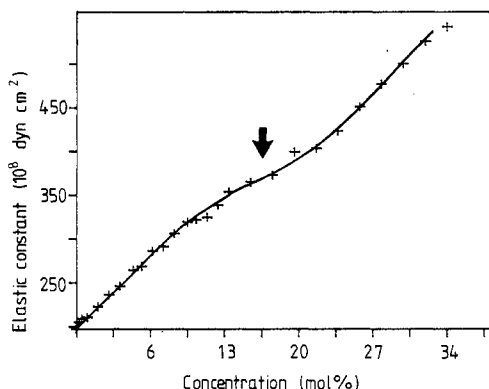


Figure 11. Adiabatic compressibility as a function of LiCl concentration (from Brillouin shifts (Tao and Lindsay 1988)). + are data points, and the full curve is a guide for the eye. The arrow marks a region of anomalous behaviour.

The salt concentration dependence of the reorientational relaxation time and the anisotropy of the polarisability may be a result of either the increased effect of pair correlations on the light scattering, or a consequence of the effect of interionic interactions on the structure and dynamics of the ionic hydration shell. We cannot separate the relative contribution of the two effects, since no reliable data are available on the single-particle reorientational relaxation time over this range of concentrations. Nonetheless our Brillouin spectra (Tao and Lindsay 1988) and refractive index measurements indicate that changes in ionic hydration probably do make a significant contribution. Neutron scattering data show that the diffusion coefficient for water in the Li^+ hydration shell is concentration dependent (Newsome *et al* 1980). It has been found that the hydration number of LiCl increases from 3.3 at 18 mol% to 5.5 at 8 mol%. The coordinates of the water molecules also change with concentration (Enderby and Neilson 1980). Further evidence of structural change is seen in the adiabatic compressibility of the solutions which is plotted as a function of LiCl concentration in figure 11. It stiffens with increasing LiCl concentration, with the exception of a clear anomaly near 20 mol%, a concentration at which other interesting changes occur. This anomaly may indicate a structural change in the solution.

Structural and dynamic properties of the DNA primary hydration shell have been studied by light scattering (Tao *et al* 1988, 1989). In contrast to LiCl solution, both the structural and dynamic properties of the DNA primary hydration shell are not sensitive to interhelical interactions. We may understand the difference between hydrated DNA and LiCl in this way: for DNA, only about a tenth of the phosphate groups of a double helix interact strongly with the phosphates of a neighbouring double helix (Lindsay *et al* 1988), so only the few water molecules that bind on these phosphates are influenced strongly by interhelical interactions; therefore the dynamics and structure of the DNA primary hydration shell are not very sensitive to DNA concentration. For LiCl, the hydrated ions are basically spherical, leaving no space for water molecules to 'hide'.

5. Conclusions

The reorientational relaxation time, τ_0 , of the water molecules in the LiCl primary hydration shell have been obtained by depolarised Rayleigh scattering. τ_0 is a strong function of LiCl concentration, varying from 0.7×10^{-11} s at 9 mol% to 1.8×10^{-11} s at 36 mol%. In deuterated solutions, τ is about 30% slower than in ordinary solution, an observation that was also made in pure D_2O and H_2O . The activation energies of 36 mol% and 26 mol% are 6.3 and 5.5 kcal mol $^{-1}$ respectively, in good agreement with

an estimation based on proton magnetic relaxation. Our results are consistent with NMR studies, but not with dielectric measurements.

The intensity of the depolarised Rayleigh scattering is much stronger than that of pure water, which suggests that the electronic polarisability of the water molecules is affected by charged ions. The increase of the intensity as the concentration increases may mean that the anisotropy of the molecular polarisability of the water molecules in the primary hydration shell is a function of LiCl concentration. This conclusion is supported by refractive index data.

Acknowledgments

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References

- Alitta F, Vasi C, Maisano G, Majolin D, Mallamace F and Migliardo 1986 *J. Chem. Phys.* **84** 4731
 Angell C A and Sare E J 1970 *J. Chem. Phys.* **52** 1058
 Angell C A 1983 *Solid State Ion.* **9 & 10** 3
 Berne B J and Pecora R 1976 *Dynamic Light Scattering* (New York: Wiley)
 Bauer D R, Brauman J I and Pecora R 1974 *J. Am. Chem. Soc.* **96** 6840
 Bockris J O'M and Saluja P P S 1972 *J. Phys. Chem.* **76** 2140
 Clementi E, Barsotti R, Fronum J and Watts R O 1976 *Theor. Chim. Acta* **43** 101
 Conway B E 1981 *Ionic Hydration in Chemistry and Biophysics* (Amsterdam: Scientific)
 Debye P 1929 *Polar Molecules* (New York: Dover)
 Enderby J E, Howells W S and Howe R A 1973 *Chem. Phys. Lett.* **21** 109
 Enderby J E and Neilson G W 1980 *Adv. Phys.* **29** 323
 ——— 1981 *Rep. Prog. Phys.* **44** 594
 Frank H S and Wen W Y 1957 *Disc. Faraday Soc.* **24** 133
 Green J L, Lacey A R and Seats M G 1987 *Chem. Phys. Lett.* **134** 385
 Hasted J B 1971 *Water: A Comprehensive Treatise* vol 3, ed. F Frank (New York: Plenum)
 Hertz H G 1973 *Water: A Comprehensive Treatise* vol 3, ed. F Frank (New York: Plenum)
 Hewish N A, Enderby J E and Howells W S 1982 *Phys. Rev. Lett.* **48** 756
 ——— 1983 *J. Phys. C: Solid State Phys.* **16** 1777
 Hsich S Y, Gammon R W, Macedo P B and Montrose C J 1972 *J. Chem. Phys.* **56** 1663
 Impey R W, Madden P A and McDonald I R 1982 *Mol. Phys.* **46** 513
 Ivanov E N 1964 *Sov. Phys.-JETP* **18** 1024
 Lindsay S M, Anderson M W and Sandercock J R 1981 *Rev. Sci. Instrum.* **52** 1478
 Lindsay S M, Powell J, Prohofsky E W and Devi-Prasad K V 1985 *Structure and Motion, Nucleic Acids and Proteins* ed. E Clementi, G Corongiu, M H Sarma and R H Sarma (New York: Adenine)
 Lindsay S M, Lee S A, Powell J W, Weidlich T, DeMarco C, Lewen G D, Tao N J and Rupprecht A 1988 *Biopolymers* **27** 1015
 Lorentz H A 1880 *Ann. Phys., Lpz.* **9** 641
 Lorenz L V 1880 *Ann. Phys., Lpz.* **11** 70
 Magini M 1983 *Ions and Molecules in Solution* ed. N Tanaka, H Ohtaki and R Tamamushi (Amsterdam: Elsevier)
 Montrose C J, Bucaro J A, Marshall-Coakley J and Litovitz T A 1974 *J. Chem. Phys.* **12** 5025
 Newsome J R, Neilson G W and Enderby J E 1980 *J. Phys. C: Solid State Phys.* **13** L923
 Okada I, Kitsuno K, Lee H and Ohtaki H 1983 *Ions and Molecules in Solution* ed. N Tanaka, H Ohtaki and R Tamamushi (Amsterdam: Elsevier)
 Pinnow D A, Candau S J and Litovitz T A 1968 *J. Chem. Phys.* **49** 347
 Pottel R 1973 *Water: A Comprehensive Treatise* vol 3, ed. F Frank (New York: Plenum)

Salmon P S 1987 *J. Phys. C: Solid State Phys.* **20** 1573

Sandercock J R 1978 *Solid State Commun.* **26** 547

Soumpasis D M, Wiechen J and Jovin T M 1987 *J. Biomol. Struct. Dyn.* **4** 535

Sridhar S and Taborek P 1988 *J. Chem. Phys.* **88** 1170

Tao N and Lindsay S M 1988 *J. Phys. Chem.* **92** 5857

Tao N, Lindsay S M and Rupprecht A 1988 *Biopolymers* **27** 1655

— 1989 *Biopolymers* at press

Washburn E W 1929 *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*
(New York: McGraw-Hill)