

NMR Relaxation Studies of Solvent D₂O in Solutions of Monosubstituted Ammonium Compounds

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Relaxation times of solvent D₂O in heavy water solutions of a series of monosubstituted ammonium compounds and rotational correlation times have been calculated. Correlation times show a gradual increase in the structure-forming tendency with chain length or bulk of alkyl groups of simple alkylammonium chlorides (RNH₃Cl). Introduction of polar group like OH, as in the case of ethanolanmonium chloride reduces the structure-forming tendency. Introduction of a phenyl group as in benzylammonium chloride increases the structure of water because of the interaction of π electron cloud with water. Cationic correlation times have also been calculated using the model of hydration of Hertz *et al.* From the temperature variation of relaxation rates, activation energies have been calculated for all the salts and glycine.

It is known that the structure of water gets altered when solutes are dissolved in it^{1,2}. Nuclear magnetic resonance is one of the potential techniques to understand the changes that occur in water when a solute is dissolved in it³⁻⁶.

Hertz and Zeidler^{7,8} have shown solvent-structure enhancement in aqueous solutions of tetraalkylammonium salts from relaxation time measurement of solvent (H₂O and D₂O). It is of interest to examine the structure of water in solutions containing solutes with both polar (hydrophilic) and non-polar (hydrophobic) character. In the present study NMR relaxation times of solvent D₂O have been measured in heavy water solutions of nine monosubstituted ammonium chlorides and glycine.

Materials and Methods

The solutes used in this study were: methylammonium, ethylammonium-, *n*-propylammonium-, *i*-propylammonium-, *t*-butylammonium- and ethanolanmonium-chlorides and ethylenediamine dihydrochloride, benzylammonium chloride, hydroxylammonium chloride and glycine. The first eight salts were prepared by careful neutralization of the respective amine and concentrating the solution. The solids that separated out were filtered off, washed with ethanol, recrystallized from ethanol, dried carefully *in vacuo* in an oven at 50-60°. These salts were always prepared afresh. Hydroxylammonium chloride (E Merck, India) and glycine (Sarabhai M Chemicals) were dried before use.

Bruker WH-270 FT-NMR spectrometer was used. Inversion recovery method⁹ was adopted for measuring relaxation times.

The solutions (0.5 M) were prepared in D₂O (Sigma) by direct weighing. The samples were deoxygenated

using freeze-pump-thaw cycles and then sealed in a capillary. The capillary was suspended in a 5 mm NMR tube containing a mixture of TMS (external reference) and CDCl₃ (locking material). The temperature of measurement was maintained constant within $\pm 0.5^\circ\text{C}$ of the desired temperature.

Results and Discussion

Measured values of relaxation times are presented in Table 1. The relaxation times of pure D₂O obtained in the present work agreed well with those reported in literature¹⁰, the deviation being of the order of <1%.

Correlation time

Heavy water is known to have slightly stronger hydrogen bonded network than water¹¹. But the structural effects characterized by relaxation studies in D₂O are smaller in magnitude than those in H₂O. This arises due to the assumption of equal quadrupolar coupling constant for D₂O in the hydration sphere and that in bulk water¹². However, calculation of correlation time in D₂O is easier because the separation of relaxation rate into intra- and intermolecular contributions⁶ is not required. The relaxation in D₂O is exclusively due to the quadrupolar interaction of deuterium and hence only intramolecular rotation must be considered. This implies that the correlation time (τ_c) can be directly calculated from the measured relaxation rate using Eq. (1).

$$\frac{1}{T_1} = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar} \right)^2 \tau_c \quad \dots(1)$$

where $1/T_1$ is the relaxation rate and coupling constant ($e^2 q Q/\hbar$) is taken as 230 ± 10 KHz (ref. 3).

Table 1—Longitudinal Relaxation Times (T_1) and Rotational Correlation Times (τ_c) of Deuterium Resonance in Heavy Water Solutions of Monosubstituted Ammonium Compounds

Sl No.	Compound	293 K		301 K		309 C	
		T_1 (s)	τ_c^\ddagger (ps)	T_1 (s)	τ_c^\ddagger (ps)	T_1 (s)	τ_c^\ddagger (ps)
1	Heavy water Lit. ^a	0.383	3.33	0.500	2.55	0.625	2.04
	Present	0.381	3.35	0.496	2.58	—	—
2	Methylammonium chloride	0.405	3.2	0.491	2.6	0.603	2.1
3	Ethylammonium chloride	0.380	3.4	0.422**	3.0	0.640	2.0
4	<i>n</i> -Propylammonium chloride	0.356	3.6	0.465	2.7	0.562	2.3
5	Isopropylammonium chloride	0.336	3.8	0.403	3.2	0.547	2.3
6	<i>t</i> -Butylammonium chloride	0.341	3.7	0.465	2.8	0.521	2.5
7	Ethanolammonium chloride	0.400	3.2	0.457	2.8	0.583	2.2
8	Ethylenediamine dihydrochloride	0.363	3.5	0.469	2.7	0.574	2.2
9	Benzylammonium chloride	0.359	3.6	0.444	2.9	0.427*	3.0
10	Hydroxylammonium chloride	0.414	3.1	0.536	2.4	1.070	1.2
11	Glycine	0.433	3.0	0.455	2.8	0.589	2.2

^aD.E Woessner, *J chem Phys*, **40** (1964) 2341.

*Temperature of measurement is 297°K.

**Temperature of measurement is 295°K

‡Value rounded to 2 significant figures.

A close look at the results in Table 1 shows that in alkylammonium chlorides (2-6 in Table 1) the τ_c of solvent D₂O increases with the chain length of the alkyl group. The lowering of τ_c of pure solvent in the presence of CH₃NH₃Cl ($\tau_c = 3.35$ ps for pure solvent and 3.2 ps in the presence of CH₃NH₃Cl) signifies breakdown of water-structure. In the presence of higher homologues τ_c values are more in comparison to the pure solvent, indicating enhanced solvent structure. A comparison of τ_c values in the presence of *n*-propyl- and isopropyl-ammonium chlorides indicates that more spherical arrangement of alkyl group favours enhancement of water-structure. However, it may be noted that *t*-butylammonium chloride solution shows a higher τ_c than that observed in *n*-propylammonium chloride solution but slightly less than that in isopropylammonium chloride solution.

Ethanolammonium chloride solution shows a τ_c value (3.2 ps) lower than that of ethyl salt solution (3.4 ps). It may be due to the fact that structured water layer around a hydrophobic alkyl group is interfered by the polar -OH group of the ethanolammonium chloride. It is also known from other physical studies¹³ that introduction of polar group decreases the hydrophobicity of alkyl groups. Hydroxylammonium chloride decreases τ_c of the solvent to a greater extent than methylammonium chloride.

Ethylenediamine dihydrochloride solution shows a higher τ_c value than ethanolammonium chloride solution. It gives two chloride ions and a cation with

two positive centres. The solvent molecules may be bound to these charge centres thus enhancing the solvent structure. Of course these bound heavy water molecules are involved in a fast exchange with molecules in the bulk but at any instant of time they are bound to the ion and are less free to rotate resulting in higher τ_c value.

The τ_c value observed for benzylammonium chloride solution is much less than that of a solution of alkylammonium chloride of similar size, but it is much higher than that of pure solvent. This is due to the hydrophilic interaction of π -electron cloud of aromatic ring with deuterons of heavy water¹⁴. The IR spectral studies of Haggins and Pimentel¹⁵ show that though the benzene ring is a weak base, it shows a behaviour that correlates well with the criteria recognised for regular hydrogen bonding systems.

Glycine shows the least correlation time in this series confirming the earlier studies, showing this zwitterion as a structure-breaker¹⁶. The bulky negative charged -COO⁻ group does not bring about ordering in the solvent structure as effectively as -NH₃⁺ and hence this result.

Ionic correlation times

An estimate of τ_c^+ would be a more meaningful indicator of solute-solvent interaction. In the evaluation of τ_c^+ , it is assumed, as a first approximation, that intramolecular relaxation rate of

a solution is the sum of contributions from the three regions¹⁷ (see Eq. 3).

$$\frac{1}{T_1} = (1 - X^+ - X^-) \left(\frac{1}{T_1^0} \right)_{\text{intra}} + X^+ \left(\frac{1}{T_1^+} \right)_{\text{intra}} + X^- \left(\frac{1}{T_1^-} \right)_{\text{intra}} \quad \dots(2)$$

Combining Eqs (1) and (2), the deuterium relaxation rate may be written as

$$\frac{1}{T_1} = \frac{3}{8} \left(\frac{e^2 q Q}{\hbar} \right)^2 (1 - X^+ - X^-) \tau_c^0 + X^+ \tau_c^+ + X^- \tau_c^- \dots(3)$$

where $X^+ = \frac{\nu^+ n_h^+ C}{55.5}$; $X^- = \frac{\nu^- n_h^- C}{55.5}$ with C as the concentration of solute in molality; X^+ and X^- are the mol fractions of D₂O in cation and anion hydration spheres respectively; ν^+ and ν^- are the stoichiometric numbers of ions formed when the salt is dissolved; n_h^+ and n_h^- are the hydration numbers of cation and anion respectively. Making use of the method of Shahidi¹⁸, hydration numbers of cations were computed from partial molal volumes of these ions¹⁹. The values of $\tau_c^-(\text{Cl}^-)$ and τ_c^0 are those given by Endom *et al.*¹⁷ (3.0 ps at 25°C) and obtained presently (3.35 ps), respectively. The values of τ_c^+ for different cations thus calculated are presented in Table 2. The cationic hydration numbers used in these calculations are also included in Table 2.

The values of τ_c^+ for ethylammonium ion onwards to *t*-butylammonium ion are much larger than that (τ_c^0) of bulk solvent as predicted. The value for D₂O in ethylammonium ion hydration sphere (3.6 ps) is very close to the value of bulk D₂O (3.35 ps). The increasing positive value for D₂O in the hydration sphere of higher homologues is as expected. The τ_c^+ for D₂O in

benzylammonium ion hydration sphere is also higher than τ_c^0 confirming higher solvent structure in this case.

One would expect the τ_c^+ in the hydration sphere of structure-breaking ions to be lower than τ_c^0 . However, negative values can not have any physical significance. This probably arises due to some erroneous assumption. It is assumed here that the structure of water everywhere except in the first hydration layer is the same as in bulk. But actually in solutions of structure-breaking solutes, the broken structure extends beyond the first layer of (n_h^+) water molecules and these have τ_c values much less than τ_c^0 . Reduced correlation times of much larger number of water molecules when clubbed together and averaged on a small number of water molecules result in a τ_c^+ value that is much less than the real value and it may even become negative. However, the negative τ_c^+ value would indicate extensive breakdown of water-structure. Lower the value of τ_c^+ , more broken is the water-structure. In the present set of compounds glycine is the one which breaks down the water-structure to the maximum extent. The same argument shows that larger values of τ_c^+ are numerically correct only if enhanced water-structure does not extend beyond the first layer.

Activation energy for relaxation of deuterium

Hindman *et al.*²⁰ calculated the activation energy of the relaxation of deuterium in pure D₂O from the plot of $\ln T_1$ versus $1/T$ over a wide range of temperatures (-18° to $+178^\circ\text{C}$). The plot showed a curvature between two linear ranges. The activation energies calculated from the two linear parts were 41.8 kJ/mol (low temperature region) and 13.8 kJ/mol (high temperature region, $>330^\circ\text{K}$). These authors attributed this to two processes: (i) at low temperature hydrogen bond breaking was responsible for the high activation energy and (ii) at high temperatures isotropic Brownian motion characterized the relaxation process.

In the present investigation we have calculated the activation energies for the relaxation processes in salt solutions from the linear plots of $\ln(1/T_1)$ versus $1000/T$ in the temperature range of 293-318 K and the values are given in Table 3. This temperature region falls in between the two temperature ranges given by Hindman *et al.*²⁰ Hence, both the processes must be contributing to the activation energy. However, the numerical value of activation energy indicates that the isotropic Brownian motion contributes largely to the observed activation energy for the relaxation process in the temperature region. The activation energies of all the salts, except that of hydroxylammonium chloride, scatter around the activation energy of pure D₂O. In the case of hydroxylammonium chloride, the

Table 2—Rotational Ionic Correlation Times (τ_c^+) of Solvent Water in Hydration Sphere of Solute at 20°C

Sl No.	Cation	Effective hydration number (n_h)	τ_c^+ (ps)
1	Methylammonium	4.1	-1.9
2	Ethylammonium	3.7	3.6
3	<i>n</i> -Propylammonium	3.5	10.8
4	iso-Propylammonium	3.4	18.2
5	<i>t</i> -Butylammonium	2.6	19.9
6	Ethanolammonium	4.7	-0.4
7	Benzylammonium	7.8	6.4
8	Hydroxylammonium	5.2	-2.2
9	Glycine (zwitterion)	7.5	-2.6

Table 3—Activation Energies (E_a) from Relaxation Times of Deuterium Resonance in D_2O Solutions of Ammonium Compounds in Temperature Range 293-318 K

Sl No.	Compound	E_a kJ/mol
1	Heavy water	21.3
2	Methylammonium chloride	18.4
3	Ethylammonium chloride	20.5
4	<i>n</i> -Propylammonium chloride	20.5
5	iso-Propylammonium chloride	20.9
6	tert-Butylammonium chloride	20.9
7	Ethanolammonium chloride	18.0
8	Ethylenediamine dihydrochloride	21.3
9	Benzylammonium chloride	21.3
10	Hydroxylammonium chloride	39.3
11	Glycine	14.2

plot of $\ln(1/T_1)$ versus $1000/T$ was non-linear. It is pertinent to note that there is a gradual increase in the activation energies of the first five alkylammonium chlorides. This observation supports the idea of increased ordering in solvent structure with increase in chain length or bulk of alkyl moiety. This is because, higher the stabilization of hydrogen bonded network greater is the energy required for either of the process indicated by Hindman *et al.*²⁰ In line with its water-structure breakdown property, glycine has the lowest activation energy while ethylenediamine dihydrochloride and benzylammonium chloride have high activation energies in keeping with their structure-enhancing property. However, activation energy is not

a sensitive indicator of structure of the solvent in different salt solutions.

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