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Concentration Dependence of the Rotational Motion of Tetraphenylborate and Tetraphenylarsonium Ions in Aqueous Solution. Effect of Their Self-Association

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The ^{13}C spin-lattice relaxation times and NOE for the para carbons of Ph_4As^+ and BPh_4^- were measured in D_2O and CD_3OD. The osmotic coefficients were also determined in the aqueous solutions of Ph_4AsCl and $NaBPh_4$. A remarkable increase in the rotational correlation time of the Ph_4As^+ ion with increasing concentration was attributed to the formation of aggregates containing two or more Ph_4As^+ ions.

The assumption that the transfer energy from one solvent to another is equal between Ph_4As^+ (or Ph_4P^+) and BPh_4^- has been widely used for dividing thermodynamic parameters into individual ionic contributions, because these ions are of similar ionic radius and of the same ionic charge.1) On the other hand, differences between Ph_4As^+ (or Ph_4P^+) and BPh_4^- in aqueous solution have been observed in various experiments: e.g., various thermodynamical measurements,2,3) the near-infrared spectra of water,4) and NMR chemical shifts of water proton.5) The differences were related to the difference in the hydration and/or in the ion-pair formation with their counter ions and/or in the aggregate formation of the Ph_4As^+ and BPh_4^- ions themselves.2-5)

The present study is focused on the ion-ion interaction particularly between the Ph_4As^+ ions and between the BPh_4^- ions in the aqueous solutions of their salts. For this purpose the concentration dependence of the rotational correlation times of the Ph_4As^+ and BPh_4^- ions was determined by measuring the ^{13}C spin-lattice relaxation rates of the para carbon of the phenyl group. The difference in the concentration dependence of the rotational correlation times is related to the formation of aggregates of the Ph_4As^+ ions and of the BPh_4^- ions.

The ^{13}C NMR spectra were recorded on a JEOL FX200 FT-NMR spectrometer at 50.1 MHz and the spin-lattice relaxation rates, R_1, were measured by the inversion-recovery method. For several samples, the measurements of R_1 were repeated 3 times or more; consistent results (within 3%) were obtained for R_1 of each sample. The ^{13}C-$\{^1H\}$ NOE (nuclear Overhauser enhancement) was determined by the gated-decoupling method. Details of the measurements have been described in previous papers.6,7) The temperature of the sample solution was controlled at 25.0 ± 0.3 °C. The osmotic coefficients of Ph_4AsCl and $NaBPh_4$ in aqueous solution at 25.0 °C were determined by vapor-pressure osmometry, in a similar manner as previously reported.[8)]

The rate of ^{13}C relaxation due to the dipolar interaction with the attached proton, R_1^D, were determined by the measured spin-lattice relaxation rate, R_1, and NOE values, η_{NOE}, according to the relation:[9)]

$$R_1^D = R_1\eta_{NOE}/1.987$$

The obtained R_1^D values of the para carbon are related to the correlation times of the C-H vectors, τ_c, by the equation:[9)]

$$R_1^D = \gamma_H^2\gamma_C^2\hbar^2 \cdot r_{CH}^{-6} \cdot \tau_c \qquad (1)$$

where r_{CH} is the C-H bond length and is taken to be 0.109 nm. The obtained R_1^D values of the para carbon and the τ_c values, which are determined from the R_1^D according to Eq. 1, are shown in Fig. 1. The τ_c values thus determined coincide with the rotational correlation times of the Ph_4As^+ and BPh_4^- ions.

The obtained τ_c values in D_2O at infinite dilution show no significant difference between the Ph_4As^+ and the BPh_4^- ion; the difference in the interaction of the Ph_4As^+ ion and of the BPh_4^- ion with water, as has been predicted by the near-infrared and NMR chemical shift of water,[4,5)] does not influence their rotational motions.

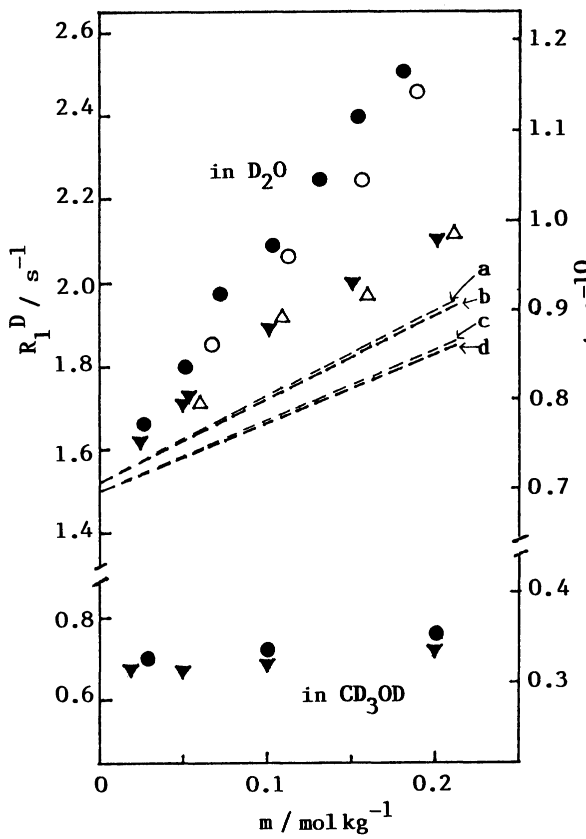

Fig. 1. Plots of the R_1^D and τ_c values of Ph_4As^+ and BPh_4^- in D_2O and CD_3OD at 25.0 °C vs. the concentration of Ph_4AsCl (●), $(Ph_4As)(SO_4)_{1/2}$ (○), $NaBPh_4$ (▼), and $LiBPh_4$ (△). The broken lines indicate calculated values of $\tau_c^o\eta_r$ (τ_c^o and η_r are the rotational correlation time at infinite dilution and relative viscosity of the solutions, respectively): (a), $LiBPh_4$; (b), $NaBPh_4$; (c), $(Ph_4As)(SO_4)_{1/2}$; (d), Ph_4AsCl.

The obtained τ_c values of Ph_4As^+ and BPh_4^- increased with increasing concentration of the salts of those ions in D_2O and the increase was particularly remarkable for the Ph_4As^+ ion. (Fig. 1) If a hydrodynamic model could be applied to the present systems, the rotational correlation time would be given by a linear function of the viscosity of the solution.[10)] The change in the τ_c values predicted from the viscosity change of the solution is represented by the broken lines in Fig. 1. The predicted increase in τ_c is much less than that observed, particularly in the aqueous solution of the Ph_4As^+ salts. The failure of the hydrodynamic model in reproducing the experimental concentration dependence of the τ_c value indicates that the medium around the Ph_4As^+ and BPh_4^- ions cannot be regarded as continuum for the rotation of those ions. Short-range interaction of the Ph_4As^+ and the BPh_4^- ions with themselves and/or their counter ions is important in the rotational motion of those ions in water.

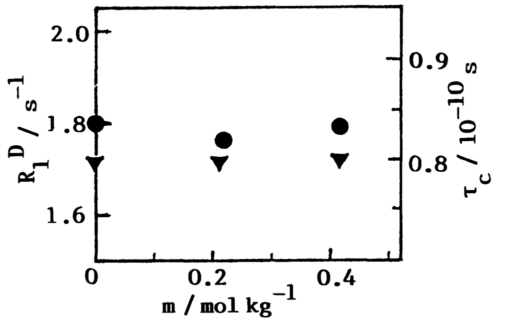

Fig. 2. Plots of the R_1^D and τ_c values of Ph_4As^+ and BPh_4^- vs. the concentration of NaCl added to the 0.05 mol/kg D_2O solutions of Ph_4AsCl (●), and $NaBPh_4$ (▼) at 25 °C.

The change in the R_1^D values of the para carbon were also measured as a function of the concentration (0.1 - 0.4 mol kg^{-1}) of NaCl added to the dilute D_2O solutions of Ph_4AsCl and $NaBPh_4$ (0.05 mol kg^{-1}), respectively. The results are shown in Fig. 2. The effect of added NaCl on the τ_c values was found to be very slight. This indicates that the interactions of Ph_4As^+ with Cl^- and of BPh_4^- with Na^+ give no specific effect on the rotational motions of the Ph_4As^+ and BPh_4^- ions. Therefore, the large increase in the τ_c value with increasing concentration as shown in Fig. 1 can be attributed to short-range interaction between the Ph_4As^+ ions and between the BPh_4^- ions, the interaction being larger between the former than between the latter. As shown in Fig. 1, the different salts of Ph_4As^+ (Ph_4AsCl and $(Ph_4As)_2SO_4$) and of BPh_4^- ($NaBPh_4$ and $LiBPh_4$) in D_2O showed only slight differences in the τ_c values; this also indicates that the increase in the τ_c values is caused not by the interaction with the counter ions but by the interaction of the bulky ions with themselves.

The τ_c values of Ph_4As^+ and BPh_4^- ions showed only slight dependence on the concentration in the CD_3OD solutions (Fig. 1), in striking contrast with the case of the aqueous solutions. This can be explained by the lack of significant short-range interaction between the Ph_4As^+ and between the BPh_4^- ions, because electrostatic interionic repulsion is stronger in methanol with a smaller dielectric constant.

The short-range interaction which increases the rotational correlation times of the tetraphenyl ions may be ascribed to forming aggregates containing the two or more Ph_4As^+ ions or BPh_4^- ions; the larger increase in the τ_c values of the Ph_4As^+ ion indicates that the tendency to form the aggregates is larger for Ph_4As^+ than for BPh_4^-. Such aggregation of bulky univalent ions is also found in aqueous solution of tetraalkylanmmonium salts.$^{11)}$

A similar diminution of the ionic rotation has also been reported for the aqueous solutions of the chloride and sulfate of $[Ru(phen)_3]^{2+}$ (phen=1,10-phenanthroline).$^{6)}$ In this case the restriction of the rotational motion of the $[Ru(phen)_3]^{2+}$ ion is caused by the formation of aggregates containing the two complex ions, where one of the phenanthroline ligands of each complex ion partially occupying an opening between the ligands of the other complex ion.$^{12)}$ The restriction of the rotational motion of the Ph_4As^+ and BPh_4^- ions may be similarly explained by a bite of the phenyl groups of the two Ph_4As^+ ions and the two BPh_4^- ions in the aggregates.

The measurement of osmotic coefficients for the aqueous solutions of Ph_4AsCl at concentrations ranging between 0.005 - 0.1 mol kg^{-1} showed large negative deviation from the Debye-Hückel theory, whereas that deviation in the aqueous solution of $NaBPh_4$ was small; e.g., the deviations are -0.255 at 0.1007 mol kg^{-1} for Ph_4AsCl and -0.043 at 0.0999 mol kg^{-1} for $NaBPh_4$. A similar negative deviation in the osmotic coefficients of Ph_4AsCl has been reported and explained in terms of the specific interaction of water molecules with the π-electron of the phenyl groups.[3)] However, considering the large tendency to form the aggregates of Ph_4As^+, which is predicted from the ^{13}C relaxation rates, the decrease in the effective number of ions in the solution may also contribute largely to the negative deviation of the osmotic coefficients.

Various thermodynamic[1a,2)] and spectroscopic studies[4,5)] suggest difference in the interaction of the Ph_4As^+ ion and of the BPh_4^- ion with water. This difference in the interaction may be closely related to the difference in the aggregate formation of the Ph_4As^+ and BPh_4^- ions themselves, but detail of the driving force to form the aggregates is not elucidated in the present stage. Further quantitative analysis for the τ_C values and the osmotic coefficients at various temperatures are now going.

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