Raman Spectroscopic Study on the Hydration Structure of Tetraethylammonium Chloride in Water

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Abstract. The hydration structure of tetraalkylammonium chloride (Et₄NCl) in aqueous solution has been studied by Raman Spectroscopy as functions of pressure and concentration. The hydration volume due to the hydrophobic hydration around trans-trans. trans-trans (tt.tt) conformer is larger than that around trans-gauche. trans-gauche (tg.tg) conformer. The hydration structures are closely correlated to the conformational equilibrium in the solution.

1. Introduction

A number of studies on the aqueous tetraalkylammonium salt solutions have been performed to investigate the nature of hydrophobic hydration and clathrate structures[1-8], because they were soluble in many polar solvents, particular in water, and their alkyl-chain length can be changed easily within the series of homologues[4].

Another remarkable feature is that tetraethylammonium ion (Et₄N⁺) shows the conformational equilibrium. The conformation of molecules is arise from intramolecular rotation and this rotation takes on trans and gauche conformations[9, 10]. Naudin. et al.[11] reported that Et₄N⁺ ion shows the conformational equilibrium between the trans-gauche. trans-gauche (tg.tg) and trans-trans. trans-trans (tt.tt) conformer for the rotation of Et-N+-Et axis in the aqueous solution, though the ethyl-chains adopt the tt.tt conformer in the crystalline state. The tg.tg and tt.tt conformers are also called Nordic cross and Greek cross, respectively. These conformations are shown in Figure 1. Theoretically tetraethylammonium ion may show other type of conformers, for example trans-trans. trans-gauche (tt.tg) and gauche-gauche. gauche-gauche (gg.gg) conformers. However, these conformers are too labile to exist in the aqueous solutions. Actually the Raman spectra attributable to these conformers are not observed in the aqueous solutions.

It is intriguing to discuss the hydration structures along with the conformational equilibrium in the tetraethylammonium salt solutions. In our preliminary studies, we measured the Raman spectra of the aqueous tetraalkylammonium bromide (Et₄NBr) solution[12, 13]. It was suggested that hydrophobic hydration may prefer the tt.tt conformer to the tg.tg conformer at R (=moles of water/moles of Et₄NBr)=19, but the hydration structure around Et₄N⁺ ion at R=4 might be different from the hydrophobic hydration.

As an extension of the previous study we have investigated the Et₄NCl solution in an effort to obtain the information of the anionic effect on the hydration structures. In this study we have observed the Raman spectral changes in the C₈N symmetric stretching and uncoupled OD stretching modes as
functions of pressures and concentration ($R$). From the C$_4$N symmetric stretching spectra we can obtain the information on a change in the conformational equilibrium, and the OD (OH) stretching spectra are used as a probe of the hydrogen-bond strength[6]. We compared the results between the aqueous Et$_4$NBr and Et$_4$NCl solutions.

2. Materials and Methods

Et$_4$NCl was obtained from Tokyo Kasei Industry Co. Ltd (Et$_4$NCl : 99.9%), and D$_2$O was obtained from Aldrich Chemical (D$_2$O : 99.8%). All sample solutions were prepared by dissolving Et$_4$NCl in 5 % D$_2$O solution (0.05D$_2$O + 0.95H$_2$O) as a solvent. The reason of using 5 % D$_2$O solution is to avoid complexity in analyzing the OH stretching Raman spectra. The OH stretching spectra of aqueous solutions are broad and the Fermi resonance effect makes the OH stretching spectra difficult, and the CH stretching band of Et$_4$N$^+$ ion overlaps the OH stretching spectra[7, 14]. The concentrations of all the solutions are expressed by $R$ (=moles of water/moles of Et$_4$NCl). Raman spectra were measured by a JASCO NR-1800 Raman spectrophotometer equipped with a CCD detector and a microscope. The exposure time of each run was 300 s. The 514.5 nm line from a Lexel argon ion was used as an exciting source with a power of 350 mW. For the high-pressure experiments, we used a diamond anvil cell (DAC). The ruby chip was used for a pressure reference[15]. To analyze the obtained C$_4$N symmetric stretching and uncoupled OD stretching spectra, we fitted the spectra with the Gaussian-Lorentzian mixed curves.

![Figure 2. Typical Raman spectra of the C$_4$N symmetric stretching mode in the aqueous Et$_4$NCl solution as a function of pressure at $R$=11.](image)

![Figure 3. Concentration dependences of the $\chi^{\text{OD, D-H}}$ of the aqueous Et$_4$NCl and Et$_4$NBr solutions. Symbols of $\Box$ and $\blacksquare$ represent the $\chi^{\text{OD, D-H}}$ of the Et$_4$NCl and Et$_4$NBr solutions, respectively.](image)
3. Results and Discussion

First of all, we discuss the pressure effects of the aqueous Et₄NCl solution. The C₄N symmetric stretching spectra of the solution as a function of pressure are shown in Figure 2. The lower and higher frequency peaks are belong to the tg.tg and tt.tt conformers, respectively[11]. To discuss more about the experimental results, we estimated the partial molar volume (\(\Delta V_{\text{tg.tg}}}^{\text{tg.tg}}\)) between the tg.tg and tt.tt conformers from the pressure dependence of the relative Raman intensities. Presuming that the proportion of the Raman scattering cross sections between the conformers is independent of a pressure, \(\Delta V_{\text{tg.tg}}}^{\text{tg.tg}}\) is given by

\[
\Delta V_{\text{tg.tg}}}^{\text{tg.tg}} = -8.314T\left(\frac{\partial \ln (I_{\text{tg.tg}}/I_{\text{tt.tt}})}{\partial p}\right),
\]

where \(R, T, p, I_{\text{tg.tg}}\) and \(I_{\text{tt.tt}}\) are gas constant, temperature, pressure, the relative Raman intensity of the tg.tg and tt.tt conformers, respectively.

Figure 3 plots the results of the concentration dependence of the \(\Delta V_{\text{tg.tg}}}^{\text{tg.tg}}\) of the aqueous Et₄NCl solution together with that of the Et₄NBr solution. The value of the \(\Delta V_{\text{tg.tg}}}^{\text{tg.tg}}\) for the aqueous Et₄NCl solution takes negative throughout the studied concentration region, indicating that the partial molar volumes of the tt.tt conformer are always smaller than those of the tg.tg conformer. It is also noticed that the \(\Delta V_{\text{tg.tg}}}^{\text{tg.tg}}\) of the aqueous Et₄NCl solution takes almost same value of the Et₄NBr solution at the same \(R\).

To discuss the observed results further, we separated the \(\Delta V_{\text{tg.tg}}}^{\text{tg.tg}}\) into two contributions as below (eq.2).

\[
\Delta V_{\text{tg.tg}}}^{\text{tg.tg}} = \Delta V_{M}^{\text{tg.tg}}}^{\text{tg.tg}} \Delta V_{\text{hyd}}^{\text{tg.tg}}}^{\text{tg.tg}}
\]

where \(\Delta V_{M}\) is the molecular volume of the conformer itself, \(\Delta V_{\text{hyd}}\) is the hydration volume influenced by interactions between the solute and solvent molecules. We calculated the intrinsic value of the \(\Delta V_{M}\) by the Alpha-Shapes programs, to be -1.34cm³mol⁻¹. Using this, we can obtain the \(\Delta V_{\text{hyd}}\).

Figure 4 plots the results of the concentration dependences of the \(\Delta V_{\text{hyd}}^{\text{tg.tg}}}^{\text{tg.tg}}\) of the aqueous Et₄NCl and Et₄NBr solutions. Generally both the \(\Delta V_{\text{hyd}}\) of the aqueous Et₄NCl and Et₄NBr solutions exist plus throughout the studied \(R\). This means that the hydration volume of the tg.tg conformer is smaller than that of the tt.tt conformer in the aqueous Et₄NCl and Et₄NBr solutions. In our previous study[13], we mentioned that the differences in the \(\Delta V_{\text{hyd}}^{\text{tg.tg}}}^{\text{tg.tg}}\) value of Et₄N⁺ ion in the aqueous Et₄NBr solution between \(R=4\) and \(19\) comes from the hydration structure around Et₄N⁺ ion and the hydration volume due to the hydrophobic hydration around tt.tt conformer is larger than that around tg.tg conformer.

![Figure 4](image-url)  
Figure 4. Concentration dependences of the \(\Delta V_{\text{hyd}}^{\text{tg.tg}}}^{\text{tg.tg}}\) of the aqueous Et₄NCl and Et₄NBr solutions. Symbols of \(\Delta\) and \(\Delta\) represent the \(\Delta V_{\text{hyd}}^{\text{tg.tg}}}^{\text{tg.tg}}\) of the Et₄NCl and Et₄NBr solutions, respectively.

![Figure 5](image-url)  
Figure 5. (a) Raman spectra of the uncoupled OD stretching mode of the aqueous Et₄NCl solution at various concentrations (R). (b) Representative curve-fitted results at \(R=6\) and \(20\).
Base on these results, we suggest that the hydrophobic hydration around tt.tt conformer in the aqueous Et₄NCl solution may be maintained at more concentrated region probably due to the anionic effect.

To consider the hydration structures further along with the conformational equilibrium, we discuss the strength of hydrogen-bond (H-bond) around Et₄N⁺ ion in the aqueous Et₄NCl solution from the uncoupled OD stretching spectra at a normal pressure (Figure 5(a)). In doing this, we fitted the uncoupled OD stretching spectra with two contributions having different hydrogen-bond strength; strong H-bond and medium H-bond[7,14,16,17]. The curve-fitted uncoupled OD stretching spectra of the aqueous Et₄NCl solution as a function of concentration are shown in Figure 5(b). The intensities ($f$) of the strong ($f_{\text{strong}}$) and medium ($f_{\text{medium}}$) hydrogen-bonds can be represented as

\begin{align}
    f_{\text{strong}} &= \frac{I_{\text{strong}}}{I_{\text{strong}} + I_{\text{medium}}}, \\
    f_{\text{medium}} &= \frac{I_{\text{medium}}}{I_{\text{strong}} + I_{\text{medium}}}.
\end{align}

Figure 6 plots the results of the concentration dependence of the $f_{\text{strong}}$ and $f_{\text{medium}}$ in the aqueous Et₄NCl solution together with that of the Et₄NBr solution. The differences in the intensity fraction between the higher and lower salt concentration region (e.g. $R$=6 and 20) in the aqueous Et₄NCl solution is smaller than that in the aqueous Et₄NBr solution. This result implies that the hydration structure in the aqueous Et₄NCl solution would not change drastically with the change in the concentration as compared to that in the aqueous Et₄NBr solution. This might be the anionic effect of Cl⁻ ion having a stronger structure-breaking property in the solutions[18].

4. Conclusions

We have shown the Raman spectral changes in the C₄N symmetric stretching and uncoupled OD stretching modes of the aqueous Et₄NCl solution as a function of pressure. The comparison of the results between the aqueous Et₄NCl and Et₄NBr solutions are made. The hydration structures are discussed in conjunction with the conformational equilibrium in the solution. An important implication is that the hydration volume due to the hydrophobic hydration around tt.tt conformer is larger than that around tg.tg conformer in the aqueous Et₄NCl solution. It is thus interesting to investigate the hydration structure of tetraalkylammonium fluoride (Et₄NF) having strong structure-making property [19]. This will be reported elsewhere.

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