A Revisit of the Conformational Stability of the Tetraethylammonium Ion in Water

by

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In this paper, we describe the conformational stability due to the local structural change of tetraethylammonium ion (abbreviated as EtN⁺) in water and alcohols. Our results indicated that the conformational stability of EtN⁺ has a close relation to the solvation of aqueous tetraalkylammonium salt (R₄NX) solutions. Furthermore, we discussed the relationship between the thermodynamic properties and microscopic information. We showed that the hydrophobic interactions and hydration are affected by the enthalpy and entropy differences of the EtN⁺ conformers in aqueous EtNX solutions, where the thermodynamic parameters of the conformers may be useful for explaining the changes.

Key words: Conformation, Tetraalkylammonium ion, Water, Raman spectroscopy, Hydrophobic hydration

1. Introduction

Numerous investigations have been conducted on the use of the tetraalkylammonium ion (abbreviated as R₄N⁺) as a model system for hydrophobic hydration and clathrate structures, via various experimental and theoretical methods, because of its good solubility in polar solvents, including water. It is considered that hydrophobic hydration plays a key role in the stabilization of proteins in aqueous media.

Another important feature of the tetraethylammonium ion (EtN⁺) is that it exists in conformational equilibrium between the trans-trans-trans-trans (tt.tt) and trans-gauche-trans-gauche (tg.tg) conformers, due to the intramolecular rotation of the Et-N⁻-Et axis in aqueous media (Fig. 1). Therefore, it would be a good idea to discuss the hydration structures along with the conformational equilibria of the EtN⁺ ion. In our preceding studies, we reported the results of the Raman spectral changes of aqueous EtNBr and EtNCl solutions, where hydrophobic hydration occurred in preference to the tt.tt conformer over the tg.tg conformer at a moderate concentration range (e.g., x = 19; x = moles of water/moles of EtN⁺ salt).

At this stage, it might be important to refer to literatures for creative discussions on these features. Here, we revisited our preceding research along with the recent studies in this area. In this review article, we describe the conformational stability of the EtN⁺ ion in water and alcohol solutions. Additionally, we discuss the relation between the thermodynamic properties and microscopic information. The present paper is organized as follows: Section 2 describes the calculation method of the difference in the partial molar enthalpy deduced from the conformational change in response to temperature variation. Sections 3 and 4 provide an overview of the results of the conformational stability of EtN⁺ (X = Cl and Br) aqueous solutions and a comparison of the conformational changes in water and alcohol solutions, respectively. Section 5 provides a summary of the results and the future outlook.

2. Estimation of the Partial Molar Enthalpy Difference Between the Conformers

The partial molar enthalpy difference (ΔHΔ→B) between the conformers (A and B) of a compound with internal rotation can be determined by the van’t Hoff equation using the equilibrium constant (K):

\[ \Delta H^\Delta \rightarrow B = -RT \ln K \],

where R, T, and p correspond to the universal gas constant, temperature, and pressure, respectively. When K is expressed as the concentration (c) of the conformers, Eq. 1 becomes

\[ \Delta H^\Delta \rightarrow B = -RT \ln (c_B/c_A) \],

In addition, the observed Raman scattering intensity (I) is proportional to the product of the concentration (c) and the Raman scattering cross-section (σ):

\[ I \propto c \sigma \].

Here, using Eq. (2) and (3), Eq. (1) can be expressed as
While that of the cases, the integrated intensity of the region of aqueous (a) Et₄NCl and (b) Et₄NBr solutions as a function of temperature, is consistent with that at 263 K through the quantum chemical calculations. Accordingly, the Et⁺ ion must be sufficiently hydrated at x = 20 despite that Et₄NX salts are sufficiently hydrated at x = 50. We, thus, analyze the response of the conformational change of the Et⁺ ion to the hydration state around the Et⁺ ion and that the differences in the hydration state are related to the conformational stability of the Et⁺ ion.

Kanno et al. proposed that the existence of the water tetrahedral structure is not essential for the “hydrophobic hydration” of R₄NX salts. In other words, high salt concentrations (low x value) also play an important role in the hydration. Therefore, it can be concluded that the tg.tg conformational preference at high salt concentrations is associated with the hydrophobic interactions between the ethyl groups due to the lack of sufficient water molecules for their hydration. However, we need to figure out why the –RT ln(\(I_{tt,tg}/I_{tg,tg}\)) values of both salts at x = 50 are very close to those at x = 20 despite that EtNX salts are sufficiently hydrated at x = 50. We, thus, analyze the response of the conformational change of the Et⁺ ion in the two different hydration environments, i.e., at x = 20 and 50.

Fig. 4 shows the Raman CH₃ rocking spectra of the aqueous (a) Et₄NCl and (b) Et₄NBr solutions (x = 20) at 263 K and 303 K. In both cases, the integrated intensity of the tt. tt conformer decreases, while that of the tg.tg conformer increases with increasing temperature. The response of the conformational equilibrium of the Et⁺ ion at x = 20, with respect to temperature, is consistent with that at x = 50, despite the difference in the hydration environment (data not shown).

Fig. 5 shows the changes in the ΔH°[^H₂O→–x] of the aqueous Et₄NCl and Et₄NBr solutions as a function of x. For the two salts, ΔH°[^H₂O→–x] showed negative values (-3.3 to -1.6 kJ/mol) as shown in Fig. 3. Assuming that the ratio of the scattering cross-section of the conformer (\(σ[^H₂O→–x]/σ[^H₂O→–x]\)) is independent of x, the value of –RT ln(\(I_{tt,tg}/I_{tg,tg}\)) would correspond to the change in the free energy difference between the conformers of the Et⁺ ion (ΔG°[^H₂O→–x]).

As shown in Fig. 3, the –RT ln(\(I_{tt,tg}/I_{tg,tg}\)) values decrease up to x = 20 for both salts, after which they remain almost constant until x = 50. This indicates that although the stability of the tg.tg conformer at a high salt concentration (x ~ 6) is higher than that of the tt. tt conformer, the difference in the conformational stability reduces with increasing water concentration, i.e., the stability of the tt. tt conformer increases as the water concentration increases. Here, the reported hydration number of the Et⁺ ion is in the range of 21–30.[2,13] Accordingly, the Et⁺ ion must be sufficiently hydrated at x = 50 but not below x = 20.

Comparing Et₄NCl and Et₄NBr, the absolute –RT ln(\(I_{tt,tg}/I_{tg,tg}\)) value of the latter is larger than that of the former throughout the x range. Our previous Raman OD stretching analysis showed that the changes in the water state as a function of x are larger in the aqueous Et₄NBr solution than in the aqueous Et₄NCl solution. These results indicate that the ionic radius (r) of the anions (rEt₄N > rPr₄N) influences the hydration state around the Et⁺ ion and that the differences in the hydration state are related to the conformational stability of the Et⁺ ion.

Fig. 2 shows the Raman spectral changes in the CH₃ rocking region of aqueous (a) Et₄NCl and (b) Et₄NBr solutions as a function of x, and their curve-fitted results. The peaks at ~895 cm⁻¹ and ~905 cm⁻¹ for the two salts are assigned to the tg.tg and tt. tt conformers of the EtN ion, respectively.[7,10] In both cases, the integrated intensity of the tt. tt conformer increases, while that of the tg.tg conformer decreases with increasing x (rise in the water concentration). To investigate the effect of the water concentration on the tt. tt – tg.tg equilibrium of the Et⁺ ion, –RT ln(\(I_{tt,tg}/I_{tg,tg}\)) was plotted as a function of x, as shown in Fig. 3. Assuming that the ratio of the scattering cross-section of the conformer (\(σ[^H₂O→–x]/σ[^H₂O→–x]\)) is independent of x, the value of –RT ln(\(I_{tt,tg}/I_{tg,tg}\)) would correspond to the change in the free energy difference between the conformers of the Et⁺ ion (ΔG°[^H₂O→–x]).

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Fig. 5 shows the changes in ΔH°[^H₂O→–x] (determined by the van’t Hoff plot [ln(\(I_{tt,tg}/I_{tg,tg}\)) vs 1/T]) of the aqueous Et₄NCl and Et₄NBr solutions as a function of x. For the two salts, ΔH°[^H₂O→–x] showed negative values (-3.3 to -1.6 kJ/mol).
throughout the x range. The obtained values are in good agreement with the results of n-pentane ($\Delta H_{\text{tv}} = -2.1 \pm 0.2$ kJ/mol).\(^{15}\) The thermal stability of the tt.tt conformer is higher than that of the tg.tg conformer for both salts; however, it decreases with x up to x = 20. Thereafter, it increases at x = 50.

To further investigate the changes in $\Delta H_{\text{gg}}$ with respect to x, $\Delta H_{\text{gg}}$ was decomposed into two terms according to the quantum chemical calculations\(^{15}\):

$$\Delta H_{\text{gg}} = \Delta E_{\text{gg}} + \Delta H_{\text{int}}$$

(6)

where $\Delta E_{\text{gg}}$ is the energy difference between the conformers in the isolated system, and $\Delta H_{\text{int}}$ is the energy difference between each conformer and the water molecules. Since the obtained $\Delta E_{\text{gg}}$ value was −3.4 kJ/mol\(^{18}\), the negative $\Delta H_{\text{gg}}$ value for both salts is mainly due to the contribution of $\Delta E_{\text{gg}}$. Moreover, the positive $\Delta H_{\text{int}}$ values with respect to x indicate that the interaction between the water molecules and the tg.tg conformer is enthalpically more stable than that with the tt.tt conformer, as shown in Fig. 5(b).

Naudin et al.\(^{7}\) analyzed 2.43 M (x = 22) aqueous Et$_4$NOH solutions, and their Raman results showed that $\Delta H_{\text{gg}}$ is −3.7 ± 0.5 kJ/mol. Using the $\Delta E_{\text{gg}}$ value, the $\Delta H_{\text{int}}$ value of the 2.43 M Et$_4$NOH solution is determined to be −0.3 kJ/mol, which is smaller than those of Et$_4$NCl and Et$_4$NBr at x = 20. Considering the hydration number of the Et$_4$N$^+$ ion, it can be suggested that the substantial hydration around the tt.tt and tg.tg conformers of aqueous Et$_4$NOH solutions caused the reduction in $\Delta H_{\text{int}}$. Comparing the results of Et$_4$NCl and Et$_4$NBr, the differences in their $\Delta H_{\text{int}}$ values below x = 20 can be explained by the change in the hydration state due to the influence of the anionic radii.

Using the thermodynamic relationship, $\Delta G = \Delta H - T \Delta S$, the subtraction of $-RT \ln(I_{\text{tv}}/I_{\text{tg}})$ from $\Delta H_{\text{tv}}$ corresponds to the entropy difference ($T \Delta S$) (Fig. 6). We find that the $\Delta H_{\text{tv}}$ values in both salts are negative throughout the x range. Although these absolute values tend to be small up to x = 20, the absolute values at x = 50 are larger than those at x = 20. Thus, it can be concluded that the anionic species (Cl$^-$ and Br$^-$) hardly affect the conformational stability of the Et$_4$N$^+$ ion at x = 20.

For the hydration of aqueous RtnX solutions at relatively low salt concentrations, the small-angle X-ray scattering and X-ray absorption results by Huang et al.\(^{17}\) showed that a crossover of the hydrophobic hydration occurs between Et$_4$N$^+$ and n-Pr$_4$N$^+$ ions. They also demonstrated that the Et$_4$N$^+$ ion in aqueous Et$_4$NBr solutions (~3 M) behave like small apolar solutes that are separated by water (solvent-separated state). Moreover, in the Fourier transform infrared (FTIR) spectra obtained by Plenizell and Stangret,\(^{19}\) a small enhancement of the absorption band intensity was observed in the OD stretching region, which was ascribed to the tetrahedral ice-like structure in the hydration shells of the Et$_4$N$^+$ ion. Accordingly, we considered that the water molecules around the Et$_4$N$^+$ ion in both salts at x = 50 undergo hydrophobic hydration. Since the $\Delta H_{\text{tv}}$ value of Et$_4$NBr at x = 50 is larger than that of Et$_4$NCl, the increase in the anionic radii induces the ordering of the hydration environment around the Et$_4$N$^+$ ion. From a classical viewpoint, it is known that the hydrophobic hydration arises from an ordering of the water structure around hydrophobic solutes (a negative entropy change)\(^{15}\). The slope of the $\Delta H_{\text{tv}}$ vs x plot is reversed at low salt concentrations (x = 50) for both salts, as shown in Fig. 6. The present results also reflect the influence of the hydrophobic hydration of aqueous Et$_4$NX solutions at x = 50. This may indicate that the hydrophobic hydration around
the Et3N+ ion contributes to the conformational stability; in other words, compared to the tg.tg conformer, the tt.tt conformer is favored for hydrophobic hydration.

The hydrophobic interactions and hydration process of aqueous $R_nNX$ solutions have been analyzed mainly by focusing on the changes in the macroscopic physical properties\textsuperscript{(1,3,19)}. Here, we investigated the hydrophobic interactions and hydration of aqueous Et4NX solutions by evaluating the cationic conformational changes and showed that the thermodynamic parameters of the conformers may be useful for explaining these changes. Our results indicated that the conformational stability due to the local structural change of Et4NX in aqueous solutions can be obtained from the information of the solvation of aqueous R$_n$NX solutions.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig6.png}
\caption{Changes in the values of $\Delta H^{\text{tg.tg} \rightarrow \text{tt.tt}} - RT\ln(I_{\text{tt.tt}}/I_{\text{tg.tg}})$ of Et4NCl (●) and Et4NBr (○) in aqueous solutions as a function of $x$.}
\end{figure}

\section{Conformational Changes of Et4NX (X = Cl and Br) in Water and Alcohols\textsuperscript{20}}

The hydrophobic hydration of R$_n$NX does not occur in alcohols. Thus, we can expect that the conformational stability of the Et3N+ ion in alcoholic solvents at low salt concentrations shows a different behavior as compared to the case in water.

Methanol (MeOH) is occasionally referred to as the “methyl-group substitution of water”; however, it is intriguing how the difference in the hydrogen bonding (H-bonding) between the water and alcohol solvents affects the conformational stability of the Et3N+ ion in the high salt concentration range. Hidaka and Kanno\textsuperscript{(21)} reported the Raman OD stretching spectra of R$_n$NCl ($R = \text{Me, Et, and } n-$Pr) in alcohols. The OD stretching frequency of alcoholic R$_n$NCl solutions shifts to higher values as compared to that of pure alcohols. This indicates that the H-bonding in alcohols becomes weaker if R$_n$NCl is dissolved. The same authors demonstrated that although the OD stretching spectral shape of deuterium oxide (D$_2$O) is similar to that of methanol-d (MeOD) solutions, the frequency in D$_2$O shifts to a lower value than that in MeOD, which indicates that the H-bonding in D$_2$O is stronger than that in MeOD.

Our previous Raman study reported the results of conformational changes of Et$_n$NCl in MeOD, EtOD, and n-PrOD with $x = 4$–20\textsuperscript{(20)}. We found that the population of the tt.tt conformer of the Et3N+ ion increases with increasing $x$ for three alcohols, while that of the tg.tg conformer decreases. This increase is independent of the alkyl-chain length of alcohols. Moreover, the $\Delta H^{\text{tg.tg} \rightarrow \text{tt.tt}}$ values indicate that the tt.tt conformer is enthalpically more stable than the tg.tg conformer throughout the $x$ range for the three alcohols. The absolute $\Delta H^{\text{tg.tg} \rightarrow \text{tt.tt}}$ values decrease with increasing $x$; the relationship between $x$ and $\Delta H^{\text{tg.tg} \rightarrow \text{tt.tt}}$ is independent of the alkyl-chain length of the alcohols. Remarkably, the conformational stability of the Et3N+ ion in three alcohols up to $x = 20$ is similar to that observed in water. Accordingly, the conformational thermodynamic stability of the Et3N+ ion at high salt concentrations is hardly related to the difference in the H-bonding between water and alcohols (i.e., the type of solvents).

\section{Summary and Future Outlook}

In this article, we reviewed the hydrophobic interactions and hydrophobic of aqueous Et4NX (X = Cl and Br) solutions from the viewpoint of conformational stability by Raman spectroscopy. We showed that the hydrophobic interactions and hydration are affected by the enthalpy and entropy differences of the Et3N+ conformers in aqueous Et4NX solutions. We showed that the analysis of the thermodynamic stability of microscopic structures, i.e., conformational equilibrium, can provide useful information on the hydrophobic interactions and hydration. Therefore, a combined study of the macroscopic properties and the thermodynamic stability of microscopic local structures is important for further understanding of the hydrophobic interactions and hydration.

In the field of materials science, R$_n$NX has been widely used for the hydrothermal synthesis of zeolites\textsuperscript{(22)}. The results presented here will provide basic information on the science of zeolites, e.g., the role of organic structure-directing agents.

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