RAMAN SPECTROSCOPIC STUDY OF HYDROPHOBIC HYDRATION OF ORGANIC MOLECULES IN AQUEOUS SOLUTION

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ABSTRACT. Raman spectra of several organic molecules which form hydrate clathrates have been measured in aqueous solution, and the hydration structure around those molecules has been investigated from the analysis of Raman linewidth data.

INTRODUCTION

It is now recognized that, when hydrocarbon molecules are dissolved in water, a structure like an "iceberg" may be formed around the solute molecules[1]. The structure resembles that of a gas hydrate where the gas molecule is encaged in a nearly spherical space formed by hydrogen bonded water molecules. Structures of various gas hydrates have so far been extensively investigated with X-ray diffraction techniques[2-4], but a study of the iceberg structures formed in solution is very difficult because of quite low solubilities of hydrocarbons in water. For this reason, spectra of hydrocarbon molecules in aqueous solution have been little reported so far, although experimental and theoretical investigations of the system from a thermodynamic viewpoint have frequently been presented in the literature.
        In this study, we succeeded in the observation of Raman spectra of benzene, cyclohexane and chloroform in aqueous solution. These molecules are known to form   hydrate clathrates of type $M \cdot 17H_2O$[2], and were selected because of their high solubilities in water, relative to other saturated hydrocarbons, and because of their strong Raman lines. It may be expected that the iceberg structure formed around the solute in aqueous solution affects the rotational motion of the solute molecule. Thus the rotational diffusion constants have been determined from the linewidths of the isotropic and anisotropic Raman spectra, and the effect of the iceberg structures on the rotational motion of the solute molecules is discussed from a comparison of the rotational diffusion constants in various solutions.
        Although we succeeded in the observation of Raman spectra for these hydrophobic organic molecules in aqueous solution, the Raman spectra were observed only for their saturated solutions, and their concentration

dependences could not be observed because of their quite low solubilities in water. It is of much interest to examine how the hydration structure changes on dilution. Thus, in order to investigate the concentration effect on the hydration structure in aqueous solution around solute molecules forming hydrate clathrates, we measured Raman linewidths of t-butyl alcohol and isopropyl alcohol in a variety of concentration of aqueous solution.

EXPERIMENTAL

Raman spectra were obtained with a Japan Spectroscopic Company model R800 laser Raman spectrophotometer and a Coherent Radiation model CR8 argon ion laser operating at 514.5 nm. Parallel $I_v(\nu)$ and perpendicular $I_h(\nu)$ polarized component spectra were recorded with a Glan-Thomson prism as an analyser, and the isotropic $I_\alpha(\nu)$ and anisotropic $I_\beta(\nu)$ component spectra were obtained using

$$I_\alpha(\nu)=I_v(\nu)-4/3 \cdot I_h(\nu), \tag{1}$$

$$I_\beta(\nu)=I_h(\nu). \tag{2}$$

Raman lines were measured at room temperature. The finite slit width effect on the observed Raman linewidth was corrected using

$$\delta_t=\delta_a[1-(S/\delta_a)^2], \tag{3}$$

where δ_t is the true (corrected) Raman linewidth (fwhh), δ_a the apparent (observed) Raman linewidth (fwhh), and S the spectral slit width[5].

The Raman lines for benzene, cyclohexane and chloroform in aqueous solution were measured for the saturated concentrations (ca. 0.04, 0.001, and 0.1 mol %, respectively), and solutions of the same concentrations were used for other reference solvents. In solutions of such low concentrations, parallel component spectra could be observed with a single scan because of rather high Raman intensities, but perpendicular component spectra could be obtained with 100 or more   accumulated scans because of extremely low Raman intensities.

The Raman lines for t-butyl alcohol and isopropyl alcohol were observed at a variety of concentration in aqueous solution and in nonpolar reference solvents. Cyclohexane was selected for the t-butyl alcohol band, and tetrachloroethylene   for the isopropyl alcohol band, because no specific intermolecular interaction might be present with the solute and because they do not disturb the Raman lines of the solute molecules.

RESULTS AND DISCUSSION

1. Benzene, cyclohexane and chloroform

The Raman lines at 991, 802 and 2251 cm^{-1} were observed for benzene,

cyclohexane and chloroform-d, respectively in aqueous solution and in reference solution. For the analysis of the rotational motion of the solute molecules, the rotational diffusion constant D_x was evaluated from the isotropic δ_α and anisotropic δ_β Raman linewidths (fwhh), using

$$D_x = \pi c (\delta_\beta - \delta_\alpha)/6. \tag{4}$$

The vibrational modes of the Raman lines used in this experiment belong to the totally symmetric species, so that the rotational diffusion constant obtained from their Raman linewidths is for the rotational motion (tumbling motion) of the solute molecule around the x axis perpendicular to the molecular z axis. Figs. 1-3 show the rotational diffusion constants obtained for benzene, cyclohexane and chloroform-d in aqueous solution and reference solution, plotted against the reciprocal viscosity of the solvent.

For the three solutes, D_x's obtained for the solutions other than aqueous solution fall on the straight lines, but D_x in aqueous solution deviates from the lines: below the lines for benzene and cyclohexane, while above the line for chloroform. This indicates that the rotational motion of benzene or cyclohexane molecules are hindered more than would be predicted from the viscosity effect and that the motion of chloroform is enhanced in aqueous solution. It is clear that other factors such as the dielectric constant cannot explain the deviation of D_x's in aqueous solution: all the solvents used are similar to each other in the solvent effect on spectroscopic properties. These facts suggest that the deviation of D_x's in aqueous solution could be attributed to the iceberg structures formed around the solute molecules.
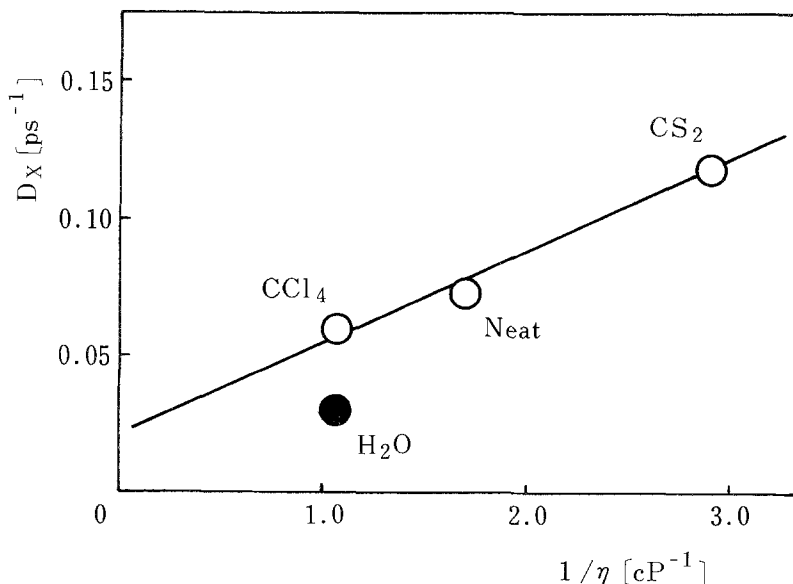

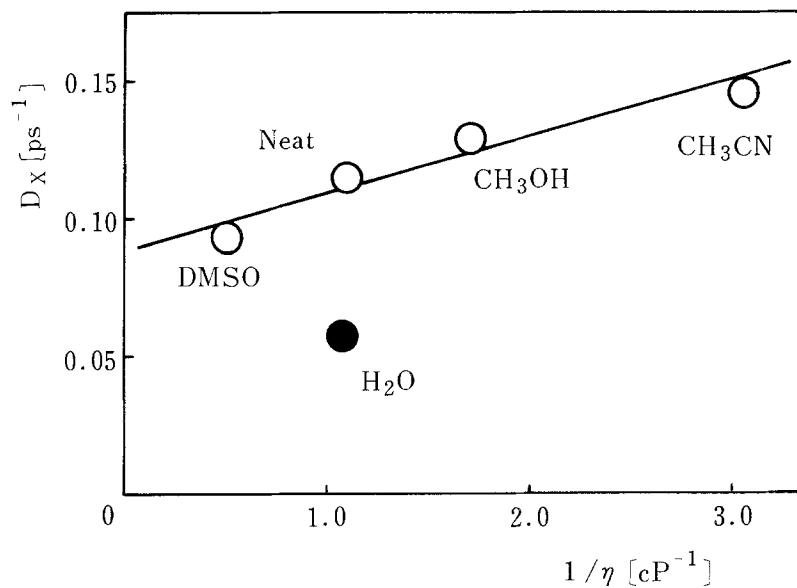Figure 1. Rotational diffusion constants of benzene.

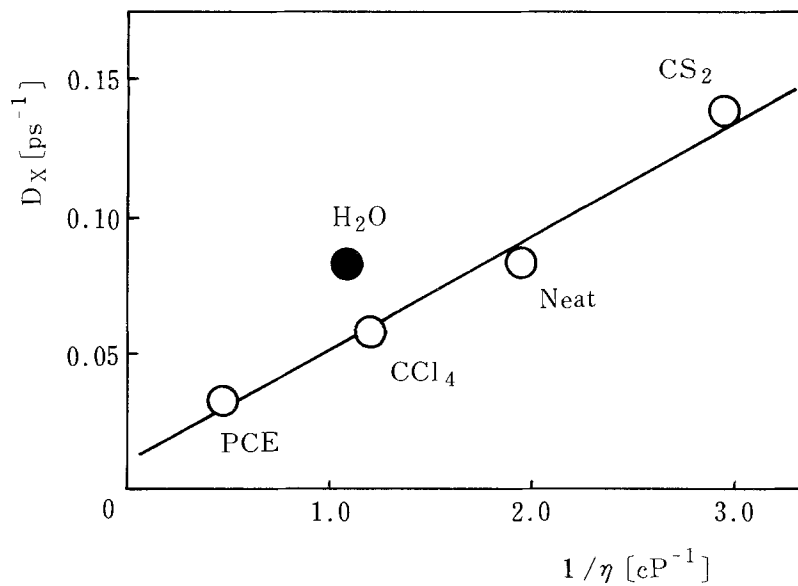Figure 2. Rotational diffusion constants of cyclohexane. DMSO is dimethyl sulfoxide.

Figure 3. Rotational diffusion constants of chloroform-d. PCE is pentachloroethane.

It is now known that various molecules form gas hydrates, and the structures of   gas hydrates have been investigated with X-ray diffraction techniques[2-4].   Benzene, cyclohexane and chloroform treated here are also known to form   hydrate clathrates of type $M \cdot 17H_2O$[2], where the solute molecule M is encaged in a nearly spherical space of diameter 6.6 Å.   On the other hand, the largest diameters of these molecules are 6.9, 6.9 and 6.4 Å, respectively.   Thus, the deviation of D_X's in aqueous solution as shown in Figs. 1-3 could be explained by considering that these organic molecules in aqueous solution are also encaged in a space of the same diameter.   This means that the hydration structure around the solute molecules in aqueous solution is similar to the crystal structure of the hydrate clathrates.

2.   t-Butyl alcohol and isopropyl alcohol

Figs. 4-5 show the isotropic Raman linewidths of t-butyl alcohol and isopropyl alcohol in aqueous solution and in nonpolar reference solvent, measured at a variety of concentrations. At first, the concentration dependence of the linewidths in nonpolar solvents is considered here.
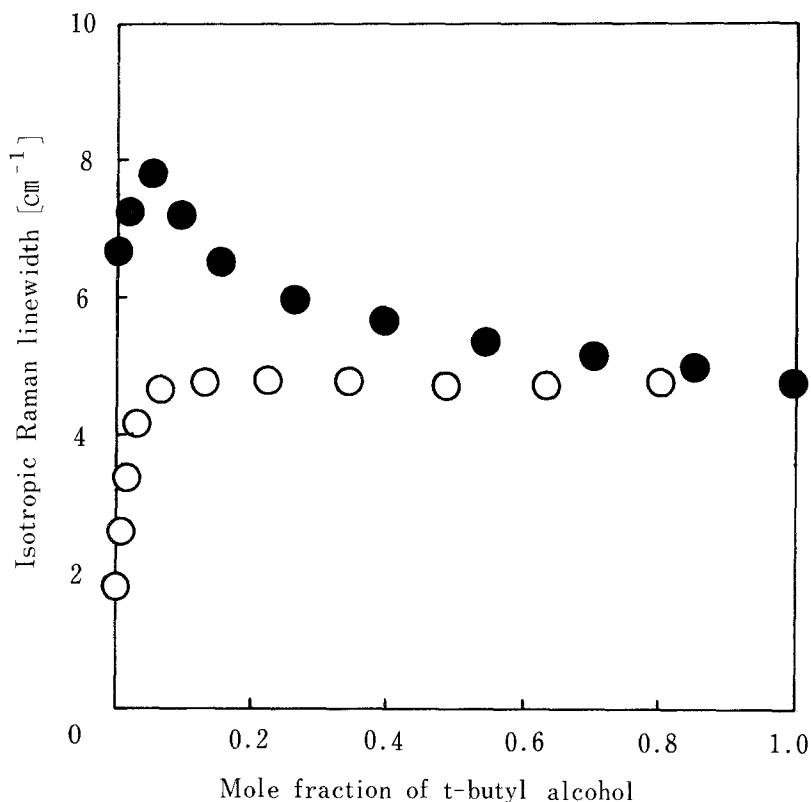

Figure 4.   Isotropic Raman linewidths of t-butyl alcohol in aqueous solution (closed circle) and in cyclohexane solution (open circle).
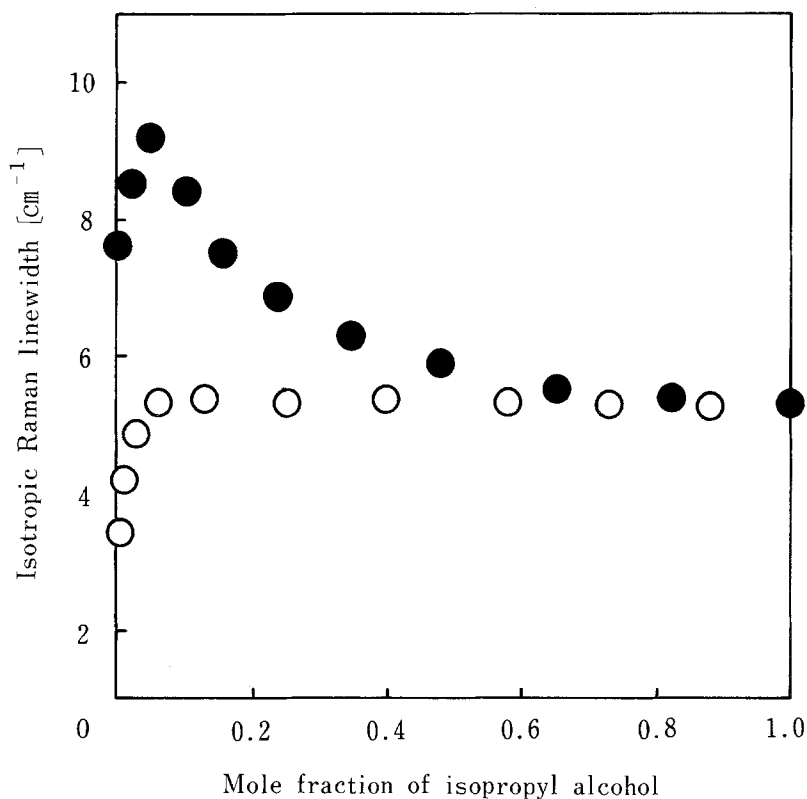
Figure 5. Isotropic Raman linewidths of isopropyl alcohol in aqueous solution (closed circle) and in tetrachloroethylene solution (open circle).

In nonpolar solvents, the Raman linewidths are almost constant in the concentration range between 0.05 and 1.0 mole fraction , while, on dilution from 0.05 mole fraction, the linewidths decrease remarkably. Such a behavior of the linewidths in nonpolar solvents suggests that the isotropic linewidth of the Raman line reflects the content of hydrogen bonded solute molecules: the larger the number of hydrogen bonded alcohol molecules   , the larger the observed isotropic Raman linewidth is. This may be reasonable because the vibrational modes of the Raman lines (at 753 and 818 cm^{-1} for t-butyl alcohol and isopropyl alcohol, respectively) are nearly assigned to the C-O stretching vibrations of the alcohol molecules.

    Based on this idea, the concentration dependence of the isotropic Raman linewidths as shown in Figs. 4-5 suggests that the content of hydrogen bonded alcohol molecules is   largest around 0.05 mole fraction. It is of much interest to note that the concentration of the largest Raman linewidths is quite close to the mole fraction of the solute molecules in the hydrate clathrates of type $M \cdot 17H_2O$. t-Butyl alcohol and isopropyl alcohol are known to form   hydrate clathrates

[6], irrespective of the hydrophilic nature of the hydroxyl group. From these facts, it may be reasonably considered that the hydration structure around the alcohol molecules in aqueous solution is similar to the crystal structure of the hydrate clathrates. That is, around 0.05 mole fraction in aqueous solution, alcohol molecules are encaged in so limited spaces that the content of hydrogen bonded molecules is the largest, giving rise to the largest isotropic Raman linewidths.

SUMMARY

In this study, Raman spectra of several organic molecules have been measured in aqueous solution, and their linewidths have been analysed. As a result, it is concluded that the hydration structure like the crystal structure of the hydrate clathrate is formed around the solute molecules in aqueous solution. The results obtained in this study indicate that the Raman linewidth well reflects the hydration structure of organic molecules in aqueous solution.

REFERENCES
[1] H.S.Frank and W.M.Evans, J.Chem.Phys. 13, 507 (1945).
[2] M.von Stackelberg and H.R.Muller, Z.Elektrochem. 24, 133 (1957).
[3] D.W.Davidson, Water, ed. by F.Franks, 2, 115 (1973), Plenum, New-York.
[4] D.W.Davidson and J.A.Ripmeester, J.Glaciol. 21, 33 (1978).
[5] K.Tanabe and J.Hiraishi, Spectrochim.Acta 36A, 341 (1980).
[6] D.N.Glew, H.D.Mak and N.S.Rath, Hydrogen-bonded Solvent Systems, p.195 (edited by A.K.Covington and P.Jones), Taylor & Francis, London (1968).