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Raman Spectral Change of Crown Ethers and Related Polyethylene Glycol Dialkyl Ethers Due to Accommodation of Water

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Raman spectra of crown ethers and related polyethylene glycol dialkyl ethers in solutions were measured. The spectra showed remarkable characteristics, which are interpreted to be due to accommodation of water. Conformations of the crowns and the ethers accommodating water are similar to those in their complexes with cations.

Raman spectral change due to complex formation of crowns with cations was found for the first time by Sato and Kusumoto[1)] and by Fouassier and Lassegues[2)] and then by Khanna and Stranz[3)] and by Hilliard et al.[4)] Recently, Takeuchi et al.[5)] carried out structure determination of the complexes of 15-crown-5 and 18-crown-6 with cations in solutions by Raman and IR measurements and normal vibration calculation, while Fukushima and Tamaki[6)] studied structure of the complexes of 12-crown-4 with cations in solutions by Raman spectroscopy and normal vibration calculation. On the other hand, Kasatani and Sato[7)] reported the Raman spectral change due to complex formation of polyethylene glycols with cations. Although solutions were treated in some of these studies, no special attention was paid to interaction of the crowns or the glycols with solvents. In the present study, we measured Raman spectra of crowns and related polyethylene glycol dialkyl ethers in solutions with a JASCO Model R800-T Raman Spectrometer using 514.5 nm line of Ar^+ laser, and found remarkable change of Raman spectra of the crowns and the ethers due to interaction with water, as described below.

In the previous work,[6)] the respective Raman spectra of 12-crown-4 in benzene, chloroform, methanol, acetonitrile, and water solutions showed no remarkable change with one another other than the change of relative intensities of some bands associated with the change of dielectric constant of solvents. On the other hand, as shown in Fig. 1, the bands of pure liquid of diethylene glycol diethyl ether at 276 and 837 cm^{-1} (Fig. 1(A)) remarkably decrease their intensities for aqueous solution (Fig. 1(C)) and two bands appear at 315 and 854 cm^{-1} (Fig. 1(C)). The spectrum of the aqueous solution resembles those of complexes of the ether with cations (refer to Fig. 1(D) as an example). The characteristic feature for aqueous solution may be interpreted as follows. The cavity in 12-crown-4 is too small to accommodate a water molecule, while diethylene glycol diethyl ether molecule, though it is not a cyclic molecule, can capture a water molecule or molecules by taking the conformation similar to those in its cation complexes.

As shown in Fig. 2, Raman spectrum of pure liquid of 15-crown-5 (Fig. 2(A)) is not much different from that of methanol solution (Fig. 2(B)). However, for aqueous solution, as shown in Fig. 2(C), intensities of the bands of pure liquid of 15-crown-5 at 319 and 825 cm^{-1} decrease and two bands appear at 338 and 848 cm^{-1} (Fig. 2(C)). The spectrum of aqueous solution is similar to those characteristic to the complexes of 15-crown-5 with cations.[5] Similar to the case of 15-crown-5, the bands at 304 and 857 cm^{-1} of tetraethylene glycol dimethyl ether in water (Fig. 3(C)) have frequencies different from those

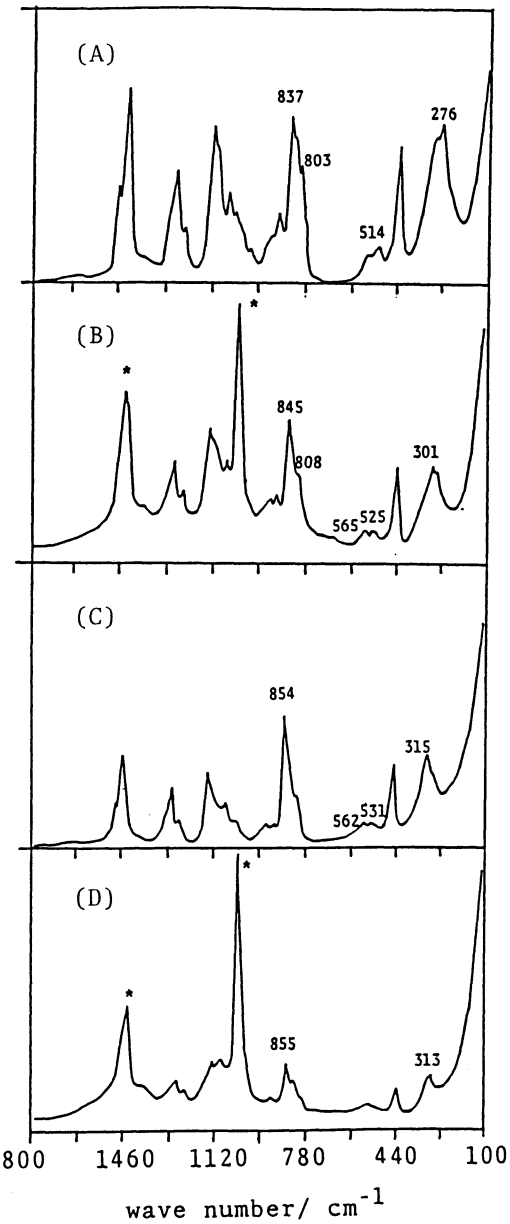

Fig. 1. Raman spectra of diethylene glycol diethyl ether (parallel spectra).
(A)pure liquid (B)methanol solution(x=0.228) (C)aqueous solution (x=0.078) (D)methanol solution with sodium bromide(x=0.058, y=0.058); x, mole fraction of ether; y, mole fraction of sodium bromide. * methanol band

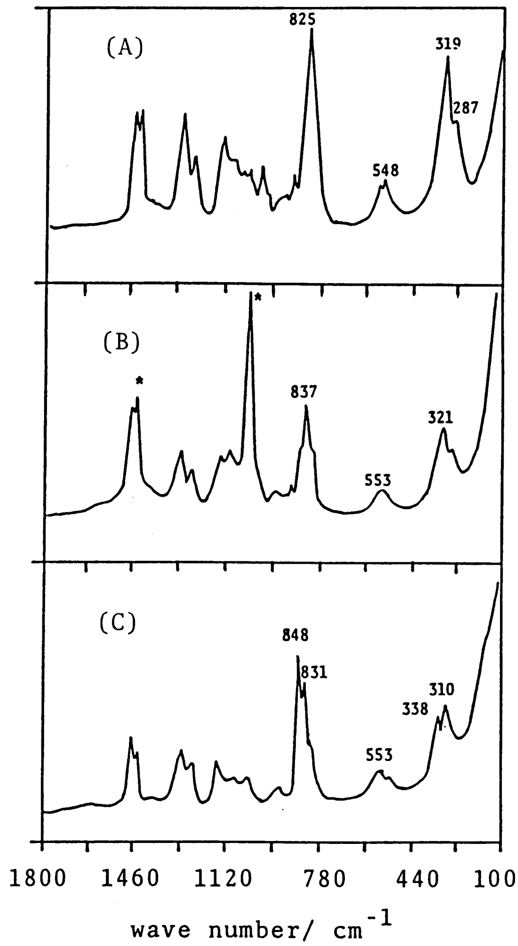

Fig. 2. Raman spectra of 15-crown-5 (parallel spectra).
(A)pure liquid (B)methanol solution (x=0.126) (C)aqueous solution (x=0.036); x, mole fraction of crown.
* methanol band

Samples:

Crowns...products of Aldrich Chemical Co., Inc.

Ethers...products of Tokyo Kasei Kogyo Co. (GR grade).

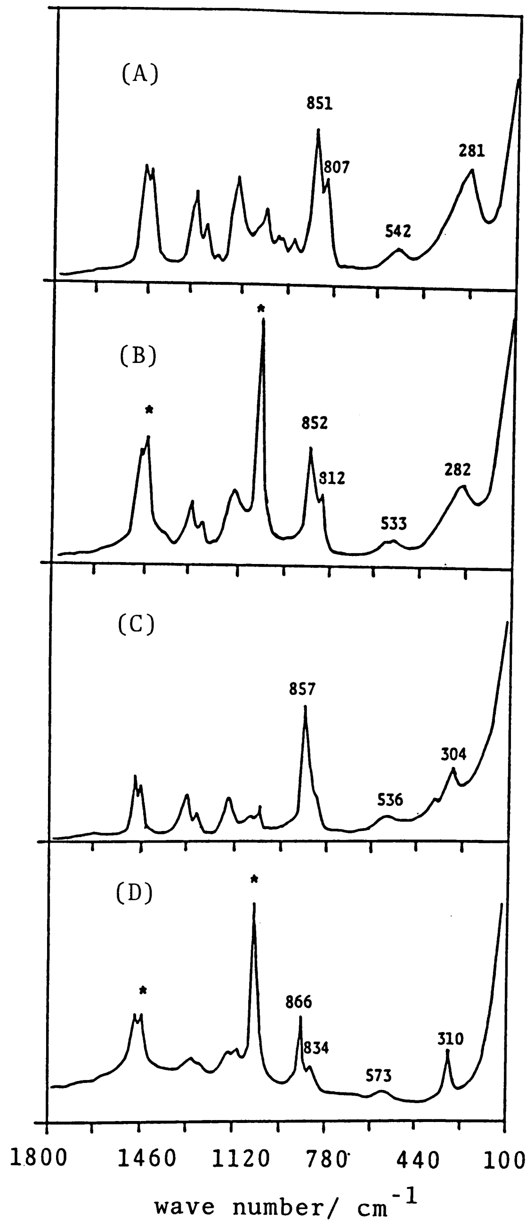

Fig. 3. Raman spectra of tetraethylene glycol dimethyl ether (parallel spectra).
(A)pure liquid (B)methanol solution(x=0.142) (C)aqueous solution (x=0.035) (D)methanol solution with sodium bromide(x=0.048, y=0.051); x, mole fraction of ether; y, mole fraction of sodium bromide. * methanol band

of the bands of pure liquid of the ether (281 and 851 cm^{-1}, Fig. 3(A)), although the spectrum of methanol solution (Fig. 3(B)) is almost the same as that of pure liquid. In addition, the spectrum of aqueous solution is similar to those of the complexes of the ether with cations (refer to Fig. 3(D) as an example).

Takeuchi et al.[5] measured spectra of methanol solutions of 18-crown-6, and obtained the spectrum for low temperature, which is similar to those of 18-crown-6-cation complexes. This resemblance suggests accommodation of methanol. We found that spectra of aqueous solutions of 18-crown-6 resemble those of 18-crown-6-cation complexes even at room temperature,[8] which suggests that 18-crown-6 has a conformation similar to those of 18-crown-6-cation complexes in the solutions.

As described above, remarkable Raman spectral feature was found for aqueous solutions of crown ethers and related polyethylene glycol dialkyl ethers. These characteristics are interpreted to be due to accommodation of water into the molecules. The molecules accommodating water have conformations similar to those of their cation complexes. This conformational change by accommodation of water is consistent with the theoretical works,[9-11] which conclude a conformation having D_{3d} symmetry for 18-crown-6 accommodating water molecules.

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