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Hydration of Cyclic Oligo(oxyethylene) Compounds. Ultrasonic Velocities and Compressibilities of Binary Systems of Water with 12-Crown-4, 15-Crown-5, and 18-Crown-6

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Synopsis. Ultrasonic velocities of binary systems of water with 12-crown-4, 15-crown-5, and 18-crown-6 were measured and the adiabatic compressibilities were evaluated therefrom. The results indicate that the most compacted hydration structure is formed at the mole ratio, approximately 2:1, of water to oxyethylene monomer unit and that the poly(oxyethylene) chain enhances structuring of the liquid water network.

Structure of aqueous solutions of poly(oxyethylene) (POE) chains, $(-OCH_2CH_2-)_m$, is one of the important subjects in the fields not only of polymer chemistry but also of surface and colloid science, since the structural aspect of this chain is closely related to the size and shape of the micelles and the phase behavior of a number of nonionic surfactants that contain the POE chain as a hydrophilic moiety.[1] Kjellander and Florin[2] have previously discussed possible structure models for POE–water systems and indicated that water molecules form a highly linked network allowing the hydrocarbon groups to be reasonably encaged. In such a water network, hydrogen bonding between water molecules and ether oxygens of the POE chain plays an important role in forming the stable structure. Thus the hydration of the POE chain is a fundamental factor for understanding the network structure and its stability.

In an earlier study,[3] we have investigated the hydration of short model compounds of POE, namely $CH_3(OCH_2CH_2)_mOCH_3$ (m=1—4) and $CH_3(OCH_2CH_2)_m$-OH (m=2 and 3), by measuring hypersonic velocities in aqueous solutions of these compounds. This study showed that a specific hydration complex of approximately $2(H_2O):1(OCH_2CH_2)$ is formed, in agreement with the results by different experimental methods.[2,4] In the present work, we have extended the hydration study of the POE chain to cyclic oligo(oxyethylene) compounds, i.e., 1,4,7,10-tetraoxacyclododecane (12-crown-4), 1,4,7,10,13-pentaoxacyclopentadecane (15-crown-5), and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6). In evaluating extent of hydration of the POE chain, the complexity arising from an effect of terminal groups is absent in these cyclic compounds, though there may be a possible steric effect associated with the limited conformational freedom of the ring molecules.

Experimental

The ultrasonic velocities in binary systems of water with 12-crown-4, 15-crown-5, and 18-crown-6 with various compositions were measured at 20.0±0.01 °C by the sing-around method with a model UVM-2 of Choompa Kogyo Co. at a frequency of 2 MHz. The densities of the solutions were also measured in order to evaluate the adiabatic compressibilities.

Results and Discussion

The adiabatic compressibilities, κ_S, were obtained by the relation

$$\kappa_S = 1/(\rho v^2), \qquad (1)$$

where ρ is the density and v is the sound velocity in the binary mixtures. The adiabatic compressibilities obtained this way for the systems of water with the three crown ethers are shown in Fig. 1. The deviations, to be denoted by $\Delta\kappa_S$, of the observed κ_S values of the mixtures from the values based on the mole-fraction mixture law are given by

$$\Delta\kappa_S = \kappa_S - (x_1\kappa_{S1} + x_2\kappa_{S2}), \qquad (2)$$

where κ_S is the observed adiabatic compressibility of the binary mixture, x_1 and x_2 are the mole fractions of the components 1 and 2 in the mixture, and κ_{S1} and κ_{S2} are the adiabatic compressibilities of the two pure components.

According to Fig. 1, the deviations $\Delta\kappa_S$ are always negative for the three systems, indicating that specific interactions exist between water molecules and POE chains. It is therefore highly suggestive of the formation of the intermolecular complexes between the crown ethers and water. The POE chain thus promotes structuring of the water network by forming hydrogen bonds between the ether oxygens and water. This implies that the ether oxygens of the POE chain are constituents of the structured water network. The close fit of the POE chain into the water lattice is geometrically favorable, since the closest oxygen–oxygen distance (0.28—0.30 nm) of POE[5] and 18-crown-6[6] with the gauche($O-CH_2-CH_2-O$) conformation is coincident with the oxygen–oxygen distance (0.285 nm) of liquid water at 25 °C.[7] Our conformational studies of POE[8] and 18-crown-6[9] have in fact indicated that these molecules in aqueous solutions much more prefer the gauche($O-CH_2-CH_2-O$) conformation with more dilution with water than the trans conformation. This consideration strongly suggests the effective incorporation of the ether oxygens of the POE chain into the structured water network around the chain. The hydrophobic CH_2CH_2 groups of the POE chain then fill out the interstitial voids of the

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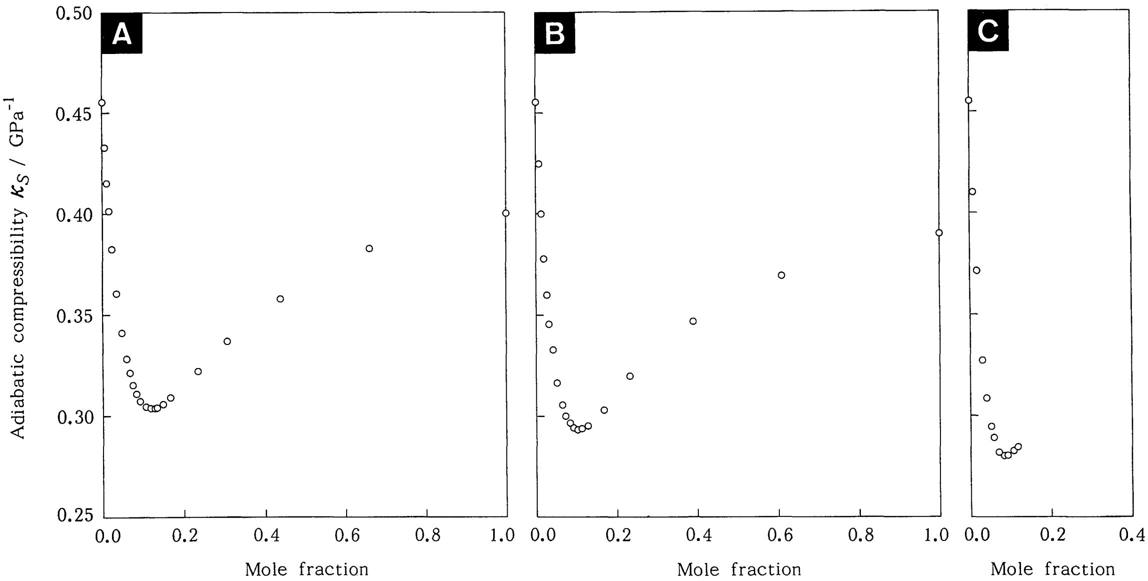

Fig. 1. Adiabatic compressibilities of the binary systems; A: water–12-crown-4, B: water–15-crown-5, and C: water–18-crown-6. Mole fraction for abscissa implies that of the crown ether. Since the water–18-crown-6 system with a large fraction of 18-crown-6 is solid at 20°C, no measurements were possible of the compressibilities in the liquid state for high concentrations.

water network, resulting in the formation of more compacted structure than the liquid structure of pure water or of the oxyethylene compounds. The observed negative values of $\Delta\kappa_S$ are thus elucidated by a model of the structured water network with the hydrophobic groups encaged.[2]

Figure 1 indicates that the absolute values of $\Delta\kappa_S$ are the largest at mole fractions of 0.113 for 12-crown-4, 0.095 for 15-crown-5, and 0.082 for 18-crown-6; the corresponding mole ratios of water to crown ether and those converted to water to oxyethylene monomer unit are shown in Table 1. The present experimental findings indicate that the most compacted hydration structure is formed at the mole ratio of approximately $2(H_2O):1(OCH_2CH_2)$ between water and the POE chain. For the compositions with more water molecules than this, the compressibility of the whole liquid mixture is increased owing to the structure of the excess bulk water, which contains a large fraction of interstitial space.[7] In more concentrated solutions than the mole ratio 2:1, on the other hand, the highly structured water network is partially broken with insufficient proton donors available to the ether oxygens of the POE chain.[2] The number of water molecules per oxyethylene unit for the most compacted hydration structure is essentially the same for the three crown ethers irrespective of the size of the POE ring. It is suggested therefore that a possible steric effect on the hydration arising from the limited conformational freedom of the ring molecule is substantially negligible.

Table 1. Mole Ratios, at Which the Absolute Values of $\Delta\kappa_S$ are the Largest, for the Binary Systems of Water with 12-Crown-4, 15-Crown-5, and 18-Crown-6

Binary system	Mole ratios	
	H_2O:Crown ether	$H_2O:OCH_2CH_2$[a]
Water–12-crown-4	7.8:1	1.96:1
Water–15-crown-5	9.5:1	1.91:1
Water–18-crown-6	11.2:1	1.87:1

a) The estimated uncertainty in the number of water molecules per oxyethylene unit is ±0.1.

The present work has indicated that the interstitial space of the water network is filled completely with the hydrophobic group of the POE chain with two water molecules per oxyethylene monomer unit. This result is consistent with the generally accepted hydration structure of the POE chain with two water molecules per oxyethylene unit.[2–4] A previous NMR study[10] showed, however, that three molecules of water were required for the hydration of each oxyethylene unit, but a later reexamination[4] has pointed out that the number of water molecules per oxyethylene unit is actually close to two instead of three. A recent infrared study[11] has indicated the presence of three different hydration complexes with water to oxyethylene mole ratios of 4:1, 2:1, and 1:1. The present and previous[3] studies on the cyclic and open-chain oligo(oxyethylene) compounds have demonstrated that, of these possible complexes, the 2:1 complex gives rise to the least compressible or the most elastic structure with the oxyethylene ether oxygens incorporated into the water lattice. In conclusion, the POE chain, whether it is cyclic or open-chain, enhances structuring of the liquid water network.

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