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THE STUDY OF WATER STRUCTURE IN AQUEOUS SOLUTIONS OF BUTOXYETHANOL BY ENTHALPY OF MIXING MEASUREMENTS

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Abstract

In order to confirm the existence of regions I and II in aqueous solutions of butoxyethanol (BE), the concentration and temperature dependences of enthalpies of mixing of aqueous BE solutions with some organic solvents were measured. It has been found that the increments of apparent enthalpies of mixing per mole of water with respect to the mole fraction of BE change irregularly at a certain concentration. This concentration nearly corresponds to the reported boundary between regions I and II. Although similar behavior has also been observed in aqueous solutions of *iso*-butoxyethanol, aqueous solutions of *tert*-butoxyethanol have shown no anomalous behaviors.

Keywords: aqueous solutions of butoxyethanol, enthalpies of mixing, water structure

Introduction

Recently, Koga and his co-workers have reported that [1–7] there exists a boundary separating regions I and II in a temperature-concentration phase diagram of a *n*-butoxyethanol+water binary system. This boundary was determined by connecting the loci of peak anomalies in third-order derivatives of Gibbs free energy, such as the composition derivative of the excess partial molar enthalpy [2] and the temperature derivative of heat capacity [7]. For example, at 25°C, the concentration which separates region I (water-rich region) and region II is reported to be around X=0.02 (X is the mole fraction of *n*-butoxyethanol).

Generally, we can easily expect that, in a water rich region (region I), the hydrogen-bonded water network structure around a hydrophobic molecule can be constructed as strongly as possible if a hydrophobic molecule has a suitable size and shape. In region II, the formation of stable water structure around a hydrophobic molecule becomes difficult because of the lack of the amount of water molecules. Furthermore, in a single-phase homogeneous solution, the change of water structure around a hydrophobic molecule with increasing its concentration may be expected to be a continuous phenomenon. Then, various properties reflecting the water-structure change will also be expected to be monotonous with increasing the concentration. Thus, we may say that the existence of a boundary between regions I and II as re-

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ported for aqueous solutions of butoxyethanol is not always a general behavior. There seems to be some conditions on a hydrophobic molecule for the presence of such a boundary.

In this study, in order to confirm the presence of this mixing scheme boundary from an entirely different point of view, the concentration dependences of the enthalpy of mixing of a small amount of aqueous butoxyethanol solution with relatively large amount of some organic solvents were measured.

Similar measurements were also made for other isomeric butoxyethanol solutions in order to know whether the appearance of such a boundary is limited only to an aqueous solution of *n*-butoxyethanol or not.

Experimental

Three kinds of butoxyethanol (*n*-butoxyethanol, *iso*-butoxyethanol, and *tert*-butoxyethanol) were purchased from Tokyo Kasei Kogyo Co., Ltd. and were purified by vacuum distillation just before use. Hereafter, we denote these three types of butoxyethanol, *n*-BE, *i*-BE and *t*-BE, respectively.

In order to discuss the behavior of water molecules within the BE solution and to determine the experimental conditions, such as temperature and the concentration of BE, liquid–liquid phase diagrams of the binary system of BE with water were examined by a following manner. A sample solution (about 1.0 g) of known concentration of BE was prepared by weighing out water and BE; it was then sealed in a small glass ampoule. After that, the ampoule was slowly warmed or cooled, at a rate of about 0.5 K min^{-1}, with shaking in a constant-temperature bath; the temperatures at which two liquid phases appeared or disappeared were accurately determined.

The enthalpies of mixing were measured when a small amount (about 0.2 g) of aqueous solutions of each BE was mixed with a large amount (25 ml) of an organic solvent (either acetone or 1,4-dioxane). These enthalpies of mixing were measured as a function of the concentration of initial BE solution (X=0–0.04, X is the mole fraction of BE) and of the temperature (15, 50°C). The calorimeter used was a twin-type conduction calorimeter manufactured by Tokyo Riko (TCC-21). Each aqueous solution of BE, sealed in a glass ampoule, was mixed with an organic solvent after the temperature of the whole system was reached constant. An ampoule containing 0.2 g of the solvent was used as a reference. The measured values of the enthalpies of mixing may be in error by as much as 4% at worst. The results shown in the following figures are averages of five or six measurements.

In this experiment, in the final solutions after mixing, the number of moles of organic solvent extends 31–39 times that of water in the acetone mixture and 26–34 times in the 1,4-dioxane mixture. Thus, we may assume that there will be no specific, organized water structure in the final solution after mixing. In other words, the concentration dependence of the observed enthalpies of mixing will reflect the concentration dependence of the state of water structure in the initial aqueous solutions of BE.

Results

Liquid–liquid phase diagrams of the BE+water binary systems are shown in Fig. 1. Liquid–liquid phase equilibrium appears in both *n*-BE+water and *i*-BE+water systems. For the *t*-BE+water system, liquid–liquid phase separation does not occur at least in the temperature range below 140°C. The critical solution temperatures and critical compositions were found to be 129.0°C, X=0.071; 47.5°C, X=0.059 for the *n*-BE+water binary systems. These values are almost identical with those already reported [8, 9]. The liquid–liquid phase diagram for the *i*-BE+water system was determined for the first time. The lower critical solution temperature and critical composition were found to be 25.3°C, X=0.070 and the upper critical solution temperature was higher than 140°C for the *i*-BE+water binary system. It is interesting to note that the two liquid region of the *i*-BE+water system extends over wider temperature-concentration range than that in the *n*-BE+water system. The reported boundary which separates regions I and II in the aqueous solution of *n*-BE is also shown in Fig. 1 by a dotted line [7]. It should be noted that the region of liquid–liquid equilibrium appears within region II. The solid line which starts at 0°C indicates the freezing-point depression curve of ice I for both *n*-BE+water and *i*-BE+water systems.

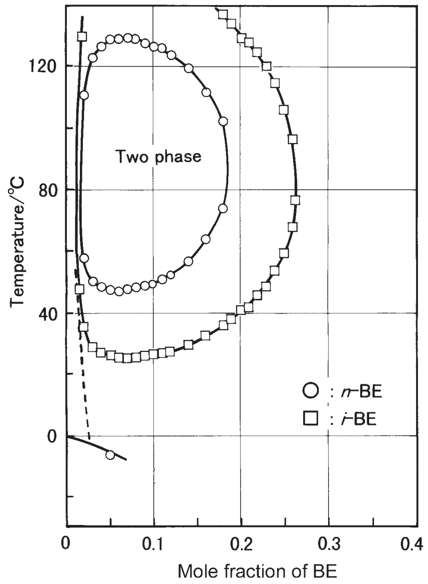

Fig. 1 Phase diagrams for *n*-BE+water and *i*-BE+water systems. The reported boundary which separates regions I and II in the aqueous solution of *n*-BE is also shown in this figure by a dotted line [7]

The results of enthalpies of mixing experiments are shown in Fig. 2 for *n*-BE aqueous solution+acetone and *n*-BE aqueous solution+1,4-dioxane systems at 15°C. The ordinate represents an apparent enthalpy of mixing per mole of water ($\Delta H_{mix}/n_w$, where ΔH_{mix} is enthalpy change observed and n_w is the number of moles of water) and the abscissa represents the concentration of the initial BE solution expressed in mole fraction. Figure 2 clearly indicates that, although the values of $\Delta H_{mix}/n_w$ increase with increasing the *n*-BE concentration (X), the increments of $\Delta H_{mix}/n_w$ with respect to X become smaller at around X=0.02. This behavior is found not only in the *n*-BE+acetone system but also in the *n*-BE+1,4-dioxane system. This fact suggests that the appearance of this irregular behavior is independent of the type of organic solvents used. However, we cannot get a definite conclusion, because we cannot carry out the same type of experiments by using non-polar solvents due to low solubility of water in these solvents. It is interesting to note that the mole fraction X=0.02 at 15°C nearly corresponds to the concentration of the reported boundary between regions I and II [6, 7] in aqueous solutions of *n*-BE. Thus, we may conclude that the results shown in Fig. 2 are strong evidences in support of the existence of such kind of boundary. Relatively large increments of $\Delta H_{mix}/n_w$ with respect to X in the concentration range between 0–0.02 are due to large endothermic heat change which is necessary to destroy stable cage-like structure of water molecules around the BE molecule. Similarly, relatively small increments of $\Delta H_{mix}/n_w$ with respect to X in the concentration range X≥0.02 will be explained by small endothermic heat in order to destroy unstable water structure around the BE molecule.

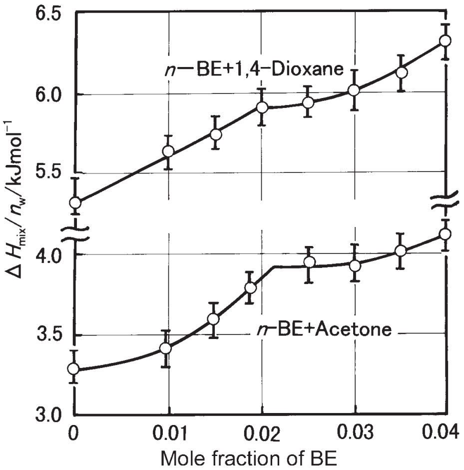

Fig. 2 The apparent enthalpies of mixing per one mole of water as a function of the moles fraction of BE in the initial aqueous solutions for *n*-BE aqueous solution+acetone and for *n*-BE aqueous solution+1,4-dioxane systems

Similar plots for the *n*-BE+1,4-dioxane system at different temperatures (15, 50°C) are shown in Fig. 3. The data at 15°C is the same as shown in Fig. 2. The results in Fig. 3 clearly indicate that the concentration at which the slope $\Delta H_{mix}/n_w$ *vs*. X changes decreases with increasing temperature: it becomes X=0.012 at 50°C. The concentration X=0.012 at 50°C also corresponds to the reported boundary between

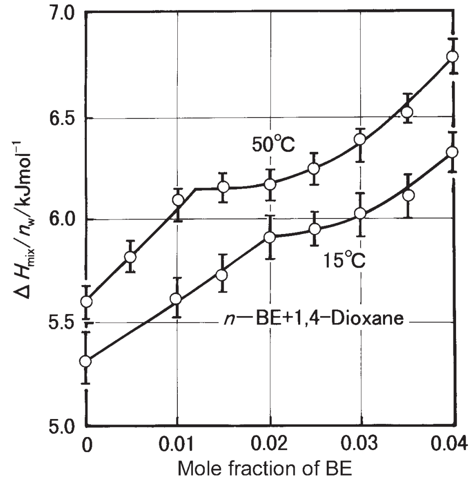

Fig. 3 The apparent enthalpies of mixing per one mole of water for *n*-BE aqueous solution+1,4-dioxane systems at different temperatures (15, 50°C)

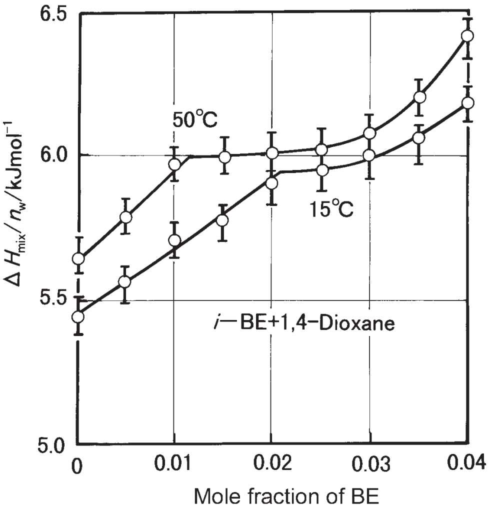

Fig. 4 The apparent enthalpies of mixing per one mole of water for *i*-BE aqueous solution+1,4-dioxane systems at different temperatures (15, 50°C)

regions I and II, showing another evidence in support of the existence of such a boundary.

In Fig. 4 similar data are shown for the *i*-BE+1,4-dioxane system at 15 and 50°C. It is important to note that even for the *i*-BE aqueous solution irregular behaviors are also found around X=0.02 at 15 and X=0.012 at 50°C. This behavior is essentially the same as that found for the aqueous solution of *n*-BE (Fig. 3). Thus, these results strongly suggest that there exists a boundary separating regions into I and II even in the aqueous solution of *i*-BE, just as in the case of *n*-BE.

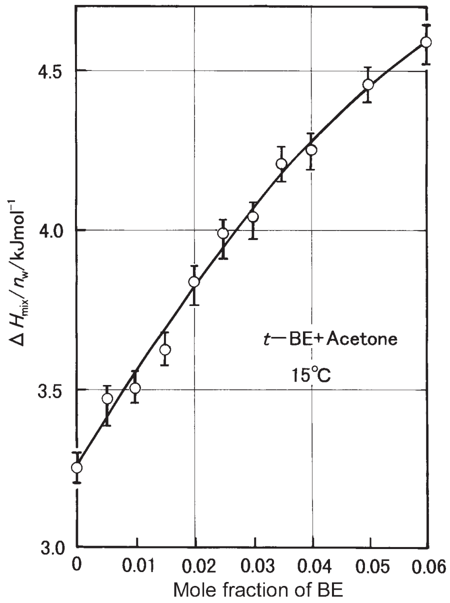

Fig. 5 The apparent enthalpies of mixing per one mole of water for *t*-BE aqueous solution+acetone system at 15°C

In Fig. 5, the apparent enthalpies of mixing per one mole of water ($\Delta H_{mix}/n_w$) for *t*-BE aqueous solution+acetone system at 15°C are shown in the same manner as in Figs 2–4. It is clear from this figure that the values of $\Delta H_{mix}/n_w$ increase almost linearly with increasing the mole fraction of *t*-BE and there is no concentration at which the slope of $\Delta H_{mix}/n_w$ *vs*. X changes irregularly. Thus, this result strongly suggests that there is no boundary separating the regions I and II in the aqueous solutions of *t*-BE.

In conclusion, a series of enthalpies of mixing measurements suggests the existence of a boundary separating regions I and II for both aqueous solution of *n*-BE and that of *i*-BE. However, the results do not suggest the existence of such a boundary for the *t*-BE+water system.

Discussion

The states of water molecules in a series of BE aqueous solutions may be classified into two typical states: (1) the formation of a strong hydrogen-bonding between an –OH group of BE molecule and water and a relatively weak one between an ethereal –O– group of BE and water; (2) the formation of a cage-like structure of hydrogen-bonded water molecules around a hydrophobic part of the BE molecule, such as

n-C_4H_9–, i-C_4H_9–, t-C_4H_9– and –CH_2CH_2– chain between the ethereal oxygen and the terminal OH group. These cage-like structures are supposed to be polyhedral networks such as 12-hedra, 14-hedra, and 16-hedra from the crystallographic analyses of clathrate-like hydrates of tetraalkyl-ammonium fluorides such as $(n\text{-}C_4H_9)_4NF$ and $(i\text{-}C_5H_{11})_4NF$ [10, 11]. It is important to note that, although these two typical states of water molecules above mentioned contribute to an energetic stability of the BE aqueous solutions individually, these two effects may interfere with each other. The formation of hydrogen-bonding, such as between –OH group and water molecule, restrain a water molecule strongly to a specific direction. However, in order to form a stable cage-like structure of water networks each water molecule should be able to rotate freely and to take a regular tetrahedral arrangement. According to the structure of hydrophobic portion of three isomers of BE molecule, the stability of the cage-like water structure around them will decrease in the order of n-BE>i-BE>t-BE [12]. This order is partly verified by the fact that the apparent enthalpies of mixing per one mole of water are more endothermic in the n-BE aqueous solution (Fig. 3) than those in the i-BE aqueous solution (Fig. 4) at 50°C. The experimental result that the existence of a boundary separating regions I and II cannot be expected in the t-BE aqueous solution may be explained by the consideration that the formation of a stable cage-like water structure is a prerequisite for an appearance of region I.

It should be noted that the liquid–liquid phase separation phenomena occur within region II, and therefore, this behavior will be independent of the presence of region I. The fact that the aqueous solutions of t-BE do not show liquid–liquid phase separation phenomena, at least below 140°C, will indicate a high stability of hydrogen-bonding between –OH group and water molecule. The phase separation phenomena both in the n-BE+water system and in the i-BE+water system will be due to the weakening of hydrogen-bonding and further destruction of water structure around hydrophobic portion of these BE molecules with increasing temperature. At present we have no information concerning the presence of two types of clusters within region II [1–3].

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