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Molar Excess Enthalpies of α,ω-Alkanediol Monoalkyl Ether+Heptane Systems at 298 K

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Enthalpies of mixing of some α,ω-alkanediol monoalkyl ether(ADAE)+heptane systems were measured at 298 K, and limiting partial molar excess enthalpies of ADAE at infinite dilution, $\lim_{x\to 0} H^E/x(1-x)$, were estimated. The ADAE used were $CH_3O(CH_2)_nOH$ (n=2, 3, 4), $C_2H_5O(CH_2)_nOH$ (n=2, 3), $C_3H_7O(CH_2)_nOH$ (n=2, 3), and $C_4H_9O(CH_2)_2OH$. The values of $\lim_{x\to 0} H^E/x(1-x)$ obtained were compared with those of normal alcohols, and discussed in the light of the intramolecular hydrogen bond contained in ADAE. The enthalpic contribution due to the intramolecular hydrogen bond in ADAE is estimated to be about 10 kJ mol^{-1}.

The solution behavior of α,ω-alkanediol monoalkyl ethers (ADAE), $C_mH_{2m+1}O(CH_2)_nOH$, in various solvents is of interest since the ADAE molecule contains both an etheric oxygen and a hydroxyl group, and hence can form hydrogen bonds in several different ways. Not only are intramolecular hydrogen bonds possible between the hydroxyl hydrogen and the etheric oxygen on the same molecule, but also intermolecular hydrogen bonds between the hydroxyl hydrogen on one molecule and either the etheric oxygen or the hydroxyl oxygen on another molecule can be formed. While, in general, investigations for the intramolecular hydrogen bond have been carried out by the use of infrared spectra,[1-5] NMR[6] or dielectric constant measurements,[7,8] it is worthwhile to obtain thermodynamic information about ADAE solutions, because few thermodynamic properties of these solutions have been investigated. In this paper, measurements of enthalpies of mixing for ADAE+heptane at 298 K are described and the results are discussed in view of the several kinds of hydrogen bonds forming in ADAE solutions.

Experimental

The α,ω-alkanediol monoalkyl ethers used were prepared by alkylation of the corresponding α,ω-alkanediols, and purified by fractional distillation in a nitrogen atmosphere. The middle fraction from each distillation was collected and analyzed by an analytical gas-liquid chromatograph (Shimadzu, Model GC-3BT) with a column packed 15% PEG6000 on Teflon; their purities were more than 99.5% for $C_mH_{2m+1}O(CH_2)_2OH$(m=1,2,3,4). As for $C_mH_{2m+1}(CH_2)_nOH$(n=3,4), peaks which seemed to show the existence of isomers were observed; their contents were estimated to be at the greatest 1 and 3% respectively. The heptane from Wako Pure Chemicals Co., Ltd. was purified using the conventional method. The purified heptane was also checked with the gas-liquid chromatograph. The result showed no impurity peaks.

Enthalpies of mixing for ADAE+heptane systems were determined by a successive dilution technique at 298 K using the isothermal displacement calorimeter described previously.[9] The precision is estimated to be ±0.5 per cent in a molar excess enthalpy of 100 J mol^{-1} for a equimolar mixture. In order to determine the limiting partial molar excess enthalpies of ADAE at infinite dilution, precise measurements of H^E at very low mole fractions of ADAE were especially needed. The concentration range covered by our calorimeter, where considerable precision can be expected, is within about 1/60–60/1 as volume fraction of components. So, the enthalpies of mixing in the dilute region were determined as follows. A previously prepared solution of a known mole fraction x_0 was diluted by the solvent, *i.e.* heptane, successively, and the enthalpy of dilution H_d^E per one mole of solution was measured at each step. The enthalpy of mixing H_0^E of the solution at a given concentration x_0 was estimated from the separately determined H^E *vs.* x curve for the pure component system with the least squares method, using the following polynomial:

$$H^E/x(1-x) = \sum_{i=0}^{n} h_i(x)^{i/2}$$

where x indicates the mole fraction of ADAE in the mixture. In this case, the enthalpies of mixing at each step in the dilute region are obtained as

$$H^E = (H_0{}^E/x_0)x + H_d{}^E$$

For each system measured, the process described above was repeated twice to evaluate H^E values in the dilute region. For the $CH_3O(CH_2)_2OH$ system, H^E changes linearly with composition from about 0.15 to 0.9 mole fraction of ADAE, because phase separation occurs in this region.[10] Hence, the enthalpy of mixing for this system was measured below the mole fraction of about 0.15.

Results and Discussion

Limiting Partial Molar Excess Enthalpy. For each system, the results were fitted by the method of least squares to the polynomial

$$H^E = x(1-x)\sum_{i=0}^{n} h_i(x)^{i/2} \tag{1}$$

Values of the coefficients h_i and the standard deviations σ for each system are collected in Table 1. In the dilute region of these systems, the remarkably unsymmetrical character of the excess enthalpies, such as seen in alcohol+nonpolar solvent systems, was observed.[11] Because of this asymmetrical dependence of H^E on x, the experimental results could not be fit by either polynomial (1) or $H^E = x(1-x)\sum_{i=0}^{n} h_i'(1-2x)^i$ in the dilute region of ADAE. So, the coefficients in Table 1 were obtained from the experimental H^E values in range of x=0.05 to 1.0. Hence, limiting partial molar excess enthalpies, $\lim_{x\to 0} H^E/x(1-x)$, could not be obtained by the use of the coefficients listed in Table 1. Even though, in order to obtain limiting partial molar excess enthalpies, several kinds of polynomials which represent the $H^E/x(1-x)$ *vs.* x relation were adopted to

Table 1. Coefficients and standard deviations for Eq. 1

	$CH_3O(CH_2)_2OH$ +heptane	$CH_3O(CH_2)_3OH$ +heptane	$CH_3O(CH_2)_4OH$ +heptane	$C_2H_5O(CH_2)_2OH$ +heptane
h_0	1.8462×10^4	2.6287×10^4	2.6581×10^4	1.9827×10^4
h_1	-8.0817×10^3	-1.2626×10^5	-1.4181×10^5	-6.4466×10^4
h_2	-3.4681×10^5	3.1505×10^5	3.8227×10^5	1.0809×10^5
h_3	1.3389×10^6	-4.3079×10^5	-5.5075×10^5	-9.0194×10^4
h_4	-1.5824×10^6	3.0772×10^5	4.0981×10^5	3.2338×10^4
h_5		-8.6433×10^4	-1.2173×10^5	
$\frac{\sigma}{\text{J mol}^{-1}}$	2.99	2.21	2.35	3.88

	$C_3H_7O(CH_2)_2OH$ +heptane	$C_4H_9O(CH_2)_2OH$ +heptane	$C_2H_5O(CH_2)_3OH$ +heptane	$C_3H_7O(CH_2)_3OH$ +heptane
h_0	1.9589×10^4	1.7371×10^4	2.5139×10^4	2.5996×10^4
h_1	-6.3408×10^4	-5.0451×10^4	-1.2214×10^5	-1.2760×10^5
h_2	1.0088×10^5	6.8248×10^4	2.9963×10^5	3.2186×10^5
h_3	-7.7523×10^4	-4.0556×10^4	-3.9506×10^5	-4.4065×10^5
h_4	2.4451×10^4	8.5129×10^3	2.6970×10^5	3.1562×10^5
h_5			-7.4262×10^4	-9.1306×10^4
$\frac{\sigma}{\text{J mol}^{-1}}$	2.60	4.18	1.65	3.34

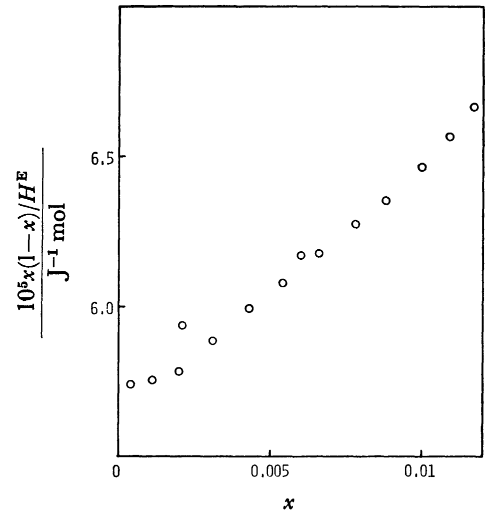

Fig. 1. Plot of $x(1-x)/H^E$ against x in dilute region for $C_3H_7O(CH_2)_3OH$-heptane system.

Table 2. Limiting partial molar excess enthalpies of ADAE at infinite dilution and the enthalpic contribution due to the intramolecular hydrogen bond in the ADAE molecules

	$\frac{\lim_{x\to0} H^E/x(1-x)}{\text{kJ mol}^{-1}}$	$\frac{H_i}{\text{kJ mol}^{-1}}$
$CH_3O(CH_2)_2OH$+heptane	17.6	−10
$CH_3O(CH_2)_3OH$+heptane	18.1	−9
$CH_3O(CH_2)_4OH$+heptane	21.2	−6
$C_2H_5O(CH_2)_2OH$+heptane	15.5	−12
$C_3H_7O(CH_2)_2OH$+heptane	15.5	−12
$C_4H_9O(CH_2)_2OH$+heptane	14.4	−13
$C_2H_5O(CH_2)_3OH$+heptane	17.3	−10
$C_3H_7O(CH_2)_3OH$+heptane	17.5	−10

our results, these curves were too steep in the dilute region of ADAE; an adequate form has not yet been found. So, the reciprocals of $H^E/x(1-x)$ were plotted against x, and the limiting partial molar excess enthalpies for all systems were estimated by extrapolation to infinite dilution "by eye." For an example, the observed points for the $C_3H_7O(CH_2)_3OH$ system are shown in Fig. 1. Values of limiting partial molar excess enthalpies determined by extrapolation to infinite dilution are listed in Table 2. The errors included in these values were estimated to be less than 5%.

Intramolecular Hydrogen Bond in ADAE. When liquids forming hydrogen bonds in the pure liquid state, such as alcohols, are diluted with nonpolar solvents, the hydrogen bonds are broken by the addition of the solvent molecules, and hence this process corresponds to an extremely large positive value of H^E. In general, the shapes of the $H^E/x(1-x)$ *vs.* x curves of such systems become very steep in the dilute region of solute. Although in the present systems the $H^E/x(1-x)$ *vs.* x curves show an appreciable rise in the dilute region, the slope is not so steep as that of normal alcohol+nonpolar solvent systems, and the difference of the limiting partial molar excess enthalpies between the two series is about several kJ mol^{-1}. This seems to mean that, in the dilute region ADAE molecules become free through the destruction of the intermolecular hydrogen bonds by the addition of solvent molecules, and each ADAE molecule forms an intramolecular hydrogen bond between the hydroxyl hydrogen and the etheric oxygen on the same molecule, and thus stabilizes itself.

To discuss the intramolecular hydrogen bond in the ADAE molecule, it will be useful to compare ADAE with normal alcohol. In a normal alcohol+nonpolar solvent system, alcohol molecules form intermolecular hydrogen bonds between hydroxyl groups in the pure alcohol state. On the other hand, at infinite dilution of alcohol in a nonpolar solvent, the intermolecular hydrogen bonds are broken and each alcohol molecule is surrounded by solvent molecules. Therefore, the value of the limiting partial molar excess enthalpy of alcohol at infinite dilution is assumed to represent the energy sufficient to break the intermolecular hydrogen bond in pure alcohol.

While many investigations have been carried out for excess enthalpies of alcohol+nonpolar solvent systems so far,[12–15] available data for limiting partial molar excess enthalpies have not been provided because of the steep rise of $H^E/x(1-x)$ *vs.* x curves in the dilute region. However, values of limiting partial molar excess enthalpies reported so far are distributed in the neighborhood of 23 to 24 kJ mol^{-1} for normal alcohol systems.[12] This figure seems to be independent of nonpolar solvents, and constant within the experimental error.[11] Brown *et al.* suggest that, for normal alcohols larger than ethanol, the strength of the intermolecular hydrogen bond hardly depends on the carbon chain length in the molecule.[16] Further, for 1,3-butanediol which has two terminal hydroxyl groups in its molecule, it was suggested previously by Murakami *et al.* that almost all the molecules form intermolecular hydrogen bonds between the hydroxyl hydrogen on one molecule and the hydroxyl oxygen on another molecule in the pure liquid state, and the amount of the intramolecular form is negligibly small.[17] It can hence be presumed that ADAE molecules also hardly form intramolecular hydrogen bonds in the pure liquid state, and it will be reasonable to assume that the relation between the strength of the hydrogen bond and the carbon chain length of ADAE is also similar to that of normal alcohols. Therefore, the difference in the values of limiting partial molar excess enthalpies for various ADAE seems to be attributed mainly to the difference in the enthalpic contribution due to formation of the intramolecular hydrogen bond between the hydroxyl hydrogen and the etheric oxygen on the same molecule.

Evaluation of the Enthalpic Contribution due to the Intramolecular Hydrogen Bond in ADAE. On the basis of the consideration in the previous section, the enthalpic contribution due to the intramolecular hydrogen bond in the ADAE molecule, H_i, can be estimated. In this estimation, the pure liquid state of normal alcohol is taken as a standard state. As the main intermolecular interactions in this state, those shown in Fig. 2(a) and (b) are considered: (a) contribution due to the intermolecular hydrogen bond and (b) contribution due to the van der Waals force including the dipolar interaction. On the other hand, in the pure liquid state of ADAE, the intermolecular interactions shown in Fig. 2(c) and (d) are also considered: (c) contribution due to two types of intermolecular hydrogen bonds and (d) contribution due to three types of van der Waals forces. The process used to evaluate H_i is given in a form of an energy level diagram in Fig. 3. In this figure, H_2 represents the limiting partial molar excess enthalpy of normal alcohol in a nonpolar solvent. H_2 includes an enthalpic contribution arising from the interruption of the van der Waals interaction among alcohol molecules shown in Fig. 2(b) through dilution with the nonpolar solvent. This contribution is represented by H_2' in Fig. 3, and then the net contribution due to the hydrogen bond becomes H_2-H_2'. H_1 represents the limiting partial molar excess enthalpy of ADAE in a nonpolar solvent. H_1 also includes an enthalpic contribution arising from the interruption of the van der Waals interactions among ADAE molecules shown in Fig. 2(d) through dilution with the nonpolar solvent. H_1' represents this contribution; then the net contribution due to hydrogen bonds (including the intramolecular hydrogen bond) becomes H_1-H_1'. As shown in Fig. 2(c), two types of intermolecular hydrogen bonds may exist in the pure liquid state of ADAE, and the energy level of this state is considered to be different from that of the pure liquid state of alcohol which is taken as the standard state. This difference between the levels is designated as H_3. With these notations, the enthalpic contribution due to the intramolecular hydrogen bond in the ADAE molecule, H_i, can be evaluated as

$$H_i = (H_1 - H_1' + H_3) - (H_2 - H_2') \qquad (2)$$

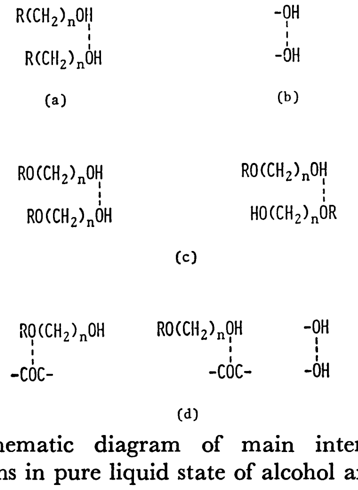

Fig. 2. Schematic diagram of main intermolecular interactions in pure liquid state of alcohol and ADAE.

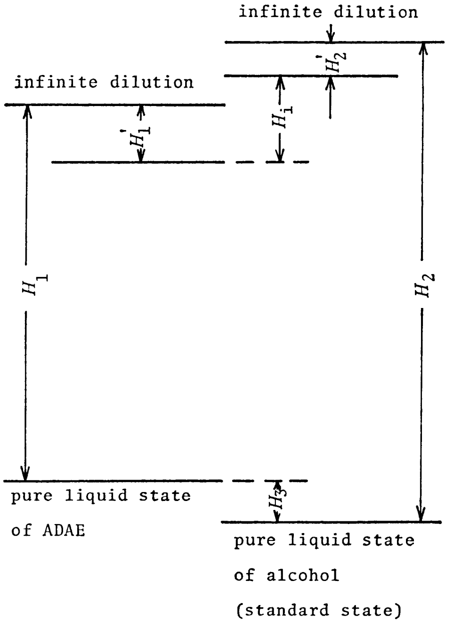

Fig. 3. Energy level diagram of ADAE and alcohol.

Values of H_1', H_2', and H_3 are evaluated as follows. If the difference in nature of the oxygen atoms contained in the ADAE molecule and the alcohol molecule is assumed to be negligible, H_1' and H_2' can be replaced by limiting partial molar excess enthalpies of ethers, $RO(CH_2)_nOR$ and ROR, where R represents an alkyl group, in nonpolar solvent, which are unable to form hydrogen bonds. One mole of ADAE is assumed to consist of one mole of alcoholic hydroxyl groups and one mole of etheric oxygen atoms, and then the pure liquid state of ADAE will be approximated by one mole of alcohol plus one mole of ether. Hence, $H_3/2$ is replaced by the enthalpy of mixing of the alcohol+ether system at equimolar fraction, $H^E(x=0.5)$. According to these assumptions, H_1', H_2', and H_3 are estimated to be 5.8 kJ mol^{-1},[18] 0.4 kJ mol^{-1},[19] and 1.5 kJ mol^{-1},[19] respectively. As for H_2, the latest value of 23.2 kJ mol^{-1} for the ethanol+hexane system[11] is used, which was measured in a sufficiently dilute region. For H_1, the values listed in Table 2 are used. Using these values and Eq. 2, H_i values for various ADAE are found and are also listed in Table 2. These results are distributed in the neighborhood of 10 kJ mol^{-1}, and it seems that the values of H_i for ADAE depend on the length of the internal methylene group in the ADAE molecule, but hardly depend on the chain length of the terminal alkyl group in the ADAE molecule. The values of H_i for ADAE having the same terminal alkyl group are in the order of $RO(CH_2)_2OH > RO(CH_2)_3OH > RO(CH_2)_4OH$. On the other hand, the values of H_i for α,ω-alkanediols ($HO(CH_2)_nOH$, $n=3$, 4) were estimated from the infrared spectra[20] and dielectric measurements,[21] and are comparable with those in the present systems. However, the dependence of H_i values on the length of the internal methylene group seems to be the reverse of that of ADAE. At present, we have no satisfactory explanation of this fact.

In conclusion, the present results suggest that the enthalpic contribution due to the intramolecular hydrogen bond contained in the ADAE molecule is smaller than that due to the normal intermolecular hydrogen bond between hydroxyl groups, and in general can be estimated to be about 10 kJ mol^{-1}.

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