

Calorimetric Study of Dilute Aqueous Solutions of Ethylene Glycol Oligomers

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The enthalpies of mixing of water and five ethylene glycol oligomers (C0Ej; j = 1–5) were measured in an ideal dilute solution at seven temperatures from 283.15 to 313.15 K by using a high-accuracy isothermal titration calorimeter. The differential enthalpies of solution of C0Ej were evaluated by applying the thermodynamic equations to the experimental results. They were negative, and their absolute values increased with decreasing temperature and increasing oxyethylene chain length. It was shown that the dissolution of C0Ej is exothermic and that the interaction between water and C0Ej molecules is stronger than the average of interactions between the same species. Moreover, the partial molar heat capacity changes and the partial molar heat capacities at 298.15 K were calculated. It was shown that the partial molar heat capacities of C0Ej in an aqueous solution are increased from the molar heat capacities of the pure liquid state owing to hydration. It was found that all the partial molar quantities per oxyethylene are almost constant. The enthalpy of mixing of some protic solvents, i.e., methanol, ethanol, 1-propanol, and ethylene glycol, with C0E5 was also measured to examine the hydration of the oxyethylene group. Our experiment showed that the differential enthalpy of solution of C0E5 is very slightly negative or even positive in contrast to the large negative value of the water system. Furthermore, it was suggested by comparing the results of C0Ej with those of C8Ej that the hydration of the hydrophobic group is also exothermic at a lower temperature and strongly dependent on temperature.

Introduction

Poly(ethylene glycol) monoalkyl ethers [C_iH_{2i+1}(OC₂H₄)_jOH, C_iE_j] are typical nonionic surfactants.^{1,2} They have been used for the thermodynamic investigations of micelle formation,^{3–7} solubilization,⁸ and microemulsion^{9,10} because they do not dissociate into ions and because both their alkyl chain length and number of ethylene oxides can be systematically changed. Since the hydration of hydrophilic and hydrophobic moieties is influential in the micellization process of C_iE_j, it is important to gain information on the hydration of the respective groups separately.

Calorimetry offers information on the molecular interaction rather directly. In this paper, therefore, the hydration of hydrophilic groups of C_iE_j is examined by the calorimetry of aqueous solutions of ethylene glycol monomer and oligomers [H(OC₂H₄)_jOH, C0E_j]. We chose five C0E_js (j = 1–5) and measured the enthalpy of mixing of water and C0E_j in the very dilute region,¹¹ instead of all the compositions,^{12,13} as a function of concentration and temperature under atmospheric pressure by the isothermal titration microcalorimeter TAM 2277. Then the partial molar enthalpy changes of C0E_j were evaluated particularly in a very dilute region to grasp the hydration of C0E_j in terms of the molecular interaction between water and C0E_j.

Experimental Section

Materials. Ethylene glycol, di-, tri-, tetra-, and pentaethylene glycols (C0E_j, j = 1–5) were purchased from Nacalai Tesque,

Inc. (C0E1), Kanto Chemical Co., Inc. (C0E2 and C0E4), Tokyo Chemical Industry Co., Ltd. (C0E3), and Aldrich Chemical Co. (C0E5), respectively. They were dehydrated by molecular sieve (0.4 nm, MERCK) and then distilled under reduced pressure. The boiling points were as follows: C0E1, bp 100–101 °C (18 mmHg); C0E2, bp 99.5–100.5 °C (1.5 mmHg); C0E3, bp 124–125 °C (1.5 mmHg); C0E4, bp 165–166 °C (1.5 mmHg); C0E5, bp 167–168 °C (0.8 mmHg). Purities were checked by gas–liquid chromatography; they were more than 99.9% for C0E1, C0E2, and C0E3 and 99.5% for C0E4 and C0E5.

Water was distilled three times, the second and third distillations being done from an alkaline permanganate solution.

Calorimetry. The enthalpy of mixing of water and C0E_j was measured by the isothermal titration microcalorimeter (TAM 2277; Thermometric AB, Sweden) controlled by Digitam 3.0 software. Details have been described by Wadsö et al.^{14,15} One to two half microliters of liquid C0E_j was injected into a 4 mL stainless steel ampule holding ca. 3.2 g of water by using a computer-controlled syringe pump (6110 Lund Pump and 612 Lund Pump 2) from a gastight syringe (Hamilton 1725LT) through a stainless steel cannula. The weight of liquid injected was accurately calculated from the density values of the liquid. The solution in the ampule was stirred by the turbine at a constant speed of 80 rpm. The heat flow was detected to 0.15 μW by high-sensitive thermopiles surrounded by a heat sink stabilized at the desired temperature of ±2 × 10^{−4} °C within an experimental error of 0.5 μW. The electrical calibration performance makes the results quantitative. Two to four runs were performed at a given temperature.

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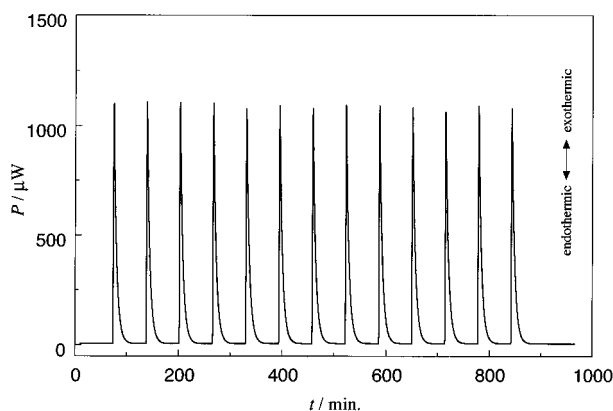


Figure 1. Heat flow vs time curve of the C0E3–water system at 303.15 K.

Thermodynamic Equations

Let us consider the mixing process of n_w moles of water and n_s moles of liquid C0Ej. The enthalpy of mixing H^M measured is expressed by

$$H^M = n_w h_w + n_s h_s - n_w h_w^0 - n_s h_s^0 \quad (1)$$

where h_i and h_i^0 are the partial molar enthalpy of component i in the aqueous solution and the molar enthalpy of pure liquid i at a given temperature T , pressure p , and molality of solute m , respectively. Then the enthalpy of mixing per unit mass of water h^M is given by

$$h^M = \frac{H^M}{n_w M_w} = \frac{h_w - h_w^0}{M_w} + m(h_s - h_s^0) \quad (2)$$

where M_w is the molar mass of water expressed in kg mol^{-1} .

By use of T , p , and m as the independent thermodynamic variables and taking account of the Gibbs–Duhem equation, the derivative of h^M with respect to m at constant T and p gives the differential enthalpy of solution of solute $\Delta_0^w h_s$:

$$(\partial h^M / \partial m)_{T,p} = h_s - h_s^0 \equiv \Delta_0^w h_s \quad (3)$$

Furthermore the derivative of $\Delta_0^w h_s$ with respect to T at constant p and m gives the corresponding partial molar heat capacity change $\Delta_0^w c_s$:

$$(\partial \Delta_0^w h_s / \partial T)_{p,m} = c_s - c_s^0 \equiv \Delta_0^w c_s \quad (4)$$

Here, c_i and c_i^0 are the partial molar heat capacity of component i in an aqueous solution and the molar heat capacity of a pure liquid i at a given T , p , and m , respectively.

The thermodynamic relations applicable to micellar solutions of water and surfactant mixture have been described in our previous paper in detail.³

Results and Discussion

The enthalpy of mixing H^M was measured as a function of n_s at a given n_w at seven temperatures from 283.15 to 313.15 K under atmospheric pressure.

Figure 1 shows the typical titration thermogram of C0E3 where 2.5 μL of liquid C0E3 was injected successively into the cell holding ca. 3.2 g of water at 303.15 K. It is seen that both the height and area of peaks are almost constant at all concentrations. The heat per injection is estimated from the corresponding peak area calculated by the Digitam 3.0 software

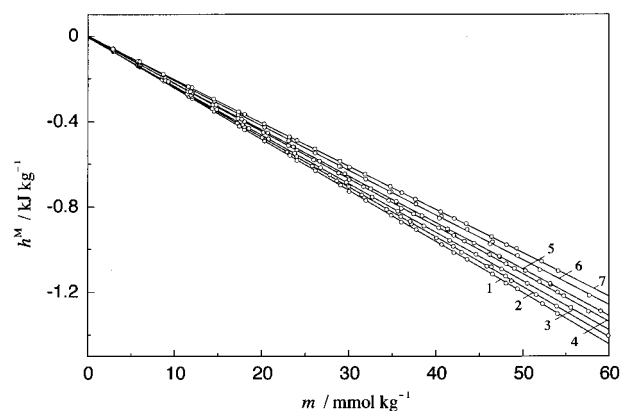


Figure 2. Enthalpy of mixing vs molality curves of the C0E3–water system at $T =$ (1) 283.15, (2) 288.15, (3) 293.15, (4) 298.15, (5) 303.15, (6) 308.15, and (7) 313.15 K.

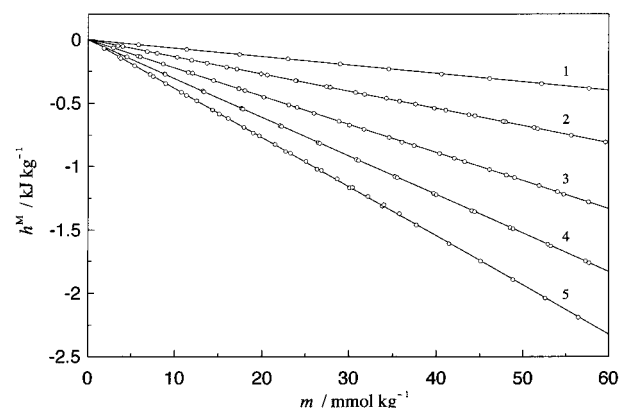


Figure 3. Enthalpy of mixing vs molality curves at 298.15 K: (1) C0E1; (2) C0E2; (3) C0E3; (4) C0E4; (5) C0E5.

program. Then the H^M value at a given n_s is estimated by summing up the area from the first peak to the one at which the total number of moles of C0Ej reaches n_s . The enthalpy of mixing per kilogram of water h^M vs molality m curves are illustrated for the C0E3 system in Figure 2. It is seen that the mixing processes are exothermic and the absolute values of h^M increase with increasing concentration and decreasing temperature. It is noted that the h^M values change almost linearly at all concentrations investigated. From eq 3, therefore, this means that the partial molar enthalpy of C0E3 does not change with concentration; i.e., the aqueous solution is considered to be ideally dilute. Although the h^M vs m plots of the other C0Ej systems are similar to those of C0E3 qualitatively, it has been found that the absolute value of h^M increases with increasing oxyethylene chain length at a given temperature as is demonstrated at 298.15 K in Figure 3.

By application of eq 3 to the h^M vs m curves, the differential enthalpies of solution of C0Ej, $\Delta_0^w h_s$, were evaluated and shown in Figure 4 and in Table 1. They are negative, and their absolute values increase with decreasing temperature and increasing oxyethylene chain length. It is suggested, therefore, that interaction between water and C0Ej molecules depends on temperature and is stronger than the average of the interaction between the same species. The interaction is probably attributable to the hydration around ether groups of C0Ej molecules and is weakened owing to thermal motion of molecules at a higher temperature. Plotting the values of $\Delta_0^w h_s$ against the oxyethylene chain length j in Figure 5, we have found that the increment of $\Delta_0^w h_s$ per oxyethylene chain is almost constant; the exothermic contribution to $\Delta_0^w h_s$ per oxyethylene group is

TABLE 1: Differential Enthalpy of Solution of C0Ej

T/K	$\Delta_0^W h_s / \text{kJ mol}^{-1}$				
	C0E1	C0E2	C0E3	C0E4	C0E5
283.15	-7.241 ± 0.0072	-14.77 ± 0.019	-24.00 ± 0.018	-32.70 ± 0.033	-41.31 ± 0.041
288.15	-7.082 ± 0.0043	-14.31 ± 0.016	-23.39 ± 0.025	-32.10 ± 0.028	-40.67 ± 0.033
293.15	-6.831 ± 0.0048	-13.88 ± 0.010	-23.10 ± 0.046	-31.33 ± 0.014	-39.73 ± 0.030
298.15	-6.641 ± 0.0041	-13.51 ± 0.011	-22.22 ± 0.018	-30.47 ± 0.016	-38.77 ± 0.047
303.15	-6.383 ± 0.0054	-13.06 ± 0.011	-21.81 ± 0.020	-29.51 ± 0.040	-37.61 ± 0.024
308.15	-6.160 ± 0.0040	-12.66 ± 0.009	-20.99 ± 0.039	-28.80 ± 0.029	-36.51 ± 0.016
313.15	-5.998 ± 0.0079	-12.28 ± 0.016	-20.33 ± 0.021	-27.73 ± 0.034	-35.32 ± 0.026

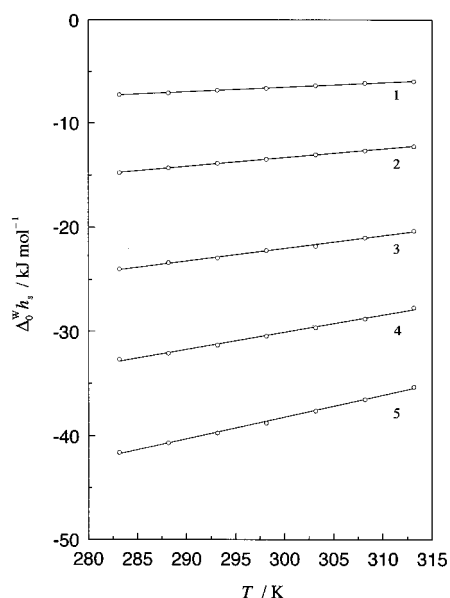
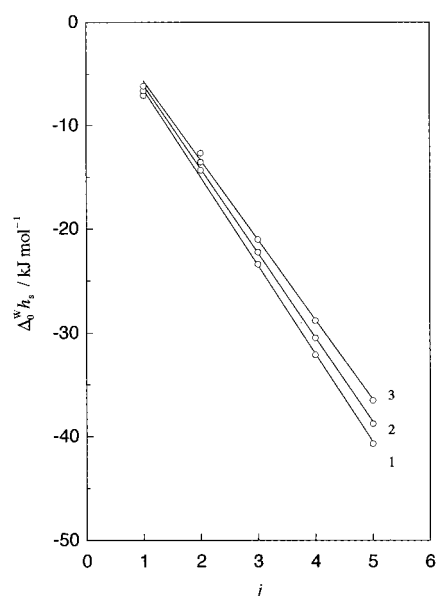


Figure 4. Differential enthalpy of solution vs temperature curves: (1) C0E1; (2) C0E2; (3) C0E3; (4) C0E4; (5) C0E5.

Figure 5. Differential enthalpy of solution vs the number j at $T =$ (1) 288.15, (2) 298.15, and (3) 308.15 K.

$-8.12 \text{ kJ mol}^{-1}$ at 298.15 K. It is very interesting to note that Dohanl et al. have found almost the same value for the homologous series of ethylene glycol dimethyl ethers.¹¹ These findings suggest that the hydration of an oxyethylene group of ethylene glycol oligomers is little affected by the terminal proton.

The partial molar heat capacity change $\Delta_0^W c_s$ was calculated by applying eq 4 to $\Delta_0^W h_s$ vs T curves in Figure 4. The values

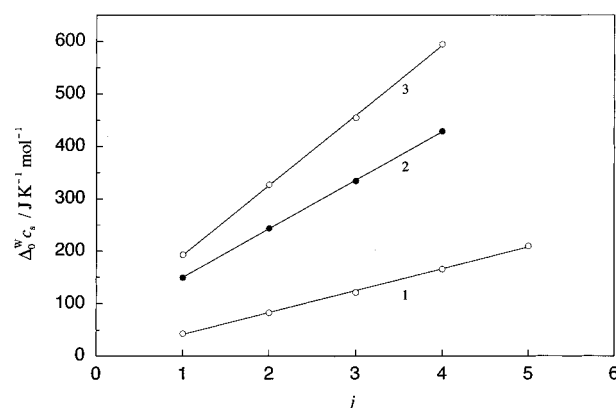
Figure 6. Partial molar heat capacity vs the number j for (1) $\Delta_0^W c_s$ and (2) c_s^0 at 298.15 K and (3) c_s at 298.15 K.

TABLE 2: Partial Molar Heat Capacities of C0Ej

	$\Delta_0^W c_s / \text{J K}^{-1} \text{mol}^{-1}$	$c_s^0 / \text{J K}^{-1} \text{mol}^{-1}$	$c_s / \text{J K}^{-1} \text{mol}^{-1}$
C0E1	43.0 ± 1.1	149.8	192.8
C0E2	82.7 ± 1.0	243.9	326.6
C0E3	121.0 ± 3.9	333.7	454.7
C0E4	165.5 ± 5.1	428.8	594.3
C0E5	209.3 ± 4.7		

^a Reference 16.

are practically independent of the molality and temperature for a given C0Ej, and then they are plotted against j in Figure 6 (curve 1). By use of the molar heat capacity of pure C0Ej c_s^0 at 298.15 K from the literature,¹⁶ the partial molar heat capacities c_s were evaluated and given in Table 2 and Figure 6 together with the c_s^0 values. It is revealed in Figure 6 that the heat capacities of C0Ej in the aqueous solution are increased from the ones of the pure liquid state and that the increment $\Delta_0^W c_s$ is also changed linearly with j . This suggests that hydration of one mole of the ethylene oxide group contributes $41.5 \text{ J K}^{-1} \text{mol}^{-1}$ to the heat capacity of C0Ej in the aqueous solution. Taking note of the linearities observed in Figures 5 and 6 and in the partial molar volume at infinite dilution per oxyethylene chain vs j plot,¹⁷ it may be presumed that C0Ej molecules are dissolved in a freely extended form with neither intramolecular nor intermolecular hydrogen bonds in the aqueous solutions. This is also consistent with the findings that the exothermic contribution to $\Delta_0^W h_s$ per oxyethylene group is almost the same for the homologous series of ethylene glycol dimethyl ethers and ethylene glycol oligomers.

Now let us look into the hydration of the oxyethylene group by comparing it with the solvation of C0Ej in some protic solvents. Recently, we obtained the differential enthalpies of solution of C0E5 in ideal dilute solutions of methanol, ethanol, 1-propanol, and ethyleneglycol (C0E1).¹⁸ The results are summarized in Table 3 together with the corresponding one of the aqueous solution. It is noted that the $\Delta_0^W h_s$ value is very slightly negative for the methanol and ethylene glycol systems

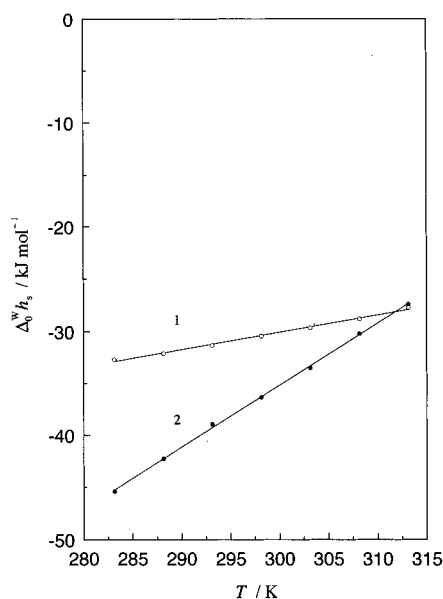


Figure 7. Differential enthalpy of solution vs temperature curves: (1) C0E4; (2) C8E4.

TABLE 3: Differential Enthalpy of Solution of C0E5 in Several Solvents at 298.15 K

solvent	$\Delta_0^W h_s / \text{kJ mol}^{-1}$				
	water	methanol	ethanol	1-propanol	ethylene glycol
	-38.77	-0.38	5.20	7.92	-0.11

and even positive for the ethanol and 1-propanol systems. The $2j + 2$ lone pairs on oxygen atoms of a C0Ej molecule are available for hydrogen bonding with the hydroxyl hydrogen of all the solvents given in Table 3. Furthermore, it is probable that some of the lone pairs of oxygen atoms in pure C0E5 are free from hydrogen bonding because the number of lone pairs is in excess of the number of hydroxyl hydrogens. In these respects, it is expected that the mixing of C0Ej with the protic solvents in Table 3 is an exothermic process and $\Delta_0^W h_s$ is negative.

However, the experiments show that $\Delta_0^W h_s$ is evidently negative only for the water system. With respect to the hydration, it has been found that the distance between the oxygen atoms for the helical conformation of C0Ej in the crystalline state¹⁹ is similar to that of liquid water,^{20,21} and most of the ethylene segments of C0Ej in aqueous solution are in a gauche conformation.^{22,23} Therefore, water and C0Ej molecules can construct a kind of network structure through the hydrogen bonds between water and C0Ej and those between water molecules. The network structure may be supported by the fact that poly(methylene oxide) and poly(trimethylene oxide) are insoluble in water.^{21,24} With respect to the solvation of 1-alkanol, on the other hand, such a network structure is unlikely because one molecule has only one hydroxyl hydrogen. Furthermore, the longer the hydrocarbon chain is, the more the hydrogen bond formation may be hindered because of the steric effect. Then the exothermic contribution to $\Delta_0^W h_s$ value is

expected to be very large for the water system but small for the other solvents. On the other hand, it is probable that the fluid structures in the pure solvents may be destroyed partly and those in pure C0Ej completely by mixing the solvent with C0Ej at a very dilute concentration. This is the endothermic contribution to $\Delta_0^W h_s$. Therefore, it is said that these two opposite contributions determine the net values of $\Delta_0^W h_s$.

Next, it is instructive to compare the $\Delta_0^W h_s$ value of C0Ej with that of CiEj. Such an example is illustrated for the C0E4 and C8E4 systems³ in Figure 7. It is clearly seen that the $\Delta_0^W h_s$ value of C8E4 is more negative and more strongly dependent on temperature than that of C0E4. These findings suggest that the hydration of hydrophobic group is also an exothermic contribution to $\Delta_0^W h_s$ and becomes less pronounced at higher temperatures, while the hydration of the hydrophilic group contributes to $\Delta_0^W h_s$ appreciably even at higher temperatures. This is very important for understanding the micellization process of CiEj surfactants and will be reported in the next paper.

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