Thermodynamics Studies on Miscibility and Interaction of Binary Surfactant Mixtures in Micelle : Calorimetry and Surface Tension Measurement

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Akio Ohta

Contents

Chapter I

General Introduction

Many studies on the mixed surfactant systems have been carried out both experimentally and theoretically.[1-3] They have aroused great interest, because the mixed surfactant systems can show superior performance such as surface tension, foamability, solubilization, microemulsion stability, and so on, as compared to single surfactant systems. It is clear that these properties are exceedingly relevant to the properties and structures of the adsorbed film and the micelle formed by surfactants. Generally the compositions in micelle and adsorbed film are different from that in bulk solution and also from each other, since they are biased toward a component to gain the lowest free energy. Since, in addition, the compositions strongly depend on the interaction between molecules in the adsorbed film and micelle, evaluating them is highly useful to shed light on the miscibility of surfactants. According to this idea, we have proposed the thermodynamic approach in order to estimate them from surface tension measurement.[4,5] Furthermore we have succeeded in estimating the activity coefficients and excess Gibbs energy of micelle formation and, then, clarifying the miscibility and interaction of surfactants in micelle quantitatively for many binary surfactant mixtures.[6-12]

Calorimetry is a powerful method to acquire information on the molecular interaction rather directly.[13] Especially the isothermal titration calorimetry has been employed widely for the investigations of micelle formation of single surfactant systems.[14-20] Recently, we also have proposed the thermodynamic equations to analyze the calorimetry data of single surfactant solution and applied them to tetraethylene glycol monooctyl ether system successfully.[18] On the other hand, the interaction

between surfactants in mixed micelle is very interesting as a subject of the calorimetry of surfactant solution. In fact some studies have been reported on the calorimetry of micelle formation of surfactants in the presence of inorganic salts,[21] co-surfactants,[22-24] or co-solvents.[25-27] As far as we know, however, there are few studies of the calorimetry from the viewpoint of the enthalpy of mixed micelle formation and the miscibility of surfactants in micelle. The main reasons for this are probably that the proper thermodynamic equations for analyzing the calorimetry data of a mixed surfactants system have not yet been established and there is a difficulty in evaluating the composition of mixed micelle.

The goal of our study is to consider the miscibility and interaction of binary surfactant mixtures in the micelle by both calorimetry and surface tension measurement comprehensively. Prior to proceeding to study the calorimetry of surfactant mixture, this thesis starts to concern with the hydration and micelle formation of nonionic surfactant of a single surfactant system by the isothermal titration calorimetry and provides a basis for a full understanding the mixed micelle formation of the mixtures. In chapter II, the effect of the size of hydrophilic group of polyethylene glycol monoalkyl ether $C_iH_{2i+1}(OC_2H_4)_jOH$ ($CiEj$) on hydration and micelle formation is investigated by measuring accurately the enthalpy of mixing of water and $CiEj$ and estimating partial molar quantities as a function of temperature. The thermodynamic equations proposed previously[18] are available to analyze the calorimetry data of mixing of pure water and liquid surfactants. However we need frequently the titration experiments of an aqueous solution of surfactant, since most of surfactants including $CiEj$

($i \geq 10$) are solids at room temperature. In chapter III, therefore, we first propose the proper thermodynamic analysis in order to obtain the enthalpy of micelle formation from the titration calorimetry of aqueous solution of surfactant. Furthermore, we will examine the effect of the length of hydrocarbon chain of *CiEj* on the micelle formation, and the hydration of surfactant monomer and micelle particles. Chapter IV describes the study on the miscibility and interaction of surfactants including *CiEj* in adsorbed films and micelles by surface tension measurement from the standpoint of the influence of the size of polar head group. In chapter V, we will develop the thermodynamic equations in order to obtain the enthalpy of micelle formation for binary mixed surfactants systems from the titration calorimetry of the aqueous solution of surfactant mixture. Finally the miscibility of some surfactant systems treated in chapter IV in micelle will be considered more minutely by evaluating the excess enthalpy of micelle formation directly.

References

1. Scamehorn, J. F., ed., *Phenomena in Mixed Surfactant Systems*, ACS Symp. Ser. 311, Am. Chem. Soc., Washington, DC, 1986.
2. Holland, P. M.; Rubingh, D. N., ed., *Mixed Surfactant Systems* ACS Symp. Ser. 501, Am. Chem. Soc., Washington, DC, 1992.
3. Ogino, K.; Abe, M., ed., *Mixed Surfactant Systems*, Surfactant Science Ser., 46, Marcel Dekker, Inc., New York, 1993.
4. Motomura, K.; Ando, N.; Matsuki, H.; Aratono, M. *J. Colloid Interface Sci.* **1990**, *139*, 188.

5. Motomura, K.; Aratono, M.; in *Mixed Surfactant Systems*, Ogino, K.; Abe, M.; eds., Surfactant Science Ser., 46, Marcel Dekker, Inc., New York, 1993, p99.
6. Aratono, M.; Villeneuve, M.; Takiue, T.; Ikeda, N.; Iyota, H. *J. Colloid Interface Sci.* **1998**, *200*, 161.
7. Villeneuve, M.; Sakamoto, H.; Minamizawa, H.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Colloid Interface Sci.* **1997**, *194*, 301.
8. Villeneuve, M.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Colloid Interface Sci.* **1998**, *208*, 388.
9. Iyota, H. Todoroki, N.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Colloid Interface Sci.* **1998**, *208*, 203.
10. Iyota, H. Todoroki, N.; Ikeda, N.; Motomura, K.; Ohta, A.; Aratono, M. *J. Colloid Interface Sci.* **1999**, *216*, 41.
11. Matsubara, H.; Ohta, A.; Kameda, M.; Villeneuve, M.; Ikeda, N.; Aratono, M., *Langmuir* **1999**, *15*, 5496.
12. Matsubara, H.; Ohta, A.; Kameda, M.; Ikeda, N.; Aratono, M. *Langmuir* submitted.
13. Desnoyer, J. E.; Perron, G.; Roux, A. H., In *Surfactant Solutions: New Methods of Investigation*; Zana, R., ed.; Marcel Dekker, Inc., New York, 1987.
14. Weckström, K.; Hann, K.; Rosenholm, J. B. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 733.
15. Olofsson, G. *J. Phys. Chem.* **1985**, *89*, 1473.
16. Anderson, B.; Olofsson, G. *J. Solution Chem.* **1989**,*18*,1019.
17. Johnson, I.; Olofsson, G. *J. Chem. Soc., Faraday Trans.* 1 **1988**, *84*,

551.

18. Aratono, M.; Ohta, A.; Ikeda, N.; Matsubara, A.; Motomura, K.; Takiue, T. *J. Phys. Chem. B* **1997**, *101*, 3535.
19. Bijma, K.; Engberts, J. B. F. N.; Haandrikman, G.; Van Os, N. M,; Blandamer, M. J.; Butt, M. D.; Cullis, P. M. *Langmuir* **1994**, *10*, 2578.
20. Olofsson, G. *Netsu Sokutei* **1992**, *19*, 76.
21. Weckström, K.; Rosenholm, J. B. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 569.
22. Johnson, I.; Olofsson, G.; Landgren, M; Jönsson, J. *J. Chem. Soc., Faraday Trans.* 1 **1989**, *85*, 4211.
23. Burrows, J. B.; Flynn, D. J.; Kutay, S. M; Leriche, T. G.; Marangoni, D. G. *Langmuir* **1995**, *11*, 3388.
24. Marangoni, D. G.; Rodenhiser, A. P.; Thomas, J. M.; Kwak, J. C. *Langmuir* **1993**, *9*, 438.
25. Callaghan, A.; Doyle, R.; Alexander, E.; Palepu, R. *Langmuir* **1993**, *9*, 3422.
26. Wärnheim, T.; Jönsson, J. *J. Colloid Interface Sci.* **1989**, *125*, 627.
27. Olofsson, G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3037.

Chapter II

Calorimetry of Micellar Solutions of Polyethylene Glycol Monooctyl Ethers

Introduction

Physicochemical properties of polyethylene glycol monoalkyl ether $C_iH_{2i+1}(OC_2H_4)_jOH$ ($CiEj$), which is a typical nonionic surfactant, have been investigated widely.[1,2] This is probably because the polar head group and alkyl chain can be varied systematically and accordingly both molecular packing and magnitude of interaction may be altered systematically. On the other hand, micelle of surfactant mixtures has more unique features than that of a single surfactant because its composition at the critical micelle concentration CMC is different from the bulk composition.[3] Also the surfactant mixtures containing $CiEj$ absorbs much interests from the standpoints of theoretical and biological aspects and industrial applications, etc. Furthermore the ternary systems composed of water, oil, and $CiEj$ have attracted attention for studying microemulsion, reversed micelles, and so on.[4-7]

So far, we have demonstrated that the thermodynamic procedure developed by our group is useful for examining the miscibility of surfactants in adsorbed films and micelles and applicable to various systems such as nonionic-nonionic and ionic-nonionic surfactant mixtures.[8-11] Thus mixtures such as $CiEj$-$CmEj$, $CiEj$-$CiEn$, and $CiEj$-$CmEn$ are good candidates for adopting our theoretical and experimental strategies and for understanding the mixed adsorption and micelle formation. Prior to proceeding to study the calorimetry of surfactant mixtures, this chapter is concerned with that of single surfactant systems of $CiEj$. The isothermal titration calorimetry was applied: the hydration and micelle formation of the $CiEj$ systems were examined thermodynamically

and provide a basis for a full understanding the mixed micelle formation of the mixtures containing C*i*E*j*.

In this study the effect of the size of hydrophilic group of C*i*E*j* on hydration and micelle formation is investigated by measuring the enthalpy of mixing of water and C*i*E*j* accurately and estimating partial molar quantities as a function of temperature. It has been known that calorimetry is one of the effective thermodynamic methods, because the information on molecular interaction are offered rather directly from the experiments. Although some studies have been reported on the enthalpy of mixing of water and C*i*E*j*,[12-14] the partial molar enthalpy changes of the respective components have not been reported as a function of temperature in detail. Recently, the thermodynamic equations have been proposed to analyze the calorimetry of surfactant solutions and applied to the aqueous solution of C8E4 successfully.[15] In this study, we chose three C8E*j*s (j = 3~5) and have considered the influence of the size of hydrophilic group of C*i*E*j* on hydration and micelle formation. In addition the hydration of hydrophobic groups have been discussed by comparing of the results of C8E*j*s with those of ethyleneglycol oligomers C0E*j*.[16]

Experimental

Materials

Tri-, tetra-, pentaethyleneglycol monooctyl ethers (C8E*j*; j = 3,4,5) were purchased from BACHEM Feinchemikalien AG (>98%). C8E3 and C8E4 were purified by the three phase extraction technique (3PHEX) developed by Kahlweit et al[17,18] from the water / C8E*j* / *n*-hexane mixture at

least for six cycles. The mixing ratios in weight were 0.46 / 0.08 / 0.46 for C8E3 from the first to the final cycle, and 0.425 / 0.15 / 0.425 from the first to the fourth cycle and 0.46 / 0.08 / 0.46 for the last two cycles for C8E4. For C8E5, however, a slight amount of more hydrophobic impurities than C8E5 could not be removed by the 3PHEX. Therefore C8E5 was purified by recrystallization from *n*-hexane solution of 30 weight percent at ca. –20°C. To remove a trace amount of water from the resulting materials and prevent them from moisture absorption, they were dried sufficiently in vacuo at 50°C. The purity was checked by a gas-liquid chromatography (>99.5%) and by observing no minimum on the surface tension vs concentration curves at 298.15K; a minimum of about 2 mN m^{-1} observed before the purification was disappeared after it.

Calorimetry

The enthalpy of mixing of water and the respective solutes was measured by the isothermal titration microcalorimeter Thermal Activity Monitor TAM 2277 (Thermometric AB, Sweden) controlled by Digitam 3.0 software. The calorimeter system has been described in detail by Wadsö et al.[19,20] Two half to four microliter of liquid C8E*j* was injected by using the computer-controlled syringe pump from the gas-tight syringe (Hamilton 1725LT) through a stainless steel cannula to ca. 3.2g of water in the 4ml stainless steel ampoule. The solution in the ampoule was stirred by the turbine at the constant speed of 120 rpm. The heat of mixing flows through high-sensitive thermopiles surrounded by a heat sink stabilized at ± 2×10^{-4} °C. The electrical calibration performance makes the results to be quantified. The weight of liquid injected was calculated from accurately

the density values of the liquid and the heat flow was detected to 0.15μW by thermopiles within the experimental error of 0.5μW. At least two runs were performed at a given temperature.

Results and Discussion

The enthalpy of mixing of water and surfactant H^M was measured as a function of the molality of surfactant m_1 at seven temperatures from 283.15K to 313.15K under atmospheric pressure. For the C8E3-water system, it was measured at three temperatures from 283.15K to 288.15K owing to its low cloud point. The H^M value per unit mass of water h^M and the molality of surfactant m_1 are defined as follows:

$$h^M = H^M / n_w M_w = (h_w - h_w^0) / M_w + m_1 (h_1 - h_1^0) \qquad [1]$$

and

$$m_1 = n_1 / n_w M_w . \qquad [2]$$

Here M_w is the molar mass of water, h_i and $h_i^\bullet$ 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 surfactant m_1, respectively.

Figure 1 shows typical titration thermograms of C8E5 where 2.5 μl of liquid surfactant was injected successively into the cell containing ca. 3.2 g of water. It is seen that both height and area of the individual peak are almost constant at low and high concentrations, while decrease gradually at concentrations around the critical micelle concentration CMC at a given temperature. Moreover we see that the height and area decrease with increasing temperature and also the CMC decreases with increasing

temperature. The heat per injection was estimated from its peak-area, and the H^M value at a given n_1 by summing up the area from the first peak to the one at which the total number of moles of C8E5 reaches n_1. The h^M vs m_1 curves of the C8E*j* systems are shown in figure 2; the mixing process is exothermic and h^M becomes more negative with increasing concentration and decreasing temperature. It is noted that h^M value changes almost linearly at low and high concentrations, while non-linearly at concentrations around the CMC. It is also seen that the absolute value of h^M increases with increasing oxyethylene chain length.

Employing T, p, and m_1 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 partial molar enthalpy change of C8E*j* $h_1 - h_1^0$:

$$\left(\partial h^{\mathrm{M}} / \partial m_1\right)_{T,p} = h_1 - h_1^0. \qquad [3]$$

By applying eq.[3] to the experimental data in Fig.2, $h_1 - h_1^0$ were evaluated and plotted against m_1 in Fig.3. The values of $h_1 - h_1^0$ are negative and the absolute values increase with decreasing temperature. As is expected from Fig. 2, they change drastically only at concentrations around CMC. Taking account that surfactant is dissolved in water both as monomer and micelle above the CMC, eqs.[1] and [3] can be written in the other forms as[15]

$$h^{\mathrm{M}} = (h_{\mathrm{w}} - h_{\mathrm{w}}^0)/M_{\mathrm{w}} + m_1^{\mathrm{m}}(h_1^{\mathrm{m}} - h_1^0) + Nm_{\mathrm{mic}}(h_{\mathrm{mic}}/N - h_1^0) \qquad [4]$$

and

$$h_1 - h_1^0 = h_{\mathrm{mic}}/N - h_1^0 - (h_{\mathrm{mic}}/N - h_1^{\mathrm{m}})\left(\partial m_1^{\mathrm{m}} / \partial m_1\right)_{T,p} \qquad [5]$$

respectively under the approximation $\partial N / \partial m_1 = 0$.[7,21] Here the

superscript "m" and subscript "mic" represent surfactant monomer and micelle, and N an average aggregation number, respectively. The enthalpy changes $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$ are referred to as the partial molar enthalpies of surfactant accompanied by the dissolution of pure one into water as monomer and that as micelle, respectively. $h_w - h_w^0$ is the partial molar enthalpy change of water, and will be evaluated and discussed later. As shown in our previous study,[15] the constant values of $h_1 - h_1^0$ at low and high concentrations correspond to $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$, respectively. In contrast to the constant values of $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$, $h_1 - h_1^0$ greatly changes with concentration around the CMC. Therefore eq. [5] suggests that the great changes of $h_1 - h_1^0$ are attributable to the change of monomer concentration with the total molality, $\partial m_1^m / \partial m_1$.

Both values of $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$ of C8E*j* are plotted against temperature in Fig.4 and listed in Table1. They are negative and their absolute values increase with decreasing temperature and increasing oxyethylene chain length. This fact suggests that the interaction between water and C8E*j* is stronger than that between same species and mainly arises from the hydration around C8E*j* molecules. Furthermore we note that the value of $h_1^m - h_1^0$ is more negative at a given temperature and increases more rapidly with increasing temperature than that of $h_{mic} / N - h_1^0$. Consequently C8E*j* molecules in monomeric state are suggested to interact with water molecules more strongly compared with that in micellar state. Here it is noted again that the contribution from one oxyethylene group to $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$ values are almost constant

and this finding supports our previous one with respect to ethylene glycol oligomers.[16]

Further insight can be drawn on this matter by plotting the $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$ values against the oxyethylene chain number j as shown in Fig.5, where the partial molar enthalpy change of C0Ej is also given.[16] It should be emphasized that the change of these enthalpies per oxyethylene group is almost constant and, in addition, that the change in $h_1^m - h_1^0$ is quite similar to that in $h_1 - h_1^0$. In the previous paper, we have mentioned that the hydration of an oxyethylene group is little affected by a small terminal group, such as proton or methyl group.[16,22] Considering the finding in Fig.5, our previous suggestion is still applicable to the present system where the terminal octyl group is greatly lager than methyl group. Some similar values for enthalpy or energy contribution have been reported for the hydration of C12Ej per oxyethylene group.[13,23]

It is important to discribe the CMC value of C8Ej before examining the enthalpy of micelle formation. It is more or less dependent on the way of determination. In this study, we employed the one proposed by Phillips. By substituting the experimental data of $h_1 - h_1^0$, $h_{mic} / N - h_1^0$, and $h_1^m - h_1^0$ into eq. [5], the derivatives $\partial m_1^m / \partial m_1$ were obtained for all systems and plotted against m in Fig.6. According to the definition by Phillips, the inflection point ($\partial^3 m_1^m / \partial m_1^3 = 0$) on these diagrams is regarded as CMC.[24] On the other hand, the constant molality of monomer being in equilibrium with micelle is also an important quantity. In order to estimate m_1^m and CMC values, the derivatives $\partial m_1^m / \partial m_1$ in Fig.6 have to be reproduced by a function of total molality m_1. It was found that a

following linear combination of two hyperbolic tangents is one of the best fitting function for this purpose.

$$(\partial m_1^{\mathrm{m}} / \partial m_1)_{T,p} = \frac{1}{2}[\mathrm{A}\tanh(\mathrm{B}m_1 + \mathrm{C}) + \mathrm{D}\tanh(\mathrm{E}m_1 + \mathrm{F}) + \mathrm{G}] \quad [6]$$

It is seen that the experimental values shown by circles are reproduced satisfactorily by the fitting functions drawn by solid lines. Since the value of m_1^{m} is obtained by solving the differential equation [6], the both values of CMC and $m_1^{\mathrm{m,c}}$ can be calculated, where $m_1^{\mathrm{m,c}}$ is referred to as a constant value of monomer concentration, and regarded to be the concentration of monomer being in equilibrium with micelle. The results were shown in Fig.7 and Table 2 together with the CMC values obtained by surface tension measurements. It is seen that the value of CMC defined here is nearly equal to that by surface tension measurements, and $m_1^{\mathrm{m,c}}$ value is a little larger than the CMC.

Now let us return to the enthalpy of micelle formation $\Delta_{\mathrm{W}}^{\mathrm{M}}h$. It is calculated by

$$\Delta_{\mathrm{W}}^{\mathrm{M}}h = h_{\mathrm{mic}} / N - h_1^{\mathrm{m}} = (h_{\mathrm{mic}} / N - h_1^{\bullet}) - (h_1^{\mathrm{m}} - h_1^{0}), \quad [7]$$

and shown in Fig.8; they are positive and decrease with increasing temperature. This shows that forming micelle diminishes the overall molecular interaction between water and C8E*j* molecules. It is worth mentioning that the volume change accompanied by micelle formation of C8E4 has been reported positive.[25] Taking account of the increase of enthalpy and volume accompanied by micelle formation of C8E*j*, it is probable that the C8E*j* molecules (mainly hydrocarbon part) become more flexible owing to dehydration by forming micelle. Although the

difference of $\Delta_W^M h$ values among the three C8E*j*s is fairly small compared to that of $h_1^m - h_1^0$ or $h_{mic}/N - h_1^0$, it is undoubtedly that $\Delta_W^M h$ increases with increasing *j*. This suggests that the hydration of oxyethylene group of C8E*j* is weakened to some degree by forming micelle. We shall return to this point later.

Besides the partial molar enthalpy of surfactant, let us now discuss the micelle formation from the standpoint of the partial molar enthalpy change of water,[15] $h_w - h_w^0$, which is calculated by substituting $h_1 - h_1^\bullet$ value into eq. [1]. The results of C8E*j* system are given in Fig.9. First it is seen that the values of $h_w - h_w^0$ are almost zero at a concentration below the CMC. This fact also supports that the aqueous solutions are regarded as ideally dilute ones. Secondly the $h_w - h_w^0$ values start to decrease sharply at a concentration around the CMC. This is in striking contrast to the increase in $h_1 - h_1^0$ accompanied by micelle formation shown in Fig.3. That is to say, the micelle formation is exothermic from the viewpoint of the enthalpy change of water, while endothermic from that of surfactants. This fact suggests that some water molecules contribute to the depression of the partial molar enthalpy of water on the occasion of micelle formation. We have discussed the reason of the decrease in $h_w - h_w^0$ value and concluded that some water molecules are trapped inside the hydrophilic atmosphere[21,26] of the micelle particles and their interaction is fairly enhanced in limited space because molecular thermal motion is restricted.[15] The increase in its absolute value with growing *j* supports our view that some water molecules are restricted in the hydrophilic atmosphere and responsible for the negative values of $h_w - h_w^0$. Furthermore the

magnitude is enhanced drastically with falling temperature, suggesting the cause for the negative $h_w - h_w^0$ is strongly temperature dependent such as hydrogen bonding.

Let us now return to the enthalpy of surfactant again. To shed light on the hydration of C8E*j* in more detail, it shall be of advantage to compare the differential enthalpy of solution of C8E*j* with that of C0E*j*. Figure 10 shows the temperature dependence of the $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$ of C8E*j* and $h_1 - h_1^0$ of C0E*j*(*j* = 4 or 5) system. The observations are summarized as follows: (i) $h_1^m - h_1^0$ of C8E*j* is more negative than $h_1 - h_1^0$ of C0E*j* at low temperatures; (ii) the slope of $h_1^m - h_1^0$ of C8E*j* is much larger than that of $h_1 - h_1^0$ of C0E*j*, therefore, $h_1^m - h_1^0$ of C8E*j* becomes less negative than $h_1 - h_1^0$ of C0E*j* at higher temperatures; (iii) $h_{mic} / N - h_1^0$ of C8E*j* is less negative than that of $h_1 - h_1^0$ of C0E*j*; and (iv) the slope of $h_{mic} / N - h_1^0$ of C8E*j* is similar to that of $h_1 - h_1^0$ of C0E*j*.

The results (i) and (ii) may suggest that C8E*j* molecule, which derived by substituting terminal hydrogen of C0E*j* molecule by the alkyl chain, interacts with water molecules more strongly compared with C0E*j* molecules. This draws the important conclusion that the interaction between the alkyl group of C8E*j* and water undoubtedly lowers the partial molar enthalpy of C8E*j*, and it depends on temperature significantly. The result (iv) may predict, with respect to the hydration of micelle, that the interaction between water and alkyl group of C8E*j* is practically vanished in micelle at all temperatures, i.e., water molecules are practically squeezed out from micelle core.[21,27] By taking into account that the micelle formation still weakens the interaction between water and C8E*j* molecules

(positive $\Delta_W^M h$) even at 313.15K where interaction between water and alkyl group of monomer of C8E*j* may be disappeared, furthermore, the results (ii) and (iii) propose the idea that the interaction between water and oxyethylene group of C8E*j* is weakened to some degree by forming micelle.

Finally let us give an overview on the micelle formation of C8E*j*. The experimental results show certainly that the micelle formation of C8E*j* causes the enlargement of enthalpy and then entropy. It is attributable to the dehydration of C8E*j* molecules. Judging from the findings derived from the thermodynamic analysis of the enthalpy of mixing, therefore, one can safely state that the driving force of micelle formation of C8E*j* is mainly the increment of entropy by dehydration of hydrophilic parts at higher temperature, while that the increment by dehydration of hydrophobic parts become dominant at lower temperature in micellization process.

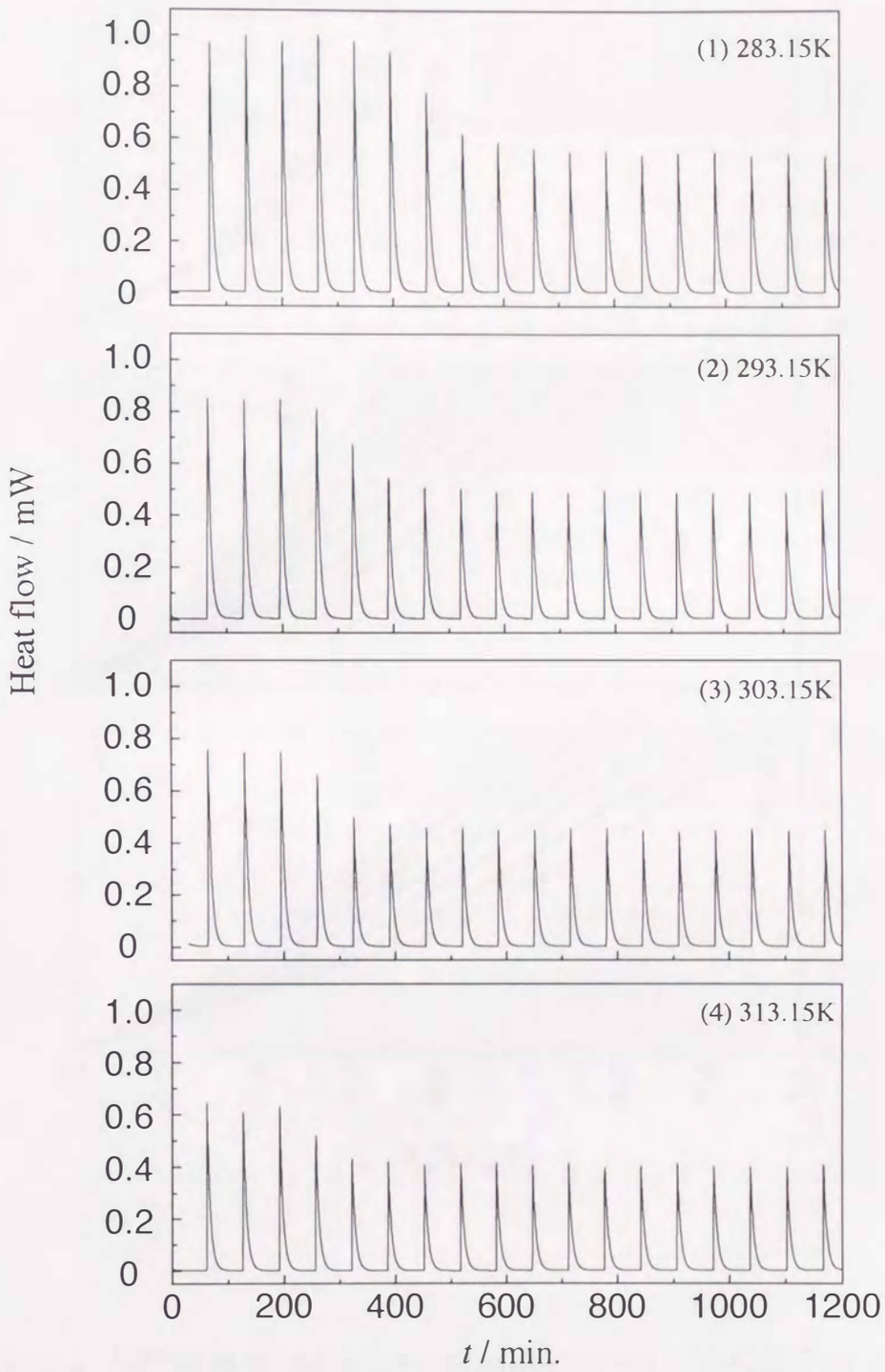

Figure 1a. Heat flow vs time curves of C8E5-water system: (1) T= 283.15 K, (2) 293.15, (3) 303.15, (4) 313.15.

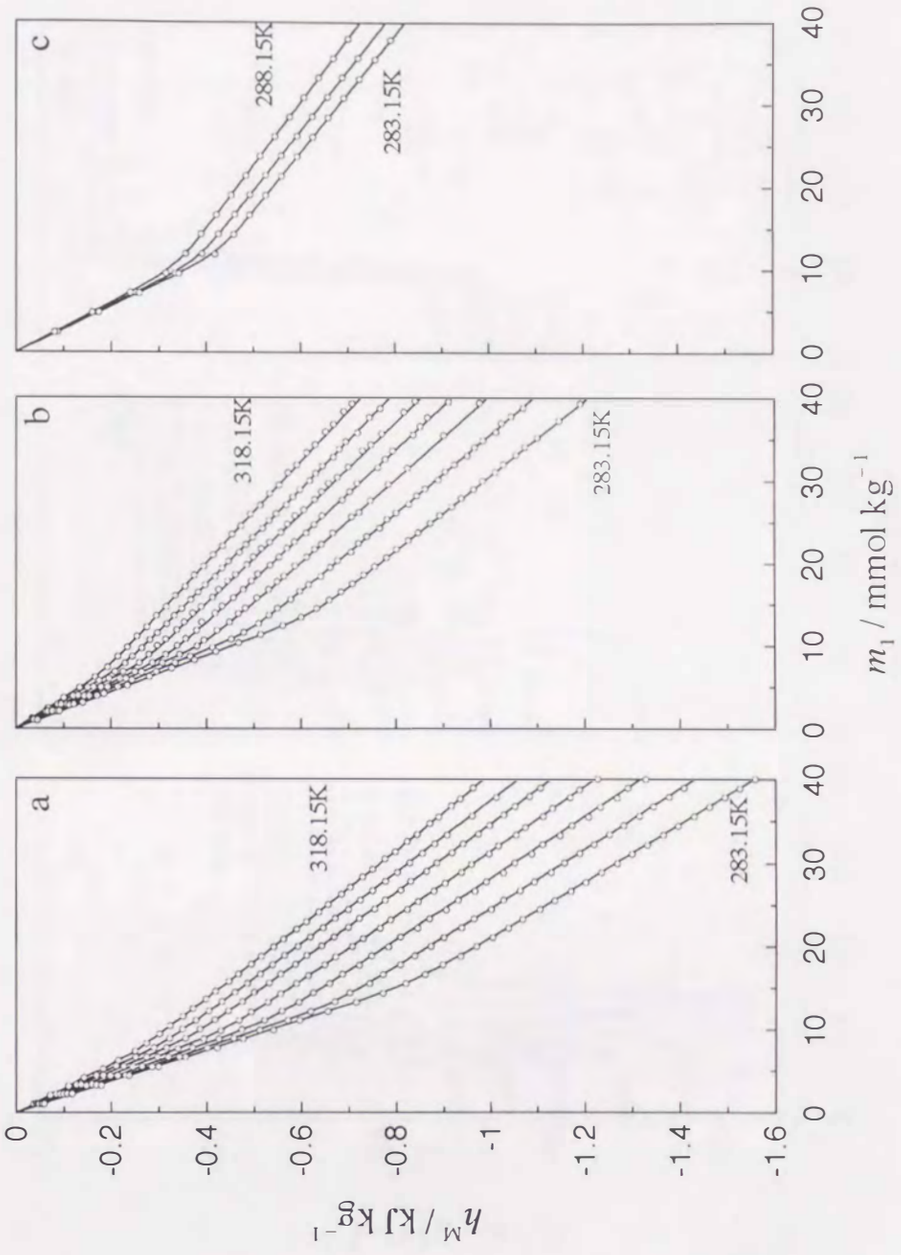

Figure 2. Enthalpy of mixing vs molality curves: (a) C8E5 (at 5K intervals), (b) C8E4 (at 5K intervals), (c) C8E3 (at 2.5K intervals).

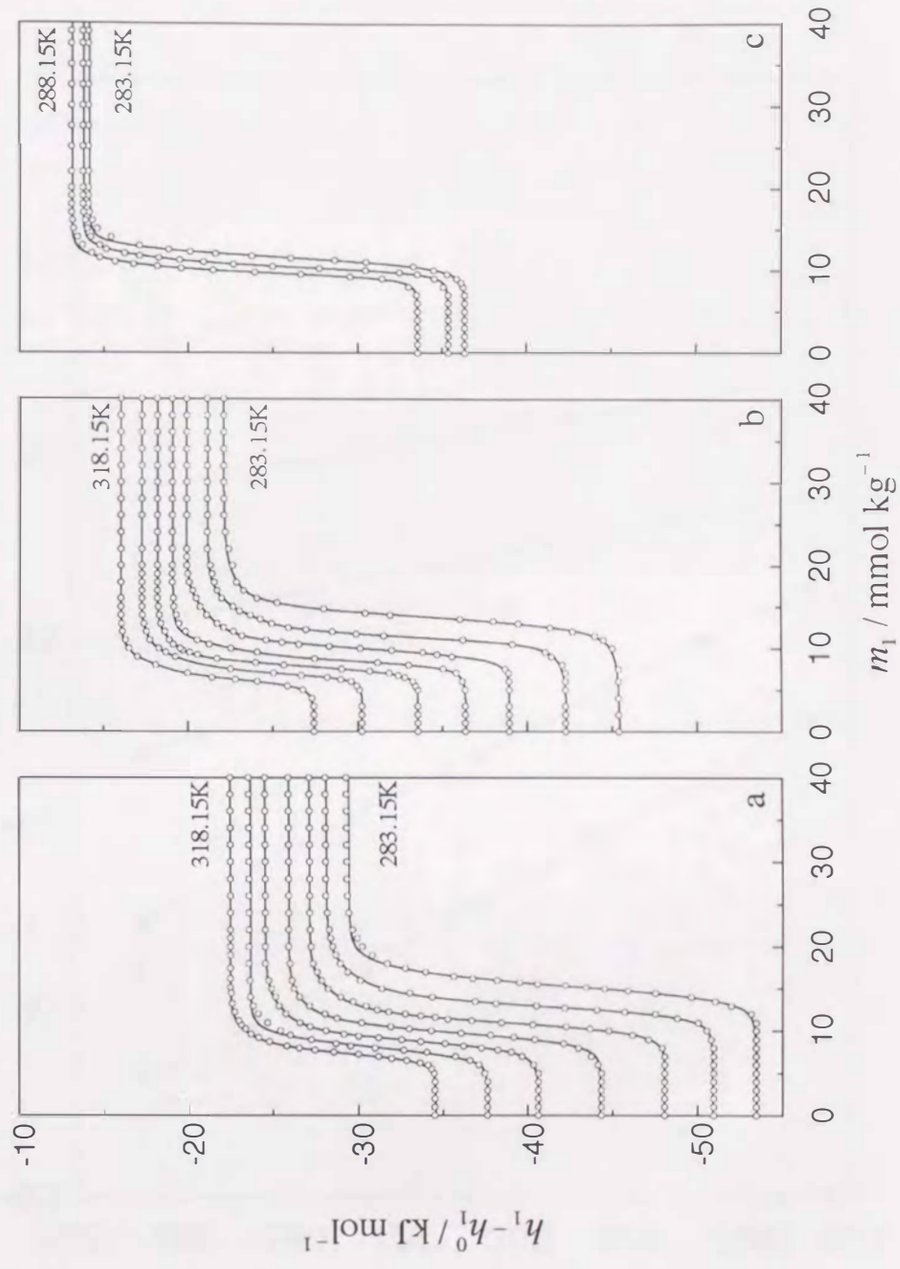

Figure 3. Partial molar enthalpy change of C8E*j* vs molality curves: (a) C8E5 (at 5K intervals), (b) C8E4 (at 5K intervals), (c) C8E3 (at 2.5K intervals).

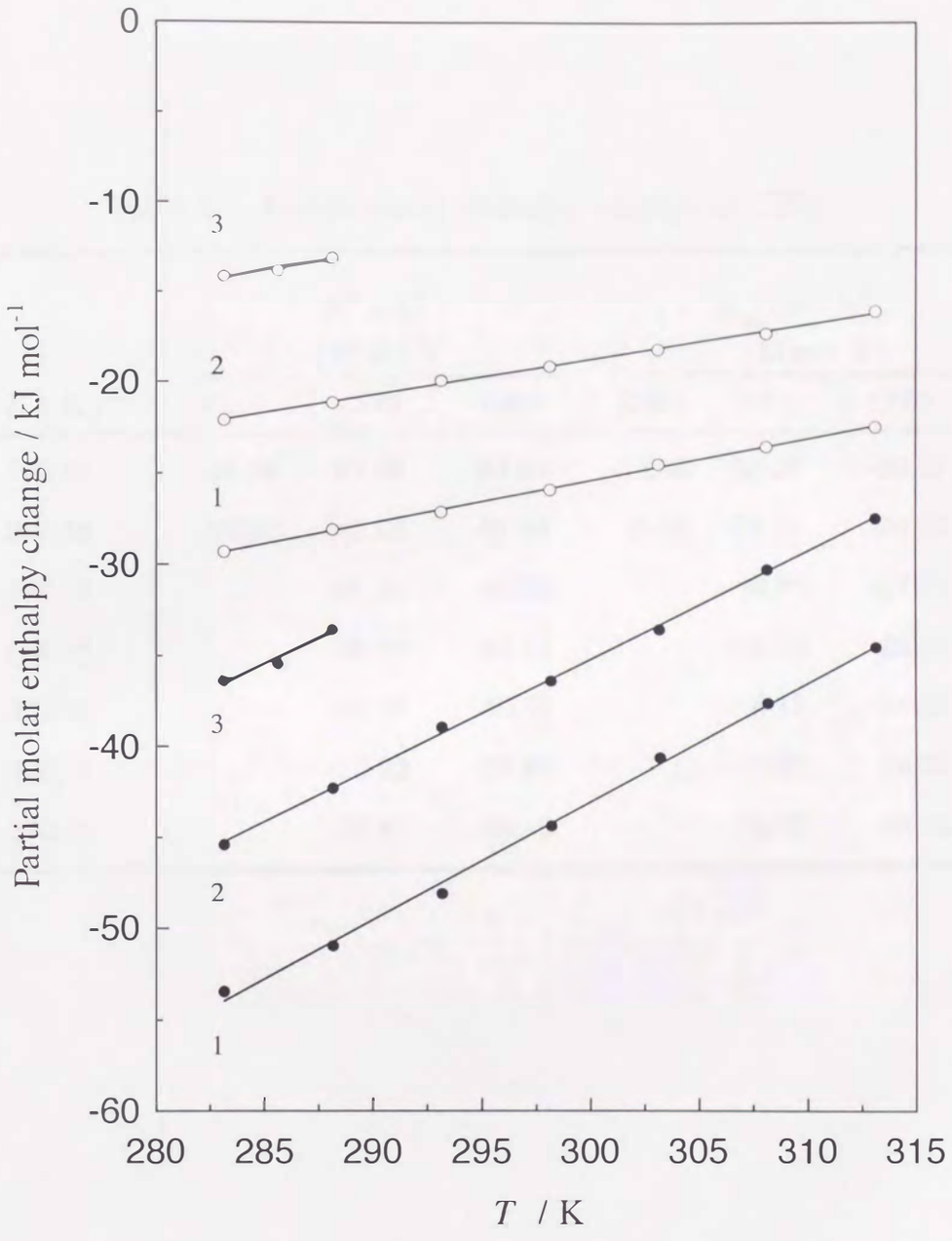

Figure 4. Partial molar enthalpy change of C8E*j* vs temperature curves: (●) $h_1^m - h_1^0$, (○) $h_{mic}/N - h_1^0$; (1) C8E5, (2) C8E4, (3) C8E3.

Table 1. Partial molar enthalpy change of C8E*j*.

	$h_1^m - h_1^0$ [kJ mol^{-1}]			$h_{mic}/N - h_1^0$ [kJ mol^{-1}]		
T [K]	C8E3	C8E4	C8E5	C8E3	C8E4	C8E5
283.15	-36.34	-45.38	-53.44	-14.08	-22.07	-29.27
288.15	-33.53	-42.25	-50.94	-13.08	-21.11	-28.05
293.15		-38.94	-48.08		-19.91	-27.10
298.15		-36.36	-44.33		-19.09	-25.88
303.15		-33.52	-40.60		-18.18	-24.49
308.15		-30.23	-37.61		-17.27	-23.52
313.15		-27.41	-34.49		-16.02	-22.42

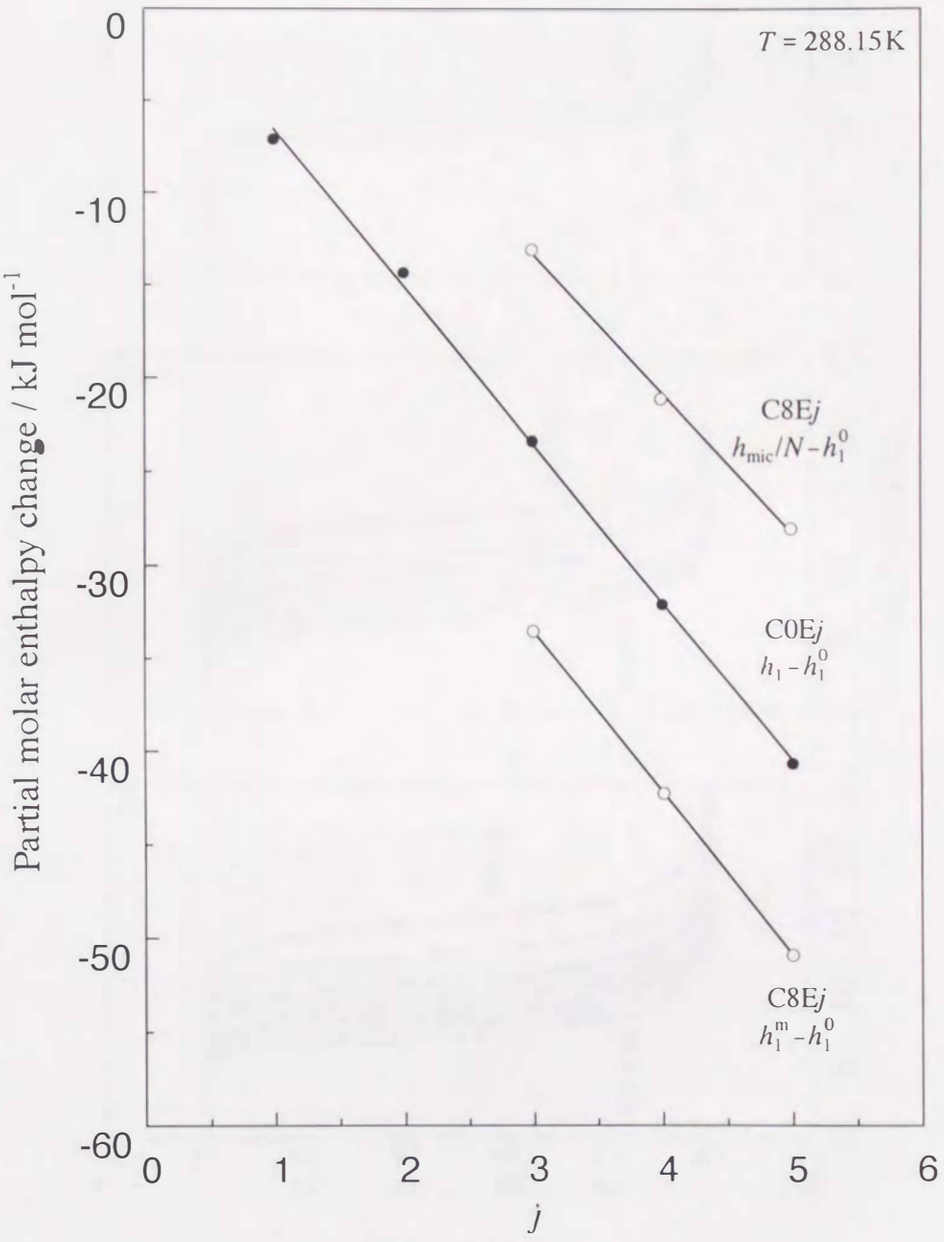

Figure 5. Partial molar enthalpy change vs the number j curves at 288.15 K. (○) C8Ej, (●) C0Ej.

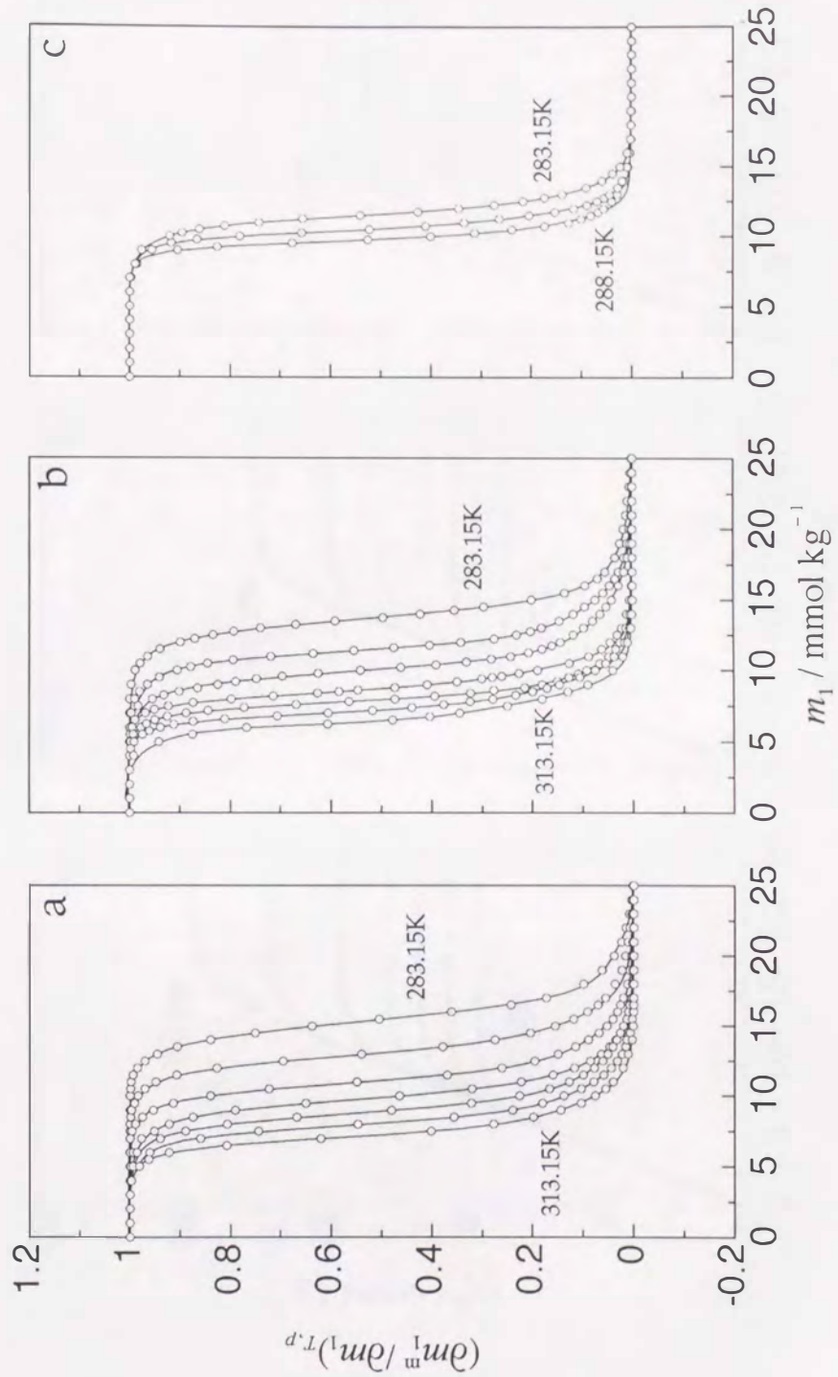

Figure 6. $\partial m_1^m / \partial m_1$ of C8E*j* vs molality curves: (a) C8E5 (at 5K intervals), (b) C8E4 (at 5K intervals), (c) C8E3 (at 2.5K intervals).

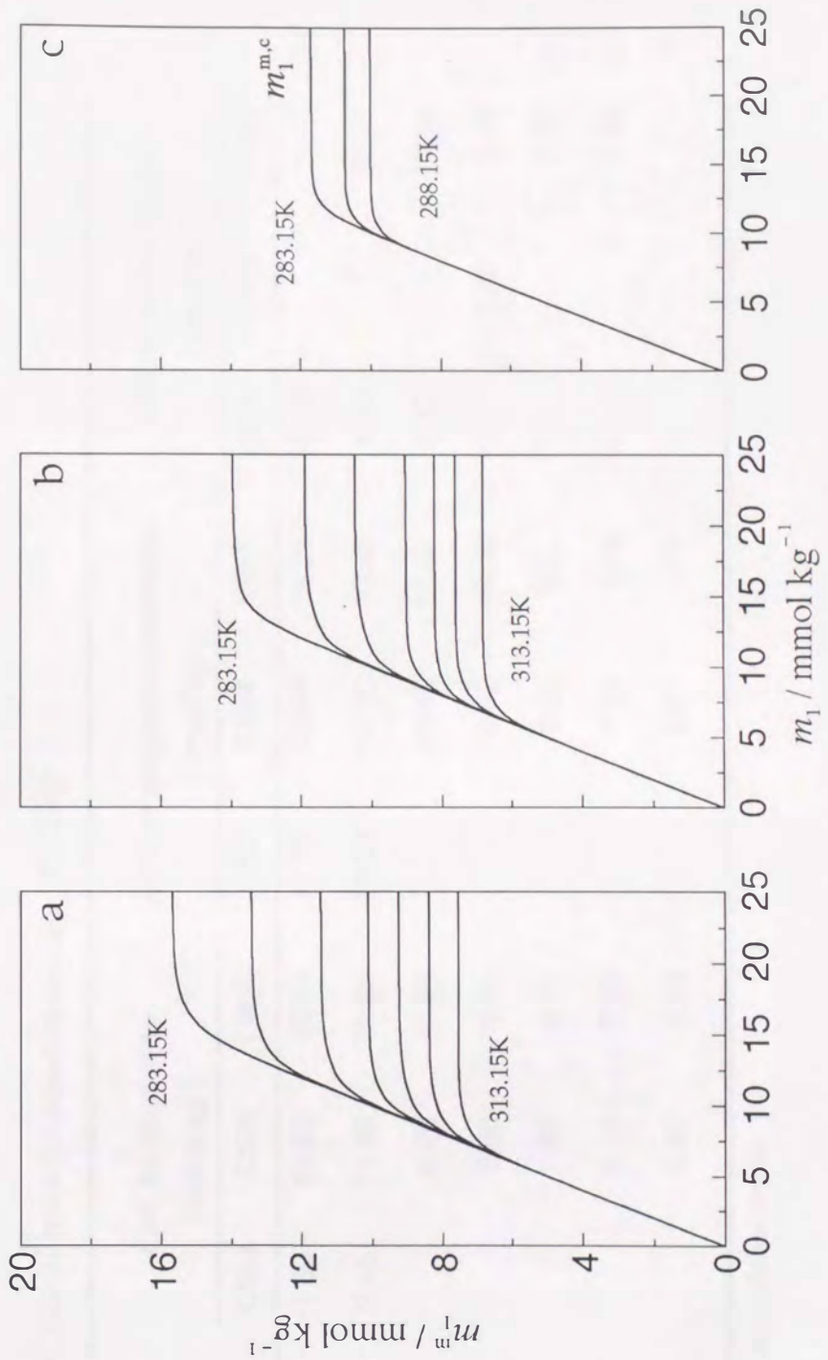

Figure 7. Monomer concentration vs total molality curves: (a) C8E5 (at 5K intervals), (b) C8E4 (at 5K intervals), (c) C8E3 (at 2.5K intervals).

Table 2. Critical micelle concentrations of C8E*j*.

	CMC by calorimetry [mmol kg^{-1}]			constant monomer concentration [mmol kg^{-1}]			CMC by surface tension [a] [mmol kg^{-1}]		
T [K]	C8E3	C8E4	C8E5	C8E3	C8E4	C8E5	C8E3	C8E4	C8E5
283.15	11.30	13.60	15.45	11.73	13.96	15.70	10.98		
288.15	9.45	11.45	13.05	10.03	11.88	13.45	9.50		13.10
293.15		9.90	11.05		10.46	11.47	8.45		10.90
298.15		8.60	9.75		9.02	10.13		8.48	9.50
303.15		7.65	8.75		8.21	9.26			8.40
308.15		6.52	7.95		7.50	8.39			7.56
313.15		6.20	7.15		6.83	7.58			

a. Ohta et. al. unpublished results

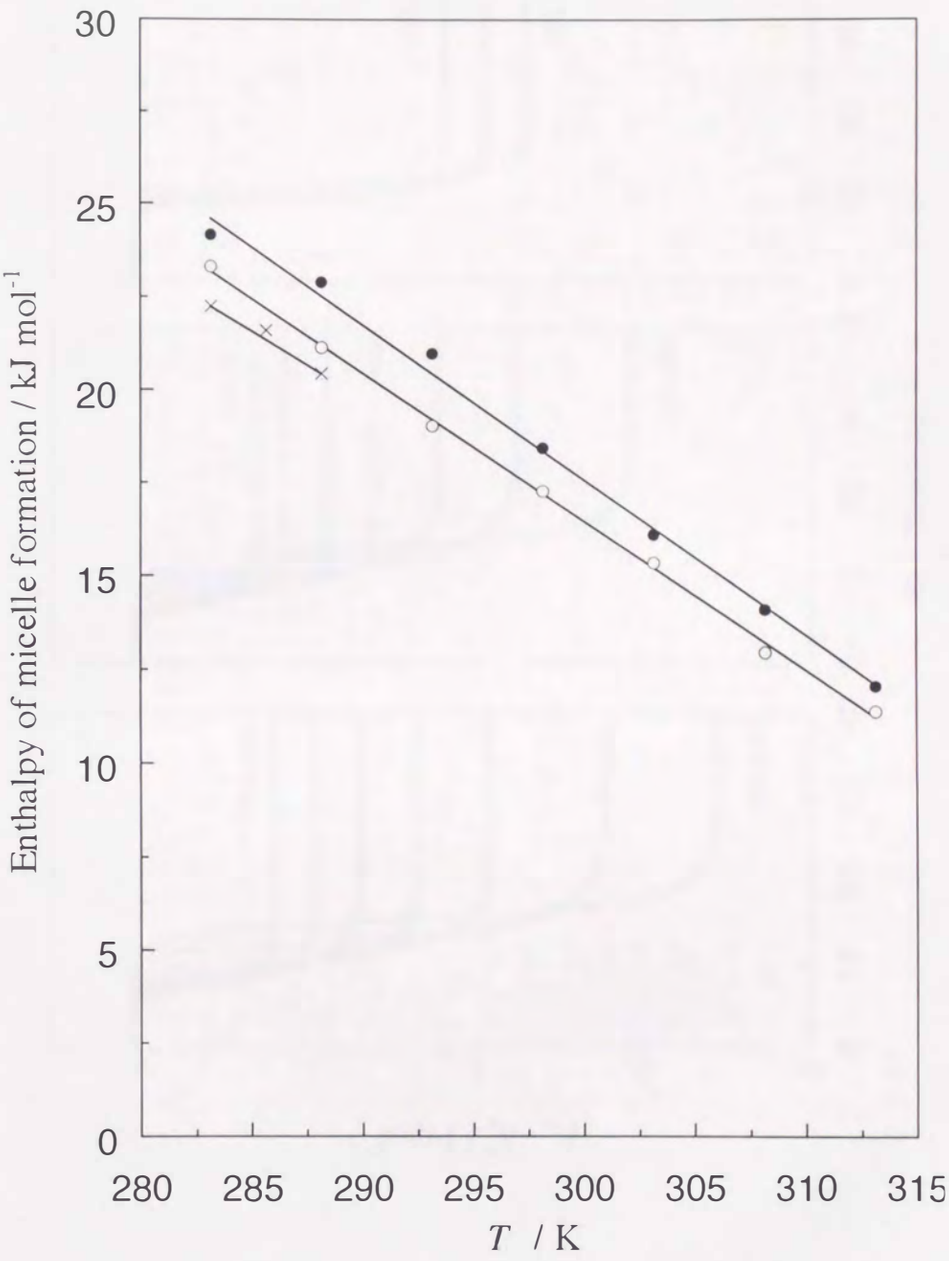

Figure 8. Enthalpy of micelle formation vs temperature curves: (●) C8E5; (○) C8E4; (×) C8E3.

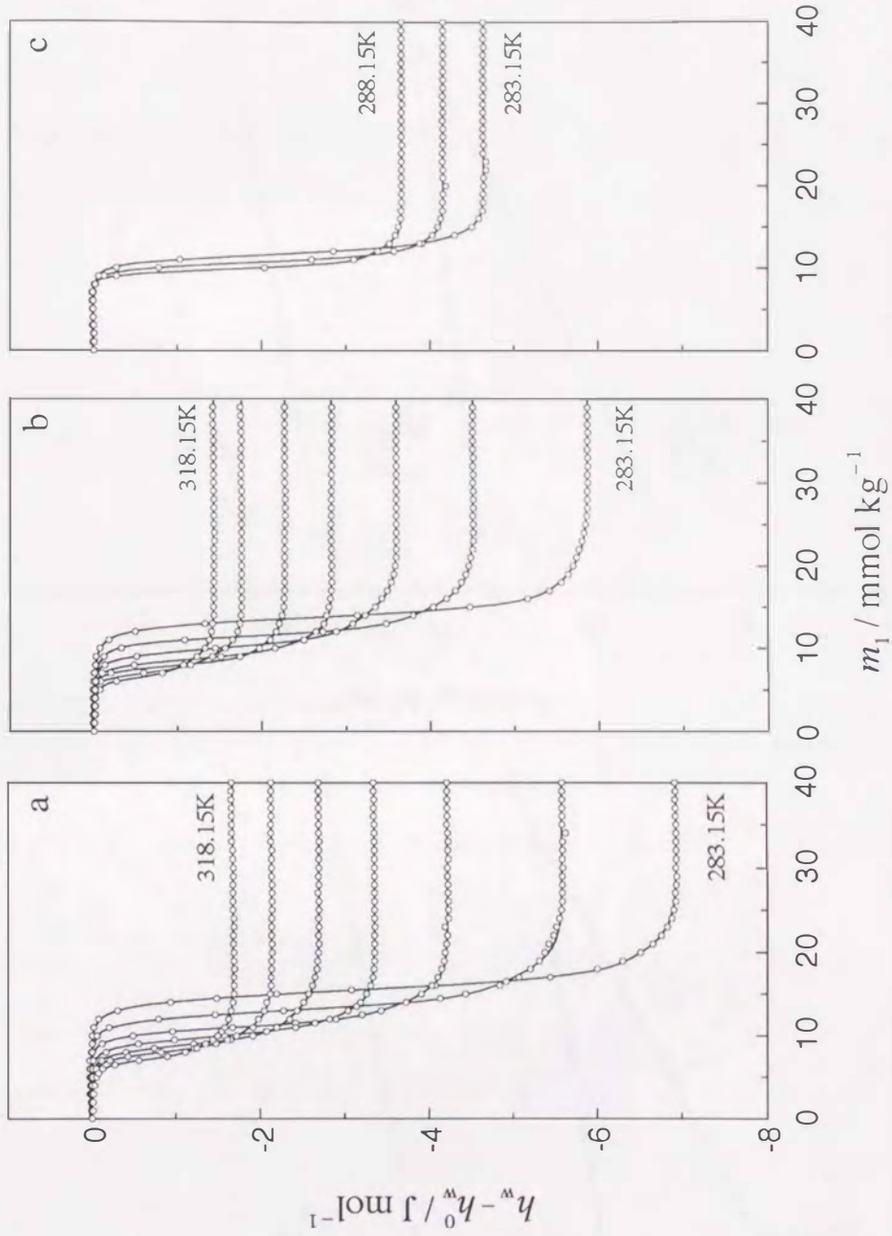

Figure 9. Partial molar enthalpy change of water vs molality curves: (a) C8E5 (at 5K intervals), (b) C8E4 (at 5K intervals), (c) C8E3 (at 2.5K intervals).

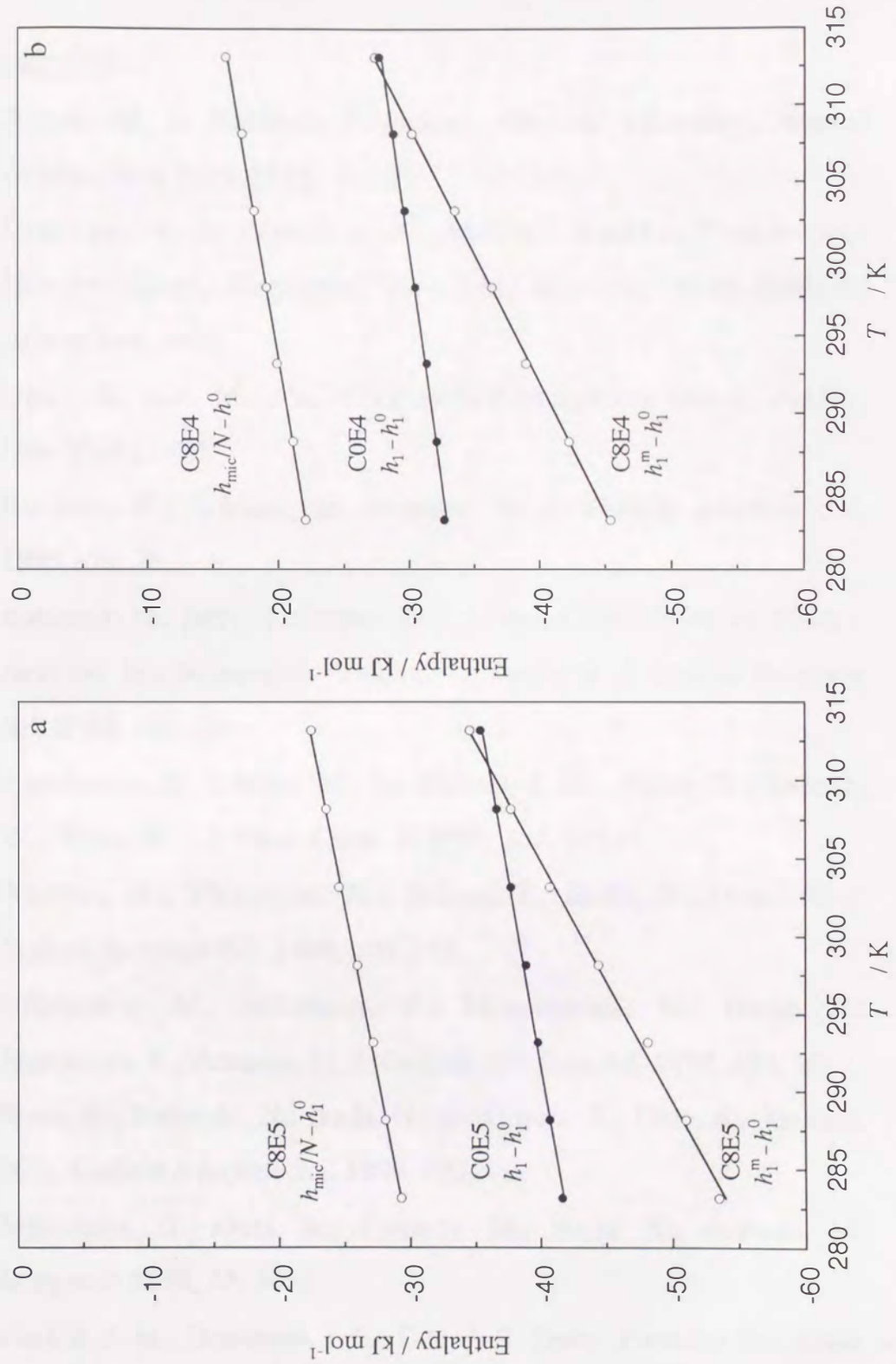

Figure 10. Partial molar enthalpy change vs temperature curves. (a) C*i*E5, (b) C*i*E4 ; (○) C8E*j*, (●) C0E*j*.

References

1. Schick, M. J. *Nonionic Surfactant: Physical Chemistry*, Marcel Dekker, New York, 1986.
2. Degiorgio, V. in *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*; Degiorgio, V.; Corti, M.; eds., North-Holland: Amsterdam, 1985.
3. Ogino, K.; Abe, M.; eds. *Mixed Surfactant Systems,* Marcel Dekker, New York, 1993.
4. Kunieda, H.; Nakano, A.; Akimaru, M. *J. Colloid Interface Sci.* **1995**,170, 78.
5. Kahlweit, M.; Strey, R.; Busse, G. *J. Phys. Chem.* **1990**, *94*, 3881.
6. Aratono, M.; Nagoya, F.; Takiue, T.; Ikeda, N. *J. Colloid Interface Sci.* **1994**, *165*, 296.
7. Amararene, A.; Gindre, M.; Le Huérou, J. -Y.; Nicot, W.; Urbach, W.; Waks, M. *J. Phys. Chem. B* **1997**, *101*, 10751.
8. Aratono, M.; Villeneuve, M.; Takiue, T.; Ikeda, N.; Iyota, H. *J. Colloid Interface Sci.* **1998**, *200*, 161.
9. Villeneuve, M.; Sakamoto, H.; Minamizawa, H.; Ikeda, N.; Motomura, K.; Aratono, M. *J. Colloid Interface Sci.* **1997**, *194*, 301.
10. Iyota, H.; Todoroki, N.; Ikeda, N.; Motomura, K.; Ohta, A.; Aratono, M. *J. Colloid Interface Sci.* **1999**, *216*, 41.
11. Matsubara, H.; Ohta, A.; Kameda, M.; Ikeda, N.; Aratono, M. *Langmuir* **1999**, *15*, 5496.
12. Corkill, J. M.; Goodman, J. F.; Tate, J. R. *Trans. Faraday Soc*. **1964**, *60*, 996.
13. Olofsson, G. *J. Phys. Chem.* **1985**, *89*,1473.

14. Weckström, K.; Hann, K.; Rosenholm, J. B. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 733.

15. Aratono, M.; Ohta, A.; Ikeda, N.; Matsubara, A.; Motomura, K.; Takiue, T. *J. Phys. Chem. B* **1997**, *101*, 3535.

16. Ohta, A.; Takiue, T.; Ikeda, N.; Aratono, M. *J. Phys. Chem. B* **1998**, *102*, 4809.

17. Schubert, K.V.; Strey, R.; Kahlweit, M. *Progr. Colloid Polym. Sci.* **1991**, *84*, 103.

18. Schubert, K.V.; Strey, R.; Kahlweit, M. *J. Colloid Interface Sci.* **1991**, *141*, 21.

19. Wadsö, I. in *Solution Calorimetry*, Marsh, K. N.; O'Hare, P.A.G.; eds., Blackwell: Oxford, 1994.

20. Bäckman, P.; Bastos, M.; Briggner, L.-E.; Hägg, S.; Hallén, D.; Lönnbro, P.; Nilsson, S. -O.; Olofsson, G.; Schön, A.; Suurkuusk, A. J.; Teixeira, C.; Wadsö, I. *Pure & Appl. Chem.* **1994**, *66*, 375.

21. Alami, E.; Kamenka, N.; Raharimihamina, A.; Zana, R. *J. Colloid Interface Sci.* **1993**, *158*, 342.

22. Dohnal, V.; Roux, A. H.; Hynek, V. *J. Solution Chem.* **1994**, *23*, 889.

23. Klose, G.; Eisenblätter, St.; Galle, J.; Islamov, A.; Dietric, U. *Langmuir* **1995**, *11*, 2889.

24. Phillips, J. N. *Trans. Faraday Soc.* **1955**, *51*, 561.

25. Wieczorek, S. A. *J. Chem. Themodyn.* **1997**, *29*, 1269.

26. Jonströmer, M; Jönsson, B.; Lindman, B. *J. Phys. Chem.* **1991**, *95*, 3293.

27. Tanford, C; Nozaki, Y.; Rohde, M. F. *J. Phys. Chem.* **1977**, *81*, 1555.

Chapter III

Calorimetry of Micellar Solutions of Pentaethylene Glycol Monooctyl and Monodecyl Ethers

Introduction

Calorimetry is a powerful method to acquire information on the molecular interaction rather directly. Especially the isothermal titration calorimetry has been employed widely for the investigations of micelle formation,[1-7] partitioning of amphipiles to the lipid membranes,[8-11] and so on. From the thermodynamic point of view, one of the advantages of the titration calorimetry is considered to be that the partial molar enthalpy change of solute can be conveniently approximated by the primary experimental results of titration heat per moles of solute injected.[12,13] Although this advantage is available, strictly speaking, only when pure solute like pure liquid of polyethylene glycol monooctyl ethers (C8E*j*) is injected, the same thermodynamic strategy has been often employed even when an aqueous surfactant solution is injected and little attention has been put on this point. Since most of surfactants including C*i*E*j* ($i \geq 10$) are solids at room temperature, we need frequently the titration experiments of aqueous solution of surfactant as many studies have been curried out in this way. Therefore, we first propose the proper thermodynamic analysis in order to obtain the enthalpy of micelle formation from the titration calorimetry of aqueous solution of surfactant. The titration experiment of aqueous C8E4 solution will demonstrate the usefulness and correctness of the thermodynamic method proposed in this study.

Now polyethylene glycol monoalkyl ethers [C*i*E*j*], are typical nonionic surfactants[14,15] and often used to investigate micellar solution or micelle formation, because the systematic studies can be carried out by changing the length of alkyl chain in hydrophobic group, or the number of

ethylene oxide in hydrophilic group. Since the hydration of hydrophilic and hydrophobic moieties are strongly influential in the micellization, it is highly useful to clarify the hydration of the respective groups in surfactant separately. From this standpoint, we have focused on the effect of the number of the EO group and reported that partial molar enthalpy and volume per ethylene oxide are almost constant and the hydration is little affected by terminal hydrophobic group in our previous study.[1,2] In this paper, therefore, we will examine the effect of the length of hydrocarbon chain of C*i*E*j* on the micelle formation, and the hydration of surfactant monomer and micelle particles.

We choose the C8E5 and C10E5, and evaluated the partial molar enthalpy change accompanied by dissolution and micelle formation by the titration calorimetry. For the C8E5 system, the enthalpy of mixing of water and pure surfactant was measured. For the C10E5 system, on the other hand, the enthalpy of mixing of water and aqueous solution of surfactant was measured, because the critical micelle concentration CMC of C10E5 is very low and its melting point is about 15℃, and the thermodynamic equations proposed in this study were applied.

Experimental

Materials

Pentaethylene glycol monodecyl ether (C10E5) was obtained from Nikko Chemicals Co., Ltd., (>99.5%) and used without further purification. Pentaethylene glycol monooctyl ether (C8E5) was purchased from

BACHEM Feinchemikalien AG (>98%) and purified by recrystallization from *n*-hexane solution of 30 weight percent at ca. –20°C. To remove a trace amount of water from the resulting materials and prevent them from moisture absorption, they were dried sufficiently in vacuo at 50°C. The purity was checked by a gas-liquid chromatography (>99.5%) and by observing no minimum on the surface tension vs concentration curves at 298.15K; a minimum of about 2 mN m^{-1} observed before the purification was disappeared after it. The critical micelle concentration, CMC, of C10E5 and that of C8E5 were 9.56 and 0.767 mmol kg^{-1} at 298.15K from the surface tension measurement, respectively.

Calorimetry

The enthalpy of mixing of water and the aqueous solutions or pure liquids of surfactants was measured by the isothermal titration microcalorimeter Thermal Activity Monitor TAM 2277 (Thermometric AB, Sweden) controlled by Digitam 3.0 software. The calorimeter system has been described in detail by Wadsö et al.[16,17] Ten microliter of aqueous solutions of C10E5 at 50.8497 mmol kg^{-1}or one to two half microliter of pure liquid C8E5, was injected by using the computer-controlled syringe pump from the gas-tight syringe (Hamilton 1725LT) through a stainless steel cannula to ca. 2.8g of water in the 4ml stainless steel ampoule. The turbine stirred the solution in the ampoule at the constant speed of 120 rpm. The heat of mixing flows through high-sensitive thermopiles surrounded by a heat sink stabilized at $\pm 2 \times 10^{-4}$ °C and was quantified by the electrical calibration performance. The weight of liquid injected was accurately

calculated from the density values of the liquid and the heat flow was detected to 0.15μW by thermopiles within the experimental error of 0.5μW. The experiments were performed at least two runs at a given temperature.

Thermodynamic equations

Prior to developing thermodynamic equations, we demonstrate that a peak area of titration thermogram per moles of surfactant in the solution injected do not give the correct partial molar enthalpy change of surfactant and enthalpy of micelle formation as mentioned in Introduction. Figures 1a and 1b are the thermograms of the titration of pure liquid C8E4 into water at 298.15 K and those of the aqueous solution of 150.80 mmol kg^{-1} of C8E4, respectively. It is seen that both the processes are exothermic and the peak area is drastically decreased around the cmc in both systems. The titration heats per moles of C8E4 in Figs.1a and 1b are plotted against the molality m_1 and compared with our previous results of the partial molar enthalpy change of C8E4 in Fig.2,[5] where the partial molar enthalpy of C8E4 at zero molality is employed as the reference state. It should be noted that the titration heat of pure surfactant (full circles) is almost, but the titration heat of aqueous surfactant solution (open circles) is not, in accord with the partial molar enthalpy (full line). Therefore we have to develop the equations being necessary for the titration calorimetry of aqueous surfactant solutions.

Consider the mixing process of n_w^0 moles of water and the aqueous solution at m_1^* mol kg^{-1} in which the n_w^* mols of water and n_1 moles of surfactant are contained. The enthalpy of mixing H^M is defined by

$$H^{M} = (n_w^0 + n_w^*)h_w + n_1 h_1 - n_w^0 h_w^0 - n_w^* h_w^* - n_1 h_1^*, \quad [1]$$

where h_i is the partial molar enthalpy of component i in the aqueous solution at a given temperature T, pressure p, and molality of surfactant m_1, the superscripts "0" and "$*$" refer to pure water and the titrant, and the subscripts w and 1 refer to water and surfactant, respectively. Now we introduce the following reduced quantity h^M:

$$h^{M} = \frac{H^{M}}{(n_w^0 + n_w^*)M_w} = \frac{X_w^0(h_w - h_w^0) + X_w^*(h_w - h_w^*)}{M_w} + m_1(h_1 - h_1^*), \quad [2]$$

where M_w is the molar mass of water expressed in kg mol^{-1}, m_1 is the molality of surfactant, and the fractions of water are defined by $X_w^0 = n_w^0/(n_w^0 + n_w^*)$ and $X_w^* = n_w^*/(n_w^0 + n_w^*)$, respectively. By choosing of T, p, and m_1 as the independent thermodynamic variables and taking account of the Gibbs-Duhem equation, the derivative of h^M with respect to m_1 is given by

$$\left(\frac{\partial h^{M}}{\partial m_1}\right)_{T,p} = \frac{1}{M_w}\frac{(h_w^* - h_w^0)}{m_1^*} + h_1 - h_1^* \quad [3]$$

at constant T and p. It should be noted that the first term of rhs of eq. [3] depends only on the concentration of the titrant.

Although eq. [3] is applicable irrespective of whether m_1 is lower or higher than CMC, it is informative to consider the contributions of monomer and micelle of surfactant to thermodynamic quantities separately when m_1 is higher than CMC. The partial molar enthalpy and the molality of surfactant are given by

$$m_1 h_1 = m_1^m h_1^m + m_{mic} h_{mic}, \quad [4]$$

and

$$m_1 = m_1^{\mathrm{m}} + N m_{\mathrm{mic}}, \qquad [5]$$

respectively. Here the superscript "m" and subscript "mic" refer to monomer and micelle aggregate, and N is the average aggregation number, respectively. Substituting eqs. [4] and [5] into eq. [2] yields the following equation,

$$h^{\mathrm{M}} = \frac{1}{M_{\mathrm{w}}}[X_{\mathrm{w}}^{0}(h_{\mathrm{w}} - h_{\mathrm{w}}^{0}) + X_{\mathrm{w}}^{*}(h_{\mathrm{w}} - h_{\mathrm{w}}^{*})] + m_1^{\mathrm{m}}(h_1^{\mathrm{m}} - h_1^{*}) + N m_{\mathrm{mic}}(\frac{h_{\mathrm{mic}}}{N} - h_1^{*}). \qquad [6]$$

Thus, the analogue of eq. [3] is given by

$$\begin{aligned}\left(\partial h^{\mathrm{M}} / \partial m_1\right)_{T,p} = {} & \frac{1}{m_1^{*}} \frac{(h_{\mathrm{w}}^{*} - h_{\mathrm{w}}^{0})}{M_{\mathrm{w}}} + \left(\partial m_1^{\mathrm{m}} / \partial m_1\right)_{T,p}(h_1^{\mathrm{m}} - h_1^{*}) \\ & + \left[1 - \left(\partial m_1^{\mathrm{m}} / \partial m_1\right)_{T,p}\right](\frac{h_{\mathrm{mic}}}{N} - h_1^{*})\end{aligned} \qquad [7]$$

under the approximation that the dependence of N on m_1 is negligibly small.

At a low concentration where no aggregates are present, eq. [7] is reduced to

$$\begin{aligned}\left(\partial h^{\mathrm{M}} / \partial m_1\right)_{T,p} = {} & \frac{1}{m_1^{*}} \frac{(h_{\mathrm{w}}^{*} - h_{\mathrm{w}}^{0})}{M_{\mathrm{w}}} + h_1^{\mathrm{m}} - h_1^{*} \\ \equiv {} & \Delta h_1 (m_1 < C)\end{aligned} \qquad [8]$$

where C represents the molality at the CMC. On the other hand, at a concentration well above the CMC, eq. [7] is reduced to

$$\begin{aligned}\left(\partial h^{\mathrm{M}} / \partial m_1\right)_{T,p} = {} & \frac{1}{m_1^{*}} \frac{(h_{\mathrm{w}}^{*} - h_{\mathrm{w}}^{0})}{M_{\mathrm{w}}} + \frac{h_{\mathrm{mic}}}{N} - h_1^{*} \\ \equiv {} & \Delta h_1 (m_1 >> C)\end{aligned} \qquad [9]$$

Subtracting eq. [8] from eq. [9] gives us the enthalpy of micelle formation

$\Delta_{\mathrm{W}}^{\mathrm{M}} h$:

$$\Delta h_1(m_1 >> C) - \Delta h_1(m_1 < C) = \frac{h_{\mathrm{mic}}}{N} - h_1^{\mathrm{m}}$$

$$\equiv \Delta_{\mathrm{W}}^{\mathrm{M}} h . \qquad [10]$$

In order to evaluate the partial molar enthalpy change according to eq.7, the h^{M} values obtained from Fig.1b were depicted as a function of m_1 in Fig.3. The important point to note is that sign conversion of slope of the h^{M} vs m_1 plots occurs at CMC region, although the titration curves in Fig.1b are exothermic over all the region. Then the partial derivative $\left(\partial h^{\mathrm{M}} / \partial m_1\right)_{T,p}$ was evaluated and plotted against m_1 in Fig.4 by open circles. It should be emphasized that the agreement between the full line and circles in Fig.4 is fairly good. Hence we conclude that both experiments of titration either by pure liquid or by surfactant solution yield correctly the enthalpy of micelle formation by appropriate thermodynamic equations.

Results and discussion

The partial molar enthalpy change of C8E5 was acquired from the analysis of enthalpy of mixing of water and pure liquid C8E5 in a similar way of ref. 5 and shown in Fig. 5. With regard to the C10E5 system, however, because of the small CMC and high melting point of C10E5, an aqueous C10E5 solution was titrated into pure water. Then the h^{M} vs m_1 plots were obtained from the heat flow vs time profile similar to Fig.1b and then the derivative $\partial h^{\mathrm{M}} / \partial m_1$ was evaluated as is shown in Fig.6. According to eq. [10] and eq. [30] in ref.5, the differences between the

constant enthalpies at lower and higher concentrations than CMC given in Figs. 5 and 6 are considered to be the enthalpies of micelle formation $\Delta_w^M h$ of C8E5 and C10E5, respectively. The results are presented in Fig. 7 and Table1 as a function of temperature. First we note that the $\Delta_w^M h$ values are positive and decrease with increasing temperature. This shows that forming micelle diminishes the overall molecular interaction between water and C*i*E*j* molecules and, therefore, that dehydration of surfactant plays an important role in micelle formation. Secondly there exist two significant differences between the enthalpies of micelle formation of C8E5 and C10E5, i.e., the difference in the enthalpy values themselves and that in their temperature dependence (heat capacity). The increase of enthalpy of C8E5 accompanied by micelle formation is larger than that of C10E5 at a temperature above 283.15K. However in contrast with the enthalpy values themselves, the decrease of the heat capacity of accompanied micelle formation is more prominent than that of C10E5. Obviously these matters are caused by the difference of hydrocarbon chain length.

To elucidate the influence of hydrocarbon chain length on the hydration and aggregation of surfactant, it is indispensable to consider the enthalpies of monomer and micellar states of surfactant separately. Let us remember that the constant values at low and high concentrations in Fig. 5 are referred to as the partial molar enthalpies of C8E5 accompanied by the dissolution of pure liquid C8E5 into water as monomer and that as micelle, $h_1^m - h_1^0$ and $h_{mic} / N - h_1^0$, respectively.[5] Here the reference state in these enthalpy changes is the pure liquid of surfactant. On the other hand, the reference state in the enthalpy change of C10E5 given in Fig. 6 is taken as

the injected aqueous solution of C10E5 at m_1^*; $h_1^m - h_1^*$ and $h_{mic}/N - h_1^*$ at low and high concentration, respectively. To compare the enthalpies of monomer and micelle between C8E5 and C10E5 separately, the reference state should be the same.

Then the titration experiment of pure liquid C10E5 into water was performed at the concentration above the CMC and at temperature above 293.15 K because the smaller CMC and higher melting point of C10E5. Figure 8a shows the h^M values of water and pure liquid C10E5 at 293.15 K to 308.15 K. Comparing the constant value of $\partial h^M/\partial m_1$ in higher concentration region $h_{mic}/N - h_1^0$, with that in Fig.6, $(h_w^0 - h_w^*)/m_1^* M_w + h_{mic}/N - h_1^*$, we can calculate $\partial h^M/\partial m_1$, in which the reference state is the pure liquid, from the $\partial h^M/\partial m_1$ value given in Fig. 6, in which the reference point is the aqueous C10E5 solution at m_1^*. The results are drawn in Fig. 8b. The constant values of $\partial h^M/\partial m_1$ below and above the CMC correspond to $h_1^m - h_1^0$ and $h_{mic}/N - h_1^0$ respectively. Now the partial molar enthalpy changes of C10E5 from pure state to monomer and micelle are compared separately with those of C8E5 as a function of temperature as is demonstrated in Fig. 9, where the partial molar enthalpy of solution of C0E5 is also drawn.[1]

First the diagram makes clear that the partial molar enthalpy change of C10E5 accompanied by the dissolution of pure liquid into water as monomer, $h_1^m - h_1^0$, depends on temperature more strongly than that of C8E5. This may be caused by that the expansion of contact area between hydrocarbon and water increases the heat capacity of surfactant. Then it is suggested that the more prominent decrease of heat capacity

accompanied by micelle formation of the C10E5 system compared to that of the C8E5 system is mainly due to the larger heat capacity of monomeric state of C10E5 compared to that of C8E5 in aqueous solution.

Next, we focus attention on the difference of the partial molar enthalpy change of micelle, $h_{\mathrm{mic}} / N - h_1^0$, between C10E5 and C8E5. Taking into account that the state of hydrocarbons of surfactants in micelle is similar to those of liquid paraffin,[18,19] it may be assumed that the enthalpy change of hydrocarbon parts of surfactant dose not change appreciably by the dissolution of pure liquid C*i*E5 into water as micelle. From this viewpoint, one can safely say that the difference in hydration of oxyethylene group is the main cause of a gap of the $h_{\mathrm{mic}} / N - h_1^0$ value between C10E5 and C8E5, i.e., the hydration ability of oxyethylene group of C8E5 in micelle particle is superior to that of C10E5. The conclusion here is closely related to the finding that the extension of hydrocarbon of surfactant leads to the increase of the aggregation number of micelle,[20] and then brings about the reduction of the effective area per molecule, which results in the decrease of the number of hydrated water molecule.[18]

Finally let us return to the examination of the $h_1^{\mathrm{m}} - h_1^0$ values of the C10E5 and C8E5 systems. It is important to note that the decrement in enthalpy of surfactant accompanied by the dissolution as monomer is greater for C8E5 having a shorter alkyl chain in this temperature region. This finding seems to be in discord with our previous statement that the hydration of alkyl chain is also an exothermic contribution to the partial molar enthalpy change as well as the polar group, which was deduced from the comparison of the enthalpy of C8E4 with that of tetraethylene glycol

C0E4.[1,2] However, this apparent contradiction itself reveals how important is the temperature dependence of the enthalpy associated with the dissolution of hydrocarbon chain as follows. Let us first note that the partial molar enthalpy change in monomer state vs temperature curves of the C*i*E5 systems cross that of the C0E5 system and designate the crossing temperature by T_c. Then, it is roughly said that the enthalpy associated with the dissolution of hydrocarbon chain is exothermic at temperature below T_c, becomes zero at T_c, and endothermic at temperature above T_c under the assumption of hydrophilic group of C*i*E5 is the same as that of C0E5. This is in accord with Shinoda's idea;[21,22] the enthalpy of solution of hydrocarbon in water is determined by a balance between a positive enthalpy of mixing and a negative enthalpy of iceberg formation, and the latter becomes dominant with decreasing temperature and negligible at high temperatures above 160 ℃. Therefore the negative and positive contributions to the enthalpy associated with the dissolution of hydrocarbon chain are compensated with each other at the temperature T_c. Examining the experimental results in Fig. 9, we conclude the compensation temperature T_c decreases with increasing the hydrocarbon chain length.

At the temperature T_m the minimum point of the CMC vs temperature curves of surfactants, the thermodynamic relation suggests that the enthalpy change of micelle formation becomes zero and, therefore, T_m is said to be compensation temperature. In this case, however, it is evident that the enthalpy contains the contributions from both hydrophilic and hydrophobic groups and then depends on the hydrophilic group of surfactant even when the hydrocarbon chain is the same.[23] From these

points of view, we propose the idea that T_m is the compensation temperature of micelle formation of a surfactant and T_c is the compensation temperature of dissolution of hydrocarbon chain of a surfactant into water. Actually T_m value is lower for C8E4 than for C8E5, but T_m values are almost the same for these two surfactants.[1,2]

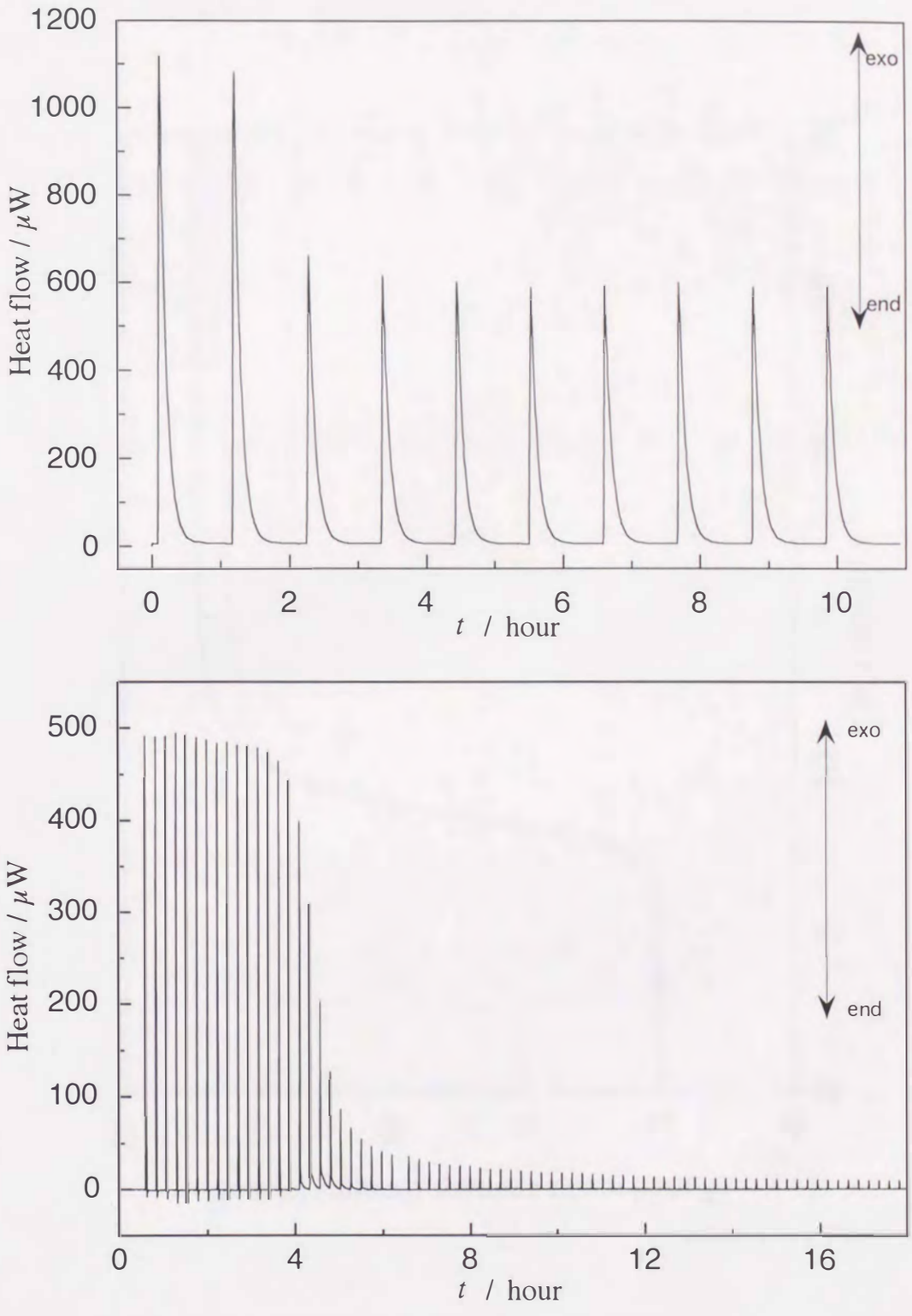

Figure 1. Heat flow vs time curves of C8E4-water system at 298.15 K: (a) injection of pure liquid C8E4 (b) injection of aqueous solution at 150.80 mmol kg^{-1} of C8E4.

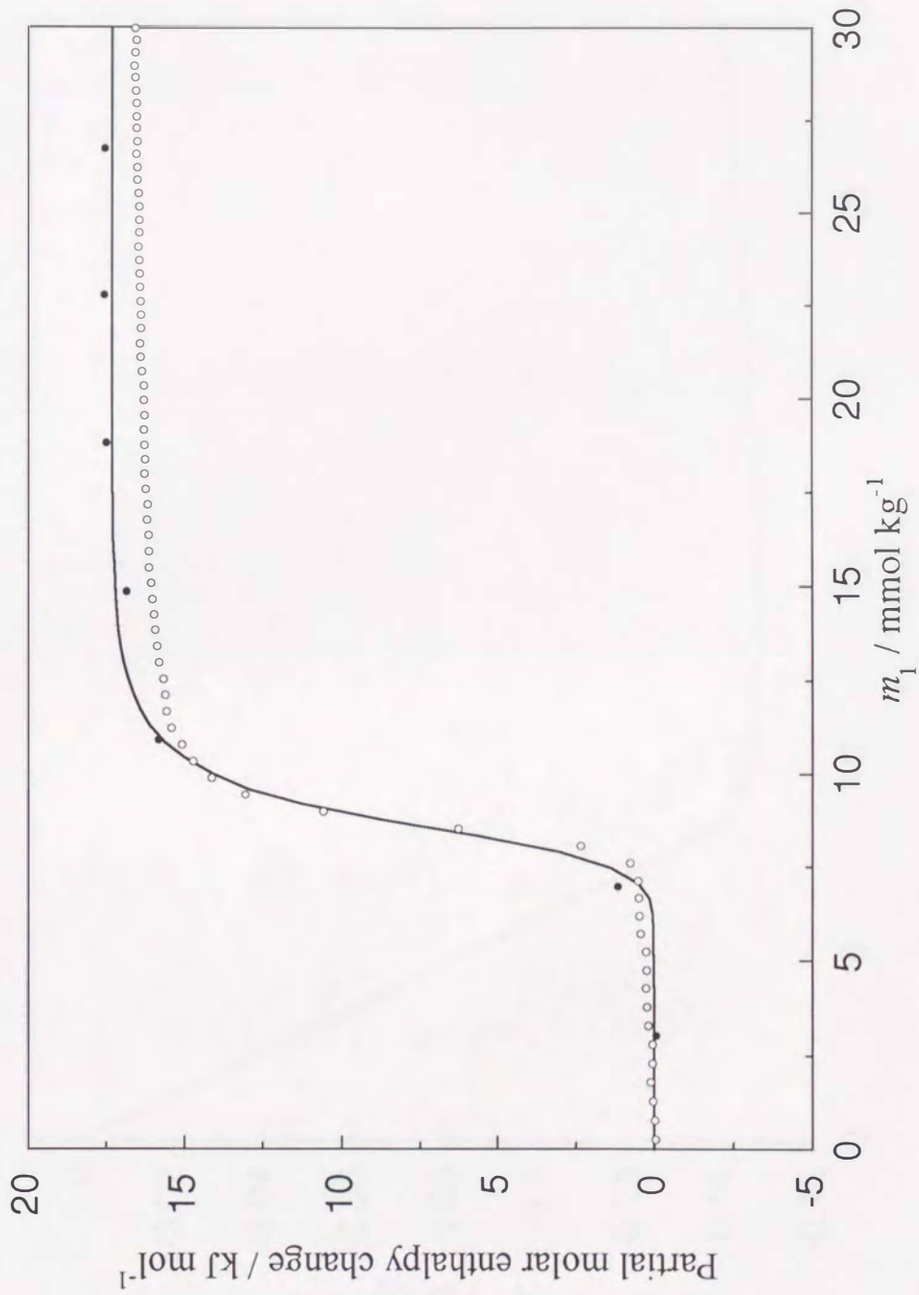

Figure 2. Comparison between partial molar enthalpy change (full-drawn line) and titration heat per injected moles of C8E4 (points): (●) injection of pure C8E4, (○) injection of aqueous solution.

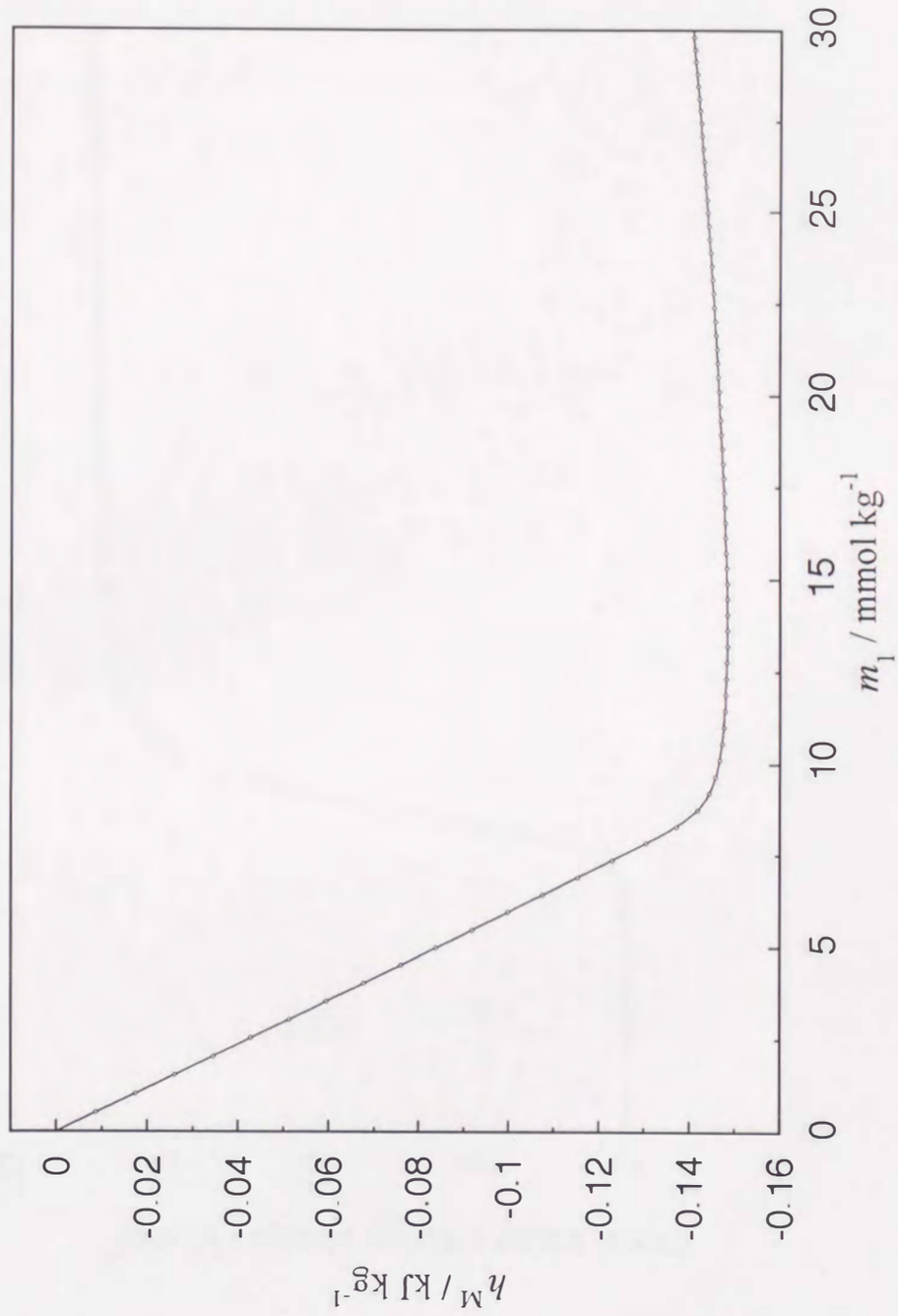

Figure 3. Enthalpy of mixing of aqueous solution of C8E4 vs molality curve at 298.15 K.

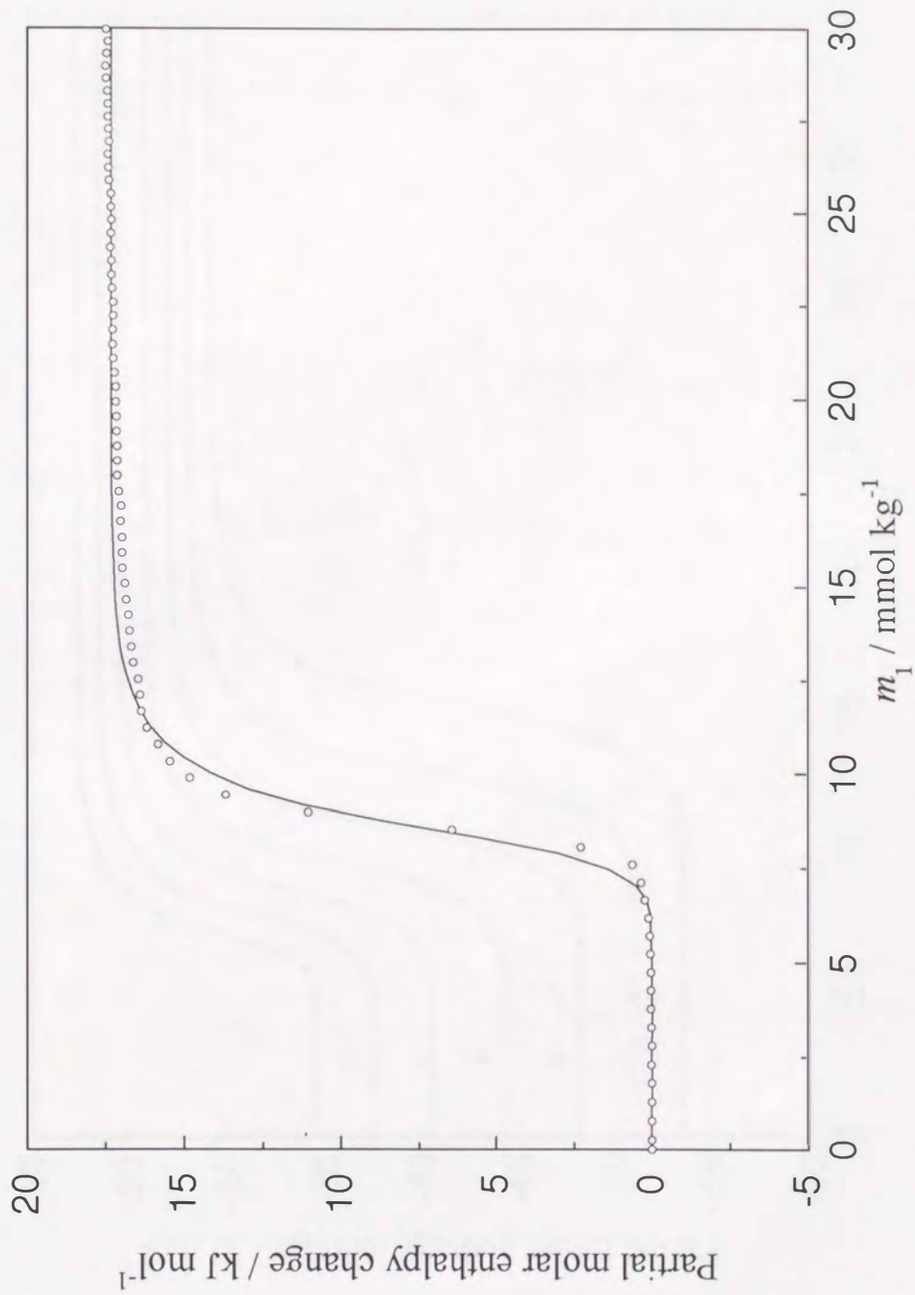

Figure 4. Partial molar enthalpy change of C8E4 vs molality curve at 298.15 K.

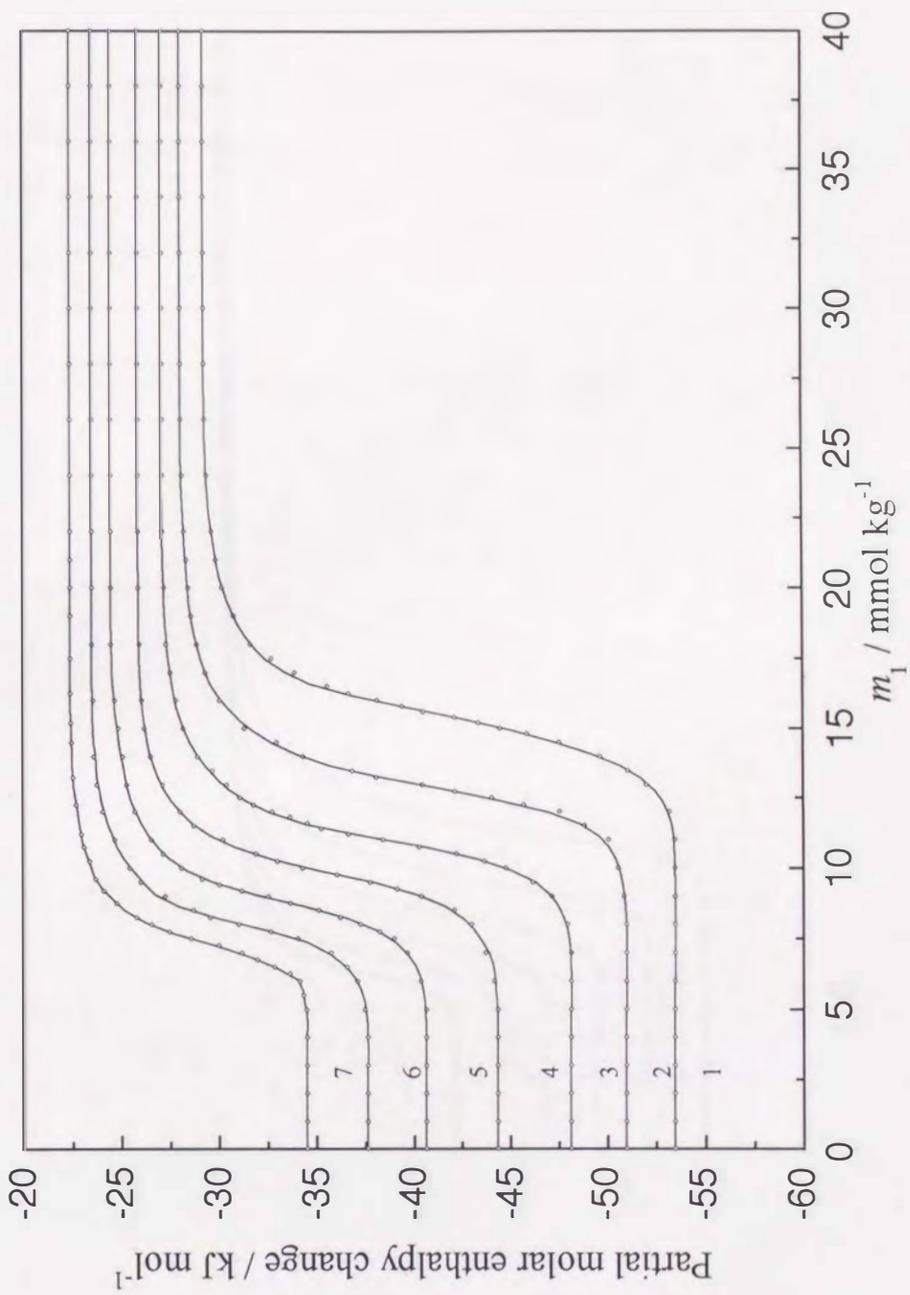

Figure 5. Partial molar enthalpy change of C8E5 vs molality curves: (1) T= 283.15 K, (2) 288.15, (3) 293.15, (4) 298.15, (5) 303.15, (6) 308.15, (7) 313.15.

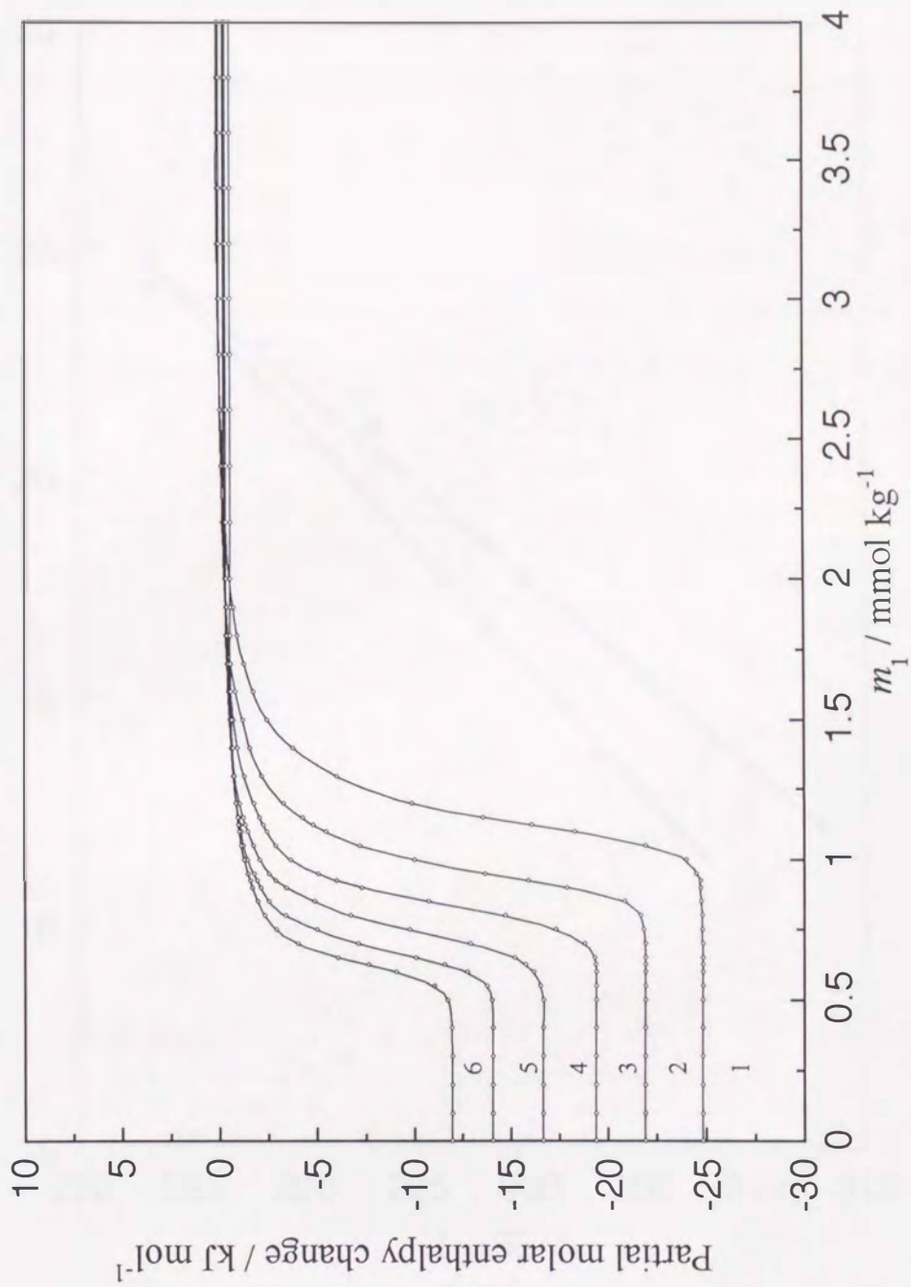

Figure 6. Partial molar enthalpy change of C10E5 vs molality curve: (1) T= 283.15 K, (2) 288.15, (3) 293.15, (4) 298.15, (5) 303.15, (6) 308.15.

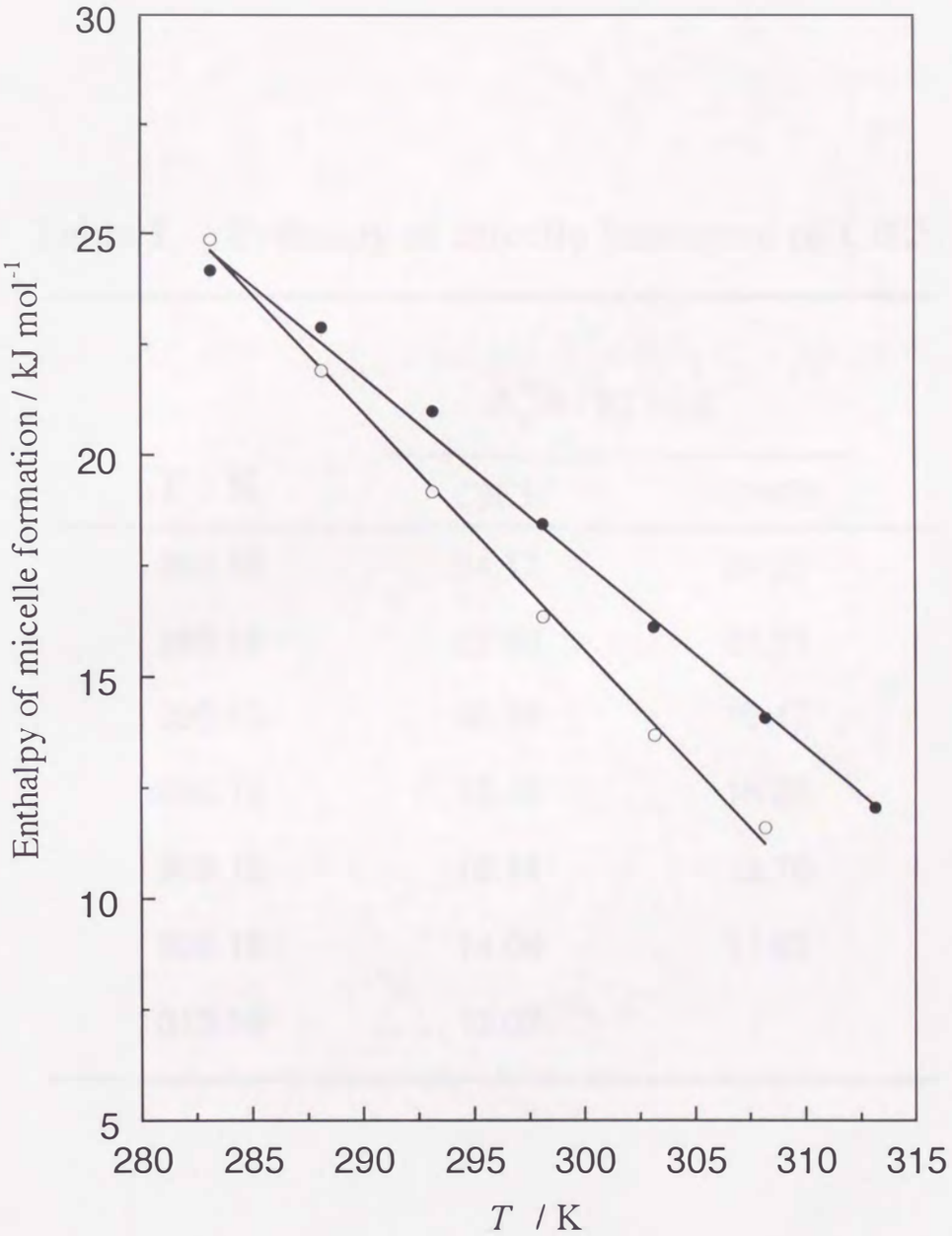

Figure 7. Enthalpy of micelle formation vs molality curves. (●) C8E5, (○) C10E5.

Table 1. Enthalpy of micelle formation of C*i*E5.

	$\Delta_w^M h$ / kJ mol^{-1}	
T / K	C8E5	C10E5
283.15	24.17	24.87
288.15	22.89	21.91
293.15	20.98	19.17
298.15	18.45	16.35
303.15	16.11	13.70
308.15	14.09	11.62
313.15	12.07	

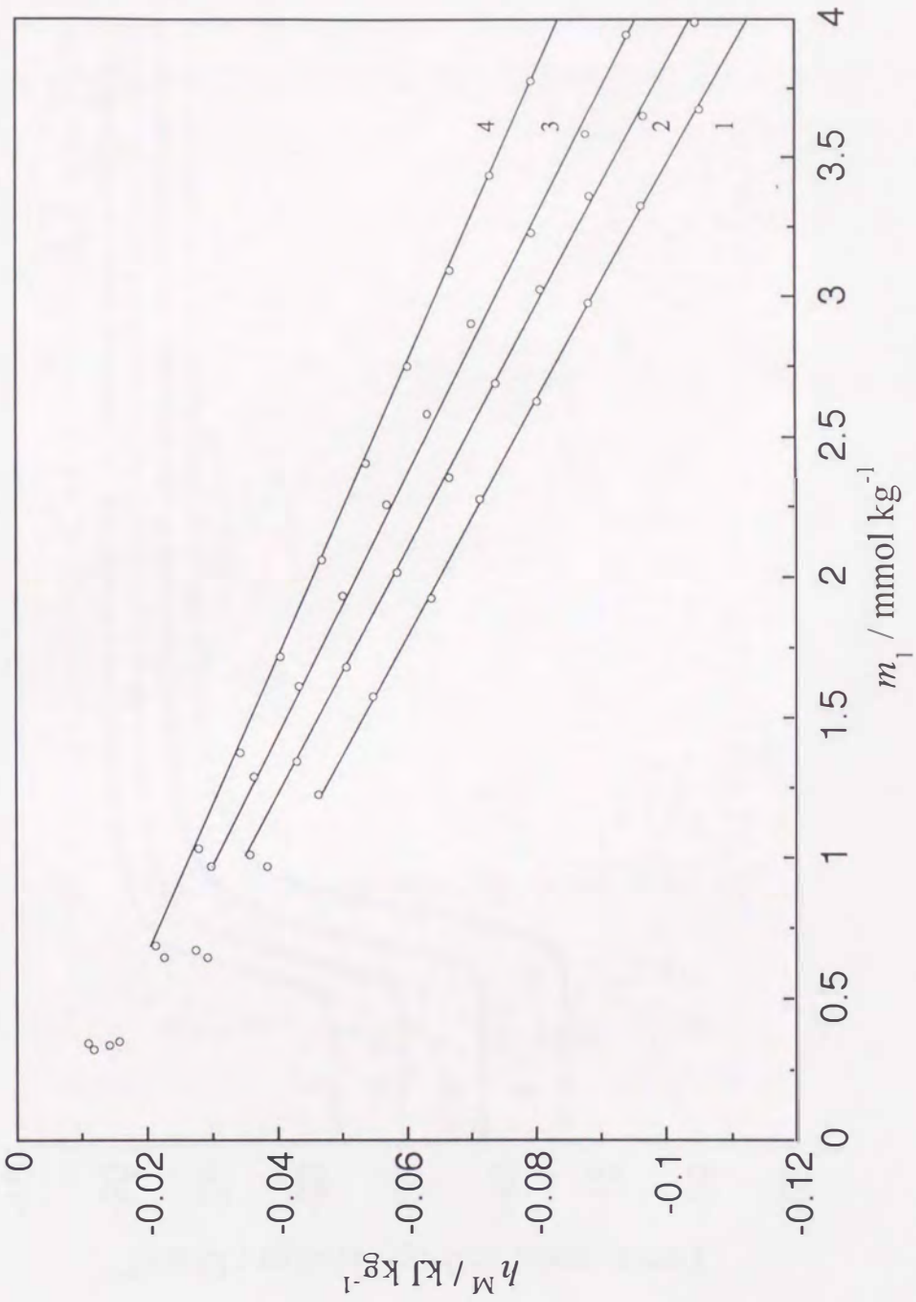

Figure 8a. Enthalpy of mixing of water and pure C10E5 vs molality curves: (1) T= 293.15 K, (2) 298.15, (3) 303.15, (4) 308.15.

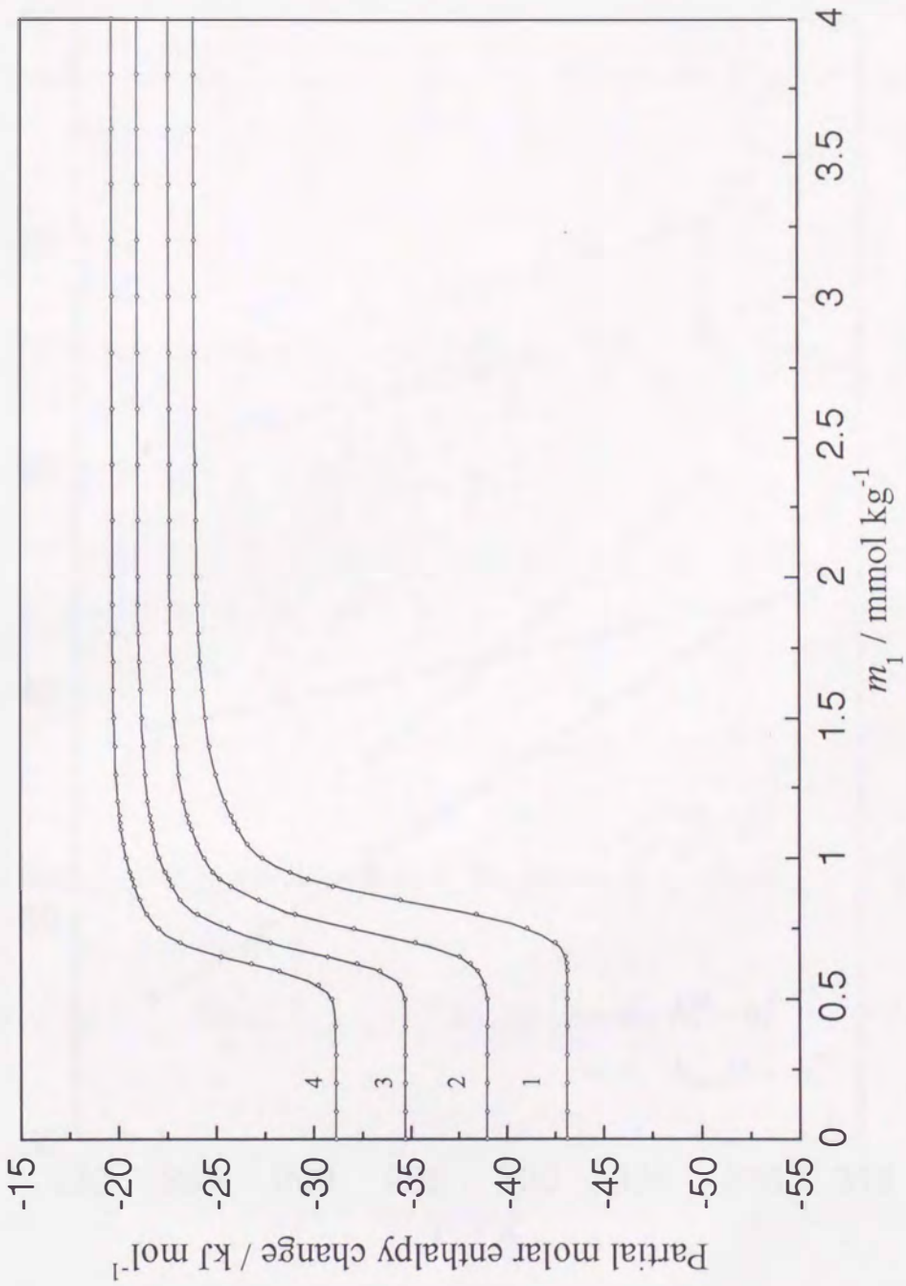

Figure 8b. Partial molar enthalpy change of C10E5 vs molality curve: (1) T= 293.15 K, (2) 298.15, (3) 303.15, (4) 308.15.

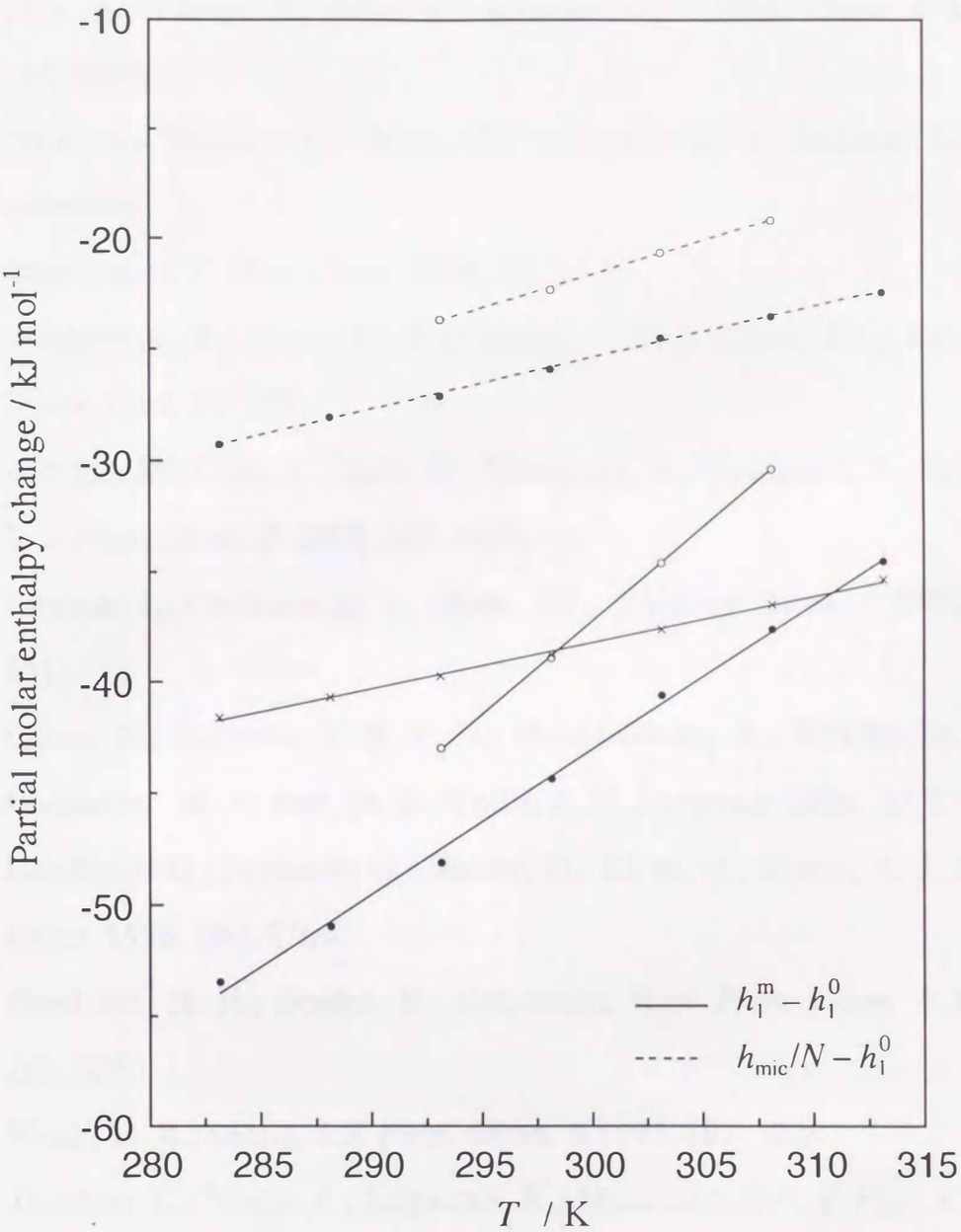

Figure 9. Partial molar enthalpy change vs temperature curves: (solid line) monomer solution, (dotted line) micellar solution ; (●) C8E5, (○) C10E5, (×) C0E5.

References and Notes

1. Ohta, A.; Takiue, T.; Ikeda, N.; Aratono, M. *J. Phys. Chem. B* **1998**, *102*, 4809.
2. Ohta, A.; Takiue, T.; Ikeda, N.; Aratono, M. *J. Solution Chem. submitted.*
3. Olofsson, G. *J. Phys. Chem.* **1985**, *89*, 1473.
4. Weckström, K.; Hann, K.; Rosenholm, J. B. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 733.
5. Aratono, M.; Ohta, A.; Ikeda, N.; Matsubara, A.; Motomura, K.; Takiue, T. *J. Phys. Chem. B* **1997**, *101*, 3535.
6. Johnson, I.; Olofsson, G. *J. Chem. Soc., Faraday Trans.* 1 **1988**, *84*, 551.
7. Bijma, K.; Engberts, J. B. F. N.; Haandrikman, G.; Van Os, N. M,; Blandamer, M. J.; Butt, M. D.; Cullis, P. M. *Langmuir* **1994**, *10*, 2578.
8. Heerklotz, H.; Lantzsch, G.; Binder, H.; Klose, G.; Blume, A. *J. Phys. Chem.* **1996**, *100*, 6764.
9. Heerklotz, H. H.; Binder, H.; Schmiedel, H. *J. Phys. Chem. B* **1998**, *102*, 5363.
10. Wenk, M. R.; Seelig, J. *J. Phys. Chem. B* **1997**, *101*, 5224.
11. Trandum, C.; Westh, P.; Jørgensen, K.; Mouritsen, O.G. *J. Phys. Chem. B* **1999**, *103*, 4751.
12. Taylor, E. L.; Bertrand, G. L. *J. Solution Chem*. **1974**, *3*, 1974.
13. Olofsson, G. *Netsu Sokutei* **1992**, *19*, 76.
14. Schick, M. J. *Nonionic Surfactant: Physical Chemistry*, Marcel Dekker, New York, 1986.

15. Degiorgio, V. in *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*; Degiorgio, V.; Corti, M.; eds., North-Holland: Amsterdama, 1985.

16. Wadsö, I. in *Solution Calorimetry*, Marsh, K. N.; O'Hare, P.A.G.; eds., Blackwell: Oxford, 1994.

17. Bäckman, P.; Bastos, M.; Briggner, L.-E.; Hägg, S.; Hallén, D.; Lönnbro, P.; Nilsson, S. -O.; Olofsson, G.; Schön, A.; Suurkuusk, A. J.; Teixeira, C.; Wadsö, I. *Pure & Appl. Chem.* **1994**, *66*, 375.

18. Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: London, 1992; Chapter 17.

19. Shinitzky, M.; Dianoux, A.-C.; Gitler, C.; Weber,G. *Biochemistry* **1971**, *10*, 2106.

20. M. Drew. *Surfaces, Interfaces, and Colloids: Principles and Applications*, 2nd ed.; Wiley-Vch, New York, 1999; Chapter 15.

21. Shinoda, K. *J. Phys. Chem.* **1977**, *81*, 1300.

22. Shinoda, K. *Principles of Solution and Solubility*, Marcel Dekker, New York, 1978; Chapter 10.

23. Chen, L. -J.; Lin, S. -Y.; Huang, C. -C. *J. Phys. Chem. B* **1998**, *102*, 4350.