Calorimetry of Surfactant Solutions. Measurement of the Enthalpy of Mixing of Tetraethylene Glycol Monooctyl Ether and Water

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The enthalpy of the mixing of water and tetraethylene glycol monooctyl ether (C_8E_4) was measured precisely as a function of concentration of surfactant and temperature by using the high-accuracy isothermal titration calorimeter. The differential enthalpies of solution of monomer and micelle and the enthalpy of micelle formation were evaluated by applying the thermodynamic relations to the enthalpy of mixing. It was shown that the dissolution of pure liquid C_8E_4 is exothermic and the micelle formation is endothermic, respectively. It was also shown that the micellization process is exothermic from the viewpoint of the partial molar enthalpy of water. The heat capacity changes accompanied by the dissolution and micellization processes were calculated. The partial molar heat capacity change vs molality curves for C_8E_4 and water were found to have a sharp maximum or minimum, and both its height and width are strongly temperature-dependent.

Introduction

Properties of micellar solutions of nonionic surfactants have been extensively studied by many methods.[1,2] So far, we have employed the thermodynamics of adsorption and micelle formation: the entropy, enthalpy, and energy of adsorption and those of micelle formation have been evaluated from the surface tension values of aqueous solutions measured as a function of temperature and concentration of surfactants.[3−5] Furthermore, we have shown that the phase diagrams of mixed adsorbed films and mixed micelles obtained from surface tension measurements are helpful to elucidate the miscibility of and molecular interaction between surfactants.[6−9] On the other hand, as is well-known, calorimetry is one of the excellent thermodynamic methods used to investigate the properties of micellar solutions because the information on the interaction between species in monomeric and micellar states can be obtained rather directly.[10,11] Therefore, it is expected to be quite useful to combine information from calorimetry with that from surface thermodynamics in order to further advance the studies on micellar solutions. We have started, then, the calorimetric studies of surfactant solutions by using the high-accuracy isothermal titration calorimeter.

The purposes of the present study are (1) to measure the enthalpy of mixing of water and nonionic surfactant as accurately as possible and (2) to estimate the enthalpy change accompanied by the dissolution of surfactant into water and that by micelle formation as a function of temperature. We chose tetraethylene glycol monooctyl ether (C_8E_4) as the nonionic surfactant because it is posssible to compare the results obtained in our study with those reported by Andersson and Olofsson at three temperatures around the critical micelle concentration (cmc)[12] and by Weckström et al. at one temperature at all compositions.[13] The surface thermodynamic study on the same system is currently under way.

Experimental Section

Materials. Tetraethylene glycol monooctyl ether, C_8E_4, was purchased from BACHEM Feinchemikalien AG and purified by the three-phase extraction technique developed by Kahlweit et al.[14,15] from the water/hexane/C_8E_4 mixture having the ratio 0.425/0.425/0.15 in weight for three times and that of 0.46/0.46/0.08 for two times. To remove the trace amount of water from the surfactant purified and to prevent it from contamination with water in the atmosphere, it was carefully stored in a desiccator with P_2O_5. The purity was checked by gas−liquid chromatography and by observing no minimum on the surface tension vs concentration curve at 298.15 K. A minimum of about 2 mN m^{-1} was observed before the purification and disappeared after it. Water was distilled three times. The second and third stages were done from alkaline permanganate solution.

Calorimetry. The enthalpy of mixing of water and C_8E_4 was measured by the isothermal titration calorimeter thermal activity monitor TAM 2277 of which the basic unit, vessels, stirrers, and so on are described in detail by Wadsö et al.[16,17] Two to four microliters of liquid C_8E_4 was injected by using the computer-controlled syringe pump (Lund 6110) from the gas-tight syringe (Hamilton 1725LT) through a stainless steel cannula to ca. 3.2 g of water in the stainless steel ampule. The solution in the ampule was stirred by a turbine at the constant speed of 120 rpm. The weight injected was accurately calculated from the density value of C_8E_4, and the heat flow was detected to 0.15 μW by a thermopile made from the Peltier element within the experimental error of 0.5 μW. Two or three series were made at a given temperature.

Thermodynamics

Let us consider the mixing process of n_w moles of water and n_s moles of C_8E_4. The enthalpy of mixing H^M is defined by

$$H^M = n_w h_w + n_s h_s - n_w h_w^0 - n_s h_s^0 \tag{1}$$

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

$$h^M = (h_w - h_w^0)/M_w + m(h_s - h_s^0) \tag{2}$$

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where M_w is the molar mass of water and m the total molality of surfactant, respectively.

By employing T, p, and m as the independent thermodynamic variables, the total differential of h^M is written by

$$dh^M = h_T^M \, dT + h_p^M \, dp + h_m^M \, dm \tag{3}$$

Here the first partial differential coefficients are given in terms of the partial molar volume v_i, the heat capacity at constant pressure $c_i = (\partial h_i/\partial T)_{p,m}$, and the isobaric thermal expansivity $\alpha_i = (1/v_i)(\partial v_i/\partial T)_{p,m}$ of component i by

$$h_T^M = (\partial h^M/\partial T)_{p,m} = \Delta_0^W c_w/M_w + m\Delta_0^W c_s \tag{4}$$

$$h_p^M = (\partial h^M/\partial p)_{T,m} = \Delta_0^W v_{\phi w}/M_w + m\Delta_0^W v_{\phi s} \tag{5}$$

and

$$h_m^M = (\partial h^M/\partial m)_{T,p} = \Delta_0^W h_s \tag{6}$$

where the following quantities are introduced

$$v_{\phi i} = v_i(1 - T\alpha_i); \quad i = w, s \tag{7}$$

and

$$\Delta_0^W y_i = y_i - y_i^0; \quad y = c, v_\phi, h; \quad i = w, s \tag{8}$$

Furthermore the second partial differential coefficients with respect to m are proved to be

$$h_{mT}^M = \partial h_T^M/\partial m = \partial h_m^M/\partial T = \Delta_0^W c_s \tag{9}$$

and

$$h_{mp}^M = \partial h_p^M/\partial m = \partial h_m^M/\partial p = \Delta_0^W v_{\phi s} \tag{10}$$

respectively. Therefore the differential enthalpy of solution of C_8E_4, $\Delta_0^W h_s$, and the corresponding heat capacity change, $\Delta_0^W c_s$, are evaluated by applying eqs 6 and 9 to the experimental values of h^M measured as a function of temperature and molality.

Now it is relevant to incorporate explicitly the contributions arising from micelle particles into eq 1, since C_8E_4 molecules aggregate to form micelle particles at a high concentration, as

$$H^M = n_w h_w + n_1 h_1 + n_a h_a - n_w h_w^0 - n_s h_s^0 \tag{11}$$

Here n_1 and n_a are the numbers of moles of monomer and micelle particles having an average aggregation number N_a, and h_1 and h_a are the corresponding partial molar enthalpies, respectively. By taking account of the mass balance equation

$$m = m_1 + N_a m_a \tag{12}$$

where m_1 and m_a are the molalities of monomer and micelle, eq 11 yields the enthalpy of mixing per unit mass of water:

$$h^M = (h_w - h_w^0)/M_w + m_1(h_1 - h_s^0) + N_a m_a(h_a/N_a - h_s^0) \tag{13}$$

Then the first partial differential coefficients are given by

$$h_T^M = \Delta_0^W c_w/M_w + m_1\Delta_0^W c_1 + N_a m_a\Delta_0^M c_a - (\Delta_0^M h_a - \Delta_0^W h_1)(\partial m_1/\partial T)_{p,m} \tag{14}$$

$$h_p^M = \Delta_0^W v_{\phi w}/M_w + m_1\Delta_0^W v_{\phi 1} + N_a m_a\Delta_0^M v_{\phi a} - (\Delta_0^M h_a - \Delta_0^W h_1)(\partial m_1/\partial p)_{T,m} \tag{15}$$

and

$$h_m^M = \Delta_0^M h_a - (h_a/N_a)m_a(\partial N_a/\partial m)_{T,p} - (\Delta_0^M h_a - \Delta_0^W h_1)(\partial m_1/\partial m)_{T,p} \tag{16}$$

where

$$\Delta_0^W y_1 = y_1 - y_s^0; \quad y = c, h, v_\phi \tag{17}$$

$$\Delta_0^M y_a = y_a^*/N_a - y_s^0; \quad y = c, v_\phi \tag{18}$$

and

$$\Delta_0^M h_a = h_a/N_a - h_s^0 \tag{19}$$

respectively. It should be noted that the new quantity c_a^* consists of the partial molar heat capacity of the micelle $c_a = \partial h_a/\partial T$ and the temperature dependence of the aggregation number and is given by

$$c_a^* = c_a - (h_a/N_a)(\partial N_a/\partial T)_{p,m} \tag{20}$$

Similarly, the quantity $v_{\phi a}^*$ is given by

$$v_{\phi a}^* = v_{\phi a} - (\mu_a/N_a)(\partial N_a/\partial p)_{T,m} \tag{21}$$

where $v_{\phi a}$ is an analogue of eq 7.

At a concentration where no aggregates are present, the right hand side of eqs 14 to 16 are reduced to

$$h_T^M = \Delta_0^W c_w/M_w + m_1\Delta_0^W c_1 \tag{22}$$

$$h_p^M = \Delta_0^W v_{\phi w}/M_w + m_1\Delta_0^W v_{\phi 1} \tag{23}$$

and

$$h_m^M = \Delta_0^W h_1 \tag{24}$$

Then the second differential coefficients are given by

$$h_{mT}^M = \Delta_0^W c_1 \tag{25}$$

and

$$h_{mp}^M = \Delta_0^W v_{\phi 1} \tag{26}$$

Furthermore, at a concentration well above the cmc, it is reasonably approximated that the $\partial m_1/\partial m$ is zero and the aggregation number does not change appreciably with the total molality at a given temperature and pressure unless T, p, and m are near the critical solution point.[18,19] Therefore, the right hand side of eq 16 is reduced to

$$h_m^M = \Delta_0^M h_a \tag{27}$$

and then the second partial differentials are given by

$$h_{mT}^M = \Delta_0^M c_a \tag{28}$$

and

$$h_{mp}^M = \Delta_0^M v_{\phi a} \tag{29}$$

By comparing eqs 24 and 27 with eq 6, the differential enthalpy of the solution of C_8E_4, $\Delta_0^W h_s = h_s - h_s^0$, is proved to be the one corresponding to the dissolution of pure liquid C_8E_4 into water as monomer, $\Delta_0^W h_1 = h_1 - h_s^0$, at a concentration below the cmc and, on the other hand, the one corresponding
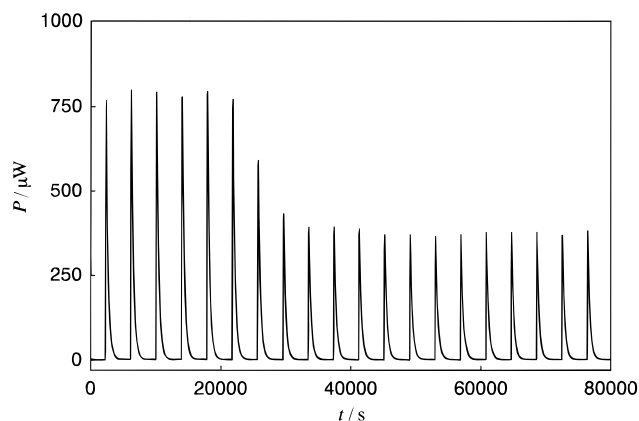
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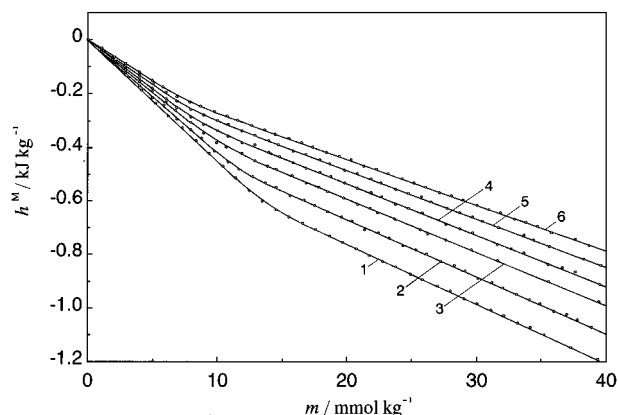

Figure 1. Heat flow vs time curve at 283.15 K.

Figure 2. Enthalpy of mixing vs molality curves: (1) 283.15, (2) 288.15, (3) 293.15, (4) 298.15, (5) 303.15, (6) 308.15 K.

Figure 3. Differential enthalpy of solution of C_8E_4 vs total molality curves: (1) 283.15, (2) 288.15, (3) 293.15, (4) 298.15, (5) 303.15, (6) 308.15 K. The solid circles represent $\delta h^M/\delta m$ at 283.15 K.

Figure 4. Differential enthalpy of monomer, micelle, and enthalpy of micelle formation of surfactant vs temperature curves. Solid circles were taken from the literature;[18] (1) $\Delta_0^W h_1$, (2) $\Delta_0^M h_a$, (3) $\Delta_W^M h_a$.

to the dissolution of pure liquid C_8E_4 into water as micelle, $\Delta_0^M h_a = h_a/N_a - h_s^0$, at a concentration well above the cmc, respectively. In what follows, $\Delta_0^W h_1$ and $\Delta_0^M h_a$ are called the differential enthalpy of solution of monomer and that of micelle, respectively. Similarly $\Delta_0^W c_1 = c_1 - c_s^0$ and $\Delta_0^M c_a = c_a^*/N_a - c_s^0$ are called the partial molar heat capacity change of monomer and that of micelle.

Results and Discussion

The enthalpy of mixing was measured as a function of n_s at a given n_w at six temperatures from 283.15 to 308.15 K under atmospheric pressure. Figure 1 shows a typical heat flow P vs time t curve, where about 2 μL of liquid C_8E_4 was injected successively into the cell for 20 times and the concentration of the final peak was well above the cmc. Here a positive P corresponds to the exothermic process. It is seen that both height and area of a peak are almost constant at low and also at high concentrations and decrease gradually at concentrations around the cmc. 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 surfactant reaches n_s. In Figure 2 are given the enthalpy of mixing per kilogram of water h^M vs molality of C_8E_4 m curves. It is seen that the mixing process is exothermic[12,13] and the absolute value of h^M increases with increasing concentration and decreasing temperature. It should be noted that the h^M value changes almost linearly at low and high concentrations, while it changes nonlinearly at intermediate concentrations around the cmc.

By applying eq 6 to the experimental data in Figure 2, the differential enthalpy of solution of C_8E_4 was evaluated and plotted against m in Figure 3. Here the $\Delta_0^W h_s$ values were obtained by evaluating the slope of a tangent line at a given con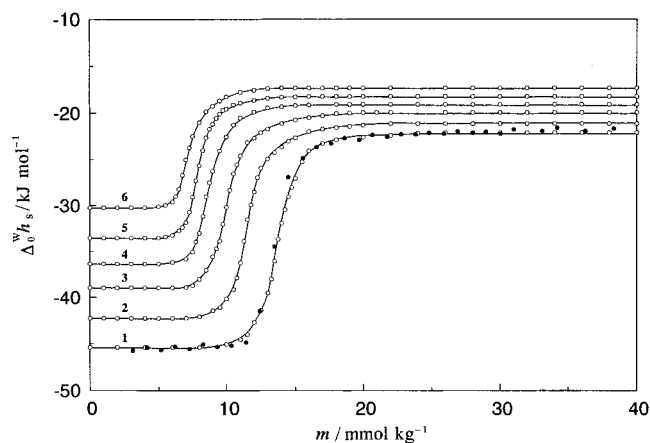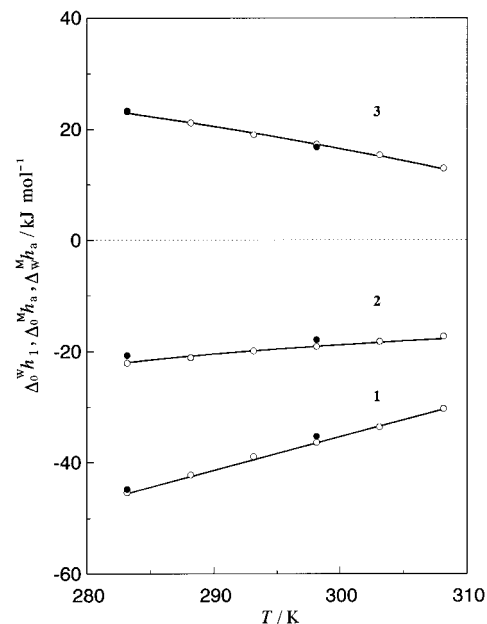centration graphically. The error for this data analysis was estimated to be from 0.22% (283.15 K) to 0.69% (313.15 K) of the $\Delta_0^W h_1$ values and 0.18% (283.15 K) to 0.52% (298.15 K) of the $\Delta_0^W h_a$ values, respectively. Furthermore the ratio of a peak area δh^M to the concentration increment δm is also plotted at 283.15 K. Although the ratio appears not strictly constant even at low and high concentrations as reported in the literature,[12,13] the values of $\delta h^M/\delta m$ and $\partial h^M/\partial m$ are in fair agreement with each other within the experimental error, and therefore, we considered them constant at low and high concentrations at a given temperature. This means that the partial molar enthalpies of monomer and aggregate are almost constant: the aqueous monomeric and micellar solutions are reasonably assumed to be ideal dilute and ideal associated ones, respectively. However, the $\Delta_0^W h_s$ value changes drastically with concentration around the cmc. Taking eq 16 and the approximation $\partial N_a/\partial m = 0$[18,19] into account, the drastic change in $\Delta_0^W h_s$ is attributable to the change of the monomer fraction in the added surfactants $\partial m_1/\partial m$.

The constant value at a low concentration, $\Delta_0^W h_1$, and that at a high concentration, $\Delta_0^M h_a$, are plotted against temperature in Figure 4. It is seen that they are both negative, and their absolute values decrease with increasing temperature. This suggests that there exists stronger interaction between water and
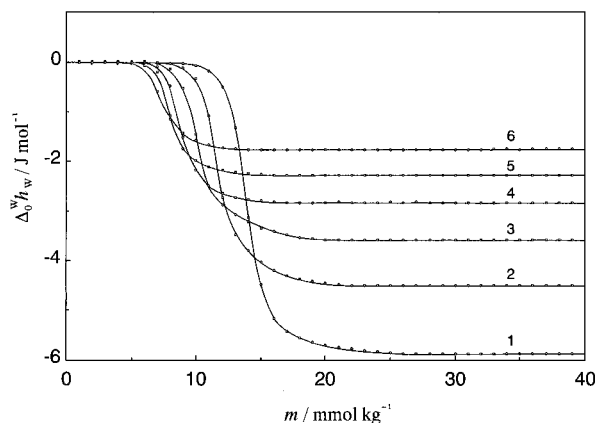
Figure 5. Differential enthalpy of dilution of water vs total molality curves: (1) 283.15, (2) 288.15, (3) 293.15, (4) 298.15, (5) 303.15, (6) 308.15 K.

C_8E_4 molecules than that between the same species and also that the interaction depends on temperature significantly. It is probable, therefore, that the interaction arises from the hydration around the hydrophilic group of C_8E_4 and that the thermal motion of molecules diminishes the hydration at a high temperature. Furthermore we note that the value of $\Delta_0^M h_a$ is less negative at a given temperature and increases rather slowly with increasing temperature compared with that of $\Delta_0^W h_1$. This means that the overall molecular interaction between water and C_8E_4 molecules is diminished by forming the micellar aggregate. This point becomes more apparent by evaluating the enthalpy of micelle formation of surfactant $\Delta_W^M h_a$ defined by

$$\Delta_W^M h_a = \Delta_0^M h_a - \Delta_0^W h_1$$
$$= h_a/N_a - h_1 \tag{30}$$

In Figure 4, it is seen that the value of $\Delta_W^M h_a$ is positive and decreases with increasing temperature. In Figure 4 are also given the literature values of three kinds of enthalpies[12] at two temperatures; the agreement is fairly good.

Now it is expected to be useful to examine the micelle formation from the viewpoint of the partial molar enthalpy of water because the hydration is an important contribution to the micellization process. The differential enthalpy of dilution of water $\Delta_0^W h_w$ is defined in eq 8 and was calculated by substituting $\Delta_0^W h_s$ values into eq 2. The results are given in Figure 5. We note first that the value is almost zero at a low concentration. This means that the partial molar enthalpies of water and C_8E_4 are almost equal to the molar enthalpy of water and the partial molar enthalpy of C_8E_4 at an infinite dilution, respectively: the aqueous solution is regarded to be an almost ideal dilute one. Next we note that the $\Delta_0^W h_w$ value starts to decrease at a concentration around cmc, which is in contrast to the increase in partial molar enthalpy of C_8E_4 by micelle formation. Since water molecules around monomeric C_8E_4 molecules do not contribute appreciably to $\Delta_0^W h_w$ values as mentioned above, water molecules in and/or around micellar particles contribute negatively to $\Delta_0^W h_w$ although its absolute value is small. Therefore it is said that the micelle formation is exothermic from the viewpoint of the enthalpy change of water, although it is endothermic from the viewpoint of the enthalpy change of surfactant.

Let us go further into the hydration of the hydrophilic group of the surfactant. The positive value of $\Delta_W^M h_a$ suggests that the interaction of surfactant with water is diminished by forming micelle. Considering that the strength of the hydrogen bond is estimated to be ~10−40 kJ mol^{-1} [20] and the magnitude of
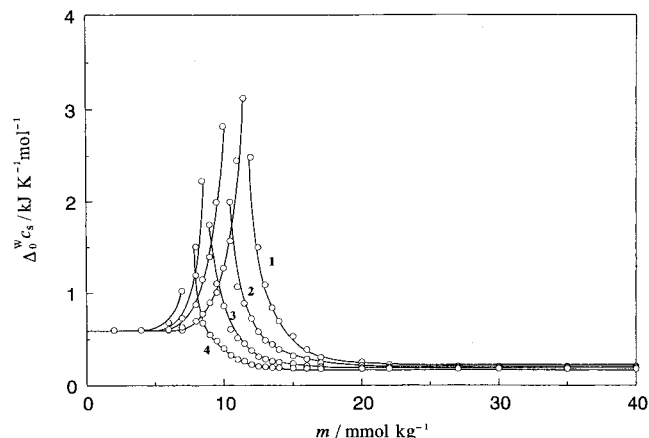

Figure 6. Partial molar heat capacity change of surfactant vs total molality curves: (1) 288.15, (2) 293.15, (3) 298.15, (4) 303.15 K.

$\Delta_W^M h_a$ is ~10−20 kJ mol^{-1} and supposing the positive $\Delta_W^M h_a$ is attributable mainly to dehydration, we may say that part of the water molecules are released from just around the hydrophilic group. Now, if the water molecules released in this way have the same properties as bulk water molecules have, the $\Delta_0^W h_w$ may not change appreciably by micelle formation. However, the experiment shows that the $\Delta_0^W h_w$ value is negative. This apparent contradiction is reasonably explained as follows: water molecules released in this way are supposed to be still trapped inside the hydrophilic atmosphere of the micelle particle, where there are 10 or more water molecules per one C_8E_4 molecule,[19,21−23] and they interact with other water molecules more strongly in the hydrophilic atmosphere than in the bulk solution because the thermal motion of water molecules may be restricted more in the former than in the latter.

It has been known that the heat capacity gives information regarding the dissolution and micellization processes.[10] By applying eq 9 to the experimental results of the temperature dependence of differential enthalpies of solution, the values of $\Delta_0^W c_s$ were estimated. The results are plotted against molality at constant temperatures in Figure 6. At a low concentration, it is seen that the $\Delta_0^W c_1$ value is almost comparable with the molar heat capacity of pure liquid C_8E_4 c_s^0.[18] This suggests that the value of the partial molar heat capacity of surfactants in the monomeric state c_1 is increased to about 2-fold of the pure liquid c_s^0 due to hydration. Furthermore, at a concentration around the cmc, it should be noted that the plot at a given temperature has a very sharp maximum, and both height and width decrease with increasing temperature. This observation is in accord with the experimental findings that the micelle formation of the present system is an endothermic process from the viewpoint of the partial molar enthalpy of C_8E_4 and that the value of $\Delta_W^M h_a$ decreases with increasing temperature as shown in Figure 4.

Furthermore, the partial molar heat capacity change of water defined in eq 8 was also calculated by

$$\Delta_0^W c_w = (\partial \Delta_0^W h_w/\partial T)_{p,m} \tag{31}$$

and is shown in Figure 7. Although the absolute value of $\Delta_0^W c_w$ is very small compared with that of $\Delta_0^W c_s$ in Figure 6, a minimum is observed on the plots at a given temperature, and both height and width of the minimum decrease with increasing temperature, which is also in accord with the finding that the micelle formation is exothermic process from the viewpoint of the partial molar enthalpy of water and that the absolute value of the partial molar enthalpy of water of micelle formation $\Delta_W^M h_w$ decreases with increasing temperature. Although the
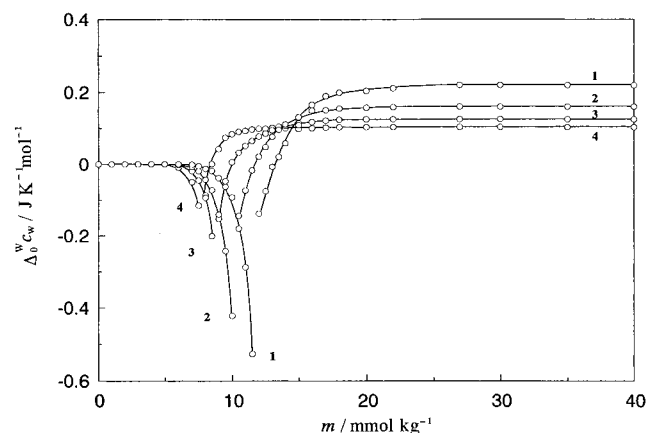
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Figure 7. Partial molar heat capacity change of water vs total molality curves: (1) 288.15, (2) 293.15, (3) 298.15, (4) 303.15 K.

heights of the maximum and minimum decrease due to the decreasing absolute values of $\Delta_W^M h_a$ and $\Delta_W^M h_w$, the decrease of the width with increasing temperature may suggest that the higher the temperature is, the closer the micelle formation is to the first-order phase transition.[10]

Supporting Information Available: Experimental data of the enthalpy of mixing given in Figure 2 (2 pages). Ordering formation is given on any current masthead page.

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