August, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 2718—2725 (1987) 2719

A Light-Scattering Study of Temperature Effect on Micelle Formation of *N*-Alkanoyl-*N*-methylglucamines in Aqueous Solution

Makoto Ōkawauchi, Mayumi Hagio, Yoshitomi Ikawa,† Gohsuke Sugihara,*
Yoshio Murata, and Mitsuru Tanaka
Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01
†San-Ei Chemical Industries, Ltd., 1-1-11 Sanwa-cho, Toyonaka 561

(Received December 10, 1986)

The physicochemical properties of *N*-alkanoyl-*N*-methylglucamine in aqueous solution have been studied by applying a Debye plot and small-system thermodynamics to an analysis of static light scattering data in the temperature range from 25 to 55 °C. A small minimum was found in a plot of the critical micelle concentration vs. temperature, instead of the monotonously decreasing tendency, as in the case of poly(oxyethylene) alkyl ether. The temperature dependence of the aggregation number of the micelle and the spread of the aggregation number distribution of micelle are both very small. The standard enthalpy change associated with micelle formation varies from positive to negative as the temperature is raised. The micellization of *N*-alkanoyl-*N*-methylglucamine surfactants is discussed separately in terms of the respective contributions from the hydrophilic and hydrophobic groups.

N-Alkanoyl-*N*-methylglucamines (MEGA-n; the chemical structure is shown in Fig. 1), nonionic surfactants, have been utilized to solubilize membrane proteins[1–3] since the time it was synthesized by Hildreth[4] in 1982. However, the physicochemical properties, such as the critical micelle concentration (cmc) and the aggregation number of micelle, at various temperatures have not yet been accurately determined. In the present study, we investigated the physicochemical properties of *N*-octanoyl-, *N*-nonanoyl-, and *N*-decanoyl-*N*-methylglucamine (MEGA-8, MEGA-9, MEGA-10) in aqueous solution at temperatures ranging from 25 to 55 °C by using a static light-scattering technique.

Ikeda et al.[5–13] have extensively studied various ionic surfactants by means of a light-scattering technique and have clearly revealed the interesting behaviors of the size and shape of surfactant aggregates. Some light-scattering studies have been made for poly(oxyethylene)-type nonionic surfactants.[14–20] For other nonionic surfactants, especially for the present MEGA-n, however, few light-scattering studies have been made in spite of the usefulness of MEGA-n in the special field of biochemistry. Thus, we have investigated the light-scattering behavior of aqueous solutions of the homologues series, MEGA-n. To analyze light-scattering data, not only Debye plots, but also small-system thermodynamics[21] have been applied. As partly described elsewhere,[20,25,26] the treatment of micelle formation by small-system thermodynamics constitutes a general theory which partly includes treatments of both mass-action and phase-separation models and can be used to clarify the thermodynamical meaning of the application of both models.

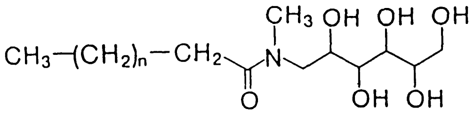

Fig. 1. The structures of *N*-octanoyl- (n=7), *N*-nonanoyl- (n=8), and *N*-decanoyl-*N*-methylglucamine (n=9).

Experimental

Materials. MEGA-8, MEGA-9, and MEGA-10 were purchased from Dojindo Laboratories and recrystallized several times from a methanol–dimethyl ether mixture and acetone. The purities of the surfactants were examined by the surface tension method. No minimum around cmc was observed for the surface tension vs. concentration curve of their aqueous solutions. Solvent water was redistilled from alkaline $KMnO_4$ after being passed through a column of an ion-exchange resin.

Methods. The light-scattering measurement was carried out using a JASCO Light Scattering Photometer LSP-1 with the unpolarized light of a mercury lamp at 436 nm. The intensities of light scattered at scattering angles, 45, 90, and 135° were measured for sample solutions in a semioctagonal cell. The semioctagonal cell was placed in a cell housing whose temperature was controlled within ±0.1 °C by circulating water around it. The reduced intensity of scattered light at 90° was calculated by

$$R_{90} = \frac{I_{90}}{I_0}\,\phi_{90}^{\mathrm{B}}\,\frac{n_0}{n_{\mathrm{B}}}, \qquad (1)$$

where I_0 and I_{90} are, respectively, the intensities of the incident and scattered light at 90°; n_0 and n_{B} are the refractive indices of the solvent and benzene, respectively. The calibration constant, ϕ_{90}^{B}, was determined by using purified benzene at 25 °C.[22] We assumed in this study that the ϕ_{90}^{B} was independent of the temperature. The angular dissymmetry Z_{45} of light scattering was determined by

$$Z_{45} = \frac{I_{45}}{I_{135}}, \qquad (2)$$

where I_{45} and I_{135} are the intensities of scattered light at 45 and 135°, respectively. A surfactant solution was directly filtered into the semioctagonal cell by using the cell-filling apparatus shown in Fig. 2. All parts of the cell-filling apparatus were cleaned in a sonicater. A membrane filter (Advan-

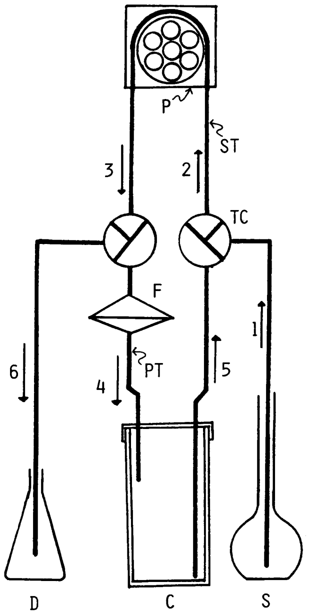

Fig. 2. Schematic diagram of cell filling system; S: sample solution, C: semioctagonal cell, D: drain solution, TC: three ways stopped cock, F: filter, P: pump, ST: silicon tube, PT: polyethylene tube.

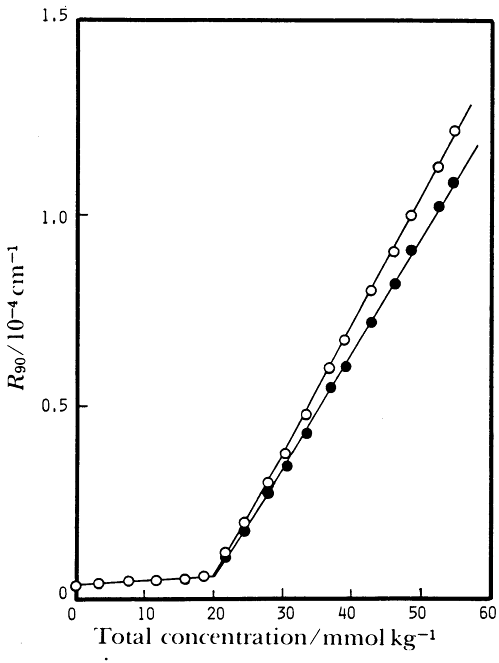

Fig. 3. Reduced scattered intensity of MEGA-9 solution as a function of total concentration at 30°C (○) and 55°C (●).

Table 1. The cmc of MEGA-n at Various Temperatures

T	cmc/mmol kg^{-1}		
°C	MEGA-8	MEGA-9	MEGA-10
25	69.0	21.4	6.7
30	66.6	20.9	6.6
35	64.9	20.5	6.5
40	63.8	20.4	6.5
45	63.2	20.3	6.6
50	63.2	20.5	6.7
55	63.7	20.8	6.9

tec) having a pore size of 0.1 μm was washed with boiling redistilled water; these parts were then arranged as shown in the figure. Firstly, the cell was filled with a sample solution or solvent which came from S through paths 1, 2, 3, F, and 4; after that, the solution or solvent was drained through paths 5, 2, 3, and 6. By repeating this procedure several times, the cell and other parts of the apparatus could be completely washed. Finally, the cell was again filled with a sample solution by the same procedure as described above and the sample solution in the cell was repeatedly circulated through path 5 to 4. A concentration change of the sample solution before and after filteration was not detected in the refractive index.

The specific refractive index increment at temperatures ranging from 25 to 55 °C was measured by means of an Otsuka Electronics Differential Refractometer R102 at 436 nm of a tungsten-halogen lamp. The calibration of the apparatus was carried out with an aqueous solution of KCl at 25 °C;[23] we assumed in this study that the calibration constant of the apparatus was independent of the temperature. The specific refractive index increment was constant over the whole concentration range measured and was almost constant at temperatures ranging from 25 to 55 °C.

Results and Discussion

The angular dissymmetry, Z_{45}, was found to be very close to unity for all the MEGA-n solutions over the whole range of the temperatures and concentrations investigated. Figure 3 shows a plot of the reduced intensity, R_{90} vs. total surfactant concentration in molality of MEGA-9 at 30 and 55 °C. Each curve has a break point indicating the beginning of micelle formation. Thus, the cmc is determined as the concentration at the break point. The values of the cmc's of MEGA-8, MEGA-9, and MEGA-10 are listed in Table 1 and the temperature dependence of the cmc's are shown in Fig. 4. It is noteworthy that a minimum appears in the cmc vs. temperature curve for MEGA-n, since the

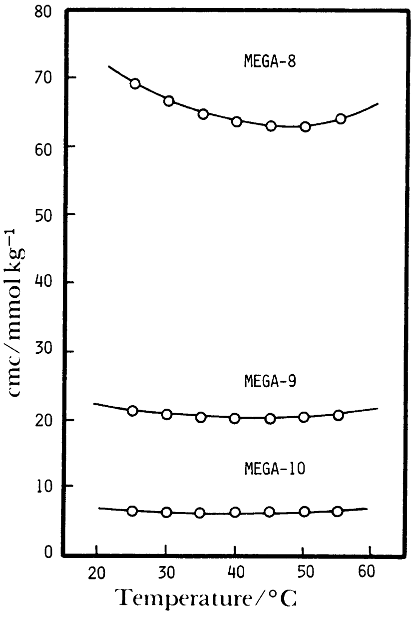

Fig. 4. Temperature dependence of cmc of MEGA-n.

existence of such a minimum has been considered to be characteristic of ionic surfactants. The cmc of poly (oxyethylene) alkyl ethers had been found to decrease monotonously with increasing temperature.[24]

From the data of R_{90} and cmc a Debye plot of MEGA-n could be made. In the absence of angular dissymmetry, the scattered light intensity at 90° from a dilute micellar solution irradiated by unpolarized light can be represented by Debye's equation:

$$\frac{K_D(C-\text{cmc})}{R_{90}-R_{90,\text{cmc}}} = \frac{1}{\overline{N}_w M_n} + 2B(C-\text{cmc}), \tag{3}$$

where K_D, the optical constant, is

$$K_D = \frac{2\pi^2 n^2}{N_A \lambda^4}(\partial n/\partial C)^2. \tag{4}$$

Further, C is the total surfactant concentration (g ml^{-1}), $R_{90,\text{cmc}}$ the reduced intensity of the solution at cmc, $\overline{N}_w$ the weight-average aggregation number of micelle, M_n the molecular weight of MEGA-n and B the second virial coefficient. n_0 and n are, respectively, the refractive indices of solvent and solution, λ the wavelength of the incident radiation and N_A Avogadro's number. Debye plots of MEGA-9 at various temperatures are shown in Fig. 5. If we draw an approximate straight line which threads through the plotted points by a least-square method, we can obtain the weight-average aggregation number of micelle as well as the second virial coefficient from the intercept and slope of this straight line, respectively. It can be seen from Fig. 5 that the respective second virial coefficients have small and negative values (2×10^{-3} mol ml g^{-2}) with a small temperature dependence. The same trends were also found for MEGA-8 and MEGA-10. It should be noted that the second virial coefficients of poly(oxyethylene) alkyl ethers change from positive to negative[16,17] in the same temperature range as the present case.

The application of small-system thermodynamics to the analysis of light-scattering data[24–27] allowed us to determine the monomeric concentration, C_1, micellar concentration, C_m, number-average and mean-square aggregation number of micelle $\overline{N}_1$, $\overline{N_1^2}$ and spread of the aggregation number distribution of micelle of MEGA-n.

In the absence of angular dissymmetry, the R_{90} of a micellar solution is given by

$$R_{90}-R_{90,0}=K_s(C_1+\overline{N_1^2}C_m), \tag{5}$$

where

$$K_s=\frac{2\pi^2 n^2}{N_0\lambda^4}(\partial n/\partial C_1^t)^2. \tag{6}$$

Here, $R_{90,0}$ is the reduced scattered intensity at 90° from solvent water, C_1^t the total surfactant concentration and N_0 the number of solvent molecules per unit volume. Equation 5 can be easily derived from Eq. 3 when $B=0$ in Eq. 3.

C_1 and C_m can be determined from the following equations:

$$\ln C_1 = \int_{\text{cmc}}^{C_1^t} K_s/(R_{90}-R_{90,0})\,dC_1^t + \ln \text{cmc} \tag{7}$$

and

$$C_m = \int_{\text{cmc}}^{C_1^t} K_s C_1^t/(R_{90}-R_{90,0})\,dC_1^t - C_1 + \text{cmc}. \tag{8}$$

From C_1 and C_m, thus obtained, $\overline{N}_1$, and $\overline{N_1^2}$ can be determined using

$$\overline{N}_1=(C_1^t-C_1)/C_m \tag{9}$$

and

$$\overline{N_1^2}=[(R_{90}-R_{90,0})/K_s-C_1]/C_m. \tag{10}$$

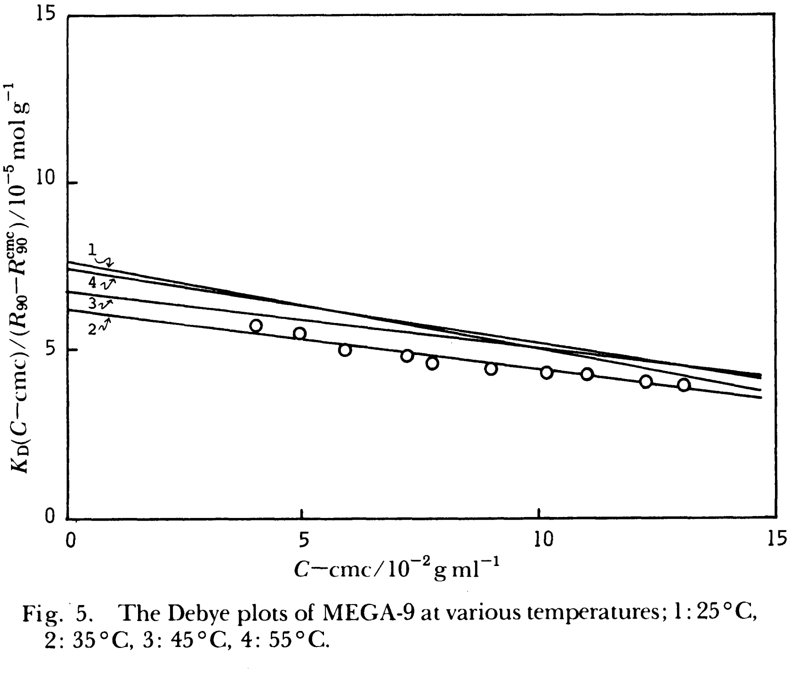

Fig. 5. The Debye plots of MEGA-9 at various temperatures; 1: 25 °C, 2: 35 °C, 3: 45 °C, 4: 55 °C.

In these calculations, the concentration (C_1^t, C_1, and C_m) units are the solute molecular number per solvent molecular number (in figures, concentrations are represented by molality).

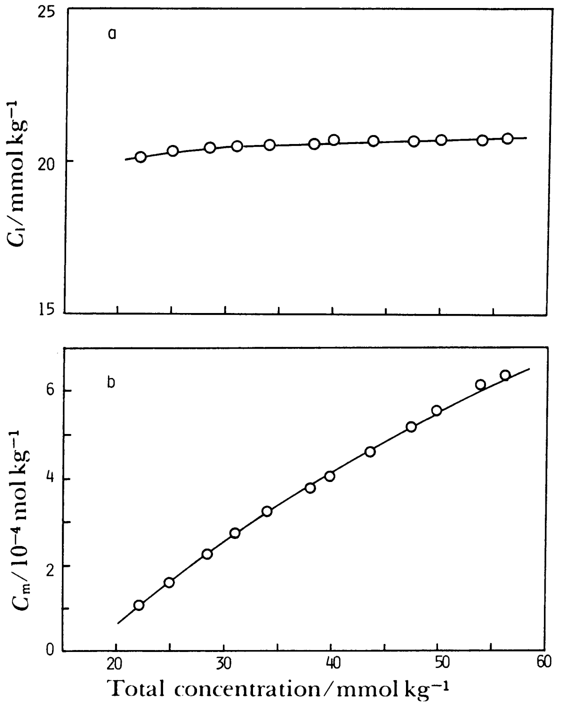

Fig. 6. Monomer concentration, C_1 and micellar concentration, C_m of MEGA-9 as a function of total concentration at 45 °C.

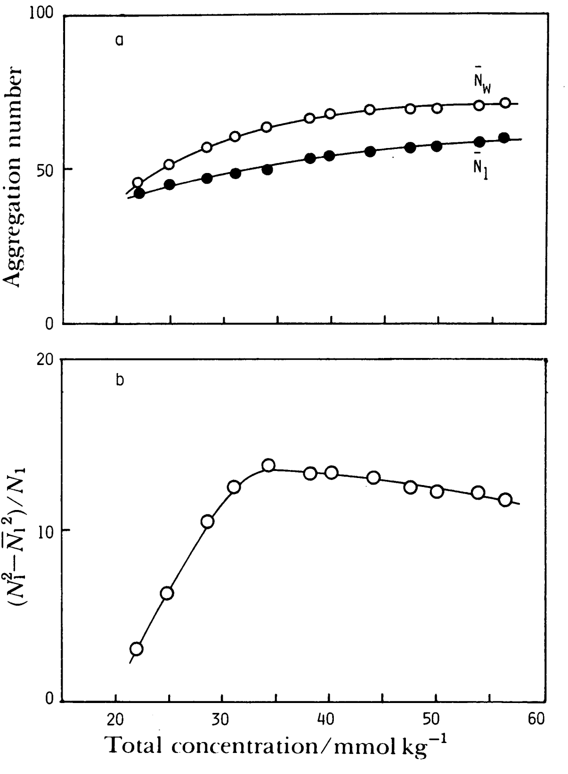

Fig. 7. Number-average and mean square aggregation number of MEGA-9 micelle (a) and the spread of aggregation number of micelle of MEGA-9 (b) at 45 °C.

Figure 6 shows the dependence of C_1 and C_m on C_1^t in the case of MEGA-9 at 45 °C. C_1 increases only slightly from cmc with increasing C_1^t, and is regarded approximately as equal to the cmc. The same trend can be seen in the cases of MEGA-8 and MEGA-10 at various temperatures. This shows that the micellization of these nonionic surfactants can be approximately treated by the phase separation model. C_m increases with an increase of C_1^t and has a value of the order of 0.01 C_1^t in the total concentration range.

Figure 7-a shows the dependence of $\bar{N}_1$ and the weight-averaged aggregation number $\bar{N}_w$ ($=\overline{N_1^2}/\bar{N}_1$) of the micelle of MEGA-9 on C_1^t at 45 °C. Both $\bar{N}_1$ and $\bar{N}_w$ increase with an increase in C_1^t. The same trend can be seen in the cases of MEGA-8 and MEGA-10 at various temperatures. The increasing tendency of $\bar{N}_1$ with C_1^t is consistent with the Eq. 11, which has been derived using a treatment based on small-system thermodynamics:[26]

$$(\partial\bar{N}_1/\partial C_1^t)=(\overline{N_1^2}-\bar{N}_1^2)/(C_1+\overline{N_1^2}C_m)\geqq 0. \tag{11}$$

Corkill et al.[28] have also derived a similar equation from the multiequilibrium model. They found that $\bar{N}_1$ of the 3-(dimethyloctylammonio)-1-propanesulfonate micelle increases with C_1^t. We also found that $\bar{N}_1$ of penta- and hexa(oxyethylene) dodecyl ether micelles increase with C_1^t under various pressures[20] at 25 °C.

The spread of the aggregation number of MEGA-9 micelle, $(\overline{N_1^2}-\bar{N}_1^2)/\bar{N}_1$, obtained from the difference between $\bar{N}_w$ and $\bar{N}_1$, is shown in Fig. 7-b, where $(\overline{N_1^2}-\bar{N}_1^2)/\bar{N}_1$, increases initially with C_1^t and then reaches an almost constant value. The same trend was observed for MEGA-8 and MEGA-10 at various temperatures. The spread of the aggregation number of the micelle of MEGA-n is much smaller than that of polyoxyethylene alkyl ether, and its C_1^t dependence is also smaller.[20]

In order to analyze the results based on small-system thermodynamics, we assumed an ideal condition for

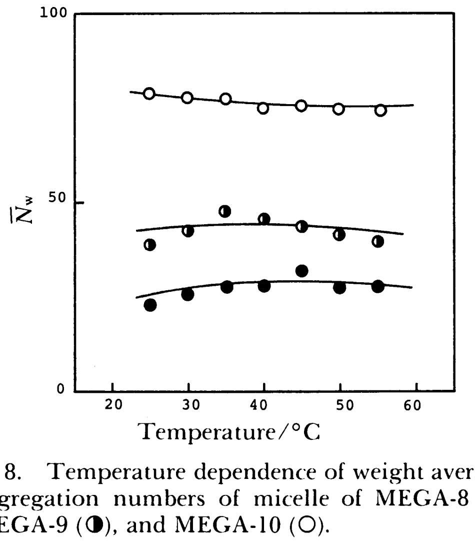

Fig. 8. Temperature dependence of weight averaged aggregation numbers of micelle of MEGA-8 (●), MEGA-9 (◑), and MEGA-10 (○).

very dilute micellar solutions of MEGA-n. This assumption can be regarded as reasonable owing to the very small value of the second virial coefficient obtained from the Debye plot.

The value of $\overline{N}_w$ extrapolated to cmc in Fig. 7 agrees well with the weight-average aggregation number obtained from the Debye plot. Figure 8 shows the temperature dependence of $\overline{N}_w$. The extrapolated $\overline{N}_w$ of MEGA-8, MEGA-9, and MEGA-10 may be regarded as being almost constant, irrespective of the temperature change, which differs remarkably from the strikingly increasing trend of $\overline{N}_w$ of poly(oxyethylene) alkyl ethers.[15] The temperature dependence of C_m and the $(\overline{N_1^2}-\overline{N}_1{}^2)/\overline{N}_1$ of MEGA-8, MEGA-9, and MEGA-10 are also very small.

From the temperature dependence of C_1, C_m, and $\overline{N}_1$, the standard Gibbs free energy, enthalpy and entropy change on micelle formation, ΔG_m°, ΔH_m°, and ΔS_m° can be estimated by the use of the following equations from small-system thermodynamics:[27]

$$\Delta G_m^\circ = RT \ln C_1 - RT/\overline{N}_1 \ln C_m, \tag{12}$$

$$\Delta H_m^\circ = -RT^2 (\partial \ln C_1/\partial T)_p - RT^2/\overline{N}_1 (\partial \ln C_m/\partial T)_p, \tag{13}$$

and

$$\Delta S_m^\circ = -RT (\partial \ln C_1/\partial T)_p + RT/\overline{N}_1 (\partial \ln C_m/\partial T)_p - R \ln C_1 + R/\overline{N}_1 \ln C_m. \tag{14}$$

These equations are (formally) the same equations as derived from the mass-action model. However, the second terms of Eqs. 12—14 and the 4 th term of Eq. 14 are much smaller than the other terms in the respective equations because of the factor $1/\overline{N}_1$; also, the smaller temperature dependence of $\ln C_m$ than that of $\ln C_1$. C_1 is nearly equal to the cmc (as described above). The equations obtained from the elimination of the terms on the respective equations described above are consistent with the equations derived from the phase-separation model. We have taken the standard states of monomer and micelle as the states of an infinite dilute solution; therefore, their standard free energies consist of self free energies as well as their interaction with water. Then, ΔG_m° represents the change of the interaction (hydrophobic and hydrophilic) of the monomer and water accompanied by the transfer of a mole of the monomer from the solution bulk into the micelle.

The temperature dependence of ΔG_m°, ΔH_m°, and ΔS_m° thus obtained, are shown in Fig. 9. The ΔG_m°, ΔH_m°, and ΔS_m° of MEGA-n decreases monotonously with the temperature. ΔG_m° is always negative and ΔS_m° positive. On the other hand, ΔH_m° changes sign from positive to negative at a lower temperature, since the hydrocarbon chain is longer. However, ΔH_m° is always positive and decreases to zero with temperature in the case of poly(oxyethylene) alkyl ether.[29—32]

In order to investigate these features of MEGA-n in detail, let us try to separate these thermodynamic parameters into contributions from the hydrophilic and hydrophobic parts of a MEGA-n molecule, assuming the additivity. ΔG_m° can be divided into three parts:

$$\Delta G_m^\circ = \Delta G_m^\circ(\mathrm{w}) + (N_c - 1)\Delta G_m^\circ(\mathrm{CH_2}) + \Delta G_m^\circ(\mathrm{CH_3}), \tag{15}$$

where $\Delta G_m^\circ(\mathrm{w})$ is the contribution of the hydrophilic part, $\Delta G_m^\circ(\mathrm{CH_2})$ the methylene group, and $\Delta G_m^\circ(\mathrm{CH_3})$ the terminal methyl group; N_c should be taken as 7, 8, and 9, respectively, for MEGA-8, MEGA-9, and MEGA-10. Similar equations are valid for ΔS_m° and ΔH_m°.

From the linear plots of ΔG_m°, ΔH_m°, and ΔS_m° vs. the number of carbon atoms in alkyl chain of MEGA-n at various temperatures, $\Delta G_m^\circ(\mathrm{CH_2})$, $\Delta H_m^\circ(\mathrm{CH_2})$, and $\Delta S_m^\circ(\mathrm{CH_2})$, can be determined (as listed in Table 2). These are the same values as those of poly(oxyethylene) alkyl ethers.[33]

$\Delta G_m^\circ(\mathrm{w})$ can be obtained by substituting the values of $\Delta G_m^\circ(\mathrm{CH_2})$ and $\Delta G_m^\circ(\mathrm{CH_3})$ (=2100 cal mol^{-1} (1 cal= 4.184 J))[24] into Eq. 15. The $\Delta H_m^\circ(\mathrm{w})$ and $\Delta S_m^\circ(\mathrm{w})$ can be determined from Eqs. 16 and 17 (see Table 3):

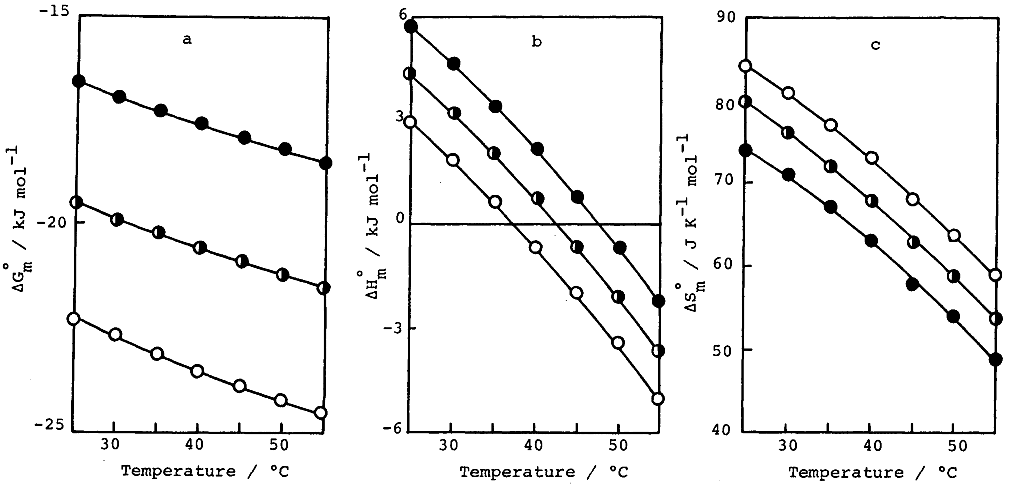

Fig. 9. Thermodynamic parameter changes on micelle formation of MEGA-8 (●), MEGA-9 (◑), and MEGA-10 (○) as a function of temperature.

Table 2. The Thermodynamic Parameters per Methylene Group of MEGA-n on Micelle Formation at Various Temperatures

T °C	$\Delta G^\circ_m(CH_2)$ kJ mol^{-1}	$\Delta H^\circ_m(CH_2)$ kJ mol^{-1}	$\Delta S^\circ_m(CH_2)$ J K^{-1} mol^{-1}
25	−2.88	−1.40	4.96
30	−2.91	−1.40	4.98
35	−2.93	−1.40	4.98
40	−2.96	−1.40	4.97
45	−2.98	−1.40	4.95
50	−3.00	−1.41	4.93
55	−3.03	−1.42	4.90

Table 3. The Thermodynamic Parameters of Contribution of Hydrophilic Parts on Micelle Formation of MEGA-n at Various Temperatures

T °C	$\Delta G^\circ_m(w)$ kJ mol^{-1}	$\Delta H^\circ_m(w)$ kJ mol^{-1}	$\Delta S^\circ_m(w)$ J K^{-1} mol^{-1}
25	9.48	21.9	41.6
30	9.26	21.5	40.4
35	9.09	20.7	37.9
40	8.88	19.7	34.4
45	8.73	18.2	29.9
50	8.59	16.6	24.7
55	8.48	14.6	18.7

$$\Delta H^\circ_m(w)=\partial(\Delta G^\circ_m(w)/T)/\partial(1/T) \tag{16}$$

and

$$T\Delta S^\circ_m(w)=\Delta H^\circ_m(w)-\Delta G^\circ_m(w). \tag{17}$$

Let us compare the contribution of $\Delta H^\circ_m(w)$ to $\Delta G^\circ_m(w)$ between poly(oxyethylene) alkyl ether and MEGA-n. In the case of MEGA-n, the enthalpy term, $\Delta H^\circ_m(w)$, is superior to the entropy term, $T\Delta S^\circ_m(w)$, while in the case of poly(oxyethylene) alkyl ether both terms are comparable.[33] This difference can be interpreted in terms of the interaction between water and the respective hydrophilic parts. The relatively large contribution of $T\Delta S^\circ_m(w)$ to $\Delta G^\circ_m(w)$ in the poly (oxyethylene) group compared to the case of the hydrophilic part of MEGA-n seems to be caused by a relatively large degree of weakening of the hydration of poly(oxyethylene) group on micellization.

The experimental results are summarized as follows. The cmc vs. temperature curve has a small minimum in the temperature range from 25 to 55 °C; also, the temperature dependence of micellar aggregation numbers, the spread of its distribution and the micellar concentration of MEGA-n are very small. The standard enthalpy change on micelle formation, ΔH°_m, changes sign from positive to negative with increasing temperature. Further, a cloud point was not observed for MEGA-8, MEGA-9, or MEGA-10, even if their solutions were heated to the boiling point and a large amount of NaCl was added into the solutions of MEGA-n (on the basis of the fact that addition of NaCl depress the cloud point of poly(oxyethylene) alkyl ethers).[34]

A suggestion concerning the solution properties of MEGA-n resulted through a comparison with those of poly(oxyethylene) alkyl ethers. The hydrophilicity of poly(oxyethylene) alkyl ether arises from the formation of two hydrogen bonds per oxyethylene group with water.[35] On the other hand, a hydroxyl group of the hydrophilic part of MEGA-n can possibly make three hydrogen bonds with water. However, by taking into account the fact that a cloud point was not observed for MEGA-n and that cmc has a shallow minimum at a certain temperature (instead of monotonous decreasing with temperature like the cmc of poly (oxyethylene) alkyl ether), it may be concluded that there is a considerable difference between the interaction of hydroxyl groups of MEGA-n with water and that of the oxyethylene groups of poly(oxyethylene) alkyl ether with water. The minimum in the temperature dependence of the cmc, as observed in ionic surfactants with ion-water dipole interaction, may result from the predominant role of the electrostatic dipole-dipole interaction of the hydrophilic part of MEGA-n with water. Further, the amide group may also play an important role in the hydrophilicity of MEGA-n. The hydrogen bond formation between hydroxyl groups in the micellar state cannot be considered as an important factor of micelle formation, since it should cause the micelle size to be much larger than the observed values.

It seems, however, that it is not always reasonable to regard the character of hydrophilic group of MEGA-n as attributable to each separate hydroxyl group. It has been well-known that for such a molecule (having several hydroxyl groups) that the steric configuration of the hydroxyl groups plays a more important role than the nature of each hydroxyl group itself. For instance, galactaric acid and D-glucaric acid are only different in the stereochemical configuration of a certain hydroxyl group; however, the former is very soluble in water and the latter is insoluble.

Finally, one should pay attention to the fact that the micellization behavior of poly(oxyethylene)-type nonionic surfactants is not common to all other types of nonionic surfactants.[31,36,37]

Thanks are due for the partial support by a research grant from the Ministry of Education (No. 60470011) and partial support of a fund from the Central Research Institute of Fukuoka University.

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