

Critical Evaluation of Micellization Behavior of Nonionic Surfactant MEGA 10 in Comparison with Ionic Surfactant Tetradecyltriphenylphosphonium Bromide Studied by Microcalorimetric Method in Aqueous Medium

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The micellization behavior of MEGA 10 has been studied at nine different temperatures by isothermal titration calorimetry (ITC), and thermodynamics of the process have been evaluated and examined in detail. The aggregation number of the nonionic surfactant has been estimated from the ITC results by a simulation procedure based on the mass action principle of micellization of the surfactant. The cmc of MEGA 10 has shown a minimum in temperature dependence as observed for ionic surfactants. For a comparison, the cmc and related thermodynamic parameters of an ionic surfactant, tetradecyltriphenylphosphonium bromide (C₁₄-TPB) studied at several temperatures in aqueous medium has been considered. The contributions of the headgroups of both the surfactants to the free energies of their respective micellization have been deciphered and presented.

Introduction

MEGA 10 [*N*-decanoyl-*N*-methylglucamine, CH₃(CH₂)₁₀-CO-(CH₂)CH₂(CHOH)₄CH₂OH], a membrane protein solubilizer¹ synthesized by Hildreth,² is a nonionic surfactant that has evidenced interesting self-association properties in aqueous medium. Unlike most of the nonionic surfactants, it can be obtained in molecularly homogeneous form so that the measured properties in solution are associated with least uncertainties. In the past, micellization and related behaviors of MEGA 10 were investigated by tensiometry and fluorometry.³ Sugihara et al.^{4a–e} have made a detailed study on the micellization behavior of MEGA 10 using the static light scattering (SLS) method and have estimated the thermodynamics of the process. Since the critical micellar concentration (cmc) of MEGA 10 modestly depends on temperature, evaluation of the energetics of the process needs very careful experimentation, which to our understanding Sugihara et al.^{4a} had performed. The temperature dependence of the cmc of MEGA 10 has a similarity with ionic surfactants in that it shows a minimum in cmc at 313 K (sodium dodecyl sulfate shows a similar pattern in the temperature dependence of its cmc with a minimum at 293 K). Desolvation of the polyoxyethylene chain in the headgroup of MEGA 10 has been considered to be the reason for the decrease in cmc in the lower range of temperature which in the upper range gets enhanced due to increased kinetic motion of the amphiphile molecules in the disrupted water structure in their surroundings.

According to recent literature, isothermal titration calorimetry (ITC) has established its claim as a potential method in the quantitative study of amphiphile self-aggregation or micellization.^{5–7} The measurement of differential enthalpy of dilution of a concentrated surfactant solution in multisteps in the microcalorimeter produces enthalpograms that can help direct

determination of cmc and enthalpy of micellization from a single run. The evaluation of the enthalpy of micellization by way of measurements of cmc at several temperatures and fitting the data into the van't Hoff equation can thus be bypassed, rendering better accuracy of the derived parameters. This has been discussed in recent literature.⁸ Interestingly, it has been shown that the enthalpy of micellization determined by the ITC method does not tally with that obtained by the van't Hoff method, and the discrepancies between the two procedures is greater for ionic surfactants than nonionics. However, case studies in this direction are only limited. Thus, there remains scope for further investigations with typical surfactant systems.

In this work, we have investigated the micellization behavior of MEGA 10 in aqueous medium and have evaluated the cmc and the thermodynamics of the process by the ITC method. Measurements were taken at different temperatures to evaluate the enthalpy of the process by the van't Hoff procedure as well as to evaluate the specific heat of the amphiphile aggregation process. In the analysis, the contributions of the polar headgroup, the terminal methyl group, and the intermediate methylene chain to the thermodynamic parameters for self-association of MEGA 10 molecules have been considered. Analysis of ITC results on the self-aggregation of the ionic surfactant tetradecyltriphenylphosphonium bromide (C₁₄TPB) has also been made, and the trends in the thermodynamic parameters have been compared with that of the nonionic MEGA 10. It has been observed that the difference of analysis between the calorimetric and van't Hoff procedures was minor for MEGA 10 and major for C₁₄-TPB. In addition to this, the aggregation number of both MEGA 10 and C₁₄TPB micelles have been evaluated by a simulation procedure based on the ITC data recently reported⁹ and used by us.¹⁰ It has been observed that the cmc of MEGA 10 and the derived thermodynamic parameters reported by Sugihara et al.^{4a} by the SLS method closely agreed with that of ours by ITC. However, the micellar aggregation numbers of MEGA 10 reported by them by the SLS method were greater than the values we determined by the ITC method.

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Experimental Section

Materials. The compound MEGA 10 used in this study was a product of Dojindo Laboratories, Kumamoto, Japan, that was obtained from Prof. G. Sugihara, Department of Chemistry, Fukuoka University, Fukuoka, Japan. It was purified by repeated recrystallization from 1:9 (v/v) mixed ethanol and ethyl ether. Safranin T was purchased from Sisco Laboratories (India) and was used as received. Doubly distilled water of specific conductance $2\text{--}4\ \mu\text{S cm}^{-1}$ was used throughout the experiments.

Methods. Isothermal Titration Calorimetry. A MicroCal Omega titration calorimeter (MicroCal Inc. Northampton, MA) was used for ITC measurements. The reaction cell and reference cell were filled with 1.34 and 1.8 mL of degassed water, respectively. The removable integrated injection stirrer syringe (capacity $350\ \mu\text{L}$) was filled with concentrated MEGA 10 solution (about 20 times its cmc), and it was mixed with water by injecting $10\ \mu\text{L}$ aliquots under stirring condition at a constant rate of 350 rpm at a constant temperature throughout the experiment. The injection duration was 30 s, and the time duration between two injections was 4 min. The concentration in the syringe was taken at a higher level so as to reach cmc during the process of dilution. The ITC experiments were done in the temperature range 293–328 K with a precision of ± 0.1 K. Using Micro Cal Origin software integration of the peaks in the enthalpogram gave the enthalpy as a function of total concentration in the cell. The enthalpy–concentration profile produced a first-order transition in the pattern, and the transition point was taken as the cmc of MEGA 10. The enthalpy of micellization was obtained from the difference between the initial and final asymptotes of the sigmoidal curve. This point is further discussed in the subsequent section.

Tensiometry. The surface tensions of MEGA 10 solutions were measured using a calibrated Kruss (Germany) tensiometer by the platinum ring detachment method. A 10 mL sample of water was taken in a vessel containing a magnetic stirrer, into which a concentrated solution of MEGA 10 was successfully added. The readings were taken after an equilibration time of 10 min. The surface tension vs concentration plot did not produce a minimum confirming the purity of the material.

Fluorometry. Fluorescence measurements were carried out with Aminco Bowman Series2 Luminescence Spectrophotometer (U.K.), by exciting the sample at 460 nm and recording the emission spectrum in the range 530–720 nm. The slit widths were 1.5 nm for excitation and 2 nm for emission. The probe used was Safranin T of concentration $1 \times 10^{-6}\ \text{mol dm}^{-3}$. Concentration of MEGA 10 was varied from 2 to 11 mM. Measurements were taken at 298 K.

Results and Discussion

Critical Micellar Concentration. The cmc of MEGA 10 was exclusively determined by the ITC method. The enthalpograms determined at nine different temperatures, 293, 298, 300.5, 303, 308, 313, 318, 323, and 328 K, are comprehensively presented in Figure 1. The curves have produced reversal of direction at approximately 303 K. Below 303 K, the micellization process was exothermic, and it became endothermic above that temperature. The cmc values were determined in terms of the sigmoidal Boltzman equation (SBE) used by us on different micelle-forming amphiphilic systems.^{7,11}

$$\Delta H_d = \frac{(\Delta H_{d(i)} - \Delta H_{d(f)})}{[1 + \exp(C_s - \text{cmc})/\Delta C_s]} + \Delta H_{d(f)} \quad (1)$$

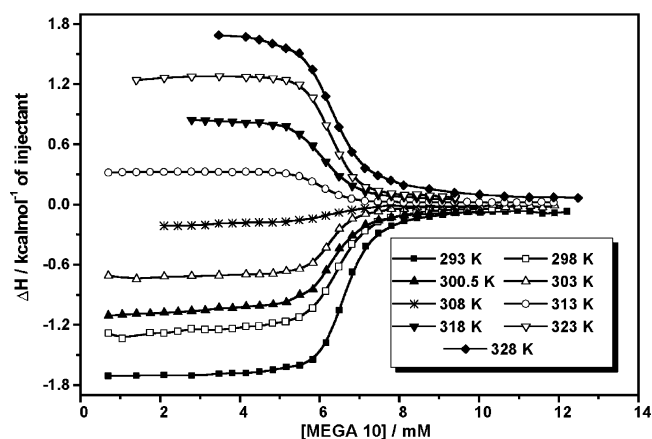


Figure 1. Enthalpograms for MEGA 10 dilution in water at different temperatures realized from ITC experiments. For details, see Experimental Section.

TABLE 1: CMC of MEGA 10 and C₁₄TPB by Calorimetry and Light Scattering at Different Temperatures

T/K	MEGA 10		C ₁₄ TPB
	cmc/mM (μcal)	cmc/mM (SLS) ³	cmc/mM (μcal) ⁶
293	6.67 ± 0.016		
298	6.45 ± 0.025	6.7	0.800 ± 0.013
300.5	6.34 ± 0.092		
303	6.29 ± 0.019	6.6	0.730 ± 0.012
308	6.1 ± 0.064	6.5	0.780 ± 0.014
313	6.08 ± 0.043	6.5	
318	6.13 ± 0.020	6.6	0.860 ± 0.011
323	6.21 ± 0.017	6.7	
328	6.38 ± 0.028	6.9	1.1 ± 0.010

where ΔH_d is the enthalpy of dilution of the surfactant, $\Delta H_{d(i)}$ and $\Delta H_{d(f)}$ are the values at the initial and final states, respectively, C_s is the concentration of the surfactant in the system, and ΔC_s is the constant interval of C_s .

The cmc values of MEGA 10 and C₁₄TPB evaluated by the above-mentioned SBE procedure at different temperatures are presented in Table 1, wherein the CMCs of MEGA 10 reported by Sugihara et al.^{4a} are also compared. The trend of the results was comparable with a vertical shift between the two, which arose because of higher cmc values of MEGA 10 by the SLS method than by calorimetry. An explanation for this discrepancy is not at hand. The sensitivities of the methods employed might be the reason for the difference. The ITC is considered to be a highly sensitive method to determine fairly accurate cmc values. Their graphical representations (Figure 2) have revealed the nature of comparison. The cmc minima at 313 and 303 K were observed for MEGA 10 and C₁₄TPB, respectively. A temperature-dependent minimum in cmc for a nonionic surfactant as observed for MEGA 10 is an infrequent observation. Such surfactants with an appreciable number of hydrophilic polyoxyethylene oxide (POE) groups (e.g., Triton X100 with average of 9.5 POEs) show a decline in cmc with increasing temperature. The MEGA 10 with five hydroxyl groups in its head got rapidly dehydrated and manifested behavior like ionic surfactants with a rise in temperature.

For physicochemical interest, we have also examined the cmc of MEGA 10 by both tensiometry and fluorometry (the dye Safranin T was the fluorescence probe¹¹). Tensiometry has produced a sharp change of the course of declination in surface tension (γ) vs $\log[\text{MEGA 10}]$ plot (taken to be the cmc) at a concentration lower than that obtained by microcalorimetry. The fluorometric method, on the other hand, produced a [MEGA

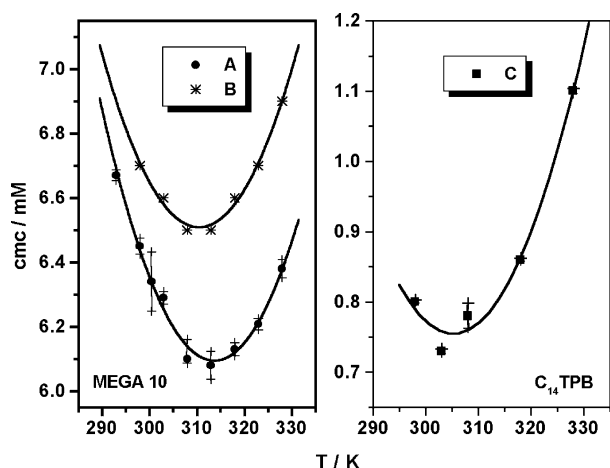


Figure 2. Dependence of cmc on temperature for MEGA 10 and C₁₄-TPB. A, MEGA 10 by calorimetry; B, MEGA 10 light scattering (results of Sugihara et al.); C, C₁₄TPB by calorimetry.

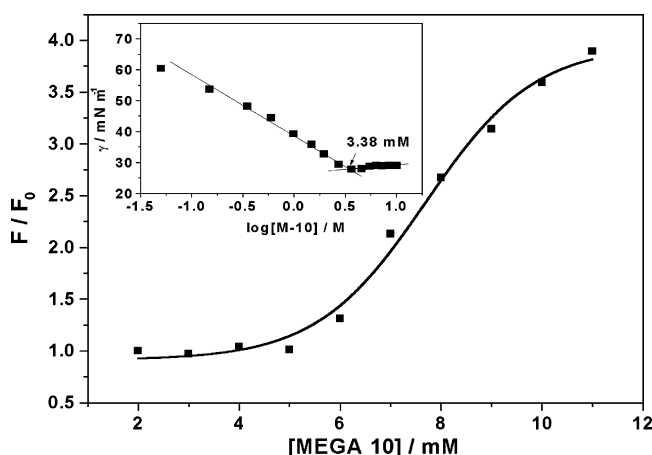


Figure 3. F/F_0 vs [MEGA 10] plot for Safranin T emission (excited at 520 nm and measured at 587 nm) at 303 K. Inset: γ vs $\log[\text{MEGA } 10]$ plot at 303 K.

10]-dependent sigmoidal pattern of the emission intensity ratio (F/F_0) of Safranin T with and without MEGA 10 to yield a cmc in terms of the sigmoidal Boltzman equation (a fluorometry-equivalent form of eq 1) that was moderately higher than calorimetry. Representative plots for tensiometry and fluorometry are presented in Figure 3. The cmc values realized by tensiometry and fluorometry at 303 K were 3.38 and 7.2 mM, respectively. Using pyrene as the fluorescence probe and cetylpyridinium bromide as the quencher, Hierrezuelo et al.¹³ have reported a cmc of 5.58 mM for MEGA 10 at 303 K, which is lower than the SLS data of Sugihara^{4a} and this work by calorimetry. In general, lower values of the cmc of MEGA 10 by tensiometry were reported in the past. The reported values in ref 4a–e were 4.68, 4.70, 4.70, 5.91, and 4.12, respectively. It may be mentioned that the Wilhelmy-type tensiometer has been found to give lower cmc values for many surfactants. On the average, the discrepancies in the present study were within $\pm 15\%$. Such a disagreement between the cmc values by calorimetry and tensiometry was not observed for C₁₄TPB.⁶ Although cmc is often a method-dependent quantity, the observation of $\sim 45\%$ lower values by tensiometry was not considered in our data analysis. To resolve the discrepancy, a detailed tensiometric study on MEGA 10 remains to be done.

Energetics of Micellization. Standard procedure for the evaluation of energetic parameters of micellization of MEGA 10 has been used. The relations considered for this purpose are

the following:

$$\Delta G_m^\circ = RT \ln X_{\text{cmc}} \quad (2)$$

where ΔG_m° is the standard Gibbs energy of micellization (according to the pseudophase micellar model), X_{cmc} is the cmc expressed in mole fraction unit, and R and T have their usual meaning.

$$\Delta H_m^\circ = \frac{d(\Delta G_m^\circ/T)}{d(1/T)} \quad (3)$$

where ΔH_m° is the standard enthalpy of micellization.

$$\Delta S_m^\circ = \frac{(\Delta H_m^\circ - \Delta G_m^\circ)}{T} \quad (4)$$

where ΔS_m° is the standard entropy of micellization

$$\Delta C_{\text{pm}}^\circ = \frac{d(\Delta H_m^\circ)}{dT} \quad (5)$$

where $\Delta C_{\text{pm}}^\circ$ is the standard specific heat of micellization.

The standard state was the state of unit activity of a hypothetical ideal solution of MEGA 10 at unit mole fraction.

Along with the evaluation of the energetic parameters using calorimetric enthalpy values, we have also evaluated them on the basis of enthalpy values determined from the van't Hoff rationale and have made a comparison between the two. In practice, a nonlinear trend in the plot between $(\Delta G_m^\circ/T)$ and T^{-1} was witnessed. A second-degree polynomial equation of the following form was used for the evaluation of ΔH_m° . Thus

$$\Delta G_m^\circ = a + bT + cT^2 \quad (6)$$

or

$$\Delta H_m^\circ = \frac{d(\Delta G_m^\circ/T)}{d(1/T)} = a - cT^2 \quad (7)$$

where a , b , and c are the coefficients of the polynomial.

The energetic parameters are presented in Table 2. It has been observed that the ΔH_m° directly determined by calorimetry on the whole was lower than that evaluated by the van't Hoff procedure using the calorimetric cmc values. The ΔH_m° values determined by Sugihara et al.^{4a} from the SLS cmc values by the van't Hoff rationale were further lower than those observed by calorimetry. The dependence of the derived ΔH_m° values on temperature is presented in Figure 4. The values have shown a linear dependence of ΔH_m° on temperature, and the $\Delta C_{\text{pm}}^\circ$ was obtained by the use of eq 5. The nature of disagreements among the three sets of values evidenced in the figure was not large. The enthalpy values determined in different ways crossed at 313 K to diverge in opposite directions in the lower-temperature region. The $\Delta C_{\text{pm}}^\circ$ values obtained from the slopes were -0.389 and -0.345 $\text{kJ mol}^{-1} \text{K}^{-1}$ by direct microcalorimetric experiments and indirect van't Hoff procedure, respectively. The ΔH_m° values of Sugihara et al. have produced $\Delta C_{\text{pm}}^\circ = -0.309$ $\text{kJ mol}^{-1} \text{K}^{-1}$. Approximately 12% discrepancies between direct calorimetry and the van't Hoff procedure as well as calorimetry and light scattering methods were observed. A comparison of $\Delta C_{\text{pm}}^\circ$ of C₁₄TPB (-0.684 $\text{kJ mol}^{-1} \text{K}^{-1}$) reported earlier by us⁸ from calorimetry with that of MEGA 10 revealed that the former was double in magnitude compared to the latter. This was the consequence of ionic processes associated with C₁₄-TPB in solution, which were absent with MEGA 10.

TABLE 2: Comparative Thermodynamic Parameters of MEGA 10 and C₁₄TPB

T/K	MEGA 10 (C ₁₄ TPB)				
	van't Hoff		$\Delta S_m^\circ / \text{kJ mol}^{-1} \text{K}^{-1}$	μcal	
	$\Delta G_m^\circ / \text{kJ mol}^{-1}$	$\Delta H_m^\circ / \text{kJ mol}^{-1}$		$\Delta H_m^\circ / \text{kJ mol}^{-1}$	$\Delta S_m^\circ / \text{kJ mol}^{-1} \text{K}^{-1}$
293	-21.9	6.47	0.097	6.63	0.097
298	-22.4 (-39.8)	5.07 (7.25)	0.092 (0.117)	5.08 (-5.96)	0.092 (0.113)
300.5	-22.6	4.34	0.089	3.94	0.088
303	-22.8 (-41.0)	3.57 (2.12)	0.087 (0.100)	2.86 (-13.2)	0.084 (0.092)
308	-23.3 (-41.2)	1.96 (-3.36)	0.082 (0.081)	0.837 (-15.5)	0.078 (0.084)
313	-23.7	0.240	0.076	-1.136	0.072
318	-24.1 (-42.2)	-1.59 (-15.4)	0.070 (0.043)	-3.22 (-21.7)	0.065 (0.064)
323	-24.4	-3.54	0.064	-4.96	0.060
328	-24.7 (-42.6)	-5.61 (-29.0)	0.058 (0.001)	-6.61 (-27.9)	0.056 (0.045)

The comparison between the calorimetric and van't Hoff methods of evaluation of thermodynamics of micellization of C₁₄TPB (shown in Table 2) has evidenced a large difference. The ionic surfactant has evidenced greater deviations from the nonionic surfactant, which was in accordance with our earlier reports.⁸ The direct calorimetric method registers integral heat, i.e., the heat of the overall process (all involved heats related to specific and nonspecific interactions), whereas the van't Hoff procedure estimates differential heat (related to the heat of micellization). In addition to its self-aggregation, the C₁₄TPB offered ionic processes (solvation, repulsive, as well as ion-dipolar interactions, etc.) in solution, which were partly absent in the case of self-association of MEGA 10 in solution. The observed differences discussed above were, therefore, not unexpected. Their interpretation and quantitative accounting ought to be a challenging task.

The ΔH_m° and ΔS_m° values of all three sets described above on MEGA 10 have shown good linear correlations between them with compensation temperatures of 321 K (direct calorimetry), 310 K (calorimetry–van't Hoff), and 319 K (Sugihara–van't Hoff).^{4a} The same was also true for C₁₄TPB, which has produced a compensation temperature of 320 K. Self-aggregating systems have observed such compensations^{5,14,15} between the associated enthalpy and entropy values, and the MEGA 10 and C₁₄TPB were no exception to this phenomenon. The compensation features of the described systems are presented in Figure 5.

In Figures 6 and 7, pairwise dependence among ΔG_m° , ΔH_m° , and ΔS_m° obtained at different temperatures are presented both for MEGA 10 and C₁₄TPB systems, respectively. Parallel features were observed for both the systems. In planes A, B, and C in both the figures, ΔH_m° vs ΔS_m° , ΔH_m° vs ΔG_m° , and ΔG_m° vs ΔS_m° dependences are depicted, respectively. The nine

points marked as 1–9 in plane C in Figure 6 correspond to the energetic parameters for MEGA 10 systems at temperatures 293, 298, 300.5, 303, 308, 313, 318, 323, and 323 K. Those marked as 1–5 in Figure 7 correspond to temperatures 298, 303, 308, 318, and 328 K for the C₁₄TPB system. For both the systems, the interdependence of ΔH_m° and ΔS_m° and ΔG_m° and ΔS_m° were fairly linear. The ΔH_m° and ΔG_m° profiles, on the other hand,

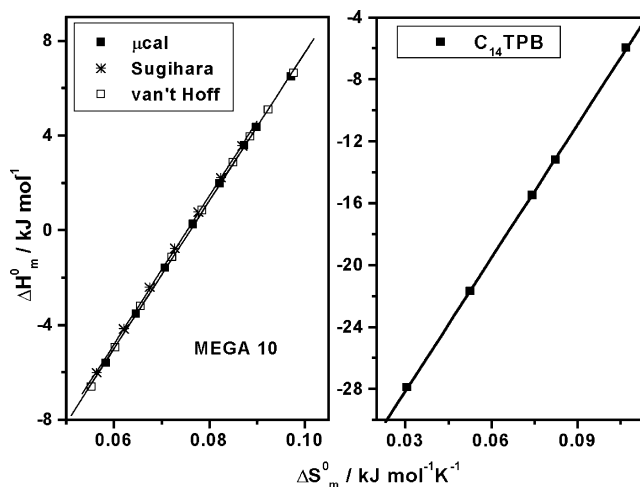


Figure 5. Enthalpy-entropy compensation plots for MEGA 10 and C₁₄TPB. In MEGA 10 section, results of microcalorimetry (this study) and light scattering (Sugihara et al.) are compared.

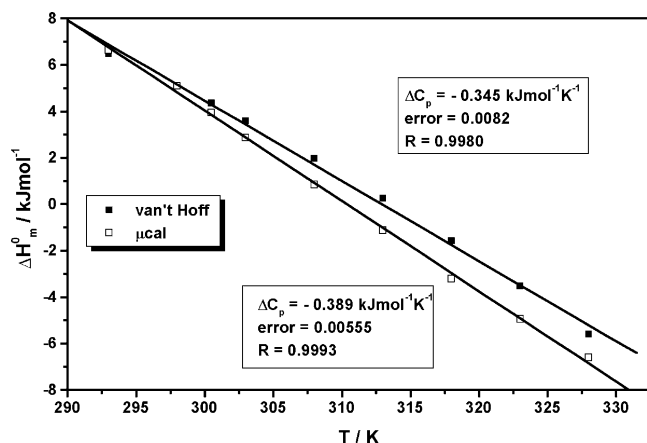


Figure 4. Dependence of ΔH_m° on temperature for micellization of MEGA 10 realized from calorimetry and van't Hoff method.

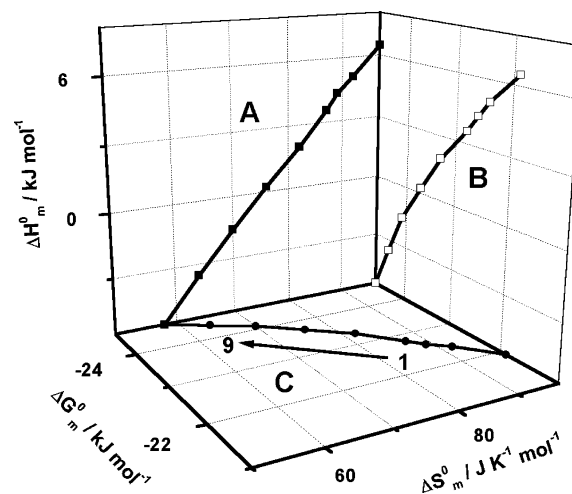


Figure 6. Pairwise thermodynamic parameter profiles for MEGA 10. Plane A, correlation of ΔH_m° with ΔS_m° ; plane B, correlation of ΔH_m° with ΔG_m° ; plane C, correlation of ΔG_m° with ΔS_m° . Points 1–9 correspond to temperatures 293, 298, 300.5, 303, 308, 313, 318, 323, and 328 K.

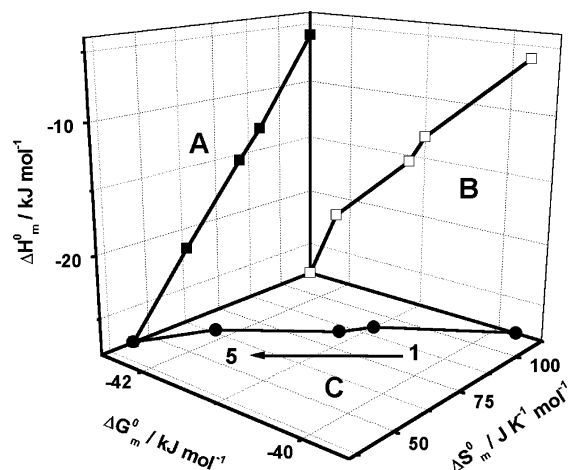


Figure 7. Pairwise thermodynamic parameter profiles for C₁₄TPB. The planes A, B, and C have the same meanings as in Figure 6. Points 1–5 correspond to temperatures 298, 303, 308, 318, and 323 K.

were curved (the degree of curvature was greater for MEGA 10 than C₁₄TPB).

The thermodynamic parameters for micellization of MEGA 10 may be deciphered for estimating the contributions of the terminal methyl group, the intermediate methylene group, and the terminal hydrophilic headgroup. The following additivity protocol^{4a} was used for the estimation of the Gibbs free energy values for the self-aggregation process

$$\Delta G_m^0 = \Delta G_m^0(\text{hy}) + (n_c - 1)\Delta G_m^0(\text{CH}_2) + \Delta G_m^0(\text{CH}_3) \quad (8)$$

where $\Delta G_m^0(\text{hy})$, $\Delta G_m^0(\text{CH}_3)$, and $\Delta G_m^0(\text{CH}_2)$ are the free energy contributions of the hydrophilic headgroup, the terminal methyl group, and the intermediate methylene groups, respectively, and n_c is the number of CH₂ groups present in the hydrophobic tail. For MEGA 10, $n_c = 9$ with $-\text{CH}_2\text{CONCH}_3\text{-CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ as the headgroup.^{4a}

Sugihara et al.^{4a} observed a very mild dependence of both $\Delta G_m^0(\text{CH}_2)$ and $\Delta G_m^0(\text{CH}_3)$ on temperature; on the average, the values were -2.9 and -8.78 kJ mol⁻¹, respectively. These values were used in eq 8 to get $\Delta G_m^0(\text{hy})$ at different temperatures. From the temperature dependence of $\Delta G_m^0(\text{hy})$, the $\Delta H_m^0(\text{hy})$ was then obtained in terms of eq 9 and $\Delta S_m^0(\text{hy})$ in terms of eq 10.

$$\Delta H_m^0(\text{hy}) = [d(\Delta G_m^0(\text{hy})/T)/d(1/T)]_p \quad (9)$$

and

$$\Delta S_m^0(\text{hy}) = [\Delta H_m^0(\text{hy}) - \Delta G_m^0(\text{hy})]/T \quad (10)$$

The deciphered $\Delta G_m^0(\text{hy})$ values obtained on the basis of calorimetric measurements are presented in Table 3. The headgroup contributions toward the free energy were nonspontaneous, whereas the contributions from CH₃ and CH₂ groups were spontaneous. These were the expected trends. The transfer of the hydrophilic headgroup from the bulk to the micelle should end up with an opposite tendency compared to the hydrophobic methyl and methylene groups. The $\Delta G_m^0(\text{hy})$ of MEGA 10 decreased with increasing temperature. Increased temperature produced desolvation of the headgroup, making its transfer energetics less nonspontaneous. The spontaneity of the transfer of the CH₃ group was more than that of the CH₂ group. The $\Delta H_m^0(\text{hy})$ obtained in terms of eq 9 was 37.3 kJ mol⁻¹. The corresponding entropy at 298 K was 200 J mol⁻¹ K⁻¹.

TABLE 3: Temperature-Dependent Headgroup Contributions to the Free Energy of Micellization of MEGA 10 and C₁₄TPB

T/K	$\Delta G_m^0(\text{hy})/\text{kJ mol}^{-1}$	
	MEGA 10	C ₁₄ TPB
293	12.89	
298	12.43	18.86
300.5	12.20	
303	11.99	18.17
308	11.54	17.87
313	11.15	
318	10.79	17.19
323	10.45	
328	10.14	16.95

The contribution of the headgroup of alkyltrimethylammonium bromide surfactants at 298 K toward the energetics of the micellization process has been recently reported.¹³ The $\Delta G_m^0(\text{hy})$ values of C₁₄TPB have been evaluated at different temperatures, which are also presented in Table 3. The results plotted according to eq 9 was linear to yield a constant $\Delta H_m^0(\text{hy})$ of 32.6 kJ mol⁻¹. It was lower than the $\Delta H_m^0(\text{hy})$ of MEGA 10, which was a consequence of the greater hydrophilicity of the headgroup of the nonionic surfactant versus the ionic. The $\Delta S_m^0(\text{hy})$ of C₁₄TPB obtained from eq 10 at 298 K was 243 J mol⁻¹ K⁻¹. The lower hydrophilicity of the ionic representative produced higher entropy toward micellization.

Aggregation Number (*N*) of MEGA 10 Micelles. There are reports on the micellar aggregation number of MEGA 10 by light scattering and fluorescence quenching methods.^{3,4} We herein report the determination of *N* by the microcalorimetric simulation method applied on other systems.^{9,10} In the simulation rationale, the mass action principle of micelle formation was used.

For *N* monomers of ionic surfactant, S⁻, forming a micelle, M_n, and binding β fraction of counterion, I⁺, the following equilibrium is valid:

$$NS^- + \beta NI^+ = M_n^{-(1-\beta)N} \quad (11)$$

The equilibrium constant is then given by the relation

$$K_m = [M_n^{-(1-\beta)N}]/([S^-]^N [I^+]^{\beta N}) \quad (12)$$

For nonionic surfactant, eq 13 results

$$K_m = [M_n]/[S]^N \quad (13)$$

The ΔG_m^0 is related with K_m by the equation

$$K_m = \exp(-N\Delta G_m^0/RT) \quad (14)$$

The demicellization constant, K_{dm} , is then

$$K_{dm} = \exp(N\Delta G_{dm}^0/RT) \quad (15)$$

In the ITC experiments, dilution of concentrated surfactant solution leads to the determination of differential heats of demicellization. Five adjustable parameters, *N*, ΔG_m^0 , ΔH_{dm}^0 , $\Delta H_{dil(mon)}$ (dilution enthalpy of monomer), and $\Delta H_{dil(mic)}$ (dilution enthalpy of micelles) were used in the simulation procedure. A nonlinear least-squares fitting procedure was considered in the computer program *Scientist*, version 2002, of MicroMath, Inc., Salt Lake City, Utah, U.S.A. In Figures 8 and 9, simulated fittings of the experimental enthalpograms at 293, 303, 323, and 328 K for MEGA 10 and at 298, 308, and 328 K for C₁₄-TPB are presented, respectively. The *N* values are given in Table

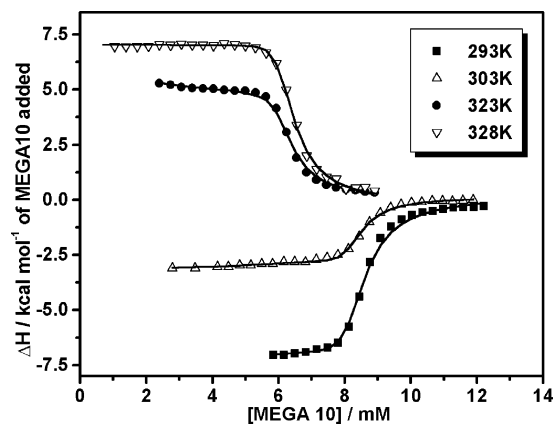


Figure 8. Simulation of enthalpograms of MEGA 10 obtained by ITC method at different temperatures for the evaluation of aggregation number.

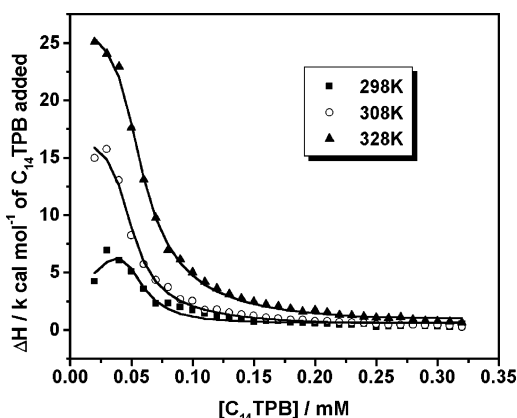


Figure 9. Simulation of enthalpograms of C₁₄TPB obtained by ITC method at different temperatures for the evaluation of aggregation number.

TABLE 4. Temperature-Dependent N and ΔG_m° of MEGA 10 (Found from Different Relations^a)

T/K	N	$\Delta G_m^\circ(\text{I})/\text{kJ mol}^{-1}$	$\Delta G_m^\circ(\text{II})/\text{kJ mol}^{-1}$	$\Delta G_m^\circ(\text{III})/\text{kJ mol}^{-1}$
293	28	-22.0	-21.3	-20.6
298		-22.4		
300.5	27	-22.7	-22.0	-21.2
303	30	-22.9	-22.3	-21.5
308		-23.3		
313	24	-23.7	-22.9	-22.0
318		-24.1		
323	29	-24.4	-23.7	-22.9
328	29	-24.7	-24.0	-23.2

^a $\Delta G_m^\circ(\text{I})/\text{kJ mol}^{-1} = RT \ln X_{\text{cmc}}$ (eq 2). $\Delta G_m^\circ(\text{II})/\text{kJ mol}^{-1} = RT[(1 - 1/N) \ln X_{\text{cmc}} + (RT/N)[\ln N^2(2N - 1)/(N - 2) + (N - 1) \ln N/(N - 1)/2(N^2 - 1)]]$ (eq 16). $\Delta G_m^\circ(\text{III})/\text{kJ mol}^{-1} = RT \ln X_{\text{cmc}} + (RT/N) \ln 2N^2$ (eq 17).

4. The fits to the experimental curves were satisfactory. The simulation method was used earlier by Blume et al.⁹ They have not made a comparison of the simulation results with that obtained by another method. We have observed lower values of N by simulation compared to fluorometry.

Sugihara et al.^{4a} have shown from light scattering experiments that N has a weak dependence on both concentration and temperature. The values reported were close to 75 with a shallow minimum at 313 K. The N values herein obtained were on the average ~50% lower than the findings of Sugihara et al. But, like their observation, a minimum in N at 313 K has also been observed by us. The lower aggregation number could be due to the experimentation done in the cmc region. It has been well-

documented that, at concentrations higher than cmc, N becomes an increasing function of surfactant concentration.¹⁶ Lower values of N by the simulation procedure have also been reported by us for sodium dodecylbenzenesulfonate, sodium dodecyl sulfate, alkyltrimethylammonium bromides, and alkyl triphenylphosphonium bromides.^{10,17,18} It may be noted that like calorimetry N estimated by the SLS method was also with reference to the results at the cmc point. In the evaluation procedure, the micellar molar mass determined at cmc was divided by the monomer molar mass to get N . The value was overestimated by the solvation of the headgroups of MEGA 10 in the micelle. However, ~50% higher value of N by SLS than calorimetry due to hydration requires justification that is given below. For this, the hydration of the headgroup region of MEGA 10 has been taken to be comparable with that of the Triton X100, where each oxygen center is solvated by four molecules of water.¹⁹ The 6 oxygen centers in the MEGA 10 molecule were thus solvated by 24 water molecules, which increased its effective molar mass. A correction for N by this value reduced the SLS determined N value at 298 K from 75 to 35, which was close to the N obtained by the method of simulation. Thus, headgroup solvation was the key factor for the discrepancy between the N determined by SLS and that determined by calorimetry.

The N values of C₁₄TPB micelles determined following the ITC protocol were 9, 6, 4, 5, and 4 at 298, 303, 308, 318, and 328 K, respectively. These values were also low like our earlier finding on cetyltriphenylphosphonium bromide¹⁸ and a recent report on the micelles of alkyltrimethylammonium bromides.¹⁷

Aggregation Number Related ΔG_m° . Two important mass action principle based equations for the estimation of ΔG_m° of nonionic surfactants were proposed by Corkill²⁰ and Moroi.²¹ We herein compare ΔG_m° values obtained from eq 2 for MEGA 10 with the values obtained from the relations of Corkill and Moroi.

Corkill's equation is as follows:

$$\Delta G_m^\circ(\text{II}) = \left(1 - \frac{1}{N}\right)RT \ln X_{\text{cmc}} + \frac{RT}{N} \left[\ln \frac{N^2(2N - 1)}{N - 2} \right] + (N - 1) \ln \frac{N(2N - 1)}{2(N^2 - 1)} \quad (16)$$

and Moroi's equation is as follows:

$$\Delta G_m^\circ(\text{III}) = RT \ln X_{\text{cmc}} + \left(\frac{RT}{N}\right) [\ln 2 + 2 \ln N] \quad (17)$$

The ΔG_m° values calculated using eqs 17 and 18 are presented in Table 4 in columns 4 and 5. The results by eq 2 are on the average ~3% higher than the Corkill proposition and ~8% higher than Moroi's proposition. Thus, the estimation of thermodynamic parameters of the process of micellization by the Corkill equation was fairly close with that by the pseudophase micellar model based eq 2. It may be mentioned that, in eq 2, the ΔG_m° is the Gibbs free energy per mole of monomer. So, implicitly, N is involved in the calculation. For high values of N , both eqs 17 and 18 reduce to eq 2. The additional terms in them have made the observed differences, since the measured N values for MEGA 10 micelles were not high.

Conclusions

The microcalorimetric study of the self-aggregation of MEGA 10 led to the following conclusions.

1. The temperature-dependent dilution enthalpograms were all well-patterned to derive information on cmc and enthalpy

of micellization of MEGA 10. The findings of Sugihara et al.^{4a} from SLS measurements and the present work were in good agreement.

2. Like ionic surfactants (e.g., C₁₄TPB), the nonionic surfactant MEGA 10 showed a minimum in temperature dependence of cmc.

3. Unlike C₁₄TPB, for MEGA 10 the enthalpy and the specific heat of micellization determined by calorimetry were in close agreement with that estimated from the van't Hoff rationale.

4. The headgroup contribution toward the free energy of micellization was less nonspontaneous for MEGA 10 than for C₁₄TPB.

5. On the basis of an ITC protocol, the aggregation number of MEGA 10 micelles could be estimated. The discrepancy between the *N* values determined by the methods of SLS and calorimetry can be accounted for on the basis of headgroup solvation.

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