

Calorimetric Study of the Micellization of Alkylpyridinium and Alkyltrimethylammonium Bromides in Water

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Titration calorimetry was employed to study the thermodynamic parameters of micellization of *N*-undecyl-, *N*-tridecyl-, *N*-tetradecyl-, and *N*-pentadecylpyridinium bromides and tetradecyl- and hexadecyltrimethylammonium bromides in salt-free aqueous solutions at 25 °C. For this purpose a model equation for the calorimetric titration curve based on the mass action model of the micellization process was derived. As adjustable parameters it contains the aggregation number n , the degree of micelle ionization p/n , and the enthalpy of micellization ΔH_M . Critical micelle concentrations cmc were determined by applying the Philips criterion to the experimental titration curves and so obtained cmc values are in excellent agreement with the literature data. Fitting of the model titration curves to those obtained experimentally shows that this procedure gives reliable values only for ΔH_M while it fails to provide any useful information on the p/n data. In addition, for surfactants with short alkyl chains and thus with low aggregation numbers ($n < \approx 50$) this fitting method provides also aggregation numbers that are close to those reported in the literature.

Introduction

Models developed to describe the thermodynamic properties of surfactant solutions have often been used to interpret calorimetric data resulting from the isothermal titrations of surfactant solutions into pure solvent.^{1–9} Most often, the purpose of calorimetric titration experiments is a direct determination of the enthalpy of micelle formation ΔH_M and the critical micelle concentration cmc. Numerous studies of surfactant systems have shown that ΔH_M can be evaluated within a two-state approximation from the calorimetric titration curve as a difference of its parts above and below cmc extrapolated to cmc.^{10–16} Only few authors, however, have applied titration calorimetry to solutions of ionic surfactants and tried to find a relationship between the composition of surfactant solution in the titration cell and the individual heat effects accompanying each injection of the titrant solution.^{17,18}

In the study we are presenting here, we employed high sensitivity titration calorimetry to determine cmc and ΔH_M for several cationic surfactants. Usually in a titration calorimetry experiment all heat effects caused by injecting the titrant solution into the titration cell, except the first one, result from mixing of two solutions of different concentrations. Therefore, they cannot be discussed simply in terms of enthalpies of dilution. In this work the simulated calorimetric titration curves were derived from the expression for the surfactant partial molar enthalpy \bar{H}_2 in the titration cell expressed in terms of the mass action model of the micellization process and in terms of the measured heat effect accompanying a single injection of the titrant solution. In the pre-micellar region, \bar{H}_2 was expressed in terms of the temperature derivative of the surfactant's mean activity coefficient γ_{\pm} , described by the Guggenheim's approximation.^{4,5,19,20} For all the measured surfactants the critical micelle concentrations determined by employing Philips criterion

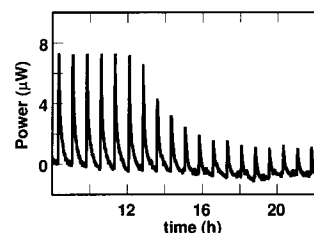


Figure 1. Typical calorimetric titration of surfactant into water; 2 mL of water was titrated with aqueous solution of $C_{13}PyBr$ (0.088 mmol/kg) at 25 °C. Each peak corresponds to 6 μL injection of the titrant solution.

ion^{21,22} on the experimental titration curves agree well with the corresponding values obtained by other methods.^{11,12,23} Fitting of the simulated calorimetric titration curves to those determined experimentally showed that the applied fitting procedure can provide only ΔH_M values while it is not able to give any information on the micelle ionization parameter p/n . Our results also show that for surfactants with a low aggregation number n such fitting may lead to good estimates of the n values.

Experimental Section

Materials. *N*-Undecyl ($C_{11}PyBr$), *N*-tridecyl ($C_{13}PyBr$), *N*-tetradecyl ($C_{14}PyBr$), and *N*-pentadecylpyridinium ($C_{15}PyBr$) bromides were synthesized from the corresponding 1-bromoalkanes and pyridinium²⁴ and purified by repeated recrystallization from acetone, while tetradecyl ($C_{14}TABr$) and hexadecyl ($C_{16}TABr$) trimethylammonium bromides were obtained from Merck and used without any further purification.

Titration Microcalorimetry. The heat effects resulting from mixing of aliquots of titrant solution from the syringe with the solution (solvent) in the titration cell were measured using TAM 2277 calorimeter from Thermometric AB, Sweden (Figure 1). Triply distilled water (2 mL) was titrated at 25 °C by a surfactant

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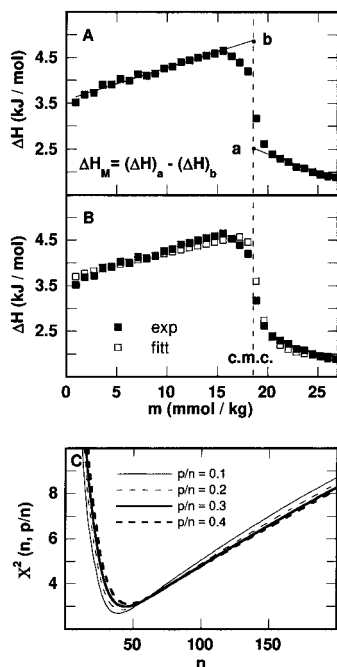
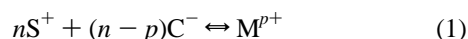


Figure 2. Calorimetric titration curve for C_{11} PyBr at 25 °C, (A) determination of ΔH_M by extrapolation method, (B) fitting of eq 14 to experimental titration curve using $p/n = 0.2$ ($\Delta H_M = -2.6$ kJ/mol, $n = 39$), C-minimization of $\chi^2(n, p/n)$ function over n at different p/n values.

solution placed in a 250 μ L syringe. Surfactant concentrations in the syringe were about 20-times higher than their cmc's. The reference cell was filled with water. The instrument was chemically calibrated by known heats of dilution of aqueous sucrose solutions²⁵ and before each experiment also by an electrical calibration. All experiments were performed at the calorimeter amplifier set between 10 and 100 μ W and were completed within 24 h. The area under a peak, which follows each injection of the titrant solution is proportional to the resulting heat effect ΔH (expressed per mole of added surfactant), which is then plotted against the total surfactant molality m in the titration vessel to construct the corresponding ΔH vs m curve (Figures 2A and 3A). The integration of peaks from the directly recorded calorimetric plots was performed using the Digitam program software.

Mass-Action Model. According to the mass-action approach, the process of micellization for cationic surfactants may be described as^{21,22}



where S^+ represents the surfactant ions, C^- the corresponding counterions, and M^{p+} is the micellar aggregate of n surfactant monomers with an effective charge of p . A surfactant solution having the concentration greater than cmc can be considered as a mixed electrolyte solution with a total surfactant molality m , expressed as

$$m = m_S + nm_M \quad (2)$$

and a degree of micellization, α ,

$$\alpha = \frac{nm_M}{m} \quad (3)$$

where m_S is the molality of surfactant ions in monomeric form and m_M is the molality of surfactant in the micellar form. The

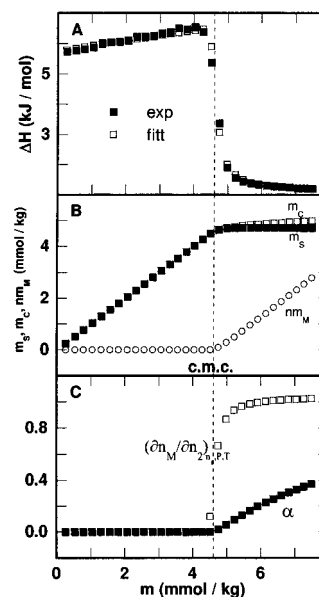


Figure 3. Analysis of calorimetric titration curve obtained for C_{13} PyBr at 25 °C, (A) fitting of eq 14 to experimental titration curve using $p/n = 0.2$ ($\Delta H_M = -5.0$ kJ/mol, $n = 50$), (B) composition of the surfactant solution below and above cmc calculated from eqs 2 and 4, (C) the corresponding degree of micellization α (eq 3) and the derivative $(\partial n_M/\partial n_2)_{n_1, P, T}$ (eq 8) as a function of the surfactant concentration.

apparent equilibrium constant for this micellization process K_M can be expressed as

$$K_M = \frac{m_M}{m_S^n m_C^{n-p}} \quad (4)$$

where m_C is the molality of the free counterions. The equilibrium between the monomeric surfactant ions, their micelles and the corresponding simple counterions can be described also in terms of composition variables n_1 (number of moles of solvent), n_2 (total number of moles of surfactant in solution), n_S (number of moles of surfactant ions in monomeric form), n_M (number of moles of surfactant ions in micellar form), n_C (number of moles of free counterions), and the corresponding partial molar enthalpies \bar{H}_1 , \bar{H}_S , \bar{H}_M , \bar{H}_C . The enthalpy of the solution in the titration cell obtained after i th injection H_i can thus be expressed as

$$H_i = n_1 \bar{H}_1 + n_S \bar{H}_S + n_C \bar{H}_C + n_M \bar{H}_M \quad (5)$$

and since $n_2 = n_S + n_M$ and $n_C = n_S + (p/n) n_M$, eq 5 becomes

$$H_i = n_1 \bar{H}_1 + n_2 (\bar{H}_S + \bar{H}_C) + n_M \Delta H_M \quad (6)$$

where the enthalpy of micelle formation ΔH_M , defined as

$$\Delta H_M = \bar{H}_M - \bar{H}_S - \left(1 - \frac{p}{n}\right) \bar{H}_C \quad (7)$$

is the enthalpy change accompanying the process in which 1 mol of surfactant ions and $(1 - p/n)$ mole of counterions pass in the solution from the unaggregated form into the micellar form. Partial differentiation of eq 6 with respect to n_2 at constant P , T , and n_1 combined with the Gibbs–Duhem equation leads to the following expression for the partial molar enthalpy of

surfactant \bar{H}_2 :

$$\bar{H}_2 = \bar{H}_S + \bar{H}_C + \Delta H_M \left(\frac{\partial n_M}{\partial n_2} \right)_{n_1, p, T} \quad (8)$$

Analysis of the Heat Effects Accompanying Titration Experiments. The heat effect q_i accompanying the i th injection of the titrant solution with concentration significantly higher than cmc into the titration cell can be expressed as

$$q_i = H_i - (H_{i-1} + H_a) \quad (9)$$

where H_i and H_{i-1} represent enthalpies of solution in the measuring cell after i th and $(i - 1)$ th injection, respectively, while H_a represents the enthalpy of the added aliquot of the titrant solution. If before the first injection the titration cell contains only solvent, with corresponding enthalpy H_1^0 , the cumulative heat effect $\sum_i q_i$, after i successive injections of the titrant solution can be presented as

$$\sum_1^i q_i = H_i - iH_a - H_1^0 = H_i - n_2 \text{ const} - H_1^0 \quad (10)$$

where n_2 is the total number of moles of added solute after i th injection and const is a constant. If the amount of solute added per injection Δn_2 is very small, this cumulative heat effect can be simplified into

$$\lim_{\Delta n_2 \rightarrow 0} \sum_1^i q_i = \lim_{\Delta n_2 \rightarrow 0} \sum_1^i \left(\frac{q_i}{\Delta n_2} \right) \Delta n_2 = \int_0^{n_2} \Delta H \, dn_2 \quad (11)$$

where ΔH is the enthalpy change accompanying each injection expressed per mol of added surfactant. Thus it follows from eqs 10 and 11 that the enthalpy of solution in the titration cell after i th injection H_i is:

$$H_i = \int_0^{n_2} \Delta H \, dn_2 + H_1^0 + n_2 \text{ const} \quad (12)$$

Finally, by taking the first derivative $(\partial H_i / \partial n_2)_{p, T, n_1}$, it follows from eq 12 that the partial molar enthalpy of the solute \bar{H}_2 at each titration point can be expressed as

$$\bar{H}_2 = \Delta H + \text{const} \quad (13)$$

The combination of eqs 8 and 13 leads to an expression for the measured quantity ΔH which includes also the enthalpy of micellization ΔH_M :

$$\Delta H = (\bar{H}_S + \bar{H}_C - \text{const}) + \Delta H_M \left(\frac{\partial n_M}{\partial n_2} \right)_{n_1, p, T} \quad (14)$$

ΔH_M can be obtained by a graphical extrapolation method which can be applied only in case of sharp transitions of calorimetric titration curves at cmc. This method is based on the assumption that micellization is an one-step process occurring at cmc in which the $(\bar{H}_S + \bar{H}_C)$ contributions just above and just below cmc are equal. Thus, according to eq 14, ΔH_M is simply a difference between the ΔH value just above cmc where $(\partial n_M / \partial n_2)_{n_1, p, T} = 1$ and the ΔH value just below cmc where $(\partial n_M / \partial n_2)_{n_1, p, T} = 0$. It can be obtained from the ΔH vs m plots as a difference between the parts of the ΔH vs m curves extrapolated

to cmc from the regions of surfactant concentration above and below cmc (Figure 2A).

The other possibility of determining ΔH_M , which involves fitting of the model calorimetric titration curve to the experimental one, is also based on eq 14. It should be applied when the experimental ΔH vs m curve is not completed and because of that the extrapolation of its part from the region beyond cmc to cmc becomes questionable. Since experimental titration process includes titration of surfactant solution below and above cmc the model titration curve must be able to cover different surfactant behavior in these two regions. It follows from eq 8 that below cmc where $(\partial n_M / \partial n_2)_{n_1, p, T} = 0$, the $(\bar{H}_S + \bar{H}_C)$ contribution can be derived from the expression for the surfactant chemical potential. Using the Gibbs–Helmholtz relation and Guggenheim approximation for the surfactant mean activity coefficient⁴

$$-\log \gamma_{\pm} = \left[\frac{A_{(T)} \sqrt{m}}{1 + \sqrt{m}} + B_{(T)} m \right] \quad (15)$$

in which m is the total surfactant molality, one obtains

$$\bar{H}_S + \bar{H}_C = \bar{H}_2^0 + 2RT^2 \left(\frac{A'_{(T)} \sqrt{m}}{1 + \sqrt{m}} + B'_{(T)} m \right) \quad (16)$$

where $A'_{(T)}$ and $B'_{(T)}$ are the temperature derivatives of coefficients $A_{(T)}$ and $B_{(T)}$, respectively, and \bar{H}_2^0 is the partial molar enthalpy of surfactant in its standard state. Above cmc it is assumed that due to small changes in concentrations of S^+ and C^- ions the $(\bar{H}_S + \bar{H}_C)$ contribution remains constant and equal to its value at cmc.

The derivative $(\partial n_M / \partial n_2)_{n_1, p, T}$, expressed as a function of m , can be obtained for given n and p/n from the apparent equilibrium constant K_M (eq 4). Introducing the degree of micellization α (eq 3), one obtains

$$\left(\frac{\partial n_M}{\partial n_2} \right)_{n_1, p, T} = \frac{n[u + g]}{1 + n[u + (1 - p/n)g]} \quad (17)$$

where

$$u = \frac{\alpha}{1 - \alpha}, g = \frac{(1 - p/n)\alpha}{1 - (1 - p/n)\alpha}$$

It has been shown that in surfactant solutions with no added electrolyte the mass action model of the micellization process combined with the cmc definition by Philips leads to the micellization constant K_M expressed as^{21,22}

$$K_M^{-1} = \frac{n(2n - p)(4n - 2p - 1)}{(2n - p - 2)} \times \left[\frac{(2n - p)(4n - 2p - 1)}{(2n - p - 1)(4n - 2p + 2)} \text{cmc} \right]^{2n - p - 1} \quad (18)$$

According to Philips²¹ the cmc can be obtained using a criterion $(\partial^3 \Phi / \partial m^3)_{\text{cmc}} = 0$ expressed in terms of property Φ , defined by the relationship $\Phi = Am_S + Bm_M$ in which A and B are constants and m_S and m_M are the molalities of surfactant ions and micelles, respectively.^{21,22} Around cmc Φ differs from the corresponding cumulative heat effect $\sum_i q_i$ only for a constant term, and thus the measured ΔH vs m curve is simply the $(\partial \Phi / \partial m)$ vs m curve. Therefore, cmc is obtained as the molality m

at which the second derivative of the experimental ΔH vs m curve with respect to m is equal to zero.

Once cmc is known, a pair of n and p/n values is chosen and the corresponding K_M is calculated. ΔH_M can then be obtained by fitting of eq 14 to the experimental ΔH vs m curve using the general linear least (chi)-square fitting procedure based on the chi-square function χ^2 defined as²⁶

$$\chi^2 = \sum_i \left[\frac{\Delta H_i - (\Delta H_i)_{\text{calc}}}{\Delta(\Delta H_i)} \right]^2 \quad (19)$$

where $(\Delta H_i)_{\text{calc}}$ is obtained from eq 14 and $\Delta(\Delta H_i)$ represents the experimental error in the measured quantity ΔH_i . For the minimization of the chi-square function $\chi^2(n, p/n)$ over n at given value of p/n the standard Simplex algorithm was used.²⁶

Results and Discussion

A result of a stepwise injections of small aliquots of the titrant surfactant solution ($m_{\text{tit}} \approx 20$ cmc) into the measuring cell containing initially water is an enthalpogram presented in Figure 1. If the individual heat bursts ΔH_i ($\Delta H_i = q_i/\Delta n_2$) are plotted against the surfactant concentration m in the titration cell, a typical sigmoidal curve with an inflection point at the cmc emerges (Figures 2A and 3A). Below cmc this curve describes the concentration dependence of the heat effects caused predominantly by the demicellization of micelles injected into solution while above cmc it reflects mainly the dilution of micelles added at each injection.

In the present work we tried to determine the thermodynamic characteristics of the micellization process for several surfactants by fitting the model functions derived from the mass action model of the micellization process (eq 1) to the corresponding experimental calorimetric titration curves (Figures 2B and 3A). Following the Philips criterion, the most characteristic property of micellization, cmc, was obtained as the concentration at which $(\partial^2 \Delta H / \partial m^2)_{\text{cmc}} = 0$. For the measured surfactants such determination of cmc was not problematic because the transitions of their ΔH vs m curves are rather sharp (Figures 2B and 3A). Comparison with the corresponding cmc data obtained in this laboratory from the emf measurements of galvanic cells consisting of an appropriate surfactant ion selective electrode and reference electrode¹² and from the measurements of specific conductivity of surfactant solutions as a function of their concentration²³ shows an excellent agreement.

Since cmc is determined according to Philips criterion^{21,22} the first micellar aggregates start forming before so defined cmc is reached. The calculation of the $(\bar{H}_S + \bar{H}_C)$ contribution at cmc from eq 16 may thus become problematic due to the presence of the already formed micelles which are not taken into account by the Guggenheim's approximation on which the eq 16 is based. The model calculations of m_S and m_C show, however, that beyond the appearance of the first aggregates they both increase linearly with the increasing total surfactant concentration up to cmc while above cmc they remain almost constant and equal to cmc. Furthermore, these calculations show that in comparison with m_S and m_C the corresponding micelle concentrations m_M are very small and can be neglected (Figures 3B and C). Apparently, as far as the $(\bar{H}_S + \bar{H}_C)$ contribution is concerned, the assumption that beyond the appearance of the first micelles the micellar concentration may be ignored while the m_S and m_C increase linearly up to cmc and then remain constant, seems reasonable. Therefore, it was used in evaluating the $(\bar{H}_S + \bar{H}_C)$ contributions from eq 16 in all of the simulated ΔH vs m curves.

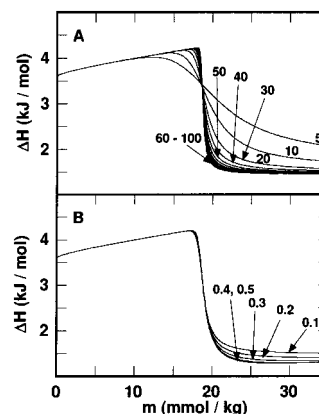


Figure 4. The dependence of the simulated calorimetric titration curve at given $\Delta H_M = -2.6$ kJ/mol, $B'(T) = 0.03$ kg/mol K, and $\text{cmc} = 18.6$ mmol/kg at 25 °C: on (A) the parameter n (varying between 5 and 100) at given $p/n = 0.2$, (B) the parameter p/n (varying between 0.1 and 0.5) at given $n = 40$.

Enthalpy of micellization has been obtained by many authors as the enthalpy difference between the parts of ΔH vs m curve above and below cmc extrapolated to cmc.^{10–16} This widely used method gives correct results only if the transition in the titration curve is completed or in other words, if in the concentration region beyond cmc the ending plateau of the titration curve is reached. Sometimes single experiment data do not show whether the observed transition ended or not. Usually this happens with surfactants with shorter alkyl chains for which the transitions are too wide or when the concentrations of the titrant solutions used in the experiments are too low. In any case, the extrapolation of the “nonended” parts of such titration curves to the corresponding cmc values may lead to unacceptably large errors in ΔH_M . Our results suggest that in such cases the curve fitting method of determining ΔH_M may be more appropriate since it makes possible to obtain reliable ΔH_M also from the titration curves that do not reach the ending plateau. Since the part of the fitting procedure that directly leads to the determination of ΔH_M involves interplay of three parameters n , p/n , and ΔH_M , their interactivity was closely investigated. The simulation of calorimetric titration curves shows that at fixed p/n and ΔH_M the curves change with n only up to $n \approx 50$ (Figure 4A), while at fixed n and ΔH_M they show only slight dependence on p/n (Figure 4B). In other words, the determination of n by the minimization of the least (chi)-square function at given p/n is possible only as long as the simulated curves show observable dependence on n , that is for $n < \approx 50$ (Figure 4A). Such minimization is presented in Figure 2C where it is shown that for $C_{11}\text{PyBr}$ at any reasonable fixed value of p/n a sharp minimum in the least (chi)-square function appears at $n \approx 40$. Similar result is obtained also with $C_{13}\text{PyBr}$ where such minimum in the least (chi) square is observed at $n \approx 50$. The relative stability and small mean square deviations of n and ΔH_M determined at p/n values between 0.1 and 0.4 (Table 1) indicate that for surfactants such as $C_{11}\text{PyBr}$ and $C_{13}\text{PyBr}$ having short alkyl chains (small n) and well defined cmc's the described curve fitting procedure can provide quite accurate ΔH_M and n values. Good agreement of the observed ΔH_M and n parameters with those recently determined in this laboratory from heat of dilution¹² and apparent molar volume²³ measurements clearly supports this conclusion.

With surfactants having longer alkyl chains and thus larger n values the fitting method is less successful. Although the correlation between the model (eq 14) and experimental calorimetric titration curve is still very good (Tables 1 and 2), it fails to provide reliable n data since the mean square deviations

TABLE 1: Enthalpy of Micellization ΔH_M and the Aggregation Number n for C_{11} PyBr and C_{13} PyBr at 25 °C Obtained from Fitting of eq 14 to the Experimental Titration Curves at Different Degrees of Micelle Ionization p/n

surfactant	cmc, mmol kg ⁻¹	n_a^a	p/n	n^b	$-\Delta H_M$, kJ mol ⁻¹	r^c
C_{11} PyBr	18.6	42	0.1	35 ± 6	2.7 ± 0.2	0.994
			0.2	39 ± 5	2.6 ± 0.2	0.993
			0.3	41 ± 4	2.5 ± 0.2	0.993
			0.4	44 ± 3	2.4 ± 0.2	0.993
C_{13} PyBr	3.6	57	0.1	40 ± 20	5.2 ± 0.3	0.998
			0.2	50 ± 10	5.0 ± 0.3	0.998
			0.3	50 ± 10	4.8 ± 0.2	0.998
			0.4	49 ± 7	4.7 ± 0.2	0.998

^a n_a values are obtained from the apparent molar volume measurements.²³ ^b The \pm values listed are the statistical root-mean-square deviations. The relative error of each experimental value of ΔH (titration point) was estimated to be $\pm 10\%$. ^c r values are the statistical correlation coefficients.

TABLE 2: Enthalpies of Micellization of C_{11} -, C_{13} -, C_{14} -, and C_{15} PyBr and C_{14} - and C_{16} TABr at 25 °C Obtained from Fits of Eq 14 Using $p/n = 0.2$,²³ ΔH_M , and by the Extrapolation Method, ΔH_M^{ex}

surfactant	cmc, mmol kg ⁻¹	$-\Delta H_M^{\text{ex}}$, kJ mol ⁻¹	$-\Delta H_M$, ^a kJ mol ⁻¹	r^b
C_{11} PyBr	18.6	2.3	2.6 ± 0.2	0.993
C_{13} PyBr	4.6	5.4	5.0 ± 0.3	0.998
C_{14} PyBr	2.7	6.9	6.4 ± 0.3	0.997
C_{15} PyBr	1.3	8.3	7.6 ± 0.3	0.998
C_{14} TABr	3.6	4.3	4.1 ± 0.2	0.999
C_{16} TABr	0.9	8.1	7.7 ± 0.2	0.995

^a The \pm values listed are the statistical root-mean-square deviations. The relative error of each experimental value of ΔH (titration point) was estimated to be $\pm 10\%$. ^b r values are the statistical correlation coefficients.

of n at $n > \approx 50$ become too large. On the other hand, the comparison with the corresponding literature data^{11,12,23} shows that it still gives accurate ΔH_M values characterized by small mean standard deviations and only weak dependence on the parameters n and p/n . As shown in Table 2 these values are also close to those obtained by extrapolation method. Since such extrapolations are safe for surfactants with longer alkyl chains due to the sharp transitions of their calorimetric titration curves one can expect that, for C_{14} PyBr, C_{14} TABr, C_{15} PyBr, or C_{16} TABr, the extrapolation method will give reliable ΔH_M values. In other words, for surfactants with longer alkyl chains no complicated fitting procedure is needed to determine their ΔH_M values.

Taken together our results show that fitting of eq 14 to the experimental calorimetric titration curves cannot provide all parameters needed for a full thermodynamic description of the micellization process. It can only lead to relatively safe ΔH_M values and for surfactants with smaller aggregation numbers also to approximate n values but fails to give any useful information on the p/n values. Since according to eq 19 the micellization constant K_M can be obtained only from cmc, n , and p/n data it follows that K_M and the corresponding standard Gibbs free energy of micellization ΔG_M^0 , together with the related entropy of micellization ΔS_M^0 , cannot be determined only by isothermal titration calorimetry. To obtain ΔG_M^0 values the corresponding n and p/n parameters have to be determined by some other method.^{12,23} They can then be combined with the measured ΔH_M values (assuming $\Delta H_M = \Delta H_M^0$) to give the corresponding ΔS_M^0 values.

Conclusions

Isothermal titration microcalorimetry has become a powerful technique for determining cmc's and enthalpies of micellization in surfactant solutions. In our contribution an attempt was made to simulate the calorimetric titration curves on the basis of a simple mass action model of the micellization process and the Philips definition of cmc. In the premicellar region these titration curves were simulated only on the basis of electrostatic interactions between the surfactant ions and their counterions described in the form of the Guggenheim's approximation of the surfactant mean activity coefficient. As a result a model titration curve was derived which contains adjustable parameters n , p/n and ΔH_M . It was shown that for all the measured surfactants the Philips criterion provides cmc values that agree well with the literature data. Fitting of the model titration curves to those obtained experimentally showed that this procedure can provide reliable values only for ΔH_M and for surfactants with low aggregation number ($n < \approx 50$) also for n . On the other hand, it fails to give any information on the degree of the micelle ionization p/n . To conclude, our results show that a full thermodynamic description of the micellization process discussed in terms of a simple mass action model cannot be realized only on the basis of the titration calorimetry data.

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