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Thermodynamics of Micellization of *N*-Octyltrimethylammonium Bromide in Different Media

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Received October 17, 1994. In Final Form: February 1, 1995[®]

The critical micelle concentrations (cmc) of *n*-octyltrimethylammonium bromide in pH 3.2, 7.0, and 10.0 media, at the temperatures 15, 20, 25, 30 and 35 °C have been determined by the electrical conductivity method. Cmc values decrease to a greater value of pH. From the conductivity data, the degrees of counterion binding of the micelles have been calculated. Thermodynamic parameters of micellization have been obtained by application of the model of Evans and Ninham in terms of hydrophobic and surface contributions, which are pH dependent.

Introduction

The formation of micelles is a cooperative process which occurs at a critical micelle concentration (cmc), characteristic of the surfactant species and various factors such as temperature and pH of the solution.¹ The cmc can serve as a measure of micelle stability in a given state, and the thermodynamics of micellization can be determined from a study of the temperature dependence of the cmc.

n-Octyltrimethylammonium bromide is a typical cationic surfactant with a cmc around 130 mM² in the absence of any other additive. The effect of temperature on the cmc of alkyltrimethylammonium bromides in aqueous solutions has been investigated by several authors for octyl, nonyl, decyl, dodecyl, tetradecyl, and hexadecyl^{3–10} and we have recently studied^{11,12} the micellar behavior of decyl, dodecyl, and tetradecyl in two different media of low and high pH at different temperatures. We have demonstrated that specific conductivity is very useful in determining cmc values and have analyzed the interactions that induce the micelle formation.

In the present work we report results of our study on the temperature dependence of the cmc in different media of *n*-octyltrimethylammonium bromide which have been obtained from conductivity measurements in the 15–35 °C temperature range at 5 °C intervals. We discuss the thermodynamic properties of the surfactant in terms of contributions from energy associated with transferring

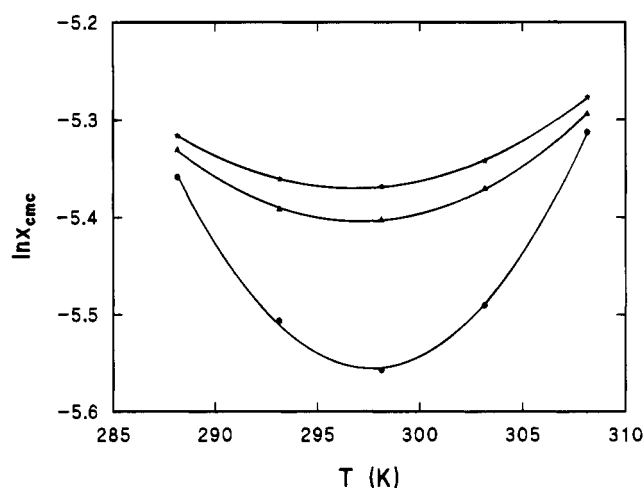


Figure 1. Experimental critical micelle concentrations (expressed in mole fractions) as a function of temperature for OTAB fitted to eq 1: ●, pH 10.0; △, pH 7.0; ★, pH 3.2.

Table 1. Critical Micelle Concentration of *n*-Octyltrimethylammonium Bromide in Media of pH 3.2, 7.0, and 10.0 at Different Temperatures

<i>T</i> (K)	cmc (mol L ⁻¹)		
	pH 3.2	pH 7.0	pH 10.0
288.15	0.2740	0.2700	0.2624
293.15	0.2620	0.2540	0.2265
298.15	0.2600	0.2512	0.2150
303.15	0.2670	0.2595	0.2300
308.15	0.2850	0.2802	0.2750

Table 2. Parameters *C*, *D*, and *E* for Fits of Equation 1 and Correlation Coefficients (*f*)

pH	10 ⁻³ <i>C</i> (K ²)	<i>D</i> (K)	<i>E</i>	<i>f</i>
3.2	7.20	-0.42	58	0.9998
7	9.00	-0.54	74	0.9998
10.0	2.18	-1.30	187	0.9997

the surfactant hydrocarbon chain out of the medium into the interior of the micelle, the associated electrostatic interactions between the head groups and counterions, and all other contributions arising from specific interactions.

Experimental Section

The surfactant *n*-octyltrimethylammonium bromide (OTAB) was obtained from Lancaster MTM Research Chemicals Ltd. (No. 8610). Three buffers were used: glycine (50 mmol dm⁻³)—

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[®] Abstract published in *Advance ACS Abstracts*, May 1, 1995.

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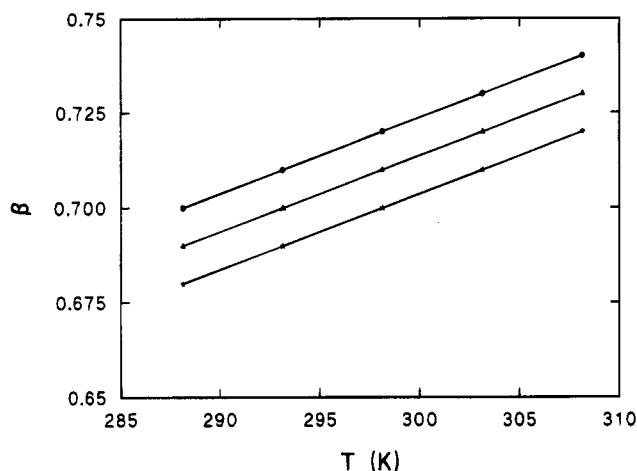


Figure 2. Dependence of the degree of counterion binding on the temperature for OTAB in different media: ●, pH 10.0; △, pH 7.0; ★, pH 3.2.

Table 3. Kinematic Viscosities (ν_o) and Densities (δ_o) of Different Media at Different Temperatures

T (K)	ν_o (mm ² s ⁻¹)	δ_o (g cm ⁻³)
pH 3.2		
288.15	1.117	1.00073
293.15	0.9821	0.99989
298.15	0.8778	0.99872
303.15	0.7783	0.99732
308.15	0.7068	0.99567
pH 7.0		
288.15	1.157	1.00947
293.15	1.010	1.00860
298.15	0.8955	1.00733
303.15	0.8029	1.00589
308.15	0.7240	1.00420
pH 10.0		
288.15	1.052	1.00045
293.15	0.9739	0.99976
298.15	0.8712	0.99867
303.15	0.7815	0.99684
308.15	0.7061	0.99477

sodium hydroxide, pH 10.0, ionic strength 0.0312; glycine (50 mmol dm⁻³)-hydrochloric acid, pH 3.2, ionic strength 0.0062; and phosphate (50 mmol dm⁻³) pH 7.0, ionic strength 0.0050. The ionic strengths of the buffers were calculated from the glycine dissociation constants¹³ $pK_a(1) = 2.3503$ and $pK_a(2) = 9.7796$ and the phosphate second dissociation constant¹³ $pK_a(2) = 7.21$. All other materials were of analytical grade and solutions were made up in double distilled water.

Critical micelle concentrations were measured by using a specific conductivity meter (Kyoto Electronics type C-117). The conductivity cell (Kyoto type K-121) was calibrated with KCl solutions in the appropriate concentration range. The cell constant was calculated using molar conductivity data for KCl published by Shedlovsky¹⁴ and Chambers et al.¹⁵ Concentrated solutions of surfactant systems of known molar composition were progressively added to the buffer solution at a constant flow rate. The measuring cell was immersed in a thermostated bath, the temperature being kept constant within ± 0.01 K.

Kinematics viscosities of the buffers were measured with a Schott-Geräte measuring system, consisting of a measuring stand, an automatic washer, a constant-temperature bath, and a calibrated Ubbelohde suspended level viscometer. Time measurements were made automatically using thermometric sensors and a electronic timer (Schott Aus 440) with precision of ± 0.01 s. The thermostat bath (C1450) was controlled within ± 0.01 K.

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Table 4. Slopes (S_m) to Conductivity Curves above the Critical Micelle Concentration and Degree of Counterion Binding (β) for OTAB in Different Media at Different Temperatures

T (K)	S_m (S cm ² mol ⁻¹)	β
pH 3.2		
288.15	20.2	0.68
293.15	22.3	0.69
298.15	23.5	0.70
303.15	25.3	0.71
308.15	26.4	0.72
pH 7.0		
288.15	19.6	0.69
293.15	21.5	0.70
298.15	22.7	0.71
303.15	24.5	0.72
308.15	25.4	0.73
pH 10.0		
288.15	18.9	0.70
293.15	20.8	0.71
298.15	21.9	0.72
303.15	23.6	0.73
308.15	24.5	0.74

Table 5. Hydrophobic Free Energy of Transfer, ΔG_{HP}° , Surface Contributions, ΔG_s° , and Enthalpy, ΔH_m° , for the Formation of Micelles of OTAB in Different Media at Different Temperatures

T (K)	ΔG_{HP}° (kJ mol ⁻¹)	ΔG_s° (kJ mol ⁻¹)	ΔH_m° (kJ mol ⁻¹)
pH 3.2			
288.15	-21.39	8.660	13.63
293.15	-22.08	9.015	5.46
298.15	-22.62	9.315	-3.41
303.15	-23.02	9.556	-13.01
308.15	-23.25	9.734	-23.35
pH 7.0			
288.15	-21.58	9.812	13.21
293.15	-22.33	9.198	2.83
298.15	-22.90	9.508	-8.14
303.15	-23.28	9.745	-20.59
308.15	-23.46	9.900	-33.69
pH 10.0			
288.15	-21.82	8.986	37.71
293.15	-22.94	9.528	12.39
298.15	-23.69	9.917	-15.16
303.15	-23.93	10.100	-44.75
308.15	-23.68	10.070	-76.73

Densities of the buffers were measured with a Anton Paar Model DMA 60/602 densimeter with a resolution of 1.5×10^{-6} g cm⁻³. Deionized double distilled water and dry air were chosen as the calibrating fluids since their densities are known precisely. Calibration was carried out prior to each measurement under the same temperature and pressure conditions. The temperature of the thermostat was maintained constant within ± 0.01 K. The temperature was measured by a digital precision thermometer (Anton Paar DT 100-20).

The pH adjustment to 3.20, 7.00, and 10.00, respectively, was made by means of a Radiometer pH-meter PHM 82.

Results and Discussion

Critical Micelle Concentration. Cmc values were determined from inflections in plots of conductivity, κ , against concentration from solutions of the OTAB at different pHs. The data points above and below the inflection were fit to two equations of the form $\kappa = Ac + B$, and by solving simultaneously the two equations, the point of intersection was obtained. Least squares analysis was employed, and correlation coefficients were greater than 0.9995 in all cases. Table 1 shows the cmc values of the OTAB as a function of the temperature and pH. Our results are in good agreement with expected

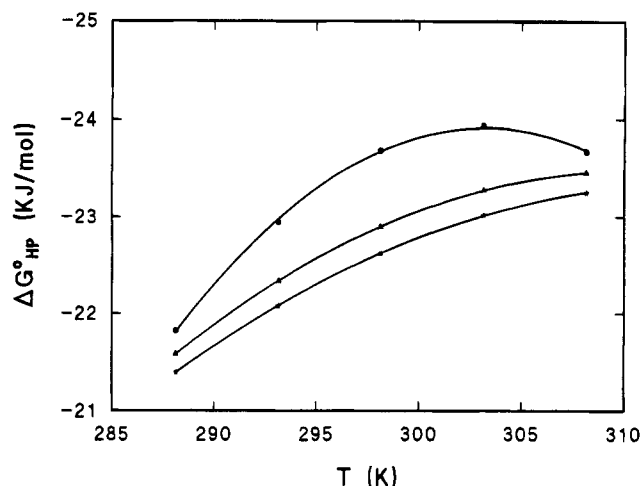


Figure 3. Free energy, ΔG_{HP}° , of transfer of a hydrocarbon tail from medium to a micelle for OTAB at each temperature: ●, pH 10.0; Δ, pH 7.0; ★, pH 3.2.

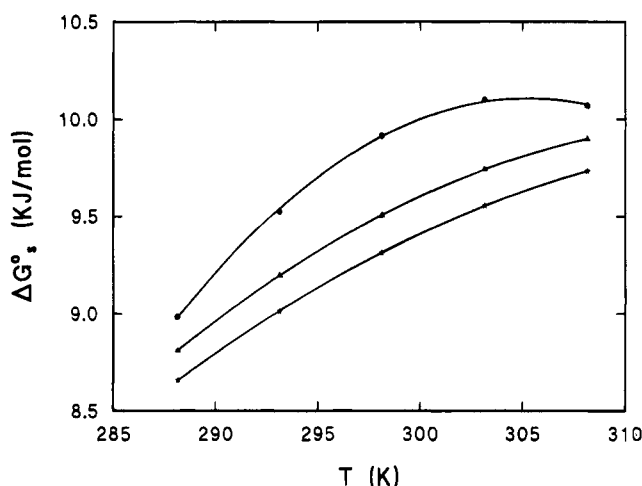


Figure 4. Free energy, ΔG_s° , of the surface for OTAB in different media at different temperatures: ●, pH 10.0; Δ, pH 7.0; ★, pH 3.2.

values.^{16,17} In all cases the variation of the cmc (expressed in mole fractions units) with temperature can be approximated by

$$\ln X_{cmc} = CT^2 + DT + E \quad (1)$$

where T is the temperature and C , D , and E are parameters. Only cmc values obtained from conductivity experiments have been used. Higher-order polynomials did not give significantly better fits. The values of C , D , and E are listed in Table 2. As can be seen in Figure 1, the minima occurs around 25 °C and is similar to that observed for a number of other surfactants.^{18,19} A peculiarity of the cmc values is that the effect of pH is to decrease the cmc as the pH is increased; i.e., the hydrophobicity of medium decreases with an increase in the pH.

Degree of Counterion Binding. The degree of counterion binding, β , was calculated from the relationship $\beta = 1 - \alpha$, α being the degree of ionization, which was determined from the gradient, S_m , of plots of κ against c

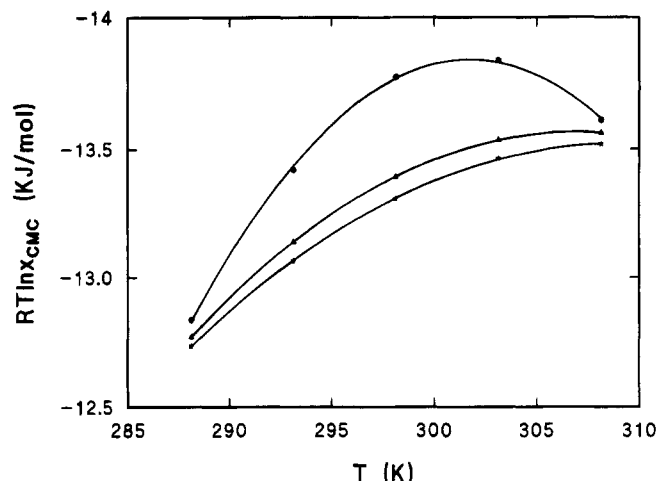


Figure 5. Free energy, $RT \ln X_{cmc}$, of micellization for OTAB in different media at different temperature: ●, pH 10.0; Δ, pH 7.0; ★, pH 3.2.

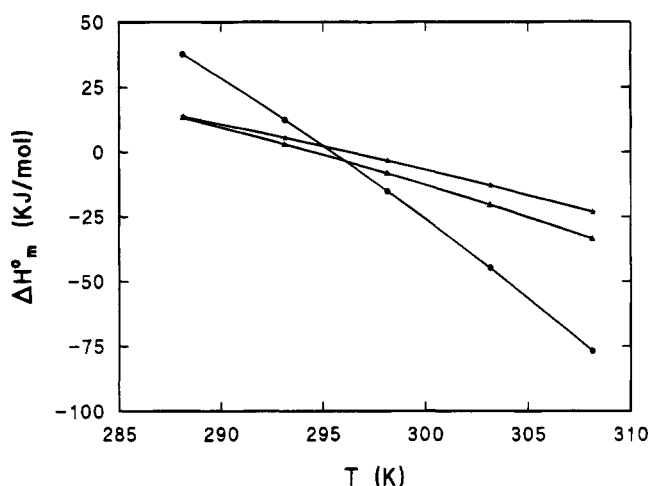


Figure 6. Enthalpy of micellization, ΔH_m° , for OTAB in different media at different temperatures: ●, pH 10.0; Δ, pH 7.0; ★, pH 3.2.

above the cmc as proposed by Evans.²⁰

$$S_m = \left(\frac{F^2}{6\pi N_A \eta_0 r_m} + \lambda_{o, Br^-} \right) \alpha \quad (2)$$

where F is Faraday's constant, N_A is Avogadro's constant, η_0 is the solvent viscosity, and r_m is the radius of the micelles.

Table 3 shows experimentally determined kinematic viscosities (ν_0) and densities (δ_0). The conversion of ν_0 into η_0 by use of δ_0 is well-known: $\eta_0 = \nu_0 \delta_0$. The values of the limiting ionic conductivity of the Br^- counterion at each temperature were taken from Robinson and Stokes.²¹ An approximate r_m value was calculated by assuming micellar sphericity and equating r_m with the length of the extended alkyl chain, l_c , calculated from²²

$$l_c = 1.5 + 1.265n_c \quad (3)$$

where $n_c = 8$ is the number of carbon atoms in the hydrocarbon chain.

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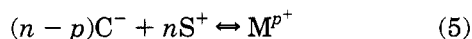
The β values calculated for OTAB are given in Table 4, together with the slopes (S_m) above the cmc. The plot of β as a function of the temperature is shown in Figure 2. β increase very slightly with increase of the temperature and is practically constant at the three pHs studied.

Thermodynamics of Micellization. In the model of Evans and Ninham,²³ the cmc is defined in terms of

$$RT \ln X_{\text{cmc}} = \Delta G_{\text{HP}}^\circ + \Delta G_s^\circ \quad (4)$$

where $RT \ln X_{\text{cmc}} = \Delta G_M^\circ$ is the total Gibbs energy per surfactant molecule associated with forming micelles, $\Delta G_{\text{HP}}^\circ$ is the hydrophobic free energy of transfer of the surfactant hydrocarbon chain from the medium to the interior of the micelle (this drives micellization) and ΔG_s° describes surface contributions, which include the energy associated with electrostatic interactions between the head groups and counterions (this opposes micellization) and all other contributions arising from specific interactions. To understand micellization the evaluation of these contributions is necessary.

One approach is to determine ΔG_s° by using a suitable model. We employed the equilibrium model, according to the method of Ueno et al.,²⁴ which relates the degree of counterion binding to the electrostatic interactions between surfactant head groups and counterions.²⁵ This provides an estimate of the free energy of transferring the surfactant hydrocarbon chain from the medium into the interior of the micelle. The equilibrium between monomers, counterions, and monodisperse micelles can be represented by



where for a cationic surfactant, C^- , S^+ , and M^{p+} represent the counterion, surfactant monomer, and micelle, respectively. The equilibrium constant for eq 5 can be related to the standard free energy of micelle formation per monomer unit by

$$\frac{\Delta G_{\text{HP}}^\circ}{RT} = -(1/n) \ln C_{\text{M}^{p+}} + \ln C_{\text{S}^+} + \left(1 - \frac{p}{n}\right) \ln C_{\text{C}^-} \quad (6)$$

For typical micelles ($n = 50-100$), the term M^{p+} is small and insensitive to large errors in the estimated $C_{\text{M}^{p+}}$ and both C_{C^-} and C_{S^+} can be replaced by the cmc (expressed in mole fractions) in the second and third terms in eq 6 to give

$$\Delta G_{\text{HP}}^\circ = RT \ln X_{\text{cmc}} + RT \left(1 - \frac{p}{n}\right) \ln X_{\text{cmc}} \quad (7)$$

where $p/n = \alpha$ is the degree of dissociation of counterions from the micelle and $(1 - p/n) = \beta$ the degree of counterion binding. Comparison with eq 4 shows that in terms of the

equilibrium model, ΔG_s° is given by

$$\Delta G_s^\circ = \beta RT \ln X_{\text{cmc}} \quad (8)$$

Values of $\Delta G_{\text{HP}}^\circ$ and ΔG_s° calculated using eqs 7 and 8 are given in Table 5. As expected, $\Delta G_{\text{HP}}^\circ$ is almost the same since all of the micelles involve the same surfactant, but the hydrophobicity of pH 10.0 medium play a significant role; at this pH the micelles are most stable. ΔG_s° increases as the pH of the medium increases.

The enthalpy of micellization can be obtained, on the assumption that β is practically constant (see Table 4) by insertion of eq 7 into a Gibbs–Helmholtz equation, which gives

$$\Delta H_m^\circ = -(1 + \beta)RT^2 \left(\frac{\partial \ln X_{\text{cmc}}}{\partial T} \right)_p \quad (9)$$

The values of ΔH_m° are given in Table 5 and are agreement with calorimetrically determined² values of ΔH_m° .

Analysis of Temperature Dependence. The results for $\Delta G_{\text{HP}}^\circ$, ΔG_s° , $RT \ln X_{\text{cmc}}$, and ΔH_m° are plotted in Figures 3, 4, and 5, and 6, respectively. The change in $\Delta G_{\text{HP}}^\circ$ with temperature is a second-order polynomial for three pH values, showing clearly a minimum for pH 10.0 near 30 °C and results from a similar dependence of $RT \ln X_{\text{cmc}}$ and ΔG_s° on temperature. Above and below 30 °C, the transfer free energy decreases and reflects an increasing solubility of hydrocarbon in the pH 10.0 phosphate medium. This increasing solubility stabilizes surfactant monomers and accounts for the minimum in cmc versus temperature for many surfactants. Similar conclusions were reached by Shinoda²⁶ from changes in the solubility of alcohols and aromatic hydrocarbons with temperature.

The model described by Evans and Ninham²³ permits analysis of the dependence of ΔG_s° with temperature as a function of n . At higher temperatures, breaks reflecting cmc become more gradual,^{27,28} suggesting decreasing aggregation numbers. As show in Figure 4, G_s° varies only slowly with T .

The enthalpy of micellization is strongly dependent on the temperature. This change can be due to the sum of two contributions of opposite sign. The removal of medium is endothermic and the transfer into the micelle is exothermic.

The changes in ΔH_m° over the temperature range studied suggest large, but nearly compensating, contributions to the free energy of transfer in the cases of pH 3.2 and 7.0 medium and a predominium of exothermic effect with increasing of temperature in the case of pH 10.0.

Acknowledgment. This work was supported by the Xunta de Galicia. The authors wish to thank Dr. A. Amigo, Universidade de Santiago de Compostela for the viscosities determinations.

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