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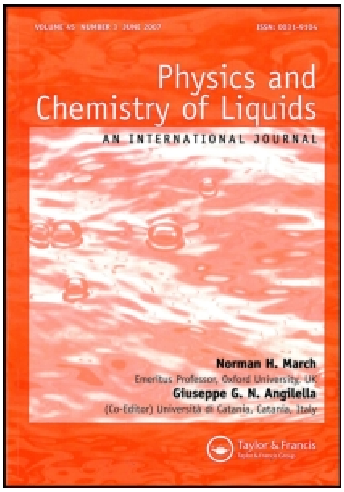

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MICELLAR PROPERTIES OF *N*-OCTYLAMMONIUM BROMIDE IN BINARY AQUEOUS MIXTURES OF BUTOXYETHANOL SYSTEM

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Micellar and thermodynamic properties of *n*-Octylammonium bromide in binary aqueous mixtures of butoxyethanol were determined employing conductivity, viscosity, ultrasonic velocity and potentiometric techniques at several temperatures. The variation of critical micellar concentration with temperature and solution composition was investigated. Thermodynamic functions such as Gibbs free energy of micellisation and transfer were evaluated. Micellar aggregation numbers of the surfactant in these binary mixtures were determined employing Guth-Simha's relationship, assuming micellar sphericity and neglecting electroviscous effect.

Keywords: Binary aqueous mixtures; micellar properties

INTRODUCTION

We have been engaged in a systematic study of the micellar properties of ionic surfactants in binary aqueous mixtures of polar organic compounds. In previous papers we have reported the micellar and thermodynamic properties of alkylpyridinium bromides, and sodium dodecylsulfate in ethylene glycol plus water mixtures [1–3].

Previous studies in alkoxy ethanol plus water mixtures have shown minima or maxima in their thermodynamic properties at low alcohol concentration [4, 5]. Formation of clathrate-like structures of alcohol

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*Corresponding author.

and water, at lower alcohol concentration, has been proposed [6–9]. In the presence of a hydrocarbon, the conversion of clathrate-like structures into more stable microphases has been observed [10–12]. The presence of a surfactant in these systems is known to stabilize the microphases, leading to the formation of microemulsions [9]. In view of the importance of alkoxyalcohols in microemulsions, we report in this paper the micellar properties of *n*-Octylammonium bromide in binary mixtures of 2-butoxyethanol plus water system using conductometric, potentiometric, ultrasonic velocity and viscosity measurements.

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Experimental

n-Octylammonium bromide (OMBr) was prepared by neutralizing *n*-Octylamine with hydrobromic acid solution as described in the literature [13]. Freshly opened bottles of *n*-butoxyethanol (C_4E_1) 99.5% (Aldrich) were used. The water used to make solutions was obtained from a Millipore-Super-Q system. Specific conductance measurements containing 12–18 different concentrations of the surfactant at fixed solvent compositions were made in a thermostated jacketed beaker with a cell (cell constant of 1.111 cm^{-1}) and an automatic conductivity CDM 83 bridge operating at 1000 Hz. Density measurements at different temperatures were obtained using an Anto*n*-Parr densimeter DMA 45 operating in the static mode. The densimeter was calibrated using densities of water and nitrogen gas [14]. The bromide-ion activities were measured using an Orion Br^- ion electrode coupled with a double junction reference electrode (Fisher Scientific 13-620-47). Ultrasonic velocity measurements were measured at a frequency of 4 MHz with a nusonics (model 6080) concentration unit using the ring-around technique.

Viscosity measurements of *n*-Octylammonium bromide in butoxyethanol/H_2O mixtures at various concentrations were determined using modified Ostwald viscometers and a Viscosity bath (Koehler Instrument). All surfactant solutions were prepared in the mixed solvent system on a molal basis and converted to other concentration units using density measurements at various temperatures.

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RESULTS

Conductivity

Plots of specific conductance vs concentration of surfactant (Fig. 1) show a break at the critical micellar concentration (cmc). The values of cmc at various butoxyethanol plus water mixtures are presented in Table I along with the values obtained by potentiometric and ultrasonic methods.

Electrochemical Studies

Plots of the emf vs log C of the surfactant at various percentages of aqueous mixtures of C_4E_1 are presented in (Fig. 2). At lower concentrations of the surfactant, the slopes of emf vs log C ranged from

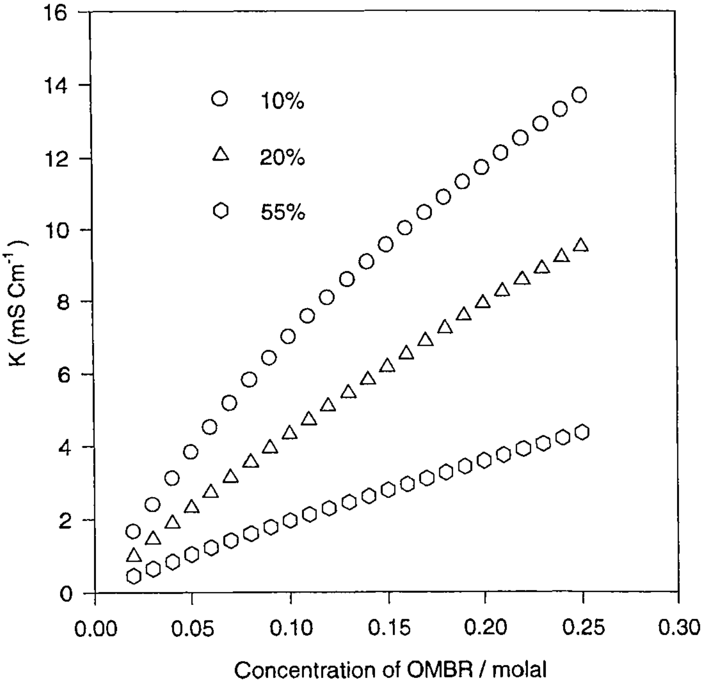

FIGURE 1 Specific conductance (k) vs concentration of OMBr in aqueous mixtures of C_4E_1.

TABLE I Values of critical micellar concentration and effective degree of dissociation of counterion (α)

wt % of C_4E_1	cmc^a	cmc^b	cmc^c	α^a	α^b
0	0.206	0.210	0.208	0.65	0.68
2	0.174		0.167		
3	0.138		0.131		
4	0.120		0.120		
5	0.091	0.098	0.075	0.62	0.59
6	0.068		0.061		
8	0.080	0.090	0.080	0.63	0.62
10	0.078	0.080		0.65	0.62
20	0.075	0.071		0.64	0.63
55	0.076	0.068	0.075	0.61	0.65

[a] conductometric.
[b] potentiometric.
[c] ultrasonic velocity method.

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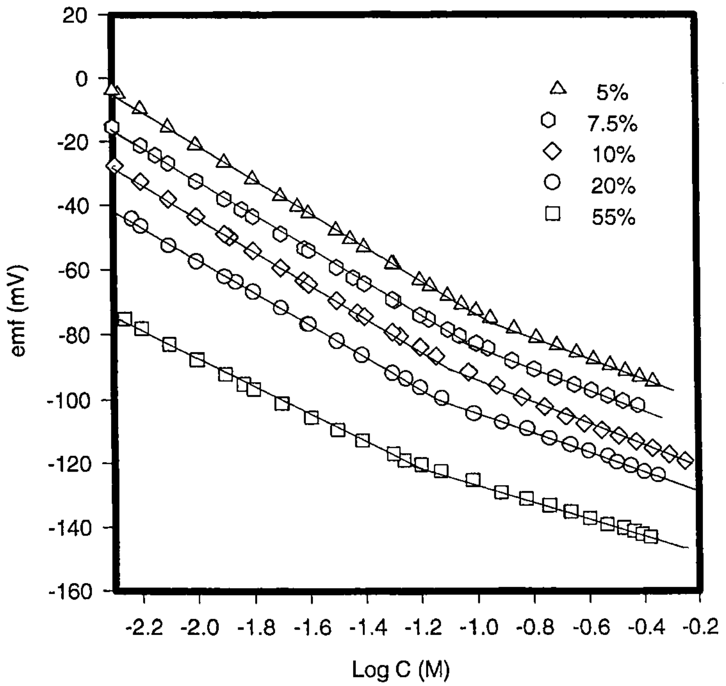

FIGURE 2 Emf plots of Br^-/DJ reference electrode system for OMBr in $C_4E_1 + H_2O$ mixtures.

57–60 mv/decade (Nernstian slope). As the concentration of the surfactant increases the slope deviates from the Nernstian slope and the break point is taken as cmc of the surfactant.

Effective Degree of Dissociation

There were two methods employed in the determination of the degree of dissociation of the counterion (α), (Tab. I).

Method 1 is the conductometric method where α was taken as a ratio of the slopes of conductivity, K, vs concentration of surfactant plots both above and below the cmc.

Method 2 is potentiometric determination of α. Plots of emf vs concentration of *n*-Octylammonium bromide below the cmc are described by the following Nernst equation:

$$E = E^o - B\log \boldsymbol{a} = E^o - B\log(\gamma C) \qquad (1)$$

where B is the Nernstian slope; $\boldsymbol{a}$, γ, and C are the activity, activity coefficient and the concentration of Br^- respectively. The values of γ were calculated using Davies equation [15].

$$\log \gamma = -\frac{AC^{1/2}}{1 + C^{1/2}} \qquad (2)$$

where

$$A = \frac{1.8246 \times 10^6}{(\varepsilon_r T)^{3/2}} \qquad (3)$$

where ε_r is the dielectric constant of the mixed solvent system ($C_4E_1 + H_2O$). The ε_r values were taken from the literature [11].

A plot of emf vs log $\boldsymbol{a}$ below cmc was analysed by linear regression to determine the values of B and E^o in different solvent mixtures. The activity of Br^- ion at all concentrations above cmc was calculated using the rearranged form of Nernst's equation.

$$\boldsymbol{a} = 10^{(E^o - E)/B} \qquad (4)$$

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In this range the activity of Br^- is given by

$$\alpha = \gamma[C_{\text{cmc}} + \alpha(C - C_{\text{cmc}})] \qquad (5)$$

where C_{cmc} is the concentration at the cmc and C is the total concentration in the bulk solution of *n*-Octylammonium bromide. On differentiating with respect to C and assuming γ to be constant above the cmc, the following equation is obtained:

$$\alpha = \frac{1}{\gamma}\frac{da}{dC} \qquad (6)$$

where da/dC is the slope of the plot of activity vs concentration above the cmc. Gamma was calculated using Davies equation with C equal to the cmc.

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Ultrasonic Velocity, Adiabatic Compressibility, Apparent Molar Volume and Apparent Molar Compressibilities

Ultrasonic velocity was calculated from the average round trip period of an ultrasonic wave in a fixed path length between the piezoelectric transducer and reflector. The period of the sound wave was measured using a frequency meter. Sound velocity measurements as a function of solute concentration were made by the addition of known weights of solute to the solution. Representative plots are shown in Figures 3 and 4. From the following relation, adiabatic compressibilities, β, were derived

$$\beta = \frac{1}{U^2 d} \qquad (7)$$

where U is the velocity of the solution and d is the density of the solution in kg m^{-3}. Representative plots can be seen in Figures 5 and 6.

The apparent molar volume, ϕ_v, was calculated from the following relationship

$$\phi_v = \frac{1000}{mdd_o}(d_o - d) + \frac{M}{d} \qquad (8)$$

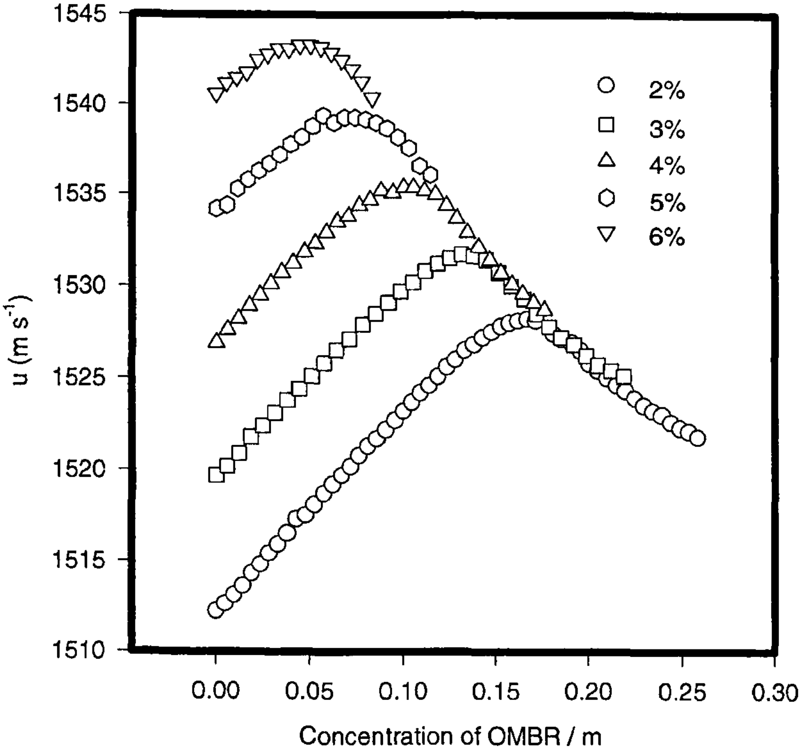

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FIGURE 3 Plot of ultrasonic velocity (U) as a function of OMBr concentration in $C_4E_1 + H_2O$ mixtures.

where m is the molality of the solution, M is the relative molar mass of the solute, d is the density of the solution, d_o is the density of the solvent, and β_o and β are the compressibility coefficients of the solvent and solution respectively.

The apparent molar volume of the miscelles, ϕ_v^{mic} was obtained using the following equation [16].

$$\phi_v = -B\left(\frac{\phi_v}{m}\right) + \phi_v^{\text{mic}} \tag{9}$$

where B is an empirical constant and m is the molarity of the solution. By extrapolation of a plot of ϕ_v vs ϕ_v/m, the values of apparent molar

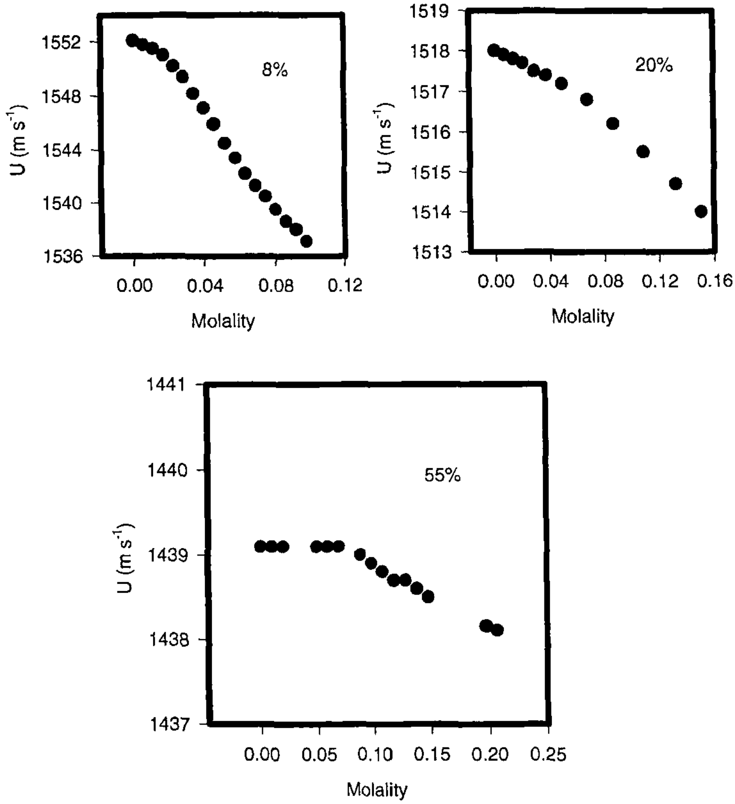

FIGURE 4 Plots of ultrasonic velocity (U) as a function of OMBr concentration in $C_4E_1 + H_2O$ mixtures.

volume of the micelle were obtained. The values of apparent molar volume at infinite dilution ϕ_v^o were obtained graphically or numerically using the following equation:

$$\phi_v = \phi_v^o + A_v C^{1/2} + B_v C \tag{10}$$

where A_v is the Debye-Huckel constant for 1:1 electrolyte and B_v is an adjustable parameter. The change in ΔV_m on miscellisation is given by

$$\Delta V_m = \phi_v^{\mathrm{mic}} - \phi_v^o \tag{11}$$

and the values are listed on Table II.

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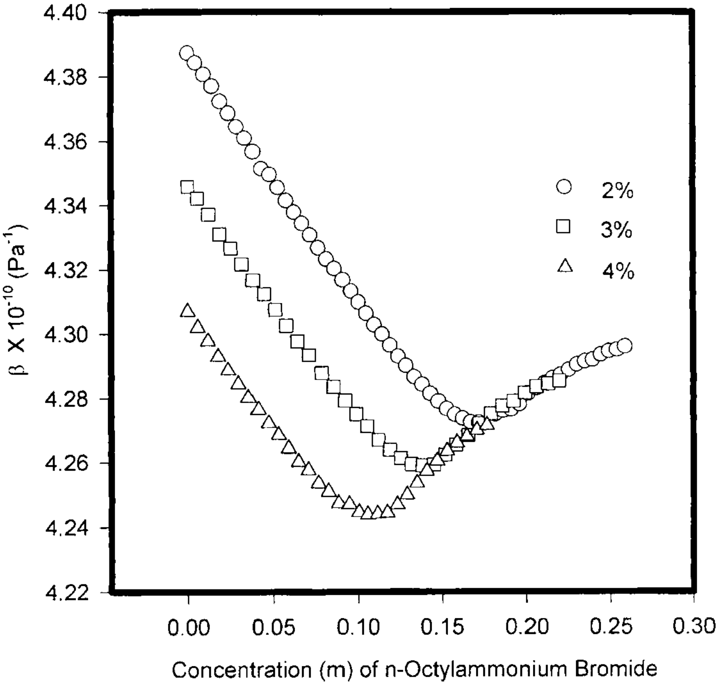

FIGURE 5 Plot of adiabatic compressibility as a function of OMBr concentration in aqueous solutions of C_4E_1.

TABLE II Change in partial molar volume and compressibility on micellisation as a function of C_4E_1

% of C_4E_1	ϕ_v^{mic*}	ϕ_v^{o*}	ΔV_m^*	$\Delta K_m^\#$
2	177.2	174.7	2.5	6.0
3	178.3	175.6	2.7	5.9
4	176.7	174.3	2.4	6.1
8	179.2	176.6	2.6	6.0
20	185.5	183.6	1.9	6.3
55	184.5	181.8	2.7	5.9

*$cm^3 \cdot mole^{-1}$
#$10^{-14} m^3 \cdot mol^{-1} \cdot Pa^{-1}$.

The apparent molar compressibilities in liquid solutions were calculated from the following relation:

$$\phi_k = \frac{1000}{md_o}(\beta - \beta_o) + \beta\,\phi_v \qquad (12)$$

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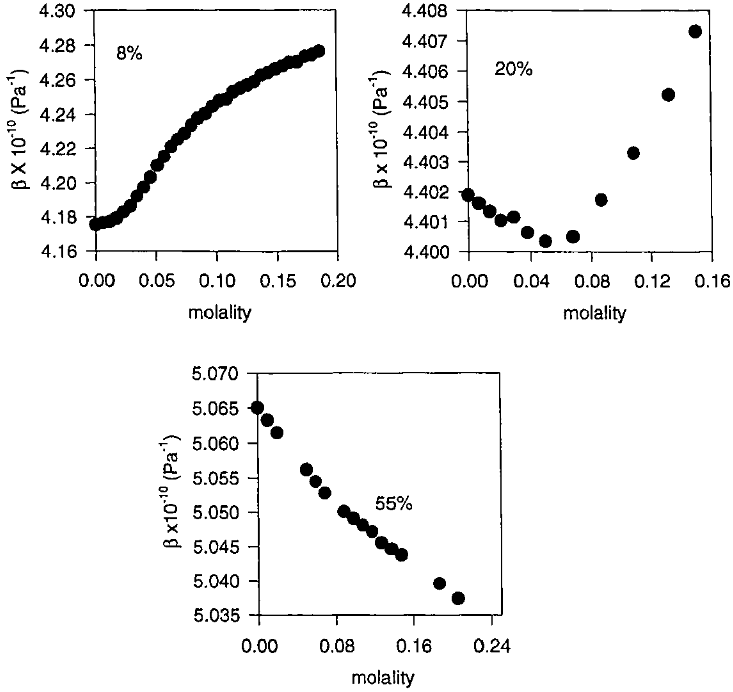

FIGURE 6 Plots of adiabatic compressibilities as a function of OMBr concentration in aqueous C_4E_1 solutions.

where β and β_o are the compressibility coefficients of the solution and solvent respectively. The apparent molar compressibility at infinite dilution (ϕ_k^o) and micellar compressibility (ϕ_k^{mic}) [17, 18] were obtained from the plots of ϕ_k vs $C^{1/2}$ to calculate the change in compressibility ΔK_{mic} upon micellisation. A typical plot of ϕ_k vs $C^{1/2}$ is presented in Figure 7 and the values of ΔK_{mic} at various butoxyethanol concentrations are presented in Table II.

Micellar Aggregation Numbers Through Viscosity Measurements

The aggregation number of short chained surfactants (C_6–C_8) can be determined through viscosity measurements. Guth and Simha [19] extended the original viscosity equation for spherical non-charged particles to obtain the relation:

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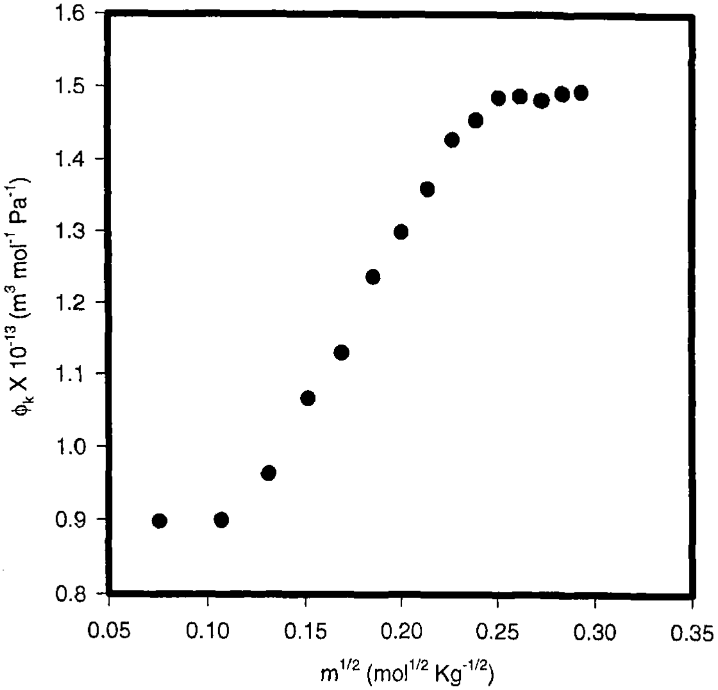

FIGURE 7 Plot of apparent molar compressibility vs $m^{1/2}$ for OMBr in 8% C_4E_1 solution.

$$\eta = \eta_0(1 + 5\phi/2 + 109\phi^2/14) \tag{13}$$

where η_0 and η are the viscosities at the cmc and in the micellar solution and ϕ is the volume fraction of the particles. For this to be applicable to ionic surfactants the micelles must be spherical, in shape, and the electroviscous effect due to micellar charge must be negligible. Volume fraction ϕ, micellar concentration, and size parameters are related by the following equation:

$$\Phi = V_m N \frac{(C_T - C_{\rm cmc})}{1000\, N_S} \tag{14}$$

where N is Avogadro's number, V_m is the volume of the micelle, C_T is the total surfactant concentration, $(C_T - C_{\rm cmc})$ is the micellar concentration and N_s is the aggregation number.

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The volume of the monomer is defined by $4/3\pi l_c^3$ where l_c is the effective length of the surfactant monomer, in the micelle. On substituting the value of V_m in terms of effective length of the surfactant monomer, the following equation is obtained:

$$\Phi = 4\pi l_c^3\, N\, \frac{(C_T - C_{\mathrm{cmc}})}{3000\, N_s} \tag{15}$$

From the above equation a plot of Φ, obtained from viscosity data, vs $(C_T - C_{\mathrm{cmc}})$ yields a straight line with a slope equal to $4\pi l_c^3 N/3000 N_s$ (Figs. 8 and 9). The aggregation numbers were calculated from the slope. The effective chain length (l_c) was estimated using Tanford's equation [20]. The values of aggregation numbers are presented in Table III.

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Thermodynamic Parameters of Micellization

Thermodynamics of micelle formation can be considered as the formation of a different micellar phase at the cmc, which is in equilibrium with the monomeric surfactant. The standard Gibbs free energy of micellisation $(\Delta^\circ G_m)$ in the case of ionic surfactant (1:1) can be calculated from [21].

$$\Delta^\circ G_m = 2RT \ln X_{\mathrm{cmc}} \tag{16}$$

The effect of a cosolute or additive on the micellisation process, given by $\Delta^\circ G_M$ can be evaluated

$$\Delta^\circ G_M = \Delta^\circ G_m \text{ (additive)} - \Delta^\circ G_m \text{ (water)} \tag{17}$$

which can be expressed as

$$\Delta^\circ G_M = 2RT \ln \frac{(X_{\mathrm{cmc}})_A}{(X_{\mathrm{cmc}})_{\mathrm{H_2O}}} \tag{18}$$

The values of $\Delta^\circ G_m$ and $\Delta^\circ G_M$ calculated are presented in Table IV.

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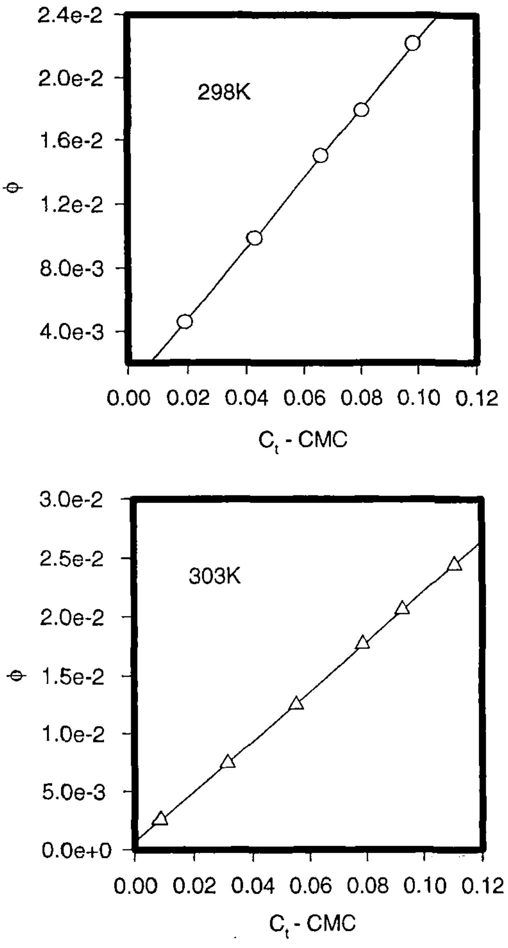

FIGURE 8 Plots of Φ vs $C_T - C_{cmc}$ of OMBr in 10% C_4E_1 at 298 and 303 K.

DISCUSSION

The cmc values of OMBr in the binary aqueous mixtures decrease rapidly with increasing butoxyethanol content and levels off at higher concentrations of butoxyethanol (Tab. I).

In all physical properties investigated in the present study a definite break was observed at the cmc values of OMBr. However the break point was not well defined at higher concentrations of butoxyethanol.

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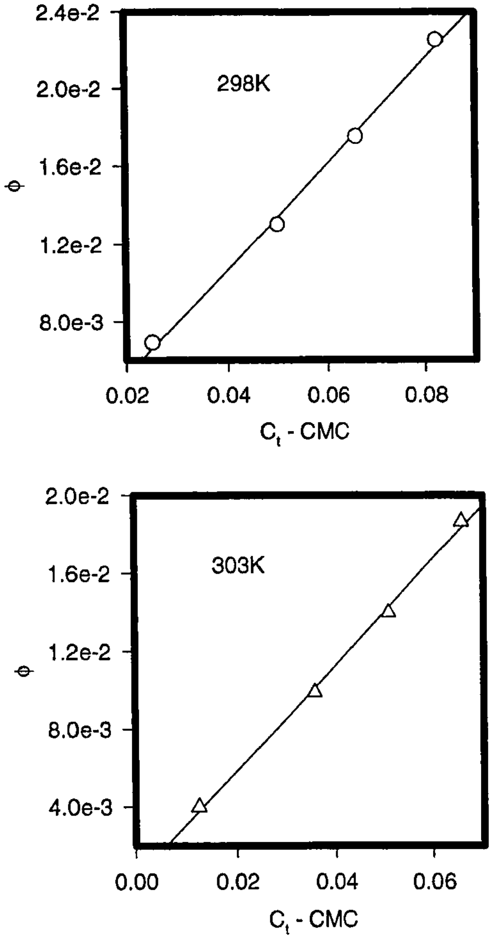

FIGURE 9 Plots of Φ vs $C_T - C_{\mathrm{cmc}}$ of OMBr in 20% C_4E_1 at 298 and 303 K.

The effective degree of dissociation of the counter-ion varied very little with the concentration of butoxyethanol.

In the study of ultrasonic velocity measurements of OMBr in various binary aqueous mixtures, the shape of curves (Figs. 3 and 4), varied with the butoxyethanol content. At lower concentration of butoxyethanol (up to 8%) the velocity increased on addition of OMBr, initially and reached a maximum (indicative of micelle formation) and then decreased. Above 8% of butoxyethanol the velocity decreased

TABLE III Aggregation numbers of *n*-Octylammonium bromide in various percentages of butoxyetanol (C_4E_1)

% of C_4E_1	Temperature (K)	N_s
0	298	20
	303	20
	308	21
	313	22
10	298	21
	303	22
	308	22
	313	22
20	298	25
	303	26
	308	26
	313	26

TABLE IV Thermodynamics of micellisation

wt. % of C_4E_1	$\Delta^\circ G_m{}^*$	$\Delta^\circ G_M{}^*$
0	−27.71	–
2	−28.56	−0.85
3	−29.71	−2.00
4	−30.40	−2.70
5	−31.77	−4.06
8	−32.06	−4.35
10	−32.08	−4.38
20	−31.81	−4,10
55	−29.55	−1.84

*units kJ per mole.

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with OMBr with a change in slope at cmc and the changes in velocity values with the addition of OMBr are relatively smaller. (Fig. 4). Similar effects were also observed in the compressibility curves.

In general the relative magnitude and the sign of compressibility depends on two factors: (1) the compressibility of the hydrocarbon core, (2) the interaction between the head groups and counter-ion binding and how the head group is solvated. When a hydrophobic solute is added to an aqueous micellar solution, it can effect the compressibility of the solution by disrupting the solvent structure and transferring to the micellar pseudo phase. Relative contributions of these factors determine the shape and sign.

In the ultrasonic velocity measurements of binary system of butoxyethanol plus water, it is observed that a maximum occurs in the sound velocity around 8% of butoxyethanol content. The maximum in

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the system was attributed to the filling up of all the cavities and to the onset of microheterogeneity in this system. Several other thermodynamic properties also show either a maximum or a minimum at this composition [22–24]. It is also known that surfactants have been found to have a large stabilizing effect on these microphase structures, leading to the formation of either microemulsions or mixed micelles [22]. In the present study we can conclude that the formation of microphases in butoxyethanol plus water is promoted by the presence of Octylammonium bromide.

Gibbs free energy of micellisation values indicate that micellisation is promoted by the presence of butoxyethanol and the negative values of $\Delta^\circ G_m$ also indicate an increase in hydrophobic interaction, resulting in the promotion of micellisation at a lower concentration of OMBr.

From the values of aggregation numbers, and ΔV_m as a function of butoxyethanol one can conclude that there is very little change in the shape or size of these micelles with increasing butoxyethanol content. The aggregation numbers determined by viscometric method were in agreement with the literature data [6, 25] and found to be independent of temperature.

The positive value of ΔK_m indicate that the micellar core behaves like a hydrocarbon core and is independent of butoxyethanol content.

CONCLUSION

The present study indicates that the presence of butoxyethanol promotes the micellization of Octylammonium bromide in these systems. The study also indicates that the surfactant stabilizes the microphases, in aqueous C_4E_1 systems leading to the formation of mixed micelles. The size and shape of these mixed micelles is independent of the butoxyethanol content.

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