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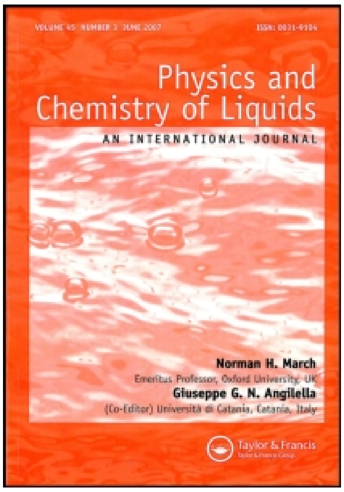

Physics and Chemistry of Liquids

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Aggregation Number of Ionic Surfactants and its Application for Alkyltrimethyl Ammonium Bromides and Sodium Tetradecyl Sulfate by Potentiometric Technique

A. A. Fafati[a]; H. Gharibi[b]; H. Iloukhani[a]; L. Safdari
[a] Department of Chemistry Faculty of Science Bu-Ali Sina University P.O. Box 65174 Hamadan Iran, [b] Department of Chemistry Faculty of Science Tarbiat Modarres University P.O. Box 14155-4838 Tehran Iran,

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AGGREGATION NUMBER OF IONIC SURFACTANTS AND ITS APPLICATION FOR ALKYLTRIMETHYL AMMONIUM BROMIDES AND SODIUM TETRADECYL SULFATE BY POTENTIOMETRIC TECHNIQUE

A.A. RAFATI[a,*], H. GHARIBI[b], H. ILOUKHANI[a] and L. SAFDARI[a]

[a]*Department of Chemistry, Faculty of Science, Bu-Ali Sina University, P.O. Box 65174, Hamadan, Iran;* [b]*Department of Chemistry, Faculty of Science, Tarbiat Modarres University, P.O. Box 14155-4838, Tehran, Iran*

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A potentiometric technique based on surfactant ion selective electrode has been used for various cationic and anionic surfactants. The data obtained contain m_1 (surfactant monomer concentration); m_2 (free counterion concentration) and α (degree of dissociation of micelle) were used for determination of aggregation number at and above cmc (critical micelle concentration). Data fitting show a relationship between aggregation number with such parameters. The correlation equation obtained shows that size of ionic micelle vary sharply after cmc. Also, the equation obtained shows size of micelle growth with increase in counterion concentration.

Keywords: Aggregation number; Potentiometric technique; Surfactant ion selective electrode; Micelle

INTRODUCTION

It is well known that the surfactants associate at and above the critical micelle concentration (cmc). This association is one way of avoiding the entropically unfavorable contact between water and the hydrophobic part of surfactant while retaining the aqueous hydrophilic part contact. The self-association is strongly cooperative and starts generally with the formation of roughly spherical micelles around cmc [1–5].

Typically the micelles have a closely spherical shape in a rather wide concentration range above the cmc. Often there is no great change in shape until the surfactant solubility limit, where liquid crystalline phases normally separate out.

Micellar aggregation number (N_g) is one of the important characteristics of surfactant solution at above cmc. This parameter has classically been determined by several methods: light-scattering [6,7], sedimentation rates in the ultracentrifuge [8,9], NMR self-diffusion coefficient [10], small-angle neutron scattering (SANS) [11–13],

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*Corresponding author. Fax: +98-811-8272404. E-mail: aa_rafati@basu.ac.ir

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freezing point and vapor pressure methods [14] are the most common methods that have been used to calculate aggregation number. The size and dispersity of micelles are sensitive to many internal (hydrophobic structure, head group type, etc.) and external (temperature, pressure, pH, electrolyte content, etc.) factors.

Recently, a potentiometric technique and use of a surfactant ion selective electrode [15–17] has led to the determination of the monomer concentration of surfactant (m_1) and free counterion concentration (m_2). The present authors have been utilizing this method to investigate the behavior of surfactant in different solutions. We develop an explicit expression for the aggregation number based on emf data from surfactant ion selective electrode and predicts effect of factors on aggregation number (N_g), and then we compare the results with other data reported earlier.

EXPERIMENTS

Dodecyltrimethyl ammonium bromide (DOTAB), tetradecyltrimethyl ammonium bromide (TTAB) and hexadecyltrimethyl ammonium bromide (HTAB) from Aldrich–Chemie (stated purity > 99%); sodium tetradecyl sulfate (> 98%) from Cambrian Chemicals Ltd.; sodium bromide (> 99%) from Merck and were used as received. All of the solutions were made in double distilled water. The surfactant selective electrodes are constructed using a method which has been described previously [18,19]. The monomer surfactant activities and free counterion activities in various solutions can be obtained from emf measurements according to the following cell:

Surfactant ion-selective electrode	Test solution containing amount of NaBr	Electrode reversible to Na or Br ion

In all experiments the temperature was controlled to within ± 0.1°C by circulating thermostated water through the jacketed glass cell, and the sample solution was continuously stirred using a magnetic stirrer. The concentration of sodium bromide as backing electrolyte was kept constant as the concentration of surfactant was varied during each experiment. The experiments have been repeated under different conditions, such as different temperatures and different electrolyte concentrations.

RESULTS AND DISCUSSION

Electrode Data

There are different ways in which the data can be used to determine the potential of the system. At surfactant concentration below the cmc the surfactant was dissociated completely; therefore, the logarithm of concentration of surfactant against the emf gives a Nernstian slope obviously the potential of electrode should be measured relative to the reference electrode. In this system three different electrochemical cells can be defined. According to Nernst's equation the following formula can be written for different electrode potentials:

$$E_{\mathrm{sur}} = E^{\circ}_{\mathrm{sur}} + \frac{RT}{F}\ln a_{\mathrm{sur}} \tag{1}$$

$$E_{Na^+} = E^{\circ}_{Na^+} + \frac{RT}{F} \ln a_{Na^+} \tag{2}$$

$$E_{Br^-} = E^{\circ}_{Br^-} - \frac{RT}{F} \ln a_{Br^-} \tag{3}$$

where a_{sur}, a_{Na^+} and a_{Br^-} are activities of surfactant ion, Na^+ and Br^-, respectively.

The potential of each electrode depends upon the logarithm of the activity of the species. In this way cells without liquid junction were constructed which can respond to three ionic species namely the surfactant monomer ion (m_1), free counterion (m_2) and third ion (co-ion) which comes from the backing electrolyte.

I. The first type of electrochemical cell can be considered between surfactant electrode and the sodium electrode for cationic or the bromide electrode for anionic surfactants as a reference electrode (Fig. 1). The activity coefficient for an ionic species measures the deviation from the ideal behavior resulting mainly from interionic interaction of an electrostatic nature. Because of this it is reasonable assume that two ions of the same sign and magnitude of charge will have nearly activity coefficients [20]. If this is true, then

$$\gamma_{Na^+} = \gamma_{sur^+} \quad \text{or} \quad \gamma_{Br^-} = \gamma_{sur^-} \tag{4}$$

and with this assumption the monomer concentration of surfactant ion can be determined below and above the cmc using the Eqs. (5)–(7):

$$E_{Cell(I)} = E_{sur} - E_{co\text{-}ion} \tag{5}$$

$$E_{Cell(I)} = E^{\circ}_{sur/co\text{-}ion} + \frac{2.303RT}{F} \log\left[\frac{m_1\gamma_{sur}}{m_{co\text{-}ion}\gamma_{co\text{-}ion}}\right] \tag{6}$$

$$E_{Cell(I)} = E^{\circ}_{sur/co\text{-}ion} + \frac{2.303RT}{F} \log\left[\frac{m_1}{m_{co\text{-}ion}}\right] \tag{7}$$

At a constant co-ion concentration, which applies for this experiment, this assumption leads immediately to:

$$E_{cell(I)} = E^{\circ}_{sur/co\text{-}ion} + (2.303RT/F)\log m_1 \tag{8}$$

II. A least-mean square method was used for determination of the slope $2.303RT/F$ and intercept $E^{\circ}{}_{sur/co\text{-}ion}$ for each set of data. The potential of the second cell would be the relative potential between counterion electrode and the membrane electrode (see Fig. 2):

$$E_{cell(II)} = E_{sur} - E_{counterion} \tag{9}$$

$$E_{cell(II)} = E^{\circ}_{sur/counterion} + (2.303RT/F)\log(a_{sur}a_{counterion}) \tag{10}$$

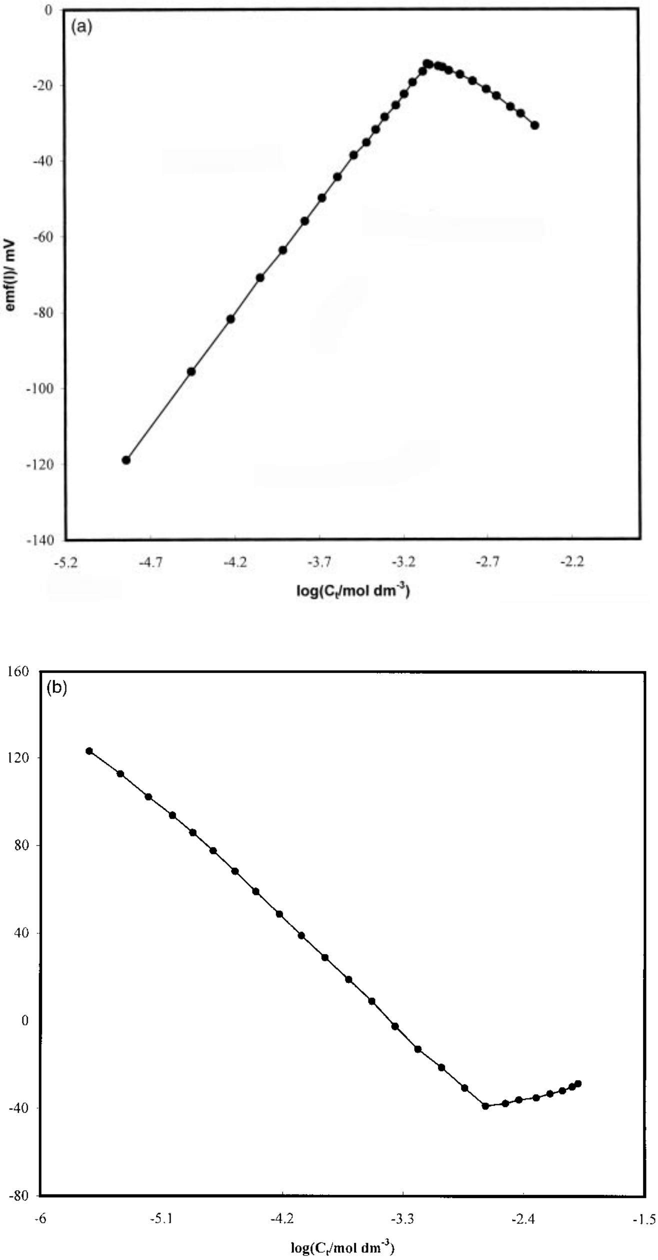

FIGURE 1 Plot of emf(I) *versus* $\log(C_t)$ typically for (a) HTAB (b) STS; in aqueous solution and 303 K.

Again in Eq. (10) the assumption is made that the cancelled activity coefficient is used, (when the concentration is increased because of electrostatic force between ions this assumption cannot be valid) so that Eq. (10) becomes

$$E_{\mathrm{cell(II)}} = E^{\circ}_{\mathrm{sur/counterion}} + (2.303RT/F)\log(\gamma_{\pm}^{2} m_1 m_2) \tag{11}$$

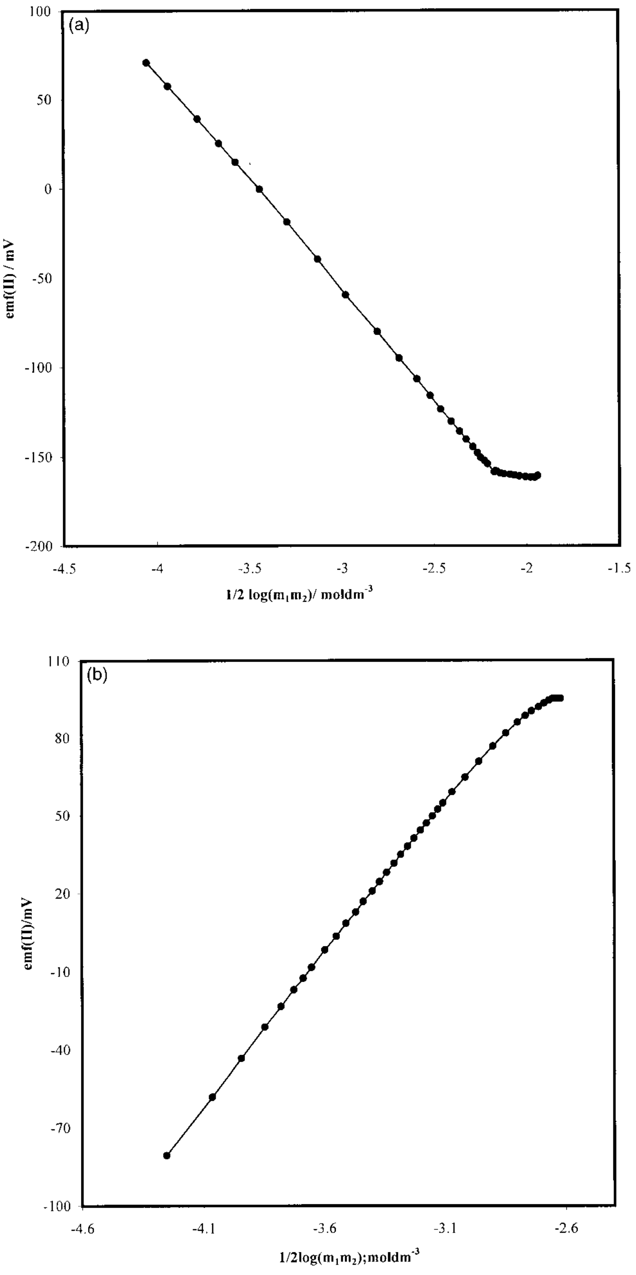

FIGURE 2 Plot of emf(II) *versus* 1/2log(m_1m_2) typically for (a) HTAB (b) STS; in aqueous solution and 303 K.

Since the surfactant is dissociated completely into ions below the cmc [21], the plot of the emf(II) against $\log(\gamma_{\pm}^2 m_1 m_2)$ obeys Nernstian behavior and the slope of the line is equal to $(+2.303RT/F)$ and the intercept is $E^{\circ}_{\text{sur/counterion}}$.The estimation of surfactant monomer ion concentration, m_1, and free counterion concentration, m_2 requires knowledge of the activity coefficient of surfactant ion and counterion in the presence of multivalent micellar ions. Free concentration (m_2) is calculated from Eq. (11). Since m_1 is known from cell(I), Eq. (8), m_2 can first be calculated from the above mentioned equation by assuming that $\log \gamma_\pm = 0$, then:

$$E_{\text{cell(II)}} = E^\circ_{\text{sur/counterion}} + (2.303RT/F)\log(m_1 m_2) \tag{12}$$

Now the calculated m_2 is used to estimate I and

$$I = 1/2(m_1 + m_2 + C_S) \tag{13}$$

where I is ionic strength and C_S is salt concentration.

In the present work the mean activity coefficient, $\gamma_\pm$, was estimated using Debye–Hückel theory. Once $\log \gamma_\pm$ is determined, then it is replaced in Eq. (11). From this m_2 is repeated until the values of log $\gamma_\pm$ and m_2 are constant.

Aggregation Number

For a series of ionic surfactant with identical head group and different alkyl chain length, the following empirical relation between cmc and N_h (the number of carbon in hydrocarbon chain) was obeyed:

$$\log \text{cmc} = A - BN_h \tag{14}$$

where A and B are constants. On the other hand, the aggregation number, N_g, of surfactant related to N_h by the following equation [22]:

$$\log N_g = A' - B'N_h \tag{15}$$

where A' and B' are constants. Combining Eq. (14) with (15) yields Huisman's equation [23] in terms of the molecular weight, MW, of the surfactant monomer as follows:

$$\log N_g = a - b\log(\text{cmc}) - \log(MW) \tag{16}$$

where a and b are constants. Fitting data at a fixed temperature for a homologous series of alkyltrimethyl ammonium bromide (C_nTAB) yields $a = 3.74$ and $b = 0.262$. Similarly for a series of n-alkyl sodium sulfates (C_nSO_4Na) these constants are 3.41 and 0.387, respectively. Also, it has been known that the cmc is related to the counterion concentration by Corrin's equation [24] (see Fig. 3):

$$\log(\text{cmc}) = a' - b'\log m_2 \tag{17}$$

where a' and b' are constants. In the other hand, Hall [25] has shown that above the cmc, the following relation is valid:

$$\log(\text{cmc}) = a' - \beta\log m_2 \tag{18}$$

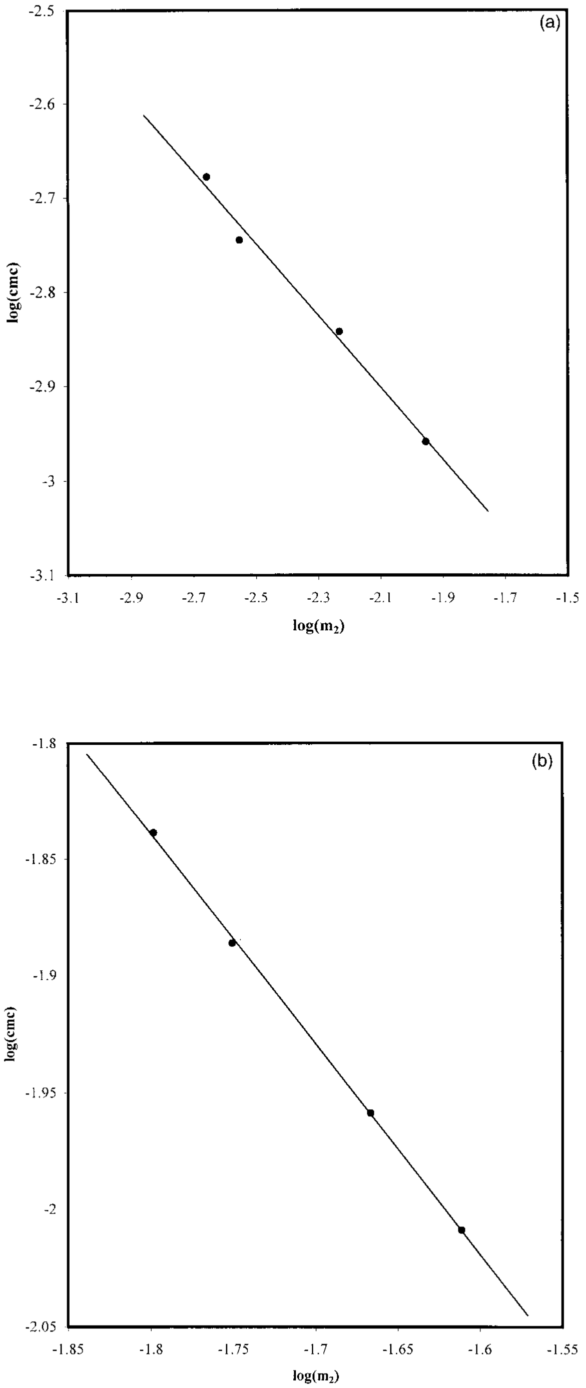

FIGURE 3 Plot of Corrin's equation (Eq. (17)) for (a) STS; (b) DOTAB; (c) TTAB; (d) HTAB at 303 K.

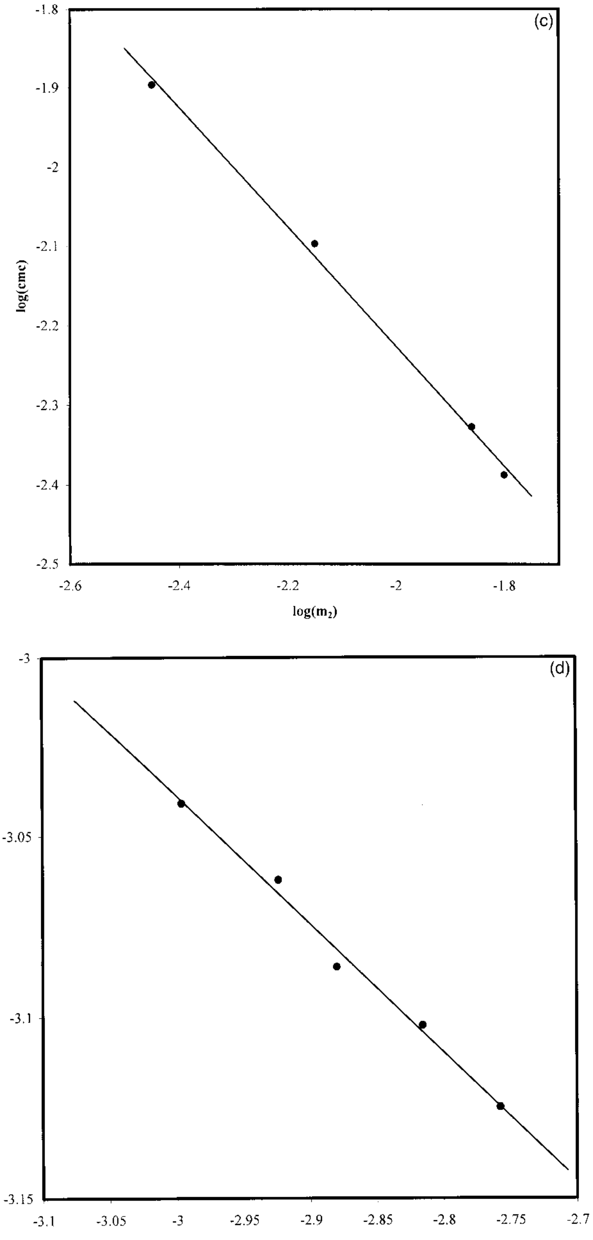

FIGURE 3 Continued.

with b' identified as the degree of counterion attachment to micelle, β. This equation is written with assumption that above the cmc, the free monomer concentration, m_1 is constant and equal to cmc.

In the electrochemical studies, it has been show that m_1 above the cmc decreases with increasing total concentration of surfactant (see Fig. 4) [26–28]. By replacing cmc with the free monomer concentration, m_1, one finds

$$\log(m_1) = a' - b' \log m_2 \tag{19}$$

Based on mass balance equation, the concentration of free counterion may be written as:

$$m_2 = m_1 + \alpha(C_t - m_1) + C_S \tag{20}$$

where α is the degree of dissociation of counterion. Substituting this equation into Eq. (19), yields:

$$\log m_1 = a' - b' \log[m_1 + \alpha(C_t - m_1) + C_S] \tag{21}$$

Combining Eqs. (16) and (21) (replacing cmc with m_1 at concentration above cmc) gives:

$$\log(N_g) = a - b\{a' - b' \log[m_1 + \alpha(C_t - m_1) + C_S]\} - \log(MW) \tag{22}$$

or

$$N_g = \gamma(\alpha C_t + \beta m_1 + C_S)^{\kappa} \tag{23}$$

where

$$\gamma = (1/MW)10^{(a-a'b)} \tag{24}$$

and

$$\kappa = bb' \tag{25}$$

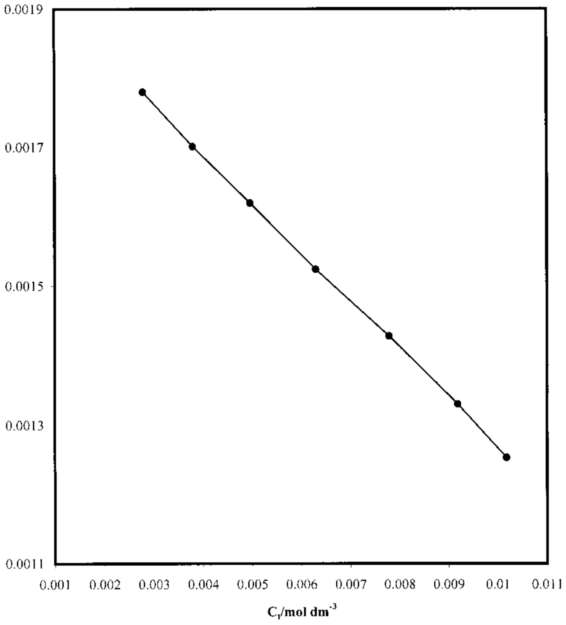

FIGURE 4 Variation of free surfactant concentration (m_1) with total surfactant concentration (C_t) after cmc, typically for HTAB at 303 K.

From data fitting for a series of *n*-alkyltrimethyl ammonium bromides and sodium tetradecyl sulfate, the values of γ and κ have been evaluated and are listed in Table I.

Figure 5 shows a plot of N_g *versus* total concentration of surfactant above cmc. These graph represent that micelles growth with increasing of surfactant concentration and this assumption cannot be true that micelles have a fixed size. In the other hand, aggregation number of ionic surfactant extremely depends to ionic strength, i.e. concentration of counterion. Figure 6 shows the variation of $\log N_g$ with $\log m_2$ for DOTAB at $T = 303\,\mathrm{K}$, typically. The above equations provide a description of the size of micelles and correlate the aggregation number (N_g) to different parameters such as total concentration of surfactant, concentration of counterion and alkyl chain length of surfactant. Since m_1 can be measured after cmc in potentiometric technique, such measurements are accurate and free of any assumption and approximation.

By determination of aggregation number of surfactant in different conditions, we will be able to determine some thermodynamic parameters of micellization such as ΔG°, ΔH° and ΔS°.

TABLE I Fitting parameters of aggregation number for a series of cationic and an anionic surfactant

Constant	*a*	*b*	*a′*	*b′*	*κ*	*γ*
Surfactant						
DOTAB	3.74	0.262	−3.4572	0.8989	0.2355	143.46
TTAB	3.74	0.262	−3.7302	0.7522	0.1971	155.04
HTAB	3.74	0.262	−4.0993	0.3535	0.0926	178.8
STS	3.41	0.387	−3.7002	0.3807	0.1473	241.08

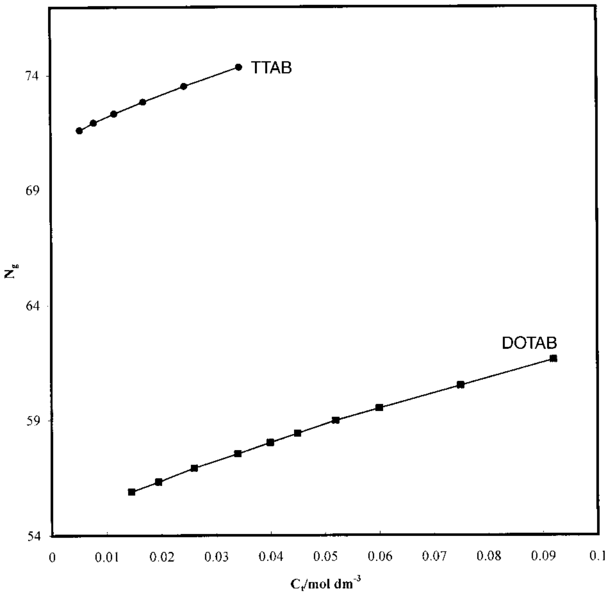

FIGURE 5 Plot of aggregation number calculated from Eq. (23) *versus* total surfactant concentration (C_t) after cmc, (■) DOTAB (●) TTAB (▲) HTAB (◆) STS; at 303 K.

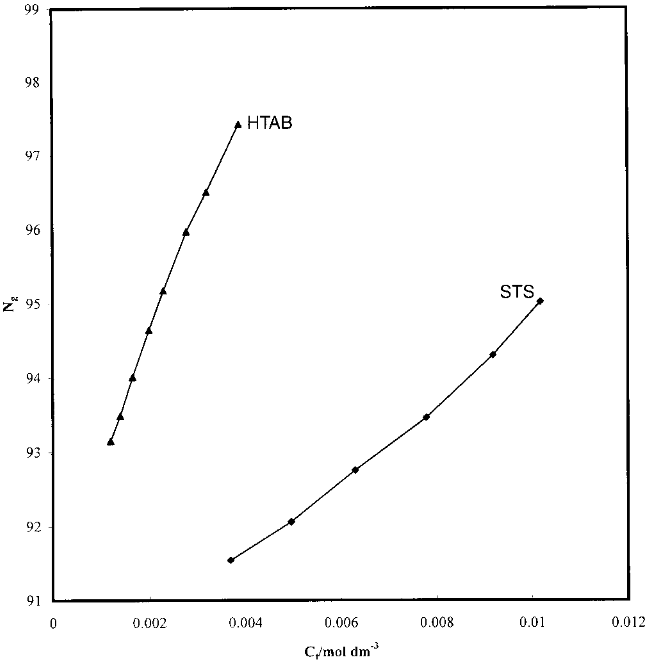

FIGURE 5 Continued.

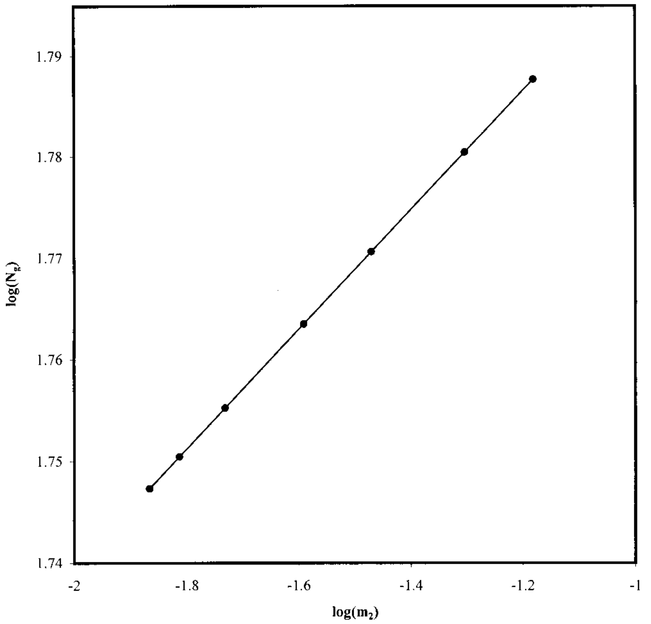

FIGURE 6 Plot of log (N_g) calculated from Eq. (23) *versus* logarithm of free counterion concentration after cmc; typically for DOTAB at 303 K.

CONCLUSION

Semiempircal equation (Eq. (23)) describe that ionic surfactants with a single long alkyl chain show aggregation numbers of less than 100 in aqueous solutions containing low or moderate concentration of electrolyte. At high electrolyte concentration, N_g increase sharply with surfactant concentration. In the other hand, micellar aggregation numbers of ionic surfactant should increase with increase in the counterion concentration, presumably because of compression of the electrical double layer surrounding the ionic heads. The resulting reduction of their mutual replusion in the micelle permits closer packing of the head groups, with a consequent increase in N_g. In agreement with the geometric considerations, aggregation numbers in aqueous solution increase with increase in the binding of the counterions to the micelle.

References

[1] J.H. Fendler, E.J. Fendler, R.T. Medary and O.A. El Seoud (1973). *J. Chem. Soc. Faraday Trans. 1*, **69**, 280.

[2] P. Mukerjee and K.J. Mysels (Eds.) (1971). *Critical Micelle Concentrations of Aqueous Surfactant Systems*. National Standard Reference Data Service, Vol. 36, U.S. National Bureau of Standard, Washington D.C.

[3] P. Molyneux, C.T. Rhodes and J. Swarbrick (1965). *Trans. Faraday Soc.*, **509**, 1043.

[4] P. Becher and M.J. Schick (Eds) (1967). In: *Nonionic Surfactants*, Chapter 15. Marcel Dekker, Inc., New York.

[5] M.J. Rosen (Ed.) (1978). *Surfactants and Interfacial Phenomena*. John Wiley & Sons, New York.

[6] P. Debye and E.W. Anacker (1951). *J. Phys.Chem.*, **55**, 644.

[7] E.W. Anacker and A.E. Westwall (1960). *J. Proc. Montana Acad. Sci.*, **9**, 4.

[8] J.B. Peri (1958). *J. Am. Oil Chem. Soc.*, **35**, 110.

[9] C.W. Dwiggins, R.J. Bolen and H.N. Dunning (1960). *J. Phys. Chem.*, **64**, 1175.

[10] B. Lindman (1983). *J. Phys. Chem.*, **87**, 1377.

[11] D.J. Cebula and R.H. Ottewill (1982). *J. Coll. Polym. Sci.*, **260**, 1118.

[12] R. Triolo, L.J. Magid, J.S. Johnson and H.R. Child (1983). *J. Phys. Chem.*, **87**, 4548.

[13] M. Corti, V. Degiorgio, J. Hayter and M. Zulauf (1984). *Chem. Phys. Lett.*, **109**, 579.

[14] T.M. Herrington and S.S. Sahi (1986). *Colloids Surf.*, **17**, 103.

[15] N. Takisawa, D.G. Hall, E. Wyn-Jones and P. Brown (1988). *J Chem. Soc.*, *Faraday Trans. 1*, **84**, 3059.

[16] W.M.Z. Wan Yunus, J. Taylor, D.M. Bloor, D.G. Hall and E. Wyn-Jones (1992). *J. Phys. Chem.*, **96**, 8979.

[17] D. Jezequel, A. Mayaffre and P. Letellier (1991). *Can. J. Chem.*, **69**, 1895.

[18] H. Gharibi (1991). Ph.D. Thesis, University of Salford.

[19] H. Gharibi, N. Takisawa, P. Brown, M.A. Thomason, D.M. Painter, D.M. Bloor, D.G. Hall and E. Wyn-Jones (1991). *J. Chem. Soc., Faraday Trans.*, **87**, 707.

[20] J.O'M. Bockris and A.K.N. Reddy (1977). *Modern Electrochemistry*. Plenum, New York.

[21] H. Gharibi, R. Palepu, D.M. Bloor, D.G. Hall and E. Wyn-Jones (1992). *Langmuir.*, **8**, 782.

[22] H.B. Kleven (1953). *J. Am. Oil Chem. Soc.*, **30**, 74.

[23] H.F. Huisman (1964). *Proc. Kon. Ned. Akad. Wetensch.*, **B67**, 367.

[24] M.L. Corrin (1948). *J. Colloid Interface Sci.*, **3**, 333.

[25] D.G. Hall (1981). *J. Chem. Soc., Faraday Trans. 1*, **177**, 1121.

[26] H. Gharibi, A.A. Rafati, A. Feizollahi, B.M. Razavizadeh, M.A. Safarpour (1998). *Colloids and Surfaces*, **145**, 47.

[27] H. Gharibi, B.M. Razavizadeh and A.A. Rafati (1998). *Colloids and Surfaces*, **136**, 123.

[28] R. Palepu, H. Gharibi, D.M. Bloor and E. Wyn-Jones (1993). *Langmuir*, **9**, 110.