Short communication

Determination of C.M.C. and Aggregation Numbers for Some Cationic Surfactants

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The physical properties of cationic surfactants in aqueous phase, although basically similar to those of anionic with the same alkyl part, generally exhibit some subtle differences. This study reports the thermodynamic analysis of some pure homologous series of cationic surfactant, for example:
$n-C_{12}H_{25}N(CH_3)_3Br, n-C_{13}H_{27}N(CH_3)_3Br,$
$n-C_{14}H_{29}N(CH_3)_3Br$ and $n-C_{16}H_{33}N(CH_3)_3Br$. The thermodynamic analysis is based on the various physical properties which were investigated, e.g., critical micelle concentration (c.m.c.), aggregation number (m_n = average aggregation number as measured by membrane osmometry), and second virial coefficient. In some cases, the thermodynamic data of the cationic system are compared to that of anionic micellar systems with the same hydrophobic(alkyl) group.

Even though a large number of studies on these surfactants has been reported in the current literature, there still remains much to be described. The purpose of this study is to report some data which are not satisfactorily described in the earlier reports, especially as regards aggregation number and the second virial coefficient, B_2.

Experimental procedures

The different cationic surfactants used were obtained in the following purity grades:
CTAB($n-C_{16}H_{33}N(CH_3)_3Br$) was used as supplied by Schuchardt, West Germany (>99 %). DTAB ($n-C_{12}H_{25}N(CH_3)_3Br$), TrTAB($n-C_{13}H_{27}N(CH_3)_3$

Dedicated to Professor Per Ekwall on his 90th birthday.

Br) and TTAB($n-C_{14}H_{29}N(CH_3)_3Br$) were synthesized as follows: the respective n-alkyl bromide (purity >99 %, Schuchardt, W. Germany) with an excess (double concentration) of trimethylamine (30% in water) was mixed and allowed to react at room temperature for about 3 weeks. The reaction which took place was:[5]

$$R-Br + H_3C-N(CH_3)_2 \rightleftharpoons R-N_+(CH_3)_3 + Br^-.$$
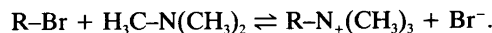
As the reaction proceeded towards the right, the mixture tended to become homogenous. After the reaction had come to equilibrium, the mixture was dried such that water and excess trimethylamine were evaporated. The dried material was a gel-like material. The product was further purified by crystallisation from acetone (3 times was sufficient). The purity was controlled by determination of c.m.c. by measuring the amount of anthracene solubilized as a function of surfactant concentration.[6–10] Membrane osmometry, the average aggregation number, m_n, of micelles was determined by using membrane osmometry, as described in detail elsewhere.[4,11–14]

Results and discussion

It was found that in all cases, the amount of anthracene solubilized was constant when the concentration was below the c.m.c. The amount solubilized was found to increase abruptly near the c.m.c. In all cases, the amount of anthracene solubilized increased linearly with concentration of detergent when above c.m.c. The average aggregation number, m_n, for the DTAB, TTAB and
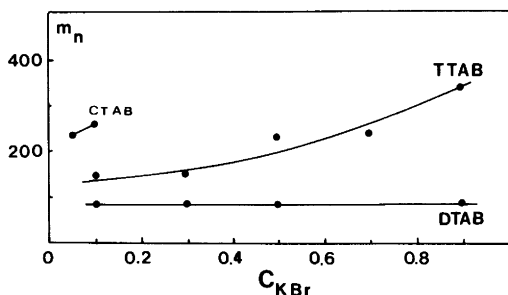
Fig. 1. Variation of aggregation number, m_n, of DTAB, TTAB & CTAB as measured by membrane osmometry, at 40 °C, as a function of added KBr (mol/dm³).

CTAB systems, as a function of added electrolyte (KBr) concentration was determined using membrane osmometry (Fig. 1). The various aggregation data[3,8,15-18] for the aqueous solutions of the different cationic surfactants, DTAB, TrTAB, TTAB and CTAB, are described below.

Critical micelle concentration (c.m.c.)

The plots of ln (c.m.c.+C_{KBr}) were found to be linear for all the systems, as also reported in the literature.[3,8,15-18] The data were derived from the following equations (at 25 °C)

DTAB
$$\ln(c.m.c.) = -6.85 - 0.635 \ln(c.m.c.+C_{KBr}). \quad (1)$$
TrTAB
$$\ln(c.m.c.) = -8.10 - 0.65 \ln(c.m.c.+C_{KBr}). \quad (2)$$
TTAB
$$\ln(c.m.c.) = -9.43 - 0.68 \ln(c.m.c.+C_{KBr}). \quad (3)$$

These data were compared with literature values. The DTAB data in the literature[17] are reported as −6.81 and −0.61 for the intercept and the slope, respectively. These values compare very well with eq. (1), which indicates that the surfactant used was of very high purity.

The c.m.c. is reported to be dependent on the alkyl chain length (n_C = number of carbon atoms) of the surfactant molecule.[3,8] The data of ln(c.m.c.) versus n_c, show that the plots are linear. The slope in pure water is −1700 J/mol (n_c), which agrees with literature values for anionic and cationic surfactants.[2,3,8] The slope changes (increases) with addition of salt, as was pointed out by us elsewhere.[8] The slopes in the case of

salt solutions is −2950 J/mol (CH₂-group), which also agrees with literature values.[3,8] These plots conclusively indicate that the synthesized materials were of very high purity.

Aggregation number (number average = m_n) *of cationic micelles*. The magnitude of m_n is 88 at temperature 40 °C, in the case of DTAB (Fig. 1). It is seen that the addition of counterion, i.e., Br⁻, has a negligible effect, even up to C_{KBr} = 0.9 M. This is in contrast to the micellar solutions of anionic surfactant, n-$C_{12}H_{25}SO_4Na$(NaDDS), of the same alkyl chain length, in which system the addition of counterion (Na⁺), has been reported to give an increase in m_n from 100 to 700, when the concentration of added NaCl concentration is increased from 0.1 to 0.8 M.[14]

The magnitude of m_n of TTAB increases on addition of counterion at 40 °C. It is seen that at 40°, the effect on m_n of KBr concentration is very large in the case of CTAB micelles (Fig. 1).

These data may be explained by considering the Krafft point of these micellar systems. The Krafft point of DTAB, in pure water, is about 0 °C, while the values for TTAB and CTAB, were found to be 11.5 and 25.8 °C, respectively. It was found that in both cases, the magnitude of the Krafft point increases at first rapidly with electrolyte concentration, and less so at KBr concentrations >0.15 M.[19]

In a recent description of a model of micellar aggregation,[20] based on the data of NaDDS, it was postulated that the following general relationship would be expected between m_n and c.m.c., for all kinds of ionic micelles:

$$\ln(c.m.c.) = K_1/(m_n)^{1/3} - K_2, \quad (4)$$

where the constant K_1 corresponds to the oil-water or micelle (interior)-water interfacial tension (~50 mN/m), and K_2 corresponds to the hydrophobic interaction arising from the free energy of transfer of the alkyl chain from water phase to micellar phase. The data given here for DTAB, however, clearly show that the relation as given in eq. (4) is incorrect, since the plot of ln(c.m.c.) versus $(1/m_n)^{1/3}$ would be a horizontal line with K_1 = infinity. It is thus seen conclusively that theoretical basis of the model described in literature,[20] is oversimplified. In any case, the model is thus found to be limited in its applicability, since it can only be used for NaDDS system at 21 °C data.
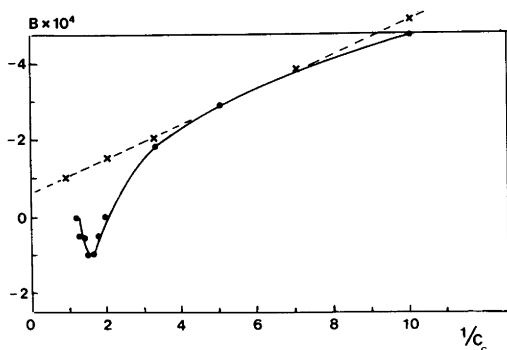
Fig. 2. Variation of second virial coefficient, B_2 (m³mol/kg²) with concentration of added electrolyte, i.e., counterion (C_c = mol/dm³), for DTAB($\times$)(C_c = KBr) and n–C$_{12}$H$_{25}$SO$_4$Na($\bullet$)(C_c = NaCl), at 40 °C.

The disagreement between eq. (4) and DTAB data of m_n versus c.m.c. can be ascribed to the neglect of consideration of the nonideality of micellar systems. We have reported elsewhere in detail,[4,8,14,21] that these micellar solutions are non-ideal because of the fact that the value of the second virial coefficient, B_2, (as measured from membrane osmometry) is not zero. Therefore, in any theoretical analysis, the nonideality must be taken into consideration. The variation of B_2 with added electrolyte ($1/C_{electrolyte}$) for both NaDDS and DTAB is given in Fig. 2. It is seen that these plots are quite different, and therefore the empirical relations used in the micellar model[20] are invalid for DTAB systems.

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