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Employment of a useful liquid membrane electrode system to characterise the micelles of bile salts and other detergents in pure and mixed states

P. K. Jana and S. P. Moulik

Department of Chemistry, Jadavpur University, Calcutta, India

Abstract: Ion-pairs or coacervates (formed by the reaction between cationic and anionic surfactants) dissolved in nitrobenzene can behave as surfactant-ion registering devices to respond to both surfactant cation and anion. The complexes of cetyltrimethyl ammonium bromide with sodium dodecyl sulfate, sodium salts of deoxycholic and chenodeoxycholic acids, and Aerosol Orange T have been used in nitrobenzene to generate such useful liquid membranes. The complex of dimethyldioctadecyl ammonium bromide and sodium cholate has been used to study the cholate ion behaviour since its complex with cetyltrimethyl ammonium bromide is water soluble. The electrochemical behaviours of the liquid membranes have been found to be fairly good and reproducible. The membrane potential measurements have been used to determine the critical micelle concentrations of the surfactants in pure as well as in mixed states to evaluate surfactant – surfactant interaction in the micelles of the latter.

Key words: Bile salts – CTAB – SDS – nitrobenzene – liquid membrane – CMC

Introduction

Estimation of surfactant concentration in solution is of considerable importance, although a suitable method is seldom available. Dye adsorption technique has been used in the determination of the concentration of ionic surfactants in solution [1–3]. The methods of surface tension and conductance have found only limited use [4–6]. Electrometric method can be adopted for ionic surfactants based on the construction of membranes selective to surfactant ions. This has advantage over the surface tension and conductance methods for it can be applied in presence of components having surface chemical and conductance properties. There are reports on the quantitative estimation of cationic and anionic surfactants including several bile salts using membranes selective to the ions of the surfactants [6–14]. The determination of strength is required to quantify their occurrence in physiological solutions, as in biles, essentially required to prevent deposition of cholesterol in the gallbladder forming stone [15]. Both liquid and solid membranes are in use for this purpose. The essential basis of the method is the incorporation of a water insoluble ion-pair (obtained by mixing a cationic and an anionic detergent) in the membrane that acts as an ion-exchanger towards either the surfactant cation or the anion of the complex to generate a membrane potential depending on the strengths of two solutions (of one of the surfactants forming the complex ion-pair) separated across it and measuring the potential using a pair of identical reversible electrodes (usually Ag/AgCl or calomel electrodes). The attempts so far made have estimated the strength of either the cationic or the anionic surfactant with the help of membrane electrodes. Use of the same membrane electrode containing the complex ion-pair for the estimation of both the constituent cation and the anion has not been reported. Such a membrane system would be, on the whole, simple, economic and less time consuming and, therefore, have better application prospects.

In a recent work [6], we have used a liquid membrane for the estimation of the concentration of cetyltrimethyl ammonium cation using its ion-pair with dodecyl sulfate anion dissolved in orthonitrobenzene. Since then we have been examining suitability of a liquid membrane system for the simultaneous estimation of the concentrations of cationic and anionic surfactants using the same membrane. We herein report the functions of such liquid membranes which can simultaneously take care of the determination of the strengths of cetyltrimethyl ammonium cation and the anions of bile salts, dodecyl sulphate and Aerosol Orange – T (AOT). It will be seen that the complex ion-pairs can register potentials corresponding to the concentrations of their constituent ions in presence of other bile salts as well, thereby making it feasible to determine the mixed micelle formation characteristics between a pair of bile salts.

Experimental

Materials

The surfactants cetyltrimethyl ammonium bromide (CTAB), Aerosol Orange T (AOT), sodium dodecyl sulfate (SDS) and the bile salts (sodium cholate (NaC), sodium deoxycholate (NaDC) and sodium chenodeoxycholate (NaCDC)) used for the study were the same as used earlier [16, 17]. Dimethyldioctadecyl ammonium bromide (DDOAB) was obtained from Sigma, USA. They were stored under proper desiccating condition to avoid contamination with moisture. A.R. grade nitrobenzene was obtained from SD Fine Chemicals, India. It was distilled and stored in cool and dark enclosure.

Doubly distilled conductivity water was used for solution preparation.

All measurements were taken in a constant temperature water bath at 303 ± 0.05 K.

The ion-pair complex of bile salts (NaDC and NaCDC) with CTAB were prepared by mixing the components in 1:1 molar ratio in aqueous medium. Water insoluble products (coacervates) were formed. The coacervates were dissolved in 1:1 (V/V) methanol and chloroform mixture and then separated in a separating funnel. The solvent was evaporated and the products were dried under vacuum and stored in a desiccator. The ion-pair of CTAB and SDS was prepared by mixing the two surfactants in 1:1 molar ratio. The salt NaBr formed in the reaction was dialysed out and the ion-pair was dried under vacuum and stored in a desiccator. The CTAB and AOT mixture in 1:1 molar ratio easily formed precipitate which was filtered, washed, dried and desiccated. The complex ion-pair of dimethyldioctadecyl ammonium bromide and NaC was prepared following the procedure adopted for the surfactant combinations of CTAB + NaDC and CTAB + NaCDC.

Among the three bile salts (NaC, NaDC and NaCDC), NaC formed soluble ion-pair with CTAB; the other salts yielded highly viscous water insoluble products or coacervates. The materials were collected, desiccated and stored. Although water insoluble, they had shown the capability to sorb water vapour.

Methods

The liquid membrane was prepared by dissolving 10 mg of the coacervate in 10 ml of nitrobenzene and aging the mixture for an hour before use. The cell used for the emf measurements is represented below

Calomel || Ref. solution | Liq. membrane

| Test solution || Calomel.

A diagramatic representation is given in Fig. 1. The whole assembly was placed in the water bath and equilibrated for half an hour prior to actual use.

In the actual procedure, the reference solution was a dilute solution of the surfactant under study at 0.01 m mol dm^{-3} (1 m mol dm^{-3} in 0.02 mol dm^{-3} NaCl for SDS and AOT). The concentration of the test solution was varied from below CMC to above CMC (at a constant concentration of NaCl 0.02 mol dm^{-3} for SDS and AOT). For each concentration of the test solution, 30 min time was given for equilibration. It was found that, although the response of the liquid membrane electrode system was quick, bile salts took nearly 15–20 mins to attain equilibrium. More time was needed for other surfactants.

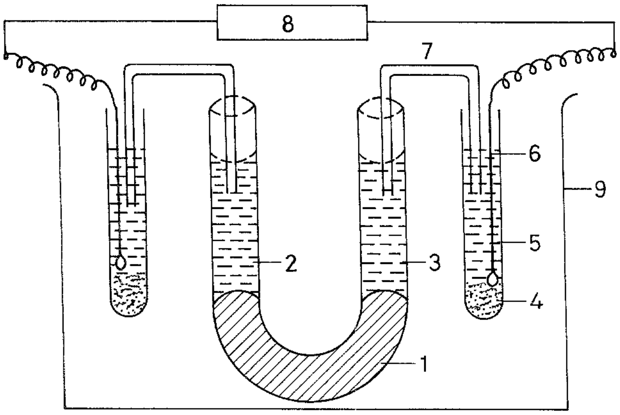

Fig. 1. A schematic representation of membrane potential measurement using a liquid membrane electrode. 1 – Liquid membrane electrode; 2 – reference solution; 3 – test solution; 4 – solid KCl; 5 – saturated KCl solution; 6 – saturated calomel electrode; 7 – salt bridge; 8 – multimeter; 9 – temperature bath

Results and discussion

Formulation of the liquid membrane

The liquid membrane essentially comprises a non aqueous water immiscible solvent in which the complex surfactant ion-pairs of the coacervates are solubilised forming a homogeneous (single phase) solution. For the determination of the concentrations of SDS, CTAB, NaC, NaDC, NaCDC and AOT, a number of organic solvents viz, nitrobenzene (NB), o-dichlorobenzene, *n*-octanol, dichloromethane, liquid parafin, cinnamic alcohol, cinnamaldehyde have been tried. Although solubility of some of the complexes in several solvents has posed a problem, good response to reversible surfactant ion specificity has been observed in NB, cinnamic alcohol and cinnamaldehyde have responsed only to CTAB. The solvent NB has also been used in the past to form liquid membrane electrodes [7–9]. CTA-C complex is water soluble, a complex of dimethyldioctadecyl ammonium cation with cholate anion has been tried to monitor the concentration of cholate.

The NB liquid membrane has been found to be stable and function for a considerable length of time (consecutive trials for 36 days have been successful) to monitor the concentrations of the bile salt anions. It is only moderately active towards CTA^+ cation (two to four days) and has shown fair activity towards DS^- and AOT^- anions. For the DS^--CTA^+ complex, the NB membrane function towards CTA^+ has been far better than DS^-. The membrane properties are sluggish for the latter.

Since the liquid membrane was used for a fairly long time (maximum up to 36 days) the solubility of NB in the test solution could be an influencing factor and, therefore, was assayed from uv-spectra. It was found that the maximum solubility of NB in the test solution was $15\ \mathrm{m\,mol\,dm^{-3}}$ at 303 K. The concentration was very low to have imparted appreciable influence on the result.

The measurement of SDS concentration by the CTA–DS contained liquid membrane was otherwise difficult. By employing $1\ \mathrm{m\,mol\,dm^{-3}}$ SDS and $20\ \mathrm{m\,mol\,dm^{-3}}$ NaCl as the reference solution and varying its concentration from 0.1–$10\ \mathrm{m\,mol\,dm^{-3}}$ at $20\ \mathrm{m\,mol\,dm^{-3}}$ of aqueous NaCl in the test solution, a system with slow response was achieved for SDS. The membrane had shown similar functions also for CTA–AOT complex.

The liquid membrane behaviour

The electro-chemical behaviours of the membrane systems are presented in Table 1. It has been observed that the electrochemical relations (1) and (2) obey for the cation and anion of the complex ion-pair (or coacervate).

$$E_m^+ = +K_+ \log a_R^+/a_T^+ \tag{1}$$

and

$$E_m^- = -K_- \log a_R^-/a_T^- \tag{2}$$

where E_m^+ and E_m^- are the membrane potentials for cation and anion responsive systems respectively; K_+ and K_- are the Nernstian equivalents of slopes for the respective cases; C_R^+ (or C_R^-) and C_T^+ (or C_T^-) are the concentrations (replacements for activities of the cation or anion) of the reference and test solutions, respectively. At the temperature of measurement (303 K), the constants K_+ and K_- are expected to be 2.303 RT/1F, i.e., 60.1 mv. Figures 2–5 demonstrate the validity of the equation in dilute solutions offering nice straight lines for both surfactant anions and cations. But the Nernstian slopes do not corroborate the results. Slopes as high as 55 mv and as low as 21 mv have been observed. Nonagreement

Table 1. Compositions and functions of the studied liquid membrane-surfactant systems at 303 K

Types of complex used in NB	Surfactants studied	Slope[a])	10^3CMC/mol dm^{-3}
CTA – DC	NaDC	44(1)	2.51
		39.5(2)	2.51
		38.4(3)	2.51
		39.0(36)	2.51
CTA – DC	CTAB	21(1)	0.89
		33(2)	0.89
		32.8(3)	0.84
CTA – DS	CTAB	55	0.91
CTA – DS	SDS	23	7.00
DDOA – C	CTAB	–	0.90
DDOA – C	NaC	18	5.18
CTA – CDC	NaCDC	44	2.04
CTA – AOT	AOT	–	2.30
CTA – DC &			
CTA – CDC	NaDC/NaCDC		
(1:1 w/w)	0:1	46.8	2.09
	1:4	28.6	2.29
	1:2	32.2	2.40
	1:1	42.3	2.51
	2:1	33.1	2.09
	4:1	33.7	2.19
	1:0	32.6	2.30
CTA – DC	NaDC/NaC		
	1:2	26.7	4.79
	1:1	36.1	3.98
	2:1	36.2	3.47

[a]), values in parantheses indicate aging in days of the membrane.

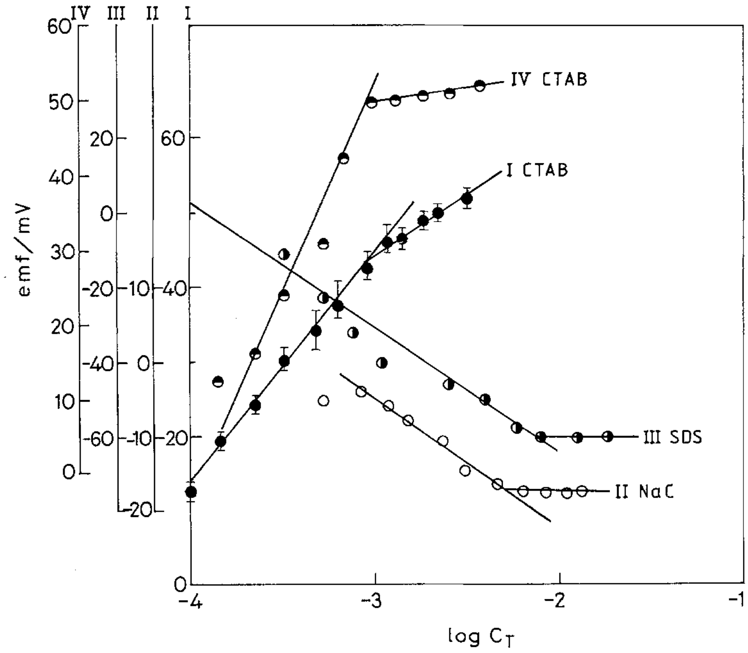

Fig. 2. Membrane potential versus log C_T plots for different surfactants at 303 K. I, CTAB with CTA – DC complex in NB; II, NaC with DDOA – C complex in NB; III, SDS with CTA – DS complex in NB; IV, CTAB with CTA – DS complex in NB

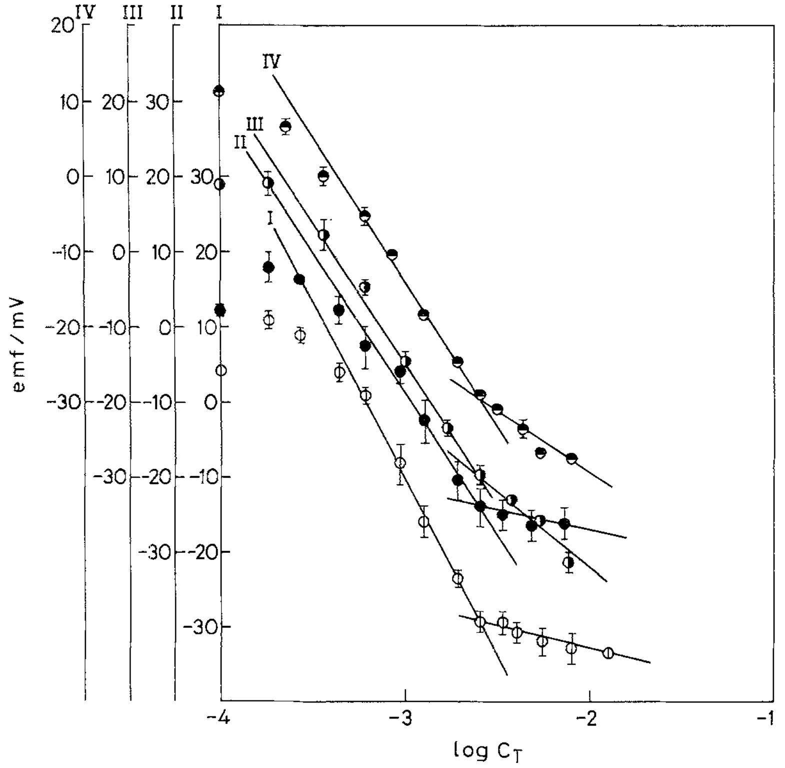

Fig. 3. Emf versus log C_T plots for the NaDC at 303 K. The ordinate scales are indicated on the plots. Ages: ○, 1 day; ●, 2 days; ◑ 3 days; ◓ 36 days

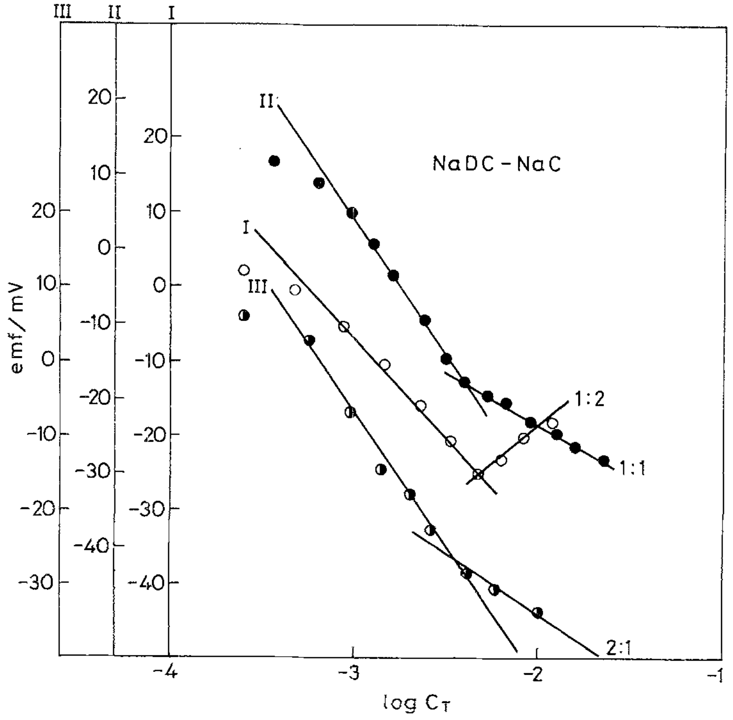

Fig. 4. Emf versus log C_T plots for the NaDC – NaC system at three different mole ratios at 303 K. Ordinate scales and mole ratios are indicated on the curves

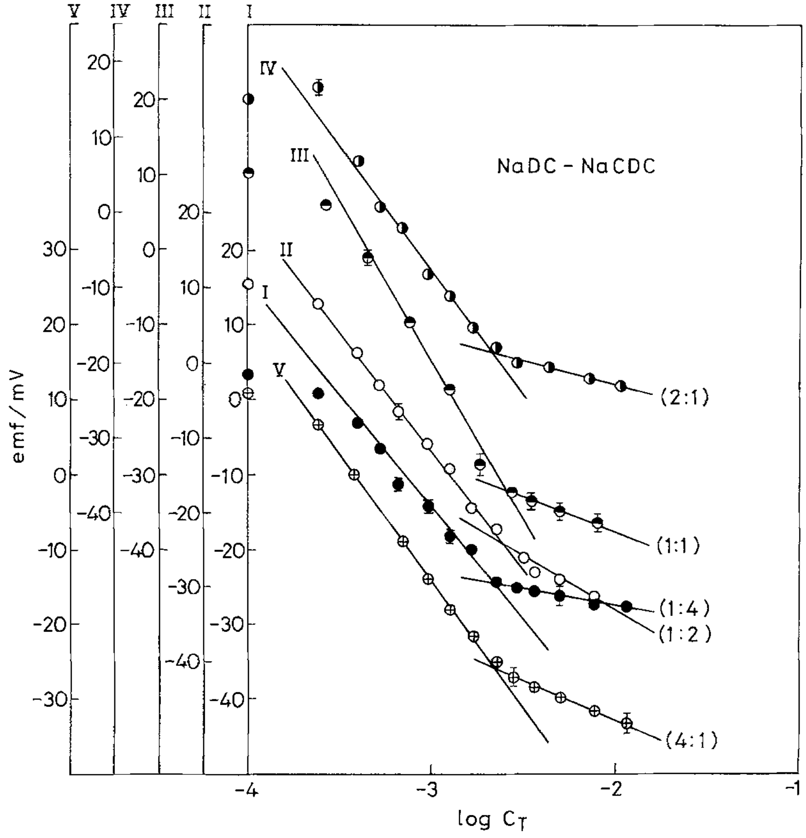

Fig. 5. Emf versus log C_T plots for the NaDC – NaCDC system at five different mole ratios at 303 K. Ordinate scales and mole ratios are indicated on the curve

of the experimental slopes with the Nernstian value has also been reported in the past [14, 18]. There is room for improvement in this area by adopting variations in the environmental compositions and conditions. The striking plus point in most of the systems is the reproducibility of the results and the distinct breaks in the initial linear courses to correspond to the critical micelle concentrations of the tried surfactants. The dual activity of the membrane electrodes both for the surfactant cation and the anion is also of striking significance. The CTAB-bile salt pairs were excellent in this respect and the electrode response was quick for the bile salt anions and less so for CTA^+ cation. For equilibration 10–15 min time was required for the former which was 30–40 min for the latter. For dimethyldioctadecyl ammonium cholate complex in NB, the response was more sluggish (> 45 mins) with a low Nernstian slope (~ 18 mv). However, a distinct break in the emf vs. concentration course to demonstrate the CMC point was observed. Similar slow response with 1 m mol dm^{-3} SDS and 20 m mol dm^{-3} NaCl as reference solution with varied concentration of SDS (from 0.1–100 m mol dm^{-3} at 20 m mol dm^{-3} NaCl) was obtained. The Nernstian slope was 23 mv with break at 7 m mol dm^{-3} as CMC. This has agreed with the reported CMC of SDS in literature [19]. Since the electrochemical principle for the functioning of the liquid membrane electrodes is not always well understood, rationalization of the discrepancy between the theory and the experiment may be an issue for future research.

CMC of pure and mixed surfactants

Determination of CMC of the individual surfactants herein studied has been possible by liquid membrane potential measurements. It has been assumed that the presence of 0.02 mol dm^{-3} NaCl has slightly affected the CMC of the studied surfactants. The standard deviations in CMC were within ± 3%. The values agree fairly well with other methods. The CMC's of the two binary combinations of bile salts, NaDC/NaC and NaDC/NaCDC mixed in different molar ratios have been also studied (Table 1). In the first case CTA^+–DC^- complex in NB was used as the membrane. A 1:1 (w/w) mixture of CTA^+-DC^- and CTA^+-CDC^- ion pairs in NB was used for the second. The first had a limitation; it could not respond to higher ratios ([NaC]/[NaDC] > 2:1). A similar problem was not observed for the other. The results in the table show a systematic variation of CMC for the mixed systems. This is exemplified in Figs. 4 and 5. According to Clint [20] the CMC of an ideal binary mixture of surfactants is given by the relation,

$$\frac{1}{\mathrm{CMC_{mix}}} = \frac{\alpha}{(\mathrm{CMC})_{\mathrm{BS}_1}} + \frac{1-\alpha}{(\mathrm{CMC})_{\mathrm{BS}_2}}\,, \tag{3}$$

where NaDC = BS_1 and NaCDC or NaC = BS_2 and α is the mole fraction of BS_1 in the mixture. In Fig. 6, the calculated and experimental CMC's are compared. Their agreement is poor; relatively low variation has been observed for the NaDC–NaCDC system.

The mole fraction of the bile salts in the mixed micelle has been calculated using Rubingh's equation [21] as applied to CTAB – bile salt and other mixtures [16, 22, 23].

$$(x^2 \ln[\mathrm{CMC_{mix}}\alpha/\mathrm{CMC_1}x]/ (1-x)^2 \ln[\mathrm{CMC_{mix}}(1-\alpha)/ \mathrm{CMC_2}(1-x)]) = 1\,, \tag{4}$$

where x is the mole fraction of surfactant 1 (NaDC) in the mixed micelle, α is the mole fraction of surfactant 1 (NaDC) in the mixture and CMC_1, CMC_2 and CMC_{mix} are critical micelle concentrations of NaDC, NaCDC or NaC and appropriate mixed micelles respectively. The results are presented in Table 2. For NaDC/NaCDC mixed system, the micellar compositions at various given mole fractions of NaDC are more or less comparable with a lower population of NaDC and higher population of NaCDC. For the NaDC/NaC system, the micellar compositions differ significantly with increase of NaDC and decrease of NaC for all the given compositions.

The interaction parameter β (calculated according to Eq. (5)) between the pair of surfactant ions in the micelle has systematically decreased with

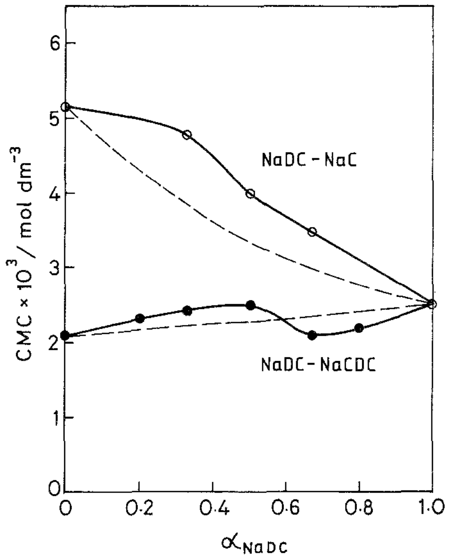

Fig. 6. Experimental and calculated CMC values of NaDC – NaC and NaDC – NaCDC systems as a function of mole fraction (α) of NaDC in binary mixtures at 303 K. Full curve, experimental; broken curve, calculated

Table 2. The experimental and calculated (according to Eq. (3)) CMC's and the parameters α, x, β, f_1 and f_2 mixed NaDC/NaCDC and NaDC/NaC systems at 303 K

System	10^3CMC/mol dm^{-3} Exptl	Calc	α	x	β	f_1	f_2
NaDC/NaCDC							
1:4	2.29	2.16	0.20	0.130	0.453	1.409	1.008
1:2	2.40	2.21	0.33	0.250	0.421	1.267	1.027
1:1	2.51	2.28	0.50	0.444	0.397	1.131	1.081
2:1	2.09	2.35	0.67	0.605	− 0.494	0.926	0.835
4:1	2.19	2.41	0.80	0.728	− 0.515	0.963	0.533
NaDC/NaC							
1:2	4.79	3.83	0.33	0.509	0.900	1.242	1.263
1:1	3.98	3.34	0.50	0.759	0.820	1.049	1.604
2:1	3.47	3.02	0.67	0.923	1.267	1.008	2.943

increasing α_{NaDC} in the pair NaDC/NaCDC and on the whole has increased with α_{NaDC} in the pair NaDC/NaC.

$$\beta = \ln\left(\frac{\mathrm{CMC}_{\mathrm{mix}}\,\alpha}{\mathrm{CMC}_1\, x}\right)/(1-x)^2 \,. \tag{5}$$

A positive β advocates repulsion between the mixed species, which is true for the first three ratios of the NaDC/NaCDC pair and all the ratios of NaDC/NaC pair. The anionic pairs, although they have correctly demonstrated positive β, the two pairs of NaDC/NaCDC (2:1 and 4:1) have yielded negative β which is unexpected.

The activity coefficients f_1 and f_2 of the component surfactants 1 and 2 respectively in the micelle have been calculated [21] using Eqs. (6) and (7) and are also given in Table 2.

$$f_1 = \exp \beta (1-x)^2 \tag{6}$$

and

$$f_2 = \exp \beta x^2 \tag{7}$$

Except for $\alpha_{\mathrm{NaDC}} = 0.80$ in the NaDC/NaCDC pair and $\alpha_{\mathrm{NaDC}} = 0.67$ in the NaDC/NaC pair, the f_1 and f_2 values moderately deviate from unity. The surfactants, therefore, do not maintain a high degree of non ideality in the mixed state in the micelles. The $\mathrm{CMC}_{\mathrm{mix}}$ vs. α_{NaDC} profiles in Fig. 5, therefore, also do not deviate much from the ideal course (Clint equation) [20]. It should be noted here that the nonideality that may arise in the mixed ionic micelles particularly due to charge interaction and counterion binding was not included in Rubingh's theory. The β values either implicitly took care of the effect or the effect was minimised by factors hitherto undefined. The absence of high degree of departure from ideal behaviour advocated in favour of the latter. The working premise of Rubingh's theory and its drawbacks were clearly presented by Motomura et al. [24] and discussed by Clint [25].

Conclusions

Cetyltrimethyl ammonium bromide can form water insoluble ion-pairs with sodium dodecyl sulfate, sodium deoxycholate, sodiumchenodeoxycholate and Aerosol Orange T which when dissolved in nitrobenzene can form liquid membranes. These liquid membranes can register potentials whose monitoring can estimate the concentration of the constituent surfactants as well as their critical micelle concentrations. The liquid membranes can respond to both the constituent surfactants in the ion-pair (the complex) and conveniently help to determine the CMC's of binary bile salt mixtures in order to understand the nature of their interaction in the micelle.

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Authors' address:

Prof. S.P. Moulik
Department of Chemistry
Jadavpur University
Calcutta - 700032
India