Colloid & Polymer Science Colloid Polym Sci 266:455–461 (1988)

Counterion binding behaviour of micelles of sodium dodecyl sulphate and bile salts in the pure state, in mutually mixed states and mixed with a nonionic surfactant

A. Bandyopadhyay and S. P. Moulik

Department of Chemistry, Jadavpur University, Calcutta, India

Abstract: The counterion binding behaviour of micelles of sodium dodecyl sulphate (SDS) and several bile salts in the pure state have been studied, as well as in mutually mixed states, and in a mixed state with polyoxyethylene sorbitan monolaurate (PSML) as a nonionic surfactant. Electrochemical measurements have shown no counterion binding by the pure bile salt micelles and their mixtures with PSML; they can bind counterions when mixed with SDS, whereas the surfactant anions of SDS micelles bind counterions in the pure state and/or in mixed states with PSML. In the SDS-PSML and SDS-bile salts combinations, the counterion association is decreased by the increased proportions of the second component. The extent of counterion binding by the different systems is presented.

Key words: Counterion binding, SDS, bile salts, mixed micelles.

Introduction

Surfactant ions above a certain concentration assemble to form multicharged micelles which usually bind counterions by way of electrostatic interaction. The phenomenon is reflected in the electrochemical behaviour of surfactant solutions. Counterion binding studies of sodium dodecyl sulphate (SDS), sodium cholate (NaC), sodium deoxycholate (NaDC), sodium chenodeoxycholate (NaCDC), sodium taurocholate (NaTC) and sodium taurodeoxycholate (NaTDC) etc. appear in the literature [1–11]: investigations on bile salts, however, are scant. Such studies on mixed micelles are also rare; some recent measurements of mixed micelles of both cationic and anionic surfactants with nonionic surfactants have been reported [7, 12, 13]. In our continued physicochemical investigations on bile salts [14] we have understood minor counterion binding by bile salt micelles. Therefore, the counterion association behaviour of SDS and several bile salts in pure as well as in mutually mixed states has been investigated. Mixed micelles of these surfactants with a nonionic detergent (polyoxyethylene sorbitan monolaurate, PSML) have been also studied. In the electrochemical method, sodium ion activity of surfactant solutions was measured with an ion selective membrane electrode and a pH meter.

Experimental

Materials

Cholic acid, deoxycholic acid, chenodeoxycholic acid and dehydrocholic acid were products of Fluka, Germany. They were prepared by converting into sodium salts and precipitating by adding hydrochloric acid. After three or four operations, the precipitated acids were recrystallised from an alcohol-water mixture and dried under vacuum. Elemental analysis for C, H and O of the compounds agreed with the calculated values within $\pm$ 0.2 %. The acids used were neutralised quantitatively with standard NaOH solutions. The concentration range of the bile salts used yielded pH values in the range 8.5–9.8, in confirmity with their pK_a values [18]. The concentration of the nonhydrolyzed bile salts were therefore more than 99.9 %, under experimental conditions, and the salts were fully ionized. For the purity and grade of sodium dodecyl sulphate (SDS) and polyoxyethylene sorbitan monolaurate (PSML), we refer to our earlier publications [15, 17]. Sodium nitrate was of BDH Anala® grade and was used as received.

All solutions were made in twice-distilled water of specific conductance 1.5–2.0 μmho cm^{-1} at 308 K.

Methods

The Na^+ activity was measured with an Na^+ selective glass membrane electrode and a digital pH meter of Elico Pvt. Ltd., Hyderabad, India. An Elico saturated calomel electrode was the reference electrode. All measurements were taken in a thermostated water bath at 308 ± 0.02 K. The deviation in the measured potential of the membrane electrode was within ± 0.05 %; the estimated Na^+ activity was uncertain to a maximum ± 0.7 %. The junction potential arising between the test solution and the calomel electrode was not eliminated by using a salt bridge. It was therefore inclusive in the ion selective membrane electrode constant, K_M^o defined in Eq. (1).

Water or aqueous PSML of definite concentration was progressively added to a solution of known ionic strength of a colloidal electrolyte or a salt, and the cell *emf* measured at each addition after equilibration of the solution. For $NaNO_3$, the equilibrium *emf* was obtained very quickly; for surfactants, the *emf* was observed to change on stirring and return to a constant value within 5 min of cessation of stirring. So, after each dilution, the solution was stirred to mix and the *emf* reading was taken when the solution was steady.

The membrane electrode potential E_M is given by the equation,

$$E_M = K_M^o + \frac{RT}{F} \ln a_{Na^+} \quad (1)$$

where K_M^o is a constant (depending on the electrode system); a_{Na^+} is the activity of sodium ion and the other terms have their usual significance.

In concentration notation,

$$E_M = K_M^o + \frac{RT}{F} \ln C_{Na^+} \cdot f_{Na^+} \quad (2)$$

where C_{Na^+} and f_{Na^+} are the concentration and the activity coefficient of the sodium ions, respectively.

Applying the extended Debye-Hückel equation for the ionic activity coefficient of uni-univalent electrolyte, Eq. (2) is transformed into

$$E_M = K_M^o + \frac{2.303\,RT}{F}\left(\log C_{Na^+} - \frac{A\sqrt{\mu}}{1 + aB\sqrt{\mu}}\right)$$

$$= K_M^o - \frac{2.303\,RT}{F}\left(\frac{A\sqrt{C_{Na^+}}}{1 + aB\sqrt{C_{Na^+}}} - \log C_{Na^+}\right). \quad (3)$$

In this equation, A and B are Debye-Hückel constants (at 308 K, $A = 0.5195$ and $B = 0.332 \times 10^8$), a is the ionic size parameter (2.5 Å) and μ is the ionic strength of the solution. E_M can be plotted against the bracketed term to find K_M^o from the intercept and (2.303 RT/F) from the slope, the latter at 308 K should be 0.0611 V. Any systematic deviation from the straight line is assigned to micelle formation affecting the activity of the counterion. Knowing K_M^o, the a_{Na^+} can be calculated. The use of this value with the Debye-Hückel activity value can then yield the degree of counterion binding by the micelles. It has been observed that electrolytes which are not surfactants yield equal K_M^o values, within the limits of experimental error.

For the colloidal electrolytes, K_M^o values depend on their types. The values varied within a narrow range. The slope of the curve of Eq. (3) has a small variation. a_{Na^+} values for surfactant solutions were found on the basis of individual K_M^o values.

Results and discussion

Graphical evaluation of K_M^o values are exemplified in Figs. 1–3. In plotting the figures, to avoid overlap the ordinate scale was shifted by Δ units for different systems, as indicated on the graphs. The validity of Eq. (3) is established in the plots; the slopes in all cases agree fairly well with the theoretical value 0.0611 V at 308 K. The intercept and slope values for all the combinations, found by least square analysis, are presented with their standard deviations in Table 1. The data reveal that the potentiometric system and the Na^+ selective membrane electrode functioned as expected. The slopes fall mostly in the range 0.061–0.063 V with the exceptions of NaDC/PSML (5 mmol · dm^{-3}) and NaC/PSML (50 mmol · dm^{-3}) systems which have

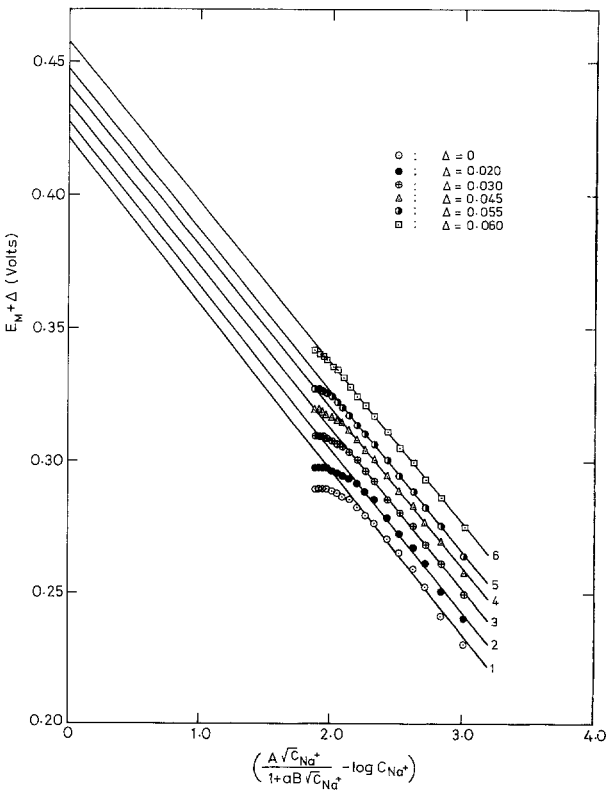

Fig. 1. Concentration-dependent membrane electrode potential, E_M in mixed surfactant solutions of SDS and PSML at 308 K. Lines 1–6 represent [PSML] 0, 0.50, 1.00, 2.50, 3.75 and 5.00 mmol · dm^{-3}, respectively

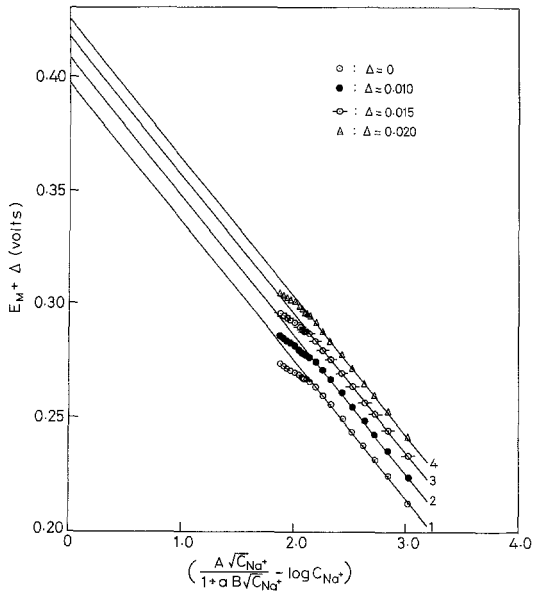

Fig. 2. Concentration-dependent membrane electrode potential, E_M in mixed surfactant solutions of 1 : 1 bile salt and SDS at 308 K Lines 1–4 represent NaDC-SDS, NaCDC-SDS, NaC-SCS and NaDHC-SDS, respectively

slopes 0.059 V and 0.064 V, respectively. The variation in slope for maximum cases is about 3 %. This is tolerable in working with surface active compounds, since their effects on the performance of membrane electrodes is hardly known. The intercepts fall in the range 0.40–0.43 V. This is attributed to the specific effects of the surfactant systems on the glass membrane, which was an unavoidable consequence. Individual K_M^o values were therefore determined to evaluate the associated Na^+ activities. Such an analysis of the quantitative performance of the membrane electrode in surfactant solutions is rare in the literature. All the slope and intercept values of Eq. (1) are therefore given in Table 1 for a ready comparison. The deviations from the straight lines in Figs. 1 and 2 indicate the stages of counterion binding by the micelles. Pure bile salts and bile salts mixed with PSML (Fig. 3) did not show counterion binding. Their E_M varied linearly with the bracketed term of Eq. (1), obtained by using the extended Debye-Hückel relation. The results are at variance with recent electrochemical studies which describe counterion association by the micelles of several bile salts [4].

Micelles may be described either by the mass action model or by the pseudo phase model. It is considered that the pseudo phase model is more applicable to nonionic micelles, whereas the mass action model is more appropriate for charged or ionic micelles. The counterion binding of micelles has been estimated by many workers in the light of the pseudo phase model [1–9, 12, 13]. Although the mass action principle was invoked by some other authors [10, 11], this simple and straightforward nature of the phase model makes it a powerful alternative. It is worth noting that where the degree of counterion binding is high, the charge of the

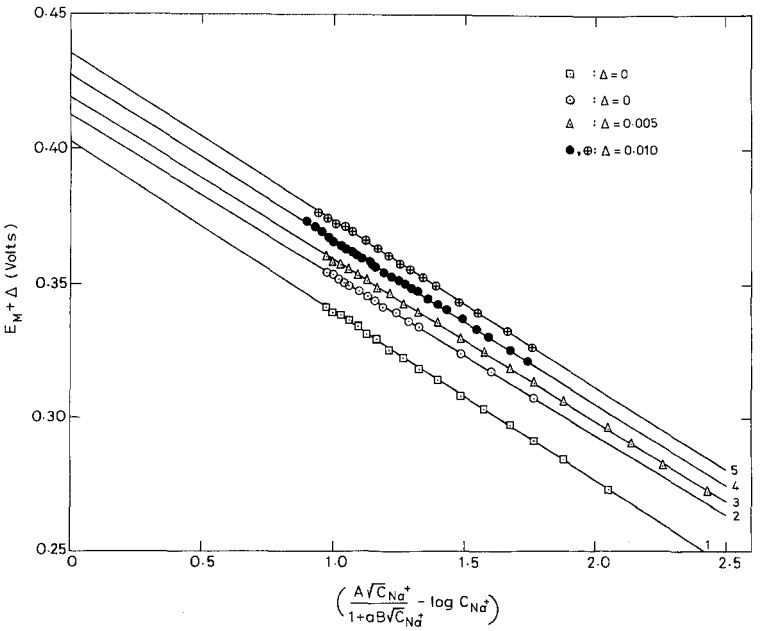

Fig. 3. Concentration-dependent membrane electrode potential, E_M in $NaNO_3$ and in pure bile salt solutions at 308 K. Lines 1–5 represent $NaNO_3$ NaDC, NaCDC, NaC and NaDHC, respectively

Table 1. Least square slopes and intercepts of Eq. (3) with their standard deviations at 308 K for various systems

System	Slope of Eq. (3) 2.303 RT/F (V)	Intercept of Eq. (3) K_M^o (V)	Corr. Coeff
$NaNO_3$	0.0633 ± 0.0003	0.4032 ± 0.0005	0.999
NaC	0.0609 ± 0.0003	0.4175 ± 0.0003	0.999
NaDC	0.0596 ± 0.0003	0.4129 ± 0.0004	0.999
NaCDC	0.0603 ± 0.0002	0.4145 ± 0.0003	0.999
NaDHC	0.0619 ± 0.0004	0.4256 ± 0.0005	0.999
SDS	0.0628 ±0.0022	0.4219 ± 0.0055	0.995
NaC in PSML (5.0 mmol · dm^{-3})	0.0623 ± 0.0003	0.4201 ± 0.0004	0.999
NaDC in PSML (5.0 mmol · dm^{-3})	0.0588 ± 0.0004	0.4131 ± 0.0004	0.999
NaDHC in PSML (5.0 mmol · dm^{-3})	0.0629 ± 0.0005	0.4255 ± 0.0006	0.999
NaC in PSML (50.0 mmol · dm^{-3})	0.0643 ± 0.0005	0.4233 ± 0.0006	0.999
NaDC in PSML (50.0 mmol · dm^{-3})	0.0626 ± 0.0006	0.4186 ± 0.0009	0.999
NaDHC in PSML (50.0 mmol · dm^{-3})	0.0615 ± 0.0003	0.4268 ± 0.0004	0.999
SDS in PSML (0.50 mmol · dm^{-3})	0.0617 ± 0.0018	0.4078 ± 0.0046	0.996
SDS in PSML (1.00 mmol · dm^{-3})	0.0610 ± 0.0008	0.4046 ± 0.0020	0.999
SDS in PSML (2.50 mmol · dm^{-3})	0.0608 ± 0.0007	0.3971 ± 0.0017	0.999
SDS in PSML (3.75 mmol · dm^{-3})	0.0608 ± 0.0004	0.3929 ± 0.0011	0.999
SDS in PSML (5.00 mmol · dm^{-3})	0.0607 ± 0.0005	0.3982 ± 0.0013	0.999
SDS-NaC (1:1)	0.0608 ± 0.0004	0.4019 ± 0.0011	0.999
SDS-NaDC (1:1)	0.0608 ± 0.0008	0.3969 ± 0.0019	0.999
SDS-NaCDC (1:1)	0.0608 ± 0.0008	0.3979 ± 0.0019	0.999
SDS-NaDHC (1:1)	0.0608 ± 0.0004	0.4049 ± 0.0011	0.999
SDS-NaC (1:5)	0.0612 ± 0.0006	0.4021 ± 0.0016	0.999
SDS-NaDC (1:5)	0.0615 ± 0.0007	0.3974 ± 0.0018	0.999

micelle is greatly reduced and both the models are more or less equally applicable to the ionic and nonionic surfactants. The analysis presented below is based on the pseudo phase model of micelles.

According to this model, the concentration of the surfactant monomer is considered constant in the post CMC region. The measured sodium ion activity is contributed by the surfactant monomers and the micelles by way of counterion dissociation. The observed activity, a_{Na^+}, is related to the concentration, C_{Na^+} and the activity coefficient, f_{Na^+} by the relation

$$a_{Na^+} = C_{Na^+} \cdot f_{Na^+} . \tag{4}$$

In the phase model,

$$C_{Na^+} = C_{Na^+}^{BP} + \alpha(C_{Na^+}^{T} - C_{Na^+}^{BP}) \tag{5}$$

where $C_{Na^+}^{BP}$ is the surfactant concentration at the break point of the activity concentration curve, $C_{Na^+}^{T}$ is its total concentration and α is the degree of dissociation of the counter Na^+. Equations (4) and (5) lead to

$$a_{Na^+} = f_{Na^+}\{C_{Na^+}^{BP} + \alpha(C_{Na^+}^{T} - C_{Na^+}^{BP})\} \tag{6}$$

Botré et al. [16] assumed both f_{Na^+} and α to be constants and used the differential form of Eq. (6) to find α.

$$da_{Na^+}/d\, C_{Na^+}^{T} = f_{Na^+} \cdot \alpha \tag{7}$$

f_{Na^+} at the CMC was used by these authors in Eq. (7) to calculate α from the slope of a plot of a_{Na^+} versus concentration. Recently, Ogino et al. [12] and Abe et al. [13] have used Eq. (7) to evaluate counterion binding of mixed micelles. It is noteworthy that f_{Na^+} may not remain constant in the post CMC region. This is because although the micelles formed are in a different phase, the concentration of the counterion produced by their dissociation increases with the increase of surfactant concentration. Equation (6) can be written as

$$a_{Na^+} = a_{Na^+}^{BP} + \alpha(a_{Na^+}^{T} - a_{Na^+}^{BP}) \tag{8}$$

where

$$a_{Na^+}^{BP} = f_{Na^+} \cdot C_{Na^+}^{BP} \quad \text{and} \quad a_{Na^+}^{T} = f_{Na^+} \cdot C_{Na^+}^{T} .$$

In the subsequent analysis, $a_{Na^+}^{BP}$ has been considered weakly dependent on surfactant concentration and

therefore a constant. This is a rational consideration, so long as measurements are taken at concentrations which are low and not very far from the CMC. On rearrangement, Eq. (8) becomes

$$a_{Na^+} = (1 - \alpha)\, a^{BP}_{Na^+} + \alpha \cdot a^{T}_{Na^+}. \qquad (9)$$

The total Na^+ ion activity, $a^{T}_{Na^+}$ has been calculated by the extended Debye-Hückel (DH) equation, assuming $a^{T}_{Na^+} = a^{DH}_{Na^+}$. In the lower range of concentration of the ionic surfactants (the measured activity) a_{Na^+} closely agrees with $a^{DH}_{Na^+}$, which differ in the higher concentration range. This is attributed to the influence of the associated monomers or micelles on the activity of the Na^+. Equation (9) is then written as

$$a_{Na^+} = (1 - \alpha)\, a^{BP}_{Na^+} + \alpha \cdot a^{DH}_{Na^+}. \qquad (10)$$

The break points in the a_{Na^+} versus $a^{DH}_{Na^+}$ plots can be used to find α from the intercept and verify it with its value calculated from the slope. Such an analysis is shown in Figs. 4 a and 5. Good linear plots after the break points advocate both $a^{BP}_{Na^+}$ and α to be fairly constant. In the lower concentration range, up to the break point, $\alpha = 1$ (100 % dissociation) and

$$a_{Na^+} = a^{DH}_{Na^+}. \qquad (11)$$

Unit slopes of the initial straight lines of Figs. 4 a and 5 corroborate Eq. (11). The mean values of α, obtained from the slope and intercept, are presented in Table 2. Pure bile salts and bile salts mixed with PSML also obey Eq. (11), showing 100 % dissociation of the counterions (Fig. 6).

The concentration of PSML was varied in the range 0.50–5.00 mmol · dm^{-3}, the lowest concentration being 10 times its critical micellar concentration [17]. Thus, SDS is expected to form mixed micelles from the beginning of its addition. The measured sodium ion activities, however, deviated from the Debye-Hückel course at concentrations higher than that shown by pure SDS (Fig. 4a). This suggested that no counterion (Na^+) binding by the mixed micelles occurs unless a threshold concentration is reached; when a sufficient number of SDS molecules are incorporated, the surface charge of the mixed micelles increases, causing counterion association. The degree of counterion binding by NaC/PSML is zero, but that of SDS/PSML mixed micelles decreases with increased PSML concentration. The variation in the degree

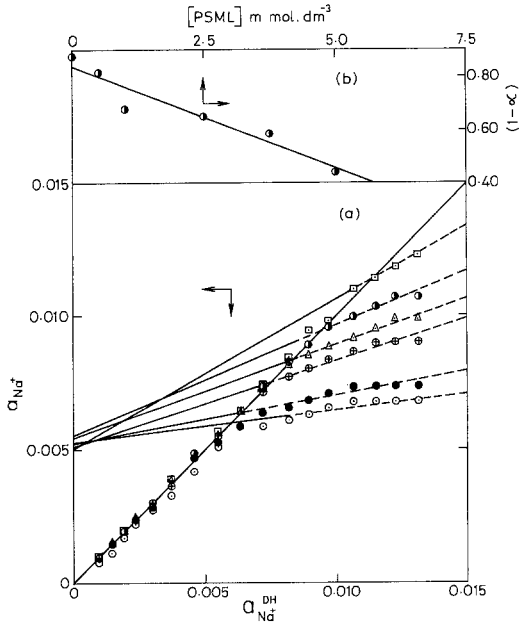

Fig. 4. (a) Dependence of the observed and calculated Na^+ activities of SDS in the presence of PSML at 308 K. Symbols represents [PSML]: 0 (⊙); 0.50 (●); 1.00 (⊕); 2.50 (△); 3.75 (◑); and 5.00 (⊡) mmol · dm^{-3} respectively. (b) PSML concentration-dependent degree of counterion association, $(1 - \alpha)$ by SDS micelles at 308 K

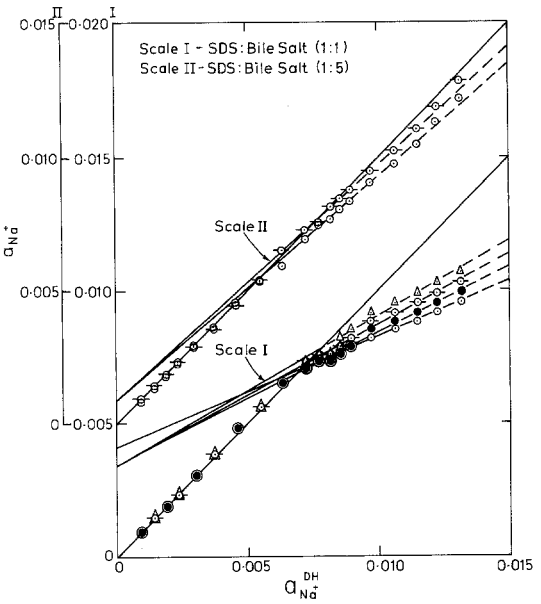

Fig. 5. Dependence of observed and calculated Na^+ activities for the mixed systems of bile salts and SDS at 1 : 1 and 5 : 1 ratios at 308 K. Symbols represent: (⊙) NaDC-SDS; (●) NaCDC-SDS; (⊕) NaC-SDS and NaDHC-SDS

Table 2. Activities at the break points, CMC[a]) and degree of counterion dissociation[b])[c]) for various systems at 308 K

System	$a^{BP}_{Na^+} \times 10^3$	CMC mmol · dm^{-3}	α
NaC	–	13.0	1.000
NaDC	–	6.0	1.000
NaCDC	–	8.0	1.000
NaDHC	–	–	1.000
SDS	6.0	8.0	0.124
NaC in PSML (5.00 mmol · dm^{-3})	–	–	1.000
NaDC in PSML (5.00 mmol · dm^{-3})	–	–	1.000
NaDHC in PSML (5.00 mmol · dm^{-3})	–	–	1.000
NaC in PSML (50.00 mmol · dm^{-3})	–	–	1.000
NaDC in PSML (50.00 mmol · dm^{-3})	–	–	1.000
NaDHC in PSML (50.00 mmol · dm^{-3})	–	–	1.000
SDS in PSML (0.50 mmol · dm^{-3})	6.35	–	0.182
SDS in PSML (1.00 mmol · dm^{-3})	7.50	–	0.320
SDS in PSML (2.50 mmol · dm^{-3})	8.30	–	0.350
SDS in PSML (3.75 mmol · dm^{-3})	9.35	–	0.412
SDS in PSML (5.00 mmol · dm^{-3})	11.35	–	0.560
SDS-NaC (1:1)	7.25	8.0	0.532
SDS-NaDC (1:1)	7.00	7.7	0.421
SDS-NaCDC (1:1)	6.90	7.6	0.493
SDS-NaDHC (1:1)	7.90	8.7	0.568
SDS-NaC (1:5)	7.50	8.3	0.885
SDS-NaDC (1:5)	5.50	6.0	0.844

[a]) NaDHC do not micellize [18]. The lowest concentration of PSML used was about 10 times its CMC (60 μmol · dm^{-3}).

[b]) Bile salt micelles in pure state and in mixed state with PSML did not exhibit counterion binding. This is in agreement with the observations of Ryu et al. [5] on sodium taurocholate and sodium taurodeoxycholate micelle.

[c]) Some reported counterion dissociation of SDS micelles at 298 K: Yamauchi et al. [1] 0.20; Kale et al. [2] 0.15; Shedlovsky et al. [8] 0.22; Satake et al. [9] 0.25; Nishikido [11] 0.25; Sasaki et al. [10] 0.27. This work on SDS agrees with that of Kale et al. [2].

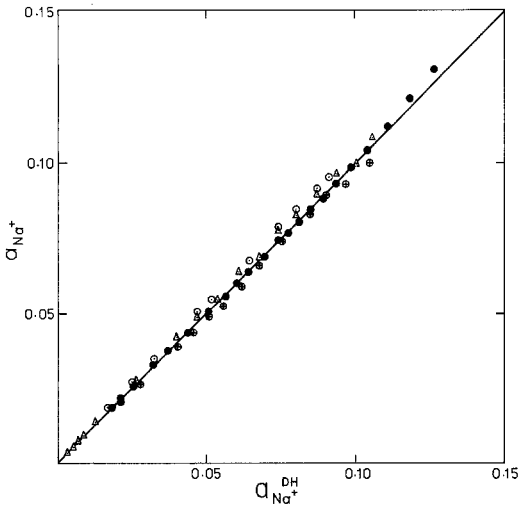

Fig. 6. Dependence of the observed and calculated Na^+ activities of different bile salts at 308 K. Symbols represent (⊙) NaDC; (●) NaC; (△) NaCDC and (⊕) NaDHC, respectively

of counterion binding $(1-\alpha)$ with PSML concentration is exemplified in Fig. 4 b. The decreasing trend is fairly linear, calculations have shown a zero degree of counterion binding at 10.94 mmol · dm^{-3} PSML at 308 K.

Individually, none of the bile salts showed counterion association. The micelles of NaC, NaCDC and NaDC have a small aggregation number (2–4 monomers per micelle), NaDHC hardly micellizes [18]. The surface charge is considered insufficient to hold counterions. The results are at variance with the reports of Rajagopalan et al. [4] of electrochemical measurements on bile salts. This is considered to be due to the authors' use of concentrations to relate *emf*, whereas we used activities. However, the mixed micelles of SDS with bile salts at 1:1 and 1:5 ratios did show counterion binding (Fig. 5). The binding in the latter mixture was lower than in the former. Assuming a linear behaviour, the ratio for $\alpha = 1$ is calculated to be 1:5.63 and 1:6.03 for NaC and NaDC, respectively, at 308 K.

Conclusion

The intrinsic function of the Na^+ ion selective membrane electrode varies slightly in surfactant solutions. In the non-micellar concentration region, the measured sodium ion activities closely agree with the activities calculated by the extended Debye-Hückel equation. Pure micelles of sodium salts of cholic, deoxycholic, chenodeoxycholic and dehydrocholic acids, as well as their mixed micelles with PSML, do not bind counterions. Mixed micelles of SDS, either with PSML or with the bile salts, bind less counterions than pure SDS micelles.

Acknowledgement

Arup Bandyopadhyay would like to thank CSIR, Govt. of India, for a Junior Research Fellowship.

References

1. Yamauchi A, Kunisaki T, Minematsu T, Tomokiyo Y, Yamaguchi T, Kimizuka H (1978) Bull Chem Soc Jpn 51:2791
2. Kale KM, Cussler EL, Evans DF (1980) J Phys Chem 84:593
3. Kale KM, Cussler EL, Evans DF (1983) J Solution Chem 11:581
4. Rajagopalan N, Vadnere M, Lindenbaum S (1981) J Solution Chem 10:785
5. Ryu K, Lowery JM, Evans DF, Cussler EL (1983) J Phys Chem 87:5015
6. Cutler SG, Meares P, Hall DG (1978) J Chem Soc Faraday Trans 1 74:1758
7. Hall DG, Price TJ (1984) J Chem Soc Faraday Trans 1 80:1193
8. Shedlovsky L, Jacob CW, Epstein MB (1963) J Phys Chem 67:2075
9. Satake I, Tahara T, Matuura R (1969) Bull Chem Soc Jpn 42:319
10. Sasaki T, Hattori M, Sasaki J, Nukina K (1975) Bull Chem Soc Jpn 48:1397
11. Nishikido N (1983) J Colloid Interface Sci 92:588
12. Ogino K, Tsubaki N, Abe M (1984) J Colloid Interface Sci 98:78
13. Abe M, Tsubaki N, Ogino K (1984) Colloid Polym Sci 262:584
14. Bandyopadhyay A, Moulik SP (1987) Ind J Bichem Biophys, in press
15. Moulik SP, Ray S, Das AR (1977) J Phys Chem 81:1766
16. Botré C, Crescenzi VL, Mele K (1959) J Phys Chem 63:650
17. Mandal AB, Moulik SP (1982) In: Mittal KL, Fendler EJ (eds) Solution behaviour of surfactants: Theoretical and applied aspects, Vol 1, Plenum Press, New York, p 521
18. Small DM (1971) In: Nair PP, Kritchevsky D (eds) The Bile Acids: Chemistry, Vol 1, Plenum Press, New York, Ch 8

Received February 27, 1987;
accepted October 13, 1987

Authors' address:

Dr. S. P. Moulik
Department of Chemistry
Jadavpur University
Calcutta – 700 032, India