ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 122 (1999) 47–52

Journal of Photochemistry and Photobiology A:Chemistry

Effects of carbohydrates on the solution properties of surfactants and dye–micelle complexation

Kamala Rani Acharya, Subhash C. Bhattacharyya*, Satya P. Moulik

Physical Chemistry Section, Chemistry Department, Jadavpur University, Calcutta 700 032, India

Received 6 August 1998; received in revised form 4 November 1998; accepted 15 December 1998

Abstract

The self aggregation of sodium dodecylsulfate (SDS), octyl phenyl polyoxyethylene ether (Triton X-100), polyoxyethylene sorbitan monolaurate (Tween 20), monopalmitate (Tween 40), monostearate (Tween 60) and monooleate (Tween 80) and the binding of the dye safranine T (ST) with micelles of the above surfactants have been studied by absorption, emission and tensiometric methods in the presence of glucose, galactose, sucrose and maltose. The carbohydrates have been observed to appreciably affect the critical micellar concentration (CMC) of the surfactants, their aggregation number and the ST–micelle binding constant. The results have been attempted to rationalize on physical chemical basis.

Keywords: SDS; Triton X-100; Tweens; Micelles; Dye–micelle binding; Additive effects; Glucose; Galactose; Sucrose; Maltose

1. Introduction

Salt addition into the solution of ion surfactants modifies the coulombic repulsions between the charged head groups and alters their aggregation and micellar structure [1,2]. The shape of micelle may also undergo a salt-induced transition (sphere-to-rod) at a threshold concentration, and a sizeable micellar growth may occur [2]. Ionic surfactants have a comparatively high CMC value than non-ionic surfactants, a much wider range of CMC is offered to the latter by the introduction of different polar groups. It is desirable to research on factors that influence the critical micellar concentration (CMC) in order to design kinetic experiments of micellar catalysis and inhibition, and hydrophobic interaction. Like CMC, micellar solubility, micellar structure and aggregation number depend on the surfactant type, the solvent medium, the presence of additives and the temperature [3–8]. Since the effectiveness of micellar solution depends on micellar size and geometry, informations on these properties along with CMC are required for the interpretation of kinetic and equilibrium results.

Addition of salts normally cause a decrease in CMC and an increase in aggregation number of ionic micelles, non-ionic surfactants are least affected by moderate addition of salt. Non-ionic compounds, viz. urea, carbohydrates, lower alkanol etc. have been found to affect the micellization characteristics of both ionic and non-ionic surfactants. In this work we have studied the effects of carbohydrates (glucose, sucrose, maltose and galactose) on the physicochemical characteristics, i.e. CMC, aggregation number of several surfactants. This constitutes a part of our photophysical studies of surfactant aggregation and dye–micelle interaction.

2. Experimental

Safranine T, ST (E. Merck, Germany), was recrystallised twice from ethanol–water mixture. The surfactants sodium dodecyl sulphate (SDS), octyl phenyl polyoxyethylene ether (Triton X-100), polyoxyethylene sorbitan monolaurate (Tween 20), monopalmitate (Tween 40), monostearate (Tween 60) and monooleate (Tween 80) were either BDH or Sigma products. Their characteristics and purity standards were the same as reported earlier [9,10]. Sucrose, glucose, galactose and maltose were Excellar grade BDH products and were used as received. Doubly distilled conductivity water was used for solution preparation.

Absorption spectra were recorded using a Shimadzu (Japan) UV–Vis spectrophotometer (160 A) with a matched pair of silica cuvettes (path length 1 cm). Fluorescence spectral measurements were recorded in a spectrofluorometer (Fluorolog F lllA spectrofluorometer, Spex, NJ, USA)

*Corresponding author.

1010-6030/99/$ – see front matter
PII: S1010-6030(99)00003-9

with a slit width of 2.5 nm. The excitation and emission wavelengths were 520 and 587 nm, respectively.

All spectral measurements were duplicated at a constant temperature of 25 ± 0.1°C and the mean values were processed for data analysis.

The concentration of ST used in the micellar solution was of the order of 10^{-5} mol dm^{-3}. The concentrations of the carbohydrates were in the range of 0.1–0.7 mol dm^{-3}.

3. Results

3.1. Critical micellar concentration

The absorbance and fluorescence intensities of ST increase in micellar solution in the presence of aqueous solution of sucrose, maltose, glucose and galactose. From the measurements of absorbance and fluorescence of the dye at different concentrations of surfactants in the presence of the sugars, the CMC values were obtained by plotting the absorbance (A) in the presence of different concentration surfactant at the absorbance maximum (520 nm). From the fluorescence measurements also the CMC values were determined from the plot the fluorescence intensity in the presence of surfactant at 587 nm (Fig. 1(A) and (B)). The values are given in Table 1. The results indicate that the CMC decreases in the presence of sugars. For confirmation of the results the CMCs of the surfactants in the presence of sugars were also determined tensiometrically (Fig. 1(C)). The decrease in CMC in the presence of the carbohydrates is prominent for ionic surfactants than the non-ionics. A linear correlation of log CMC with [sugar] has been observed, a

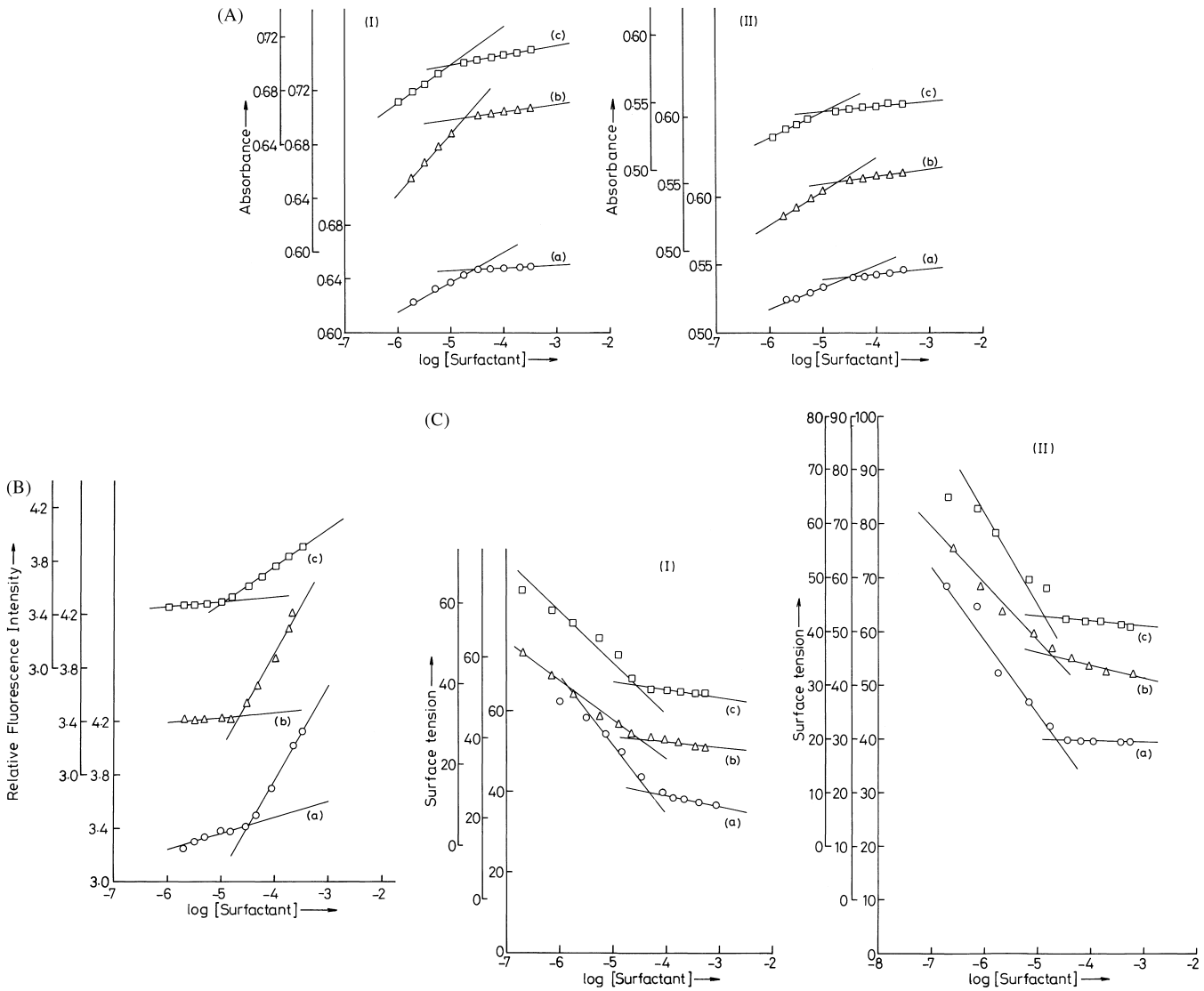

Fig. 1. (A) Plot of absorbance vs. log[surfactant]. (I) Tween 20, (II) Tween 40 in the presence of glucose, (a) 0.1 M, (b) 0.3 M (c) 0.5 M; (B) Plot of fluorescence intensity vs. log[Tween 20] in the presence of glucose (a) 0.1 M, (b) 0.3 M, (c) 0.5 M; (C) Plot of surface tension vs. log[surfactant] (I) Tween 20, (II) Tween 40, in the presence of sucrose (a) 0.1 M, (b) 0.3 M, (c) 0.5 M.

Table 1
The effects of carbohydrates on CMC of surfactants at 298 K

[Carbohydrate] mol dm^{-3}	10^4 CMC/mol dm^{-3}					
	SDS	Tween 20	Tween 40	Tween 60	Tween 80	Triton X-100
Sucrose						
0.1	50.0	0.30	0.21	0.15	0.09	2.1
0.3	44.0(34.0[a])	0.24(0.22[a] 0.23[b])	0.16(0.19[a])	0.13(0.14[a])	0.08(0.08[a])	1.7(1.9[a])
0.5	32.5(27.8[a])	0.20(0.21[a] 0.20[b])	0.12(0.13[a])	0.11(0.12[a])	0.065(0.07[a])	1.5(1.6[a])
Glucose						
0.1	61.0	0.24(0.25[b])	0.19	0.17	0.07	2.2
0.3	49.0	0.20(0.22[b])	0.17	0.15	0.06	2.0
0.5	40.0	0.16(0.15[b])	0.13	0.10	0.05	1.6
Maltose						
0.1	55.0	0.30	0.21	0.16	0.08	2.1
0.3	45.	0.26	0.14	0.13	0.065	2.0
0.5	40.0	0.20	0.12	0.10	0.055	1.6
Galactose						
0.1	60.0	0.23(0.29[b])	0.20(0.20[b])	0.18(0.17[b])	0.085	2.1

[a]By tensiometry.
[b]By fluorimetry.
CMC $\times 10^4$ mol dm^{-3}, micelles, SDS: 80.0, Tween 20: 0.5, Tween 40: 0.25, Tween 60: 0.23, Tween 80: 0.10, Triton X-100: 2.4.

graphical illustration is given in Fig. 2. The trend follows the relation (1)

$$\mathrm{CMC} = a - b\ [\mathrm{sugar}] \tag{1}$$

The values of the constants a and b are given in Table 2. The addition of sugar favours the formation of structure of water matrix, possibly due to hydrogen bonding. The more structured is the water, the lower is the CMC. The process of micellization is a consequence of hydrophobic interaction [11], and it is hindered by the forces of mutual repulsion acting between the hydrophilic parts (the ionic head groups) of surfactant molecules [12].

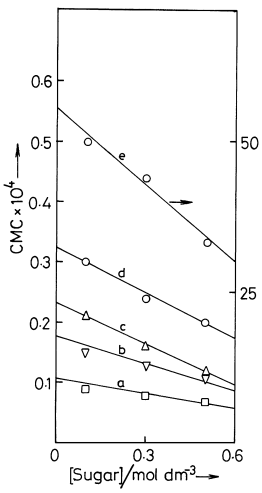

Fig. 2. Plot of critical micelle concentration of surfactants vs. [sucrose] (a) Tween 20, (b) Tween 40, (c) Tween 60, (d) Tween 80 (e) SDS.

3.2. Binding constants

For the quantification of the complexation process, the micelle has been considered to be in pseudophase, i.e. the monomer concentration is constant and equal to the CMC. The concentration of the micelle is equal to ([S] − CMC)/n where [S] and n are the concentration of the surfactant and the micellar aggregation number, respectively. For concentration of [S] much larger than the CMC, the micellar concentration [M] virtually equals to [S]/n and the dye interacts with the micelles according to the following complexation equilibrium,

$$\mathrm{D} + \mathrm{M}\,(\mathrm{or}\,[S]/n) \overset{K_c}{\rightleftharpoons} \mathrm{DM} \tag{2}$$

where D, M and DM represent the dye, micelle and dye–micelle complex, respectively and K_c is the complexation constant. For the determination of K_c the modified equation of Lang [13] has been used.

$$\frac{[S]l}{n(\varepsilon-\varepsilon_o)} = \frac{l}{(\varepsilon_c-\varepsilon_o)}\left\{[D] + [S]/n - \frac{(\varepsilon-\varepsilon_o)[D]}{(\varepsilon_c-\varepsilon_o)}\right\} + \frac{l}{K_c(\varepsilon_c-\varepsilon_o)} \tag{3}$$

where the new term l represents the path length and ε_o, ε and ε_c are the extinction coefficients of the dye in water, in micelle and the dye–micelle complex, respectively. The identical K_c values were also obtained from the Benesi–Hildebrand equation [14]. In processing the results, the n values derived from the fluorescence measurements and reported in the next section were used. The K_c values derived

Table 2
The a, b, A and B values from Eqs. (1) and (4) for different surfactants in the presence of carbohydrates at 298 K

	Surfactants					
	SDS	Tween 20	Tween 40	Tween 60	Tween 80	Triton X-100
Sucrose						
10^4a	41.0	0.25	0.22	0.16	0.09	2.6
10^4b	55.5	0.33	0.24	0.18	0.11	2.4
A	4.8	5.03	5.09	5.11	5.12	5.12
B	0.84	0.70	0.70	0.71	0.73	0.84
Glucose						
10^4a	52.0	0.20	0.18	0.15	0.08	1.7
10^4b	66.0	0.27	0.22	0.19	0.08	2.3
A	4.7	5.16	5.2	5.23	5.28	5.19
B	0.78	0.40	0.45	0.50	0.53	0.60
Maltose						
10^4a	39.0	0.28	0.23	0.15	0.11	2.0
10^4b	58.0	0.33	0.23	0.18	0.12	2.4
A	4.8	5.12	5.19	5.2	5.27	5.17
B	0.83	0.50	0.55	0.60	0.65	0.75

from the slope and intercept of the straight lines (Fig. 3) according to the Eq. (3) are presented in Table 3.

The dye–micelle complex in the presence of sugars have different extents of affinity similar to that observed in their absence. The order of the binding constants (K_c) represents the binding efficacies of the dye ST with the surfactant micelles in the presence of the carbohydrates. The linear plots of log K_c versus [sugar] for different surfactants are given in Fig. 4. They fit the following equation (Eq. (4)) for glucose, sucrose and maltose, where A and B are the required constants.

$$\log K_c = A + B\ [\text{sugar}] \tag{4}$$

The value of the intercept A refers to log K_c without sugar, i.e. the complexing magnitude in aqueous medium. The values in Fig. 4 corroborate this. The K_c has been found to vary inversely with the CMC. The values of the constants A and B are given in Table 2.

3.3. Fluorescence behaviour of the dye in the presence of sugars

The enhancement of the fluorescence intensity of dyes and other compounds in micellar medium has been reported [15,16]. The fluorescence of ST at a constant concentration is enhanced in aqueous solutions of surfactants. The degree of enhancement of fluorescence intensity is larger in the presence of sugars. Using a dye concentration of 10 μmol dm^{-3} and surfactant concentration of 1 mmol dm^{-3}, a nearly two-fold increase in intensity was observed in the presence of 0.5 M glucose and 0.5 M sucrose. The fluorescence intensity increased with increasing number of hydroxyl groups in the sugar. At constant [dye] and [sugar], the flourescence intensity (F) has increased with [surfactant] forming a plateau [F_{max}]. Considering a 1 : 1 complexation of the dye with the micelle the ($F_{max} - F_o$) can be taken to be proportional to [D_{comp}] as

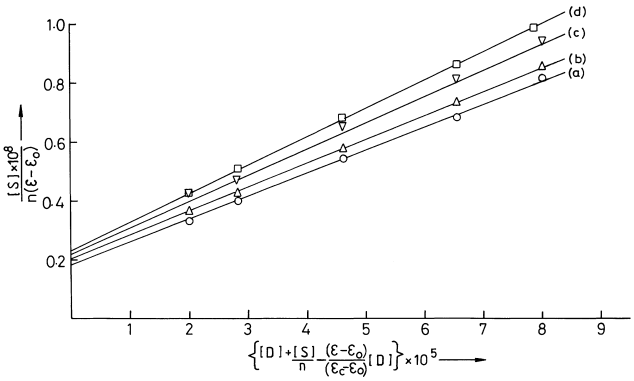

Fig. 3. Plot of $[S]/\{n(\varepsilon - \varepsilon_o)$ vs. $\{[D] + [S]/n - ((\varepsilon - \varepsilon_o)[D])/(\varepsilon_c - \varepsilon_o)\}$ (a) Tween 20, (b) Tween 40, (c) Tween 60, (d) Tween 80.

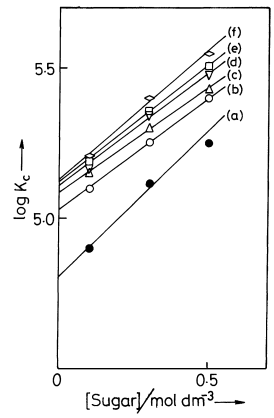

Fig. 4. Plot of log K_c vs. [sucrose] (a) SDS, (b) Tween 20, (c) Tween 40, (d) Tween 60, (e) Tween 80, (f) Triton X-100.

Table 3
The ST–micelle binding constant, K_c and the aggregation number, n for surfactants in the presence of carbohydrate at 298 K

[Carbohydrate]/mol dm^{-3}	10^{-5} K_c/10^{-5} K_c'/n					
	SDS	Tween 20	Tween 40	Tween 60	Tween 80	Triton X-100
Sucrose						
0.1	0.75	1.5	1.6	1.8	2.0	1.6
	0.80	1.2	1.6	1.7	1.9	1.5
	95	85	98	115	125	142
0.3	1.5	1.8	2.1	2.4	2.5	2.3
	1.4	1.6	2.0	2.2	2.3	2.2
	106	86	100	120	130	150
0.5	1.8	2.3	2.7	3.0	3.2	2.8
	1.4	2.1	2.6	2.9	3.1	2.8
	128	90	112	126	132	160
Glucose						
0.1	0.70	1.6	1.8	1.9	2.5	1.3
	0.80	1.4	1.8	1.9	2.5	1.5
	90	82	95	115	133	140
0.3	0.9	1.8	2.2	2.3	2.7	2.7
	0.9	1.7	2.0	2.3	2.8	2.6
	104	85	100	124	128	145
0.5	1.5	2.4	2.8	2.9	3.5	3.1
	1.4	2.1	2.7	3.0	3.6	2.8
	120	90	110	125	130	150
Maltose						
0.1	0.80	1.4	1.7	1.9	2.1	1.7
	0.65	1.3	1.6	1.9	2.2	1.7
	95	84	96	114	125	144
0.3	1.6	1.8	2.2	2.5	2.6	2.4
	1.4	1.8	2.1	2.3	2.4	2.3
	110	86	100	120	130	150
0.5	1.8	1.9	2.6	3.1	3.3	2.8
	1.8	2.1	2.6	3.2	3.4	2.8
	125	88	110	125	132	160
Galactose						
0.1	0.71	1.4	1.7	1.85	2.4	1.3
	0.65	1.3	1.65	1.80	2.4	1.3
	90	84	94	115	125	140

n values in absence of additives: SDS: 50, Tween 20: 86, Tween 40: 92, Tween 60: 112, Tween 80: 124, Triton X-100: 134.

reported earlier [15]. $[D_{comp}]$ is the maximum concentration of dye–micelle combine. At any other state of enhanced fluorescence (F),

$$[F - F_o] = K[D'_{comp}] \quad (5)$$

$$[F_{max} - F_o] = K[D_{comp}] \quad (6)$$

$[D'_{comp}]$ is the complex corresponding to F. Considering the complexation equilibrium (2) and combining Eqs. (5) and (6) we get,

$$\frac{1}{(1 - F_R)} = \left(\frac{K'_c}{n}\right)\frac{[S]}{F_R} - K'_c[D_T] \quad (7)$$

F_R is the ratio of the enhanced fluorescence intensity at any stage to its maximum value, i.e. a measure of the fraction of the dye in the complexed form, i.e. $F_R = (F - F_o)/(F_{max} - F_o)$ $[D_T]$ is total concentration of dye.

A plot of $(1 - F_R)^{-1}$ versus $[S]/F_R$ should be linear to yield K'_c and n from the intercept and the slope, respectively. The K'_c and n values are presented in Table 3. The derived n and K'_c values are aggregation number and binding constant of the dye with micelle in the presence of sugars, respectively. For SDS a sharp increase in the n values was observed in the presence of sugar where as in the case of non-ionic surfactants, the increase in n value was not so large.

4. Discussion

The results indicate that sugars have appreciable effect on micellization characteristics of ionic surfactants SDS and non-ionic surfactants Tweens and Triton X-100. The effect of sugars, i.e. glucose, sucrose, maltose and galactose on the CMC of the surfactants are given in Table 1. The CMC of a surfactant may increase or decrease depending on the nature and type of the additive. For ionic micelles, the thermodynamic parameters are complex since both hydrophobic and electrostatic interaction are involved in the interaction process. For non-ionic surfactants the thermodynamic parameters are obviously less complex. Sugars are non-ionic

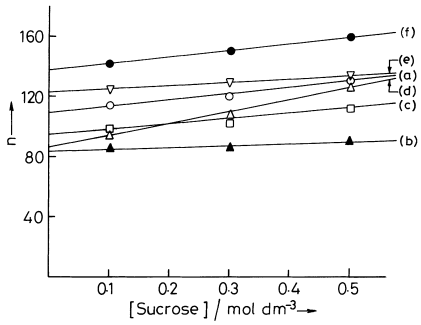

Fig. 5. Plot of aggregation number vs. [sucrose] (a) SDS, (b) Tween 20, (c) Tween 40, (d) Tween 60, (e) Tween 80, (f) Triton X-100.

compounds. Their effects on non-ionic surfactants has a different dimension than on the ionic surfactant SDS. From Table 1 it is found that the CMCs of ionic and non-ionic surfactants decrease in the presence of sugars. For ionic surfactant the decrease is more compared to the non-ionics. Kanungo et al. [17] have reported that the CMC of CTAB, a cationic surfactant increased gradually with the addition of glucose and sucrose. It was reported earlier [18] that the CMC of CTAB in aqueous dextrose solution initially increases and then decreases with the addition of sugar. According to Fendler and Fendler [1], the CMC of non-ionic surfactant Triton X-100 decreases with increasing concentration of sucrose. For the authentication of our results, we determined the CMC values spectrophotometrically, tensiometrically and spectrofluorimetrically. All the three methods gave the same trend in CMC. It is considered that due to hydrophobic interaction icebergs are formed around the non-polar tails of the surfactants which need to be united during micelle formation. In the presence of carbohydrates water–water interaction is replaced by water–sugar interaction, the chances of iceberg formation to protect the monomers becomes less. As a consequence micelle formation is favoured and CMC is lowered. In glucose and galactose there are six O–H linkages and the effect of the two are identical. Similarly sucrose and maltose have 12 O–H linkages and the effect of the two are also identical. This is a straight forward correlation of CMC with the studied carbohydrates. The decrease in CMC of surfactants is accompanied with an increase in the aggregation number of the micelles (Fig. 5) as shown in Table 3. The lowering of CMC is in favour of carbohydrate induced phasing out of the amphiphiles accompanied by a favourable micellar growth. Lesser entrapment probability of the non-polar-ends of the amphiphile molecules by inefficient ice-berg formation leads to a better intramolecular association leading to increasing of n. The decreasing effect of the sugars on CMC of surfactants is correlated in the Eq. (1). The n values for the studied surfactants in the presence of glucose and sucrose are given in Table 3.

The binding constant values of ST with surfactants in the presence of sugars follow the Eq. (4). The B value for SDS is greater than those for Triton X-100 and Tweens (Table 2). Obviously the sugars affected the micellization of SDS more than the non-ionics. The difference lies in the ion–dipole interaction between the anions of the SDS and the polar carbohydrates and the dipole–dipole interaction between the polyoxyethylene head groups and the carbohydrates for the non-ionic surfactants. The former reduces the repulsion factor with a consequence of effective lowering of CMC.

5. Conclusions

The CMC values of SDS, Triton X-100 and Tweens decrease where as the aggregation numbers increase in aqueous carbohydrate medium. The effects are more for the ionic surfactant SDS. The CMC and n both linearly depend on [carbohydrate]. The interaction of ST with micelles increases in the presence of carbohydrates. The activities of different carbohydrates in this respect are more or less equal.

Acknowledgements

The work was supported by a senior fellowship of U.G.C. to K. Acharya.

References

[1] J.H. Fendler, E.J. Fendler, Catalysis in Micellar and Macromolecular Systems, Academic Press, New York, 1975.
[2] K. Acharya, S.C. Bhattacharya, S.P. Moulik, Ind. J. Chem. 36A (1997) 137.
[3] P. Lianos, R. Zana, J. Phys. Chem. 84 (1980) 3339.
[4] M. Alamgreen, S. Swarup, J. Phys. Chem. 87 (1983) 876.
[5] J.E. Lofroth, M. Alamgreen, J. Phys. Chem. 86 (1982) 1636.
[6] S.C. Bhattacharya, H. Das, S.P. Moulik, J. Photochem. Photobiol. A Chem. 79 (1994) 109.
[7] P. Ray, S.C. Bhattacharyya, S.P. Moulik, J. Photochem. Photobiol. A Chem. 108 (1997) 267.
[8] K. Acharya, S.C. Bhattacharya, S.P. Moulik, J. Photochem. Photobiol. A Chem. 109 (1997) 29.
[9] S.P. Moulik, S. Gupta, A.R. Das, Can. J. Chem. 67 (1984) 356.
[10] S.P. Moulik, S. Roy, A.R. Das, J. Phys. Chem. 81 (1977) 1766.
[11] R.D. Vold, M.J. Vold, Colloid and Interface Chemistry, Addison-Wesley, Reading, MA, 1983.
[12] S. Voyutsky, Colloid Chemistry, Mir Publishers, Moscow, 1978.
[13] R.P. Lang, J. Am. Chem. Soc. 84 (1962) 1185.
[14] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
[15] S.C. Bhattacharya, H. Das, S.P. Moulik, J. Photochem. Photobiol. A Chem. 74 (1993) 239.
[16] S. Basu, J. Photochem. Photobiol. A Chem. 56 (1991) 339.
[17] S.K. Kanungo, B.K. Sinha, J. Ind. Chem. Soc. LXI (1984) 964.
[18] A.K. Rakshit, S. Narayan, Ind. J. Chem. 25A (1986) 95.