Effect of Surfactants on Kinetics of Alkaline Fading of Crystal Violet & Acid-catalyzed Inversion of Sucrose

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The kinetics of (i) alkaline fading of Crystal Violet (CV$^+$) $[=\overset{+}{C}\{-\phi N(CH_3)_2\}_3]$ and (ii) acid-catalysed inversion of sucrose have been investigated in aqueous media in the presence of cationic surfactant cetyltrimethylammonium bromide (CTAB), anionic surfactant sodium dodecyl sulphate (SDS) and neutral surfactant Triton X-100 (TX). At [surfactant] above and below their cmcs CTAB accelerates the rate of alkaline fading of the dye, being active specially above its cmc; SDS strongly inhibits the reaction well below its cmc; and TX is only feebly catalytic. The rate enhancement and inhibition are rationalized in terms of various factors like dye-surfactant complexation, double layer effect around micelles of CTAB or formation of mixed micelles by SDS and also possible shift of monomer⇌dimer equilibrium of CV$^+$. In contrast, the surfactants show hardly any effect on the acid-catalyzed inversion of sucrose which, as expected, occurs only in the aqueous phase due to strong hydrophilicity of both sucrose and hydrogen ions, throughout the surfactant concentration ranges employed.

Recently Kundu and coworkers have studied the medium effects on the kinetics of alkaline fading of Crystal Violet (CV$^+$) $[=\overset{+}{C}\{-\phi N(CH_3)_2\}_3]$[1a] and acid-catalyzed inversion of sucrose (Suc)[1b] in a host of aquo-or ionic solvents with varying acid-base characters. The results indicated that the kinetics of these reactions were amply guided by the relative solvation of the reactants, viz. CV$^+$ and OH$^-$ or Suc and H$^+$ respectively in these solvents. It is well known[2-19] that surfactants often affect the kinetics of various types of organic reactions particularly above their critical micelle concentrations (cmc). The surfactant molecules may interact with the reactant molecules and thus change their solvation behaviour variously. Despite extensive investigations on the role of surfactant, there appears to be little understanding of the effect of the surfactants on the structural aspects of reactant organic substrates, the possible specific surfactant-substrate interactions, vis-a-vis their effects on miceller catalysis in general.

In the present paper we report our results of investigations on the effects of cationic surfactant, cetyltrimethylammonium bromide (CTAB), the anionic surfactant sodium dodecyl sulphate (SDS) and the non-ionic surfactant Triton X-100 (TX) on the kinetics of alkaline fading of CV$^+$ as well as H$^+$-catalyzed hydrolysis of Suc both above and below the respective cmc regions of the surfactants. Notably Dyunstee and Grunwald[4] have studied the kinetics of alkaline fading of CV$^+$ in the presence of CTAB and SDS at one concentration far above the cmc of the respective surfactants. However, in view of the fact that dyes having a tri-

phenylcarbonium ion (e.g. CV$^+$) are usually prone to undergo complexation[20] with these surfactants it was considered extremely useful to extend these reaction kinetics even to the pre-micellar concentration (pmc) region and analyze the results of spectral scans for such solutions. This may help in understanding the catalytic effects of micelles free from those unrelated to micellization. Besides, since the complexation processes might induce shift in cmc's[21a] of the surfactants, as OH$^-$ often does[21b], the determination of their cmc's in presence of CV$^+$, sucrose and OH$^-$ was considered equally useful.

Materials and Methods

The Crystal Violet chloride (E Merck), TX (Reidel) and sucrose (AR, Glaxo) were used as received. CTAB and SDS (both AR, BDH) were purified by the methods described earlier[22a] and their purity verified from surface tension (γ) measurement of their solutions by the absence of any minima in γ-concentration profiles[22b]. The cmc values of the samples in pure water were found to be 8-9 × 10^{-4} mol dm^{-3} for CTAB, 8 × 10^{-3} mol dm^{-3} for SDS and 2.2 × 10^{-4} mol dm^{-3} for TX, which agree fairly well with the respective literature data[22]. Sodium hydroxide (GR, E Merck) and HCl (AR, Glaxo) were used as such. All solutions were prepared in triply distilled water and all the experiments were carried out at 25°C.

The rate constants for alkaline fading of CV$^+$ were determined by following the decrease in its absorbance at 590 nm[23] in the presence of various surfactants at four different concentrations of

NaOH employing a Systronic spectrophotometer [model MK (II)−106]. While the CV$^+$ concentration was kept fixed at 0.65×10^{-5} mol dm^{-3}, the range of surfactant concentration employed were 1.2×10^{-4}-5.7×10^{-3} for CTAB; 2.5×10^{-5}-6.0×10^{-4} for TX and 1×10^{-5}-7.3×10^{-2} mol dm^{-3} for SDS. The required NaOH concentrations were of the order of 10^{-3} mol dm^{-3} (ranging from 0.55×10^{-3}-1.36×10^{-3} mol dm^{-3}) for CTAB and TX as also for water, whereas for SDS the NaOH concentration was of the order of 1 mol dm^{-3} (ranging from 0.3-0.7 mol dm^{-3}), except for the three initial concentrations of SDS (1×10^{-5}-3.5×10^{-5}) where about 10^{-2} mol dm^{-3} NaOH (ranging from 0.5×10^{-2} to 1.3×10^{-2} mol dm^{-3}) was required.

The rate constants for the inversion of Suc were obtained by observing the angle of rotation of monochromatic sodium (D) light, with the help of a Hilger standard polarimeter (MK III) (Watts Microptic, England). These observations were made with a 10% sucrose solution in the presence of surfactant concentrations varying from 1.2×10^{-4}-5.7×10^{-3} for CTAB, 2.5×10^{-5}-6.0×10^{-4} for TX and 1.2×10^{-5}-7.3×10^{-2} mol dm^{-3} for SDS. For the infinity readings the reaction mixtures were kept overnight. All these measurements were performed at 25°C.

The cmc values of CTAB and SDS in the presence of the substrates were determined from the measurement of conductance of solutions using a Phillips PR 9500/90 conductivity bridge, while those of TX in the presence of substrates were obtained by measuring the surface tension (γ) of solutions by drop weight method using a stalagmometer. In such measurements the substrate concentrations were kept constant at the values at which the kinetics of their respective solutions were followed. Because, in the presence of 1 mol dm^{-3} NaOH the conductance of the SDS−NaOH mixed solutions would not change appreciably, the cmc of SDS in the presence of 1 mol dm^{-3} NaOH was also estimated from γ-values.

Spectra of the dye-surfactant solutions covering a range of 460 to 630 nm were taken at a fixed CV$^+$ concentrations [0.85×10^{-5} for CTAB and TX and 0.65×10^{-5} mol dm^{-3} for SDS] varying the [surfactant] in the range of 1.5×10^{-4}-5.0×10^{-3} for CTAB, 2.0×10^{-5}-2.0×10^{-3} for TX and 1×10^{-5}-6.4×10^{-2} mol dm^{-3} for SDS.

Results

Alkaline fading of Crystal Violet:

As is well known[1,24] coloured CV$^+$ in aqueous solution remains in equilibrium with the colourless

Table 1—Rate Constants (k_{sf}) of Alkaline, Fading of Crystal Violet in Presence of Various Surfactants at Different Concentrations and 25°C

[Concentrations in mol dm^{-3} and k_{sf} in dm^3 mol^{-1} s^{-1}]

CTAB		SDS		TX	
$C_{sf} \times 10^3$	k_{sf}	$C_{sf} \times 10^2$	$k_{sf} \times 10^3$	$C_{sf} \times 10^4$	k_{sf}
5.70	5.7	7.28	6.3	6.0	0.8(0.7)
4.80	7.2	6.30	6.8	4.0	0.8(0.7)
3.80	8.3	5.39	7.9	2.0	0.8(0.7)
2.90	8.3	4.54	7.8	1.0	0.8(0.7)
1.90	7.7	3.59	8.7	0.5	0.8(0.7)
1.35	6.3	2.70	8.6	0.25	0.8(0.7)
0.95	5.0	1.80	8.5		
0.75	1.5(1.3)	0.90	9.3		
0.48	0.6(0.5)	0.35	5.2(1.7)		
0.24	0.2(0.2)	0.27	4.5(1.6)		
		0.18	4.2(1.4)		
		0.13	3.7(1.2)		
		0.09	2.1(0.7)		
		0.06	2.8(0.9)		
		0.004	55(27)		
		0.002	153(82)		
		0.0012	187(100)		

$(k^0_{H_2O})^{25°}C = 0.19$ dm^3 mol^{-1} sec^{-1} (see ref. 1a)

Data in parentheses refer to k^0_{sf} as obtained by use of Eq. (3)
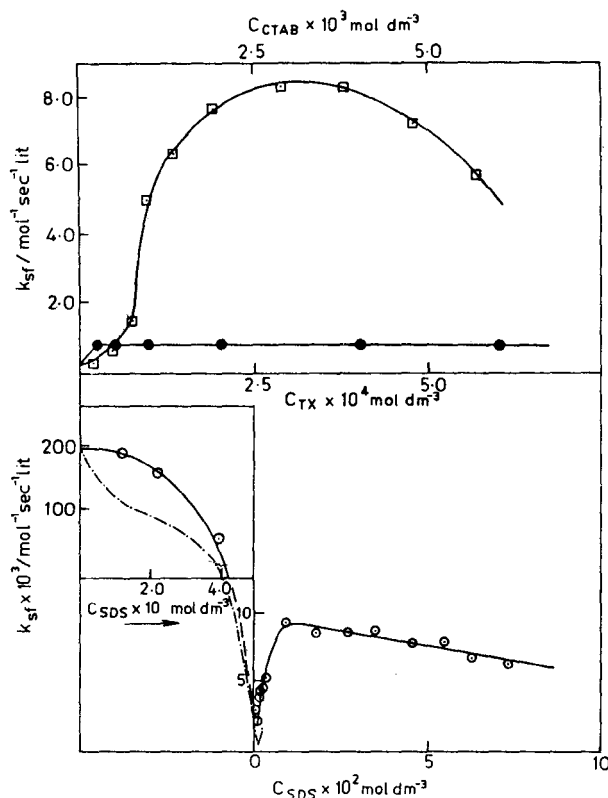

Fig. 1—Variation of rate constants (k_{sf}) for alkaline fading of Crystal Violet in presence of SDS (o), TX (●) and CTAB (□) of varying concentrations at 25°C [------- curve represent the variation of k^0_{sf} with SDS concentration]

carbinol (CVOH) (Eq. 1). In the presence of alkali, the backward reaction becomes practically insignificant as compared to the forward one, i.e. fading of CV$^+$ and the decoloration reaction could be followed spectrophotometrically.

$$CV^+ + OH^- \rightleftharpoons CVOH \qquad \ldots (1)$$

The rate of reaction (1) would be given by Eq. (2)

$$\frac{d[CV+]}{dt} = k_{sf}[CV^+]^{-m}[OH^-]^n = k_1[CV^+]^m \ldots (2)$$

where m and n are the orders with respect to CV$^+$ and OH$^-$ respectively, k_1 is the pseudo-unimolecular rate constant; and k_{sf} the second order rate constant in the presence of surfactants. The k_{sf} values, as also the m and n values were obtained following standard procedures[1a,24] and determining the pseudo-first order rate constants at four different [OH$^-$]. The k_{sf} values are given in Table 1.

Notably, as the reaction is essentially between two oppositely charged ions, a considerable primary salt effect arising out of electrostatic interactions between the charged species present in the solution would be involved[24]. The rate constant free from such effect (k_{sf}) could be obtained using Bronsted-Bjerrum equation[24] (see Eq. 3).

$$\log k_{sf} = \log k_{sf}^0 + 1.02\, z_1 z_2 \mu^{1/2}(1+\mu^{1/2})^{-1} \qquad \ldots (3)$$

where z_1 and z_2 are charges on the reactant ions and μ is the ionic strength of the solution.

Admittedly, application of Eq. (3) to micellar solutions above cmc region is not permissible in view of the uncertainties in the degree of aggregation of surfactant molecules in the presence of OH$^-$ and CV$^+$. However, since we are specially interested in pmc region, the k_{sf}^0 values for such regions employing Eq. (3) were computed and the values are presented in Table 1 and plotted versus [surfactant] in Fig. 1. Notably the $k_{sf}^0 - C_{SDS}$ profile (Fig. 1) is more or less similar to that of $k_{sf} - C_{SDS}$ profile, although correction of the ionic strength effect in the pmc region of the SDS shifts the $k^0 - C_{SDS}$ profile slightly downward, as the concentration of NaOH used in that region is of the order of 0.01 mol dm^{-3}. But for CTAB and TX, the effect is fairly insignificant as the concentration of NaOH used is of the order of 0.001 mol dm^{-3}.

The spectra of the dye in aqueous as well as surfactant added solutions at different concentrations of CTAB, TX and SDS are shown in Fig. 2a-c. Because of similarity of such curves in the cases of CTAB and TX only a few representative curves are shown in Fig. 2(b) and (c). The conductance (L) or surface tension (γ) values for the

respective surfactants at varying concentrations, in the presence of fixed [CV$^+$] (0.65×10^{-5} mol dm^{-3}) or [NaOH] (1.0 mol dm^{-3}) are given in Table 2. The cmc values thus obtained are presented in Table 3.

Inversion of sucrose

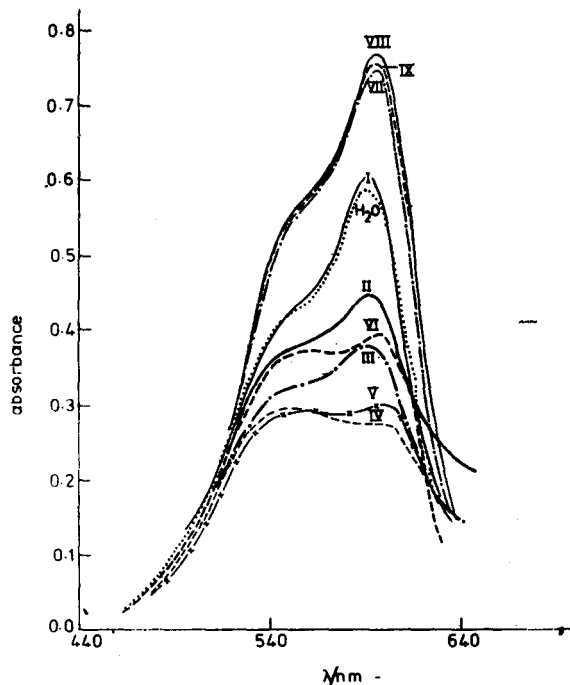The reaction for the acid-catalyzed inversion of sucrose[1b] can be represented by Eq. (4)[1b]

Fig. 2a—Spectra of CV$^+$ [0.65×10^{-5} mol dm^{-3}] at 25°C in presence of SDS at various concentrations [I = 1.16×10^{-5}, II = 6.96×10^{-5},   III = 9.28×10^{-5},   IV = 6.96×10^{-4}, V = 9.28×10^{-4},   VI = 1.04×10^{-3},   VII = 2.65×10^{-3},   VIII = 4.41×10^{-3}, 1.77×10^{-2}, IX = 4.4×10^{-2}; 5.3×10^{-2} and 6.4×10^{-2} mol dm^{-3} SDS]
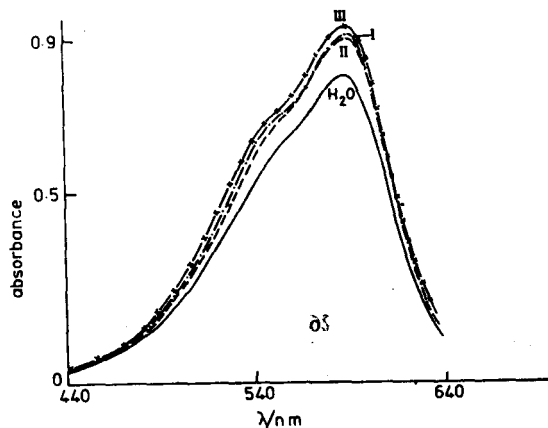

Fig. 2b—Spectra of CV$^+$ [0.85×10^{-5} mol dm^{-3}] at 25°C in presence of CTAB at various concentrations [I = 2.85×10^{-3}, II = 1.90×10^{-3}, III = 0.24×10^{-3} mol dm^{-3} CTAB]
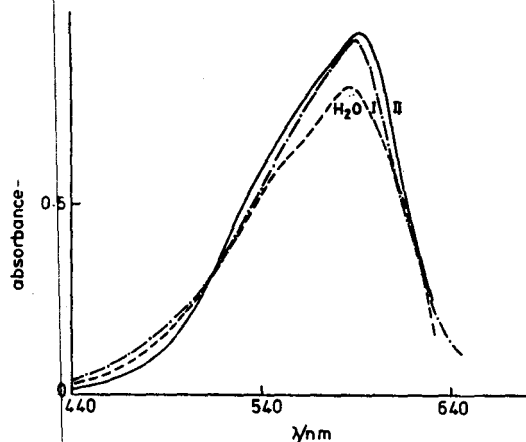
Fig. 2c—Spectra of CV^+ [0.85×10^{-5} mol dm^{-3}] at 25°C in presence of TX at various concentrations [I = 1.36×10^{-4}, II = 16.26×10^{-4} mol dm^{-3} TX]

Table 2—Conductance (L) and/or Surface Tension (γ) of CTAB, SDS and TX Solutions of Different Concentrations in Presence of Crystal Violet (0.65×10^{-5} mol dm^{-3}), Sucrose (10%) and/or Sodium Hydroxide (1 mol dm^{-3}) at 25°C

[C_{sf} in mol dm^{-3}, L values in mhos; γ in dyne/cm^1]

CTAB + Crystal Violet		SDS + Crystal Violet		SDS + NaOH	TX + Crystal Violet	
$C_{sf} \times 10^2$	$L \times 10^4$	$C_{sf} \times 10^2$	$L \times 10^3$	γ	$C_{sf} \times 10^3$	γ
0.86	6.50	8.15	5.26	29.80	1.94	32.35
0.57	5.71	5.43	4.17	30.25	1.30	33.20
0.48	3.23	4.52	3.85	30.25	1.08	33.50
0.29	3.44	2.72	2.17	30.30	0.65	34.00
0.25	3.45	2.41	2.19	—	0.43	34.20
0.19	2.94	1.81	1.49	30.15	0.22	34.80
0.16	2.70	1.51	1.59	—	0.11	37.20
0.12	1.76	1.21	1.16	30.10	0.06	39.70
0.085	2.22	0.91	0.87	30.00		
0.048	1.18	0.45	0.57	30.40		
0.024	0.63	0.30	—	30.50		
		0.23	0.29	31.50		
		0.18	—	34.00		
		0.10	—	37.50		
		0.05	—	42.40		

CTAB + Sucrose		SDS + Sucrose		TX + Sucrose	
0.71	4.9	6.79	3.43	1.96	36.87
0.59	4.1	5.66	2.82	1.30	36.92
0.48	3.5	4.53	2.56	1.10	36.90
0.36	3.1	2.26	1.63	0.94	36.97
0.30	2.7	1.70	1.22	0.65	36.70
0.24	2.3	0.85	0.83	0.40	36.60
0.18	1.9	0.57	0.64	0.20	36.20
0.12	1.9	0.28	0.034	0.16	34.93
0.06	1.2	0.17	0.022	0.10	34.60
0.03	0.7				

Table 3—CMC Values (in mol dm^{-3}) of CTAB, SDS and TX Solutions in Presence of Crystal Violet (0.65×10^{-5} mol dm^{-3}), Sucrose (10%) and/or Sodium Hydroxide (1 mol dm^{-3}) at 25°C

| Surfactant	cmc values in presence of		
	CV^+	Suc	$NaOH$
CTAB	9.0×10^{-4}	8.0×10^{-4}	—
SDS	4.4×10^{-2}	8.0×10^{-3}	2.4×10^{-3}
TX	2.3×10^{-4}	2.2×10^{-4}	—

Literature values of Cmc's (mol dm^{-3}) of the surfactants in water (a) CTAB: $8-9 \times 10^{-4}$; (b) SDS: $8-9 \times 10^{-3}$ and (c) TX: $2-4 \times 10^{-4}$ [vide ref 21a and relevant references therein]

Table 4—Rate Constants (k_i) for Acid-Catalyzed Inversion of Sucrose in Presence of Surfactants at Different Concentrations at 25°C

[C_{sf} in mol dm^{-3}; k_i in min^{-1}]

CTAB		SDS		TX	
$C_{sf} \times 10^4$	$k_i \times 10^3$	$C_{sf} \times 10^3$	$k_i \times 10^3$	$C_{sf} \times 10^4$	$k_i \times 10^3$
1.24	2.4	1.16	2.2	0.28	2.0
2.38	2.6	2.24	1.9	0.54	2.2
4.79	2.2	4.56	2.0	1.09	2.9
9.50	2.3	9.05	2.0	2.16	2.6
19.0	2.6	18.10	2.0	4.32	2.3
26.5	2.0	27.15	1.9	6.49	2.3

$(k_i)_{H_2O} = 1.9 \times 10^{-3}$ min^{-1} (see ref. 1b)

$$C_{12}H_{22}O_{11} + H_2O \overset{H^+}{\rightleftharpoons} 2\ C_6H_{12}O_6 \qquad \ldots (4)$$
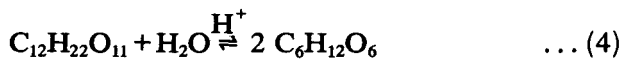
At constant [H^+] the reaction follows pseudo-first order kinetics which could be studied polarimetrically. The values of the rate constants (k_i) were obtained as usual[1b] from the slopes of the first order linear plots of $-\ln (R_t - R_\infty)$ versus t where R_t and R_∞ represent the angle of rotation at time t and final (infinity) time respectively. The k_i values obtained at [HCl] = 0.25 mol dm^{-3} are given in Table 4.

The cmc values of the detergents in the presence of 10% sucrose solution were also estimated from respective conductance (L) or surface tension values (given in Table 2) and are presented in Table 3.

Discussion

Kinetics of alkaline fading

Figure 1 shows that with addition of CTAB at concentrations well below its cmc, the k_{sf} value increases, though rather slowly, from k_{H_2O} (the k-values in water)[1a] up to its cmc. Beyond cmc, the k_{sf} values increase steadily with increase in [surfactant] eventually showing a broad maximum

around $[CTAB] = 3.3 \times 10^{-3}$ mol dm^{-3}. As for TX the k_{sf} value increases by about four times the k_{H_2O} value and then remains the same even beyond cmc of TX. The magnitude of increase in k_{sf} is small as compared to that observed above cmc of CTAB. The addition of SDS, on the other hand, retards the rate of reaction at a galloping rate for concentrations well below the cmc of the surfactant (inset in Fig. 1). The decreasing trend in k_{sf} values continues up to $C_{SDS} \approx 1 \times 10^{-3}$ mol dm^{-3}. The rate constant then increases, at first steeply and then slowly, to pass through a maximum at the original cmc of SDS (8×10^{-3} mol dm^{-3}). Beyond this there is again a very slow decrease in k_{sf} values.

Cmc in presence of CV$^+$

When CV$^+$ (0.65×10^{-5} mol dm^{-3}) is added to SDS, its cmc value increases from 8×10^{-3} to 4.4×10^{-2} mol dm^{-3}, contrary to that observed in the presence of salts[21b]. This seemingly unusual shift in cmc indicates a strong dye-surfactant interaction. The cmc values of CTAB and TX on the other hand, remain unperturbed in the presence of CV$^+$ pointing to the not-so-strong dye-surfactant interaction. For understanding the observed kinetic behaviour as well as shift in cmc value of SDS, analysis of the spectra (Fig. 2a-c) should be of particular use.

Spectral analysis

The cationic dye molecules (monomeric) are known to exist in equilibrium with their oligomers (mostly dimers)[21a,25]. Aqueous solutions of CV$^+$, as also the solutions containing the surfactants, show a prominent peak around 590 nm (Fig. 2a-c) presumably due to the monomeric species. An additional peak around 550 nm, prominent in presence of SDS only, probably arises out of the existence of the dimers.

For SDS, depending on its concentration the spectra exhibit extensive variations (Fig. 2a). Three distinct regions are discernible. At very low [SDS], the spectra in general and the peak heights around 590 nm in particular begin decreasing. The feeble dimer shoulder around 550 nm broadens as more SDS is added. The monomer: dimer peak height ratio falls from a value $\gg 1$ to around unity at about 6.96×10^{-4} mol dm^{-3} SDS (Fig. 2a, curve IV) where a maximum broadening of the dimer shoulder along with maximum lowering in absorbance at 590 nm is observed. Beyond this [SDS] the dimer shoulder again gradually recedes away to a hump as feeble as that in pure water. The monomeric peak intensity increases again, eventually surpassing the absorbance value in wa-

ter till 4×10^{-2} mol dm^{-3} SDS. Notably, this is the cmc of SDS in the presence of CV$^+$ (vide Table 3). The monomer: dimer peak height ratio in this region again rises to a value exceeding that in pure water. Ultimately, above this cmc the spectra as well as absorbance at 590 nm become invariant as is also the monomer:dimer peak height ratio.

Plots of variation of the peak absorbance λ value ($\lambda = 590$ nm or 550 nm) versus log [dye]/[surfactant] which are known[21a] to indicate the types of interactions prevailing at any particular [dye]: [surfactant] ratio are shown in Fig. 3 in the case of SDS. Similar plots, resembling a 'potential well', have been observed for other cationic dye molecules as well[21a]. The right hand side of the curves are assumed to be guided[21a] chiefly by coulombic interactions, indicating that ion-ion interactions are prevailing at low [SDS]. Thus observed increase in [dimer] up to 6.96×10^{-4} mol dm^{-3} SDS indicates that the negatively charged surfactant ions induce dimerization of the dye cations[21,25] via electrostatic forces. As these dipositive dimeric species are stabilized by increased coulombic interactions with SDS anions, the $2 CV^+ \rightleftharpoons (CV)_2^{2+}$ equilibrium is shifted gradually in favour of the dimer. At higher [SDS] (left hand side of Fig. 3), hydrophobic effect becomes prominent. Submicellar aggregates of SDS are formed gradually and ion-ion interactions (acting in cooperation with hydrophobic forces) become less important[21a]. The observed increase in absorbance 590 nm values and a declining trend in 550 nm shoulder (Fig. 2a, curves V-VIII) then indicate breaking down of dimeric dye units to monomeric cations and their stabilization via hydrophobic interactions with SDS oligomers. Above 4.4×10^{-2} mol dm^{-3} SDS, as the monom-
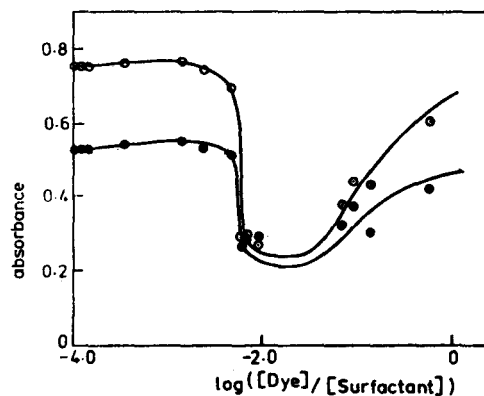

Fig. 3—Plots of absorbance λ [$\lambda = 590$ nm or 550 nm] values against log [Dye]/[Surfactant] for fixed dye concentrations of 0.65×10^{-5} mol dm^{-3} and varying SDS concentrations ranging from $\approx 1 \times 10^{-5}$ to 6.4×10^{-2} mol dm^{-3} [○ = OD at 590 nm; ● = OD at 550 nm]

eric dye species are incorporated in the extended SDS-dye mixed micelles[26], essential constancy of the forces involved lead to the plateau of curves in Fig. 3 and practically invariant absorbance values (Fig. 2a curve IX). Only a slight variation could be expected in micellar dilution. The non-availability of the surfactant molecules, engaged in SDS-dye interactions, for micellar aggregation also accounts for the increase in cmc value of SDS from 8×10^{-3} to 4.4×10^{-2} mol dm^{-3} in the presence of the dye.

In the case of CTAB, however, the coulombic forces are repulsive in nature and do not cooperate with hydrophobic forces, while non-ionic TX molecules exert only hydrophobic effects. Expectedly then, the conversion of monomer to dimer is not induced by these surfactants. On the other hand, these two are expected to form complexes with the monomeric dye species via hydrophobic[27] and/or charge transfer[20] interactions and thus shift the monomer ↔ dimer equilibrium in favour of the monomer. This is what has been observed (Fig. 2b and c), as the absorbance values, in general, and those at 590 nm in particular, increase, the dimer hump gets feebler. But this rather inappreciable change in absorbance values, in comparison to that observed in the presence of SDS and the constancy of cmc values even in the presence of CV$^+$, seems to corroborate the view that dispersion and charge transfer interactions are very weak in nature as compared to ion-ion interactions[21]. However, as micelles are formed, the large hydrophobic moieties may have sufficient dispersive interactions[27] resulting from collective effect of large number of molecules incorporated.

Effect of varying [OH$^-$] on cmc

While cmc values of CTAB and TX are not changed by addition of 10^{-3} mol dm^{-3} NaOH, the cmc decreases to a value 2.4×10^{-3} mol dm^{-3} for SDS in the presence of 1 mol dm^{-3} NaOH (vide Table 3). Since these are [OH$^-$] employed in kinetic studies, it is expected that apart from its role as reactant, OH$^-$ also alters the interactions present in SDS solutions. Unfortunately, the estimation of cmc of SDS in the presence of both CV$^+$ and OH$^-$ is forbidden by the chemical reaction that sets in. However, it appears justified to assume that in presence of OH$^-$ the dye-surfactant mixed micelles will be formed at concentration less than 4×10^{-2} mol dm^{-3} but above 2.4×10^{-3} mol dm^{-3} SDS.

Catalytic effect of surfactants

Having established the types of interactions operative in dye-surfactant solutions, the analysis of the k_{sf} − [surfactant] profiles appears rewarding. In the case of CTAB, the initial slow rise in k_{sf} values is attributable to increase in [dye monomer] on the addition of CTAB. When micellization starts, the dye (CV$^+$) molecules, instead of being incorporated within the micellar pseudophase[5], possibly adhere to the outer surface, despite coulombic repulsion, through dispersive type interactions. More explicitly, these organic dye cations (CV$^+$) construct the inner Helmholtz plane (IHP)[28] of the micellar 'microelectrodes', through dispersion interactions in competition with the little hydrated hydrophobic micellar counter ion Br$^-$. Now the approach of hydrophilic reagent OH$^-$ from the bulk to the outer Helmholtz plane (OHP) of these positively charged microelectrodes will obviously depend on the potential difference $(\phi_{IHP} - \phi_b)^{15,29}$, where ϕ_{IHP} and ϕ_b are the potentials at the IHP of the micelle and at the bulk respectively (Fig. 4). Thus with increased addition of CTAB, ϕ_{IHP} increases which facilities more OH$^-$ ions to approach to the microelectrode-water interface and the result is the linear increase in k_{sf} values with [CTAB].

Admittedly, the presence of Br$^-$ ions, which are known to get specifically adsorbed[28] on Hg-surface and possibly on these microelectrode surfaces as well, will hinder the specific adsorption of CV$^+$ forming IHP and also the approach of hydrophilic OH$^-$ towards IHP, usually defined as micelle-water interphase[8], to some extent, so that the desired increase of k_{sf} values as discussed above, may be substantially restricted. The observed broad hump at 3.3×10^{-3} mol dm^{-3} CTAB may be attributed to the completion of the process of accommodating CV$^+$ molecules at the IHP's of the micelles and mere dilution[30] through more micelle formation at still higher [CTAB]. In the case of neutral surfactant TX, ϕ_{IHP} is not at all altered by the addition of TX above cmc and the situation remains the same as at pmc. The rate constants are thus held constant throughout, after an initial enhancement due probably to increased dye monomer contribution.

In the case of SDS, at very low [surfactant] the rate constant is almost identical to that in pure water (inset in Fig. 1), where absorbance $_{590}$ values are also nearly the same (Fig. 2a). As more SDS is added, the [monomeric dye] is decreased substantially resulting in a rapid decrease in k_{sf} values, as observed up to $C_{SDS} = 6.96 \times 10^{-4}$ mol dm^{-3}. From this concentration up to cmc (4.4×10^{-2} mol dm^{-3} of SDS in the absence of NaOH), the concentration of "monomeric dye-SDS oligomer" in-
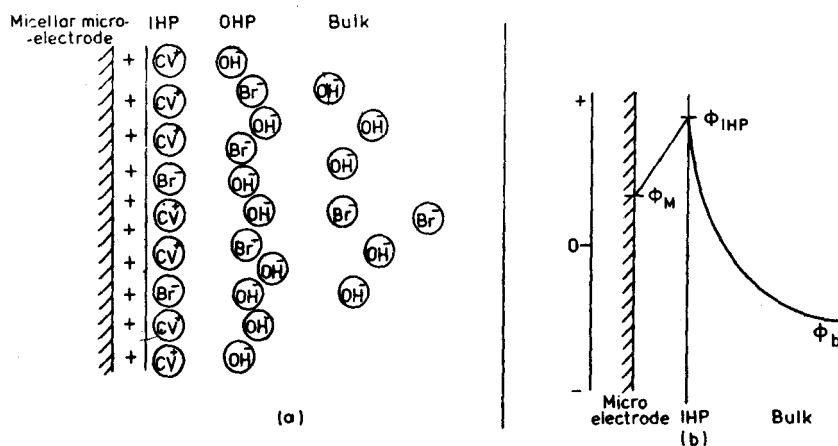
Fig. 4—Distribution of (a) ions and (b) potential around micellar 'micro-electrodes' of CTAB

teracted product increases. While the increased number of monomeric species should enhance the rate of reaction, the negative charge of the SDS oligomers present in these complexes would retard the same by repelling the neucleophile, OH^- ion. Thus the k_{sf} values increase again in this region but the extent of increase is small as compared to the fall and even as the absorbance$_{590}$ values surpass the value in water, the k_{sf} values remain much less than k_{H_2O}. The width of this region, upto which k_{sf} goes on increasing, is however uncertain owing to micelle formation inthe presence of OH^-. From kinetic data, the hump almost at the original cmc of SDS seems to suggest that mixed micelle formation in the presence of 1 mol dm^{-3} NaOH occurs at this concentration. Beyond cmc hardly any dye molecule is left behind. Further addition of SDS is likely to cause simple micellar dilution and hence a very slow decrease in k_{sf} values as has been observed. Obviously the interphase or Stern layer model put forward in the case of CTAB is not applicable here as the reactant CV^+ molecules are the part of the micro-electrode itself and the situation here refers to the pseudophase model[5,18]. Unfortunately, the limitation in using high CV^+ concentrations set by high extinction coefficient of the dye forbid detailed analysis of the suitability of the model.

The results presented above point to following interesting features. (i) It is demonstrated that the surfactants may have significant interactions with the dye molecules even at the pmc region. (ii) In contrast to the popular belief that the kinetic effects involving the surfactants are important only well above their cmc, significant effects might be present in the pmc region as well. In fact, in the present study the decreasing trend in k_{sf} values caused by the addition of SDS was almost over

before the micelles were formed. For TX also, although very little, the effect on k_{sf} observed was achieved at pmc. (iii) When the rate of any reaction is affected by micelles, depending on the type and magnitude of the interaction between the organic molecules and the surfactants, either the 'pseudophase model' or 'interphase model' may be operating. Thus for strong coulombic type of reactant-surfactant interactions extending up to the formation of mixed micelles the pseudophase model seems to be valid, as in the case of SDS. In the case of others involving non-coulombic type interactions, the 'interphase model', better defined by the double layer property of micellar micro-electrodes, is applicable, as was found for CTAB.

In the case of kinetics of inversion of sucrose the rate constants (k_i) practically remain unaltered from that in pure water by the addition of surfactants in both pmc and cmc regions. If one considers that H_3O^+ ions interact differently with the cationic and anionic surfactants and are expected to occupy the 'Stern layer' of SDS micelles, and be repelled by that of CTAB micelles this result appears rather perplexing. On the other hand, this is quite expected in view of the fact that sucrose molecules, with so many hydrophilic groups, undergo strong H-bonded interaction with water molecules, as no electrostatic sucrose-surfactant interaction is being expected. The hydrophobic part of the substrate molecule being well shielded by the hydrophilic OH^- groups, the weak hydrophobic interaction operative between the sucrose-surfactant organic moieties is not able to overcome the effect of hydrophilic bonding and the substrate sucrose molecules remain in the bulk phase. As a result, the reaction occurs chiefly in aqueous phase and the k_i values remain constant. Further support to this observation is obtained

121

from the fact that cmc's of the surfactants remain unaltered in the presence of sucrose. Thus the observed kinetic results with sucrose point out that in such catalysis under investigation, the reaction site is of primary importance.

Acknowledgement

Thanks are due to Dr K Das for helpful discussions and to the CSIR, New Delhi for the award of a research associateship to one of them (JD).

References

1 (a) Mondal U, Sen S, Das K & Kundu K K, *Can J Chem*, 64 (1986) 300; (b) Mondal U, Das K & Kundu K K, *Can J Chem*, 64 (1986) 1638.

2 Fendler J H & Fendler E J, *Catalysis in micellar and macromolecular systems* (Academic Press, New York) 1975.

3 (a) Cordes E H & Dunlap R B, *Acc chem Res*, 2 (1969) 329; (b) Cordes E H ed *Reaction kinetics in micelles* (Plenum Press, New York) 1973; (c) Cordes E H & Geitler C, *Prog bioorg Chem*, 1 (1973) 2; (d) Cordes E H, *Pure appl Chem*, 50 (1978) 617; (e) Albrizzio J, Archila J, Rodulfo T & Cordes E H, *J org Chem*, 37 (1972) 871.

4 Duynstee E F J & Grunwald E, *J Am chem Soc*, 81 (1959), 4540, 4542.

5 Bunton C A, (a) *Pure Appl Chem*, 49 (1977) 969; (b) *Prog Solid State Chem*, 8 (1973) 239; (c) In *solution chemistry of surfactants*, Vol. 2, edited by K L Mittal (Plenum Press, New York) 1977; (d) *Catal Rev Sci-Eng*, 1 (1979) 20; (e) Bunton C A, Carrasco N, Huang S K, Paik C H & Romsted L S, *J Am chem Soc*, 100 (1978), 5420; (f) Bunton C A, Romsted L S & Smith H J, *J org Chem*, 43 (1978), 4299; (g) Bunton C A, Romsted L S & Savelli G, *J Am chem Soc*, 101 (1979), 1253; (h) Al-Lohedan H, Bunton C A & Romsted L S, *J phys Chem*, 85 (1981), 2123; *J org Chem*, 47 (1982) 3528; (i) Al-Lohedan H, Bunton C A & Moflet J R, *J phys Chem*, 87 (1983) 332; (j) Bunton C A, Mhola M M, Moffet J R, Monaners D & Savelli G, *J org Chem*, 49 (1984) 426.

6 Berezin I V, Martiner K & Yatsimerskii A K, *Russ chem Rev*, 42 (1973) 787.

7 Martiner K, Yatsimerskii A K, Vhevashov A & Berzin I V in *Micellisation solubilization and micro-emulsions*, Vol. 2, edited K L Mittal (Plenum Press, New York) 1977, pp. 489.

8 (a) Broxton T J, *Aust J Chem*, 34 (1981) 2313; 35 (1982) 2557; 36 (1983) 2203; 37 (1984) 47; (b) Broxton T J & Sango D B, *Aust J Chem*, 36 (1983) 711.

9 Romsted L S in *Micellization, solubilization and micro-emulsions*, Vol. 2 edited by K L Mittal (Plenum Press, New York) 1977, pp. 509.

10 Nome F, Rubira A F, Franco C & Ionesku L G, *J phys Chem*, 86 (1982) 1881.

11 Dougherty S J & Berg J C, *J Colloid Interface Sci*, 48 (1974) 110; 49 (1975) 135.

12 Brown J M & Darwent J R, *J Chem Soc Chem Commun*, (1969) 171.

13 Dash A C, Dash B & Mahapatra P K, *J chem Soc Dalton*, (1981) 2063, (1983) 1503 and other relevant references therein.

14 Gern L H, *Can J Chem*, 63 (1985) 578.

15 (a) Lelivre J & Gaboriaud R, *J chem Soc Faraday Trans I*, 81 (1985), 335; (b) Gaboriaud R, Charbit G & Dorion F, in *Surfactants in solutions*, Vol. 2, edited by K L Mittal (Plenum Press, New York) 1984, 949.

16 (a) Funasaki N, *J phys Chem*, 83 (1979) 237, 1988; (b) Funasaki N & Murata A, *Chem pharm Bull*, 28 (1980) 805.

17 (a) Quina F H, Chaimovich H, *J phys Chem*, 83 (1979) 1844; (b) Chaimovich H, Bonilha J B S, Politi M J & Quina F H, *J phys Chem*, 83 (1979) 1851; (c) Quina F H, Politi M J, Cuccovia I M, Martins-Franchetti S M & Chaimovich H in *Solution behaviour of surfactants theoretical and applied aspect*, Vol. 2, edited by K L Mittal & F J Fendler, (Plenum Press, New York) 1982, pp. 1125.

18 (a) Cipiciani A, Linda P, Savelli G & Bunton C A, *J phys Chem*, 87 (1983) 5262; (b) Bunton C A, Frankson J & Romsted L S, *J phys Chem*, 84 (1980) 2607; (c) Bunton C A, Hamed F H & Romsted L, *J phys Chem*, 86 (1982) 2103; (d) Bunton C A, Huang S K, *J org Chem*, 37 (1972) 1790; 40 (1976) 41; (e) Bunton C A, Chan S, Huang S K, *J org Chem*, 39 (1974) 1262.

19 Fendler E J & Fendler J H, *Adv phys-org Chem*, 8 (1970) 27.

20 (a) Hayashi H, *Bull chem Soc*, Japan 34 (1961) 119; (b) Rohatgi-Mukherjee K K, Choudhuri R & Bhowmick B B, *J colloid interface Sci*, 106 (1985) 45.

21 (a) Moulick S P, Ghosh S & Das A R, *Colloid polym Sci*, 257 (1979) 645; (b) Evans D N & Ninham B N, *J phys Chem*, 87 (1983) 5020, 5025.

22 (a) Suzuki C H, *Bull chem Soc Japan*, 44 (1971) 2630; (b) Mukherjee P, Cardinal J R, *J phys Chem*, 82 (1978) 1620.

23 *International Critical Tables*, Vol. VII (McGraw Hill, New York) 1930.

24 Carsaro G, *J chem Educ*, 41 (1964) 48.

25 Levshin L V & Gorshkov V K, *Opt Spectrosc*, 10 (1961) 401.

26 Corkill J M, Goodman J F & Tate J R, *Trans Faraday Soc*, 60 (1964) 986.

27 (a) Ben Naim A, *Hydrophobic interactions*, (Plenum Press, New York) (1980); Franks F, Pedlay M D & Reid D S, *J chem Soc Faraday Trans-I*, 72 (1976) 359; (c) Clark A H, Franks F, Padley H D & Reid D S, *J chem Soc Faraday Trans I*, (1977) 290; (d) *The hydrophobic interactions*, *Faraday Soc Symp* (1982); Hertz H G & Leiter A, *Zeit physik Chem Neue Folge*, 33 (1982) 451.

28 Bockris J O'M & Reddy A K N, *Modern electrochemistry*, Vol. 2 (Plenum Press, New York) 1970.

29 Treiner C, Lebesnerais A & Micheletti C, in *Adv Chem Ser* edited by W F Furter, no. 177 (American Chemical Society, Washington) 1979, pp. 109.

30 Bunton C A & Wolfe B, *J Am chem Soc*, 95 (1973) 3742; (b) Bunton C A, Minch M J, Hidalgo J & Sepulveda L, *J Am chem Soc*, 95 (1973) 3262; (c) Buist G J, Bunton C A, Robinson L, Sepulveda L & Stan M J, *J Am chem Soc*, 92 (1970) 4072.