

Influence of non-ionic surfactants on the degree of association and extent of absorption of acid dyes on nylon 6

S R Karmakar, S K Vaidya & M A Desai

Department of Textile Chemistry, Faculty of Technology & Engineering, M.S. University of Baroda,
Baroda 390 001, India

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The interaction of acid dyes and non-ionic surfactants in solution has been studied by the surface tension, viscosity and polarographic techniques. Positive entropy change and low enthalpy change suggest that aggregation is an entropy-determined phenomenon brought about by the hydrophobic bonding. A higher increase in reduced viscosity in the presence of surfactants is explained as an electro-viscous effect due to aggregation. The increase in particle size of acid dyes, determined by polarographic diffusion coefficient, also suggests that the critical micelle concentration decreases with increase in the amount of surfactants. From the sorption behaviour of acid dyes in the presence and absence of surfactants on nylon 6, a possible mechanism of interaction in the dyeing process is discussed from the practical dyeing point of view to produce retarding and levelling effects.

Keywords: Acid dyes, Aggregation number, Dye sorption, Diffusion coefficient, Non-ionic surfactant, Surface tension, Viscosity

1 Introduction

The results of interaction of non-ionic surfactants and some acid dyes in aqueous solution have been reported earlier^{1,2}. One of the most striking features of these studies is the association of dye and surfactant in solution where more than one mole of dye is bound by each mole of surfactant, indicating the existence of micelles in addition to that of hydrophobic bonding responsible for binding.

A literature survey indicates that very little information is available on the surface tension of acid dyes in surfactant solution. Some of the workers³⁻⁵ have, however, tried to demonstrate that anionic dyes tend to concentrate at air-water interface and the break in the curve of surface tension vs. concentration of surfactant due to micelle formation but they have not discussed the results from the thermodynamic point of view. Though considerable work⁶⁻⁸ has been done on the rate of uptake of acid dyes, the behaviour of non-ionic surfactants with respect to level dyeing on nylon is not clear because of the dearth of information about the system containing both dye and surfactant.

In the present work, the interaction of acid dyes and non-ionic surfactants of varying ethylene oxide lengths in solution has been investigated by

the surface tension, viscometric and polarographic techniques. Also, the influence of surfactants on the rate of sorption of some acid dyes on nylon 6 has been investigated.

2 Materials and Methods

2.1 Materials

2.1.1 Dyes and Surfactants

Six commercial dyes, viz. Acid Red 88, Acid Red 14, Acid Red 18, Acid Brown 14, Acid Blue 113 and Acid Blue 120, were used. The method of purification of these dyes and their structures and colour index numbers have been reported earlier¹. Three non-ionic surfactants with increasing length of the ethylene oxide chain links, viz. Hyoxid X 100, Hyoxid X 200 and Hyoxid X 400 (supplied by Hico Products Ltd, Bombay), were used. The specifications and properties of these surfactants have been reported earlier¹.

2.1.2 Fibre

Nylon 6, 15-denier monofilaments were used. They were purified by treating with 0.01 M sodium carbonate and 0.05% Lissapol N at 60°C for 30 min followed by washing with water, drying and conditioning.

2.2 Methods

2.2.1 Measurement of Surface Tension

The stock solutions (1.0×10^{-3} M) of dye and surfactant were prepared in double distilled water and the exact volumes were mixed together to get the solutions with different surfactant-to-dye (S/D) ratios. The surface tension of these solutions was measured by means of a du Nouy surface tension balance (in each case on the three separate samples of the same solution) after allowing the surfaces to age for 30 min prior to measurement. The surface tension of double distilled water was 72.05 dynes/cm at 30°C. Measurements were carried out at 30, 40 and 50°C. The critical micelle concentration (CMC) of surfactants was determined as the concentration at the intersection of the two lines obtained by plotting the surface tension against concentration. Several thermodynamic parameters like free energy, heat and entropy of micellization were determined.

2.2.2 Measurement of Viscosity

An Ubbelohde dilution viscometer was used. The efflux time for water at 30°C was 193 s. The kinetic energy correction under these conditions is small and was therefore neglected. The measurements were carried out at 30, 40, 50 and 60°C and the reduced viscosities were determined from the flow time at different concentrations of surfactants.

2.2.3 Determination of Dye Aggregation

A Systronic polarograph (type 1632) was used to measure the diffusion current (i_d) of dye solution at 30°C. The dropping mercury electrode had the following characteristics: $m = 1.224$ mg/s [in pure water at zero applied potential vs. standard calomel electrode (SCE)] and a drop time of about 2 s (in pure water at 0.75 V vs. SCE). The height of mercury head was 78 cm. Since the current is diffusion controlled, the diffusion coefficient (D) of the reductive particles was calculated from the Ilkovic equation⁹ and since the diffusion coefficient can be related to molecular weight of diffusing species, the apparent molecular weights of the dyes and, consequently, the aggregation numbers were determined using the procedure suggested by Hilson and McKay¹⁰.

2.2.4 Determination of Dye and Surfactant Sorption

Nylon fibres (1.0 g) were treated with agitation in 100 ml baths containing dye and/or surfactant. The dye concentration, if not zero, was $1.25 \times$

10^{-5} M except in the case of Acid Blue 120 where it was 1.10×10^{-5} M. Dye bath was buffered at pH 3.7. Dyeing was started at 50°C and the temperature was raised to 95°C in 30 min. The fibres were dyed for 3 h. After every 15 min, 0.5 ml solution was pipetted out and diluted to 5 ml with blank solution and optical density was measured. The amount of dye sorbed by the fibre was then calculated from the standard calibration graph of the dye. The amount of surfactant sorbed was determined from the blue complexes with ammonium cobalt thiocyanate and extracted with 1,2-dichloroethane and measured spectrophotometrically¹¹.

3 Results and Discussion

The data on surface tension were plotted against the logarithms of the surfactant concentrations in the presence/absence of acid dye. Fig. 1 shows the typical plots in presence of some acid dyes. It is observed that the surface tension decreases gradually to reach a constant value (CMC) after which it remains constant with further increase in the concentration of surfactant. Thus, by extrapolating the two lines forming the plots, the CMC values are estimated. Some such typical CMC values for Hyoxid X 100, Hyoxid X 400 and six dyes at 30 and 50°C are given in Table 1. The CMC values drop with the addition of a dye, the extent of drop depending on the hydrophobic nature of the dye. Between the two surfactants, the one having longer ethylene oxide chain in the molecule (Hyoxid X 400) invariably gives lower CMC values than the one having shorter chain (Hyoxid X 100) at both the temperatures in the presence or absence of dye. In the earlier studies², it was shown that the complex of the dye-surfactant contains more dye than the surfactant on the molar basis.

The CMC values increase with increase in temperature from 30°C to 50°C. This effect is more marked with shorter ethylene oxide chain in the surfactant molecule and can be attributed to the effect of temperature on the solubilization of non-ionic surfactants. The interaction of dye with surfactants decreases with increasing solubilization of the surfactant at 50°C. The phenomenon has a practical bearing on the dyeing of nylon with acid dyes at 100°C in the presence of non-ionic surfactants.

Various thermodynamic parameters were determined using the following equations for solutions of surfactants in pure water, the interaction involved being water-surfactant, water-dye and surfactant-dye.

$$\Delta G_{\text{mic}}^{\circ} = RT \ln \text{CMC}$$

$$\Delta H_{\text{mic}}^{\circ} = RT^2 (d/dT) \ln \text{CMC}$$

$$\Delta S_{\text{mic}}^{\circ} = (\Delta H_{\text{mic}}^{\circ} - \Delta G_{\text{mic}}^{\circ})/T$$

The values of various thermodynamic parameters calculated from CMC values are given in Table 2. The results show that there is a change in free energy as the aggregation proceeds or, in other words, spontaneous changes occur. The changes in $\Delta G_{\text{mic}}^{\circ}$ depend on the nature of the dye; its negative value decreases with the increase in the number of sulphonic acid groups and in-

creases with increase in the hydrophobicity of the dye molecules. The decrease in the negative values of enthalpy with increase in sulphonic acid group is a strong evidence for more solubilization due to disaggregation of dye. Increase in $\Delta H_{\text{mic}}^{\circ}$ with increase in the hydrophobicity of dye is accounted for desolvation when forming aggregates. The values of entropy change for all the dyes are positive and this strongly suggests that hydrophobic bonding plays an important role in the aggregation of these dyes.

The results of the viscosity measurements of aqueous solutions of acid dyes in Hyoxid X 400 at 30°C along with the reference curve R (for surfactant only) are shown in Fig. 2. Data represent the character of the complex formation. Reduced

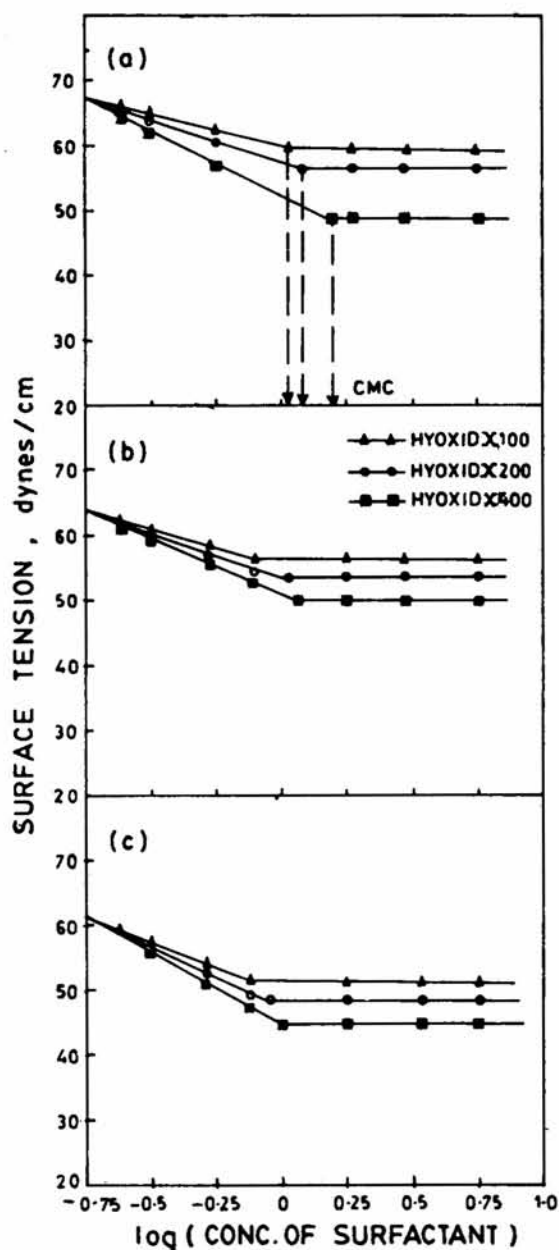


Fig. 1—Surface tension vs. surfactant conc. at $0.1 \times 10^{-3} M$ of (a) Acid Red 18, (b) Acid Brown 14, and (c) Acid Blue 120

Table 1—Effect of surfactant and temperature on critical micelle concentration (CMC) of acid dyes

Dye ^a	Surfactant	CMC $\times 10^{-3} M$ at	
		30°C	50°C
None	Hyoxid X 100	0.9	1.1
	Hyoxid X 400	0.4	0.8
Acid Red 88	Hyoxid X 100	0.5	1.0
	Hyoxid X 400	0.2	0.3
Acid Red 14	Hyoxid X 100	0.6	1.0
	Hyoxid X 400	0.3	0.4
Acid Red 18	Hyoxid X 100	0.7	0.9
	Hyoxid X 400	0.3	0.5
Acid Brown 14	Hyoxid X 100	0.8	1.1
	Hyoxid X 400	0.5	0.6
Acid Blue 113	Hyoxid X 100	0.7	1.1
	Hyoxid X 400	0.4	0.4
Acid Blue 120	Hyoxid X 100	0.5	1.0
	Hyoxid X 400	0.2	0.3

^aDye concentration, $3.0 \times 10^{-5} M$

Table 2—Thermodynamic parameters for the micellization of acid dyes in Hyoxid X 400 at 30°C

Dye	$\Delta G_{\text{mic}}^{\circ}$ kcal/mol	$\Delta H_{\text{mic}}^{\circ}$ kcal/mol	$\Delta S_{\text{mic}}^{\circ}$ e.u.
Acid Red 88	-5.2	-4.6	2.7
Acid Red 14	-4.9	-2.8	6.8
Acid Red 18	-4.8	-2.3	8.3
Acid Brown 14	-4.6	-1.8	9.2
Acid Blue 113	-4.7	-2.2	8.3
Acid Blue 120	-5.1	-3.9	3.9

viscosity increases initially and passes through a maximum. Further increase in surfactant concentration suppresses the electro-viscous effect, as practically all the dye anions would be in the complex. The position of maximum reduced viscosity depends on the nature of the dye. The maximum value is higher for Acid Blue 120 at S/D ratio 0.16:1 than for Acid Blue 113 because of higher hydrophobicity and binding affinity of the former. Also, the latter dye shifted towards lower concentration of surfactant (S/D::0.12:1). Similar behaviour is also observed with hydrophilic dyes and the order of efficacy is the same as that observed by earlier methods². This large vis-

cosity value at particular S/D ratio for any acid dye entails either some sort of molecular rearrangement in the dye molecule or interaction with surfactant. Since a non-ionic surfactant does not carry any ionisable group, binding has to be accomplished by intermolecular forces. Reduced viscosity decreases with increase in temperature of solution, as at higher temperature the mobility of the molecule increases, resulting in increase in flow rate. Reduced viscosity decreases as a linear function of temperature up to 60°C. Analogous, but less extreme, changes in viscosity curve were obtained on the other two surfactants containing comparatively smaller ethylene oxide units.

Preliminary polarographic experiments on the association of acid dyes in the absence of surfactants suggest that aggregation number remains fairly constant with dye concentration up to $0.4 \times 10^{-3} M$ for Acid Red 88, Acid Red 14 and Acid Red 18 and thereafter it increases sharply due to the formation of dimers. The aggregation of Acid Blue 120 was found to be maximum even at $0.2 \times 10^{-3} M$ and it decreases with further increase in dye concentration. This dye does not dissociate completely and the diffusing species were not the dye ion. This observation thus places higher limits on the concentration of dye solutions ($0.4 \times 10^{-3} M$ and $0.2 \times 10^{-3} M$) which are expected to be for monomeric form and would usefully be studied in the presence of surfactant. The aggregation numbers in presence of non-ionic surfactants at S/D ratio 0.4:1 are given in Table 3. It is seen that the aggregation number of acid dyes increases with the addition of surfactants and the order of efficacy is of the same magnitude as obtained by the other methods². The aggregation number increases considerably with increase in ethylene oxide units in the surfactants, the dye-surfactant aggregates being much larger than those of dyes alone. This suggests that

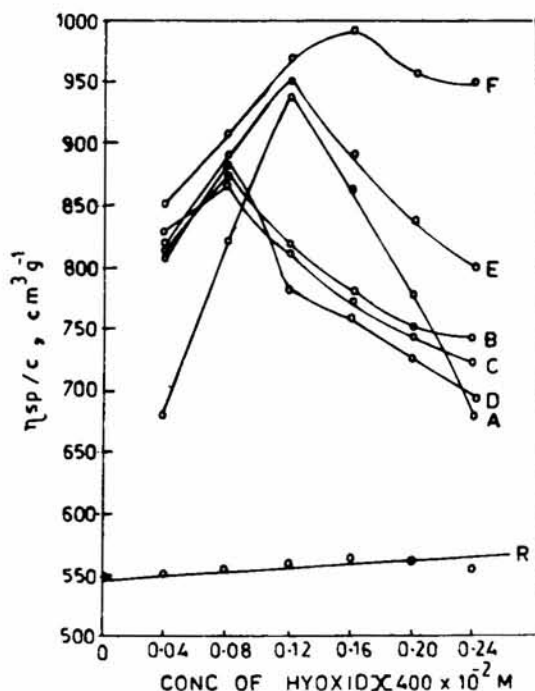


Fig. 2—Reduced viscosity vs. surfactant conc. at $1 \times 10^{-2} M$ of (A) Acid Red 88, (B) Acid Red 14, (C) Acid Red 18, (D) Acid Brown 14, (E) Acid Blue 113, and (F) Acid Blue 120 [R is the reference curve for Hyoxid X 400-water]

Table 3—Effect of addition of non-ionic surfactants on the aggregation number of acid dyes in water at 30°C
[Surfactant-dye ratio, 0.4:1]

Dye	Dye conc. $\times 10^{-3} M$	Aggregation number			
		None	Hyoxid X 100	Hyoxid X 200	Hyoxid X 400
Acid Red 88	0.4	0.80	0.92	0.99	1.15
Acid Red 14	0.4	0.25	0.27	0.29	0.38
Acid Red 18	0.4	0.02	0.03	0.05	0.07
Acid Brown 14	0.2	0.37	0.68	0.90	1.07
Acid Blue 113	0.2	0.56	0.72	0.83	1.15
Acid Blue 120	0.2	0.86	0.95	1.07	1.27

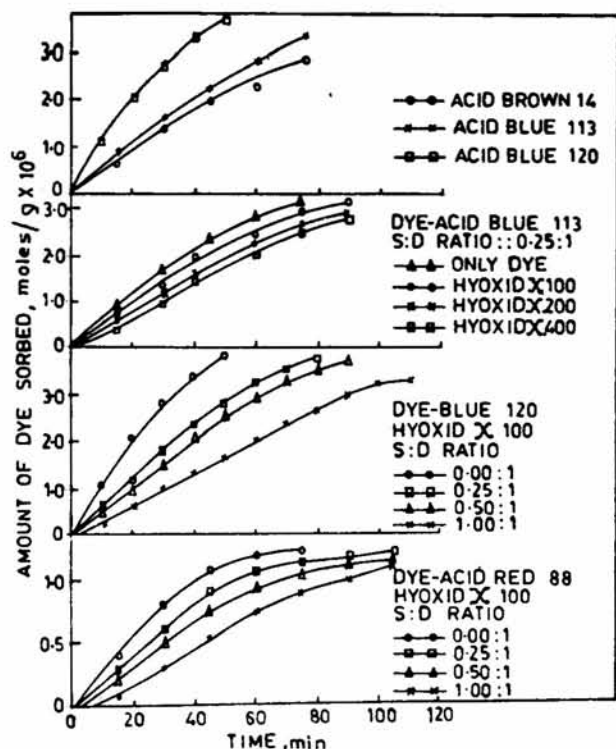


Fig. 3—Sorption of acid dyes in absence/presence of non-ionic surfactants

interaction takes place between dye molecules and surfactant molecules. Further, it indicates that the complex tends to contain more dye than the surfactant molecules. These values agree well with the corresponding values for the micelles of the non-ionic surfactants studied by other methods.

3.1 Dyeing

The rate of sorption of acid dyes on nylon fibre in the presence/absence of surfactants is shown in Fig. 3. The number of sulphonic acid groups in the dye molecule and hydrophobicity influence the rate and extent of dyeing¹². With the addition of surfactant to the dye-bath, the rate of sorption of the dye decreases, the effect being more marked with increasing S/D ratio and length of the ethylene oxide chain in the surfactant molecule. With the formation of a complex, the concentration of free dye in the bath decreases², which, in turn, lowers the rate of sorption. The

complex may slowly break with time, generating free dye molecules and thus the extent of dyeing over a long period is not affected by the surfactant.

4 Conclusion

The addition of a surfactant to the acid dye solution binds some dye in the form of a complex, exhibiting spontaneous drop in free energy and positive change in entropy as determined from the critical micelle concentration (CMC) at different temperatures. This suggests hydrophobic binding between the dye and the surfactant molecules in the complex. The CMC values determined from the surface tension data as well as the viscosity are influenced by the increase in the hydrophobicity of the dye. The surface tension values at CMC show increase with longer chain of ethylene oxide in the surfactant molecule. The CMC values increase with increase in temperature. The aggregation number, as determined by the polarographic data, and viscosity increase with the addition of surfactant, particularly with surfactant having longer chain length of ethylene oxide. All these factors influence the rate of dyeing by affecting the concentration of free dye in the dye-bath which is probably the rate determining species. However, the equilibrium sorption is not affected by the presence of surfactants.

References

- 1 Karmakar S R, Kulkarni P P & Savsani M P, *Indian J Text Res*, 13 (1988) 45.
- 2 Karmakar S R, Patel S G & Pandya N R, *Indian J Text Res*, 14 (1989) 93.
- 3 Wurzhmitt B, *Z Anal Chem*, 130 (1950) 105.
- 4 Craven B R & Datyner A, *J Soc Dyers Colour*, 83 (1967) 41.
- 5 Giles C H & Saufer A H, *J Soc Dyers Colour*, 87 (1971) 301.
- 6 Delany M J & Datyner A, *J Soc Dyers Colour*, 87 (1971) 263.
- 7 Cagarra J, Valldeperas J, Navarro J A & Navarro A, *J Soc Dyers Colour*, 99 (1983) 291.
- 8 Valko E I, *Rev Prog Color Relat Top*, 3 (1972) 50.
- 9 Ilkovic D, *Collect Czech Chem Commun*, 6 (1934) 498.
- 10 Hilson P J & Mekay R B, *Trans Faraday Soc*, 61 (1965) 374.
- 11 Anon, *Colour Chronicle (Sandoz)*, April/June 1987, 22.
- 12 Datye K V & Vaidya A A, *Chemical processing of synthetic fibres and blends* (John Wiley & Sons, New York) 1984, 258.