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Interaction of Methyl Orange with Submicellar Cationic Surfactants

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The interaction of aqueous Methyl Orange (MO), an azo dye, with alkyltrimethylammonium and *N*-hexadecylpyridinium halide surfactants in submicellar concentration ranges has been investigated. The interaction gives rise to a new absorption band of MO with a maximum at ca. 370 nm, and the appearance of the new band has been attributed to change in the chromophore microenvironment in water structure enforced closely packed ion pairs of the dye with submicellar cationic surfactant. The strength of the interaction depends on the alkyl chain length of the surfactant, the surfactant head group and the counter ions.

Methyl Orange (MO) interacts strongly with cationic surfactants in submicellar concentration range and gives rise to a new absorption band centred near 370 nm.[1—3] Similar absorption bands of MO as well as of some other azo dyes have been reported to be caused by cationic polymers[1—4] and simple electrolytes.[5—8] However, the mechanisms of these interactions are still not well understood.

According to Reeves and Harkaway, aqueous MO forms dimers in the presence of cationic polymers and very dilute cationic surfactants.[3] They attributed the 370 nm band to interactions of paired dyes stacked in sandwich structures with parallel transition dipoles. On the other hand, circular dichroism experiments clearly showed that the new band of MO cannot be due to its dimer.[8] More over, no such band was detected for aggregation of MO[9] or other azo dyes.[10]

Vijlder was of the opinion that the appearance of a similar band in the presence of a large excess of simple electrolytes is caused by certain changes in the chromophore microenvironment due to replacement of hydrating water dipoles by metal ions.[7] However, the very low concentration of cationic surfactant required to produce this band is not enough to replace the hydrating water dipoles unlike in large excess of simple electrolytes.

In the present paper, we report the results of an investigation on the interaction of MO with various cationic surfactants in the submicellar concentration ranges.

Experimental

MO, obtained from IDPL India, was recrystallized twice from water. Hexadecyltrimethylammonium bromide (CTAB), tetradecyltrimethylammonium bromide (TTAB), dodecyltrimethylammonium bromide (DTAB) and *N*-hexadecylpyridinium bromide (CPB) were of Sigma products. *N*-hexadecylpyridinium chloride (CPC) was obtained from Hexel Corporation, USA. The surfactants were purified by recrystallization from acetone.

The absorption spectra were recorded by a Hitachi-330 spectrophotometer using a matched pair of 1 cm path length cells fitted in a thermostated cell holder.

Results and Discussion

The absorption spectra of MO in aqueous solutions of varying concentrations of CTAB are shown in Fig. 1. At very low concentrations of the surfactants, i.e., below cmc (9.2×10^{-4} mol dm^{-3}), the absorption of the 463 nm ($\epsilon_{\max}=2520\pm10$ m^2 mol^{-1}) band of MO decrease rapidly with increase in the concentration of the surfactant. It can be seen from the figure that the decrease in intensity of this band is accompanied by an increase in the absorption in the lower wavelength region with an absorption maximum at 375 nm. An isosbestic point

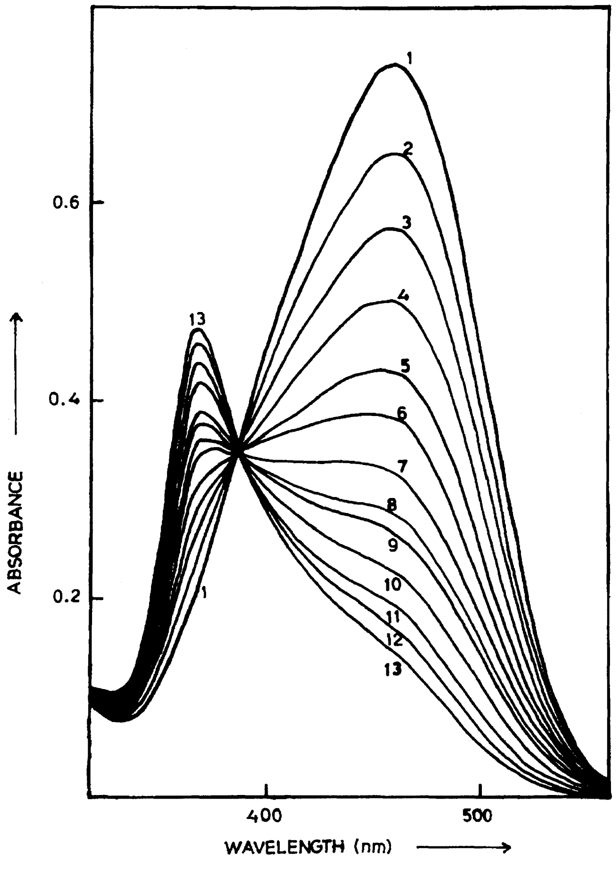


Fig. 1. Visible spectra of aqueous MO in presence of varied amounts of CTAB in submicellar concentration range: [MO] = 2.96×10^{-5} mol dm^{-3}; [CTAB]$\times10^5$ mol dm^{-3}=(1) 0.0, (2) 1.0, (3) 1.5, (4) 2.0, (5) 2.5, (6) 3.0, (7) 3.5, (8) 4.0, (9) 4.3, (10) 5.0, (11) 6.0, (12) 7.0, and (13) 9.0.

was observed at 388 nm. The decrease in intensity of the 463 nm band accompanied by an increase in intensity of the 375 nm band continues till the concentration of the surfactant reaches ca. 1×10^{-4} mol dm^{-3}. With a further increase in the surfactant concentration upto ca. 5.5×10^{-4} mol dm^{-3}, the absorbance of the $\lambda_{\max}$ remains constant whereas there was a slight bathochromic shift of the $\lambda_{\max}$ with a slow increase in the absorbances in the longer wavelength side. On further addition of the surfactant, the 375 nm band disappeares with a corresponding appearance of a new band with absorption maximum at 431 nm. The intensity of the 431 nm band attains a constant value at and above the concentration of ca. 1×10^{-2} mol dm^{-3} of the surfactant.

The variations in the spectra of MO in presence of other cationic surfactants, viz., DTAB, TTAB, CPB, and CPC were found to be similar to that in the presence of CTAB. However, the position of the $\lambda_{\max}$ of the new band at ca. 370 nm and the corresponding λ_{iso} were different for different surfactants, whereas the $\lambda_{\max}$ of the band observed at high concentrations of the surfactants was 431 nm for all the cases (Table 1). The 431 nm band has been attributed to the dye in micelles.[3] The maximum of the new band of MO in the submicellar concentrations of the surfactants shifts to lower wavelengths with the increase in the alkyl chain length of the alkyltrimethylammonium bromide surfactants indicating a dependence of the interaction on the hydrophobicity of the surfactant (Table 1). The $\lambda_{\max}$ of this band in CPB is at 373 nm, which is at a lower wavelength than that in CTAB, whereas in CPC it is observed at a still lower wavelength of 369 nm which shows a dependence of the interaction on the surfactant head group and counterion also.

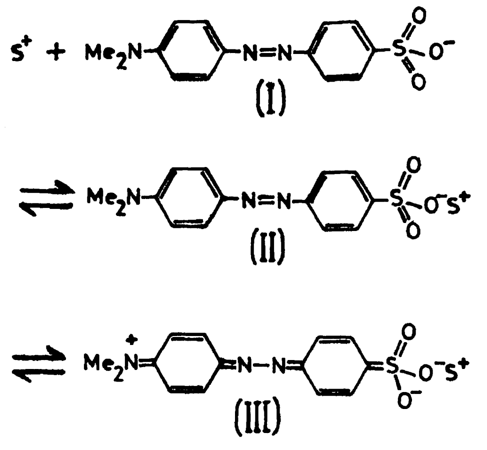
It is interesting to note that the effect of large excess of simple electrolytes[5–8] and cationic polymers[1–4] on the spectral behavior of MO, i.e., the appearance of the new band, is similar to the effect of very dilute cationic surfactants. However, the position of the $\lambda_{\max}$ in simple electrolytes and cationic polymers are different, i.e., at 358 and 370 nm respectively.[1–8] It was noticed that even KOH and NaOH in large excess give rise to such absorption band with $\lambda_{\max}$ at 355 nm. These observations suggest that the submicellar cationic surfactants, cationic polymers and large excess of simple electrolytes and alkali metal hydroxides cause similar changes in the electronic distribution of the chromophore of MO leading to an increase in the transition energy by as large as ca. 66 kJ mol^{-1}. MO does not exhibit such metachromic behavior in organic solvents such as methanol or ethanol indicating an important role of the water structure in the interaction. On the other hand, there is no replaceable proton in the base form of the dye which exists in pure water. Thus, the new band of aqueous MO in presence of excess of simple electrolytes, cationic polymers or very dilute cationic surfactants does not seem to be further deprotonation of the base form of the dye.

Table 1. Absorption Maxima and Isosbestic Points of Spectra of the Base Form of MO in Presence of Various Cationic Surfactants in Their Submicellar Concentration Ranges[a]

Surfactant	Alkyl chain length	$\lambda_{\max}$ ±1 nm	$\lambda_{\max}$ ±1 nm
DTAB	12	377 (2250)	389 (1150)
TTAB	14	376 (2110)	389 (1150)
CTAB	16	375 (2020)	388 (1120)
CPB	16	373 (1930)	387 (1090)
CPC	16	369 (1780)	384 (1010)

a) Values in parentheses are the molar extinction coefficients (in ±20 m^2 mol^{-1}). The molar extinction coefficients at the $\lambda_{\max}$'s were obtained from Eq. 3.

It has been reported that MO aggregates in aqueous solution when the concentration of the dye exceeds ca. 6×10^{-4} mol dm^{-3} but the aggregated species of the dye does not show any band in the shorter wavelength side.[9] Circular dichroism measurements also showed that the shorter wavelength band is not due to any aggregated species of MO.[8] Therefore, the suggestion of Reeves and Harkaway[3] that the new band arises due to induced stacking of the dye may be ruled out. Vijlder suggested that the near-UV band of MO arises due to certain marked changes in the chromophore microenvironment caused by breaking of water structure, competitive hydration and ion-pair formation.[5–7] Eventhough the model suggested by Vijlder is more acceptable than that of Reeves and Harkaway, the former model also has a limitation, i.e., it can as such explain the metachromacy of MO only when the concentration of the electrolyte is sufficient enough for ion-ion interaction to take place. Although cationic polymers and very dilute cationic surfactants produce similar effect, the mechanism has to be somewhat different from that of large excess of simple electrolytes. We feel that the dye anion, D^- forms water structure enforced ion pair with the surfactant ion, S^+.[11–13] The poor solubility of the interaction products conforms to such ion pair formation. These water structure enforced ion pairs are closely packed like contact ion pairs of simple electrolytes.[14] It is the closely packed ion pair, S^+D^- which gives rise to the new band at ca. 370 nm in presence of dilute cationic surfactants. As a consequence of the ion-pair formation, the negative charge of the sulfonato group of MO becomes localized on a particular oxygen atom to which the S^+ ion is attached. In such situation, the two other oxygen atoms in the sulfonato group will have an electron-withdrawing effect on the MO chromophore rendering the latter to be electron-deficient (Scheme 1).



Scheme 1.

The slight variations in the $\lambda_{\max}$ of MO in the ion pairs with different cationic surfactants can be attributed to differences in compactness of the ion pairs where the hydrophobicity of the surfactant tail, nature of the head group and the counterion determine the compactness.

An additional factor affecting the absorption band may be a modification of the microenvironment of the chromophore. The hydrophobic tail of the surfactant is most likely to orient itself around the hydrophobic chromophore replacing the water dipoles.[7] The removal of the water dipoles from the chromophore microenvironment is partial unlike that caused by large excess of simple electrolytes.[7] The situation in cationic polymers may be similar to that in the surfactants. This explains the lesser shift of the MO absorption band in cationic surfactants and polymers than in large excess of simple electrolytes.

Determination of Equilibrium Constants. Eventhough the solvent takes part in the dye-surfactant interaction, the solvent concentration is virtually unaffected. Therefore, we express the interaction of MO with submicellar cationic surfactants in terms of the equilibrium:

$$\mathrm{S}^+ + \mathrm{D}^- \overset{K_\mathrm{c}}{\rightleftharpoons} \mathrm{S}^+\mathrm{D}^- \tag{1}$$

or,

$$K_\mathrm{c} = [\mathrm{S}^+\mathrm{D}^-]/\left([\mathrm{S}^+][\mathrm{D}^-]\right). \tag{2}$$

The equilibrium constants have been determined from the absorbances at $\lambda_{\max}$ of the new bands using the equation:[15]

$$\frac{[\mathrm{S}^+]_0[\mathrm{D}^-]}{d-d_0} = \frac{1}{\epsilon_\mathrm{c}-\epsilon_0}\left([\mathrm{S}^+]_0+[\mathrm{D}^-]_0-\frac{d-d_0}{\epsilon_\mathrm{c}-\epsilon_0}\right) + \frac{1}{(\epsilon_\mathrm{c}-\epsilon_0)\,K_\mathrm{c}} \tag{3}$$

where $[\mathrm{S}^+]_0$ and $[\mathrm{D}^-]_0$ are the initial concentrations of the surfactant and the dye, d and d_0 are the observed absorbances of MO in presence and in absence of the surfactant and ϵ_c and ϵ_0 are the molar extinction coefficient of the ion pair and the free base form of the dye respectively. Iterative method was used to calculate the values of K_c and the results obtained at various temperatures are given in Table 2.

It can be seen from Table 2 that the equilibrium constants are very high. Such high values of equilibrium constants can be attributed to combined electrostatic and hydrophobic interaction and are quite common for interactions between oppositely charged large organic ions.[11,13,16,17] The equilibrium constant of the interaction is dependent on the alkyl chain length of the surfactant. It is interesting to note that a plot of logarithm of the K_c values vs. corresponding alkyl chain length of the surfactants for the alkyltrimethylammonium bromide surfactants is found to be quite linear. This observation goes in parallel to those observed for cmc[18] and solubilization constants by micelle[19] where logarithms of the cmc as well as solubilazation constants (were reported to vary linearly with the alkyl chain lengths of the surfactants). Therefore, it is evident that hydrophobic interaction is playing a major role in the interaction of the dye with the submicellar cationic surfactants.

The equilibrium constants of the interaction of MO with three different surfactants having same alkyl chain length, viz., CTAB, CPB, and CPC have been found to increase in the order CTAB>CPB>CPC whereas their cmc decrease in the order CTAB≈CPC>CPB[20,21] indicating that there is no direct correlation between the K_c values and the cmc values. The stronger interaction with CPB compared to that with CTAB may be

Table 2. Equilibrium Constants for the Interaction of MO with Submicellar Cationic Surfactants at Various Temperatures

Surfactant	Temperature ($\pm$0.1 K)	Equilibrium constants[a] ($\mathrm{dm^3\,mol^{-1}}$)
DTAB	293	9.77×10^2
DTAB	298	8.23×10^2
DTAB	303	7.11×10^2
TTAB	293	8.25×10^3
TTAB	298	6.93×10^3
TTAB	303	5.73×10^3
CTAB	293	4.64×10^4
CTAB	298	4.01×10^4
CTAB	303	3.43×10^4
CPB	293	8.00×10^4
CPB	298	7.37×10^4
CPB	303	6.00×10^4
CPC	293	1.13×10^5
CPC	298	1.06×10^5
CPC	303	9.40×10^4

a) Error limit=±5 %.

Table 3. Equilibrium Constants and Other Thermodynamic Parameters of the Interaction of Aqueous MO with Submicellar Cationic Surfactants at 298 K

Surfactant	$-\Delta G$	$-\Delta H$	ΔS
	kJ mol^{-1}	kJ mol^{-1}	J mol^{-1} K^{-1}
DTAB	16.6	24.2	−25.5
TTAB	21.9	26.4	−15.1
CTAB	26.3	22.4	13.1
CPB	27.8	18.7	30.5
CPC	28.7	17.0	39.2

due to the higher hydrophobicity of pyridinium segment compared to that of the trimethylammonium segment. Moreover, the sulphonato group can come to more proximity of the *N*-alkylpyridinium nitrogen (planer structure) compared to that of tetraalkylammonium nitrogen (tetrahedral structure) and therefore, the dye-surfactant ion pair is more firmly held in the former than in the latter.

It has been reported that among *N*-alkylpyridinium halide surfactants, the cmc decreases in the order $Cl^- > Br^- > I^-$.[16] The reverse order observed for the K_c values for CPB and CPC indicates different role of the counter ion in micellization and the interaction of MO with submicellar cationic surfactants. The higher effectiveness of Cl^- ion than Br^- ion may be due to their differences in hydration and effects on water structure.[7,14,22] Cl^{-1} ion has a greater salting-out effect or water structure making ability compared to Br^{-1} ion.[23,24] In addition, it can be noted here that the micelles of CPB are apparently rod-like whereas the micelles of CPC are spherical.[22]

The calculated thermodynamic parameters of the interactions, viz., ΔH and ΔS (obtained from the equilibrium constants at 293, 298 and 303 K) are given in Table 3. The ΔH values are large and negative for all the systems. There was no definite trend in the ΔH values for the three alkyltrimethylammonium bromide surfactants and a large increase in entropy is thus responsible for the large decrease in ΔG with increase in alkyl chain length. In case of the hexadecyl surfactants, despite a decrease in the negative of enthalpy, the free energy of the interaction increases in the order CTAB<CPB<CPC due to a larger increase in entropy.

Conclusion

From the present study we can conclude that the interaction of MO with aqueous submicellar cationic surfactants, is a water structure enforced closely packed ion-pair formation. The large blue shift of the MO absorption band is due to a change in chromophore microenvironment where the surrounding water dipoles are partly replaced by the surfactant tails. The strength of the interaction depends on the alkyl chain length, the nature of the head group as well as counter ion of the surfactant.

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