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Azo dyes interactions with surfactants. Determination of the critical micelle concentration from acid–base equilibrium

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Abstract

The critical micelle concentrations (CMC) for three surfactants, CTAB, TX-100 and SDS, were determined from the shift in the ionization equilibrium of two optical probes, methyl orange (MO) and acid alizarin violet N (AVN). At constant pH, the ratio of the acid and base forms of these dyes was considerably altered in the presence of micelles, as evidenced by pronounced changes in their absorbance spectra. CMC were also obtained from surface tension measurements, in the presence and absence of the optical probes, under comparable experimental conditions. The results indicate that the optical probes have no effect on the CMC values. Good agreement between the conventional, non-invasive, surface tension method and our method was observed with TX-100. For CTAB, the difference is explained in terms of interactions between optical probes and surfactant preaggregates; for SDS it has been attributed to electrostatic repulsion. Thermochromic measurements show that both the enthalpy and entropy of ionization of MO undergo abrupt changes near the CMC of SDS and hence such measurements can form the basis for a new method for CMC determination.

Keywords: Azo dyes; Ionization; Thermodynamics; Surface tension; Surfactants

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1. Introduction

Several methods for determining the CMC of surfactants have been reported in the literature. Among these are light scattering [1], surface tension [2] and spectrophotometry [3,4]. CMC values for mixed micelle systems have been obtained using both theoretical and experimental methods [5]. Recently, a new method for the determination of CMC using a kinetic approach has been proposed [6]. The effect of micelles on absorption spectra, ionization constants, enthalpies, entropies and free energies of ionization of azo dyes has been studied [7–11]. At and above the CMC, abrupt changes in thermodynamic parameters of ionization were observed. The magnitude of these changes depends on the nature of dye, micelle and pH.

This paper presents a novel method for the determination of CMC that makes use of the effect of micelles on the shift of ionization equilibrium of an optical probe, an azo dye that is introduced into solutions containing different concentration of surfactant system. A wavelength at which absorbance of the dye solution is most sensitive to acid–base ratio is then selected for monitoring the effect of surfactant addition on absorbance. The CMC obtained by this procedure is then compared with that from the well-established surface tension method. It ought to be stated that this new approach is related to, but quite distinct from, the “spectral change method” in which color changes of

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dyes in the presence of surfactants have been variously attributed to the formation of ion pairs [12], micelles [13], and insoluble complex salts [14]. Color changes can also occur as a result of the formation of dye dimers and higher aggregates bound to the surfactant [14]. This method may be viewed as an illustration of Le Chatelier's principle in a new domain.

2. Experimental

2.1. Materials

Acid alizarin violet N (4-hydroxy-3-(2-hydroxy-1-naphthyl azo)benzene sulphonic acid) was obtained from Aldrich as sodium salt ($C_{16}H_{11}O_2N_2SO_3Na$) and purified by recrystallization from ethanol. Methyl orange was obtained from BDH. CTAB (cetyl-trimethyl-ammonium bromide), TX-100 (*p*-octyl-phenol (oxy-ethene)$_n$, $n = 9.5$) and SDS (sodium dodecyl sulphate) were Sigma chemicals and were used without further purification. Phosphoric acid, acetic acid and boric acid were all of analytical grade. Reported CMC ranges at 25 °C are: 0.09–1 mM for CTAB [6,15], 0.2–10 mM for SDS [16,17], and 0.2–2 mM for TX-100 [18,19]. These values may be sensitive to pH, ionic strength, counter-ion concentration, solvent polarity and temperature [16]. They can also vary with the method of determination.

2.2. Methods

Spectrophotometric measurements were performed on a Helios α-Unicam spectrophotometer that was controlled by Vision software package via an RS-232 real time interface. The temperature was controlled by a DBS-PCB 150 Peltier thermostat and measured to within ±0.1 °C by a thermocouple immersed in the cell. Measurements were carried out on 6.8×10^{-5} M AVN solutions at pH 7.00, and on 4.0×10^{-5} M and 8.0×10^{-6} M MO solutions at pH 3.50. Universal buffer was used throughout. Repetitive scans were recorded in the wavelength range of 350–700 nm and visible absorbance spectra were collected for dye solutions containing several surfactant concentrations. Surface tension measurements were carried out using a CSC Du Nouy tensiometer equipped with a 17 mm diameter platinum ring. Measurements were performed at 22.0 °C.

3. Results and discussion

3.1. Ionization constant effect on absorption spectra

Fig. 1a shows spectra of AVN solutions, at pH 7.00, for which [CTAB] varies in the range 0–8.0 mM. At low [CTAB], the spectrum initially exhibits both blue and hypochromic shifts. This behavior may be due to the association of AVN with CTAB preaggregates. As CTAB is further added, the spectra move towards the basic form.

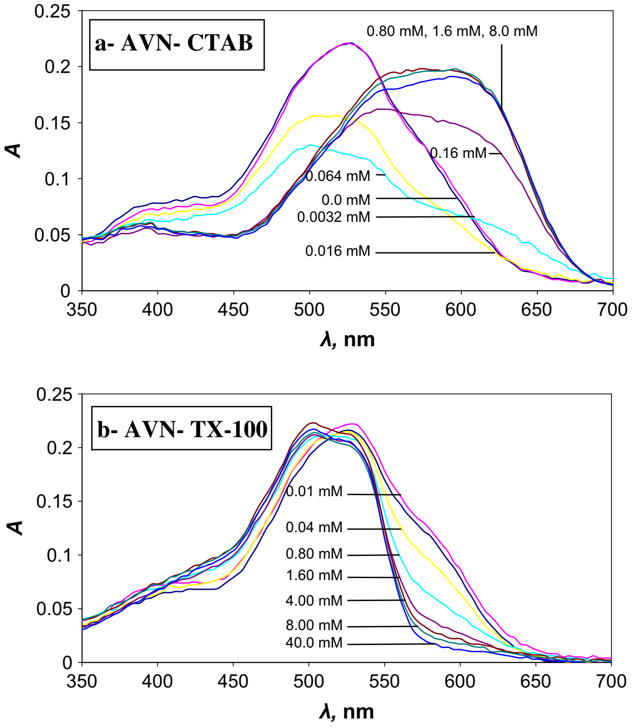

Fig. 1. Dependence of absorption spectra of AVN–surfactant solutions on (a) [CTAB] and (b) [TX-100]. [AVN] = 6.80×10^{-5} M, $T = 22.0$ °C, pH = 7.00, $I = 0.11$ M.

At [CTAB] < 1.0 μM, these spectra nearly overlap ($\lambda_{max} = 520$ nm), indicating little or no dye–surfactant interactions. As [CTAB] is progressively increased, a blue shift is observed with $\lambda_{max} = 500$ nm. This shift probably arises from interactions between AVN and CTAB preaggregates. These preaggregates have been known to perturb the monomer–dimer equilibrium of the dye [20]. However, continued addition of CTAB causes a red shift, i.e. towards the basic form of AVN. At and above CMC, a broad band centered at 600 nm is observed, indicating that AVN is now completely solubilized within CTAB. A small hypochromic shift (particularly near 500 nm) occurs at higher [CTAB]. This effect may be attributed to the enlargement of micelle size and better accommodation of the AVN species. Overall, these spectral changes suggest that, at and above the CMC, AVN exists predominantly in the basic form within micellar CTAB.

The effect of TX-100 on the AVN spectrum is shown in Fig. 1b. In contrast to CTAB, an increase in [TX-100] results in a shift toward the acid form. The most significant change occurs in the 520–560 nm range. This behavior suggests that the microenvironment within TX-100 micelles promotes the acid form of AVN.

The opposing effects of CTAB and TX-100 on AVN spectra are consistent with the reported pK_a values of AVN in CTAB and TX-100 [20]. At 25.0 °C, the pK_a of AVN is 7.00 in water, falls to 6.40 in the presence of micellar CTAB and increases to 8.09 in micellar TX-100 [20]. Fig. 2 shows the effect of SDS on MO spectra at pH 3.5. It is apparent that changes in [SDS] in the interval 0–1 mM have little effect on the spectrum. In addition, at SDS concentrations well above the CMC, the spectra again become much less sensitive to continued SDS addition. The red shift indicates that micellar SDS promotes the acidic form of MO. This conclusion is borne out by the finding that pK_a for MO, at 25.0 °C, increases from 3.67 in water to 3.97 in 10 mM SDS [7]. Further discussion of the acid–base properties of AVN and MO as well as the effect of CTAB, TX-100, and SDS on their pK_a and spectra is found elsewhere [8,20].

3.2. CMC from absorbance changes

Absorbance changes at the broad acid peak centered at 628 nm for CTAB and the shoulder at 580 nm for TX-100 were fairly pronounced and hence were selected for analysis. At these wavelengths, the spectral changes may be attributed solely to dye ionization. The base portion of the CTAB–AVN spectrum is complicated by the effect of CTAB on dye tautomerization and dimerization as a consequence of the formation of premicellar aggregates [20,21]. Fig. 3 shows that, for both systems, absorbance remains essentially insensitive to surfactant addition until near the CMC. Moreover, little change is observed well beyond the CMC. The highly pronounced effect of surfactant concentration on absorbance in the CMC region implies that AVN can act as a suitable reporter molecule for CMC determination. Fig. 3 also shows parallel and abrupt changes in the surface tension of these solutions.

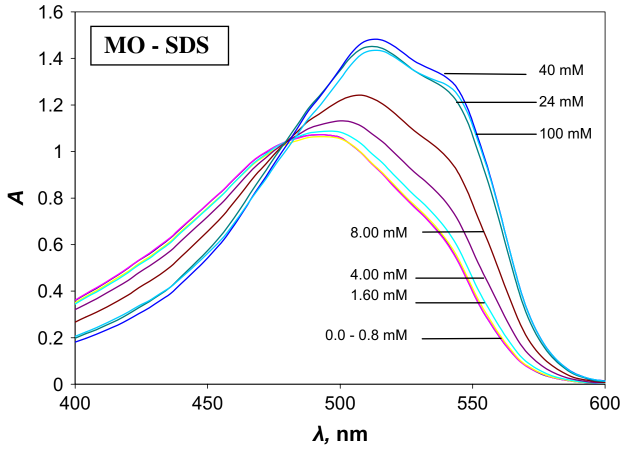

Fig. 2. Dependence of absorption spectra of MO–SDS solutions on [SDS]. [MO] = 4.00 × 10^{-5} M, T = 22.0 °C, pH = 3.50, I = 0.03 M.

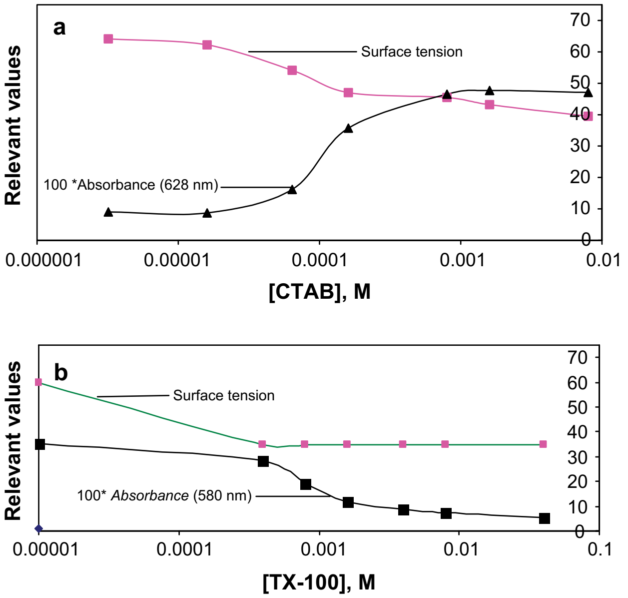

Fig. 3. Dependence of surface tension and absorbance (multiplied by 100) of AVN–surfactant solutions on (a) [CTAB] and (b) [TX-100]. Values are given in the presence and absence of AVN. [AVN] = 6.80 × 10^{-5} M AVN, T = 22.0 °C, pH = 7.00, I = 0.11 M.

In the case of SDS, AVN cannot be used as a reporter molecule because this surfactant has no observable effect on the dye's pK_a, and hence on its spectrum [20]. However, since (as mentioned earlier) SDS increases the pK_a of MO, this dye can potentially be used as a reporter molecule. Fig. 4 shows the dependence of MO absorbance at 540 nm on [SDS]. Surface tension changes are also shown for comparison. As in the previous two cases, abrupt changes in both properties occur near the CMC. It has been reported that under certain conditions, the optical probe perturbs the surfactant system and hence modifies the CMC values [22–25]. In order to ascertain whether the dye affects the surface tension, and hence the CMC, measurements were performed on all

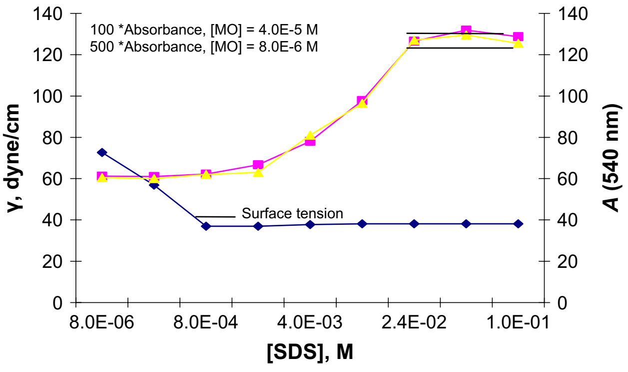

Fig. 4. Dependence of surface tension and absorbance of MO–SDS solutions on [SDS]. λ = 540 nm, T = 22.0 °C, pH = 3.50, I = 0.03 M.

surfactant systems in the presence and absence of dye, at the highest concentrations used in this work. There was no measurable effect of the dye on surface tension, and hence on the CMC, of these surfactants.

CMC values have been traditionally assigned to coincide with abrupt changes in physical [1–3] and chemical [6] properties of solutions that accompany the increase in the surfactant concentration. For TX-100, this procedure gives identical CMC (0.70 mM) with both the present method and the surface tension method. However, for CTAB the CMC of 0.060 mM is significantly lower than that from surface tension (0.10 mM), whereas for SDS the CMC was 1.0 mM vs. 0.80 mM from surface tension measurements.

In the case of CTAB, the most significant change in surface tension almost coincides with the inflection point of the plot of absorbance vs. [CTAB]. The lack of agreement between the two methods in this case can be attributed to positively charged premicellar aggregates that interact strongly with the negatively charged AVN. This interaction alters the thermodynamic properties of AVN, and hence its spectrum. By contrast, the repulsive interaction between SDS and MO anions appears to retard the surfactant aggregation resulting in a CMC increase. Thus, whereas surface tension measures bulk properties, the spectrum is often sensitive to changes in molecular interactions and properties. Finally, spectral changes have been known to deviate from other bulk properties because of these interactions [26].

3.3. CMC from enthalpy and entropy of ionization

The dependence of the enthalpy and entropy of ionization of MO on [SDS] was obtained using the thermochromic method [8,27,28]. Visible spectra of MO in formic acid–formate buffer were obtained in the temperature range 20–55 °C. The ionic strength of solutions was maintained at 0.100 M. For best sensitivity, the pH of the buffer was initially adjusted to lie in the vicinity of the pK_a of MO. The data were then fitted to an expression of the form:

$$\log R = a/T - b + cT \tag{1}$$

where $R = (A - A_a)/(A_b - A)$, A being the observed absorbance at 540 nm (λ_{max} for the acidic form), A_a and A_b are absorbances of most acidic and basic solutions. The constants a, b and c are obtained from regression analysis. The above equation has been derived on the assumption that pK's of both buffer and dye vary according to an expression of the form $pK = a/T - b + cT$, differing only in the values of the constants. A second assumption is that both the activity ratio of buffer species (a_{B^-}/a_{HB}) and the activity coefficient ratio of indicator species (γ_{D^-}/γ_{HD}) are independent of temperature. Eqs. (2) and (3) can be obtained from Eq. (1) by direct differentiation followed by substitution into van't Hoff relation.

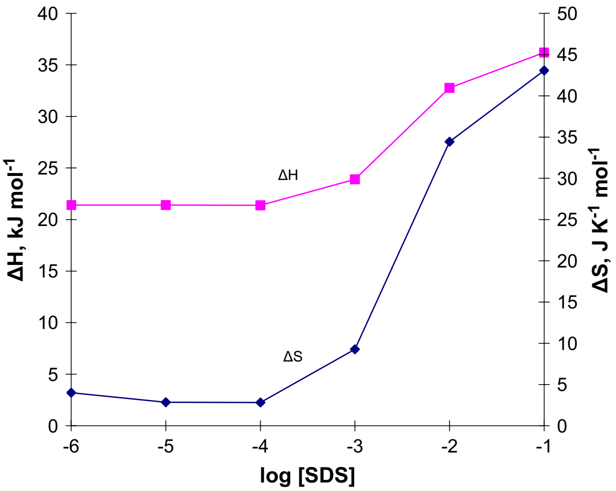

Fig. 5. Dependence of enthalpy and entropy changes for the ionization of MO on [SDS]. $T = 25.0$ °C, $I = 0.10$ M.

$$\delta\Delta H = \Delta H_B - \Delta H_D = 2.303R\left(a - cT^2\right) \tag{2}$$

$$\delta\Delta S = \Delta S_B - \Delta S_D = 2.303R(b - 2cT) \tag{3}$$

Here, the subscripts B and D refer to buffer and dye. $\delta\Delta H$ and $\delta\Delta S$ obtained in this work are apparent (as opposed to true, or thermodynamic) values since they can vary with ionic strength. Since ΔH_B and ΔS_B have already been independently determined [8], those for MO can now be calculated. The enthalpy and entropy of ionization of MO as a function of [SDS] have already been reported [8]. Fig. 5, which shows the dependence of these parameters on [SDS], reveals that significant changes begin at ca. 0.50 mM SDS, corresponding to the CMC of SDS. This result shows that the CMC obtained from thermochromacy compares well with that obtained from surface tension (Table 1).

Table 1
CMC for CTAB, SDS and TX-100 as obtained from absorbance and surface tension measurements

Surfactant	Dye	CMC (mM)		Literature (25 °C)
		Absorbance	Surface tension	
CTAB	AVN	0.060	0.10	0.09–1.0 [5,14]
TX-100	AVN	0.70	0.70	0.2–2.0 [17,18]
SDS	MO	1.0	0.80	0.2–10 [15,16]

Some literature values are given in the last column for comparison.

4. Conclusion

The good agreement between the surface tension method and the present method suggests that the alteration of the acid–base equilibrium of the reporter molecule can be reliably used for CMC determination under conditions when dye and surfactant do not form premicellar aggregates or exert significant electrostatic interactions. The change in the microenvironment of the dye, resulting from its solubilization within the micelle, changes the pK_a and consequently causes a shift of equilibrium between acid and base forms of the dye. This change is sensitive to the surfactant type and has potential applications in solution thermodynamics and in the determination of the thermodynamic parameters of ionization in different microenvironments. It can be used for rapid CMC determination of a wide range of surfactants and is well suited for experiments in the undergraduate physical chemistry laboratories. Investigation of systems containing surfactants and reporter molecules of various charge types should yield further insight into the types of interactions and their possible influence on CMC.

Acknowledgments

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