Chapter III
Chapter III: RESULTS AND DISCUSSION

III.A. Sulfonephthalein dye - cationic surfactant.

III.A.i. Spectral characteristics and acid base equilibria of aqueous PR, CR and CP.

Three forms of aqueous PR, viz., DH$_2$, DH$^-$ and D$^{2-}$ have absorption bands in the visible region with $\lambda_{\text{max}}$ at 506, 431 and 559 nm, respectively [Rosendorfova 1980, Zaslavsky 1991, Drummond 1989] (Table III.A.1). The changes in the spectra of aqueous PR with variation in pH in the ranges 4.91 to 9.01 have been shown in Fig.III.A.1. The spectral variations clearly indicate a gradual change of the dye from its DH$^-$ form to the D$^{2-}$ form with increase in the pH. The $pK_a$'s of the dye in water corresponding to the second deprotonation equilibrium have been found to be 7.74 in low ionic strength ($I = 0.01$) phosphate buffer systems [Perrin 1963] which agree well with the literature values [Rosendorfova 1980, Zaslavsky 1991, Drummond 1989] (Table III.A.2). The spectral variation in the aqueous dye solutions in acidic to highly acidic conditions have been shown in Fig.III.A.2. It can be seen from the figure that below pH 3.37 as the pH is further decreased, the DH$^-$ form of the dye gradually changes to the DH$_2$ form. The $pK_{a1}$ of the dye in water corresponding to this first deprotonation equilibrium of the dye has been found to be 0.90 in Glycine-NaCl-HCl buffer systems [Dean 1992]. The spectra of aqueous solutions of CR and CP at varying pH were analogous to those of PR (Table III.A.1). The corresponding $pK_{a1}$ values of CR and CP in water have also been determined and included in Table III.A.2.
Table III.A.1. Spectral characteristics of the sulphonephthalein dyes and their deprotonated dye-surfactant ion pairs with cationic surfactants.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}^a$ of DH$_2$ form / nm</th>
<th>$\lambda_{\text{max}}^a$ of DH$^+$ form / nm</th>
<th>$\lambda_{\text{max}}^a$ of D$^{2-}$ form / nm</th>
<th>$\lambda_{\text{max}}^a$ of D$_{12}^{2-}$ form / nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR</td>
<td>506</td>
<td>433(424)</td>
<td>559(572)</td>
<td>572</td>
</tr>
<tr>
<td>CR</td>
<td>518</td>
<td>434(424)</td>
<td>573(583)</td>
<td>583</td>
</tr>
<tr>
<td>CP</td>
<td>527</td>
<td>434(423)</td>
<td>578(590)</td>
<td>590</td>
</tr>
</tbody>
</table>

$^a$ Values within the parentheses correspond to micellized dye.

Fig.III.A.1. The UV-visible absorption spectra of aqueous PR ($2.5 \times 10^{-5}$ mol dm$^{-3}$) at 298 K and varying pH of: (1) 4.91, (2) 6.64, (3) 7.26, (4) 7.58, (5) 8.06, (6) 8.23 and (7) 9.01.
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Table III.A.2 Ionization characteristics of the sulphonephthalein dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>pK$_a^b$ in water</th>
<th>pK$_{a2}^c$ in water</th>
<th>Observed minimum pK$_{a2,IP}^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR</td>
<td>0.90</td>
<td>7.74</td>
<td>5.87</td>
</tr>
<tr>
<td>CR</td>
<td>1.10</td>
<td>8.15</td>
<td>6.20</td>
</tr>
<tr>
<td>CP</td>
<td>1.55</td>
<td>8.50</td>
<td>6.48</td>
</tr>
</tbody>
</table>

$^b$ In glycine-NaCl-HCl buffer system, $^c$ In phosphate buffer system
$^d$ For ion pairs of the dyes with CTAB

Fig. III.A.2. The UV-visible absorption spectra of aqueous PR (2.5×10$^{-5}$ mol dm$^{-3}$) at various pH and at 298 K. pH: (1) 3.11, (2) 2.44, (3) 2.20, (4) 1.95, (5) 1.51, (6) 1.28, (7) 0.95, (8) 0.67, (9) 0.55, (10) 0.41 and (11) 0.33.
III.A.ii. Spectral behavior of the aqueous dyes in the presence of cationic surfactants.

The spectra of $2.5 \times 10^{-5}$ mol dm$^{-3}$ aqueous PR solution alone and in the presence of varying amounts of CTAB at 298 K have been shown in Fig.III.A.3. It can be seen from the figure that the dye exists in the $DH^-$ form in pure aqueous solutions [Shapovalov 2007]. The absorption of the 431 nm band of the dye starts decreasing with the appearance of a band with $\lambda_{\text{max}}$ at 572 nm as the concentration of CTAB is increased above $5.0 \times 10^{-5}$ mol dm$^{-3}$. The intensity of this new band increased up to about $9.0 \times 10^{-4}$ mol dm$^{-3}$ of the surfactant.

![Fig.III.A.3](image)

**Fig.III.A.3.** The UV-visible absorption spectra of aqueous PR ($2.5 \times 10^{-5}$ mol dm$^{-3}$) alone and in presence of CTAB at 298 K. Concentrations of CTAB ($10^{-4}$ mol dm$^{-3}$): (1) 0.0, (2) 1.0, (3) 2.0, (4) 3.0, (5) 4.0 and (6) 5.0. Spectra (7) is in 0.05 mol dm$^{-3}$ NaOH and (8) in 0.05 mol dm$^{-3}$ NaOH and 0.02 mol dm$^{-3}$ CTAB.

The spectra recorded between $5.0 \times 10^{-5}$ and $5.0 \times 10^{-4}$ mol dm$^{-3}$ of surfactant concentrations passed through a clear isosbestic point at 490 nm indicating the
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existence of an equilibrium between the free dye and a species formed due to interaction between the dye and the surfactant. The CMC of CTAB in water has been found to be $9.2 \times 10^{-4}$ mol dm$^{-3}$ in pure water at 298 K, which agrees well with literature [Colichman 1951]. So the formation of the species giving rise to the 572 nm band may be a premicellar phenomenon, which the present work attempts to address thoroughly. On further addition of the surfactant the intensity of the band again gradually decreased with corresponding increase in absorbance in the range of wavelength from 350 to 500 nm giving rise to a band with $\lambda_{\text{max}}$ at 424 nm as shown in Fig.III.A.4. The 424 nm band observed at higher concentrations of the surfactant may be attributed to the DH$^-$ form of the dye solubilized in the micelles.

![Absorbance vs. Wavelength](image)

**Fig.III.A.4.** The UV-visible absorption spectra of aqueous PR ($2.5 \times 10^{-5}$ mol dm$^{-3}$) alone and in presence of CTAB at 298 K. Concentrations of CTAB ($10^{-4}$ mol dm$^{-3}$): (1) 0.0, (2) 6.0, (3) 8.0, (4) 50.0, (5) 100 and (6) 150.

Similar spectral variations of the dye were observed also on addition of other surfactants, viz., TTAB, DTAB, CPB and CPC which are shown in Fig.III.A.5-III.A.8, respectively. Other sulphonephthalein dyes, viz., CR and CP shows similar spectral
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Fig. III.A.5. The UV-visible absorption spectra of aqueous PR (2.5×10^{-5} mol dm^{-3}) alone and in presence of TTAB at 298 K. Concentrations of TTAB (10^{-3} mol dm^{-3}): (1) 0.0, (2) 0.6, (3) 0.8, (4) 1.0 and (5) 1.5.

Fig. III.A.6. The UV-visible absorption spectra of aqueous PR (2.5×10^{-5} mol dm^{-3}) alone and in presence of DTAB at 298 K. Concentrations of DTAB (10^{-3} mol dm^{-3}): (1) 0.0, (2) 6.0, (3) 8.0 and (4) 10.0.
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Fig. III.A.7. The UV-visible absorption spectra of aqueous PR (2.5×10⁻⁵ mol dm⁻³) alone and in presence of CPB at 298 K. The concentrations of CPB/10⁻⁴ mol dm⁻³: (1) 0.00, (2) 0.60, (3) 0.80, (4) 1.00 and (5) 2.50.

Fig. III.A.8. The UV-visible spectra of aqueous PR (2.5×10⁻⁵ mol dm⁻³) alone and in presence of CPC at 298 K. Concentrations of CPC /10⁻⁴ mol dm⁻³: (1) 0.00, (2) 0.75, (3) 1.00, (4) 1.25, (5) 1.50, (6) 1.75, (7) 2.00 and (8) 2.50.
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Fig. III.A.9. The UV-visible absorption spectra of aqueous CR (2.5×10^{-5} \text{ mol dm}^{-3}) alone and in presence of CTAB at 298 K. Concentrations of CTAB /10^{-4} \text{ mol dm}^{-3}: (1) 0.0, (2) 1.0, (3) 2.0, (4) 2.5, (5) 3.0, (6) 4.0 and (7) 5.0.

Fig. III.A.10. The UV-visible absorption spectra of aqueous CP (2.5×10^{-5} \text{ mol dm}^{-3}) alone and in presence of CTAB at 298 K. Concentrations of CTAB /10^{-4} \text{ mol dm}^{-3}: (1) 0.0, (2) 1.0, (3) 2.5, (4) 5.0 and (5) 8.0.
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variations in presence of cationic surfactants (Fig.III.A.9-III.A.10). Although the ability of the different surfactants to cause same effect in the spectra of the dye was different, there was no difference in the $\lambda_{\text{max}}$ of the new band (at 572 nm) of the dye upon changing the surfactant. With CPC and CPB, the spectral variations were comparable to those with CTAB. However, the increase in the absorbances of the 572 nm band was noticed with increase in the chain length of the alkyltrimethylammonium bromide surfactants.

The DH- form ($\lambda_{\text{max}}$ at 431 nm) of the dye exists in the neutral pure aqueous solution. On addition of CTAB up to $8.0 \times 10^{-4}$ mol dm$^{-3}$ the pH of the dye solutions was found to decrease gradually from 5.44 to 4.90. Similar pH variations of aqueous solution on addition of cationic surfactants were observed earlier in case of another dye [Dutta 1993]. It is interesting to note that the $\lambda_{\text{max}}$ (572 nm) of the absorption band of the dye, in presence of very low concentrations of the surfactant is exactly same as the absorption band of the D$_2^-$ form in micellar CTAB solution under basic conditions as shown in Fig.III.A.3 [Resendorfova 1980]. The shift of the band from 559 nm in water to 572 nm in the presence of micellar alkyltrimethylammonium bromide surfactants under basic conditions was earlier attributed to change of microenvironment of the dye solubilized micelle under basic conditions [Karukstis 1998, Dutta 1993]. The 572 nm band of PR observed in the presence of CTAB at the low premicellar concentrations of the surfactant in the present case may also be attributed to the D$_2^-$ form of the dye.

It is interesting to note that the 572 nm band of PR initially increased with increasing concentration of the surfactant up to its CMC in the absence of the dye but starts decreasing gradually as more surfactant is added above the CMC. Now, the question to be answered here is – how does this 572 nm band, which decreases the appearance of micelles, arise? Involvement of micelles at far below CMC apparently cannot explain the appearance of the 572 nm band because the band again starts decreasing as the concentration of the surfactant exceeds the CMC of the pure surfactant. Had micelles been involved in the appearance of the band, one would have expected the intensity of the band to remain same if not increase with increasing surfactant concentration above CMC.

Anionic and nonionic surfactants showed no effect on PR below CMC, although they increased their pK$_{a2}$ in water above CMC [Drummond 1989, Dutta 1995]. This
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indicates, the primary requirement of electrostatic attraction between the dye and the surfactant for the interactions giving rise to the band at 572 nm.

It was reported earlier that aqueous phenazanium dyes form closely packed hydrophobic ion pairs [Diamond 1963] with SDS in submicellar solutions where the dye undergoes protonation due to combined electrostatic-hydrophobic interaction without addition of any acid [Dutta 1992]. Evidence of hydrophobicity-induced protonation of dye has been observed also in an analogous ion pair between neutral red and SDS in aqueous solution of pH 7.0 of phosphate buffer [Dutta 1993b]. In the present case, the observed decrease in the pH of PR solution from 5.44 to 4.90 on addition of CTAB up to $8.0 \times 10^4$ mol dm$^{-3}$, is indicative of deprotonation of the dye. It is possible that due to strong hydrophobicity the oppositely charged dye and surfactant ions form a very closely packed ion pair, localizing the original negative charge of the dye anion, paving way for a second deprotonation of the dye. The ion pairs break down as micelles are formed with increasing concentration of surfactant above CMC [Nasiruddin Khan 2006]. Solubilization of the dye by micelle probably wins in a competition with ion pair formation and subsequent deprotonation of the dye. Thus, one can propose that at very low concentrations, these cationic surfactants form similar ion pairs with anionic DH$^-$ of the present sulfonephthalein dyes to give dye-surfactant ion pairs (DSIP), viz., $S^+\cdot DH^-$, which subsequently are deprotonated to form deprotonated dye-surfactant ion pairs (DDSIP), viz., $S^+\cdot D^-$ (Fig.III.A.11). This type of protonation or deprotonation of the dye seems possible in view of the reported unusual nature of such ion pairs [Diamond 1963]. Here it can be mentioned that ion association in micellar solutions through SO$_3^-$ group of sulphonephthalein dye with the cationic micelles is reported to promote electron withdrawal from the aromatic rings through conjugated $\pi$-systems leading to ionization of easily dissociable groups in the dyes [Bailey 1968, Savvin (1978a, 1978b)]. The electrons on sulphonic acid group might interact with the aromatic $\pi$-system through d-orbitals on sulfur as suggested by Yakatan [Yakatan 1972].

Surface tension data of the dye-surfactant solutions may be helpful in understanding the origin of the appearance of the 572 nm band of the dye and the reason for the disappearance of the band above the CMC.
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![Schematic representation of deprotonation of anionic dyes](image)

**Fig. III.A.11.** Schematic representation of the deprotonation of anionic dyes by monomeric cationic surfactants. PR, $X_1 = X_2 = H$; CR, $X_1 = CH_3$, $X_2 = H$; CP, $X_1 = H$, $X_2 = CH_3$.

**III.A.iii. Surface tensions of cationic surfactants in the presence of the sulfonephthalein dye.**

The variations observed in the surface tension, $\gamma$ of aqueous CTAB solutions in the absence and in the presence of $3.6 \times 10^{-5}$ mol dm$^{-3}$ PR are shown in Fig. III.A.12. In the absence of the dye, $\gamma$ of the aqueous surfactant solutions initially decreases gradually on increasing the concentration of the surfactant and levels off at some concentration of the surfactant, the break point being the CMC of the pure surfactant, CMC*. The observed CMC values are in good agreement with the literature values (Table III.A.3).

In the presence of the dye, the surface tension starts to decrease at a much lower concentration of the surfactants and also levels off at a much lower concentration of the surfactant than in absence of the dye, where the break point can be attributed to the CMC of the surfactant in the presence of the dye or the CMC of the DSIP, CMC$_{IP}$. These DSIP micelles were earlier referred to as dye rich induced micelles [Kusumoto 1979, Sato 1980] premicellar aggregation [Garcia-Rio 2007] or mixed micelles [Hiskey 1954] The efficiency increased with increase in the chain length in absence as well as in the presence of the dye.
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Fig. III.A.12. Plots of surface tension and absorbance of PR ($3.6 \times 10^{-5}$ mol dm$^{-3}$) as a function of the logarithm of CTAB concentrations at 298 K. Symbols: (○) surface tension of aqueous solution of pure surfactant, (△) surface tension of aqueous CTAB solution in presence of PR, (♂) absorbance at 431 nm, (○) absorbance at 572 nm.

Table III.A.3. Critical micelle concentration (CMC), pC$_{20}$ and surface excess concentration ($\Gamma_s$) of the cationic surfactants in absence and in the presence of phenol red at 298 K.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>CMC (mol dm$^{-3}$)</th>
<th>pC$_{20}$</th>
<th>$\Gamma_s$ (mol/1000 m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Literature values</td>
<td>a</td>
<td>b</td>
</tr>
<tr>
<td>DTAB</td>
<td>$1.6 \times 10^{-2}$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>$6.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>TTAB</td>
<td>$3.6 \times 10^{-3}$</td>
<td>$3.9 \times 10^{-3}$</td>
<td>$7.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>CTAB</td>
<td>$9.2 \times 10^{-4}$</td>
<td>$9.1 \times 10^{-4}$</td>
<td>$6.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>CPB</td>
<td>$9.2 \times 10^{-4}$</td>
<td>$9.0 \times 10^{-4}$</td>
<td>$5.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>CPC</td>
<td>$9.0 \times 10^{-4}$</td>
<td>$9.1 \times 10^{-4}$</td>
<td>$8.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>CTAB with KBr</td>
<td>$1.4 \times 10^{-4}$</td>
<td></td>
<td>$5.0 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

(a) in absence and (b) in the presence of phenol red.
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The surface tension of the surfactant at the CMC\textsubscript{IP} observed in the presence of the dye is found to be slightly different from that at CMC* observed in the absence of the surfactant. As the concentration of the surfactant in the presence of the dye is gradually increased to the CMC*, a small change is observed in \( \gamma \) and it soon becomes equal to that in the absence of the dye. In the case of the alkyltrimethylammonium bromide surfactants, \( \gamma \) at CMC\textsubscript{IP} is higher than that at CMC* where the difference between the two decreases with increase in the chain length (Fig.III.A.12 – III.A.14). In the case of CPB, \( \gamma \) at CMC\textsubscript{IP} is almost same as that at CMC* but still the CMC* can be located from the change in the trend in the \( \gamma \) vs. concentration curve (Fig.III.A.15). However, in the case of CPC, \( \gamma \) at CMC\textsubscript{IP} is significantly lower than that at CMC* (Fig.III.A.16). Thus, with all surfactants, both CMC\textsubscript{IP} and CMC* can be located in the presence of the dye. The difference between the two CMC values, the so called

\[
\begin{align*}
\text{Surface tension (mN/m):} & \quad 75 \quad 65 \quad 55 \quad 45 \quad 35 \quad 25 \\
\text{Absorbance:} & \quad 1.0 \quad 0.8 \quad 0.6 \quad 0.4 \quad 0.2 \quad 0.0 \\
\log[\text{TAB}]: & \quad -6.0 \quad -5.0 \quad -4.0 \quad -3.0 \quad -2.0
\end{align*}
\]

Fig.III.A.13. Plots of surface tension and absorbance of PR (3.6x10^{-5} \text{ mol dm}^{-3}) as a function of the logarithm of TTAB concentrations at 298 K. Symbols: (○) surface tension of aqueous solution of pure surfactant, (△) surface tension of aqueous TTAB solution in presence of PR, (●) absorbance at 431 nm and (○) absorbance at 572 nm.
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**Fig.III.A.14.** Plots of surface tension and absorbance of PR (3.6×10⁻⁵ mol dm⁻³) as a function of the logarithm of DTAB concentrations at 298 K. Symbols: (○) surface tension of aqueous surfactant solution, (Δ) surface tension of aqueous DTAB solution in presence of PR, (□) absorbance at 431 nm and (○) absorbance at 572 nm.

**Fig.III.A.15.** Plots of surface tension and absorbance of PR (3.6×10⁻⁵ mol dm⁻³) as a function of the logarithm of CPB concentrations at 298 K. Symbols: (○) surface tension of aqueous surfactant solution, (Δ) surface tension of aqueous CPB solution in presence of PR, (□) absorbance at 431 nm and (○) absorbance at 572 nm.
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Fig.III.A.16. Plots of surface tension and absorbance of PR (3.6×10^−5 mol dm^−3) as a function of the logarithm of CPC concentrations at 298 K. Symbols: (○) surface tension of aqueous surfactant solution, (Δ) surface tension of aqueous CPC solution in presence of PR, (◊) absorbance at 431 nm and (○) absorbance at 572 nm.

lowering of CMC, increases with surfactant in the order: DTAB<TTAB<CTAB<CPB <CPC (Table III.A.3), which is same as the order of decrease in CMC_{ip} in the presence of the dye.

The above observations in the behavior of the surface tension on addition of the surfactant in the presence of the dye are consistent with the closed-packed ion pair formation between the dye and surfactant ions of opposite charge due to combined electrostatic and hydrophobic forces [Dutta {1992, 1993(b)}, Perrin 1963]. Aromatic anions are reported to cause major and unexpected changes to the structure of monolayers of cationic surfactant at the air-water interface [Bell 1997]. Any change in the structure of the monolayer at the air-water interface is expected to affect the surface tension of the liquid. In the present case, the dye-surfactant ion pairs probably form a monolayer at the air-water interface analogous to the reported monolayer of CTAB with p-tosylate counterion [Bell 1997]. The area per surfactant molecule in the monolayer of CTAB with p-tosylate counterion was reported to increase by one-quarter to generate space for the p-tosylate ions within the monolayer [Bell 1997]. Formation of close-packed ion pairs between the sulfonephthalein dyes and the cationic surfactants in the present case is equivalent to formation of a new nonionic surfactant
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with a larger head group which is a favorable species from hydrophobic and electrostatic consideration [Colegate 2005]. Such ion pair nonionic surfactant is expected to have greater affinity towards the air-water interface and will also occupy larger surface area per surfactant. Therefore the ion pair surfactant is also expected to have higher efficiency and lower CMC [Rosen 1989] than the corresponding pure cationic surfactants as has actually been observed in the present case (Fig.III.A.12 - III.A.16, Table III.A.3).

The surface excess concentration at surface saturation of the surfactants, viz., $\Gamma_s$ has been calculated using the Gibbs adsorption Eq. III.A.1.: [Rosen 1989]

$$d\gamma = -4.606 \frac{R}{T} \Gamma_s \; d \log C_1$$

III.A.1.

where, $d\gamma$ is the change of surface tension at surface saturation and $C_1$ is the surfactant concentration. The $\Gamma_s$ of the surfactants in the presence of the dye has been found to be smaller than that in the absence of the dye (Table III.A.3). This indicates that a larger surface area is required for the ion pair surfactant than that required for the surfactant alone.

The effectiveness of a surfactant is a measure of the amount of reduction in surface tension by the surfactant at the CMC [Rosen 1989]. The effectiveness of the surfactants in the presence of the dye (at CMC$_{wp}$) has been found to be slightly less than that in the absence of the dye (at CMC$_*$) Fig.III.A.13. The difference increased with the chain length of the alkyltrimethylammonium bromide surfactants as can be seen in Fig.III.A.12 - III.A.14. The difference between the two CMC values also increased with increase in the chain length in the case of the alkyltrimethylammonium bromide surfactants (Table III.A.3). The effectiveness of CPB in the absence of the dye has been found to be approximately equal to that in the presence of the dye. However the effectiveness of CPC in the presence of the dye has been found to be greater than that in the absence of the dye. The effectiveness of a surfactant is reported to increase with better packing of the surfactant at the surfactant monolayer in the air-water interface [Rosen 1989]. The observed greater effectiveness CPC in the presence of the dye than in the absence, despite lower $\Gamma_s$ of the ion pair than pure CPC (Table III.A.3) suggests that a smaller surface area per surfactant or ion pair may not be a requirement for a better packing at the interface.
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The pyridinium head groups of CPC and CPB may contribute towards stronger specific interactions and better packing of their ion pairs compared to the tetraalkyl ammonium head groups of CTAB [Vlachy 2009]. In addition to that, the Cl\(^-\) counterion of CPC may contribute towards better packing of the ion pairs than the Br\(^-\) counterion of CPB. The reported larger contribution of Cl\(^-\) counterion than the Br\(^-\) counterion towards micellization [Rosen 1989] and submicellar dye-surfactant interactions [Dutta 1993(a)] may be mentioned in this context. In the case of the alkyltrimethylammonium surfactants, the difference between the effectiveness of the ion pair surfactant and the pure surfactant decreases with decreasing chain length. This can be attributed to a presence of pure surfactant along with the ion pair surfactant in the surface monolayer, where the ratio of ion pair to pure surfactant decreases with decrease in the chain length. The significantly decreasing difference between CMC\(_{IP}\) and CMC\(*\) with decreasing chain length of the alkyltrimethylammonium surfactants also indicate decreasing ion pair formation and the overall subsequent effects with decreasing chain length. The closer value of \(\gamma\) at CMC\(_{IP}\) to that of CMC\(*\) in the case of CPB compared to that in the case of CTAB implies a dependence of the surface tension behavior of the DSIP on the type or size of the head group. The value of \(\gamma\) at CMC\(_{IP}\) for CPC is lower than that at CMC\(*\), which indicates a dependence also on the counter ion.

The effect of added salt on \(\gamma\) of CTAB-PR system has been shown in Fig.III.A.17. As expected, addition of 0.01 mol dm\(^{-3}\) KBr markedly reduced the surface tension. The presence of 3.6\times10\(^{-5}\) mol dm\(^{-3}\) PR in the KBr-CTAB solutions further reduced the \(\gamma\) at surfactant concentrations below CMC\(_{IP}\). The plot of \(\gamma\) vs. concentration of CTAB for the PR-KBr-CTAB system is closer to that for the PR-CTAB system than that for the KBr-CTAB system. Thus the dye increases the efficiency of the cationic surfactant more than that caused by the salt. The presence of the salt caused greater reduction of \(\gamma\) at the CMCs indicating that the salt increased the effectiveness of CTAB. That the observed dye-surfactant interaction is not merely a salt effect is also evident from the changes in the electronic spectra of the dyes with increasing surfactant concentration in absence and the presence of KBr. The addition of the surfactant lead to the deprotonation of the dye-surfactant ion pair whereas the addition of the salt simply masked the deprotonation as evident from the absorbances of the two bands at 431 and 572 nm.
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**Fig.III.A.17.** Plots of surface tension and absorbance of PR ($3.6 \times 10^{-5}$ mol dm$^{-3}$) as a function of the logarithm of CTAB concentrations in presence of 0.01 mol dm$^{-3}$ KBr at 298 K. Symbols: (○) surface tension of aqueous solution of pure surfactant, (Δ) surface tension of aqueous CTAB solution in presence of PR, (◇) absorbance at 431 nm, (○) absorbance at 572 nm.

**III.A.iv. Correlation of surface tension with absorbance.**

The correlation between the variations in the absorptions at 431 and 572 nm with the corresponding variations in $\gamma$ observed on the addition of the cationic surfactants seems to be interesting. One can see from Fig.III.A.12 - III.A.17 that in the aqueous solution of $3.6 \times 10^{-5}$ mol dm$^{-3}$ PR the 572 nm band of the dye, as indicated in the figure by the absorbance at its $\lambda_{\text{max}}$, started to appear at the cost of the absorbances of the 431 nm band as the concentration of the surfactant reached the CMC$_{\text{ip}}$. The intensity of the 572 nm band increased with increase in the concentration of the surfactant until the concentration reached CMC*, the CMC of the pure surfactant. But with further increase in the concentration of the surfactant above the CMC*, the intensity of the 572 nm band started to decreased gradually. It was shown earlier that the sulfonephthalein dyes in these aqueous closed packed dye-cationic surfactant ion pairs undergo a further deprotonation. The microenvironment around the dye-surfactant
ion pair, i.e., the surrounding water structure plays an important role in the stabilization of the ion pair by a further deprotonation of the dye in the ion pair. It has been reported that the surface of polyoxyethylated nonionic surfactant micelles have negative zeta potential in presence of various electrolytes which favors the presence of anions, where the anions are either preferably solvated in the micelles or generated by expulsion of cations from the micelles [Ohki 2006]. Similarly, when the present close packed dye-surfactant ion pairs aggregate to form micelle, as the surfactant concentration approaches CMC$_{ip}$, the dye ion may lose a proton since a negative zeta potential at the ion pair micelle surface favors the presence of anions. The resulting deprotonated dye in the ion pair gives rise to the new bands with absorption maxima at 572, 583 and 590 nm for PR, CR and CP, which correspond to the $D_2^-$ forms of the dyes respectively. At this point one can opine that even though the ion pair formation is a result of specific interactions between the dye and the surfactant ions and these specific interactions exist in the ion pairs in the monolayer at the air-water interface, the deprotonation of the dye in the ion pair micelles is a result of cooperative interaction since it occurs only on micelle formation by the ion pairs [Hayakawa 1999, Novo 2007].

Similar spectral variations were observed for aqueous solutions of PR with other cationic surfactants and also for CR and CP with the CTAB. However, other more hydrophobic sulfonephthalein dyes, viz., bromothymol blue, thymol blue, bromophenol blue, etc., have precipitated out upon addition of the cationic surfactants below CMC and hence no spectral variation analogous to those in the case of PR, CR and CP were observed. These precipitates were reported to be 1:1 salt between a sulfonephthalein dyes and a cationic surfactants formed below CMC [Mukerjee 1955]. Thus, the hydrophobicity of the dye plays a crucial role in the dye-surfactant interaction, particularly for micelle formation by dye-surfactant ion pairs and the subsequent deprotonation of the dye in the ion pair micelles. There is probably a ceiling value for hydrophobicity of the dyes above which the dye-surfactant ion pair is precipitated out below the CMC of the surfactants and hence there is no question of spectral observation corresponding to any deprotonation of the dye. The spectra recorded for PR, CR and CP with surfactant concentrations between the two CMCs for all dye-surfactant combinations passed through clear isosbestic points which enables study of the equilibrium involved between the dye and the surfactant below CMC*.
Results and discussion

IIIA.v. Equilibrium study.

We assume the following type of an equilibrium to exist between the free mono anionic form of the dye (DH\(^-\)), the surfactant ion (S\(^+\)) and the deprotonated dye-surfactant ion pair (S\(^+\)D\(^2\)) in the concentration range of the surfactant below the CMC* as shown below:

\[
[DH^-] + [S^+] \approx [S^+DH^-] \approx [S^+D^2] + [H^+]
\] III.A.2

or, \[K_c = [S^+D^2][H^+] / [DH^-][S^+]\] III.A.3

where, \(K_c\) is the overall equilibrium constant. The DH\(^-\) form of the dyes has no absorbance above 560 nm. So, if \(A\) and \(\varepsilon\) are the absorbance and the molar absorption coefficient of the dye at the \(\lambda_{max}\) (572 nm) of the deprotonated ion pair, S\(^+\)D\(^2\), in the presence of the surfactant, respectively, taking [DH\(^-\)]\(_0\) as approximately equal to the total initial concentration of the dye, [D]\(_0\) (as [D\(^2\)]\(_0\) \approx 0) and [S\(^+\)]\(_0\) as the total initial concentration of the surfactant, then

\[
K_c = [H^+] (A/\varepsilon) / ([D]_0 - A/\varepsilon) ([S^+]_0 - A/\varepsilon)
\] III.A.4

or, \[\log K_c = \log [H^+] + \log [(A/\varepsilon) / {([D]_0 - A/\varepsilon) ([S^+]_0 - A/\varepsilon)}] \] III.A.5

or, \[\log K_c = \log K_c + \text{pH}\] III.A.6

where, \(K_c = (A/\varepsilon) / {([D]_0 - A/\varepsilon) ([S^+]_0 - A/\varepsilon)}\) III.A.7

The equilibrium constants (\(K_c\)) were determined by using Eq.III.A.4 from the absorbance values of the \(\lambda_{max}\)'s of the deprotonated ion pairs in the surfactant concentration ranges where the spectra passed through the isosbestic point and the results are shown in Table III.A.4. With CTAB, the order of ease of deprotonation of the dyes is \(\text{PR} > \text{CR} > \text{CP}\). It is interesting to note that the pK\(_{a2}\) in water of these dyes also decrease in the same order. The equilibrium constants of PR decreased considerably with decrease in chain length of the surfactant, whereas they are comparable with surfactants of similar chain length, \textit{viz.}, CTAB, CPB and CPC. This consolidates the assumption of hydrophobicity induced deprotonation of dye in the ion pair.
Table III.A.4. Equilibrium constants of the induced deprotonation for various submicellar dye-surfactant systems at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Surfactant</th>
<th>Average $K_e^3/10^4$ dm$^3$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR</td>
<td>CTAB</td>
<td>42.1</td>
</tr>
<tr>
<td>PR</td>
<td>TTAB</td>
<td>2.57</td>
</tr>
<tr>
<td>PR</td>
<td>DTAB</td>
<td>0.13</td>
</tr>
<tr>
<td>PR</td>
<td>CPB</td>
<td>37.1</td>
</tr>
<tr>
<td>PR</td>
<td>CPC</td>
<td>59.3</td>
</tr>
<tr>
<td>CR</td>
<td>CTAB</td>
<td>14.6</td>
</tr>
<tr>
<td>CR</td>
<td>TTAB</td>
<td>9.03</td>
</tr>
<tr>
<td>CR</td>
<td>CPB</td>
<td>12.7</td>
</tr>
<tr>
<td>CR</td>
<td>CPC</td>
<td>18.7</td>
</tr>
<tr>
<td>CP</td>
<td>CTAB</td>
<td>10.1</td>
</tr>
<tr>
<td>PR</td>
<td>CTAB$^b$</td>
<td>11.0</td>
</tr>
</tbody>
</table>

$^a$ Experimental error is within 5%  
$^b$ In buffered medium of pH 4.89

However, when the pH is increased to within less than one pH unit away from the $pK_a$ of the dye, *i.e.*, to above 6.74, the concentration of the free $D^2^-$ form of the dye become significant, even in the absence of the surfactant, which again increases with increase in the pH. Therefore, for a study of the effect of pH variation near the $pK_a$ on the equilibrium constant, the concentration of the free $D^2^-$ form has to be taken into account. Under such situation,

$$[DH^-]_0 = [D]_0 - [D^2^-]_0 = [D]_0 - A_0/\varepsilon$$

III.A.8

So,

$$[DH^-] = [D]_0 - A_0/\varepsilon_0 - (A - A_0)/\varepsilon$$

III.A.9

where $A_0$ and $\varepsilon_0$ are the absorbance at the $\lambda_{max}$ in the absence of the surfactant and the molar extinction coefficients of the free $D^2^-$ form of the dye. Thus, at a pH near the $pK_a$ of the dye, $K_e$ in the Eq.III.A.7 is given by,
Results and discussion

\[ K_e = \frac{(A/e)}{\left(\frac{[D]_o - A_0/e_0 - (A - A_0)/e}{([S^+]_o - A/e)}\right)} \quad \text{III.A.10} \]

Adjustment of pH of the aqueous dye solutions by using the low ionic strength standard buffer systems [Perrin 1963] narrowed down the surfactant concentration range in which the deprotonation of the dye in the ion pair is observed, probably due to increase in the ionic strength. However, in a considerable range of the concentrations of the surfactants, the spectra arising from the deprotonated ion pair passed through isosbestic points. The equilibrium constant, \( K_e \) has been computed for different dye-surfactant systems at varying pH using Eqs. III.A.5, III.A.6 and III.A.9 from the absorbance values at the \( \lambda_{\text{max}} \)’s of the deprotonated ion pairs in the surfactant concentration ranges where the spectra passed through isosbestic points.

The plots of \( \log K_e \) values against pH have been shown in Fig.III.A.18 – III.A.20 for different dye-surfactant systems. The plots have been found to be linear with negative slopes, which show that \( K_e \) increases linearly with \([H^+]\) as assumed in Eq. III.A.6. The intercept of the straight line again gives an average value of the overall equilibrium constant, \( K_c \). The \( K_c \) values obtained from these plots have been shown in Table III.A.5. The \( K_c \) values obtained using Eq.III.A.4 and those obtained from the

![Fig.III.A.18. Plot of \( \log K_e \) vs. pH of the interaction of PR with cationic surfactants: DTAB (X), TTAB (O), CTAB (D) and CPB (A).]
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Fig. III.A.19. Plot of log $K_e$ vs. pH of the interaction of CR with cationic surfactants: DTAB (X), TTAB (□) and CTAB (○).

Fig. III.A.20. Plot of log $K_e$ vs. pH of the interaction of CP with cationic surfactants: DTAB (X), TTAB (□) and CTAB (○).

plots are in agreement. However, the slopes have been found to be less than the expected value of unity in all cases, which may be due to presence of some more factors in the interaction. The $K_e$ values have been found to be large which is in agreement with reports in similar systems indicating a hydrophobic contribution to the interaction [Neumann 1990, Dutta {1993, 1992}, Priyadarsini 2003]. The values of $K_e$ as well as $K_c$ for dye-alkyltrimethylammonium surfactant systems have been found to increase considerably with increase in chain length of the surfactant in the cases of all three dyes in agreement with earlier reports on similar interactions [Dutta 1992,
**Table III.A.5.** $pK_c$ values for the deprotonated dye-surfactant ion pair formation obtained from the intercept of plots of $\log K_e$ vs. pH at 298K.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>PR (dm$^3$ mol$^{-1}$)</th>
<th>CR (dm$^3$ mol$^{-1}$)</th>
<th>CP (dm$^3$ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DTAB</td>
<td>-4.1</td>
<td>-3.2</td>
<td>-2.7</td>
</tr>
<tr>
<td>TTAB</td>
<td>-2.9</td>
<td>-2.7</td>
<td>-1.6</td>
</tr>
<tr>
<td>CTAB</td>
<td>-2.0</td>
<td>-1.6</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

Cimoncic 1998, Dutta 1993]. The equilibrium constants between CTAB and different dyes were however found to decrease in the order PR>CR>CP, i.e., with increasing hydrophobicity of the dye. This contrasts with the reported observation of a greater equilibrium constant of complex formation of decylpyridinium chloride with higher hydrophobicity of dye [Cimoncic 1998]. Since a deprotonation equilibrium is also involved in addition to the dye-surfactant ion pair (or complex) formation in the present case as shown in Eq. III.A.3, a lower $pK_{a2}$ of the dye in water is expected to increase the value of equilibrium constant. The $pK_{a2}$ of PR, CR and CP in water are 7.74, 8.15 and 8.50, respectively. Therefore the observed trend of decreasing the equilibrium constant with different dyes and same surfactant can be attributed to increasing $pK_{a2}$ of the dyes in the same order. The plots of $\log K_e$ vs. the alkyl chain length of the surfactants have been found to be quite linear (Fig.III.A.21). Interestingly, this observation goes in parallel with the earlier observations of linearity of plots of logarithms of CMC [Lindamann 1980], solubilization constant of solubilization by micelle [Abu-Hamadiyyah 1990] and equilibrium constants of methyl orange-alkyltrimethylammonium bromide surfactant interaction in submicellar concentration ranges vs. alkyl chain length of surfactants [Dutta 1993]. This is an analogy of the present deprotonated ion pair formation with other interactions of surfactants which are driven mostly by hydrophobic effect.
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![Graph](image)

**Fig.III.A.21.** Plot of chain length of surfactant (carbon number, n) vs. log K_c of PR (○), CR (■) and CP (Δ) at pH 7.0 and 298 K.

The values of standard enthalpy ($\Delta H^\circ$) and standard entropy ($\Delta S^\circ$) of the interaction at 298.15 K for PR-CTAB and PR-TTAB systems have been determined, from van’t Hoff plot (Fig.III.A.22 – III.A.23) for the equilibrium constants determined at three temperatures, viz., 298.15, 308.15 and 318.15 K. It was assumed that the $\Delta H^\circ$ remained constant within this small range of temperature. The $\Delta H^\circ$ and $\Delta S^\circ$ values were found to be -15.0 kJ mol$^{-1}$ and -97 Jmol$^{-1}$K$^{-1}$, for the former and -15.8 kJmol$^{-1}$ and -120 Jmol$^{-1}$ K$^{-1}$ for the later, respectively. Negative enthalpy change in the interaction means an entropy gain in the surrounding by breaking up of water structure. Negative entropy change in the interaction indicates more orderliness in the ion pairs as compared to the free dye and surfactant ions.

![Graph](image)

**Fig.III.A.22.** Plots of ln K_c vs. 1/T (van’t Hoff plot) for PR-CTAB system.

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The $pK_a$ of the dye-surfactant ion pairs in water, $pK_{a2,\text{IP}}$ have been calculated directly by using Eq. III.A.11:

$$pK_{a2,\text{IP}} = pH - \log\{(d_b - d)/(d - d_a)\}$$  \hspace{1cm} \text{III.A.11}$$

where, $d_b$ and $d_a$ are the absorbances at the $\lambda_{\text{max}}$ of the doubly deprotonated form of the dye when all the molecules are in the base (doubly deprotonated) form of the conjugated acid form, respectively. No pH variation was made for the determination of $pK_{a,\text{IP}}$ as the presence of buffer components affect the ion pair formation. The values of $pK_{a,\text{IP}}$ were calculated using the observed pH of the solutions and those with CTAB which have been included in Table III.A.2. These $pK_{a2,\text{IP}}$ values are possibly underestimated values as the formation of $[\text{S}^+\text{DH}^-]$, as shown in equilibrium (III.A.3), may not be complete. The $pK_{a,\text{IP}}$ have been found to decrease initially with increasing concentration of surfactant, reach a minimum at the concentration of the surfactant corresponding to the highest absorbances of the submicellar band and then increase again. This trend can be easily anticipated from the trend of change in spectral absorbances of the dyes with variation in concentration of surfactant (Fig.III.A.3 - III.A.4). The results show that the ion pair formation can lower the $pK_{a2}$ by more than two units.
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III.A.vi. The situation above the CMC of the pure surfactant.

The surface tension of the dye-surfactant solutions above CMC$_{IP}$ does not change on increase of the surfactant concentration for a small concentration range which is a characteristic of the surfactant Fig.III.A.12 - III.A.16. However, on further increase in the concentration of the surfactant, as the CMC$^*$ is approached the surface tension quickly adjusts itself with the surface tension value of the surfactant observed above CMC$^*$ in the absence of the dye. This observation indicates that pure surfactant ions replace the ion pairs from the monolayer at the air-water interface as the concentration of the surfactant approaches the CMC$^*$. This adjustment in the surface tension coincides with the commencement of the decrease of the absorbance due to the deprotonated ion pairs at 572 nm observed with increase in the surfactant concentration (Fig.III.A.12 - III.A.16). On further increase in the concentration of the surfactant beyond the CMC$^*$, the absorbance of the 572 nm band started to decrease gradually with corresponding increase in absorbance in the lower wavelength region having an absorption maximum at 424 nm. At pH lower than 5.80 in buffered solutions or in unbuffered solutions, the 572 nm band arising due to the deprotonated ion pairs almost disappeared at very high concentrations of the surfactants. However, at pH 5.80 or higher in buffered solutions showed lesser decrease in the D$^{2-}$ band with increase in the surfactant concentration to beyond the CMC$^*$, and the band did not disappear at very high concentrations of the surfactant. This indicates the presence of some protonated ion pairs in the micelles which was previously termed as presence of specific interaction of between the dye and head groups of cationic surfactants in the micelles [Rosendorfova 1980].

The decrease in the 572 nm at higher concentrations of the surfactant can be attributed reversal of the deprotonation of the dye of the ion pair to the monoanionic DH\textsuperscript{−} form or decomposition of the ion pairs and subsequent protonation to the DH\textsuperscript{−} form [Mukerjee 1955, Micheau 2004, Buwalda 2001]. The formation of the band at 424 nm is due to appearance of the DH\textsuperscript{−} form of the dye solubilized in micelle as the shift of the absorption maximum of the DH\textsuperscript{−} form of the dye from 431 nm to 424 nm can be attributed to solubilization of the DH\textsuperscript{−} form of the dye in the micelles. Overcompensation of charge on the micelles at large excess of the surfactant may facilitate the observed reversal of deprotonation [Samoshina 2005, Mazei 2006]. Whether the dye-surfactant ion pair remains intact in the micelles dominated by the
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pure cationic surfactant or the dye is exchangeable between the micelles of the cationic surfactants and the bulk aqueous medium like in neutral micelles [Novo 2007], could not be ascertained from the present data. A reported decomposition of ion pair of cyanine cations with anions of sulfonephthalein and xanthene dyes by added ionic surfactants can be mentioned in this context [Shapovlov 2005]. However, above the CMC*, the observed equal surface tensions of the aqueous surfactant solutions in the presence of the dye and in the absence of the dye shows the monolayer at the air water interface to consist of only the surfactant ions. A present model for the premicellar and micelle forming behavior of the anionic dye - cationic surfactant systems has been summarized in Fig.III.A.24.
Fig. III.A.24. Premicellar and micelle formation behavior of anionic dye cationic surfactant ion pairs in aqueous solutions: deprotonation of dye in ion pair micelles.
III.B. **Neutral red - anionic surfactant.**

III.B.i. **The acid base equilibria and spectral properties of neutral red in aqueous solutions.**

Neutral red (NR), in aqueous solutions at moderate pH, exists in equilibrium between two forms, *viz.*, HD⁺ and D [Shang 2007, Dutta 1993b]. The base form, D has absorption maximum at 450 nm. On the other hand, the acid form, HD⁺, has been reported to have different absorption maximum in the range of 535 to 545 nm. The observed differences in the absorption maximum values of HD⁺ has been attributed to effects of different buffer systems used [Dutta 1993b]. The same reason has also been reported to be responsible for the different reported values of pKₐ₁ in water of NR in the range of 6.5 to 7.4 [Dutta 1993b]. The variation in the spectra of aqueous NR with pH in the neutral or moderate pH range in phosphate buffer system has been shown in Fig.III.B.1 [Dutta 2004]. The absorption maximum of the HD⁺ form and the pKₐ₁ in water corresponding to the dissociation of the HD⁺ form have been reported to be 527 nm and 6.75 (±0.02), respectively in phosphate buffer system [Perrin 1963].

In highly acidic solutions, NR accepts another proton to form H₂D²⁺ which is evident from the variation of the spectra of the dye with variation in the pH in highly acidic solutions as shown in Fig.III.B.2. It can be seen from the figure that as the pH is gradually decreased in the highly acidic solutions, the absorbances of the 527 nm band of the HD⁺ form of the dye decreases with corresponding increase in higher wavelength side forming a band at 598 nm. A clear isosbestic point has been observed at 569 nm which indicates the presence of an equilibrium between two forms of the dye in the solutions. The 598 nm band of the dye has been found to reverse on increasing the pH. The 598 nm band can thus be attributed to the doubly protonated H₂D²⁺ form of the dye. The pKₐ of the dye corresponding to acid dissociation of the H₂D²⁺ form of the dye in water, pKₐ₂, has been found to be 0.26 in glycine buffer system [Perrin 1963]. Thus, the three forms of aqueous neutral red, *viz.*, D, HD⁺ and H₂D²⁺ have absorption bands in the visible region with λ_{max} at 450, 528 and 598 nm, respectively, and the two pKₐ's, *viz.*, pKₐ₁ and pKₐ₂ corresponding to acid dissociation of HD⁺ and H₂D²⁺ are 6.75 and 0.26, respectively.
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Fig. III.B.1. The UV-visible absorption spectra of aqueous NR (5.0×10⁻⁵ mol dm⁻³) at 298 K and various pH: (1) 4.48, (2) 6.22, (3) 6.39, (4) 6.57, (5) 6.79, (6) 6.93, (7) 7.24, (8) 7.41 and (9) 8.50.

Fig. III.B.2. The UV-Visible absorption spectra of aqueous NR (5.0×10⁻⁵ mol dm⁻³) at 298 K and various pH: (1) 2.95, (2) 0.74, (3) 0.52, (4) 0.30, (5) 0.20, (6) 0.12 and (7) 0.05.
III.B.ii. **The spectral variations of aqueous NR in submicellar anionic surfactants.**

The spectra of 5.00×10⁻⁵ mol dm⁻³ aqueous NR at a fixed pH of 2.90 in the absence and the presence of SDS of varying concentrations are shown in Fig.III.B.3. On increasing the concentration of SDS in the submicellar concentration range, the absorbances of the 528nm band of NR gradually decreased with a corresponding increase in the absorbance in the higher wavelength side forming a shoulder in the wavelength range of 569 to 750 nm (Fig.III.B.3). The intensity of the shoulder increased on increasing the surfactant concentration up to ca. 2.00×10⁻⁴ mol dm⁻³. On further addition of the surfactant the intensity of the shoulder started to decrease with corresponding increase of the absorbances of the 527nm band as can be seen in Fig.III.B.4. The shoulder totally disappeared at SDS concentration of ca. 4.00×10⁻⁴ mol dm⁻³. On the other hand, on increasing the surfactant concentration above 2.00×10⁻⁴ mol dm⁻³, the λ_max gradually shifted from 528 to 508nm and then to 538nm at concentration of SDS above CMC (Fig.III.B.5) [Dutta 1993(b), Moulik 1993].

![Fig.III.B.3.](image)

**Fig.III.B.3.** The UV-visible absorption spectra of aqueous NR (5.0×10⁻⁵ mol dm⁻³) at SDS concentrations (10⁻⁴ mol dm⁻³) (1) 0.0, (2) 0.4, (3) 0.8 and (4) 2.0 respectively, at pH 2.90 and 298 K. The broken line is the difference spectra of 4 and 1.
Results and discussion

Fig.III.B.4. The UV-visible absorption spectra of aqueous NR (5.0×10^{-5} mol dm^{-3}) at SDS concentrations (10^{-4} mol dm^{-3}): (4) 2.0, (5) 4.0, (6) 8.0, (7) 20.0 and (8) 30.0 mol dm^{-3} respectively, at pH 2.90 and 298 K.

Fig.III.B.5. The UV-visible absorption spectra of aqueous NR (5.0×10^{-5} mol dm^{-3}) at SDS concentrations (10^{-4} mol dm^{-3}): (8) 30.0, (9) 40.0, (10) 60.0, (11) 80.0 and (12) 300.0 mol dm^{-3} respectively, at pH 2.90 and 298 K.
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The presence of the base form of the dye, i.e., D can be ruled out at pH 2.90 or lower, which is about 4 pH units or more away in the low pH side than pK_{a1} of the dye. The \( \lambda_{\text{max}} \) of 538 nm observed above the cmc of the surfactant is attributed to the acid form, HD\(^+\) of the dye solubilized by the micelles. The red shift of 10 nm of the band may be due to micellization of the HD\(^+\) form of the dye as such shifts of other cationic dyes are known [Moulik 1993, Rohatgi-Mukherjee 1985]. A spectral shoulder between 569 to 750 nm of aqueous NR reported earlier in the presence of submicellar SDS at pH 7.00 was ascribed to formation of the dicationic form, viz., H\(_2\)D\(^{2+}\) of the dye [Dutta 1993b]. Difference spectra obtained by subtracting the absorbances of spectra 1 from that of spectra 4 in the submicellar concentration range at pH 2.90 also showed a \( \lambda_{\text{max}} \) at 598 nm (Fig.III.B.3). A comparison of the spectra in Fig.III.B.2 with Fig.III.B.3 shows that the 598 shoulder/bands of the two figures are actually same. The shoulder observed in the submicellar solutions can therefore be rightly attributed to the dicationic form, H\(_2\)D\(^{2+}\) of the dye. Similarly, the 508nm band in of the dye in the presence of the surfactant can be attributed to the HD\(^+\) form of the dye. The observed shift of the \( \lambda_{\text{max}} \) from 528 to 508nm can be attributed to HD\(^+\) form of the dye solubilized in less polar environment in the micelles [Drumond 1989, Dutta 1993, Paul 1999, Moulik 1993].

The formation of this shoulder, or in other words, the H\(_2\)D\(^{2+}\) form of the dye in the aqueous submicellar SDS solutions at a pH 2.90 or higher is interesting. The cmc of sodium dodecyl sulfate in pure water is 8.31x10\(^{-3}\) mol dm\(^{-3}\) [Rosen 1989]. Although the cmc should decrease in the presence of the buffer components and the dye, it is unlikely to decrease to about 2x10\(^{-4}\) mol dm\(^{-3}\) to cause any change to the dye to give rise to the shoulder at 598 nm. So, any type of involvement of micelles in the appearance of this band at the surfactant concentration below 4.00x10\(^{-4}\) mol dm\(^{-3}\) is unlikely. Thus the interaction between the dye and the surfactant at concentration around 2x10\(^{-4}\) mol dm\(^{-3}\) and formation of the shoulder at 598 nm may be a premicellar phenomenon.

As reported earlier [Dutta 1992, Rafati 2008], it is possible that due to presence of strong electrostatic and hydrophobic interaction between the oppositely charged dye and surfactant ions, the ions form a close packed dye-surfactant ion pairs (DSIP), HD\(^+\)S\(^-\), in an analogous way that has been proposed in Section III.A [Diamond 1963]. In the close packed DSIP's the original charges on the ions are localized. The localization of the original positive charge of the dye cation paves way for a second protonation of the dye, i.e., a protonated dye-surfactant ion pair (PDSIP), H\(_2\)D\(^{2+}\)S\(^-\)
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(Fig.III.B.6), is formed as in the case of phenothiazine dyes with SDS [Dutta 1992]. This PDSIP probably breaks down as micelles are formed with the concentration of surfactant exceeding the cmc like in the cases reported earlier resulting in the disappearance of the 598 nm band [Dutta 1992]. An isosbestic point was observed at 569 nm in the concentration range of the surfactant between $4.00 \times 10^{-5}$ and $2.00 \times 10^{-4}$ mol dm$^{-3}$ which is an indicative of the presence of equilibrium between the free dye HD$^+$ and the protonated $H_2D^{2+}-S^-$ form in the submicellar concentration range.

![Fig.III.B.6. Schematic representation of the protonation of NR by submicellar concentration of SDS.](image)

The variations in the absorbances at 598 and 527 nm of aqueous NR at pH 2.90 in the presence of varying concentrations of SDBS and SDSN in the submicellar concentration ranges are shown in Fig.III.B.7 and Fig.III.B.8. The spectral behaviors of the dye solutions in the presence of these two surfactants have been found to be similar to that observed for SDS suggesting occurrence of similar interactions of the dye with these two surfactants also. The positions of the absorption maxima and the isosbestic points were also found to be same as in the case of all three surfactants. The intensities of absorbance of the aqueous dye solutions at 598 nm in presence of varying concentrations of the three dyes decrease in the order SDS>SDBS>SDSN suggesting a decrease in the strength of the interaction in the same order.

The spectral variations in the 569 - 750 nm regions with variation in the concentration of SDS were considerably reduced upon increase in the ionic strength of
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Fig.III.B.7. The UV-visible absorption spectra of aqueous NR (5.0×10⁻⁵ mol dm⁻³) at SDBS concentrations (/10⁻⁴ mol dm⁻³) of (1) 0.0, (2) 0.4, (3) 0.6, (4) 0.8 and (5) 2.0 mol dm⁻³ respectively, at pH 2.90 and 298 K.

Fig.III.B.8. UV-visible absorption spectra of aqueous NR (5.0×10⁻⁵ mol dm⁻³) at SDSN concentrations (/10⁻⁴ mol dm⁻³): (1) 0.0, (2) 0.8, (3) 1.0, (4) 1.6 and (5) 2.0 mol dm⁻³ respectively, at pH 2.90 and 298 K.
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the solutions, e.g., in the presence of 0.1 mol dm⁻³ NaBr. This observation also indicates that an increase in the ionic strength is not the reason for increase in the absorbance in the 569 nm - 750 nm region.

III.B.iii. The surface tension behavior of the NR dye – anionic surfactant systems.

Variations in surface tensions of the buffered aqueous surfactant solutions at pH 2.90 with variation in SDS concentration in the presence and absence of NR of concentration of 5.00×10⁻⁵ mol dm⁻³ are shown in Fig.III.B.9. The absorbance data of the dye in the solutions at 598 nm and 527 nm are included in the figure to help in correlating the surface tension data with the absorbances. The variation in the surface tension of the buffered solution on increasing the concentration of SDS in absence of the dye has been found to be as expected (Fig.III.B.9). The surface tension gradually decreased with increase in the concentration of the surfactant, reached a minimum at

![Graph showing surface tension vs log[SDS] and absorbance vs log[SDS]](image)

Fig.III.B.9. Plots of surface tension (mN/m) and absorbance of aqueous NR (5.0×10⁻⁵ mol dm⁻³) solutions as a function of the logarithm of SDS concentrations at pH 2.90 and 298 K. Symbols: surface tension in presence (Δ) and absence (□) of NR, absorbances at 527 (○) and 598 nm (○).
[SDS] = 2.51\times10^{-3} \text{ mol dm}^{-3} and then almost leveled off. The concentration 2.51\times10^{-3} \text{ mol dm}^{-3} is therefore the cmc of the surfactant in the buffered medium.

The plot of the surface tension vs. [SDS] in the presence of the buffer and the dye has been found to be unusual (Fig.III.B.9). In the submicellar concentration range, the surface tension decreased more rapidly indicating a considerably higher efficiency of the surfactant in the presence of the dye. It can be recalled that the value of \( pC_{20} \), which is the concentration of the surfactant required to lower the surface tension by 20

\[ \text{Table III.B.1. Critical micelle concentration of the surfactants (CMC) and DSIP (CMC}_{IP} \), pC}_{20} \text{ and surface excess concentration at surface saturation (}\Gamma_s\text{) in pure water, in presence of buffer and in the presence of buffer and NR (5.0\times10^{-5} \text{ mol dm}^{-3} ) at 298 K.} \]

<table>
<thead>
<tr>
<th>Physical property</th>
<th>In presence of</th>
<th>SDS</th>
<th>SDBS</th>
<th>SDSN</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMC(^a) / (mol dm(^{-3}))</td>
<td>Water</td>
<td>8.30\times10^{-3}</td>
<td>1.18\times10^{-3}</td>
<td>1.22\times10^2</td>
</tr>
<tr>
<td></td>
<td>(8.31\times10^{-3})(^c)</td>
<td>(1.20\times10^{-3})(^c)</td>
<td>(1.20\times10^{-2})(^c)</td>
<td></td>
</tr>
<tr>
<td>CMC(_{IP})(^b) / (mol dm(^{-3}))</td>
<td>Buffer &amp; NR</td>
<td>7.94\times10^{-3}</td>
<td>6.30\times10^{-3}</td>
<td>1.26\times10^{-4}</td>
</tr>
<tr>
<td>CMC(^a) / (mol dm(^{-3}))</td>
<td>Buffer</td>
<td>2.51\times10^{-3}</td>
<td>1.00\times10^{-3}</td>
<td>3.98\times10^{-3}</td>
</tr>
<tr>
<td></td>
<td>Buffer &amp; NR</td>
<td>2.23\times10^{-3}</td>
<td>1.12\times10^{-3}</td>
<td>5.01\times10^{-3}</td>
</tr>
<tr>
<td>pC(_{20})</td>
<td>Buffer</td>
<td>3.25</td>
<td>4.01</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>Buffer &amp; NR</td>
<td>3.72</td>
<td>4.18</td>
<td>3.40</td>
</tr>
<tr>
<td>(\Gamma_s) / (mol / 1000 m(^2))</td>
<td>Buffer</td>
<td>1.60\times10^{-3}</td>
<td>1.34\times10^{-3}</td>
<td>1.31\times10^{-3}</td>
</tr>
<tr>
<td></td>
<td>Buffer &amp; NR</td>
<td>2.08\times10^{-3}</td>
<td>1.89\times10^{-3}</td>
<td>1.55\times10^{-3}</td>
</tr>
</tbody>
</table>

\(^a\)Experimental error limits = ±3\%, \(^b\)experimental error limits = ±6\%, \(^c\)the values in parentheses are literature values from ref. [Rosen 1989].
Results and discussion

mN m⁻¹ is a measure of the efficiency of the surfactant. The \( pC_{20} \) has been found to be 3.25 and 3.72 in absence and the presence of the dye, respectively (Table III.B.1). This increase in the efficiency of the surfactant in the presence of the dye can be attributed to formation of the close packed DSIP, HD⁺S⁻, where the ion pair itself behaves like a nonionic surfactant having an efficiency higher than SDS alone. Nonionic surfactants usually have higher efficiency than the corresponding ionic surfactants [Rosen 1989]. The ion pair formation is a specific interaction between the dye and the surfactant ions and this specific interaction should exist also in the ion pair monolayer at the air/water interface. The surface tension of a solution is affected by any change in the structure of the monolayer at the air-water interface. It was reported that presence of \( p \)-tosylate causes major and unexpected changes to the structure of the monolayer of hexadecyltrimethylammonium bromide (CTAB) at the air-water interface [Bell 1997].

The area per surfactant molecule in the monolayer of CTAC with \( p \)-tosylate counterion was reported to increase by one quarter to accommodate the \( p \)-tosylate ions within the monolayer. Similarly, in the present case, the nonionic dye-surfactant ion pair surfactant has a larger head group than that of SDS and therefore occupies a larger surface area per surfactant in the monolayer at the air-water interface compared to that of SDS. A larger surface area per surfactant leads to a lower CMC of the ion pair surfactant.

The surface tension decreased as the concentration of SDS was increased up to ca. \( 1.0 \times 10^{-4} \) mol dm⁻³ and above that again started to increase [Fig.III.B.9]. The surface tension reached a maximum as the concentration of SDS reached ca. \( 2.0 \times 10^{-4} \) mol dm⁻³ and then again started to decrease with further increase in [SDS]. The first minimum of the surface tension may correspond to the cmc of the DSIP surfactant, HD⁺S⁻. Although the surface tension is expected to remain almost unchanged above CMC, the surface tensions often show a minimum at the CMC in the presence of impurity, here, the dye being the impurity [Moroi 1992]. The CMC of the DSIP surfactant, \( CMC_{IP} \), for HD⁺S⁻ has been estimated as \( 7.9 \times 10^{-5} \) mol dm⁻³ (Table III.B.1). It is possible that the protonation of the dye in the DSIP takes place as soon as the DSIP surfactants start forming micelles of their own. Such ion pair micelles can also be termed as premicelles [Reeves 1977]. Interestingly, the maximum of the surface tension and the maximum of the absorbance at 598 nm correspond to the same concentration of the surfactant. This suggest involvement of the same species, \( \text{v.i.z.}, \) PDSIP, \( \text{H}_2\text{D}^{2+}\text{S}^- \) in appearance of the
shoulder at 598 nm and increase in the surface tension above $1.0 \times 10^4$ mol dm$^{-3}$ of SDS. The increase in surface tension may be due to replacement of some ion pairs in the air-water interface by the PDSIP. The nonionic ion pair surfactants are transformed into cationic surfactant with a different head group on protonation of the dye in the close packed ion pair. The increase in the surface tension is probably due to conversion of nonionic ion pair surfactant to cationic protonated ion pair surfactant because a cationic surfactant is expected to have lower efficiency of the compared to the corresponding nonionic surfactant. Although the ion pair formation is a specific interaction between the dye and the surfactant ions, the protonation of the dye in the ion pair micelles is a result of cooperative interaction since the protonation takes place only after the ion pair micelles start forming [Hayakawa 1999, Novo 2007].

The dye solutions showed similar variations in the presence of SDBS and SDSN also as can be seen in Fig.III.B10 and Fig.III.B11. In the case of SDBS, the CMC$_{IP}$ ($6.30 \times 10^{-5}$ mol dm$^{-3}$) is slightly smaller than that with SDS. The increase in the surface tension at above the CMC$_{IP}$ of the DSIP of SDBS was also less compared to that of

![Fig.III.B.10. Plots of surface tension (mN/m) and absorbance of aqueous NR ($5.0 \times 10^{-5}$ mol dm$^{-3}$) solutions as a function of the logarithm of SDBS concentrations at pH 2.90 and 298 K. Symbols: surface tension in presence ($\Delta$) and absence (○) of NR, absorbances at 527 (○) and at 598 nm (○).](image)
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Fig. III.B.11. Plots of surface tension (mN/m) and absorbance of aqueous NR (5.0x10^{-5} \text{ mol dm}^{-3}) solutions as a function of the logarithm of SDSN concentrations at pH 2.90 and 298 K. Symbols: surface tension in presence (Δ) and absence (□) of NR, absorbances at 527 (○) and at 598 nm (○).

SDS. On the other hand, no minimum of surface tension was observed in the NR-SDSN system. The CMC_{IP} of DSIP of SDSN has been assumed to be the concentration at which the surface tension initially leveled off and estimated to be 1.26x10^{-4} \text{ mol dm}^{-3}. The lower maximum in the surface tension curve for SDBS than that for SDS may be due to lesser replacement of the ion pair surfactants of the monolayer of the air-water interface in the case of SDBS than in the case of SDS. Absence of such maximum in the case of SDSN may be due to absence of such substitution in the monolayer. This is expected because the PDSIP formation with SDSN is the minimum among all three surfactants as has been indicated by the absorption intensities in the three cases at 598 nm (Fig. III.B.9 - Fig. III.B.11.).

When the concentration of the surfactant was increased above the concentration corresponding to the maximum absorbance at the wavelength of 598 nm, the surface tension decreased gradually but remained lower than that in absence of the dye. The
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slope of the surface tension vs. surfactant concentration at surface saturation, i.e., near CMC, in the presence of the dye was smaller than that in its absence. This indicates a lower surface excess concentration, $\Gamma_s$, (as defined by Eq. III.A.1) of the surfactant in the presence of the dye than its absence at surface saturation.

In the case of all three surfactants, the $\Gamma_s$ in the presence of the dye have been found to be greater than that in absence of the dye (Table III.B.1). This observation may be attributed to gradual break up of the ion pairs and corresponding gradual decrease in the fraction of the ion pairs at the monolayer at the air/water interface. Overcompensation of charge on the ion pair micelles at large excess of the surfactant may facilitate the observed reversal of deprotonation [Samoshina 2005, Mazei 2006]. The CMC's of all three surfactants in the presence of the dye have been found to be almost same as that in its absence (Table III.B.1). Similarly, the surface tensions at the CMC, which is also a measure of the effectiveness of a surfactant, have been found to be same in the presence as well as absence of the dye for all three surfactants. This suggests occupation of the monolayer at the air-water interface by the pure surfactants alone at concentrations above the CMC even in the presence of NR.

A summary of the different interactions, viz., the DSIP formation, monolayer formation by the DSIP's at the air-water interface, micelle formation by the DSIP's, formation of PDSIP in the ion pair micelles, formation of pure micelles with solubilized dye and replacement of the ion pair in the monolayers by pure micelles at different surfactant concentration ranges have been illustrated in Fig.III.B.12.

III.B.iv. The submicellar dye-surfactant equilibrium in the NR systems.

The presence of isosbestic points in the aqueous NR spectra in the submicellar solutions indicates the presence of equilibria between the free dye, [HD$^+$] and the PDSIP, H$_2$D$^{2+}$·S$^-$. The equilibrium of the submicellar PDSIP formation between NR and SDS can be represented by [Dutta 1992]:

$$K_c = \frac{[H^+] + [HD^+] + [S^-]}{[H_2D^{2+}S^-]}$$  III.B.1

or,

$$K_c = \frac{[H_2D^{2+}S^-]}{([H^+] [HD^+] [S^-])}$$  III.B.2
Fig. III.B.12. Illustration of the various cationic dye - anionic surfactant interactions at different concentration ranges of the surfactant, \textit{viz.}, below CMC of the ion-pair surfactant (CMC$_{IP}$), between CMC$_{IP}$ and CMC of the pure surfactant and above CMC.
where \([S]\) and \(K_c\) are the concentration of the monomeric surfactant and the equilibrium constant of the interaction, respectively. The equilibrium constants have been determined using the Eq. III.B.3 derived from Eq. III.B.2:

\[
K_c = \frac{(d-e_0[H^+]_0)/((\varepsilon - e_0)) / \{[H^+][(H^+]_0 - [H_2D^{2+}\cdot S^\cdot ]([S]_0 - [H_2D^{2+}\cdot S^\cdot ])}
\]

where \([H^+]_0\) and \([S]_0\) are the initial concentrations of the dye and the surfactant, respectively; \(d\) and \(\varepsilon\) are the absorbance and molar absorption coefficient of the PDSIP \([H_2D^{2+}\cdot S^\cdot ]\) at the \(\lambda_{\text{max}}\) 598 nm in the presence of the surfactant, respectively and \(e_0\) is the molar absorption coefficient of the dye at 598 nm in the absence of the surfactant. An iterative method in C language was used for computation of the equilibrium constants. Only those absorbance values of the \(\lambda_{\text{max}}\) of the PDSIP in the submicellar surfactant concentration ranges were used in the calculations whose spectra passed through the isosbestic point.

The equilibrium constants determined for the submicellar interactions of NR with SDS and SDBS at fixed pH of 2.90 have been shown in Table III.B.2 along with the thermodynamic parameters. The large equilibrium constant values can be compared with those observed in similar systems [Dutta 1992]. The equilibrium study was not performed with SDSN because the spectral variations were too less with this surfactant. \(\Delta G^0\) was calculated by using the Eq. III.B.4.:

\[
\Delta G^0 = -RT \ln K_c.
\]

The equilibrium constant and the \(\Delta G^0\) of the interaction with the two surfactants show that the interaction of PDSIP formation is stronger with SDS than that with SDBS. The \(\Delta H^0\) and \(\Delta S^0\) were determines by van’t Hoff plot from the \(\Delta G^0\) values at 293K, 298K and 303K assuming the \(\Delta H^0\) to be constant within this small temperature range. The van’t Hoff plots have been shown in Fig. III.B.13 and Fig. III.B.14 and the \(\Delta H^0\) and \(\Delta S^0\) values have been included in Table III.B.2. Both negative standard enthalpies and positive standard entropies observed for the present systems favor the interaction. A greater strength with SDBS then with SDS is expected due to greater hydrophobicity of SDBS than that of SDS. However, the observed greater strength with SDS than with
SDBS can be attributed to the much higher positive entropy of interaction observed for the former than the latter the interaction being driven by enthalpy as well as entropy.

The plots of logarithm of log $K_e$ vs. pH at 298K for both surfactants are shown in Fig. III.B.15 and Fig. III.B.16. It can be seen from the figures that log $K_e$ increases linearly with the experimental pH in both cases. The linearity is expected as $K_e$ is inversely proportional to $[H^+]$ in Eq. III.B.2. The linearity of the plots also suggests the validity of Eq. III.B.2 which is based on 1:1 dye-surfactant interaction. The intercept of the plots give the overall equilibrium constant, $K_e$, which have been included in Table III.B.2. However, the intercepts have been found to be less than the expected value of unity in all cases, which may be due to presence of some more factors in the interaction.
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Table III.B.2. Equilibrium constants ($K_c$) and thermodynamic parameters of NR-SDS and NR-SDBS systems at pH 2.90 and at different temperatures.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>Temperature /K</th>
<th>$K_c$ /mol$^{-1}$</th>
<th>$K_c'$ /mol$^{-1}$</th>
<th>$\Delta G^\circ$ /kJ</th>
<th>$\Delta H^\circ$ /kJ mol$^{-1}$</th>
<th>$\Delta S^\circ$ /J mol$^{-1}$ K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS</td>
<td>293</td>
<td>1.67×10$^7$</td>
<td></td>
<td>40.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>298</td>
<td>1.46×10$^7$</td>
<td>9.92×10$^4$</td>
<td>40.9</td>
<td>9.3</td>
<td>106.0</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>1.23×10$^7$</td>
<td></td>
<td>41.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SDBS</td>
<td>288</td>
<td>4.51×10$^6$</td>
<td></td>
<td>36.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>293</td>
<td>4.06×10$^6$</td>
<td>1.72×10$^4$</td>
<td>37.1</td>
<td>24.9</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>2.73×10$^6$</td>
<td></td>
<td>37.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Experimental error limits = ±5%.

Thus, from a linear equation between log $K_c$ and pH, we get

$$\log K_c = m \log [H^+] + \log K_c'$$

Fig. III.B.15. Plots of log $K_c$ vs. pH of NR-SDS system at 298 K.

The slopes for NR-SDS and NR-SDBS have been found to be 0.75 and 0.96, respectively. Assuming $m$ to be unity (which is actually not far from unity), we get
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Fig. III.B.16. Plots of log $K_c$ vs. pH of NR-SDBS system at 298 K.

$$K_c = K_{c'} / [H^+] \quad \text{III.B.6}$$

which is essentially the same as Eq. III.B.2 with

$$K_{c'} = [H_2D^{2+}\cdot S'] / [HD^+] [S']. \quad \text{III.B.7}$$

Thus, the observed linear relation between the logarithm of $K_c$ and pH in fact supports our assumption that the interaction product between NR and the submicellar anionic surfactants are doubly PDSIP, i.e., $H_2D^{2+}\cdot S'$ as shown in Eq. III.B.2. The constant $K_{c'}$, where,

$$K_{c'} = K_c [H^+] \quad \text{III.B.8}$$

may be considered as another equilibrium constant which is independent of the hydrogen ion concentration or pH. The values of $K_{c'}$ for the dye with SDS and SDBS have been found to be $9.92 \times 10^4$ and $1.72 \times 10^4$ mol dm$^{-3}$, respectively, at 298K [Table III.B.2]. The higher pH-independent equilibrium constant, $K_{c'}$ with SDS than that with SDBS again indicates a stronger interaction in the NR-SDS system than that in the case of NR-SDBS system.


III.C. **Triphenylmethane dyes - anionic surfactant.**

III.C.1. **The acid base equilibria and spectral properties of aqueous triphenylmethane dyes.**

The electronic spectra of the aqueous solutions of the triphenylmethane dyes, viz., pararosaniline (RN), crystal violet (CV), ethyl violet (EV) and malachite green (MG) at 298 K have been shown in Fig.III.C.1. The absorption maxima of the dyes have been found to be at 547, 590, 595 and 617 nm, respectively, which agreed well with the literature values (Table III.C.1). These absorption maxima have been reported to be due to helical isomers of the dyes, called isomer A (Table III.C.1) [Duxbury 1993]. The electronic spectra of the aqueous triphenylmethane dyes show a shoulder to the lower wavelength region of the absorption maxima, which have been reported to be

![Graph showing the UV-visible absorption spectra of aqueous triphenylmethane dye. Spectra are: pararosaniline, crystal violet, ethyl violet and malachite green.](image)

**Fig. III.C.1.** The UV-visible absorption spectra of aqueous triphenylmethane dye. Spectra are: pararosaniline, crystal violet, ethyl violet and malachite green.
**Results and discussion**

Table III.C.1. Spectrophotometric characteristics of different forms of triphenylmethane dyes.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Isomer B ((\lambda_{\text{max}}, \text{nm}))</th>
<th>Isosbestic point ((\text{nm}))</th>
<th>Isomer A ((\lambda_{\text{max}}, \text{nm}))</th>
<th>Isosbestic point ((\text{nm}))</th>
<th>PDSIP ((\lambda_{\text{max}}, \text{nm}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Para rosiniline</td>
<td>514</td>
<td>531</td>
<td>547</td>
<td>566</td>
<td>587</td>
</tr>
<tr>
<td>Crystal violet</td>
<td>540</td>
<td>566</td>
<td>590</td>
<td>615</td>
<td>634</td>
</tr>
<tr>
<td>Ethyl violet</td>
<td>543</td>
<td>572</td>
<td>595</td>
<td>616</td>
<td>640</td>
</tr>
<tr>
<td>Malachite green</td>
<td>550</td>
<td>596</td>
<td>617</td>
<td>640</td>
<td>657</td>
</tr>
</tbody>
</table>

due to their distorted helical isomers, called isomer B [Lewis 1939]. The relative intensities of the isomer A and B \((I_A \text{ and } I_B)\) depend on solvent dielectric constant and the \(I_A : I_B\) ratio increases with decrease in dielectric constant [Valiente 1991]. For example, for RN, the band at 547 nm is due to the symmetrical helical isomer, isomer A and the shoulder observed at 514 nm is due to the distorted helical isomer, isomer B. The corresponding absorption maxima of the distorted helical isomers of CV, EV and MG have been found to be at 540, 543, and 550 nm, respectively. On increasing the concentration, the aqueous dyes change from the isomer A to isomer B, a phenomenon, also attributed to dimerization [Sarkar 1999, Duxbury 1993, Lueck 1992, Stork 1972].

In dilute aqueous solutions \((-2.5\times10^{-5} \text{ mol dm}^{-3}\)), the triphenylmethane dyes exist in monocationic form. The dyes have been reported to exist in three forms with different colors in aqueous solutions, viz., as monocationic form in weakly acid solution, as dicationic form in strongly acidic solutions and as tricationic form in very strongly acid solutions. [Finar 1973]. The colored quinoid structures of these dyes change to colorless carbinol forms in acidic solutions and finally the two forms exist in equilibrium proportions. On the other hand, all these dyes are unstable in alkaline conditions [Sengupta 2000] and decompose leading to a range of products [Chen 2007]. Thus the changes in the aqueous dyes in acidic as well as in alkaline conditions
complicate the study of the premicellar and micelle formation behavior in anionic surfactant solutions in the presence of these dyes, analogous to that described in Section IIIB. However a careful analysis of the rates of fading by acid isomerization and alkaline decomposition of these dyes has revealed that the dyes are quite stable within a small range of pH to permit a study of the aqueous solutions of anionic surfactants in the presence of these dyes in that particular pH range, which has been elaborated in the following subsections.

III.C.ii. Effect of pH on fading of the triphenylmethane dyes.

The spectral variations observed in aqueous RN upon alkaline decomposition and isomerization from colored quinoid to colorless carbinol in acidic medium at 298 K in terms of time scan curves at the absorption maxima of the dye in the basic and acidic solutions have been shown in Fig.III.C.2 and Fig.III.C.3, respectively. The fading of the dyes has been studied in the pH range from 0.5 to 10.5 pH. Above pH 10.5, the decomposition is too fast to be studied by conventional method. The first order [Al-Shihri 2003, Sengupta 2000] rate constants for the alkaline decomposition of the dyes have been determined using the equation [Sengupta 2000]:

$$\ln (d_t - d_\infty) = - kt + \ln(d_0 - d_\infty)$$

III.C.1

where, $d_0$, $d_t$ and $d_\infty$ are the absorbances at the absorption maximum of the aqueous dye solution at the start, time ‘t’ and at infinite time, respectively. On the other hand, for the the coloured quinoid (Q) - colorless carbinol (C) reversible reactions, $Q \rightleftharpoons C$, the reactions can be assumed to be unimolecular in both directions [Adams 1914]. The rate of transformation of the colored to colorless form can be expressed as [Adams 1914]

$$- \frac{dQ}{dt} = k_r[Q] - k_b[C]$$

III.C.2

Putting $[C] = [Q]_0 - [Q]$, $[Q]_0$ being the initial concentration of Q, one can get [Adams 1914]

$$\ln ([Q] - [Q]_\infty) = -(k_r + k_b) t + \ln ([Q]_0 - [Q]_\infty)$$

III.C.3

which takes the form of equation III.C.1 in terms of the absorbances. Hence, equation
Fig. III.C.2. Time scan curves of aqueous RN at 298 K and various pH in basic condition.

Fig. III.C.3. Time scan curves of aqueous RN at 298 K and various pH in acidic condition.
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III.C.1 can be used for analysis of fading of the dyes in the acidic solutions.

Some representative plots of $\ln(d_t - d_\infty)$ vs. $t$ for the dyes at different pH have been shown in Fig.III.C.4, Fig.III.C.5, Fig.III.C.6 and Fig.III.C.7, respectively. The plots have been found to be linear with negative slopes. The first order rate constants for the dyes at 298 K determined from the slopes have been given in Table III.C.2.

Fig.III.C.4. Plots of $\ln(d_t - d_\infty)$ vs. time (minute) of aqueous RN at 298 K and various pH: 1.52 (□), 1.88 (○), 2.38 (△), 8.47 (○), 9.41 (×) and 10.46 (×).

Fig.III.C.5. Plots of $\ln(d_t - d_\infty)$ vs. time (minute) of aqueous CV at 298 K and various pH: 1.26 (□), 2.20 (○), 3.34 (△), 8.36 (○), 9.44 (×) and 10.41 (×).
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**Fig. III.C.6.** Plots of ln(d_t - d_a) vs. time (minute) of aqueous EV at 298 K and various pH: 1.56 (□), 2.27 (○), 2.38 (△), 8.52 (×) and 10.39 (×).

**Fig. III.C.7.** Plots of ln(d_t - d_a) vs. time (minute) of aqueous MG at 298 K and various pH: 1.67 (□), 2.39 (○), 2.50 (△), 8.93 (○), 9.84 (×) and 10.27 (×).

The plots of the rate constants of the fading of the dyes vs. pH can be seen in Fig. III.C.8. It is interesting to note that the plots of the two reactions at low and high pH together take a U shape showing a minimum at about pH 5.00 in case of all the four dyes. Thus the plots indicate that the dyes are quite stable within the pH range of about 4.00 to 6.50. It can be mentioned here that the aqueous solutions of the triphenylmethane dyes are very weakly acidic. The pH of the aqueous solutions of these
Results and discussion

The spectral variations of aqueous triphenylmethane dyes by anionic surfactants.

The variations in the electronic spectra of $2.5 \times 10^{-5}$ mol dm$^{-3}$ aqueous RN solution on addition of SDS can be seen in Fig.III.C.9. With increase in the SDS
Results and discussion

Fig. III.C.9. The UV-visible absorption spectra of aqueous RN (2.5×10⁻⁵ mol dm⁻³) alone and in the presence of SDS at 298 K. Concentrations of SDS /10⁻⁴ mol dm⁻³: (1) 0.0, (2) 0.6, (3) 0.8, (4) 1.0, (5) 2.0, (6) 3.0, (7) 6.0 and (8) 20.0. The broken line is the difference spectra of 8 and 1.

concentration, the intensity of the absorption band of the helical isomer form at 547 nm started to decrease with simultaneous gradual appearance of the band of the distorted helical form at 514 nm. This was accompanied by increase in the absorption intensity in the higher wavelength region from ≈ 566 to 700 nm. This continued up to SDS concentration of 2.0×10⁻³ mol dm⁻³. All of the spectra in this concentration range of SDS passed through isosbestic points at 531 and 566 nm. As the concentration of the surfactant was increased to above 2.0×10⁻³ mol dm⁻³, the absorbances in the band at 514 and in the region 566 to 700 nm again started to decrease (Fig. III.C.10). This was accompanied by shifting of the 547 nm band to 551 nm with increase in the intensity of the band and continued up to SDS concentration of 2.0×10⁻² mol dm⁻³. The 551 nm band can be attributed to RN solubilized in the SDS micelles [Ramanathan 2003]. Ramanathan et al. reported analogous red shift in the case of aqueous RN in presence of SDS and attributed the observed red shift to incorporation of the dye to micelles [Ramanathan 2003].
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Fig.III.C.10. The UV-visible absorption spectra of aqueous RN (2.5×10⁻⁵ mol dm⁻³) in the presence of SDS at 298 K. Concentrations of SDS /10⁻⁴ mol dm⁻³: (8) 20.0, (9) 60.0, (10) 100.0 and (11) 200.0.

Analogous spectral variations of the spectra have been observed on the addition of SDS also in the case of the other three triphenylmethane dyes, viz., CV, EV and MG as shown in Fig.III.C.11-Fig.III.C.16, the spectral characteristics of which have been included in Table III.C.1. However, in the case of MG, only the absorbances in the range of the distorted helical form of the dye (from 540 to 596 nm) increased taking the form of a shoulder which did not take the form of a band. Similar observations have been made also with other anionic surfactants, viz., SDBS (Fig.III.C.17 - Fig.III.C.18) and SDSN (Fig.III.C.19). Ramanathan et al. attributed the decrease in the absorbance of 546 (547 as observed in the present study) nm band of aqueous RN on the addition of SDS below CMC to dye-surfactant salt formation. However, it is an accepted fact that mere salt or ion pair formation does not lead to any change in electronic spectra of the associated ions [Lewis 1942]. On the other hand the present spectral observations with the triphenylmethane dyes at lower concentrations of the surfactants can be
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**Fig.III.C.11.** The UV-visible absorption spectra of aqueous CV ($2.5 \times 10^{-5}$ mol dm$^{-3}$) alone and in the presence of SDS at 298 K. Concentrations of SDS /10$^{-4}$ mol dm$^{-3}$: (1) 0.0, (2) 0.6, (3) 2.0, (4) 4.0, (5) 6.0, (6) 8.0 and (7) 10.0. The broken line is the difference spectra of 7 and 1.

**Fig.III.C.12.** The UV-visible absorption spectra of aqueous CV ($2.5 \times 10^{-5}$ mol dm$^{-3}$) alone and in the presence of SDS at 298 K. Concentrations of SDS /10$^{-4}$ mol dm$^{-3}$: (1) 0.0, (7) 10.0 and (8) 100.0.
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Fig. III.C.13. The UV-visible absorption spectra of aqueous EV (2.5\times 10^{-5} \text{ mol dm}^{-3}) alone and in the presence of SDS at 298 K. Concentrations of SDS /10^{-4} \text{ mol dm}^{-3}: (1) 0.0, (2) 0.6, (3) 0.8, (4) 1.0, (5) 2.0, (6) 4.0 and (7) 8.0. The broken line is the difference spectra of 7 and 1.

Fig. III.C.14. The UV-visible absorption spectra of aqueous EV (2.5\times 10^{-5} \text{ mol dm}^{-3}) alone and in the presence of SDS at 298 K. Concentrations of SDS /10^{-4} \text{ mol dm}^{-3}: (1) 0.0, (7) 8.0 and (8) 100.0.
Results and discussion

Fig.III.C.15. The UV-visible absorption spectra of aqueous MG (2.5×10^{-5} mol dm^{-3}) at SDS concentrations (10^{-4} mol dm^{-3}) of (1) 0.0, (2) 0.4, (3) 0.8, (4) 1.0 and (5) 2.0, respectively and 298 K. The broken curve is the difference spectra of 5 and 1.

Fig.III.C.16. The UV-visible absorption spectra of aqueous MG (2.5×10^{-5} mol dm^{-3}) at 298 K and SDS concentrations (10^{-4} mol dm^{-3}) of (1) 0.0, (5) 2.0, (6) 10.0, (7) 60.0 and (8) 100.0 respectively.
Results and discussion

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{The UV-visible absorption spectra of aqueous RN (2.5\times10^{-5} mol dm^{-3}) alone and in the presence of SDBS at 298 K. Concentrations of SDBS /10^{-4} mol dm^{-3}: (1) 0.0, (2) 0.2, (3) 0.6, (4) 1.0, (5) 2.0 and (6) 6.0. The broken line is the difference spectra of 6 and 1.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure2.png}
\caption{The UV-visible absorption spectra of aqueous RN (2.5\times10^{-5} mol dm^{-3}) alone and in the presence of SDBS at 298 K. Concentrations of SDBS /10^{-4} mol dm^{-3}: (1) 0.0, (6) 6.0, (7) 20.0 and (8) 100.0.}
\end{figure}
Results and discussion

Fig.III.C.19. The UV-visible absorption spectra of aqueous RN (2.5×10⁻⁵ mol dm⁻³) alone and in the presence of SDSN at 298 K. Concentrations of SDSN /10⁻³ mol dm⁻³: (1) 0.0, (2) 1.0, (3) 3.0, (4) 4.0, (5) 6.0, (6) 8.0 and (7) 20.0 respectively. The broken line is the difference spectra of 7 and 1.

explained in a way similar to that for the analogous premicellar phenomena observed in the case of NR described in section III.B.

It is interesting to note that the absorbances of aqueous RN, in the absence of the surfactant, increased in the range of 566 to 700 nm with gradual decrease in the 547 nm band on decreasing the pH below 2.88 to 0.76 showing an isosbestic point at 566 nm (Fig.III.C.20). The spectra obtained below 0.76, in the absence of the surfactant, however, did not pass through the isosbestic point and decreased with time which can be attributed to conversion of the colored quinoid form of the dye to the colorless carbinol form [Sengupta 2000]. CV and EV also behaved in similar manner on pH variation in the absence of the surfactant (Fig.III.C.21-Fig.III.C.23). In the case of MG none of the spectra passed through any isosbestic point on decreasing the pH (Fig.III.C.23). This may be due to fast conversion of the quinoid form to the carbinol form which overshadow any increase in absorbances in the higher wavelength range unlike in the cases of RN, CV and EV. It can be seen from Fig.III.C.20 of aqueous RN
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**Fig.III.C.20.** UV-visible absorption spectra of aqueous RN \(2.5\times10^{-5}\) mol dm\(^{-3}\) at 298 K and various pH: (1) 2.88, (2) 2.25, (3) 1.92, (4) 1.79, (5) 1.37, (6) 1.13 and (7) 0.76.

**Fig.III.C.21.** UV-visible absorption spectra of aqueous CV \(2.5\times10^{-5}\) mol dm\(^{-3}\) at 298 K and various pH: (1) 2.68, (2) 2.33, (3) 2.27, (4) 2.13, (5) 2.02 and (6) 1.84.
Fig.III.C.22. The UV-visible absorption spectra of aqueous EV ($2.5 \times 10^{-5}$ mol dm$^{-3}$) at 298 K and various pH: (1) 6.50, (2) 4.64, (3) 3.12, (4) 2.68, (5) 2.54 and (6) 2.43.

Fig.III.C.23. The UV-visible absorption spectra of aqueous MG ($2.0 \times 10^{-5}$ mol dm$^{-3}$) at 298 K and various pH: (1) 3.75, (2) 2.21 (3) 1.72, (4) 1.44, (5) 0.76 and (6) 0.59.
that on lowering the pH, the absorbances in the higher wavelength range increase and take the form of a band with $\lambda_{\text{max}}$ at 577 nm. This increase in the absorbances in the higher wavelength ranges and formation of the band at 577 nm can be attributed to conversion of the monocationic (D\textsuperscript{+}) form of the dyes to the dicationic (DH\textsuperscript{2+}) form. On the other hand the isosbestic point at 531 nm in the case of RN can be attributed to the equilibrium between the helical and the distorted helical structures of the dye [Duxbury 1993]. The analogous observations made with CV, EV and MG can be explained in the same way. The increase in the intensity of the 514 nm band at the cost of the intensity of the 547 nm band observed together with appearance of the shoulder/band due to the dicationic form indicates that the distorted helical structure of the dye is favored in the dicationic form.

III.C.iv. The surface tension behavior of the triphenylmethane dye – anionic surfactant systems.

The plots of surface tensions of the aqueous solutions of the surfactant in the absence and in the presence of the dyes along with the absorbances at the $\lambda_{\text{max}}$'s of the helical monocationic form and the quinoid dicationic forms as functions of the concentrations of SDS and SDBS are shown in Fig.III.C.24 to Fig.III.C.31. One can see from these figures that there exist some correlations between the absorbances and surface tensions in parallel with that observed with NR – anionic surfactant systems. The CMC\textsubscript{IP} can be easily located for all the dye-surfactant combinations, which are significantly lower than the corresponding CMC\textsuperscript{*} in all cases. The CMC\textsubscript{IP}'s of the DSIP's were found to decrease in the order MG>>RN>CV>EV in the cases of both surfactants (Table III.C.2 & Table III.C.3). Absence of an amino group makes MG somewhat different from the other three dyes. The hydrophobicity of the dyes other than MG increases in the order RN<CV<EV. The observed decrease in CMC\textsubscript{IP} with increasing hydrophobicity of the dyes may indicate closer contact of the ions and more non-ionic like nature of the DSIP with higher hydrophobicity of the dye. It means hydrophobicity of the dyes plays an important role in the interaction.

The surface tensions at CMC\textsubscript{IP} of the DSIP's have been found to be higher than that of the pure surfactant in all cases indicating lower effectiveness of the DSIP's.
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Fig.III.C.24. Plots of surface tension (mN/m) and absorbance of aqueous RN (2.5×10^{-5} mol dm^{-3}) solutions as a function of the logarithm of SDS concentrations at 298 K. Symbols: surface tension in presence (Δ) and absence (○) of RN, absorbances at 547 (○) and at 587 nm (○).

Fig.III.C.25. Plots of surface tension (mN/m) and absorbance of aqueous CV (2.5×10^{-5} mol dm^{-3}) solutions as a function of the logarithm of SDS concentrations at 298 K. Symbols: surface tension in presence (Δ) and absence (○) of CV, absorbance at 591 (○) and at 636 nm (○).
Fig.III.C.26. Plots of surface tension (mN/m) and absorbance of aqueous EV (2.5×10⁻⁵ mol dm⁻³) solutions as a function of the logarithm of SDS concentrations at 298 K. Symbols: surface tension in presence (Δ) and absence (○) of EV, absorbances at 595 (△) and at 640 nm (○).

Fig.III.C.27. Plots of surface tension (mN/m) and absorbance of aqueous MG (2.5×10⁻⁵ mol dm⁻³) solutions as a function of the logarithm of SDS concentrations at 298 K. Symbols: surface tension in presence (Δ) and absence (□) of MG, absorbance at 617 (△) and at 658 nm (○).
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Fig. III.C.28. Plots of surface tension (mN/m) and absorbance of aqueous RN (2.5×10$^{-5}$ mol dm$^{-3}$) solutions as a function of the logarithm of SDBS concentrations at 298 K. Symbols: surface tension in presence (∆) and absence (○) of RN, absorbance at 547 (○) and at 587 nm (○).

Fig. III.C.29. Plots of surface tension (mN/m) and absorbance of aqueous CV (2.5×10$^{-5}$ mol dm$^{-3}$) solutions as a function of the logarithm of SDBS concentrations at 298 K. Symbols: surface tension in presence (∆) and absence (○) of CV, absorbances at 591 (○) and at 636 nm (○).
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**Fig. III.C.30.** Plots of surface tension (mN/m) and absorbance of aqueous EV (2.5×10⁻⁵ mol dm⁻³) solutions as a function of the logarithm of SDBS concentrations at 298 K. Symbols: surface tension in presence (Δ) and absence (○) of EV, absorbance at 595 (○) and at 640 nm (●).

**Fig. III.C.31.** Plots of surface tension (mN/m) and absorbance of aqueous MG (2.5×10⁻⁵ mol dm⁻³) solutions as a function of the logarithm of SDBS concentrations at 298 K. Symbols: surface tension in presence (Δ) and absence (○) of MG, absorbances at 617 (○) and at 658 nm (●).
Results and discussion

Table III.C.2. Critical micelle concentration of SDS and triphenylmethane dye ion pairs (CMC\textsubscript{IP}), pC\textsubscript{20} and surface excess concentration at surface saturation ($\Gamma_s$) in pure water and in the presence of triphenylmethane dyes (2.5\times10^{-5} mol dm\textsuperscript{-3}) at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$^a$CMC\textsubscript{IP} / (mol dm\textsuperscript{-3})</th>
<th>pC\textsubscript{20}</th>
<th>$\Gamma_s$ / (mol / 1000 m\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>8.30\times10^{-3}</td>
<td>3.05</td>
<td>7.54\times10^{-4}</td>
</tr>
<tr>
<td>RN</td>
<td>1.26\times10^{-4}</td>
<td>4.18</td>
<td>2.36\times10^{-4}</td>
</tr>
<tr>
<td>CV</td>
<td>1.01\times10^{-4}</td>
<td>4.50</td>
<td>2.41\times10^{-4}</td>
</tr>
<tr>
<td>EV</td>
<td>6.31\times10^{-5}</td>
<td>4.55</td>
<td>2.49\times10^{-4}</td>
</tr>
<tr>
<td>MG</td>
<td>6.31\times10^{-4}</td>
<td>4.30</td>
<td>3.15\times10^{-4}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental error limits = ±3%.

Table III.C.3. Critical micelle concentration of SDBS and triphenylmethane dye ion pairs (CMC\textsubscript{IP}), pC\textsubscript{20} and surface excess concentration at surface saturation ($\Gamma_s$) in pure water and in the presence of triphenylmethane dyes (2.5\times10^{-5} mol dm\textsuperscript{-3}) at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$^a$CMC\textsubscript{IP} / (mol dm\textsuperscript{-3})</th>
<th>pC\textsubscript{20}</th>
<th>$\Gamma_s$ / (mol / 1000 m\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>1.18\times10^{-3}</td>
<td>4.05</td>
<td>5.93\times10^{-4}</td>
</tr>
<tr>
<td>RN</td>
<td>1.00\times10^{-4}</td>
<td>4.25</td>
<td>2.46\times10^{-4}</td>
</tr>
<tr>
<td>CV</td>
<td>7.94\times10^{-5}</td>
<td>4.65</td>
<td>2.67\times10^{-4}</td>
</tr>
<tr>
<td>EV</td>
<td>5.01\times10^{-5}</td>
<td>4.88</td>
<td>2.91\times10^{-4}</td>
</tr>
<tr>
<td>MG</td>
<td>3.98\times10^{-4}</td>
<td>4.55</td>
<td>3.18\times10^{-4}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Experimental error limits = ±3%.
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compared to the corresponding pure surfactants (Fig.III.C.24 to Fig.III.C.31). In the case of RN, CV and EV, the $\Gamma_s$ increases in the order RN<CV<EV, which is the order of increasing hydrophobicity of the dyes. The $pC_{20}$, which is a measure of the efficiency, of the DSIP's of these dyes also increases in the order RN<CV<EV. The above observations are in parallel to the observations made for photometric sensitivities of the dyes which was found to be in the order RN<CV<EV which was attributed to increasing hydrophobicity for the dyes in the same order [Lee 1989]. The behavior of MG with respect to the efficiency and effectiveness of the corresponding DSIP’s was also analogous to the other three dyes. The $pC_{20}$ of MG has been found to be higher than that of RN but less than that of CV as in the case of the spectrophotometric sensitivities reported by Lee et al [Lee 1989]. On the other hand, the surface excess concentration, $\Gamma_s$ at the CMC_{IP} for MG is also higher than those for the other three dyes. The surface tension at CMC_{IP} of MG has also been found to be significantly lower than those of the other three dyes.

Similar trends in CMC_{IP}, $pC_{20}$, and $\Gamma_s$ have been observed for the dyes also with SDBS Fig.III.C.28 to Fig.III.C.31 and Table III.C.2 & Table III.C.3). The difference between CMC_{IP} and CMC* have been found to be smaller in the case of SDBS compared to SDS with all four dyes. The smaller difference between CMC_{IP} and CMC* can be attributed to lower CMC* of SDBS (1.18x10^{-3} mol dm^{-3}) than SDS (8.30x10^{-3} mol dm^{-3}).

A comparison between the surface tension data of the aqueous triphenylmethane dyes – anionic surfactant systems with the absorbances at the absorption maxima corresponding to the helical monocationic forms and the dicationic forms indicate that the dye in the DSIP’s are protonated to the dicationic forms and exist as PDSIP’s as the DSIP’s start forming micelles by themselves analogous to that observed with NR in the previous section. The protonation of the dye in the DSIP to the doubly positive form cannot be attributed to the surface potential of the micelles alone because the surface potentials of the pure anionic surfactants should become more negative than that of the DSIP micelles [Healy 1990]. Whereas in the present case the absorptions due to the doubly positive dye form gradually disappeared when the surfactant concentrations are increased above the cmc of the pure surfactants. Lee et al. observed this shoulder in presence of other anions and attributed to the formation of ion pair [Lee 1989]. Lovell et al. also reported the association of this shoulder of CV with ion pair formation
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[Lovell 1999]. However some change in electronic distribution must take place in addition to ion pair formation to cause any change in the electronic spectra [Dakiky 2000]. Therefore some specific interaction, viz., close packed ion pair formation, causing electronic redistribution of the dye due to localization of the positive charge of the dye should be the key factor for appearance of the shoulder corresponding to the doubly protonated dye.

Valient et al [Valient 1991] noted that the distorted helical structure of the triphenylmethane dyes is favored by increase in the dielectric constant of the medium. Similarly, in the present case, the conversion of the dyes from their helical structure to the distorted helical structure as the PDSIP’s are formed can be attributed to high dielectric constant at the surface of the DSIP micelles where the dye is located.

III.C.v. The situation above the CMC of the pure surfactant.

The surface tension of the surfactants in the presence of the dyes, i.e., the surface tension of the DSIP’s, become equal to that of the corresponding pure surfactant as the surfactant concentration exceeds the CMC* as was observed in the cases of the sulfonephthalein dyes with cationic surfactants and neutral red with anionic surfactants. This indicates that as the surfactant concentration exceeds the CMC*, these dye-surfactant systems also regain air-water interfacial monolayer consisting of pure surfactant alone. The intensity of the band due to the PDSIP’s gradually decreases as the surfactant concentration approached the CMC* indicating reversal of the dye in the PDSIP to monocationic dye which can be attributed to transfer of the dye of the PDSIP from the DSIP micelle surface to the interior of pure surfactant micelles where the dielectric constant is lower than that in the bulk. Thus the premicellar aggregation reported to be responsible for destruction of the in pairs as the DSIP micelles changes to pure surfactant micelles [Garcia-Rio 2007]. This assumption is supported also by the fact that the absorbances due to the distorted helical structures, which is favored by higher dielectric constant, gradually disappeared along with the disappearance of the shoulder due to the deprotonated form, as the CMC*'s were approached. Therefore, above the CMC*, the dyes exist only in a solubilized state in the helical monocationic form in pure surfactant micelles.