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**Partitioning of Reactive Yellow 86 between Aqueous and Micellar Media studied by
Differential Absorption Spectroscopy**

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Abstract

The present study describes the partitioning of a reactive dye, reactive yellow 86 between aqueous and micellar media of a cationic surfactant, Cetyltrimethyl ammonium bromide (CTAB) as well as an anionic surfactant, Sodium Dodecyl Sulphate, SDS. In a systematic investigation, we have recorded the UV/Visible absorption spectra of the dye as a function of surfactant's concentration above and below the critical micelle concentration (CMC). Absorption spectra display red shift in case of CTAB and hypochromic shift upon using SDS. The partition coefficient (K_x) was calculated using differential absorption data and the value of free energy of partition (ΔG_p) was calculated using this K_x value. The results revealed that the dye is solubilized in CTAB micelles to greater extent than in SDS micelles.

Key Words: Dye, surfactant, solubilization, spectroscopy, micelle, partition coefficient.

33 INTRODUCTION

34 In recent years, the surfactants oriented research has undergone a dramatic development where
35 more emphasis has been focused to exploit the applications of surfactant systems to achieve
36 specific targets in chemical and technological areas of organic chemistry, physical chemistry,
37 petroleum and mineral processing, cosmetics and pharmaceuticals. Surfactants offer key role as
38 industrial cleaners, wetting, dispersing and leveling agents^[1, 2] as well as they are potentially
39 useful for green chemistry applications, being used as micellar catalysts, where they have
40 replaced harmful organic solvents.^[3-7] One of the most common industrial applications of
41 surfactants can be found in textile industry as surfactants are widely used to improve dyeing
42 process by increasing solubility, stabilizing the dispersed state and promoting uniform
43 distribution of the dye. The use of surfactants is not only limited to adsorption and fixation of
44 dyes on substrate, but also to address environmental problems for the removal of loosely bound
45 dyes and other toxic organics from the substrate via solubilization process.^[8,9] The importance of
46 solubilization lies in the fact that it enables us to get rid of organic co-solvents that may may
47 contaminate the environment by causing pollution and may lead to health problems.^[10,11] The
48 intrinsic nature of micelles, being heterogeneous in nature for encapsulating polar as well as non-
49 polar compounds enables them to serve aforementioned purpose.^[2, 12]

50 In premicellar region, monomers of surfactant interact with the dye molecules to form ion
51 association complexes, while, in post micellar region dye molecules are likely to be incorporated
52 into micelles.^[9] Hydrophobic effect is dominant to decide the locus of additive within micelle,
53 although, the effects of electrostatic interactions are not too weak to be ignored.^[13,14]

In 1954, Rattee and Stephens were the first to produce reactive dyes at the Imperial Chemical Industries, Manchester, which were later introduced commercially in 1956. The chromophore groups of these dyes are capable to directly interact with the substrate.^[15]

The spectra of many dyes are sensitive to polarity of solvent, the phenomenon being called solvatochromism. Positive solvatochromism exhibits red shift due to the enhanced polarity of the environment around the dye, while in case of negative solvatochromism, a blue shift is often observed. In positive solvatochromism, the excited state is more polar than the ground state, while in negative solvatochromism, the ground state is more polar.^[16]

Earlier, we reported the solubilization of some drugs such as Chloroquine Diphosphate, and Pefloxacin mesylate using the micellar solutions.^[17-18] In the present study, we attempted to explore the solubilization process of the reactive yellow 86 (RY 86) dye with a cationic surfactant [Cetyltrimethyl ammonium bromide (CTAB)] and an anionic surfactant [Sodium Dodecyl Sulphate (SDS)] using spectroscopic techniques. We anticipate that the observations from this study will be helpful to choose the best optimized conditions for spontaneous solubilization of dye in the micellar solution. Figure 1 represents the structure of the reactive yellow 86.

71

72 **Figure1.** Chemical structure of Reactive yellow 86

73 MATERIALS AND METHODS

74 In the present study, we extensively used differential UV/Visible spectroscopy as a useful tool to
75 demonstrate, qualitatively and quantitatively, whether interaction between two components
76 occurs or not. We found this technique very useful to probe the partition behavior of solubilize
77 between solvent and micellar phase and to get the values of partition constant. In simple
78 UV/visible spectra, we made base line correction by keeping distilled water in both cells using
79 Hitachi, U-2800 spectrophotometer. Later on, the aqueous solution of dye was taken in sample
80 cell and its spectra were recorded at different dye concentration. Finally, the surfactant was
81 dissolved in dye solution and spectra were recorded at different surfactant concentration to
82 observe changes in dye spectra due to the presence of surfactants. For the differential
83 spectroscopy, initially, the aqueous solution of dye was prepared and divided it into two portions.
84 A part of this solution was used as reference and the other one was used to prepare surfactant
85 solution. The base line correction was made by keeping dye solution in the reference as well as

sample compartments. Afterwards, a series of surfactant solutions were run to get differential UV/Visible spectra of the respective compositions.^[15, 16, 19]

Analytical grade, Cationic surfactant, Cetyltrimethyl ammonium bromide, CTAB and an anionic surfactant Sodium Dodecyl Sulphate, SDS was purchased from Sigma Aldrich and were used as received, while Reactive dye, Reactive yellow 86 (IUPAC name, sodium 7-((4-(4,6-dichloro-1,3,5-triazin-2-ylamino)-2-ureidophenyl)dizenyl)naphthalene-1,3,6-trisulphonate) was generously provided by Sandal dyestuff, Faisalabad, Pakistan. For all experiments, double distilled water was used, which was processed using still apparatus (Model IM-100). The stock solution of the dye was prepared in distilled water and was further diluted so that maximum absorbance may not exceed 1 and the Lambert-Beer law could be applied. The concentration of dye solution was kept at 1.5×10^{-5} M and surfactants were dissolved in it ranging from pre micellar to post micellar concentration (from 0.8mM to 1.2mM for CTAB and from 7.5 mM to 14.5 mM for SDS).

The differential UV/Visible spectroscopy can be used to measure the absorbance of dye-surfactant solution while removing the effect of dye absorbance at the same time. The increase in value of differential absorbance (ΔA) with surfactant concentration suggests stronger dye-surfactant interaction and indicates continuous inclusion of dye molecules within micelle. The differential absorbance is zero below critical micelle concentration CMC and increases rapidly beyond it. The values of ΔA at different surfactant concentration, above CMC, are inserted in Kawamura equation to get value of partition coefficient that is measure of degree of solubilization.^[20-23]

RESULTS AND DISCUSSION

108 ***Partitioning of RY86 in CTAB micelles***

109 Figure 2(a) shows the simple UV/Visible spectrum of reactive yellow 86 ($1.5 \times 10^{-5} \text{M}$) in the
110 absence and presence of CTAB. The peak at 420 nm shows the maximum absorbance and was
111 selected for the subsequent study. The shift in spectra confirms the interaction between dye and
112 surfactant. The change in environment of dye molecules from polar water to non-polar core
113 causes red shift in the spectrum of dye containing solution. The cumulative effect of electrostatic
114 and hydrophobic interactions causes anionic dye molecules to be accommodated within the
115 micelles of cationic CTAB. From Figure 2(b), the observed increase in absorbance with
116 increasing concentration of CTAB indicates incorporation of large amounts of dye molecules
117 into the micelle of surfactant. The *CMC* of CTAB is reduced (from 1.00mM to 0.89mM) due to
118 two main factors (i) an increase in entropy upon mixing surfactant with solubilized dye in
119 micelle and (ii) decrease in electrical work of micellization due to decrease in repulsion between
120 surfactant heads caused by solubilized dye. The aforementioned factors enable dye to drive
121 surfactant unimers close to each other and initiate micellization before *CMC*. The *CMC* of
122 CTAB in presence of RY86 was also determined by data of electrical conductivity, as displayed
123 in Figure 2(c). The value of *CMC* obtained from UV/Visible spectroscopy (0.89mM) and
124 conductivity (0.93mM) are in close agreement with each other. The slight difference between
125 two *CMC* values is due to the fact that *CMC* does not have a sharp value rather it represents a
126 range of concentration within which micellization takes place.^[19]

Figure 2. (a) Simple UV/Visible absorption spectra of Reactive yellow 86 in the presence of different CTAB concentration. (b) Plot of simple absorbance of Reactive yellow 86 as a function of CTAB concentration. (c) Plot of electrical conductivity of CTAB in presence of RY86 as a function of concentration at 298K.

The dye molecules are solubilized in outer portion of micelle and are under lateral pressure which tends to push it into the core of micelle. However, the attraction between anionic dye and cationic surfactant pushes the dye molecule in palisade layer very close to surface which thereby exhibits large K_x value. This phenomenon of solvatochromism is indicative of penetration of dye into palisade layer of micelle. The attraction between opposite charges, however, does not allow deep penetration of dye into micelle.^[20] The initial decrease in absorbance could be due to surfactant-assisted self-aggregation of dye molecules that reduces repulsion between dye molecules. The subsequent increase in the absorbance could be due to adsorption of dye molecules on the surface of oppositely charged CTAB.^[21, 23] The results from absorbance study reveal that the absorbance increases rapidly till CMC , while in post micellar region this increase was slow due to maximum incorporation of dye molecule as indicated by the saturation plateau in Figure 2(b) and 4(b). The slow increase in absorbance after CMC can be explained on the basis that greater amount of surfactant added in solution produces large number of micelles and increase in absorbance is due to incorporation of dye molecules into newly formed micelles.^[17, 25, 26-32]

Initially, the interaction between dye anions D^{n-} and surfactant cation S^+ produces dye-surfactant ion pair complex, DS.

Self-aggregation of DS, causes absorbance to increase in premicellar region.

At *CMC*, dye molecules enter into micelles as normal monomers and absorbance reaches its limiting value.

M and DM represent empty micelles and dye containing micelle respectively.

Solubilization, being a dynamic process causes dye molecules to spend different residence time at different positions between core and the surface because there is imbalance between the hydrophilic and hydrophobic forces which do not let dye molecules to acquire a stable position within micelle, rather keeps it fluctuating between surface and core, thus, giving random values of absorbance.^[13, 14, 17-18, 21-24]

The position of dye molecules within micelle depends on the balance between hydrophilic and hydrophobic forces. For anionic RY 86, hydrophilic forces are dominant and dye molecules are oriented near the surface of micelle as evident from high value of partition coefficient for dye-CTAB system.^[29, 30]

The long range electrostatic attraction between dye and surfactant molecules brings them close to each other while the short range dispersive and the hydrophobic interactions are responsible to align hydrophobic parts of dye and surfactant with each other in parallel fashion. The aforementioned forces act cooperatively with each other.

The qualitative as well as quantitative view of dye-surfactant interaction is provided by differential spectroscopy. It helps to calculate the value of partition coefficient and free energy of partition. The continuous increase in the differential absorbance with CTAB concentration (Figure 3(a)) is indicative of continuous inclusion of additive molecules within micelle. [17-18, 28, 30]

The value of partition coefficient was determined by the differential absorbance method reported by Kawamura et al. [20] according to the following equation;

$$\frac{1}{\Delta A} = \frac{1}{K_c \Delta A_\infty (C_d + C_s^{mo})} + \frac{1}{\Delta A_\infty} \quad (1)$$

In equation 1, C_d is the concentration of dye in term of molarity; C_s^{mo} is analytical concentration of surfactant calculated as $C_s - CMC_o$. Here, CMC_o is CMC of surfactant in water and C_s is surfactant concentration. ΔA is differential absorbance and ΔA_∞ represents its value at infinite concentration of surfactant, where all dye molecules are supposed to have been solubilized. K_c is the partition constant having value in the units of dm^3/mol calculated from slope of straight line plotted according to equation 1. The dimensionless quantity partition coefficient, K_x is obtained as $K_x = K_c n_w$, where n_w is number of moles of water per dm^3 . [17-18] Figure 3(b) displays the plot to calculate partition coefficient according to Kawamura model and table 1 shows data for calculation of partition coefficient.

Table 1:

Concentration of surfactant, C_s , differential absorbance, ΔA , reciprocal of differential adsorption, $1/\Delta A$, analytical concentration of surfactant, C_s^{mo} for calculation of partition coefficient of reactive yellow 86 in CTAB micellar Media

$10^3 C_s/$ (M)	$10^2 \Delta A$	$1/\Delta A$	$10^5 C_s^{mo}/$ (M)	$10^5 (C_s^{mo}+C_d)/$ (M)	$(C_s^{mo}+C_d)^{-1}$ (M) ⁻¹
1.21	2.7	37.03	20.96	22.47	4451.14
1.17	2.5	40	17.18	18.68	5351.63
1.14	2.3	43.48	13.64	15.13	6607.30
1.10	2	50	10.29	11.79	8479.94
1.07	1.6	62.5	7.14	8.64	11572.37
1.05	1.4	71.43	4.16	5.66	17651.98
1.01	1.1	90.91	1.35	2.85	35090.55

The value of free energy change for the transfer of dye molecules from aqueous to micellar phase was calculated using the following relation;

$$\Delta G_p = -RT\ln K_x \tag{2}$$

In equation 2, “ R ” is the general gas constant and T is absolute temperature.

196 The large values of K_x (1.12×10^6) indicates large scale transfer of dye molecules from the
 197 aqueous to the micellar media of CTAB, while, the large negative value of ΔG_p (-34.5 kJ/mol) is
 198 an indicative of the spontaneous nature of partitioning and a sign of stability of system.^[29, 30]
 199 Scheme 1 indicates binding of RY86 molecules with CTAB while scheme 2(a) shows
 200 partitioning of dye molecules with CTAB micelles.

201
 202 Figure 3. (a) Plot of differential absorbance of Reactive yellow 86 as a function of CTAB
 203 concentration. (b) Relationship between $(\Delta A)^{-1}$ and $(C_d + C_s^{mo})^{-1}$ for the calculation of partition
 204 coefficient (K_x) for Reactive yellow 86/CTAB system.

205

206 *Partitioning of RY86 in SDS micelles*

207 Figure 4(a) shows simple UV/Visible spectrum of reactive yellow 86 (1.5×10^{-5} M) in the absence
 208 and presence of SDS. The shift in spectra indicates interaction between dye and surfactant;
 209 however, it is the repulsive interaction due to similar charges on dye and SDS. There is
 210 hypochromic shift but no bathochromic or hypsochromic shift because the polarity around head
 211 groups of dye remains same either it is in pure water or in SDS micelle. Similar charges on
 212 surface of SDS micelle and RY86 inhibit the dye to penetrate in micelle and keep dye at micelle
 213 surface^[14-18] as indicated in scheme 2(b). Due to electrostatic repulsion between similar charges,

the only force responsible for partitioning of dye in SDS micelle is hydrophobic interaction. The increase in absorbance with concentration of SDS (Figure 4(b)) indicates limited partitioning of dye molecules into the micelle as repulsion between similar charges opposes deep penetration.^[23-24]

Figure 4. (a) Simple UV/Visible absorption spectra of Reactive yellow 86 in the presence of different SDS concentration. (b) Plot of simple absorbance of Reactive yellow 86 as a function of SDS concentration. (c) Plot of electrical conductivity of SDS in presence of RY86 as a function of concentration at 298K.

Figure 5(a) shows continuous increase in the differential absorbance with increasing SDS concentration which is indicative of hydrophobic partitioning of dye molecules within micelle.^[17-18, 28-30] Figure 4(b) and 4(c) shows that the dye increases *CMC* of SDS (from 8.2mM to 8.52mM) which can be ascribed to the repulsion between similar charges on dye and SDS partially increasing electrical work of micellization. In fact, the presence of dye molecules inhibits the close approach of surfactant molecules and causes delay in micellization. The electrostatic repulsion compels dye to keep its anionic sulfonate groups out of micelle and dye molecules remain half buried in micelle, as displayed scheme 2(b). When SDS was added to dye solution no red or blue shift is observed because chromophores of dye are still in water molecules and there is no change in polarity around chromophores. After reaching *CMC*, there is

little increase in absorbance due to formation of more micelles and incorporation of dye molecules in newly formed micelle causes little increase in absorbance.^[17-18] Similar models regarding electrostatic and hydrophobic interaction by surfactants have been proposed by Ghosh *et al.*^[3,7], Malik *et al.*^[4], Saha *et al.*^[5] and Sar, *et al.*^[6].

Figure 5(b) displays the plot to calculate partition coefficient according to Kawamura model and table 2 shows data for calculation of partition coefficient.

Table 2:

Concentration of surfactant, C_s , differential absorbance, ΔA , reciprocal of differential adsorption, $1/\Delta A$, analytical concentration of surfactant, C_s^{mo} for calculation of partition coefficient of reactive yellow 86 in SDS micellar Media

$10^3 C_s /$ (M)	$10^2 \Delta A$	$1/\Delta A$	$10^5 C_s^{mo} /$ (M)	$10^5 (C_s^{mo} + C_d)$ (M)	$(C_s^{mo} + C_d)^{-1} /$ (M) ⁻¹
13.4	2.8	35.7	519.28	520.78	192.018
11.72	2.6	38.47	351.87	353.37	283
11.03	2.4	41.67	282.94	284.43	351.57
9.87	1.8	55.56	166.84	168.34	594.03
9.15	1.3	76.93	94.63	96.13	1040.23
8.72	0.9	111.11	52.09	53.59	1865.97

8.52	0.7	142.85	32.27	33.77	2961.11
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244

245 Table 3 shows the values of partition coefficient and free energy of partition for dye/SDS system.
246 The values of K_x for SDS micelle is lower (4.5×10^4) than in CTAB micelles (1.12×10^6). This
247 indicates that the dye is partitioned in SDS micelle to lesser extent than in CTAB ones. The
248 negative value of ΔG_p (-26.38 kJ/mol) is an indicative of the spontaneous nature of partitioning
249 and a sign of stability of system.^[29, 30]

250

251 Figure 5. (a) Plot of differential absorbance of Reactive yellow 86 as a function of SDS
252 concentration. (b) Relationship between $(\Delta A)^{-1}$ and $(C_d + C_s^{mo})^{-1}$ for the calculation of partition
253 coefficient (K_x) for Reactive yellow 86/SDS system.

254

255

256 *Comparison of partitioning of RY86 within SDS and CTAB micelle*

257 RY86 is partitioned between aqueous and micellar media of CTAB to greater extent than in SDS
258 micelles. As shown in Scheme 1, the interaction between CTAB micelle and RY86 takes place
259 due to attraction between opposite charges. Dye molecules will initially adsorb at the surface of
260 micelle due to electrostatic interaction. However, this macromolecule has two aromatic rings
261 which have affinity for nonpolar core of micelle and therefore the electrostatic attraction alone is
262 not able to support it at surface. In fact, the dye molecules move into micelle in such a way that
263 their hydrophilic parts *viz.* sulfonate groups (SO_3^-) remain close to surface and aromatic rings
264 penetrate into core as evident from scheme 2(a). Dye molecules are, thus, solubilized into the
265 palisade layer of micelle.

266

267 Unlike incorporation of RY86 in CTAB micelles where both electrostatic as well as hydrophobic
268 forces are involved, partitioning of dye molecules within SDS micelles are favored by
269 hydrophobic forces only. In this scenario, the solubilization takes place to less extent than in case
270 of CTAB as clear from lower value of partition constant in SDS micelle (4.5×10^4) than in CTAB
271 micelle (1.12×10^6). Opposite charges on dye and CTAB causes larger negative value of ΔG_p in
272 case of dye/CTAB system, facilitating spontaneity of solubilization. While in case of dye/SDS
273 system, the repulsion between similar charges makes solubilization less spontaneous. If it
274 requires to remove dyes from water by micellar enhanced ultrafiltration, it is suggested to select
275 oppositely charged surfactant so that removal of impurity may be reinforced by electrostatic as
276 well hydrophobic forces. Dye spectra undergo red shift in presence of CTAB due to change in

277 polarity around its chromophores while in SDS causes no red shift as there is no such change in
278 polarity.

279 Repulsive interaction by SDS head groups have also been proposed by Saha *et al.*^[31], Ghosh *et*
280 *al.*^[32-34] and Mukherjee *et al.*^[35].

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Table 3.

Partition coefficient, K_x and free energy of partition, ΔG_p ; for reactive yellow 86 /CTAB and reactive yellow 86 /SDS systems.

Systems	K_x	$\Delta G_p /$ (kJ mol ⁻¹)
RY86-CTAB	1.12×10^6	-34.50
RY86-SDS	4.5×10^4	-26.38

Scheme 1. Binding of RY 86 with CTAB

292

293 **Scheme 2** (a). Partitioning of RY 86 in micelle of CTAB.

294

295

296

297 **Scheme 2 (b).** Partitioning of RY 86 in micelle of SDS

298 **CONCLUSION**

299 In the present study, the solubilization of anionic dye, reactive yellow 86 has been investigated in
300 the micellar media of CTAB (a cationic surfactant) and SDS ((an anionic surfactant). For this
301 purpose, simple and differential UV/Visible absorption spectra were recorded. The results

revealed the higher degree of solubilization of reactive yellow 86 in micelles of cationic surfactant (CTAB) than anionic SDS. The shift in UV/visible spectra of dye in the presence of CTAB is an indicative of strong interaction between the two phases. The dye has relatively higher value of K_x and more negative value of ΔG_p in CTAB micelles than in SDS micelles. It is because both electrostatic and hydrophobic forces favor partitioning of dye in CTAB micelle while solubilization in SDS micelle is governed by hydrophobic force only because electrostatic repulsion hinders partitioning in SDS micelle.

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