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## **CHAPTER 5 : STUDY OF SOLUBILITY OF INDICATOR DYES IN AQUEOUS SOLUTION OF PURE AND MIXED SURFACTANTS\***

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The present chapter deals with studies on aggregation and micro-environmental properties of surfactants by monitoring solubility of a suitable indicator solute in an aqueous solution of surfactant as a function of the surfactant concentration. In the present work cationic, anionic and neutral surfactants, viz., cetyl trimethyl ammonium bromide (CTAB) sodium dodecyl sulphate (SDS) and triton X 100 (TX 100) have been studied in aqueous solution. Aggregation properties of binary mixtures of SDS and TX 100 have also been studied. As indicator solutes we have chosen three dyes namely ketocyanine dye A, ketocyanine dye B and the E<sub>T</sub> (30)-betaine dye as shown in figure 5.1. A novel method has been proposed for determining the critical micelle concentration (*cmc*), solubility in micellar phase (*s<sub>m</sub>*) and the distribution coefficient (*K*) (of the dye between aqueous and micellar phase). The Hildebrand parameter,  $\delta_H^2$ , representing cavity formation energy has been determined for the micelle – water interface.

### **5.1 Determination of critical micelle concentration (cmc) and the solubility in the micellar phase**

Micellisation is essentially a dynamic process involving equilibrium between the surfactant molecules (*S*) in the aqueous phase and those in the micelles as represented by the following equation.

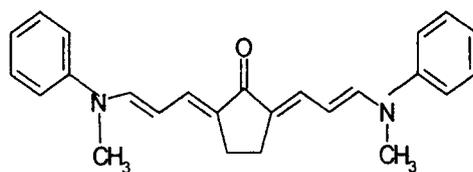
$$n S (\text{aqueous phase}) = S_n (\text{micellar phase}) \quad (5.1)$$

An indicator solute distributes itself between the two phases. Any property (*P*) of the solute that has dependence on its local environment can be used to reveal the equilibrium process.

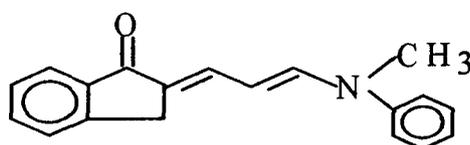
The value of *P* is expected to be different in the two phases.

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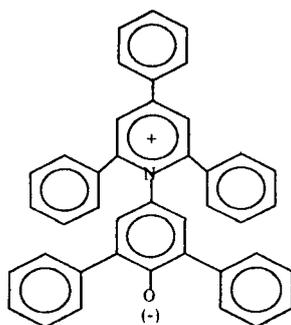
\* A. Maitra, N. Deb, S. Bagchi., *J. Mol. Liq.* (2007), doi:10.1016/j.molliq.2007.11.008



Ketocyanine dye A (KCD A)



Ketocyanine dye B (KCD B)



ET(30) betaine dye

**Figure 5.1: Indicator solutes used in the present study e.g. ketocyanine dye A, ketocyanine dye B and ET(30) betaine dye**

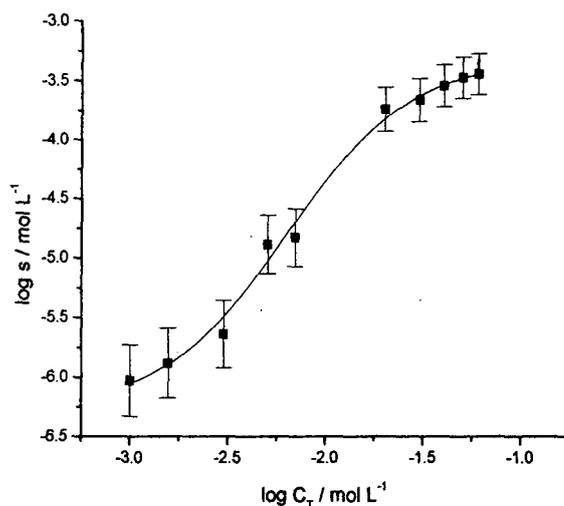
The measured value of  $P$  in a micellar medium can be assumed to be represented by a mole fraction average of the aqueous phase property ( $P_{aq}$ ) and micellar phase property ( $P_m$ ), as given by the following equation [1-6].

$$P = (n_{aq} P_{aq} + n_m P_m) / (n_{aq} + n_m) \quad (5.2)$$

Where  $n$  refers to the number of moles of the solute and the subscripts  $m$  and  $aq$  denote the micellar phase and the aqueous phase respectively. Calculation of value of  $P_m$  and  $P_{aq}$  requires knowledge of  $n_m$  and  $n_{aq}$  which in turn are related to the distribution coefficient ( $K$ ) of the indicator solute between the two phases. It has been shown that the parameters are related as [5, 7]

$$P = P_m + (P_{aq} - P_m)(1 - v(C_T - cmc)) / (1 + (K - 1)v(C_T - cmc)) \quad (5.3)$$

where  $v$  is the molar volume of the surfactant,  $C_T$  is the total surfactant concentration. The property  $P$  can be any additive property. It is known that  $\log s$ , where  $s$  represents solubility, is related to Gibbs free energy of solution [8]. In the present work we have taken  $\log s$  as the property  $P$ . The variation of  $\log s$  as a function of  $\log C_T$  has been studied. Figure 5.2 is a representative plot showing such variation. Value of  $\log s$  increases abruptly after a certain concentration. Data points can be fitted to a Boltzmann sigmoid equation. It has been proposed that the value of  $cmc$  can be obtained from the inflexion point of the Boltzmann sigmoid curve obtained by plotting a solute property as a function of  $C_T$  [9,10]. Truly speaking,  $\log s (= P)$  is related to  $\log (C_T - cmc)$  by the Boltzmann sigmoid equation as can be seen from equation (5.3). Thus the fitting of the experimental data point to Boltzmann sigmoid plot involving  $\log s$  and  $\log C_T$  is only an approximate one and hence the assignment of concentration at the inflexion point as  $cmc$  is likely to be in error. In this work an iterative procedure has been adopted as follows. Equation (5.3) can be rearranged as.



**Figure 5.2:** A plot  $\log s$  vs.  $\log C_T$  for SDS + TX 100 mixed binary system

$$\log s = \log s_{aq} + (K \log s_m - \log s_{aq}) \nu (C_T - cmc) + (1 - K) \nu P (C_T - cmc) \quad (5.4)$$

In the present procedure the value of concentration of surfactant at the inflexion point of  $\log s$  vs  $\log C_T$  plot is taken as the guess value of  $cmc$ . The parameter  $\log s_{aq}$  was then determined by linear regression analysis using equation (5.4). It follows from equation (5.3) or (5.4) that  $\log s = \log s_{aq}$  at  $C_T = cmc$ . Thus the value of the concentration for which  $\log s = \log s_{aq}$  was found out from the  $\log s$  vs  $\log C_T$  curve. This gives the output value of  $cmc$ . The above procedure was then repeated using the output  $cmc$  value as the input to get a new output  $cmc$ . The iteration was continued until the input and output  $cmc$  values are within  $\pm 2\%$ . Thus with SDS, the value of  $cmc$  obtained by this procedure comes as 7.4 mM which is in good agreement with the literature value. Once  $cmc$  is determined, values of  $\log s_m$ ,  $\log s_{aq}$ , and  $K$  can be found out by a linear regression analysis using equation (5.4). Values of molar volume ( $\nu$ ) for SDS and CTAB have been taken as  $0.246 \text{ L mol}^{-1}$  [11] and  $0.324 \text{ L mol}^{-1}$  [12]. The value for TX 100 has been estimated from the molecular dimension as  $0.294 \text{ L mol}^{-1}$  [5]. For mixed surfactant system the molar volume has been calculated by the relation.

$$v = x_1 v_1 + x_2 v_2 \quad (5.5)$$

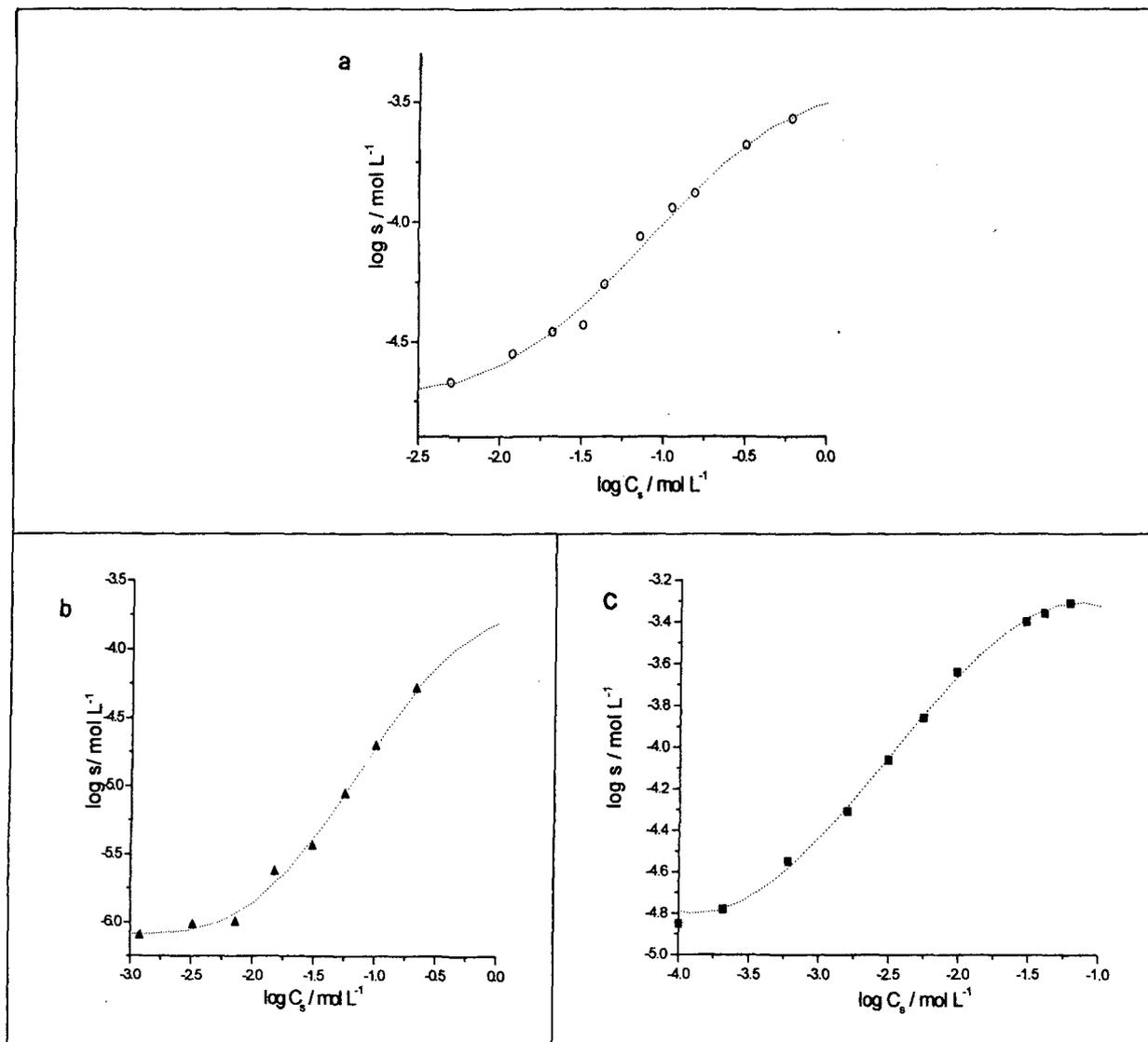
where  $x$  is the mole fraction and subscripts  $_1$  and  $_2$  represent surfactant component 1 and 2 respectively. Values of the relevant parameters along with the fitting statistics are given in tables 5.1 and 5.4. Figure 5.3 shows the experimental  $\log s$  values as a function of the concentration of surfactant in the aggregated form ( $C_S = C_T - cmc$ ) along with the best fit line for some representative systems.

## 5.2 Results and discussions

### 5.2.1 Homomicelles

Table 5.1 shows the values of  $cmc$  along with the solubility of indicator solutes in the aqueous ( $s_{aq}$ ) and in the micellar ( $s_m$ ) phase formed by pure surfactants. Note that the value of  $s_{aq}$  is greater than the solubility in pure water for all the indicator solutes. The slightly enhanced solubility is rationalisable in view of the presence of free surfactant monomers in the aqueous phase according to the two-phase model. The value of  $s_m$  is significantly greater than that of  $s_{aq}$  for the dyes indicating an increased solubility of the dyes in the micellar phase. Value of molar based distribution coefficient,  $K$ , for a particular solute is however dependent on the nature of the micelle. Thus CTAB, forming cationic micelle is characterized by a larger value of  $K$  compared to SDS, which forms anionic micelle. It has been established from spectroscopic studies that the indicator solutes used in the present study are located at the micelle-water interface [7, 13, 14]. In the present work the solutes are dipolar and the negative part of the molecule, viz., the carbonyl oxygen for the ketocyanine dyes and phenoxide group of the betaine dye can approach the cationic micelle more freely. Thus the greater value of  $\log K$  for CTAB compared to that of SDS can be rationalized. The spectroscopic parameter viz.,  $E_T(30)$  for the betaine dye and the energy of maximum fluorescence for the ketocyanine dyes indicate that the micropolarity around the chromophoric part of the dyes is in between that of water and ethanol [13-15]. To get an idea about the micropolarity of the region where the dye is solubilised we proceed as follows.

It is customary to write any property ( $XYZ$ ), linearly related to the Gibbs energy of a solute-solvent system, in terms of LSER by the following equation [16, 17],



**Figure 5.3:** Representative plots of  $\log s$  as a function of  $\log C_s$  for  $E_T(30)$  betaine dye in SDS (a), ketocyanine dye A in CTAB (b) and ketocyanine dye B in TX 100 (c). The dotted line represents best fit curve using  $\log s_m$ ,  $\log s_{aq}$  and  $\log K$  as given in table 5.1

**Table 5.1. Solubility of the indicator dyes in micellar phase ( $s_m$ ) and in aqueous phase ( $s_{aq}$ ), and the distribution coefficient ( $K$ ) along the fitting statistics for different micellar systems**

system	cmc (mM)	log $K$	$-\log s_m$	$-\log s_{aq}$	$R^2$	$\sigma$
<b>Ketocyanine dye A (KCD A)</b>						
aq-SDS	7.40	1.32 ± 0.04	4.27 ± 0.05	6.00 ± 0.06	0.99	0.0001
aq-CTAB	0.78	1.63 ± 0.04	3.70 ± 0.05	6.14 ± 0.06	0.99	0.0010
water <sup>a</sup>	-	-	-	6.82 ± 0.06	-	-
<b>Ketocyanine dye B (KCD B)</b>						
aq-SDS	7.40	2.63 ± 0.04	3.23 ± 0.05	4.58 ± 0.05	0.97	0.006
aq-TX100	0.40	3.03 ± 0.04	3.24 ± 0.04	4.85 ± 0.05	0.99	0.003
aq-CTAB	0.80	2.92 ± 0.04	3.16 ± 0.04	5.32 ± 0.06	0.90	0.010
water <sup>b</sup>	-	-	-	5.75 ± 0.06	-	-
<b>E<sub>T</sub>(30)-Betaine dye</b>						
aq-SDS	7.60	1.71 ± 0.04	3.43 ± 0.05	4.74 ± 0.05	0.96	0.0002
aq-CTAB	0.78	2.10 ± 0.04	3.46 ± 0.05	3.99 ± 0.05	0.96	0.0003
water <sup>c</sup>	-	-	-	5.70 ± 0.06	-	-

$R^2$  = correlation coefficient

$\sigma$  = standard deviation

<sup>a</sup> ref. 30; <sup>b</sup> ref. 24; <sup>c</sup> ref. 31

**Table 5.2. Values of  $\delta_H^2$  of micelle water interface for different surfactants**

**Homomicelles**

surfactant	$\alpha^{(a)}$	$\pi^{*(a)}$	$\delta_H^2$
CTAB	0.87	0.68	1.06
SDS	1.14	0.52	1.00
TX 100	1.06	0.56	1.01

<sup>(a)</sup> Ref. 5

$$XYZ = XYZ_0 + \text{cavity formation energy} + \Sigma \text{solute-solvent interaction energy} \quad (5.6)$$

The term  $XYZ_0$  denotes a constant and depends only on the solute. The summation in the above equation extends over all the modes of solute-solvent interaction. Using Kamlet-Taft version of LSER [18], we can write

$$XYZ = XYZ_0 + m \delta_H^2 + p \pi^* + a \alpha + b \beta \quad (5.7)$$

In equation (5.7) the cavity term is written as a product of coefficient  $m$  and the Hildebrand solubility parameter,  $\delta_H^2$ , of the solvent [19]. The solute-solvent interaction is written in terms of nonspecific dipolarity-polarisability interaction and specific interaction, e.g. hydrogen bond donation (HBD) and hydrogen bond acceptance (HBA). Empirical solvatochromic parameters  $\pi^*$ ,  $\alpha$ ,  $\beta$  have been used as descriptors of dipolarity-polarisability, HBD, HBA respectively [20-23]. In a recent communication we have shown that the value of  $\log s$  for the ketocyanine dye B in pure solvent is related to these parameters as [15].

$$\log s = -3.05 + 1.20 \alpha + 3.80 \pi^* - 3.54 (\delta_H^2 / 1000), n = 14, R^2 = 0.871, \sigma = 0.0002 \quad (5.8)$$

It is known that the ketocyanine dyes reside in the water micelle interface [13, 25]. The polarity of this region resembles that of aqueous alkanols [26]. In our earlier communication we have shown that the correlation equation (5.8) is also valid for water + ethanol mixture [24]. Thus we assume the relation (5.8) to hold good for the locus of solubilisation of the dye in micelle. In that case the LHS of equation (5.8) would be replaced by  $\log s_m$ . The parameters  $\alpha$ ,  $\beta$  and  $\pi^*$  for micellar media provided by the pure surfactant under study have recently been determined from spectroscopic studies. Values of  $\alpha$  and  $\pi^*$  for the micellar media have been listed in table 5.2. We have estimated the value of  $\delta_H^2$  for the micellar media using equation (5.8) and the known values of  $s_m$ ,  $\alpha$  and  $\pi^*$ . Thus study of solubility provides a method for the estimation of  $\delta_H^2$  for a micellar medium. Estimated values of  $\delta_H^2$  have been given in table 5.2. Note that for all the micelles the values of  $\delta_H^2$  for the locus of solubilisation of the dye, that is, micelle-water interface lies between those for water (2.29) and ethanol (0.68). We have calculated the values of  $\delta_H^2$  for the water + ethanol mixtures as

a function of composition using known enthalpies and volume of mixing and those quantities for pure solvents [19]. Values are given in table 5.3. It comes out that the value of  $\delta_H^2$  for the micellar phases used in these studies is close to the value of  $\delta_H^2$  at 0.5 mole fraction of water.

### 5.2.2 Heteromicelles

Solubility of the ketocyanine dye B in micellar media formed by binary mixture of SDS and TX-100 has been studied in detail. Values of *cmc* for the surfactant mixture compares well (within  $\pm 5\%$ ) with the value obtained by fluorescence method using the probe. Table 5.4 lists values of solubility of the dye in the micellar and the aqueous phase along with the values of distribution coefficient (*K*) as a function of the composition of surfactant mixture as obtained by the present analysis. Statistical parameters representing the fit are also given in table 5.4. Variation of  $\log K$  as a function of  $x_{SDS}$ , the mole fraction of SDS in the binary surfactant mixture has been shown in figure 5.4. The parameter  $\log K$  is directly related to the free energy change in bringing a solute molecule from the aqueous phase to the micellar phase. According to the linear solvation energy relationship (LSER) formalism,  $\log K$  value can be thought of as a sum of terms due to contribution from the different modes of solvation interaction, namely, dipolarity, hydrogen bond donation (HBD acidity) and hydrogen bond acceptance (HBA basicity) and cavity formation. LSER analysis indicates that the relative contribution of different interaction towards  $\log K$  are as follows: dipolarity  $\sim 2-3\%$ , HBD / HBA  $\sim 25-30\%$  and cavity  $\sim 40-45\%$  [27]. In the case of anionic SDS micelle the negative end of the ketocyanine dye B (carbonyl oxygen) remains away from the micelle which the positive part (*N*-atom), being sterically hindered cannot come close to the micelle. The interaction involves here is mainly electrostatic. On the other hand, for TX 100 micelle, HBD interaction of the head group with the carbonyl oxygen is important. Lower value of  $\log K$  for anionic SDS micelle relative to that of neutral TX 100 micelle as observed in our experiment indicates that HBD interaction dominates over electrostatic effects. In the mixed micellar system the variation of  $\log K$  with mole fraction is not linear.

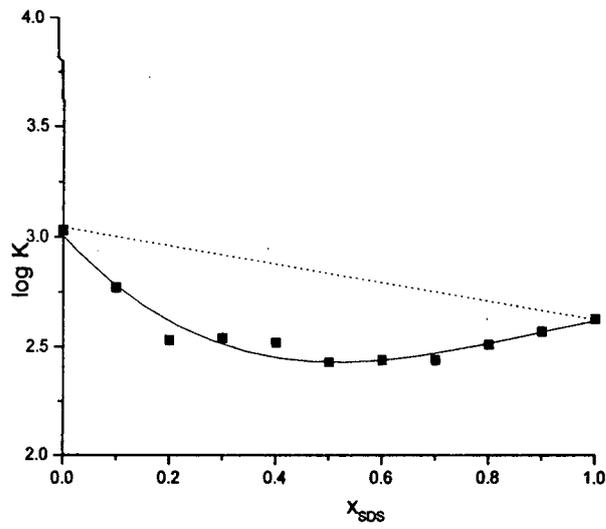


Figure 5.4: A plot of  $\log K$  as a function of  $x_{SDS}$  for SDS + TX 100 mixed binary system

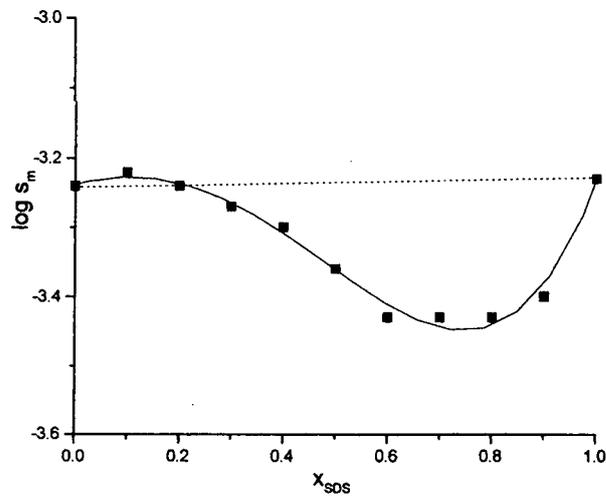


Figure 5.5: A plot of  $\log s_m$  as a function of  $x_{SDS}$  for SDS + TX 100 mixed binary system

**Table 5.3. Values of  $\delta_H^2$  for water + ethanol mixture**

$x_w$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\delta_H^2$	0.68	0.73	0.79	0.86	0.94	1.05	1.17	1.33	1.53	1.84	2.29

**Table 5.4. Solubility of the indicator dye in micellar phase ( $s_m$ ) and in aqueous phase ( $s_{aq}$ ), and the distribution coefficient ( $K$ ) along the fitting statistics for hetero-micellar system formed by SDS + TX 100**

$x_{SDS}$	$cmc/mM$	$\log K$	$-\log s_m$	$-\log s_{aq}$	$R^2$	$\sigma$
0.0	0.34	$3.03 \pm 0.04$	$3.24 \pm 0.05$	$4.85 \pm 0.05$	0.99	0.0030
0.1	0.36	$2.77 \pm 0.04$	$3.22 \pm 0.05$	$5.32 \pm 0.05$	0.99	0.0050
0.2	0.37	$2.53 \pm 0.04$	$3.24 \pm 0.05$	$5.61 \pm 0.05$	0.98	0.0003
0.3	0.38	$2.54 \pm 0.04$	$3.27 \pm 0.05$	$5.52 \pm 0.05$	0.98	0.0003
0.4	0.40	$2.52 \pm 0.04$	$3.30 \pm 0.06$	$5.34 \pm 0.06$	0.96	0.0090
0.5	0.42	$2.43 \pm 0.04$	$3.36 \pm 0.06$	$5.42 \pm 0.06$	0.96	0.0050
0.6	0.54	$2.44 \pm 0.04$	$3.43 \pm 0.06$	$5.47 \pm 0.06$	0.96	0.0018
0.7	0.71	$2.44 \pm 0.04$	$3.43 \pm 0.06$	$5.55 \pm 0.06$	0.97	0.0050
0.8	0.92	$2.51 \pm 0.04$	$3.43 \pm 0.06$	$5.81 \pm 0.06$	0.98	0.0003
0.9	0.94	$2.57 \pm 0.04$	$3.40 \pm 0.05$	$5.60 \pm 0.05$	0.98	0.0050
1.0	7.40	$2.63 \pm 0.04$	$3.23 \pm 0.05$	$4.58 \pm 0.05$	0.97	0.0060

 $R^2$  = correlation coefficient $\sigma$  = standard deviation

Note that at the SDS rich region ( $0.5 < x_{SDS} < 1.0$ ) the  $\log K$  values show only a slight decreasing trend. But the variation of  $\log K$  is more prominent in the TX 100 rich region. Figure 5.5 shows a plot of  $\log s_m$  as a function of  $x_{SDS}$ . Values of  $\log s_m$  are almost constant in the range ( $0.0 < x_{SDS} < 0.3$ ), and the curve showing the variation over the entire range passes through a minimum. Thus the dye is less soluble in mixed micelle. In the event of ideal solvation, the standard free energy of solution in a binary mixture will be given by the mole fraction averaged value [19, 28] and  $\log s_m$  in a binary surfactant mixture will be a linear function of molefraction [8, 24]. Non linear variation of  $\log K$  and  $\log s_m$  with mole fraction is indicative of nonideality of surfactant mixture. Interaction between the surfactants in the SDS + TX 100 mixture is well documented in the literature [15, 29]. Thus the results obtained from solubility measurements also point to surfactant – surfactant interaction in the binary mixture.

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