Chapter II
Chapter-II

ACID-BASE EQUILIBRIUM OF SULPHONEPHTHALEIN DYES IN ANIONIC SURFACTANT SYSTEMS *

2.1 Introduction

Dye–surfactant interactions in aqueous buffered systems have been drawing interest of many researchers due to their industrial applications [Barni 1991] and pertinence to biological process [Sarmiento 1992, Tomlinson 1979, Tanford 1980, Breslow 1991]. Knowledge of acid-base equilibria in dye–surfactant systems is also useful in analytical chemistry since surfactants are often used to sensitize electronic absorption of dyes for spectral determination of metal ions in buffered media [Diaz Garcia 1986, Hinze 1979]. Knowledge of CMC of surfactant in the buffered media is also useful for such studies in choosing the concentration of surfactant for the purpose. Observed shifts in


Most of the reports on acid-base equilibria in dye-surfactant systems involve dyes where, both of the acid and base forms are completely bound to the micelles [Drummond 1989, Pesavento 1992, Moulik 1993]. Several reports can be seen in the literature on partition equilibrium study of dyes in aqueous micellar systems [Rychlovsky 1988, Shah 1998, Novarro 2001, Sabate 2001b, Mishra 1999]. A method of studying the interaction of such acid-base indicator dye with surfactant is by eliminating either of the acid or base form of the dye from the system by keeping the pH of the system far away from the $pK_{a,w}$ and study the interaction of the other form with surfactants [Drummond 1989abcd, Minch 1975, Pesavento 1992, Moulik 1993]. However, a problem arises as some of the indicator dyes are unstable at extreme pH. Moreover, buffer components, ionic strength and specific interactions, which may affect $pK_{a,w}$,
may differ at extreme pH from those at any other pH of interest. A few of the studies reported so far have dealt with acid base equilibrium of indicator dyes in aqueous ionic micellar medium where the dye is partially bound to micelles [Sabate 2001a, Dutta {1993, 1995}, Hazarika 1993].

Partition equilibrium of dyes in aqueous micellar systems, has been studied by several authors using a combined concentration term for the two forms of an acid-base indicator in a well-buffered solution. The equilibrium constants of the association of the dyes to micelles were usually determined by using a B-H type plot [Drummond 1989, Pesavento 1992, Moulik 1993, Dutta {1993, 1995}, Gehlan 1995]. However, use of B-H type plot for determination of partition equilibrium constant in the method may result in large error due to difficulty in separating equilibrium constant and molar extinction coefficient from the product of the two [Hazarika 1993, Pearson 1965, Emslie 1965].

Partition equilibrium of dyes in aqueous micellar systems, has been studied by Dutta et al. using a combined concentration term for the two forms of an acid-base indicator in a well-buffered solution [Dutta {1993, 1995}, Hazarika 1993]. In the present paper it has been shown that a modification of the method enables to obtain the partition constant of such indicator dye between the micellar pseudophase and aqueous phase along with the CMC of the surfactant and in well-buffered solutions without use of any B-H type plot. The method requires spectral data of the dye solution of an absorption band, which decreases with addition of the surfactant, as a function of surfactant concentration. Though there are several methods for determination of CMC, reports of new and more efficient methods continues to appear in the literature [Temres 1973,
Ledakowicz 1997]. In addition, some of the present methods of CMC determination are either laborious or less efficient in buffered systems. Hence, the aspect of CMC determination has also been emphasized.

The dyes chosen were bromothymol blue (BTB), bromophenol blue (BPB) and thymol blue (TB), in aqueous anionic surfactant solutions by using the present modified method and the surfactants chosen were sodium dodecyl sulfate (SDS), sodium dodecyl sulfonate (SDSN) and sodium salt of linear alkyl benzene sulfonate (LABS, mostly dodecyl). These systems were chosen because the acid forms of these anionic acid-base indicator dyes bind to the anionic micelles, whereas, the doubly negative base forms do not bind due to higher electrostatic repulsion [Dutta 1995].

2.2 Experimental

BTB, BPB and TB, all products of S.D. Fine Chemicals, India were recrystallized from water and dried before use. SDS also from S.D. Fine Chemicals, was extracted from ether, dried, then recrystallized from methanol-water mixture and again dried. SDSN was obtained from Merck, Germany and was used as such. Industrial grade LABS was supplied by Kumud Enterprises, Calcutta was recrystallized twice from methanol-water mixture and dried. Buffer components of AR grade chemicals purchased from BDH, India and were used as such.

The visible spectra were recorded on a Hitachi U2001 spectrophotometer using a thermostated cell holder. The temperatures were
maintained within ±1 K. The wavelengths and absorbances were reproducible within ±0.5 and ±0.002 respectively. The pHs were measured using a Systronics (India) pH System-361. The buffer solutions were prepared following the tables of Perrin having ionic strength of 0.01 [Perrin 1963].

2.3 Theory

The various equilibria and species involved in the case of the sulphonephthalein indicators in aqueous anionic micellar systems can be summarized as shown in Scheme II (1) [Dutta 1995].

The pK_{a,w} of the sulphonephthalein dyes in the present experimental pH ranges can be defined by the equilibrium

\[ BH_w^- \rightleftharpoons K_{a,w} B_w^{2-} + H^+ \]  \hspace{1cm} (1)

or,

\[ K_{a,w} = \frac{[B_w^{2-}][H^+]}{[BH_w^-]} \]  \hspace{1cm} (2)

where, BH_w^- and B_w^{2-} are the acid and its conjugate base form, respectively.

The presence of the two forms of the dye in equilibrium makes it difficult to study the interactions of such indicator dyes with surfactant micelles near their pK_{a,w}. We have proposed a method to remove this difficulty by considering a combined activity or concentration term for both forms as follows.
Scheme II (1). The various equilibria and the species involved in the dye-surfactant systems studied.

\[
\begin{align*}
BH_w^- & \rightleftharpoons K_{a2,w} B_w^{2-} + H_w^+ \\
BH_m^- & \rightleftharpoons K_{a2,m} B_m^{2-} + H_m^+
\end{align*}
\]

Scheme II (2) Structure of the BH\(^-\) forms of the chosen indicators:

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X(_1)</td>
</tr>
<tr>
<td>BTB</td>
<td>CH(CH(_3))(_2)</td>
</tr>
<tr>
<td>TB</td>
<td>CH(CH(_3))(_2)</td>
</tr>
<tr>
<td>BPB</td>
<td>Br</td>
</tr>
</tbody>
</table>

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If \([D_w]\) is the total dye concentration in the aqueous solution, one can get from Eq. (2) that

\[
[D_w] = BH_w^- (1 + K_{a,w} / [H^+])
\]  \hspace{1cm} (3)

and

\[
[D_w] = B_w^{2-} (1 + [H^+] / K_{a,w}).
\]  \hspace{1cm} (4)

It follows from Eqs. (3) and (4) that the ratio of \([BH_w^-] / [B_w^{2-}]\) is a constant at a constant pH. Therefore, in whatever form the dye is incorporated into the micelles, the ratio of the two forms of the dye in aqueous medium remains constant at a constant pH. Thus, a combined concentration term for the dye in the aqueous medium, \(i.e., [D_w]\) can be used for determination of the dye–micelle association constant in buffered medium even though both forms of the dye exist in solution. We further assume that the electrostatic potential (or the effective pH) remains virtually constant at the micelle surface (though different from the bulk) with the variation in surfactant concentration. Thus, in analogy to Eqs. (3) and (4) we can write for the dye molecules which are bound to the micelles that

\[
[D_m] = BH_m^- (1 + K_{a,m} / [H^+])
\]  \hspace{1cm} (5)

or

\[
[D_m] = B_m^{2-} (1 + [H^+] / K_{a,m})
\]  \hspace{1cm} (6)
where, $BH_m^-$ and $B_m^{2-}$ are the concentrations of the acid and conjugated base forms of the dye, respectively, and $[H_m^+]$ and $K_{a,m}$ are hydrogen ion concentration and the acid dissociation constant of the dye in the micellar pseudophase.

In a well-buffered micellar solution, one can write,

$$K_{ass}$$

$$D_w + S_m \rightleftharpoons D_m$$ (7)

or

$$K_{ass} = [D_m] / [D_w][S_m]$$ (8)

where, $K_{ass}$ is the association constant of the dye with micelles at constant pH and $[S_m]$ is the concentration of micellized surfactant.

The association of the dyes with the micelles is determined by electrostatic and hydrophobic interactions. In case of an anionic dye and anionic surfactant system the association is opposed by electrostatic repulsion between the similar electrical charges on the dye forms but is favored by hydrophobic interactions of the dyes and the micelles. Thus, the association of the of the doubly anionic base form of the dye with the anionic micelles is much less compared to the association of the mono anionic acid form due to stronger electrostatic repulsion in the former. Thus, $[BH_m^-] >> [B_m^{2-}]$, in the case of sulfonephthalein dyes and anionic micelles systems. Therefore, one can consider $[D_m]$ as approximately equal to $BH_m^-$. Thus,
\[ K_{a_{ss}} = \frac{[D_m]}{[D_o][S_m]} \]  

(9)

If \( d_o \), \( d \) and \( d_m \) are the absorbances of the dye in absence of surfactant, in presence of surfactant of concentration \([S]\), and in excess of surfactant respectively, at fixed \( pH \) at an wavelength of the band where absorbances decrease with increase in concentration of the surfactant, then \( d_o = \varepsilon_o[D_o], \; d_m = \varepsilon_m[D]_o \) and \( d = \varepsilon_m[D]_o + \varepsilon_o[D_o] - \varepsilon_m[D_m] \), where, \( \varepsilon_o \) and \( \varepsilon_m \) are the apparent molar absorption coefficients of the dye, \([D]_o\) and \([D_m]\) are the total concentration and the concentration of micellized dye respectively. Substituting these concentration terms in Eq. (8),

or, \( K_{a_{ss}} = \frac{[D_m]}{[[D_o] - [D_m]][S_m]} \)  

(10)

or, \( K_{a_{ss}}[S_m] = \frac{(d_o - d) / (\varepsilon_o - \varepsilon_m)}{\{(d_o/\varepsilon_o - (d_o - d) / (\varepsilon_o - \varepsilon_m))\}} \)  

(11)

or, \( K_{a_{ss}}[S_m] = \frac{(d_o - d) / (\varepsilon_o - \varepsilon_m)}{\{(d_o\varepsilon_o - d_o\varepsilon_m - d_o\varepsilon_o + d_o\varepsilon_o) / \{\varepsilon_o(\varepsilon_o - \varepsilon_m)\}\}} \)  

(12)

or, \( K_{a_{ss}}[S_m] = (d_o - d) / (d - \varepsilon_m[D_o]) \)  

(13)

or, \( K_{a_{ss}}[S_m] = (d_o - d)/(d - \varepsilon_m[D_o]) \)  

(14)
or, \[ K_{\text{ass}}[S_m] = \frac{(d_o - d)\/(d - d_m)} \] \[ Now, \text{putting } [S_m] = [S_o] - \text{CMC,} \]
\[ \frac{(d_o - d)\/(d - d_m)} = -K_{\text{ass}} \text{CMC} + K_{\text{ass}}[S_o] \] \[ \text{(16)} \]

A plot of \( (d_o - d)\/(d - d_m) \) as \([S_o]\) should be linear with slope equal to \( K_{\text{ass}} \) and intercept of the abscissa equal to CMC (or the intercept of the ordinate equal to \(-K_{\text{ass}}\text{CMC}\)). The \( pK_a \)s were determined using Eq. (17):
\[ pH = pK_{a2} - \log\{(A_b - A_a)/(A_a - A_b)\} \] \[ \text{(17)} \]
where, \( A_a \), \( A_b \) and \( A_x \) are absorbances of the indicator in a strong acidic medium, in strong basic medium and at an intermediate \( pH \) respectively, at \( \lambda_{\text{max}} \) of the acid or base form.

### 2.4 Results and Discussion

The spectral characteristics of the dyes in water are given in Table II (1). The spectra of BPB at a constant \( pH \) of 3.2 in varying concentration of SDS is shown in Fig. II (1). The two bands with absorption maxima at 438 and 591 nm can be attributed to the acid (i.e., BH) and the base (i.e., \( B^- \)) forms of BPB respectively. When SDS is added to the aqueous dye solutions at a fixed \( pH \) at which both acid and base forms are present, the absorption band of the base forms gradually decreases to near zero with corresponding increase in the other band as reported earlier [Dutta 1995]. This indicates that with increase in the concentration of the anionic micelle more and more of the base form of the dyes are converted into the acid form. The near disappearance of the band of the base forms at high concentration of the surfactant indicates that the only the acid form associate with the micelles. This is expected because the electrostatic
Fig. II (1) Spectra of BPB (2 × 10^{-4} mol dm^{-3}) in presence of various concentrations of SDS at pH 3.20 and 313 K. [S] × 10^{-3} mol dm^{-3} : 1 (1.0); 2 (2.0); 3 (3.0); 4 (4.0); 5 (5.0); 6 (6.0); 7 (7.0).
repulsion between the doubly anionic $B_{w}^2-$ and the anionic surfactant is stronger than the hydrophobic attractive interaction between the two ions, whereas, in the case of mono anionic $BH^{-}$ and the anionic surfactant, the hydrophobic attraction is stronger than the electrostatic repulsion.

**Table II (1).** Some physical characteristics of the sulphonephthalein dyes at 313 (-0.5) K:

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{max}$ (+0.5) (nm)</th>
<th>$\lambda_{max}$ (+0.5) (nm)</th>
<th>$pK_{a2,w}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPB</td>
<td>438</td>
<td>591</td>
<td>3.49(3.52)</td>
</tr>
<tr>
<td>BTB</td>
<td>432</td>
<td>616</td>
<td>7.10(7.10)</td>
</tr>
<tr>
<td>TB</td>
<td>451</td>
<td>597</td>
<td>8.80(9.05)</td>
</tr>
</tbody>
</table>

There is a fixed ratio of the two forms of the dye at any fixed pH. Incorporation of a fraction of the $BH_{w}^{-}$ form into the micelles causes an imbalance between the two forms of the dye in aqueous phase and therefore a fraction of the $B_{w}^2-$ form is converted into the $BH_{w}^{-}$ form. The effect of increasing the concentration of SDS on the spectra of TB and BTB is similar to that of BPB. In case of TB the bands corresponding to absorption maxima at 451 and 597 nm can be attributed for the respective acid and base form of the indicator [Fig. II (2)]. The effect of other anionic surfactants on the spectra of sulphonephthalein dyes is similar to that observed for SDS. Fig. II (3), Fig. II
Fig. II (2) Spectra of TB (2 X 10^{-4} \text{ mol dm}^{-3}) in presence of various concentrations of SDS at pH 8.50 and 313 K. [S] X 10^{-3} \text{ mol dm}^{-3} : 1 (1.0); 2 (2.0); 3 (3.0); 4 (4.0); 5 (5.0); 6 (5.5); 7 (6.0); 8 (7.0).
Fig. II (3) Spectra of BTB (2 X 10^{-4} \text{ mol dm}^{-3}) in presence of various concentrations of SDS at pH 6.70 and 313 K. [S] X 10^{-3} \text{ mol dm}^{-3}: 1 (1.0); 2 (2.0); 3 (3.0); 4 (4.0); 5 (5.0); 6 (6.0).
**Fig. II (4)** Spectra of BTB (2 $\times$ 10$^{-4}$ mol dm$^{-3}$) in presence of various concentrations of LABS at pH 7.42 and 313 K. [S] $\times$ 10$^{-3}$ mol dm$^{-3}$: 1 (1.0); 2 (2.0); 3 (3.0); 4 (4.0); 5 (5.0); 6 (6.0); 7 (7.0)
Fig. II (5) Spectra of BTB (2 X 10^{-4} mol dm^{-3}) in presence of various concentrations of SDSN at pH 7.03 and 313 K. [S] \times 10^{-3} mol dm^{-3} : 1 (1.0); 2 (2.0); 3 (3.0); 4 (4.0); 5 (5.0); 6 (6.0).
2.4.1 Determination of CMC.

CMC locates a rather narrow concentration domain inside which the fraction of any additional surfactant placed in solution that micellizes goes from 0 to almost 1. Most solution properties are sensitive to the state of aggregation of the surfactant and frequently a physical property vs surfactant concentration plot is virtually linear for stretches both below and above the CMC. However a CMC based on extrapolation will depend upon the surfactant concentration at which the extrapolation commences. Hence there are methodological differences between CMC determinations which include choice of a characteristic point to be designated as CMC, nature of the plot employed in the determination, concentration range used when extrapolation is involved, type of data collected and effect of added indicators [Mukerjee 1971, Annacker 1994].

The present work is the result of our quest for a simplified spectroscopic method of CMC determination involving indicator dyes which can be simultaneously used for determining the association constant of the dye with the surfactant as well as the equilibrium constant of the dye partition.

CMC’s of the surfactant systems were determined by using Eq. (16), spectroscopically. It is evident that for the linear relationship [Eq. (16) ] to hold a plot of \((d_o - d)/(d - d_m)\) as \([S_o]\) should be linear with slope equal to \(K_{as}\) and intercept of the abscissa equal to CMC (or the intercept of the ordinate equal to \(- K_{as}\).CMC). The plots of \((d_o - d)/(d - d_m)\) vs. \([S_o]\) for BPB-SDS system at different temperatures and at pH 3.20 are shown in Fig.II (6). The plots have
Fig. II (6). \( \frac{(d_0 - d)}{(d - d_m)} \) vs. \([S_0]\) at various temperatures, BPB-SDS at 3.20 pH: ■, 298K; ▲, 303 K; ●, 308K; ○, 313K.
been found to be quite linear which indicates the validity of the present method. One can note how easy it is to locate the CMC from the plot unlike the conventional spectroscopic method for determination of CMC using dye [Mukerjee 1971]. The values of \([S_0]\) corresponding to the points on the abscissa where the straight lines meet are the CMC's of the surfactants in the respective buffer media. The points below \([S_0] = \text{CMC}\) fall on the abscissa due to absence of micelles. The versatility of the method is in the simultaneous determination of the CMC's of the surfactant system and the \(pH\) dependent association constant of the dye with the surfactant.

The CMC and \(K_{as}\) values determined at 313 K for the different systems are shown in Table II (2). Some systems could not be studied at temperatures lower than 313 K because precipitation was observed at lower temperatures. It is interesting to note that the \(K_{as}\) values decreases with increase in \(pH\) for a particular dye-surfactant system. This can be anticipated as the relative concentration of the acid form of the dye, which binds preferentially to the micelles, decreases with increase in \(pH\). Similar trends have been observed for variation in \(K_{as}\) and CMC with varying \(pH\) and temperature in all the dye-surfactant systems studied. It can be seen from the table that the CMC's in buffered media are much lower than that of the surfactant in pure water. We have plotted the CMC’s vs. temperature at different \(pH\) for some systems in order to see the dependence of CMC on temperature and \(pH\) [Fig. II (7)]. In general, the CMC decreased with increase in temperature and \(pH\). It can be seen from the figure that the lowering of CMC due to formic acid-KOH buffer
Table II (2). The pH dependent association constants $K_{ass}$ and the pH independent equilibrium constants $K_s$ of the sulfonephthalein dyes with anionic surfactants at 313 ($\pm 0.1$) K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Surfactant</th>
<th>pH</th>
<th>CMC* / 10^{-3} \text{ mol dm}^{-3}</th>
<th>$K_{ass}$ / \text{ dm}^{-3} \text{ mol}^{-1}</th>
<th>$K_s$ / \text{ dm}^{-3} \text{ mol}^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPB</td>
<td>SDS</td>
<td>3.20</td>
<td>5.5</td>
<td>89</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.40</td>
<td>5.8</td>
<td>69</td>
<td>124</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.89</td>
<td>6.1</td>
<td>40</td>
<td>141</td>
</tr>
<tr>
<td>BTB</td>
<td>SDS</td>
<td>6.47</td>
<td>1.7</td>
<td>900</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.70</td>
<td>1.9</td>
<td>830</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.90</td>
<td>2.2</td>
<td>780</td>
<td>1200</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.06</td>
<td>2.3</td>
<td>790</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.26</td>
<td>2.4</td>
<td>650</td>
<td>1300</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.49</td>
<td>2.5</td>
<td>470</td>
<td>1300</td>
</tr>
<tr>
<td>LABS</td>
<td></td>
<td>7.42</td>
<td>3.1</td>
<td>309</td>
<td>955</td>
</tr>
<tr>
<td>SDNS</td>
<td></td>
<td>7.03</td>
<td>8.7</td>
<td>335</td>
<td>620</td>
</tr>
<tr>
<td>TB</td>
<td>SDS</td>
<td>8.50</td>
<td>2.6</td>
<td>125</td>
<td>188</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.10</td>
<td>2.7</td>
<td>55</td>
<td>165</td>
</tr>
</tbody>
</table>

*Experimental error limits: ($\pm 0.2 \times 10^{-3}$ mol dm$^{-3}$) for CMC and ($\pm 5\%$) for $K_{ass}$. 
Fig. II (7). CMC against temperature for different surfactants at different pH: •, (BPB-SDS, pH 3.20); □, (BPB-SDS, pH 3.40); ▲ (BPB-SDS, pH 3.89); ×, BTB-LABS, pH 7.03); O, (BTB-LABS, pH 7.42); +, (TB-SDS, pH 8.50); □, (TB-SDS, pH 9.10).
system (form pH 3.20 to 4.02) is comparatively less than by phosphate (from pH 6.47 to 7.49) and borate (from pH 8.50 to 9.10) buffer systems.

2.4.2 Determination of equilibrium constant.

In a system of dye and surfactant where the base form is very negligible associated with the micelles (due to electrostatic repulsion) compared to the acid form, we can summarize the various equilibria as shown in Scheme II (1) [Dutta 1995]. The equilibrium constant $K_a$ which is independent of pH can be related to $K_{ass}$ by

$$K_a = K_{ass}(1 + K_{a2,w}[H^+])$$

(18)

The pH independent association constants, $K_a$ have been calculated using Eq. (18) and the values are included in Table II (2). It can be seen from the table that the $K_a$ values are fairly constant at constant temperature. This indicates the validity of the present method and its basic assumption that a combined activity term for the two forms of the dyes can be used in well-buffered aqueous solutions. The slight increase in $K_a$ with increase in pH in the systems can be attributed to higher absorption of Na$^+$ ions in the stem layer of the micelles which may screen the repulsion between the similarly charged dye and micelles. The values of $K_{ass}$ and $K_a$ presented in the tables agree well with literature values in similar systems. [Dutta 1995, Mishra 1999] For a common dye, viz. BTB with varying surfactant, the strength of the interaction, as
indicated by the equilibrium constants, is in the order SDNS < LABS < SDS. The strength of the interaction of the three dyes with a common surfactant, viz., SDS varies in the order BPB < TB < BTB which is in the order of increasing hydrophobicity of the dyes [Dutta 1995, Mishra 1999] [Scheme II (2)].

2.4.3 Thermodynamics of the dye-surfactant interaction.

The driving force for micellization is mainly the hydrophobic force. Micellization involves positive entropy due to destruction of the ordered iceberg structure of water around the hydrocarbon tail of the monomeric surfactant. However in presence of dyes there occurs a change not only in the water structure but also in the micellar pseudophase and in the microenvironment of the dyes [Pearson 1965, Mukerjee 1971, Annacker 1994]. Such perturbations depend upon various factors including the nature and strength of dye-surfactant interactions [Dutta 1992,1993,1995, Moulik 1993, Mishra 1999, Hazarika 1993, Mukerjee 1971, Dolzjicova 1997]. Determination of the thermodynamic parameters is therefore of great utility in the study of dye-surfactant interaction.

We have determined the $\Delta H^o$ and $\Delta S^o$ for the systems using the van't Hoff plot assuming the $\Delta H^o$ to be nearly constant in the small experimental temperature range between 298 and 313 K using average value of $K_s$ obtained at different $pH$. Some representative van't Hoff plots are shown in Fig. II (8). The linearity of the plots consolidates the assumptions made in the present partition equilibrium method. The thermodynamic parameters are given in Table II (3). The observed small negative enthalpy change indicates weak dye-micelle
Fig. II (8). $(1/T) / (10^{-3} \text{K}^{-1})$ vs. $\ln K_s$ for various dye-surfactant system at different pH: ▲, BTB-LABS (pH 7.03); ○, BTB-LABS (pH 7.42); ■, BPB-SDS (pH 3.20); △, BPB-SDS (pH 3.40); ×, BPB-SDS (pH 3.89); ●, TB-SDS (pH 9.10).
Table II (3). Thermodynamic parameters of the interaction of sulfonephthalein dyes with anionic surfactants at 298 K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Surfactant</th>
<th>$-\Delta G^*$ / k J M$^{-1}$</th>
<th>$-\Delta H^*$ / k J M$^{-1}$</th>
<th>$-\Delta S^*$ / JM$^{-1}$K$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPB</td>
<td>SDS</td>
<td>12.7</td>
<td>19.4</td>
<td>21.1</td>
</tr>
<tr>
<td>TB</td>
<td>SDS</td>
<td>11.7</td>
<td>15.6</td>
<td>12.5</td>
</tr>
<tr>
<td>BTB</td>
<td>LABS</td>
<td>14.9</td>
<td>21.3</td>
<td>20.3</td>
</tr>
</tbody>
</table>
interaction between dye and micelle due to similar charge on both. The greater
$\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ for the interaction between BTB nonionic surfactant, viz.,
TX100 roughly shows the negative effect of the similar charge on the
interaction of the dyes with the anionic surfactants. The observed weak
interaction between the dyes and anionic surfactants is driven by strong
hydrophobic interaction. The small negative entropy changes can be attributed
to more ordering in the bound system compared to the free dyes and micelles.

2.5 Conclusion

A combined activity term for the two forms of an indicator dye can be
used in well-buffered aqueous solutions for study in dye-surfactant systems.
The present method can be employed to the study of partition equilibria of acid­
base indicator dyes between aqueous and micellar pseudo-phases of aqueous
dye-surfactant systems of similar charge type and determination of CMC of the
surfactants in buffered media.

REFERENCES

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