Acid dissociation constants of N-alkyl p/o-hydroxy styryl pyridinium dyes in surfactant solutions

Bijay K Mishra, Pradipta K Behera & Rajalaxmi Rath
Centre of Studies in Surface Science and Technology,
Department of Chemistry, Sambalpur University, Jyoti Vihar 768 019, India

Received 4 September 2000; revised 9 November 2000

Some N-alkyl p/o-hydroxy styryl pyridinium halides, the alkyl moieties being methyl, hexyl and decyl, have been synthesised and the acid dissociation constants of these compounds in aqueous and surfactant solutions have been determined using spectrophotometric method. The alkyl chain does not have any substantial effect on the $pK_a$ values in aqueous and cationic surfactant (cetyl trimethylammonium bromide: CTAB) system. However, with longer alkyl chain the $pK_a$ values increase in anionic surfactant (sodium dodecyl sulphate: SDS). These results have been attributed to the variation in solubilization sites of the surfactants.

Acid-base equilibrium in micellar media differs significantly from that in the aqueous media. The shifts in the $pK_a$ values of indicators have been paid much attention due to their role to investigate the environment characteristics. It has been suggested that the shift in the $pK_a$ may be due to (i) electrostatic potential between the micelle surface and bulk aqueous phase, and (ii) specific molecular interaction such as ion-pair formation between oppositely charged indicator species and head groups of monomeric surfactants.

Dutta et al. have proposed a model for the indicator-surfactant systems in which either the acid or the base form of the indicator predominantly binds to the micelle. In this model, the shifts in $pK_a$ of an indicator in micellar solutions are calculated from the knowledge of the association constant of the indicator with the micelles at any desired concentration of the surfactant. Moulik et al. have investigated the acid-base equilibrium for dye, neutral red, in AOT micelles and have proposed the residence site of neutral red to be the interfacial region of SDS microemulsion, have studied the acid-base equilibria of neutral red in benzene-in-oil microemulsion and they reported the $pK_a$ to be 6.88 and 7.05 in microemulsions with n-propanol and n-butanol as the cosurfactant respectively.

In continuation of our earlier work in dye-surfactant interactions, herein we report an investigation of acid dissociation constants of some N-alkyl a/p-hydroxy styryl pyridinium iodide/bromide (I) in cationic and anionic surfactant systems.

Materials and Methods

The compounds N-methyl 4-(p-hydroxy styryl) pyridinium iodide (p-OHC$_3$), N-methyl 4-(o-hydroxy styryl) pyridinium iodide (o-OHC$_3$), N-hexyl 4-(p-hydroxy styryl) pyridinium iodide (p-OHC$_6$), N-hexyl 4-(o-hydroxy styryl) pyridinium bromide (o-OHC$_6$), N-decyl 4-(p-hydroxy styryl) pyridinium bromide (p-OHC$_{10}$) and N-decyl 4-(o-hydroxy styryl) pyridinium bromide (o-OHC$_{10}$) were prepared by condensing appropriate y-picolinium salts with p/o-hydroxy benzaldehyde. The uncorrected melting point values recorded in acid bath are reported in Table 1. The IR spectral data obtained from spectra recorded in a Perkin-Elmer RX1-FT IR spectrophotometer are in accordance with the structures of the compounds. The experimental concentrations of the hydroxy compounds were maintained at 2x10$^{-5}$ M in 5% methanol (E-Merck, AR) solution. CTAB and SDS (E-Merck) were purified before use. The pH was maintained at 7-12 with buffers prepared from citric acid, boric acid, phosphoric acid, sodium hydroxide and hydrochloric acid in different compositions. An Elico LI-120 digital pH meter was used for pH measurements. The electronic spectra were recorded on a Shimadzu UV-vis-200 spectrophotometer maintaining temperature at 300±0.5 K by using INSREF Ultracryostat. The $pK_a$ values have been determined by using the absorbance values of the
Table I—Absorption maxima of N-alkyl oř-p-hydroxy styryl pyridinium dyes in aqueous, SDS and CTAB solutions at neutral (λ\text{ionic}: ionic species) and alkaline pH (λ\text{merocyanine}: merocyanine species) at 300±0.5 K

<table>
<thead>
<tr>
<th>Comp.</th>
<th>M P in °C</th>
<th>Aq. medium (SDS (1×10^{-4}M))</th>
<th>SDS (1×10^{-3}M)</th>
<th>CTAB (5×10^{-4}M)</th>
<th>CTAB (5×10^{-3}M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>λ\text{ionic} (nm)</td>
<td>λ\text{merocyanine} (nm)</td>
<td>λ\text{ionic} (nm)</td>
<td>λ\text{merocyanine} (nm)</td>
</tr>
<tr>
<td>C_{1p}-OH</td>
<td>211</td>
<td>368</td>
<td>447</td>
<td>378</td>
<td>457</td>
</tr>
<tr>
<td>C_{1p}-OH</td>
<td>225</td>
<td>376</td>
<td>447</td>
<td>378</td>
<td>457</td>
</tr>
<tr>
<td>C_{1p}-OH</td>
<td>235</td>
<td>372</td>
<td>447</td>
<td>378</td>
<td>457</td>
</tr>
<tr>
<td>C_{1p}-OH</td>
<td>244</td>
<td>373</td>
<td>444</td>
<td>375</td>
<td>444</td>
</tr>
<tr>
<td>C_{1p}-OH</td>
<td>240</td>
<td>366</td>
<td>444</td>
<td>370</td>
<td>450</td>
</tr>
</tbody>
</table>

Results and Discussion

Absorption spectra in aqueous medium

The longest wavelength of the absorption band of all the dyes under study in 5% methanol-water medium appears around 366-378 nm. In p-hydroxy series, with increase in hydrophobic chain at pyridinium nitrogen, the λ_{max} values increase but not to a significant extent (3 nm from C_{1} to C_{6} and 4 nm from C_{1} to C_{10}). When hydroxy group is placed in the ortho position of N-methyl substituted dyes, the band suffers a hypsochromic shift up to 7 nm. While studying the substituent effect on electronic spectra of some benzylidines, Kuanar and Mishra have reported a hypsochromic shift up to 2-12 nm due to ortho substitution of -Cl, -OMe and -NH_{2} groups. In alkaline pH, the absorption spectrum of ortho-hydroxy derivative suffers bathochromic shift up to 78 nm. While the para hydroxy counterpart experiences a bathochromic shift of 71 nm. In alkaline pH, the large shift may be rationalized by proposing ortho and para-quinonoid structures for o-hydroxy and p-hydroxy dyes respectively (Scheme I).

Both the quinonoid forms absorb at same wavelength i.e. at 444 nm indicating a similar vectorial electron flow from the nitrogen atom towards the electron withdrawing carbonyl group. Similar to the cyanine counter parts, the merocyanine formed from the three cyanine dyes in alkaline medium does not experience the effect of alkyl chain towards the electronic spectra.

Absorption spectra in micellar medium

From the alkali fading kinetics of rosaniline hydrochloride, Mishra et al. have proposed that SDS micelles contain around 9% hydrophobic patches. These hydrophobic patches help in solubilizing substrates with similar charge as that of micellar surface. In the present study sodium dodecyl sulphate (SDS) and cetyltrimethyl ammonium bromide (CTAB) are used as the anionic and cationic surfactants for the formation of the micelles. The surfactants have CMC at 8×10^{-3} M and 9×10^{-4} M respectively. To see the effect of [surfactant] on λ_{max} and pK_{a} value the concentration above and below the CMC are chosen.

The shift of absorption maxima in SDS surfactant medium indicates that the dyes are localized either at...
Table 2—pKₐ values of N-alkyl α/β-hydroxy styryl pyridinium halides in aqueous and surfactant systems at 300±0.5 K

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Aq. medium</th>
<th>SDS (1×10⁻⁵M)</th>
<th>SDS (1×10⁻³M)</th>
<th>CTAB(5×10⁻⁴M)</th>
<th>CTAB(5×10⁻³M)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_{max} (nm)</td>
<td>pKₐ (nm)</td>
<td>λ_{max} (nm)</td>
<td>pKₐ (nm)</td>
<td>λ_{max} (nm)</td>
</tr>
<tr>
<td>C₄-α-OH</td>
<td>444</td>
<td>8.50±0.04</td>
<td>450</td>
<td>9.57±0.03</td>
<td>455</td>
</tr>
<tr>
<td>C₄-p-OH</td>
<td>444</td>
<td>8.69±0.08</td>
<td>444</td>
<td>9.00±0.03</td>
<td>444</td>
</tr>
<tr>
<td>C₆-α-OH</td>
<td>450</td>
<td>8.32±0.08</td>
<td>464</td>
<td>11.43±0.03</td>
<td>475</td>
</tr>
<tr>
<td>C₆-p-OH</td>
<td>450</td>
<td>8.48±0.04</td>
<td>468</td>
<td>11.06±0.03</td>
<td>480</td>
</tr>
<tr>
<td>C₁₀-α-OH</td>
<td>450</td>
<td>8.32±0.04</td>
<td>464</td>
<td>11.61±0.08</td>
<td>475</td>
</tr>
<tr>
<td>C₁₀-p-OH</td>
<td>450</td>
<td>8.51±0.04</td>
<td>480</td>
<td>11.29±0.02</td>
<td>480</td>
</tr>
</tbody>
</table>

Fig. 1—Absorption spectra of C₁₀-p-OH(2×10⁻⁵M) in SDS (1×10⁻³M) micellar solution at pH 9.14, 9.70, 10.08, 10.43, 10.68, 10.92, 11.24 and 11.62

Acid dissociation constant of dyes

The equilibrium during the dissociation of the dyes is shown in Scheme I. Due to a wide difference in the λ_{max} value of the molecular and ionic peaks, spectrophotometric determination is found to be the best tool for pKₐ measurement. Further the λ_{max} of the ionic species is found to be the analytical wavelength in almost all cases. The isosbestic points obtained in the absorption spectra by varying pH of the medium are indicative of equilibrium between the molecular and ionic species (Fig. 1).

The pKₐ values of these compounds are found to be around 8.69. No significant change in the pKₐ values due to change in alkyl chain at nitrogen was observed. However, the change of position of hydroxy group in the benzene ring has a noticeable effect on the pKₐ value. The α-hydroxy derivative has a lower pKₐ value than the p-hydroxy compound. The decrease in pKₐ value in the case of the former may be attributed...
to the ortho effect. The trend in $pK_a$ values is different in presence of charged micelles. The $pK_a$ values increase in anionic surfactant whereas decrease in cationic surfactant. The cationic dyes are localized close to the anionic surface of the SDS micelle and the OH$^-$ at alkaline $p$H is repelled by the anionic surface. And hence a high $p$H is necessary to interact with the dyes to enable them to dissociate. The effect of alkyl chain is clearly felt in SDS micellar medium. With increasing alkyl chain the $pK_a$ value increases. This is obvious due to relatively strong interaction of the dyes having high hydrophobicity with the micelles. Similarly, in CTAB micelles the $pK_a$ values are found to be less than that in systems without surfactant and that in anionic micelles. The decrease is more for C$_{10}$ dye because of comparatively a strong binding of dye with the cationic micelle when compared to dyes with smaller alkyl chain. The position of hydroxy group does not have any effect on the $pK_a$ values in differently charged micellar system.

Thus the charges at the interface as well as hydrophobic patches of the micelles are found to have major contribution on the acid dissociation constant of substrates with varied hydrophobicity.

Acknowledgement

BKM acknowledges the financial assistance from UGC, New Delhi through the UGC Research Award in Chemistry for the IXth plan period.

References