Adsorption of styryl pyridinium dyes on CTAB treated silica

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Cetyltrimethylammonium bromide (CTAB) adsorbs on silica surface and modifies the surface. The adsorption behaviour of some monochromophoric and bischromophoric styryl pyridinium dyes on CTAB treated silica (CTAB-silica) has been investigated. The adsorption model proposed by Gu and Zhu has been utilized to explain the type of adsorption isotherm. A low coverage of dye on CTAB-silica has been explained through apolar bonding. The rate constants of adsorption have also been determined. The adsorption behaviour of the dyes on CTAB-silica has been compared with that on silica, alkali treated silica and PEG treated silica surfaces.

Adsorption of cetyltrimethylammonium bromide (CTAB) on silica has been studied by various workers. Israelachvili et al. have reported a compact monolayer of CTAB on muscovite mica at concentration just below the critical micelle concentration (CMC) of CTAB. In this case the adsorption is due to the interaction of CTAB head group with the surface of the adsorbent. Similarly Rennie et al. have studied the structure of adsorbed CTAB on silica surface and reported that the surfactants are adsorbed on silica surface in bilayers when CTAB concentration is around the CMC. This bilayer makes the silica surface cationic. Similar surface modifications of various adsorbents have been studied by Somasundaran et al. In our earlier communications we have reported the area of coverage ($A'$) and rate of adsorption ($k_w$) of some monochromophoric and bischromophoric dyes on silica, alkali treated silica and PEG treated silica surfaces. The variation in the adsorption properties is found to change significantly in accordance with the charge at the silica surface. In the present study the silica surface has been modified by the use of surfactant like CTAB and the adsorption behaviour of some styryl pyridinium dyes has been investigated.

The interest on doping styryl pyridinium dyes on CTAB treated silica stems from the report of Groh et al. Styryl pyridinium dyes are found to be active non-linear optical material. When the monolayer film of these dyes on glass is tilted against laser beam the activity increases due to a specific orientation of the chromophore. Due to hydrophobic and hydrophilic interactions of the dyes with the CTAB treated silica surface the dye may assume desired orientation. The present work is an attempt to study the anchoring pattern of the dyes on CTAB treated silica surface.

Materials and Methods

The monochromophoric (1-5) and bischromophoric (6-11) styryl pyridinium dyes were prepared by the method reported earlier. The compounds were recrystallised before use.
CTAB (Sisco, Bombay) was purified by crystallising twice from methanol. Chloroform was purified by washing it with equal volume of water and then drying over CaCl₂. It was distilled before use. Triply distilled water was used throughout the study and all experiments were conducted at natural pH. Silica (Glaxo) of 125-150 μm with a BET-surface area of 137 m²/g (nitrogen adsorption) was obtained by the method reported earlier. The average diameter of the pore on silica surface was determined to be 80 Å. The silica (100 mg) was then treated with 500 cm³ of CTAB solution ([CTAB] = 7.6 × 10⁻⁴ M) in conductivity water for 72 h at 301 ± 0.2 K with occasional stirring; filtered and washed with distilled water several times till no bromide ion was obtained in the filtrate. The BET area of CTAB-treated silica was found to be 112 m²/g with pore diameter 52 Å.

The adsorption isotherms were established by measuring the concentration of the dyes spectrophotometrically before and after adsorption with a fixed amount of CTAB-treated silica. For this, a Hitachi UV-vis spectrophotometer was used. From the change in the concentration with varying time, the kinetic data were obtained by plotting time versus log (OD₀ - ODₜ) / (OD₁ - ODₜ) where OD₀, OD₁, ODₜ and ODₜ are the optical density values at zero, at infinity (24 hours) and at a given time, t, respectively. The plots were found to be linear with correlation coefficient = 0.99. The adsorption process was almost over within 10 minutes. Each result was an average of three to four experiments with 2% error.

Results
Silica gel, after treatment with CTAB solution, is assumed to have a coat of cationic surfactant where the cationic head group is anchored at the silica surface masking the silanol group. After the treatment of dye solution with CTAB treated silica (CTAB-silica) the adsorption of the dye can be marked visually producing shining, coloured silica. When the dye-CTAB-silica is isolated and treated with alkali, desorption of the dye occurs immediately. After keeping the solution for some time no readsorption of the dye on the silica surface is observed. The absorption spectra of supernatant solution are compared with the dye solution in alkali medium having almost same absorption value (optical density = 1.2). The spectra in both cases are found to be the same indicating the desorption of dye only from the adsorbent surface.

Adsorption isotherm
The plots of equilibrium concentration and adsorbed concentration on CTAB-silica in aqueous medium at constant temperature (301 ± 0.2 K) have been shown in Figs 1 - 4. Within the experimental concentration of the dyes the adsorption isotherms for all the dyes except methoxy substituted monochromophoric dyes are found to have single plateaus. In the case of methoxy substituted monochromophoric dyes the adsorption isotherms have two plateaus.

To explain the adsorption isotherm both Langmuir (Eq. 1) and modified Freundlich equation (Eq. 2) were used.

\[
(C_i/A_i) = (1/A_0 b) + (C_i/A_0) 
\]

... (1)

where \( C_i \) is the concentration of the dye at the adsorption equilibrium, \( A_i \) is the amount dye adsorbed at
equilibrium, $A_m$ and $b$ are the Langmuir constants related to the capacity and energy of adsorption respectively. Gu and Zhu\(^4\) have proposed a model to explain the $S$ adsorption isotherm where the adsorbates form hemimicelles on the adsorbent surface with an average hemimicellisation number of $'n'$. 

$$K$$

Adsorbent + $n$ Adsorbate $\rightleftharpoons$ Adsorbent-(Adsorbate)\(_n\)

By combining Langmuir and Freundlich equation they have proposed a modified equation.

$$\log (\frac{\tau}{\tau_m}) = \log K + n \log C \quad \ldots (2)$$

where $\tau$ is the amount of dye adsorbed at concentration $C$ and $\tau_m$ is the amount adsorbed in the limiting adsorption at high concentration. When $n$ is around one or less, $K$ may be treated as binding constant of adsorbate and adsorbent. The corresponding adsorption parameters with regression coefficients are given in Tables 1 and 2.

**Adsorption kinetics**

Analysis of the rate of adsorption data of Table 3 reveals that the rate constants of adsorption of $\_\text{NMe}_2\_\text{NMe}_2\_\text{NMe}_2\_\text{NMe}_2$ substituted bischromophoric dyes are less than the corresponding methoxy substituted bischromophoric dyes but reverse is the case in monochromophoric dyes. With increasing chain length the rate of adsorption decreases in the case of monochromophoric dyes. In the case of bischromophoric dyes with increase in spacer length in methoxy substituted bischromophoric dyes the rate of adsorption increases whereas in $\_\text{NMe}_2\_\text{NMe}_2\_\text{NMe}_2\_\text{NMe}_2$ substituted bischromophoric dyes the order is tetramethylene $>$ trimethylene $>$ hexamethylene spacers.

**Discussion**

Cetyltrimethylammonium bromide (CTAB) has a cationic head group having a surface area of $30 \pm 3 \text{ A}^2$(ref. 2). When silica gel with surface area $137 \text{ m}^2/\text{g}$ is treated with $7.6 \times 10^{-4} M$ of CTAB, the adsorption can lead to a condensed monolayer if $100\%$ adsorption is assumed. A condensed monolayer of CTAB on silica converts the silica surface to have hydrophobic characteristics. During the adsorption process the silanol groups on the silica are covered by the cationic head groups and the hydrophobic tails are exposed to water. From reflectivity studies Rennie et al.\(^2\) have shown that CTAB forms bilayer on silica surface where the upper layer surfactants have hydrophilic head groups exposed to bulk water and their hydrophobic tails remain entangled with the tail groups of the surfactants proximal to silica surface. They have, further, reported that, with decrease in [CTAB] the percentage of bilayer on the silica surface decreases. The formation of bilayers of surfactants on various solid surfaces has been reported by several workers\(^15\)\(^-\)\(^19\). In the present study the adsorption of cationic dyes on CTAB-silica surface clearly envisages that at least a part of the adsorbent surface has a monolayer of CTAB where the cationic dyes bind through hydrophobic interaction. In comparison to alkali treated silica and normal silica, the ease of desorption in CTAB-silica also suggests that the dyes do not bind directly to the silica surface.
Table 1: Langmuir isotherm fitting (Eq. 1) for the adsorption of styryl pyridinium dyes on CTAB-silica.

<table>
<thead>
<tr>
<th>Dyes</th>
<th>$R^2$</th>
<th>$A_m \times 10^5$</th>
<th>$B \times 10^4$</th>
<th>$-\Delta G^{\circ}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.972</td>
<td>1.58</td>
<td>0.427</td>
<td>36.7</td>
</tr>
<tr>
<td>2</td>
<td>0.929</td>
<td>2.20</td>
<td>0.098</td>
<td>33.0</td>
</tr>
<tr>
<td>3</td>
<td>0.972</td>
<td>1.89</td>
<td>0.545</td>
<td>37.3</td>
</tr>
<tr>
<td>4</td>
<td>0.966</td>
<td>2.62</td>
<td>0.089</td>
<td>32.8</td>
</tr>
<tr>
<td>5</td>
<td>0.973</td>
<td>1.82</td>
<td>1.026</td>
<td>32.9</td>
</tr>
<tr>
<td>6</td>
<td>0.615</td>
<td>1.70</td>
<td>0.131</td>
<td>33.7</td>
</tr>
<tr>
<td>7</td>
<td>0.999</td>
<td>9.92</td>
<td>0.209</td>
<td>34.9</td>
</tr>
<tr>
<td>8</td>
<td>0.907</td>
<td>1.04</td>
<td>11.889</td>
<td>45.0</td>
</tr>
<tr>
<td>9</td>
<td>0.980</td>
<td>1.00</td>
<td>2.771</td>
<td>41.3</td>
</tr>
<tr>
<td>10</td>
<td>0.999</td>
<td>3.15</td>
<td>1.842</td>
<td>34.3</td>
</tr>
<tr>
<td>11</td>
<td>0.991</td>
<td>15.10</td>
<td>0.168</td>
<td>34.3</td>
</tr>
</tbody>
</table>

* Adsorption from chloroform medium.

Table 2: Adsorption parameters obtained from Eq. 2 and energy of hemimicellisation for the adsorption of the styrylpyridinium dyes on CTAB-silica, silica*, alkali-silica* and PEG-silica* from aqueous and chloroform media.

<table>
<thead>
<tr>
<th>Dye</th>
<th>CTAB-silica</th>
<th>Silica</th>
<th>Alkali-silica</th>
<th>PEG-silica</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R^2$</td>
<td>$N$</td>
<td>$\log K$</td>
<td>$-\Delta G^{\circ}$</td>
</tr>
<tr>
<td>1</td>
<td>0.974</td>
<td>0.645</td>
<td>2.813</td>
<td>25.093</td>
</tr>
<tr>
<td>2</td>
<td>0.997</td>
<td>0.941</td>
<td>3.981</td>
<td>24.341</td>
</tr>
<tr>
<td>3</td>
<td>0.983</td>
<td>0.622</td>
<td>2.729</td>
<td>25.284</td>
</tr>
<tr>
<td>4</td>
<td>0.976</td>
<td>0.713</td>
<td>2.836</td>
<td>22.285</td>
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<tr>
<td>5</td>
<td>0.987</td>
<td>0.812</td>
<td>3.999</td>
<td>28.329</td>
</tr>
<tr>
<td>6</td>
<td>0.999</td>
<td>1.070</td>
<td>5.217</td>
<td>28.052</td>
</tr>
<tr>
<td>7</td>
<td>0.986</td>
<td>0.578</td>
<td>2.937</td>
<td>29.231</td>
</tr>
<tr>
<td>8</td>
<td>0.988</td>
<td>0.833</td>
<td>4.050</td>
<td>27.905</td>
</tr>
<tr>
<td>9</td>
<td>0.999</td>
<td>0.759</td>
<td>4.050</td>
<td>27.905</td>
</tr>
<tr>
<td>10</td>
<td>0.999</td>
<td>0.439</td>
<td>2.069</td>
<td>27.197</td>
</tr>
<tr>
<td>2*</td>
<td>0.990</td>
<td>0.895</td>
<td>3.868</td>
<td>25.886</td>
</tr>
<tr>
<td>5*</td>
<td>0.993</td>
<td>0.675</td>
<td>2.809</td>
<td>23.979</td>
</tr>
</tbody>
</table>

* Adsorption from chloroform medium.

Table 3: Area of coverage and rate constants during adsorption of styryl pyridinium dyes on CTAB treated silica at 301 ± 0.2K.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Area of coverage (Å²/molecule)</th>
<th>Rate constant ($k_r \times 10^4$ s⁻¹)</th>
<th>Dye</th>
<th>Area of coverage (Å²/molecule)</th>
<th>Rate constant ($k_r \times 10^4$ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1961</td>
<td>9.09</td>
<td>8</td>
<td>2404</td>
<td>10.59</td>
</tr>
<tr>
<td>2</td>
<td>1939</td>
<td>25.17</td>
<td>9</td>
<td>2341</td>
<td>6.67</td>
</tr>
<tr>
<td>3</td>
<td>1400</td>
<td>7.10</td>
<td>10</td>
<td>3518</td>
<td>12.80</td>
</tr>
<tr>
<td>4</td>
<td>3001</td>
<td>15.50</td>
<td>11</td>
<td>830</td>
<td>4.70</td>
</tr>
<tr>
<td>5</td>
<td>1892</td>
<td>9.09</td>
<td>2*</td>
<td>1046</td>
<td>5.72</td>
</tr>
<tr>
<td>7</td>
<td>3403</td>
<td>4.07</td>
<td>5*</td>
<td>854</td>
<td>10.13</td>
</tr>
</tbody>
</table>

* Adsorption from chloroform medium.
Adsorption isotherm

The adsorption of cationic surfactant on silica gel results in the adsorption isotherms having one or more than one plateaus. Existence of more than one plateau in the adsorption theorem is an indication of the presence of multilayer in the adsorption phenomena. However, the adsorption of the cationic dyes on CTAB-silica yields adsorption isotherms having almost one plateau at the experimental concentration of the dye.

The adsorbents that form micelle on aqueous medium, are proposed to form hemimicelle on adsorbent in aqueous medium. The formation of hemimicelle is, generally, attributed to hydrophobic interaction of the adsorbates. Formation of hemimicelle is evidenced from a conspicuous increase in adsorption, which is attributed to the onset of surfactant aggregation on the surface through lateral interaction. To explain the adsorption isotherm of CTAB on silica, Gu and Zhu have combined Freundlich and Langmuir equations to obtain the number of adsorbate per hemimicelle on the adsorbent. In the present study the adsorption of the cationic dye on the CTAB-silica has been monitored. Because the exact charge on the effective surface of the adsorbent is not known both Langmuir equation and the equation derived by Gu and Zhu have been utilized to study the adsorption phenomena.

Both the equations are linear in characteristics and the correlation coefficients have been used as indicators to choose the suitable equation (Tables 1 and 2). The data of Table 2 clearly envisage that the combined equation of Langmuir and Freundlich can explain the adsorption behaviour of all the dyes. The n values (number of adsorbate per hemimicelle) are found to be less than one except in the case of 7. The ‘n’ values for adsorption of the dyes on CTAB-silica is less than that of the adsorption of the dyes on silica as well as alkali treated silica (Table 2). This is due to the hydrophobic nature of the surface of the CTAB-treated silica. The n values for the adsorption of dyes on PEG-treated silica is less than one and the results have been attributed to adsolubilization phenomena. Though n value with less than one does not have any physical significance for hemimicellisation number, it can be considered as probability of anchoring of an adsorbate on the adsorbent as monomer. Formation of hemimicelle in water medium is due to hydrophobic interaction of the hydrophobic groups of the dyes. In nonpolar environment hydrophobic interaction decreases and consequently inhibits hemimicellisation. From the ease of desorption of the adsorbed dyes it has been proposed that the adsorption of dye on CTAB-silica is due to the interaction of hydrophobic group of the dye with the exposed hydrophobic chains of CTAB on the CTAB-silica. A probable orientation scheme of the dye on the CTAB-silica is given in Fig 5.

It provides a nonpolar environment resulting in inhibition of hemimicellisation of the dye and thus the average number of hemimicellisation decreases. Corollary to this with increased hydrophilic characteristics of the dye the hemimicellisation increases. The n values (Table 2) of all the dyes clearly support this proposition. In the case of monochromophoric dyes n values of butyl derivatives are more than the corresponding amyl derivatives. Similarly in the case of bischromophoric dyes with increase in spacer length the hydrophobic characteristic increases which leads to decrease in hemimicellisation and consequently decrease in n values.
Further, when the functional groups i.e. -NMe₂ and -OMe are considered, NMe₂ is more hydrophilic than the OMe group. This is clearly reflected from the corresponding \( n \) values of the dyes. The log \( K \) values are found to be less (some times \( 10^4 \) times) when compared to the values obtained during the adsorption of the dyes on normal or alkali treated silica (Table 2). This low value is the obvious result of adsorption due to apolar bonding, which is comparatively weak. It is interesting to note that with increase in hydrophobicity the binding constant decreases for each series of dyes with the same functional group. The change in free energy due to hemimicellisation (or binding with the adsorbed CTAB) \( (\Delta_{nm} G) \) has been obtained using Eq. 3.

\[
\Delta_{nm} G = -RT \ln K
\]

The data are given in Table 2. The values are found to be within the range of -22.9 to -29.2 kJ/mole.

When log \( K \) is correlated with \( n \) a good correlation is obtained (Eq. 4, Fig.6).

\[
\log K = 4.675 \pm 0.465 n - 0.046
\]

\[
R^2 = 0.93, \ SD = 0.281
\]

The adsorption of 2 and 5 from chloroform medium onto CTAB-silica has been investigated. The \( n \) values are found to be 0.895 and 0.674 respectively which are very close to the values of butyl and amyl substituted -NMe₂ dyes (2 and 4) when studied in aqueous medium. The log \( K \) values are also found to be in the same range as in aqueous medium of the respective dyes. These results corroborate the dominance of apolar bonding in the adsorption process.

Area of coverage

The area of coverage \( (A') \) of each dye on the CTAB-silica has been determined by considering (i) the effective area for adsorption on CTAB-silica is 112 m²/g and (ii) the effective anchoring area of the dye is 75 Å²/molecule.

The \( A' \) values are found to be in the range of 830 Å² to 3518 Å² per molecule. The apparent large surface area of the dye molecules, when compared to the values on adsorbents like silica, alkali-silica and PEG-silica, is probably a consequence of the presence of porosity on the silica surface. Due to the adsorption of CTAB, it is likely that the pores are either filled up or blocked by CTAB. The decrease in pore diameter after adsorption of CTAB also supports this proposition.

The structure-\( A' \) relationship as mentioned below is found to be highly interesting.

Monochromophoric dyes:

(i) For -OMe substituted dyes with increase in chain length the \( A' \) values decrease.

(ii) For -NMe₂ substituted dyes with increase in chain length the \( A' \) values increase.

Bischromophoric dyes:

(i) For -OMe substituted dyes with increase in spacer length the \( A' \) values increase.

(ii) For -NMe₂ substituted dyes with increase in spacer length the \( A' \) values decrease.

These changes in the behaviour of the dyes during adsorption may be attributed to the complexity in the structure of dyes. The complexity is a result of the possible effective functional groups such as benzene and pyridinium nuclei, olefinic double bond of styryl unit, substituents in the benzene nucleus, alkyl chains of monochromophoric dyes and methylene units of bischromophoric dyes.

However, the \( A' \) values obtained in chloroform medium for 2 and 5 are found to be 1046 Å² and 854 Å² respectively. The trend is found to be reversed when compared to the \( A' \) values on silica and alkali treated silica. This difference may be attributed to the compatibility of the chain length of the dye 5 with that of the surfactant.

Adsorption kinetics

The rate of adsorption obeys first order kinetics with respect to the concentration of the dye. Assuming the area for adsorption to be very large, pseudounimolecular rate constants have been calculated and reported in Table 3. The rate constant values are found to be more than that obtained in normal silica. No linear correlation are obtained of the rate constants with \( n \), log \( K \) and \( A' \) values.

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