Formation Constants of Intermolecular Charge Transfer Complexes of Quinaldine Ethiodide & of 2-Hydroxystyryl Derivatives of Quinoline Ethiodide in Ethanol & Chloroform

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The formation constants and the molar absorptivities of the intermolecular charge transfer complexes of quinaldine ethiodide, 2-(2'-hydroxystyryl) quinoline ethiodide and 2-(4'-hydroxystyryl) quinoline ethiodide have been determined in ethanol and in CHCl$_3$ at different temperatures. The results are discussed in terms of temperature, solvent polarity and dye molecular structure. In general, the intermolecular charge transfer complexes of the hydroxystyryl cyanine derivatives are more stabilized in ethanol than in CHCl$_3$.

The longer wavelength band observed in the spectra of quinaldine ethiodide and its hydroxystyryl derivatives was assigned to an intermolecular charge transfer (CT) transition$^{+*}$. Generally, the structure and mechanism of solvation of styryl cyanine dyes having wide applications as photosensitizers$^6$ and in biological processes$^7$, are considered to be of interest for the study of the spectral sensitization. A detailed study of the electronic spectra of these compounds is, therefore, called for.

In continuation of our work on the spectra of styryl cyanine dyes$^5$,$^7$, the present communication includes the determination of formation constants and molar absorptivities of intermolecular CT complexes of quinaldine ethiodide (I), 2-(4'-hydroxystyryl) quinoline ethiodide (II) and 2-(2'-hydroxystyryl) quinoline ethiodide (III) in solvents of different polarities, such as ethanol and CHCl$_3$ and at different temperatures. The results are discussed in terms of temperature, solvent polarity and dye molecular structure. Further a comparison has also been made of the results obtained in this study with those of the CT complexes of the hydroxystyryl-4-phenylthiazole ethiodide derivatives reported earlier$^7$.

Materials and Methods

Quinaldine ethiodide was prepared by the method of Sutherland and Compton$^4$. The separated product was recrystallised from ethanol in yellow needles. 2-(2'-and 4'-hydroxystyryl) quinoline ethiodides were prepared by the reaction of quinaldine ethiodide with the corresponding aldehyde in the presence of a few drops of piperidine as catalyst by a method similar to that described before$^8$. The styryl derivatives obtained were recrystallised several times from ethanol. The purity of the compounds was checked by elemental analyses.

Spectral grade quality solvents (E. Merck) were used in this investigation.

Stock solutions (10$^{-3}$M) were made by dissolving the accurately weighed amount of the compound in the appropriate volume of the solvent. Dilute solutions for spectral measurements were obtained by accurate dilution.

Procedure and measurements— A series of solutions containing compounds I-III at different concentrations were prepared in ethanol and chloroform. The solutions were equilibrated at the desired temperature (±0.2°) and their visible spectra recorded rapidly on a UNICAM SP 8000 ultraviolet spectrophotometer. The reference cell contained the pure solvent at the same temperature.

Results and Discussion

Representative spectra of III in ethanol and CHCl$_3$ in the temperature range 30-50° within the CT complex region are given in Fig. 1.

The formation of CT complex (AB) of the compounds under investigation involves the transfer of an electron from the negatively charged iodide ion to...
the positively charged nitrogen atom of quinaldine ion (compound I) or to 2-(hydroxystyryl) quinoline ion (compounds II and III) within the solvent separated ion-pair as shown in Eq. (1).

$$\text{(X}=\text{-CH}_3 \text{ I, -CH=CH}_2 \text{ II, -CH=CH} \text{ III)}$$

The formation constant $K_t$ and the molar absorptivity ($\epsilon_{AB}$) of the intermolecular CT complex (AB) in ethanol and chloroform were determined at different temperatures (Table 1), using Eq. (2)

$$\frac{L}{\epsilon_{AB}} = \left( \frac{1}{K_t \epsilon_{AB}} \right) P + \frac{1}{\epsilon_{AB}}$$

where $L$ and $P$ represent respectively, $C_{OA}C_{OB}/C_{OA} + C_{OB} - C_{AB}$ and $1/C_{OA} + C_{OB} - C_{AB}$. $C_{OA}$ and $C_{OB}$ represent the initial molar concentrations of A and B respectively, $C_{AB}$ is the molar concentration of the CT complex (AB). Since $C_{OA} = C_{OB} = C_0$, where $C_0$ is the initial molar concentration of the compound, $L = C_0^2/2C_0 - C_{AB}$ and $P = 1/C_0 - C_{AB}$ in Eq. (2) is the absorbance due to the CT complex. Since the absorbance measurements were carried out at the $\lambda_{\text{max}}$ of the CT complex, one can consider the measured absorbance at this $\lambda_{\text{max}}$ to be equal to the absorbance due to the CT complex only. This fact was confirmed by the good linear relationship obtained on plotting the absorbance against the concentration of the compound. This indicated the existence of only one absorbing species which should be the CT complex.

In order to obtain more accurate values of $K_t$ and $\epsilon_{AB}$, Eq. (2) was solved iteratively. Thus, for different initial concentrations of each compound, $L/E_{AB}$ and $P$ values were calculated assuming that $2C_A >> C_{AB}$ and plotting one against the other to get the required linear plot. The method of least squares was used to define the best linear plot through the experimental points, and from which the values of $K_t$ and $\epsilon_{AB}$ were determined. Since $K_t$ is large, it becomes necessary to use these initial values of $K_t$ and $\epsilon_{AB}$ to determine $C_{AB}$ using Eq. (3)

$$C_{AB} = 2C_0 - \frac{\epsilon_{AB}C_0^2}{\epsilon_{AB}} + \frac{1}{K_t}$$

After obtaining $C_{AB}$, the values of $L/E_{AB}$ and $P$ were revised accordingly and a new set of values of $K_t$ and $\epsilon_{AB}$ (second iteration) were obtained. Further iterations were made until constant values of $K_t$ and $\epsilon_{AB}$ were obtained.

The linear relationship between $L/E_{AB}$ and $P$ values obtained from the fourth iteration, which give more accurate values of $K_t$ and $\epsilon_{AB}$ for all the compounds investigated in ethanol at 30°, are shown in Fig. 2. The $K_t$ and $\epsilon_{AB}$ values of the intermolecular CT complexes in ethanol and in CHCl$_3$ at different temperatures are collected in Table 1.

Effect of temperature on the formation constant ($K_t$) — An examination of the results presented in Table 1 reveals that $K_t$ decreases with increasing temperature except in the case of compound (III) in ethanol. This can be interpreted on the principle that by increasing temperature the extent of dissociation of CT complex exceeds the extent of association of the separated ions as a result of decrease of their

![Fig. 2 — Fourth iteration of $L/E_{AB}$ vs. $P$ linear relationship at 30°. (a) For compound (I); (b) for III; (c) for II.]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_t \times 10^{-5}$ in ethanol</th>
<th>$K_t \times 10^{-5}$ in CHCl$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25°</td>
<td>30°</td>
</tr>
<tr>
<td>I</td>
<td>0.87</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>(1.71)</td>
<td>(1.73)</td>
</tr>
<tr>
<td>II</td>
<td>1.66</td>
<td>1.48</td>
</tr>
<tr>
<td></td>
<td>(5.18)</td>
<td>(4.94)</td>
</tr>
<tr>
<td>III</td>
<td>9.93</td>
<td>13.87</td>
</tr>
<tr>
<td></td>
<td>(5.13)</td>
<td>(5.26)</td>
</tr>
</tbody>
</table>

*Molar absorptivity ($\epsilon \times 10^{-4}$) are given in parentheses and are expressed in mol$^{-1}$ cm$^2$
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solvation. However, the increase in the formation constant of the CT complex of compound (III) in ethanol on increasing the temperature can be ascribed to the fact that the dissociation of this CT complex is more than balanced by the decrease in the ionisation power of ethanol leading to high $K_f$ value.

Effect of solvent polarity on $K_f$— At a fixed temperature, it is evident that the $K_f$ value of the CT complex of compound (I) is higher in chloroform as compared to that in ethanol. This can be ascribed to the non-polar character of CT complex which is expected to more stabilized in less polar chloroform. On the other hand, the CT complexes of compounds (II) and (III) are more stabilized in ethanol than in CHCl$_3$, which can be attributed to a specific ethanol-CT complex interaction. This behaviour is similar to the one observed for the CT complexes of the hydroxystyryl 4-phenylthiazole ethiodide derivatives. Thus generally one can conclude that the CT complexes of the hydroxystyryl cyanine derivatives are more stabilized in protic solvents relative to aprotic ones. It may be noted that the specific interaction between ethanol and 2-(2' or 4'-hydroxystyryl) quinoline ethiodide was previously indicated by the spectra of these compounds in mixed solvents.

However, the CT complex of compound (II) appeared to unstable in CHCl$_3$ as revealed by the decrease in the intensity of the CT complex band with time.

Effect of solvent polarity and temperature on $\epsilon$— The variation of $\epsilon$ values with solvent polarity reveals that the CT complex of compound (I) is being stabilized in CHCl$_3$ relative to ethanol, while that of compound (III) is being stabilized in ethanol relative to CHCl$_3$, which is in accordance with our above conclusion. The irregular variation of $\epsilon$ with temperature (Table 1) can be ascribed to the fact that $\epsilon$ is not a good measure for absolute intensity of a transition, rather one has to consider the integrated intensity (oscillating strength $f$). The oscillating strengths of the CT complex bands of the compounds under investigation in CHCl$_3$ and in ethanol at different temperatures have been calculated and are recorded in Table 2.

Effect of molecular structure on $K_f$— At a fixed temperature and in the same solvent, the $K_f$ values of the CT complexes of compounds (I-III) show the following increasing order: $1 < II < III$

| Table 2 — Oscillator Strength ($f$) Values for the Intermolecular CT Complex Band of Compounds I, II and III in Ethanol and CHCl$_3$ at Different Temperatures |
|-----------------|-----------------|-----------------|-----------------|
| Compound | $25^\circ$ | $30^\circ$ | $40^\circ$ |
| I | 13.86 | 13.76 | 13.45 |
| II | (14.85) | (14.76) | (14.61) |
| III | 19.86 | 17.78 | 16.54 |
| | $40^\circ$ | $50^\circ$ |
| I | 11.58 | 11.89 |
| II | (6.14) | (5.69) |
| III | (12.22) |

This order is in line with the extent of conjugation existing in the cation of each of these compounds, resulting in more electron delocalization in the same order. This in turn increases the affinity of the cation to accept electron from the iodide ion (high $K_f$). However, the higher conjugation in the cation of compound (III) relative to that in compound (II) is probably due to the high inductive effect of the OH group in ortho position in case of the former compound.

References
2. MAHMOUD, M. R. & ABDEL-HAMIDE R., under publication.