

## Interionic Charge Transfer Enhanced by Hydrophobic Interaction

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**Synopsis.** A water solution containing Rhodamine 6G and Na-tetraphenylborate exhibits a new absorption band at 540 nm, which has the characteristics of a charge-transfer (CT) band. In organic solvents, however, such a CT band is not found. This indicates that hydrophobic interactions enhance the charge transfer interaction.

Spectroscopic studies on the charge transfer interaction in water solution have been made in connection with the biological interest.<sup>1–6</sup> However, very little has been reported about the effect of hydrophobic interactions on the charge transfer interaction.

In the present report we show evidence to support the view that hydrophobic interactions play an important role in the formation of the charge transfer (CT) complex.

### Experimental and Results

When the sodium salts of tetraphenylborate ( $\text{BPh}_4^-$ ) is added to a water solution of Rhodamine 6G ( $\text{Rhod } 6\text{G}^+$ ), a purple color appears instantaneously. At the same time, the characteristic fluorescence of the  $\text{Rhod } 6\text{G}^+$  ion decreases on adding the  $\text{BPh}_4^-$  solution. On the contrary, no evidence of any CT interactions with  $\text{BPh}_4^-$  was found for  $\text{Rhod } 6\text{G}^+$  in organic solvents such as ethanol, acetonitrile, and *N*-methylformamide. These results indicate that water enhances the CT interaction between the organic ions both possessing large hydrophobic groups.

The UV/VIS absorption spectra of the water solutions of mixtures of  $\text{Rhod } 6\text{G}$  and Na-tetraphenylborate were examined on a Shimadzu UV 200S double beam spectrophotometer at 25 °C. The results are shown in Fig. 1. The appearance of isosbestic points confirms the presence of a new complex. The absorption maximum of the new band was determined as  $\lambda = 540 \text{ nm}$  from the concentration dependence of the peak position of the spectra. We analysed the spectra on the basis of a modified Rose-Drago equation<sup>7</sup>:

$$\frac{ab}{d-d_0} = \left( a + b - \frac{d-d_0}{\epsilon_C - \epsilon_A} \right) \frac{1}{\epsilon_C - \epsilon_A} + \frac{1}{K(\epsilon_C - \epsilon_A)} \quad (1)$$

where  $d_0$ ,  $d$ ,  $\epsilon_A$ ,  $\epsilon_C$ ,  $a$ ,  $b$  and  $K$  denote the absorbances of  $\text{Rhod } 6\text{G}^+$  and mixtures, the molar absorptivities of  $\text{Rhod } 6\text{G}^+$  and complex, the initial concentrations of  $\text{Rhod } 6\text{G}^+$  and  $\text{BPh}_4^-$ , and the equilibrium constant for the complex. By means of an iterative method, the constant was determined as

$K = 1.02 \times 10^5 \text{ l/mol}$  at 25 °C. This is fairly comparable with the  $K$  values of the ion pair of  $[(i\text{-C}_6\text{H}_{11})_3(n\text{-C}_4\text{H}_9)\text{N}]^+\text{BPh}_4^-$  determined by conductometry<sup>8</sup> or of fluorenylsodium by spectrophotometry.<sup>9</sup> These facts strongly suggest the new entity to be an interionic CT complex with 1:1 stoichiometry. Therefore, equilibrium (2) should be considered;



Thus the new absorption at 540 nm is ascribable to the CT band arising from the excitation of the complex.

### Discussion

From Table 1, it is evident that the CT interaction between  $\text{Rhod } 6\text{G}^+$  and  $\text{BPh}_4^-$  is not affected by the solvent polarity, but it is strongly dependent upon the nature of the solvent, the lipophilicity or hydrophobic solvation capability. In organic solvents, the solvent-solute pairs must be formed predominantly in comparison with the solute-solute pairs, because of their relatively strong hydrophobicity. Hence, it is difficult to form the tight binding donor-acceptor ion pairs. This leads to the interruption of the subsequent charge

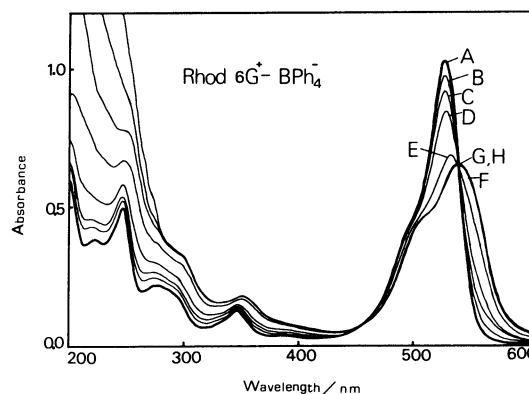


Fig. 1. Absorption spectra of  $\text{Rhod } 6\text{G}^+$  ( $1.12 \times 10^{-5} \text{ mol/l}$ ) in water with various amounts of  $\text{BPh}_4^-$  at 25 °C. A none, B  $1.06 \times 10^{-6} \text{ mol/l}$ , C  $0.19 \times 10^{-5} \text{ mol/l}$ , D  $0.38 \times 10^{-5} \text{ mol/l}$ , E  $0.76 \times 10^{-5} \text{ mol/l}$ , F  $1.52 \times 10^{-5} \text{ mol/l}$ , G  $3.42 \times 10^{-5} \text{ mol/l}$ , H  $6.83 \times 10^{-5} \text{ mol/l}$ .

TABLE 1. SOLVENT DEPENDENCE ON THE CT-COMPLEX FORMATION BETWEEN  $\text{Rhod } 6\text{G}^+$  AND  $\text{BPh}_4^-$  IONS

Solvent	Dielectric constant	Spectral evidence	Complex formation
Water	78.54 <sup>a</sup> )	A new band appears at 540 nm.	yes
Ethanol	24.30 <sup>b</sup> )	A shift in the $\text{Rhod } 6\text{G}^+$ spectrum is observed.	no
Acetonitrile	37.45 <sup>b</sup> )	A shift in the $\text{Rhod } 6\text{G}^+$ spectrum is observed.	no
<i>N</i> -Methylformamide	182.4 <sup>b</sup> )	A shift in the $\text{Rhod } 6\text{G}^+$ spectrum is observed.	no

a) The Chemical Society of Japan, Ed. "Kagaku Binran, Kiso-hen II", Maruzen (1957) p. 1166. b) A. J. Bard, Ed. "Electroanalytical Chemistry", Marcel Dekker, Inc., New York (1969) Vol. 3, Appendix 1.

transfer since CT interaction involves short range forces, so that the formation of the CT complex is reduced. This explains why the CT band is not found in solvents such as ethanol, acetonitrile and *N*-methylformamide. On the contrary, when water is used as a solvent the stacking between the donor and acceptor ions must be promoted, for solvent water enhances the hydrophobic interactions between the two ions.<sup>10-11</sup> Once stacking take place between two pi-electron systems, the charge transfer from donor to acceptor occurs easily, because intermolecular charge transfer is most strongly favored in the case where "active orbital" overlapping between donor and acceptor is possible.<sup>12</sup> This is the main reason why Rhod 6G<sup>+</sup> forms a CT complex with BPh<sub>4</sub><sup>-</sup> in water solution.

Subsequently, we have estimated the overall free energy change on complex formation as  $\Delta G = -26$  kJ/mol. Let  $\Delta G_{HI}$  be the free energy change due to the hydrophobic interaction we can split  $\Delta G$  into two contributions;

$$\Delta G = \Delta G_{E,C} + \Delta G_{HI} \quad (3)$$

where  $\Delta G_{E,C}$  is the contributions from electrostatic and CT interactions. Sheraga<sup>13</sup> calculated  $\Delta G_{HI}$  values for various types of hydrophobic interactions;  $\Delta G_{HI} = -1.3 \sim -6.3$  kJ/mol were determined. These values are relatively small in comparison with the  $\Delta G$ . In spite of the fact, the hydrophobic effect on the CT

interaction must be significant, because  $\Delta G_{HI}$  describes the tendency to form the tight binding ion pairs, and only a fraction of the pairs yield the CT complex.

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