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Surfactant Effect on the Hydrophobic Interaction between Rhodamine 6G and Sodium Tetraphenylborate

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The hydrophobic interaction occurring between rhodamine 6G and tetraphenylborate was investigated spectroscopically by varying the medium with the addition of surfactants or ethanol. The ion aggregates formed between the two ions were destroyed by the additives. The dye existed as monomeric species in the presence of a cationic surfactant whereas it was incorporated with anionic and nonionic surfactants. For the complete dissociation more than the critical micelle concentration (cmc) was required with a nonionic surfactant while less than cmc was necessary with the others.

Introduction

The absorption spectra of aqueous solutions containing dye cations and hydrophobic anions, such as tetraphenylborate (TPB⁻), show spectral changes conspicuously at longer wavelengths with respect to dye blank due to the association of dye and anion.¹⁻⁵ When both cation and anion are large, univalent, and poorly hydrated, water structure forces the two ions to form an ion-pair to minimize their disturbance to itself and to maximize water-water binding.⁶ The opposite charges assuredly facilitate the association. The tendency of water molecules to self-associate should be responsible for the ion-pairing. Thus the factors which could modify the tendency should be likely to influence the formation of ion-pairs. The addition of 1,4-dioxane or urea, which decreases or increases the dielectric constant of medium, respectively, is found to interfere with the formation of ion-pairs and eventually to destroy completely the ion-pairs into single ions.⁷

The widespread use of dyes, such as rhodamine B, rhodamine 6G, and acridine red, in tunable lasers has stimulated a number of studies on spectroscopic and structural properties in relation to the lasing mechanism.^{8,9} Since many of the commonly used dyes tend to aggregate and form dimers in solution, most of studies have been concerned with understanding the spectral effects particularly blue shifts in the absorption spectra produced by dimerization.^{9,10} However, spectral changes attributed to hydrophobic interaction have attracted little attention, insofar as we are aware, despite the

fact that theoretical treatments of dimer spectra give predictions regarding the red shifts.

Many peculiarities have been found in the spectroscopic properties of dyes with a detergent around cmc. The studies of fluorescence decay and the analysis of absorption bands of pinacyanol¹¹ and cyanine dyes^{3,12} with sodium dodecyl sulfate (SDS) and of rhodamine 6G (Rh6G⁺) with SDS¹³ were carried out to clarify the nature of the interaction between dye and detergent. Again, in these studies hydrophobic interactions were largely neglected.

In the present paper therefore the absorption and fluorescence emission behaviors of Rh6G⁺ and TPB⁻ mixed solutions are reported in the presence of a surfactant for the purpose of understanding the nature of hydrophobic interaction between the two ions. Cetyltrimethylammonium bromide (CTAB), SDS, or Triton X-100 (TX-100) was used as a cationic, anionic, or nonionic surfactant. Since the absorption spectrum of dye and the formation of micelle are greatly influenced by the pH and ionic strength of the medium, respectively, the two variables are necessarily controlled.^{8,14}

Experimental

Rhodamine 6G (Aldrich) and sodium tetraphenylborate (Fluka) of reagent grade as sources of cation, Rh6G⁺, and of anion, TPB⁻ respectively were dissolved in distilled water and stored in polyethylene bottles. All solutions containing Rh6G⁺ were wrapped with aluminum foil to prevent photodissociation. TX-100 (Shinyo Pure Chemicals), SDS and

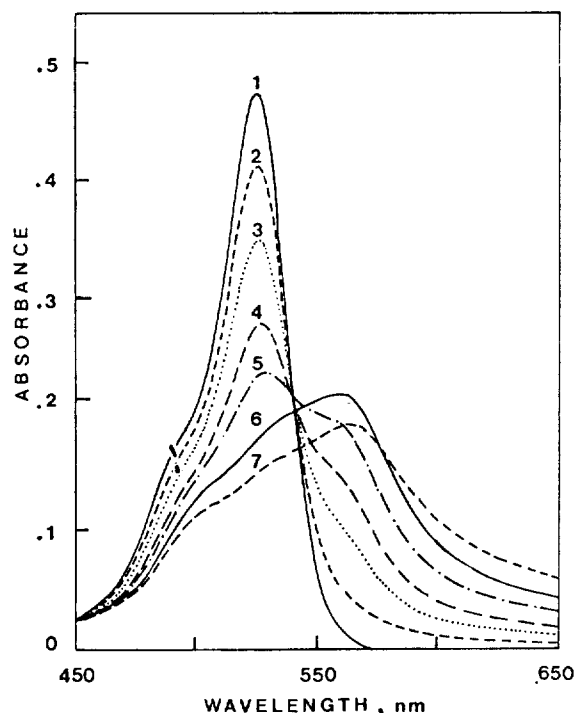


Figure 1. Absorption spectra of Rh6G^+ and its ion-associate with TPB^- at pH = 6.2. $[\text{Rh6G}^+] = 5.0 \times 10^{-6} \text{ M}$, $[\text{TPB}^-] \times 10^6 \text{ M}$: (1) 0; (2) 1.0; (3) 2.0; (4) 3.0; (5) 4.0; (6) 5.0; (7) 6.0.

CTAB (BDH Chemicals) of reagent grade were used as received. The ionic strength was adjusted to 0.001 M with NaCl (Tedia) and pH with NaH_2PO_4 and Na_2HPO_4 (Hayashi Pure Chemicals). Absolute ethanol (Riedel de Haen) was used to vary solvent composition.

Visible spectra were made on a Shimadzu UV-240 spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Hitachi 650-60 spectrofluorimeter. The excitation wavelength was fixed at 500 nm to avoid spectral overlap with Rayleigh scattering.

Results and Discussion

Figure 1 shows the absorption spectrum of $5.0 \times 10^{-6} \text{ M}$ Rh6G^+ and the spectral variation caused by the increase of TPB^- concentration up to $6.0 \times 10^{-6} \text{ M}$. The aqueous solutions reveal broad bands near 570 nm and 490 nm. The latter band is not clearly discernible but its appearance may be judged from the increase of absorbance ratio of the maximum at 527 nm to that near 490 nm. These observations are attributed to the association of ion-pairs, which is promoted by the presence of TPB^- presumably due to the increased hydrophobicity of the ion-pair in comparison with individual ions. As the dissociation constant⁹ of the dye dimer is 5.9×10^{-4} , more than 98.5% of the dye exist as the monomeric form in the absence of TPB^- . The absorbance increase at 580 nm and the concurrent decrease at 527 nm were linear with $[\text{TPB}^-]$ less than ≈ 0.6 times of the dye concentration.

The hydrophobic interaction with TPB^- is apparently not hindered by the presence of the hydrogen atom on amino group in Rh6G^+ . Dye cation such as thionine and toluidine blue do not exhibit such a hydrophobic interaction with TPB^- only because of the capability of hydrogen atom on amino groups of forming hydrogen bonds with water molecules.⁷

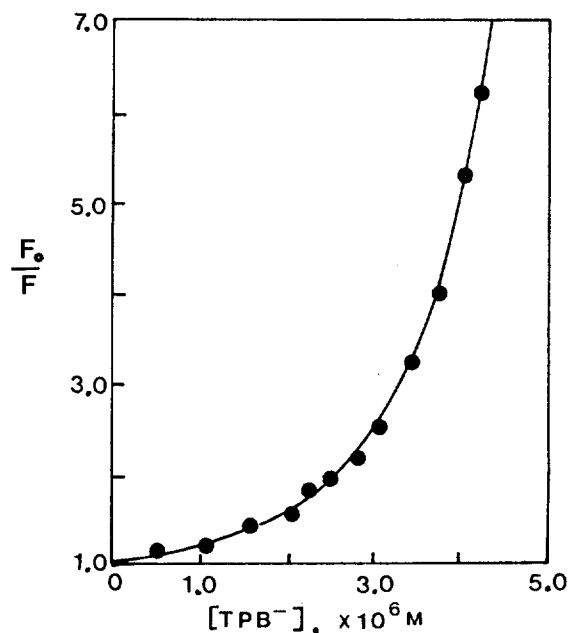


Figure 2. Plot of F_0/F vs. TPB^- concentration at 555 nm. $\lambda_{\text{ex}} = 500 \text{ nm}$.

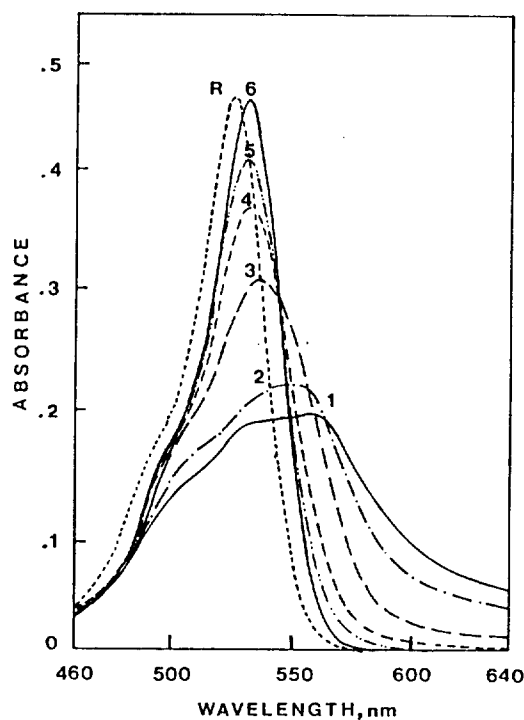


Figure 3. Effect of TX-100 on the absorption spectrum of $5.0 \times 10^{-6} \text{ M}$ Rh6G^+ and $5.0 \times 10^{-6} \text{ M}$ TPB^- mixed solution at pH = 6.2. $[\text{TX-100}] \times 10^4 \text{ M}$: (1) 0; (2) 0.086; (3) 0.86; (4) 3.00; (5) 5.13; (6) 6.90. R is the spectrum of $5.0 \times 10^{-6} \text{ M}$ Rh6G^+ .

The fluorescence intensity decreased continuously at all wavelengths upon the addition of TPB^- as illustrated in Figure 2. The deviation from linearity in a Stern-Volmer plot even at very low $[\text{TPB}^-]$ supports the aggregation of ion-pairs.

Effects of TX-100 on absorbance and fluorescence emission spectra were examined. Figure 3 presents the variation of absorption spectrum of $5.0 \times 10^{-6} \text{ M}$ Rh6G^+ and $5.0 \times$

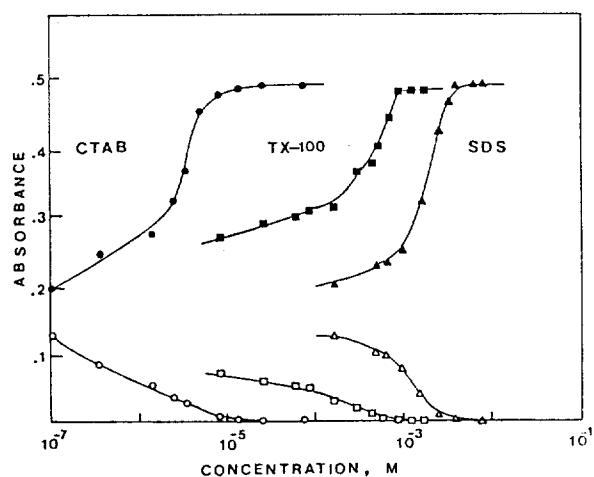


Figure 4. Variation of absorbances at the maximum (closed points) and at 580 nm (open points) vs. concentration of CTAB (circles), TX-100 (rectangles), or SDS (triangles).

10^{-6} M TPB⁻ mixed solution as a function of [TX-100]. Even at 8.6×10^{-6} M TX-100 far below cmc (3×10^{-4} M) in pure water¹⁵ the broad spectrum experiences a drastic change, particularly in the long wavelength region where the absorption by the ion-associates dominates. The cmc of TX-100 in 0.001 M NaCl solutions was measured by fluorimetry and obtained to be close to that in pure water. With the increase of [TX-100] both hypsochromic and hyperchromic shifts are accompanied and the spectrum approaches to that of Rh6G⁺ alone above cmc with a red shift by 5 nm. The red shift is presumably caused by the micellar environment. The results imply that TX-100 dissociates Rh6G⁺ · TPB⁻ ion aggregates and a complete dissociation occurs above 9.0×10^{-4} M. A complete dissociation here is assumed when the spectrum is superposable on that of Rh6G⁺ alone irrespective of spectral shifts. In addition the surfactant provides Rh6G⁺ with an environment different from aqueous media manifested by the spectral change.

Identical studies were performed with SDS (cmc = 7.7×10^{-3} M) in pure water¹⁵ and CTAB (cmc = 9.2×10^{-4} M) in pure water¹⁵ and the results are summarized in Figure 4 where absorbances at the maximum and 580 nm are plotted vs. surfactant concentration. For all these surfactants it can be seen that the deaggregation increases with the increase of surfactant concentration. The dissociation is essentially completed at about 4.0×10^{-3} M and 2.6×10^{-5} M for SDS and CTAB, respectively, which are estimated to be smaller than the cmc¹⁶ in 0.001 M NaCl solutions.

The absorption maxima in the fully dissociated solutions are located at 527, 532, and 533 nm for CTAB, TX-100, and SDS, respectively. This spectral behavior appears to suggest that the nature of interference by CTAB is somewhat different from that by the nonionic or anionic detergent. This is further supported by the change of relative fluorescence quantum yield upon the addition of surfactant. The relative fluorescence quantum yield, I_F/A_{500} , was estimated from the peak height of the fluorescence spectrum (I_F) and the absorbance at the exciting wavelength (A_{500}).³

The addition of CTAB does not cause any significant spectral shift but enhances the fluorescence quantum yield which becomes steady from about 2.6×10^{-5} M CTAB as displayed in Figure 5A. On the other hand, by the addition of

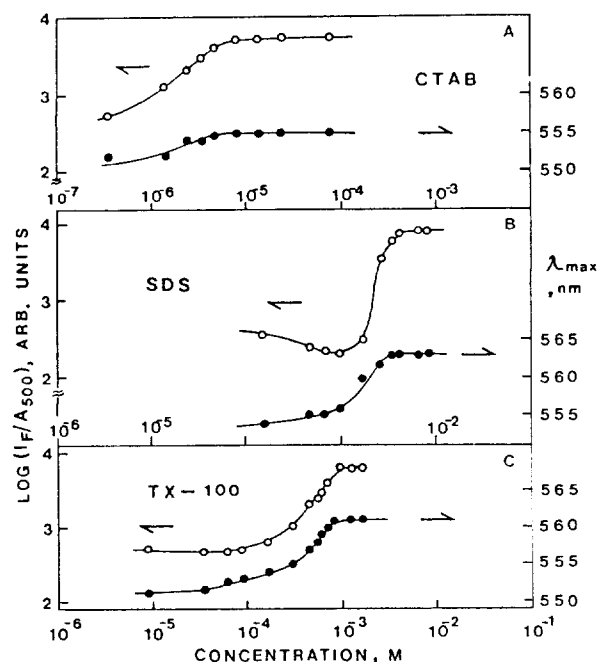


Figure 5. Log (I_F/A_{500}) and wavelength of peak fluorescence vs. concentration of CTAB (A), SDS (B), TX-100 (C).

SDS the wavelength of peak fluorescence is shifted from 555 nm to 563 nm (Figure 5B) above 4.8×10^{-4} M SDS. Below about 6.5×10^{-4} M SDS, fluorescence is emitted predominantly from monomeric Rh6G⁺ species whereas above 4.0×10^{-3} M SDS, Rh6G⁺ incorporated into SDS presumably fluoresces. Between the two limits both species contribute to the fluorescence intensity.

Similar results are obtained with TX-100 as shown in Figure 5C. The fluorescence quantum yield of Rh6G⁺ and TPB⁻ shows gradual increase with the increase of [TX-100] and reaches back to that of Rh6G⁺ alone from above 9.0×10^{-4} M TX-100. Moreover, the maximum fluorescence wavelength starts to deviate from 551 nm at 8.6×10^{-6} M TX-100, and reaches a plateau, 561 nm above 9.0×10^{-4} M TX-100 after a gradual increase with TX-100. The spectral behavior illustrates that the aggregates of Rh6G-TPB ion pair, which is predominant species below cmc, gradually dissociate and simultaneously Rh6G⁺ and its ion pair, Rh6G-TPB, incorporate into the micelle and the process is apparently completed above 9.0×10^{-4} M TX-100.

To provide a further evidence, the absorbance and fluorescence intensity of Rh6G⁺ and TPB⁻ solutions were examined by varying the mole fraction of ethanol in an aqueous solution. As the mole fraction of ethanol increased, both the absorbance and fluorescence intensity increased and when it reached at 0.085 the mixed solution attained to the levels of Rh6G⁺ alone in pure water with spectral shifts of approximately 5 nm. From this observation it may be inferred that the dye is predominantly solvated with ethanol whose microenvironment resembles the one provided by SDS or TX-100.

The enhancement of fluorescence intensity compared with the aqueous solution by the addition of SDS or TX-100 may be explained in terms of the hydrophobic environment and/or the immobilization of dye molecules in the micellar media. The enhancement of similar nature has been reported in recent reports^{3,12,13} using cyanine dyes with SDS. The enhancement in these systems were attributed to the inhibition

of radiationless decay by the micellar environment which immobilize the cyanine dyes to some extent. The polarity present in the local environment of the dyes was not related to the fluorescence yield.¹² The microviscosity of SDS micelle measured near room temperature is reported to be about 15-30 cp,¹⁷ which is significantly higher than in methanol. Although the exact location of the dye within the micellar region is not known we may assume that TX-100 micelle has similar microenvironment as SDS micelles based on the experimental results that in both micellar media, Rh6G⁺ showed nearly the same fluorescence spectral behavior.

On the other hand, the most effective deaggregation by CTAB is apparently achieved in a different way. Rh6G⁺ is effectively repelled from like-charged CTA⁺ or its micelle electrostatically due to the relatively high concentration of surface charge and exists predominantly as monomeric species as evidenced by essentially no spectral shift. Instead it is quite possible that TPB⁻ may be incorporated into the micellar media,¹⁸ which inhibits the ion-pairing and aggregation.

Attractive electrostatic interaction occurring between surfactant and Rh6G⁺ may be not strong enough to differentiate significantly the spectral behaviors in the presence of SDS from those in TX-100. However, the minimum concentration of TX-100 required to dissociate completely Rh6G⁺-TPB⁻ aggregates was larger than its cmc in pure water while that of SDS was found to be less than its cmc in pure water possibly due to the weaker electrostatic interaction with TX-100.

In summary, the hydrophobic interaction led to the formation of Rh6G⁺-TPB⁻ aggregates is overwhelmed by a stronger micellar interaction with the dye or the ion pairs. The cationic dye predominantly exists as a monomeric species while it may incorporate into nonionic or anionic micellar environment.

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Surface Enhanced Raman Scattering of Methoxybenzonitriles in Silver Sol

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The surface-enhanced Raman scattering (SERS) of methoxybenzonitrile in a silver sol was investigated. All of ortho-, meta-, and para-substituted benzonitriles were found to adsorb on the silver surface via the nitrogen lone pair electrons. The benzene ring of meta derivative seemed likely to stand perpendicular to the silver surface, while the benzene rings of both ortho and para derivatives assumed tilted stances with respect to the surface. The SERS technique appeared to be a useful means to study the substituent electronic effects.

Introduction

The surface-enhanced Raman scattering (SERS) technique has been demonstrated to be a powerful tool in the study

of interfacial structures at the molecular level¹. Specifically, information regarding the chemical identity, structure and orientation of the species at the interfaces can be readily inferred from the SER spectra.

The benzonitrile molecule has a very interesting char-

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