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Hydrophobic Interaction between Rhodamine 6G and Tetraphenylborate Anions

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The hydrophobic interaction occurring between rhodamine 6G and tetraphenylborate anions has been investigated with surfactants by absorption and fluorescence studies. In the order of tetraphenylborate, tetrakis(4-fluorophenyl)borate, and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate the hydrophobicity is found to be increased.

Introduction

Tetraphenylborate (TPB⁻) anion has been used to investigate the nature of interaction with cationic dyes, such as methylene blue, rhodamine 6G, and crystal violet.¹⁻⁵ The ion aggregates associated between dye cation and TPB⁻ show characteristic absorption behavior at longer wavelengths and cause fluorescence intensity to decrease with respect to the dye blank. The spectral variations are attributed to the hydrophobic interaction originated from water structure to minimize the disturbance of dye cation and TPB⁻ to water and to maximize water-water bonding.⁶ The ion pairs have commonly applied to analytical chemistry, especially for the separation of ions by extraction and precipitation.⁷ TPB⁻ is generally known as an effective precipitating reagent for K⁺ and NH₄⁺.⁸ Several attempts have been made to improve physico-chemical properties of TPB⁻ as an agent for precipitation and solvent extraction in aqueous solutions.⁹ The strongly electron-withdrawing trifluoromethyl substitution, in particular, highly increased the lipophilicity and decreased the solubility of ion pair to promote the extraction into organic solvents.⁹ However, studies on absorption or fluorescence behavior owing to the hydrophobic interaction have attracted little attention yet.

In the present paper, therefore, analyses on the absorption and fluorescence spectral changes of rhodamine 6G with TPB⁻, tetrakis(4-fluorophenyl)borate, and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anions are reported for the

purpose of understanding the difference of the hydrophobicity of three borates. Among them, TFPB⁻ is expected to enhance the formation of ion aggregates most due to the trifluoromethyl substitution.

Experimental

Rhodamine 6G (Aldrich, GR) was used as a cationic source, Rh6G⁺. Sodium tetraphenylborate (Fluka AG, GR) sodium tetrakis(4-fluorophenyl)borate (Aldrich, GR), and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (Dojindo, GR) as sources of boron complex anions, TPB⁻, TFB⁻, and TFPB⁻, respectively, were dissolved in distilled water and stored in polyethylene bottles. TFPB⁻ is dissolved in small amount of methanol and diluted with distilled water because of its low solubility. Triton X-100 (Merck) and cetyltrimethylammonium bromide (CTAB) (BDH chemicals Ltd.) of reagent grade were used as received. Ionic strength and pH were adjusted with NaCl (Shinyo, GR) and a CH₃COOH-CH₃COONa buffer, respectively. Visible spectra were taken on a Shimadzu UV-240 spectrophotometer and fluorescence emission spectra were recorded on a Hitachi 650-60 spectrofluorimeter.

Results and Discussion

Figure 1 shows the absorption spectra of 4.0×10^{-6} M Rh6G⁺ and the spectral variation caused by the increase of

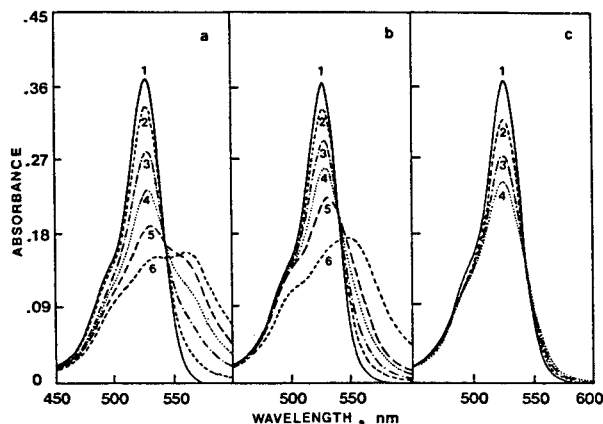


Figure 1. Absorption spectra of Rh6G⁺ and its ion aggregates with TPB⁻ (a), TFB⁻ (b), and TFPB⁻ (c) at pH = 5.0 and $\mu = 0.01$ M. $[\text{Rh6G}^+] = 4.0 \times 10^{-6}$ M. Concentration of borate, 10^{-6} M; (1) 0.0; (2) 0.8; (3) 1.6; (4) 2.4; (5) 3.2; (6) 4.0.

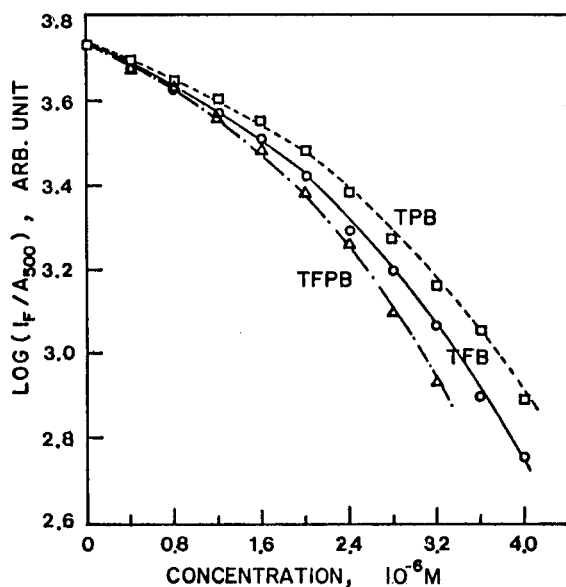


Figure 2. Plot of $\log(I_F/A_{500})$ vs. the concentration of borates. $[\text{Rh6G}^+] = 4.0 \times 10^{-6}$ M.

tetraphenylborate concentrations. The mixed 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 ratio of absorbance at maximum to that near 500 nm. These spectral changes are attributed to the aggregation of dyes which is promoted by the borates due to the increased hydrophobicity of the ion pair in comparison with individual ions. As crystal violet and borate system⁵, the aggregates are probably consisted of not only double ion pair but charged ion pair formed by the adsorption of the Rh6G⁺ ion to the ion pair. The dyes in the aggregates apparently exhibit the absorption characteristics of dye dimer. As the dissociation constant¹⁰ of dimer of the dye dimer is 5.9×10^{-4} , essentially all the dye exist as the monomeric form in the absence of borates.

The fluorescence emission intensity decreased proportionally at all wavelengths on the addition of the borates, which supports the formation of ion aggregates since the ion aggregates are known to be nonfluorescent.¹¹ To estimate

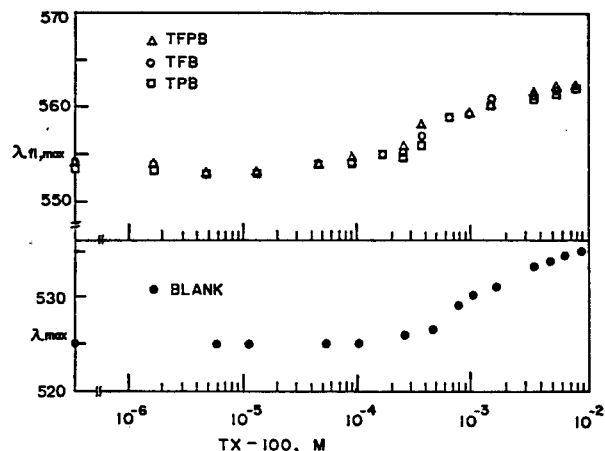


Figure 3. Variations of wavelength of maximum absorbance (λ_{max}) for Rh6G⁺ only and of fluorescence ($\lambda_{fl,max}$) vs. $[\text{TX-100}]$ for Rh6G⁺ and borate mixed solutions. $[\text{Rh6G}^+] = 4.0 \times 10^{-6}$ M and concentration of borates, 2.4×10^{-6} M. $\lambda_{fl,max}$ for the dye blank essentially overlaps with those for the mixed solutions.

the extent of the ion aggregates the relative fluorescence quantum yield,¹² $\log(I_F/A_{500})$ was calculated from the peak height of the fluorescence emission spectrum, I_F , and the absorbance at the exciting wavelength, A_{500} . A plot of $\log(I_F/A_{500})$ vs. the concentration of borates is shown in Figure 2. The result suggests that the hydrophobicity is increasing in the order $\text{TPB}^- < \text{TFB}^- < \text{TFPB}^-$. TFB⁻ is recently found to be more hydrophobic than TPB⁻ using crystal violet as a probe.⁵ However, the relative hydrophobicity of TFPB⁻ were not reported.

The observed absorption spectra (Figure 1) may be analyzed by a simple exciton theory.¹³ According to the theory a dye monomer peak may split into a higher energy band, H band, and a lower one, J band, as a result from the interaction between adjacent dye cations in the aggregation of ion pair. The theory also predicts that H band is always larger than J band in a parallel dimer configuration, whereas J band gives larger absorbance in an oblique dimer structure.

As can be seen from Figure 1, TPB⁻ apparently promotes the dimers of the J band more than TFB⁻ or TFPB⁻. This implies that the dimers of the H band is more promoted by TFPB⁻ than by TPB⁻ since more dimers are formed with TFPB⁻ (Figure 2). The different behavior by three borates may be explained in terms of solute-solvent interaction in addition to hydrophobic interaction.

The solute-solvent interaction in perfluorohydrocarbons is much weaker than that in the corresponding hydrocarbons solvents.¹⁴ The interaction between Rh6G⁺ and TFPB⁻, albeit not perfluorinated, may be assumed to be weak compared with TPB⁻ or TFB⁻. Furthermore, the negative charge in TFPB⁻ is probably more delocalized than the other borates, and thus the electrostatic interaction with Rh6G⁺ may be less significant than that with TPB⁻ or TFB⁻. Therefore, the interaction between dyes itself is expected to become more important in the aggregates with TFPB⁻ than that with TPB⁻ or TFB⁻. The more important the dye-dye interaction, the more ion pairs in the aggregates are tend to be held in a parallel dimer configuration, under which the dispersion forces should be greatest. Moreover, the coulombic repulsion can be minimized if the charged amino groups in Rh6G⁺

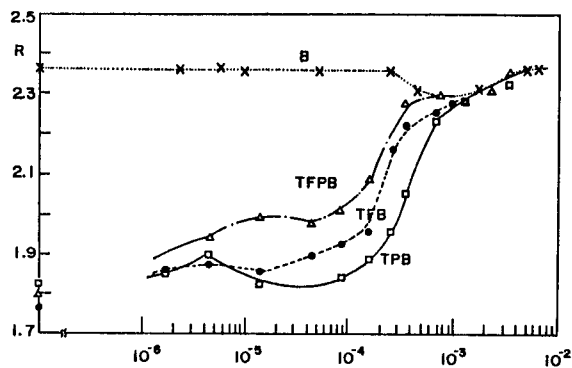


Figure 4. Plot of R vs. $[TX-100]$ for $4.0 \times 10^{-6}M$ Rh6G $^{+}$ and $2.4 \times 10^{-6}M$ borate mixed solutions. B is for the dye blank.

lie along the far edges as possible. Therefore, in the order $TFPB^{-} < TFB^{-} < TPB^{-}$, the absorption spectra shows the lower energy band to be enhanced, as expected.

Effect of TX-100. Upon the addition of TX-100, a non-ionic surfactant, to $4.0 \times 10^{-6}M$ Rh6G $^{+}$, the absorption and fluorescence emission spectra showed gradual bathochromic shift above cmc ($3.0 \times 10^{-4}M$)¹⁵ (Figure 3). Before the cmc, essentially no spectral changes were observable. Concomitantly the ratio of the absorbance at maximum to that at shoulder, R , (Figure 4) decrease somewhat and regain the initial value at higher $[TX-100]$. The variation of R appears to indicate that at the beginning of micelle formation some dye cations may be incorporated to form dimer-like structure¹² which eventually dissociates into monomeric species upon dilution with a large number of micelles.

In the presence of borate anions, however, the corresponding ratios show quite different behavior as shown in Figure 4. For each of three borates, the ratio increases with the increase of $[TX-100]$ and shows slight decrease resulting in a broad maximum, followed by sigmoidal increase as recently reported.⁵ The initial increase of R possibly shows the enhancements both of the dissociation of the aggregates and of the incorporation of Rh6G $^{+}$ containing species into TX-100. Accompanied with the increases of the R , the J band increased while the H band decreased, and at the R maximum the J band showed the greatest absorbance. This spectral change appears to show that the dimers of near parallel configuration in the ion aggregated are partially converted to those of oblique configuration upon the exposure of TX-100.

Beyond the shallow maximum the R and the J band decreased whereas the H band increased. The result implies that the dye containing species may apparently come together, due to the tendency of association of the surfactant, to result in the formation of dimer-like structure¹² with the parallel configuration, which causes the ratio to decline.

In the region of sigmoidal increases the dissociation of the ion aggregates continues and the dye species of dimer-like structure are progressively diluted with the surfactant, and eventually the R values follow the identical curve with Rh6G $^{+}$ alone.

For $TFPB^{-}$, the dependence of R on $[TX-100]$ follows a similar pattern as TPB^{-} , but shows larger R values at all concentrations. At a given $[TX-100]$ there seem to exist less aggregates of dimer-like structure with $TFPB^{-}$ and TPB^{-} . TFB^{-} behaves in between $TFPB^{-}$ and TPB^{-} . The result may be attributed to the difference in hydrophobicity of the anion.

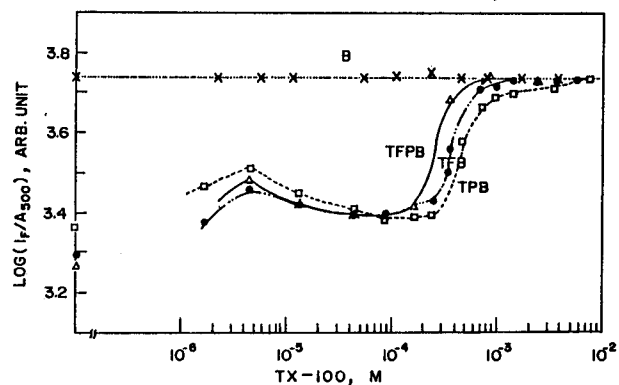


Figure 5. Plot of $\log(I_F/A_{500})$ vs. $[TX-100]$ for $4.0 \times 10^{-6}M$ Rh6G $^{+}$ and $2.4 \times 10^{-6}M$ borate mixed solutions. B is for the blank.

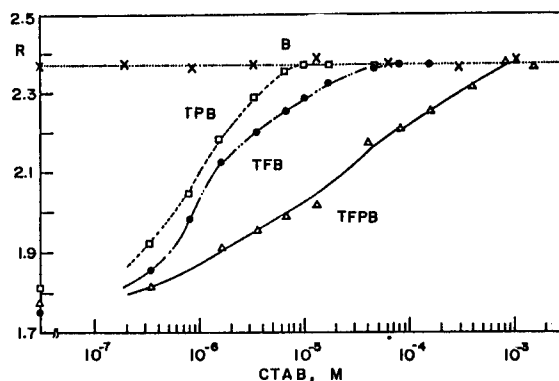


Figure 6. Plot of R vs. $[CTAB]$ for $4.0 \times 10^{-6}M$ Rh6G $^{+}$ and $2.4 \times 10^{-6}M$ borate mixed solutions. B is for the blank.

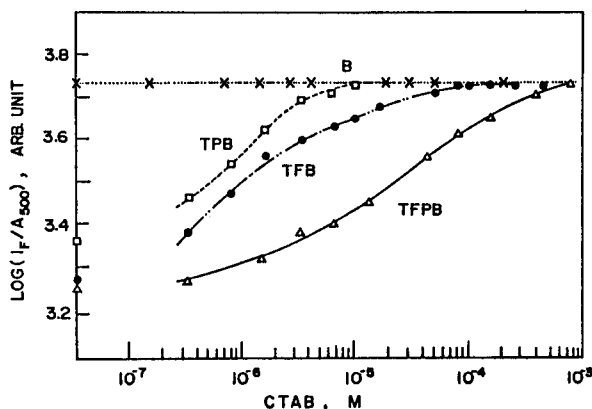


Figure 7. Plot of $\log(I_F/A_{500})$ vs. $[CTAB]$ for $4.0 \times 10^{-6}M$ Rh6G $^{+}$ and $2.4 \times 10^{-6}M$ borate mixed solutions. B is for the blank.

Since $TFPB^{-}$ is the most hydrophobic, it apparently has the strongest interaction with TX-100. As a result, the formation of dimer-like structure of Rh6G $^{+}$ on the surfactant appears to be the least promoted in the presence of $TFPB^{-}$.

A supporting evidence is shown in Figure 5, where the relative fluorescence quantum efficiency is plotted vs. $[TX-100]$. General feature is quite similar with the variation of the R and thus the same explanation can be applied. Before about $8.6 \times 10^{-5}M$, however, TPB^{-} has the largest value simply because the value was the highest initially.

Effect of CTAB. Similar studies were performed with a cationic surfactant, CTAB, as shown in Figure 6 and 7. Both

figures reveal almost identical curves. It is therefore suggested that the effect of a surfactant on ion aggregates can be equally analyzed either with the relative fluorescence quantum efficiency or with the R .

In the absence of borates, $Rh6G^+$ apparently shows essentially no association with CTAB. $Rh6G^+$ is electrostatically repelled from CTAB or its micelle, and exists predominantly as monomeric species as evidenced further by no spectral shifts. In the presence of borate anions, however, it is quite possible that borates may be incorporated into the micellar media.

Contrary to TX-100, however, TPB^- has the largest values among three borates at all [CTAB], which may be interpreted in terms of the ionic interaction between CTAB and borate anions. That is, since TPB^- has the strongest ionic interaction among three borates, its ion aggregates dissociate more easily, resulting in larger R and relative fluorescence quantum efficiency. However, the effect of hydrophobicity should not be neglected, although it may be difficult to determine its contribution to the overall dissociation. It seems certain that the smaller the hydrophobicity of a borate anion is, the easier the dissociation of ion aggregates becomes upon the addition of CTAB. The order of hydrophobicity obtained above partially supports the result in Figure 6 and 7. The ion aggregates with TPB^- appears to be completely dissociated well before the cmc ($9.2 \times 10^{-4}M$)¹⁵ of CTAB, whereas approximately $8.0 \times 10^{-5}M$ and $9.0 \times 10^{-4}M$ CTAB are required to dissociate completely the ion aggregates with TFB^- , and $TFPB^-$, respectively. Thus, it may be concluded that the hydrophobicities of the borates studied are increasing in the order $TPB^- < TFB^- < TFPB^-$.

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Dipole Moment Derivatives and Infrared Intensities in Chloromethanes

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The results of *ab initio*(MP2/6-31G) molecular orbital calculations of the dipole moment derivatives and gas phase IR intensities in chloromethanes are reported. The theoretical polar tensors are analyzed into the net charge, charge-flux, and overlap contributions. The charge-flux contribution was found to be dominant in the Cl atom polar tensor, while the net charge effect was the most prominent contribution for the H atom polar tensor. The Cl atom polar tensor appeared, in a good approximation, to be transferable among various chloro molecules. On the other hand, for the prediction of IR spectra of complex hydrocarbons containing chlorine atoms, some empirical adjustment of the H-atom polar tensor seemed to be made depending on the number of Cl atoms bound to the certain carbon atom.

Introduction

The determination of the absolute intensities of infrared absorption bands is one of the most fundamental methods in studying the structure and electronic properties of polyato-

mic molecules. As the integrated intensity is intimately related to the electronic charge movements during vibration, the measurement of infrared intensities has been a powerful tool in understanding the charge distribution in molecules and their redistributions during vibration¹.

One of the fundamental challenges facing a vibrational molecular spectroscopist is to predict the spectrum of a new

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