Aggregation of Crystal Violet with Tetraphenylborate Anions in Aqueous Solutions

Beom-Gyu Lee, Rae-Seok Jung, and Kang-Jin Kim*

Department of Chemistry, Korea University, Seoul 136-701. Received October 24, 1988

The hydrophobic interaction between tetraphenylborate (TPB-) or tetrakis (4-fluorophenyl)borate (TFB-) and crystal violet has been investigated in aqueous solutions by absorption spectrophotometry. Both of the anions promote the aggregation of the ion pairs formed between crystal violet and TPB- or TFB-. When crystal violet and borate anion are nearly equimolar, insoluble floating aggregates can be observed. Based on the relative absorbance of H and J bands and on the effect of TX-100, TFB- is found to be more hydrophobic than TPB-.

Introduction

Tetraphenylborate anion (TPB-) has been used to investigate the nature of hydrophobic interaction with cationic dyes, such as methylene blue,[1,2] rhodamine 6G,[3] and crystal violet.[4] The ion aggregates associated between dye cation and TPB- show characteristic absorption behavior at longer wavelengths with respect to the dye blank. The spectral variations caused by the addition of TPB- 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.[5]

The formation of the ion aggregates can be interfered by some additives such as 1,4-dioxane and urea which modify the tendency of water[2] to lead the hydrophobic interaction. The ion aggregates can be destroyed by the addition of surfactants[3] which exert dispersion and/or electrostatic forces to the dye and TPB-. However, spectral changes attributed to hydrophobic interaction are not widely studied, insofar as we are aware, although ion pairs have become commonly applied to analytical chemistry, especially for the separation of ions by extraction and precipitation.[6] TPB- is generally known as an effective precipitating reagent for K^+ and NH_4^{+}.[7]

Several attempts have been made to improve physicochemical properties of TPB- as an agent for precipitation and solvent extraction in aqueous solutions.[8] However, studies on absorption behavior owing to the hydrophobic interaction have attracted little attention yet.

In the present paper, therefore, an analysis on the absorption spectral changes of crystal violet with TPB- and TFB- is reported for the purpose of understanding the difference of the hydrophobicity between the two borates. TFB- is expected to enhance the formation of ion pair aggregates due to the substitution by an electron withdrawing group on phenyl rings and the results are compared with those with TPB-

Experimental

Crystal violet (Aldrich, GR) was used as a cationic source, CV+. Sodium tetraphenylborate (Fluka AG, GR) and sodium tetrakis (4-fluorophenyl) borate (Aldrich, GR) were dissolved in distilled water and stored in polyethylene bottles to avoid adsorption loss. All organic solvents of best grade obtained from Junsei Chemical Company were used without purification. Triton X-100 (Merck) of reagent grade was used as received. Ionic strength and pH were adjusted with NaCl and a
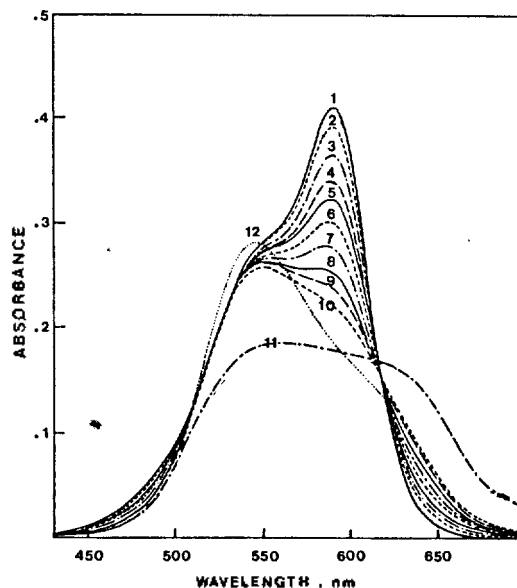

Figure 1. Absorption spectra of CV+ and its ion aggregates with TPB- at pH = 5.0 and $\mu = 0.01$M. [CV+] = 4.0×10⁻⁶M. [TPB-]. 10⁻⁶M: (1) 0.0; (2) 0.4; (3) 0.8; (4) 1.2; (5) 1.6; (6) 2.0; (7) 2.4; (8) 2.8; (9) 3.2; (10) 3.6; (11) 4.0; (12) 400.

CH_3COOH-CH_3COONa buffer, respectively. Visible spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Results and Discussion

Spectral Characteristics. Figure 1 and 2 show the absorption spectra of aqueous 4.0 × 10⁻⁶M CV+ solution and the spectral variation caused by the increase of TPB- and TFB- concentrations, respectively. The spectrum of CV+ is characterized by a band at 589 nm and a shoulder near 550 nm. With the increase of anion concentration the mixed solutions reveal considerable absorbance around 640 nm and apparent growth near the shoulder in the light of the decrease at 589 nm. These observations are attributed to the formation of the soluble aggregates of ion pair, which is possibly promoted by borate ions due to the enhanced hydrophobicity of the ion pair compared with the individual ions. Since the dimerization constant[9] of CV+ was estimated to be 6×10², under which most of the dye cation exist as the monomeric form in 4.0 × 10⁻⁶M CV+ without the borates. The decrease in absorbance at 589 nm and the concomitant increase at 637 nm, an arbitray chosen wavelength, were linear with respect
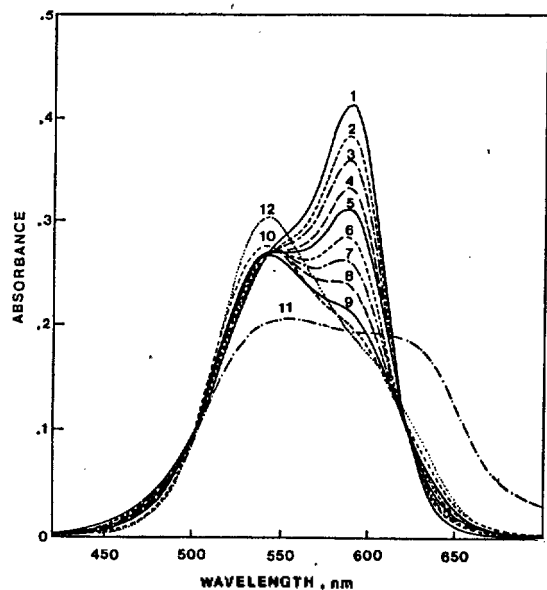
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Figure 2. Absorption spectra of CV$^+$ and its ion aggregates with TFB$^-$ at pH = 5.0 and μ = 0.01M. [CV$^+$] = 4.0 × 10^{-6}M. [TPB$^-$], 10^{-6}M: (1) 0.0; (2) 0.4; (3) 0.8; (4) 1.2; (5) 1.6; (b) 2.0; (7) 2.4; (8) 2.8; (9) 3.2; (10) 3.6; (11) 4.0; (12) 400.

Figure 3. Variation of absorbance at 589 nm (A) and 637 nm (B) vs. concentration of TPB$^-$ (open circles) and TFB$^-$ (closed circles) obtained from Figure 1 and 2.

to the concentration of borate ions up to 3.6 × 10^{-6}M, *i.e.* 0.9 times of CV$^+$ concentration, and thus quantitative analyses of the borate ions are possible. These are illustrated in Figure 3, where TFB$^-$ causes the absorbance of monomeric CV$^+$ to decrease faster than TPB$^-$. This may indicate that TFB$^-$ is more hydrophobic than TPB$^-$. The data for TPB$^-$ are in good agreement with those by Kobayashi *et al.*[4] Apparently the spectrophotometric determination of TPB$^-$ is more sensitive than a potentiometric titration.[10] No comparison is possible for TFB$^-$ yet.

Over a narrow concentration range of TPB$^-$ near 4.0 × 10^{-6}M, the spectra change abruptly (Spectrum 11 of Figure 1) and some floating aggregates were observed. The addition of TFB$^-$ of similar concentration as TPB$^-$ also resulted in the formation of insoluble aggregates. However, as the concentration of borate anions increased further, no insoluble aggregates were observable and the absorbance near 545 nm showed a continuous increase while that at 637 nm dimished slightly. Also, insoluble aggregates were not formed either in the presence of surfactants or in nonaqueous solvents under the experimental conditions. The results suggest that only when both CV$^+$ and borate anion are nearly equimolar, the insoluble aggregates are formed. Under the excess of either of the component ions, the soluble ion aggregates presumably consist of double ion pairs[1] and charged species. The latter species are likely formed by the adsorption of the ion in exess to the ion pair and resist combining into lager aggregates which will settle down from the solution. On the other hand, near stoichiometric composition the ion pairs are formed at the very beginning due to the hydrophobic interaction by water. The ion pairs thus formed are considered electrostatically neutral species. The ion pairs are relatively easily coagulated into the insoluble aggregates.

The observed spectral changes due to the addition of borate ions (Figures 1 and 2) show characteristically the presence of dimer and may be analyzed by a simple exciton theory.[11] According to the theory the splitting of dye
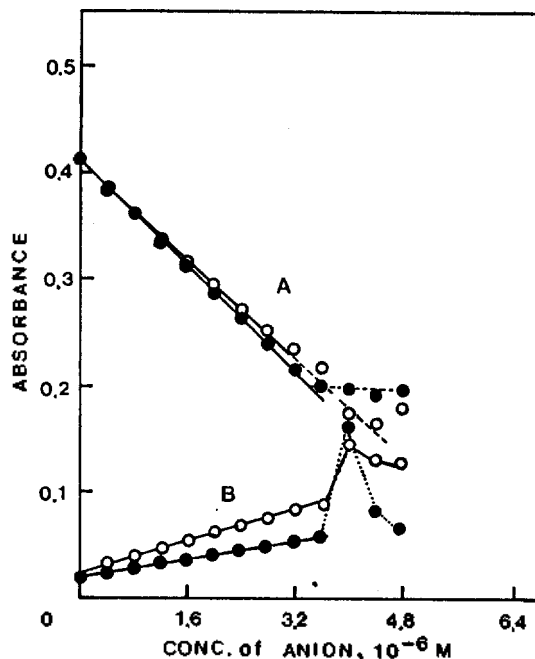
monomer peak into a higher energy band, H band, and a lower energy band, J band, results from a point dipole-dipole interaction between adjacent dye cations in the aggregation of ion pair. The theory also predicts that H band is always larger than J band in a parallel dimer configuration, whereas J band gives larger absorbance in an oblique dimer structure. Aqueous rhodamine B[11] and aqueous methylene blue[12] were proved to have a parallel configuration by dimerization, since the H band of these dyes in water was observed to be larger than the J band.

As can be seen from Figure 1 and 2 at low borate concentrations, TFB$^-$ apparently promotes the dimers of the H band to be more populated than TPB$^-$ while the J band is relatively larger with TPB$^-$ than with TFB$^-$. TFB$^-$ yields more dimers of parallel configuration than TPB$^-$. The different behavior by the two borates may be related to the difference in their hydrophobicities. That is, it appears that the more hydrophobic an anion is, the more the dye cations in aggregates are expected to be held in a parallel dimer configuration. When two adjacent dye cations are in a parallel configuration the dispersion forces should be greatest. Moreover, the coulombic repulsion can be minimized if the charged amino groups in CV$^+$ lie along opposite edges as possible.

As the concentration of borates becomes in excess of [CV$^+$] the J band is progressively converted to the H band. That is, the aggregation of parallel structure becomes more favorable to a much extent at higher borate concentrations.

Effect of TX-100. Upon the addition of TX-100, a nonionic surfactant, to 4.0 × 10^{-6}M CV$^+$, the absorption spectrum shows a gradual bathochromic shift above cmc (3.0 × 10^{-4}M)[3] and the maximum absorption occurs at 599 nm which corresponds to a shift of 10 nm from that in the absence of the surfactant. The shift reflects the different environment around CV$^+$. Concomitantly the ratio of the ab-
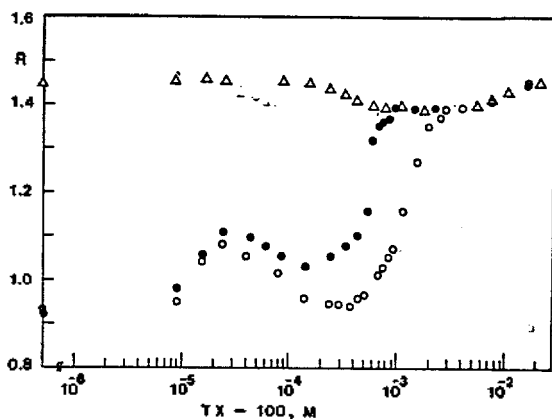
Figure 4. Plot of R vs. concentration of TX-100 for CV$^+$ alone (triangles), CV$^+$ with TFB$^-$ (closed circles), and CV$^+$ with TPB$^-$ (open circles). Concentration: CV$^+$, 4.0×10^{-6}M; TFB$^-$, 2.4×10^{-6}M; TPB$^-$, 2.8×10^{-6}M.

sorbance at maximum to that at shoulder, R, (Figure 4) decrease to 1.39 from the initial value 1.45, 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 arranged to form a dimer-like structure[13] which eventually dissociates into monomeric species upon dilution with a large number of micelles.

In the [TX-100] region below about 3×10^{-5}M, the initial moderate rise of the R possibly indicates the increases both of the dissociation of the aggregates into ion pairs and of the incorporation of CV$^+$ and/or the ion pair into TX-100. Most of the dye species in the surfactant seem to show monomeric absorption behavior. Accompanied with the increase of the R, the J band increased while the H band decreased, and at 3.0×10^{-5}M TX-100 the J band showed the greatest absorbance. This spectral change may be interpreted that at the exposure of the surfactant in the low concentration region, the ion aggregates are presumably not completely destroyed, but the dimers of parallel configuration in the ion aggregates appears to the partially converted to those of oblique configuration.

Between 3.0×10^{-5}M and about 3.0×10^{-4}M, however, 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 structure[13] with parallel configuration, which causes the ratio to decline.

Above 3.0×10^{-4}M the dissociation of the ion aggregates continues with the concentration of TX-100, and the dimer-like structure are progressively diluted with the surfactant and converted into monomeric species. Complete dissociation was estimated to occur at 9.4×10^{-4}M and 3.6×10^{-3}M TX-100 for the TFB$^-$ and TPB$^-$, respectively, and eventually the R values follow the identical curve with CV$^+$ alone.

For TFB$^-$, the dependence of R on [TX-100] below 3×10^{-3}M follows a similar pattern as for TPB$^-$, but shows larger R values at all concentrations of the surfactant. This probably means that at a given [TX-100] there exist less aggregates of dimer-like structure with TFB$^-$ than with TPB$^-$. The difference of R dependence on [TX-100] may be explained by the difference in hydrophobicities of the anions. Since TFB$^-$ is considered to be more hydrophobic than TPB$^-$

Table 1. Solvent Effects on the Absorption Spectra for CV$^+$ and CV$^+$-TPB$^-$ Mixed Solutions and Specification of the Solvents. [CV$^+$] = 4.0×10^{-6}M, [TPB$^-$] = $4.0 \times 10^{+6}$M

no.	solvent	refractive index[a]	λ_{max} nm	R[b] CV$^+$	R[b] CV$^+$-TPB$^-$	$E_T(30)$[c] kcal/mol	π^*,[d]
1	2-butanol	1.3972	589	1.37	1.37	—	47.1
2	1-butanol	1.3993	592	1.38	1.39	0.46	50.2
3	2-propanol	1.3772	589	1.36	1.32	0.46	48.6
4	1-propanol	1.3856	589	1.41	1.39	0.51	50.7
5	acetone	1.3588	589	1.35	1.34	0.72	42.2
6	ethanol	1.3614	588	1.38	1.38	0.54	51.9
7	methanol	1.3284	585	1.37	1.36	0.60	55.5
8	DMF	1.4282[c]	595	1.33	1.33	0.88	43.7
9	acetonitrile	1.3441	587	1.32	1.35	0.85	46.0
10.	DMSO	1.4783	602	1.31	1.31	1.00	45.0
11	H$_2$O	1.331	589	1.45	0.94	1.09	63.1
12	formamide	1.4475	595	1.54	1.51	0.98	56.6

[a] J. A. Dean, "Handbook of Organic Chemistry", McGraw-Hill Co., New York. [b] R is the ratio of the absorbance at maximum to the shoulder. [c] Reference 15. [d] Reference 16. [e] Values at 25 °C. others at 20 °C.

as proposed above, TFB$^-$ apparently has a stronger interaction with TX-100. As a result, the formation of dimer-like structure of CV$^+$ on the surfactant appears to be less promoted with TFB$^-$ compared with TPB$^-$. Apparently, in the presence of nonionic surfactant the hydrophobic interaction between CV$^+$ and anions is overwhelmed by a stronger dye-surfactant interaction.

Effect of solvent polarity. The absorption spectra of CV$^+$ itself and of the aggregates are originated from a π-π^* transition and the transition is generally known to show a bathochromic shift with the increase of solvent polarity. The effect of solvent polarity has been theoretically treated.[14] Because of difficulties in assessing the complex nature of solvent-solute interactions, however, empirical parameters of solvent polarity are more frequently employed.[14]

To understand the nature of the environment around CV$^+$ in micellar media, the absorption spectra of a mixed solution of CV$^+$ and TPB$^-$ in a number of organic solvents were obtained and the results are summarized in Table 1.

A relative constancy in the R manifests that no new absorbing species is formed in any of these solvents except water. The R in water is conspicuously different from others. In connection with these data the microenvironment of CV$^+$ in TX-100 micellar media appears to be somewhat similar to that provided by the nonaqueous solvents.

The solvent effect on the position of spectral maxima, λ_{max}, is not considerable, reaching only from 589 nm in water and 2-butanol to 602 nm in DMSO (Table 1). Nevertheless, it may be considered suitable to apply the $E_T(30)$ scale to plot the variation of $1/\lambda_{max}$, since it is the most comprehensive solvent scale based on a transition of a cationic dye.[15] However, the plot did not give reasonable linear correlation, implying that the $E_T(30)$ scale is not particularly suitable to the present system. Another widely known solvent polarity, the π^* scale, was utilized to plot $1/\lambda_{max}$, but also resulted in a poor correlation. Finally, the variation was plotted as a function of $(n^2-1)/(2n^2+1)$, where n is the solvent refractive index, as
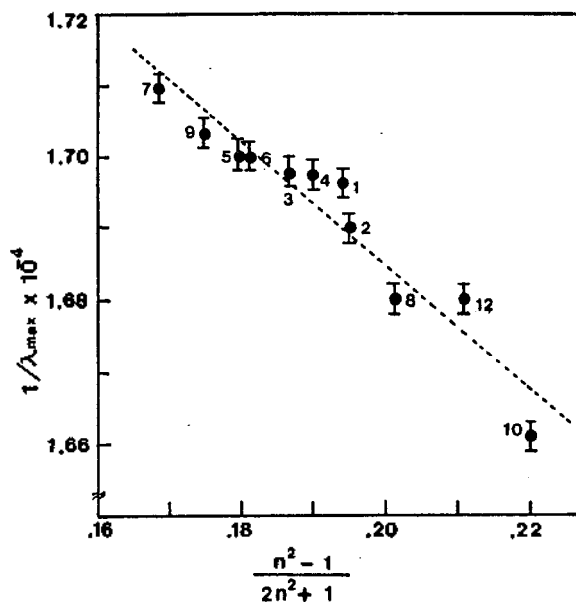
Figure 5. Plot of $1/\lambda_{max}$ vs. $(n^2-1)/(2n^2+1)$ for a mixed solution of CV^+ and TPB^- in various solvents. Concentrations: CV^+, $4.0 \times 10^{-6}M$; TPB^-, $4.0 \times 10^{-6}M$. The numbers correspond to the solvents in Table 1.

shown in Figure 5. The value for water is excluded because it lies far above the line. This plot shows a relatively good linear relationship of the observed solvent shift, which is somewhat different from the result with methylene blue.[2] The refractive index of a solvent probably plays an important role in the spectral variation of the present system. More experimental information using different types of dyes and a wide range of organic solvent should be accumulated to establish a firm conclusion on this complicated solvent polarity.

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Acid-Catalyzed Migration of the Methyl Substituent in the Dienone-Phenol Rearrangement of *p*-Quinol Ether

Young-Sook Paik Hahn

Department of Chemistry, Kyung Hee University, Suwon 449-900. Received November 14, 1988

4-Methoxy-4-methylcyclohexa-2,5-dienone 1 in aqueous sulfuric acid underwent the normal dienone-phenol rearrangement with methyl group migration. The fact that methyl is migrating group and methoxy is remaining group can be rationalized by the stabilization of positive charge at C-4 during the transition state. Methoxy methyl dienone 1 ($(H_0)_{1/2} = -4.6$) is less basic than 4,4-dimethylcyclohexa-2,5-dienone whose half protonation acidity is reported as -3.15 or -3.66. This basicity difference comes from the unstabilization of the protonated methoxy methyl dienone 1 due to the electron withdrawing inductive effect of a methoxy group.

Introduction

The intramolecular 1,2-shift[1] of group R to a cationic center has been studied extensively. The group R undergoing the rearrangement is commonly alkyl, aryl, or hydrogen. The order of relative migratory aptitude of the group R is