

Relative Hydrophobicity of Triphenylmethane Dyes as Revealed by Interaction with Tetraarylborate Anions

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The ion aggregates formed between cationic triphenylmethane dyes and tetraphenylborate (TPB) or tetrakis(4-fluorophenyl) borate (TFB) anions have been investigated spectroscopically. The photometric sensitivities of the dyes are found to be increasing in the order pararosaniline < malachite green < methyl violet 2B < crystal violet < ethyl violet. Cetyltrimethylammonium bromide (CTAB) and Triton X-100 (TX-100) destroy the ion aggregates. By comparing the concentration of surfactant beyond which dye-borate mixed solutions behave identically with the dye blank, the order of hydrophobicity appears to be parallel with that of photometric sensitivity.

Introduction

Ion pairs of monovalent anions with cationic triphenylmethane dyes have been frequently used in spectrophotometric determinations of metal chelates and many organic anions.¹⁻³ Researches with such dyes have up to now been performed on extractability¹ with organic and inorganic anions, on separation⁴ by liquid chromatography, on stability constants⁵ with tetrafluoroborate, and on hydrophobic effects in the alkaline fading reaction⁶ of the dyes or in the formation of ion aggregates.^{7,8}

When anions in particular are large, monovalent, and poorly hydrated, the water structure forces the cations and anions to form ion aggregates to minimize their disturbance to water.⁹ As a result the adsorption spectra of aqueous solutions show spectral changes both at longer and at shorter wavelengths with respect to dye blank.⁷ The spectral changes which are attributed to hydrophobic interaction between cationic dyes and hydrophobic anions have not been widely studied. The relative hydrophobicity of triphenylmethane dyes may be responsible for the differences in extractability of ion aggregates,¹ in separation on a reverse-phase column⁴, and in stability constants.⁵

In this paper we report a simple and alternative way of evaluation for the relative hydrophobicity of triphenylmethane dyes by absorption spectrophotometry.

Experimental

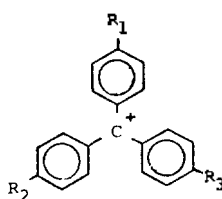
Structure of those cationic triphenylmethane dyes (Aldrich) used are shown below. Sodium tetraphenylborate (Fluka AG, GR) and sodium tetrakis(4-fluorophenyl) borate (Aldrich, GR) were used as anionic sources, TPB and TFB, respectively. Dyes and anions are dissolved in distilled water and stored in polyethylene bottles to avoid adsorption loss. Triton X-100 (Merck), and cetyltrimethylammonium bromide (B.D.H.) of reagent grade were used as received. Ionic strength and pH were adjusted with NaCl and a CH₃COOH-CH₃COONa buffer, respectively. Visible spectra were recorded on a Shimadzu UV-240 spectrophotometer.

Results and Discussion

Spectral Characteristics. Absorption spectra of dilute aqueous solutions of a triphenylmethane dye, under which

Table 1. Photometric Sensitivities (10⁴M⁻¹) of Triphenylmethane Dyes for TPB and TFB at the Respective Absorption Maximum. Dye Concentration: 4.0 × 10⁻⁶M. Concentration Range of TPB or TFB: 0.40–2.8 × 10⁻⁶M

pH/μM	MG		MV2B		CV		EV	
	TPB	TFB	TPB	TFB	TPB	TFB	TPB	TFB
4.0/0.01	5.5	5.6	5.9	5.9	6.0	6.3	7.0	7.5
5.0/0.01	5.4	5.4	5.9	5.9	6.1	6.5	7.1	7.6
6.0/0.01	5.1	5.2	5.8	5.8	5.9	6.1	6.9	7.2
6.0/0.1	5.0	5.2	5.6	5.6	5.8	6.0	7.0	7.3
7.0/0.01	4.9	5.0	5.5	5.6	5.5	5.6	6.8	7.0



Ethyl violet (EV): R₁=R₂=R₃=N(C₂H₅)₂

Crystal violet (CV): R₁=R₂=R₃=N(CH₃)₂

Methyl violet 2B (MV2B): R₁=R₂=N(CH₃)₂,
R₃=NHCH₃

Malachite green (MG): R₁=R₂=N(CH₃)₂,
R₃=H

Pararosaniline (PR): R₁=R₂=R₃=NH₂

the formation of dimers are not significant, show two additional bands by the addition of tetraarylborate anions, one occurring in the blue side, *H* band, and the other in the red, *J* band, of the intense peak of the dye blank. The *H* band is not clearly discernible and generally appears as a shoulder. These spectral changes are attributed to the ion aggregates formed between dye and anion.^{3,7}

With the increase of tetraarylborate concentration up to about 0.7 times of dye concentration, the intense peak decrease linearly, over which a quantitative determination of the dye is possible. Table 1 compares the photometric sensitivity³ defined by the magnitude of the absorbance decrease/anion concentration at the respective absorption maximum. Under the similar conditions the photometric sensitivity of PR was obtained to be about 1.0 × 10⁴M⁻¹.

Although the hydrogen atoms on amino groups in MV2B and PR may form hydrogen bonds with water molecules, the hydrophobic interaction with the tetraarylborate anions is apparently not completely eliminated.¹⁰ Increase of pH resulted in a slight lower photometric sensitivities for all the dyes

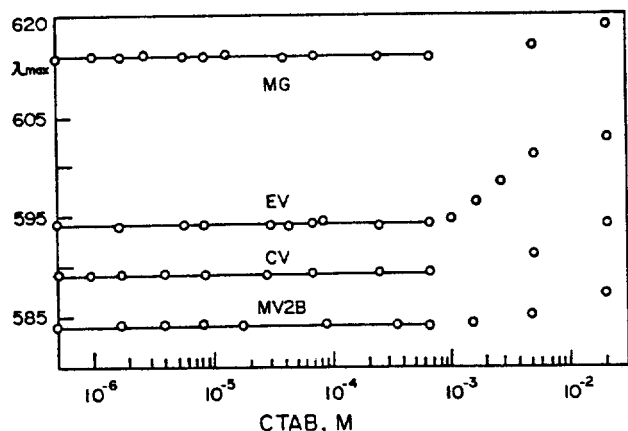


Figure 1. Variation of absorption maximum vs. [CTAB] for 4.0×10^{-6} M triphenylmethane dye solutions.

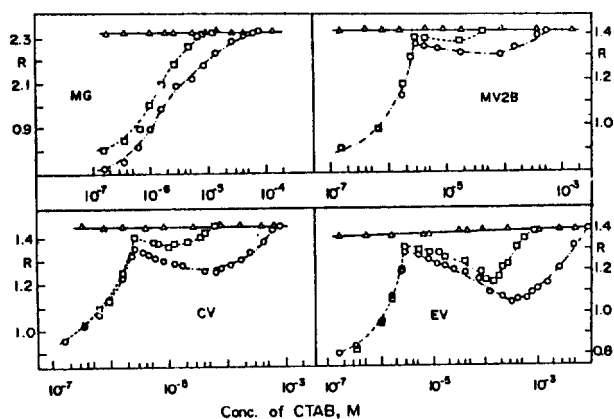


Figure 2. Plots of R vs. [CTAB] for 4.0×10^{-6} M triphenylmethane dyes and 2.4×10^{-6} M TPB (□) or TFB (○). Dye blanks are shown by solid lines.

possibly due to the chemical instability of the dye toward hydroxide ion.⁶

The photometric sensitivities of the dyes are increasing in the order $PR < MG < MV2B < CV < EV$. Also, it is noted that more hydrophobic⁸ TFB exhibits systematically larger photometric sensitivities for all the dyes than TPB. The larger and more hydrophobic the anion, the greater the disturbance to water structure,⁹ and so the more ion aggregates are formed. Thus, it is reasonable to assume that the more hydrophobic an anion is, the larger becomes the decrease of the absorbance at the intense peak of the dye upon the addition of the anion. Thus, the increasing order of photometric sensitivity of the dyes may be assumed to be parallel with that order of hydrophobicity. This possibility was further evaluated below by the effects of surfactants on the absorption spectra.

Effect of CTAB. Upon the addition of CTAB to 4.0×10^{-6} M dye solutions in the absence of the borate anions, absorption spectra show gradual bathochromic shifts beyond the cmc (9.2×10^{-4} M) as shown in Figure 1, indicating that some dyes are incorporated into and immobilized in the micellar media in spite of the electrostatic repulsion between dyes and micelles.⁶ The difference in the shifts are not clearly distinguishable between dyes, however, EV shows not only the largest shift, but a relatively sharp break near the cmc.

Table 2. C_d Values of CTAB^a

anion	MG	MV2B	CV	EV
TPB	1.0×10^{-5}	4.0×10^{-5}	6.0×10^{-5}	8.0×10^{-4}
TFB	6.0×10^{-5}	5.0×10^{-4}	8.0×10^{-4}	9.0×10^{-3}

^aConcentration of dye: 4.0×10^{-6} M; concentration range of anion: 2.4 – 2.8×10^{-6} M.

However, the ratios, R , of the absorbance at the absorption maximum to that at the shoulder which occurs about 40 nm to the red of the absorption maximum, remained constant (Figure 2).

In the presence of the borate anions the corresponding ratios show quite different behavior. Around 2.5×10^{-6} M CTAB the R values show a sharp maximum, followed by a broad minimum except MG. The variation of the R vs. [CTAB] may be interpreted in terms of the interaction with CTAB. During the initial rise to the maximum the ion aggregates formed between dyes and anions are dissociated and the anions are presumably incorporated into CTAB. The incorporation of tetraarylborate may reduce the electrostatic repulsion between dyes and the cationic surfactant, which enables dye molecules to adsorb on to the tetraarylborate-containing surfactant species. Beyond the maximum, therefore, the dye containing surfactant species apparently come together due to the tendency of association of the surfactant, or alternatively, a dye from the bulk solution may be adsorbed to the dye-containing surfactant, to result in the formation of dimer-like structure.¹¹ Both processes cause the R to decline. Beyond the minimum, however, the dimer-like structures are progressively diluted with CTAB and converted into monomeric species, and eventually the R follows the identical behavior with dye blank.

It is noted from Figure 2 that in the increasing order of photometric sensitivity the R minimum becomes deeper and moves to a higher concentration of CTAB. The result possibly suggests that the more hydrophobic a dye is, the more dimer-like structures are formed due to stronger interaction with CTAB. The shallow minimum was not developed with MG possibly because of its very weak interaction with CTAB.

It is also noted that the concentration of CTAB from which the R value becomes identical with that of respective dye blank, denoted by C_d , are different as summarized in Table 2. The C_d increases in the order $MG < MV2B < CV < EV$ for both TPB and TFB. This order coincides with that of photometric sensitivity. This result appears to be reasonable since more CTAB should be required to dissociate completely the ion aggregates formed between dyes and tetraarylborate anions having stronger hydrophobic interaction. That is, larger C_d appears to indicate the existence of stronger interaction between dye and tetraarylborate anion.

It may be interesting to relate the relative hydrophobicity to the number of methyl or methylene group in the dye. Taniguchi and Iguchi⁶ reported that the volume changes associated with the incorporation of triphenylmethane dyes into micellar phase were of hydrophobic origin, and that the magnitude of the volume change was reasonably increasing with the increase of number of methyl and methylene groups. In the triphenylmethane dyes PR, MG, MV2B, CV, and EV utilized here there are, respectively, 0, 2, 3, 6, and 10

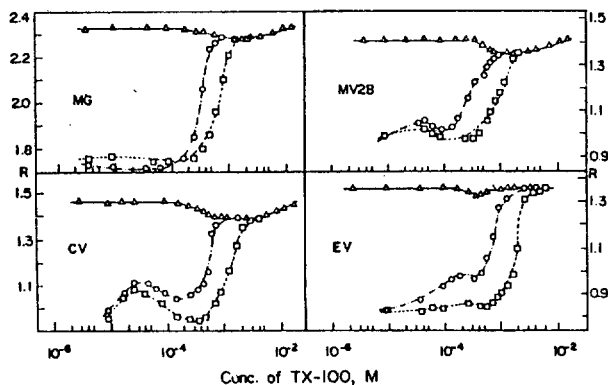


Figure 3. Plots of R vs. $[TX-100]$ for $4.0 \times 10^{-6}M$ triphenylmethane dyes and $2.4 \times 10^{-6}M$ TPB(\square) or TFB(\circ). Dye blanks are shown by solid lines.

Table 3. C_d Values of TX-100^a

anion	MG	MV2B	CV	EV
TPB	1.2×10^{-3}	2.0×10^{-3}	3.6×10^{-3}	6.0×10^{-3}
TFB	7.0×10^{-4}	8.2×10^{-4}	9.4×10^{-4}	2.4×10^{-3}

^aConcentration of dye: $4.0 \times 10^{-6}M$; concentration range of anion: $2.4-2.8 \times 10^{-6}M$.

such groups.

For a given dye, C_d is smaller with TPB than that with TFB. Since the dimer-like structures are possibly promoted by incorporated tetraarylborate, their dissociation becomes more difficult with more hydrophobic TFB.

It may be concluded that the hydrophobicity of the dyes increase in the same order as C_d .

Effect of TX-100. Similar studies were performed with TX-100 and Figure 3 shows the variation of R vs. $[TX-100]$. Contrary to CTAB, at the beginning of micelle formation ($[cmc] = 3 \times 10^{-4}M$) some dyes in the absence of borate anions are apparently incorporated into TX-100 to form dimer-like structure. The R values in the presence of borates vary similarly to those in Figure 2, and a similar interpretation may be applied although the maxima are broader and much lower due to the relatively easy incorporation of the dyes into TX-100.

Table 3 lists the C_d values defined above. Again the C_d value is increasing in the order $MG < MV2B < CV < EV$, as

expected since more TX-100 should be necessary to dissociate the dimer-like structure of a dye having larger hydrophobicity. However, the C_d values for TX-100 are smaller with TFB than with TPB, which is in reverse order with that obtained for CTAB. This discrepancy appears to come from the different mechanism to form dimer-like structures in micellar environment. Into TX-100, dyes are incorporated directly by the interaction with the surfactant, and the dimer-like structures are formed either between dye-containing surfactants or by the adsorption of an additional dye from the bulk solution to the dye-containing TX-100. The borate anions subsequently assist the dissociation of the dimer-like structures on surfactants because of their hydrophobic interaction with dyes. Thus, more hydrophobic TFB completes the dissociation at smaller concentration of TX-100 than TPB. Consequently, more hydrophobic TFB appears to show smaller C_d values.

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