

- 102, 6351 (1980); (e) K. Tatsuta, K. Akimoto, and M. Kinoshita, *J. Am. Chem. Soc.*, **101**, 6118 (1979).
7. (a) J. -G. Jun and B. P. Mundy, *Bull. Korean Chem. Soc.*, **8**, 489 (1987); (b) J. -G. Jun and B. P. Mundy, *Bull. Korean Chem. Soc.*, **8**, 310 (1987); (c) D. Wilkening and B. P. Mundy, *Synth. Commun.*, **14**, 227 (1984).
8. (a) R. L. Danheiser, C. A. Kwasigroch, and Y. -M. Tsai, *J. Am. Chem. Soc.*, **107**, 7233 (1985); (b) R. L. Danheiser and D. M. Fink, *Tetrahedron Lett.*, **26**, 2513 (1985).
9. M. E. Flaugh, T. A. Crowell, and D. S. Farlow, *J. Org. Chem.*, **45**, 5399 (1980).

Medium Effect on the Formation of Ion-Pair between Methylene Blue and Tetrphenylborate in Dilute Solutions

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The hydrophobic interaction leading to the formation of ion-pair between MB⁺ and TPB⁻ was investigated spectroscopically by varying the medium with the addition of 1,4-dioxane or urea. Beyond 0.01 mole fraction of 1,4-dioxane in water or above 2.0M urea the ion-pair appeared to be completely dissociated into individual ions. The ion-pair was not observed in common organic solvents and the absorption maxima of MB⁺ were correlated relatively well with the π^* -scale.

Introduction

The visible absorption spectra of aqueous solution containing methylene blue cation (MB⁺) and tetrphenylborate anion (TPB⁻) show spectral changes, especially at long wavelengths presumably due to the aggregation of MB⁺ and TPB⁻.¹ The new absorption behavior could be clearly differentiated from the well-studied metachromatic effects in methylene blue both in solutions of pure MB⁺ of varying concentrations and in systems where the dye is adsorbed on solid surfaces. They consist of a shift of the long wavelength peak to a shorter wavelength. The metachromacy of aqueous MB⁺ solutions can be related to the formation of dimer, (MB⁺)₂.²

Since both the cation and the anion are large, univalent, and poorly hydrated, the water structure forces the two ions to form an ion-pair, MB-TPB, to minimize their disturbance to itself and maximize the water-water bonding.³ The opposite charges on the anion and cation facilitate the association. The ion-pairs can be associated further to produce double ion-pairs again by the water structure as suggested recently.⁴ The tendency of water molecules to self-associate should be responsible for the ion-pairing. Therefore, the factors which could modify this tendency should be likely to influence the formation of ion-pairs.

For the purpose of elucidating the nature of ion-pair formation, in this paper the absorption and fluorescence emission behaviors of MB⁺ and TPB⁻ mixed solutions are reported by varying the composition of the medium with the addition of 1,4-dioxane and urea. The addition 1,4-dioxane into water decrease the dielectric constant of medium whereas urea increases it. In addition, the effects of replacing MB⁺ with other cationic dyes having similar structure and of changing water with common organic solvents were investigated.

Experimental

Chemicals. Methylene blue, thionine, and toluidine blue

(all from Merck, GR) were used as cationic sources, MB⁺, Thio⁺, and TB⁺, respectively. Sodium tetrphenylborate (MCR, GR) as a source of boron complex anion, TPB⁻, was dissolved in distilled water and stored in a polyethylene bottle to prevent contamination from glasswares containing boron. N-methylformamide (NMF), N-methylpropionamide (NMP), dimethylformamide (DMF), and 1,4-dioxane, from Fluka, 1,2-dichloroethane (DCE), formamide, and pyridine, from Junsei, and dimethylsulfoxide (DMSO), acetonitrile, CH₂Cl₂ and alcohols used from Aldrich Co. were all reagent grade. For all solutions the concentrations of MB⁺ and TPB⁻ were 1.0×10^{-6} M and 1.0×10^{-5} M, respectively.

Methods. Visible spectra were made on a Cary 17D spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Hitachi 650-60 spectrofluorimeter. All solutions containing MB⁺ were stored in polyethylene bottles wrapped with aluminum foil to minimize the photodecomposition of MB⁺. Measurements were made at room temperature.

Results and Discussion

Figure 1 shows the absorption spectra of 1.0×10^{-6} M MB⁺ in water (a) and in methanol (b), and of mixed solutions of 1.0×10^{-6} M MB⁺ and 1.0×10^{-5} M TPB⁻ in water (c) and methanol (d). The mixed solution in water reveals a broad absorption spectrum in comparison with other spectra. Particularly, it has a considerable absorbance around 710 nm and there exists a significant contribution near 623 nm in the light of the decrease in absorbance of MB⁺ at the absorption maximum, 666 nm. The species responsible for the spectral change that is present only in the mixed aqueous solution was attributed to the aggregation of MB-TPB ion-pairs.^{1,4}

Since both monovalent MB⁺ and TPB⁻, large and hydrophobic, contribute to tightening up their surrounding water, there would be a tendency for the water structure to force these ions into a single cavity in order to minimize disturbance of the water structure.³ The tendency of water mole-

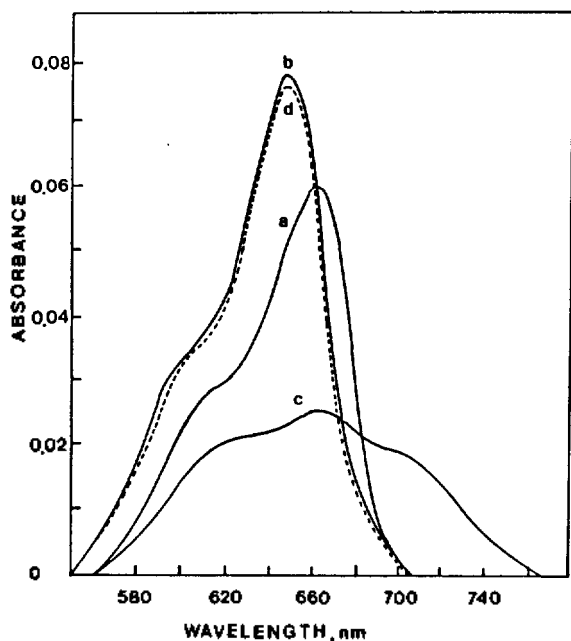


Figure 1. Absorption spectra of MB⁺ in water (a), MB⁺ in methanol (b), MB⁺ and TPB⁻ in water (c), and MB⁺ and TPB⁻ in methanol (d). Concentrations: MB⁺, 1.0×10^{-6} M; TPB⁻, 1.0×10^{-5} M.

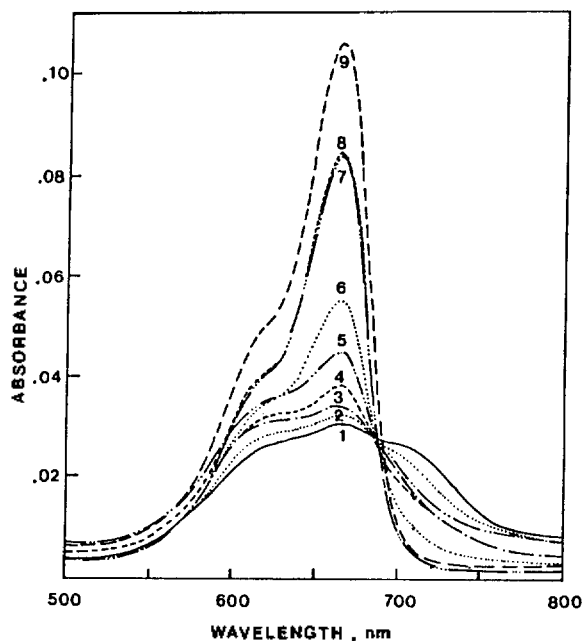


Figure 2. Effect of 1,4-dioxane on the absorption spectrum of mixed aqueous solutions of MB⁺ and TPB⁻. Concentrations of 1,4-dioxane (M): (1)0.0, (2)0.06, (3)0.11, (4)0.23, (5)0.35, (6)0.65, (7)0.82, (8)1.2, (9)3.3.

cles to self-associate is responsible for the anomalous ion-pairing. Factors which modify these tendencies should be likely to reduce the porportion of the dye in the aggregation.

Effect of 1,4-Dioxane. 1,4-Dioxane is completely miscible with water and permits continuous decrease of the dielectric constant of the medium from 78.6 to 2.2.^{5,6} Water and 1,4-dioxane have about the same viscosity. Figure 2 illustrates the variation of absorption spectrum of MB⁺ and TPB⁻ mixed solution as a function of 1,4-dioxane concentra-

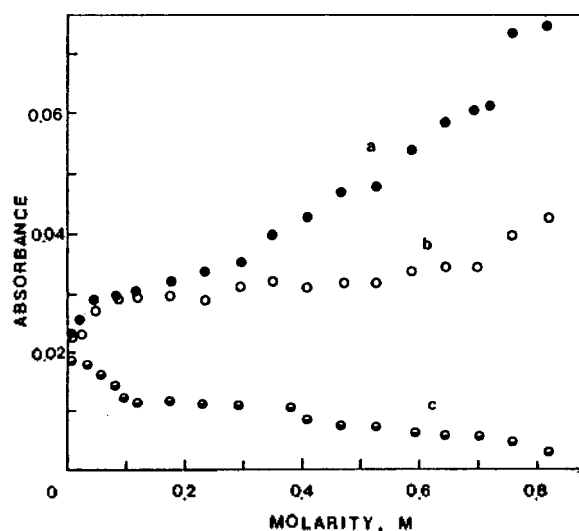


Figure 3. Variation of absorbances at 666 nm (a), 623 nm (b), and 705 nm (c) vs. the molar concentration of 1,4-dioxane in MB⁺ and TPB⁻ mixed aqueous solution.

tion in dioxane-water mixed solvents. As the concentration of 1,4-dioxane increases the spectrum approaches to that of MB⁺ alone. This can be clearly seen in Figure 3 where the absorption changes at 705 nm, 666 nm, 623 nm are plotted against 1,4-dioxane concentration in mixed solvent. With the increase of 1,4-dioxane concentration, the absorbance at 705 nm decreases while those at 666 nm and 623 nm increase. Beyond 0.6 M 1,4-dioxane, the absorption spectrum of MB⁺-TPB⁻ systems became similar to that of MB⁺ alone. The result demonstrates that the addition of 1,4-dioxane to MB⁺-TPB⁻ solutions provides the solvent with a solvating capability for both MB⁺ and TPB⁻ and thus reduces the association tendency of the two ions and that a complete dissociation into individual ions occurs above about 0.01 mole fraction of 1,4-dioxane near which the dielectric constant of the medium should be very close to that of water.

The fact that 1,4-dioxane interferes with the ion pair formation between MB⁺ and TPB⁻ is further supported by the change of the fluorescence emission spectrum of MB⁺ and TPB⁻ in 1,4-dioxane-water. Addition of 1,4-dioxane does not cause spectral shift but changes fluorescence intensity. The solution was excited at 600 nm rather than at the wavelength corresponding to the maximum of fluorescence excitation spectrum, 666 nm, to avoid spectral overlap with the spectrum due to Rayleigh scattering. With the increase of 1,4-dioxane concentration the fluorescence intensity increased monotonically. At about 0.01 mole fraction of 1,4-dioxane the fluorescence emission and excitation spectra of MB⁺ containing TPB⁻ in the mixed solvent became almost identical to the corresponding spectra without TPB⁻ in pure water. This result confirms that beyond 0.01 mole fraction of 1,4-dioxane MB⁺ exist as individual ions instead of forming ion-pairs with TPB⁻. Therefore, even a minute decline of dielectric constant caused by addition of 1,4-dioxane may completely destroy the ion-pair between the large, monovalent, and hydrophobic MB⁺ and TPB⁻.

Effect of Urea. The use of dissolved urea is suggested as a probe for investigating the contribution of water structure to hydrophobic bonding.⁷ Urea possesses three potential hydrogen bonding centers on each molecule. Urea appreci-

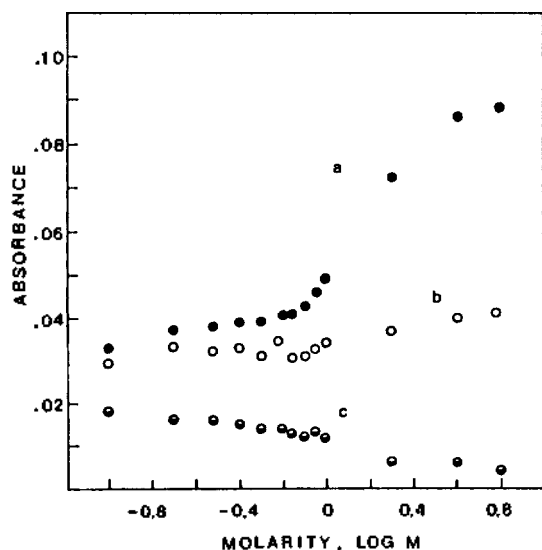


Figure 4. Variation of absorbances at 666 nm (a), 623 nm (b), and 705 nm (c) vs. the molar concentration of urea in MB⁺ and TPB⁻ mixed aqueous solution.

ably increases the dielectric constant of water. The variation of absorption spectrum on adding urea was studied.

A similar result as Figure 2 was obtained. That is, with the increase of dissolved urea the absorbance around 710 nm was diminished while that near 666 nm was increased. At slightly above 2.0 M urea, the spectrum of MB⁺ and TPB⁻ mixed solution became identical with that of MB⁺ alone. The dependence of absorbances at 623, 666, and 705 nm on urea concentration is summarized in Figure 4. The absorbance ratio of the maximum to the shoulder at 623 nm was about 1.1 without urea and was increased to 1.9 at 2.0 M urea. The latter value is nearly the same as that of MB⁺ alone at 2.0 M urea. Beyond 2.0 M urea, the ratio remains at 1.9 despite of the increase in absorbance.

The data explain assuredly that urea interferes with the ion-pair formation in water. The formation of hydrogen bonding between urea and water causes the water structure less rigid. At high concentrations of urea, the cooperative structure of water itself should be markedly reduced.

Effect of Substituent. The following dye cations having different substituents are compared with MB⁺ for ion-pair formation in water.

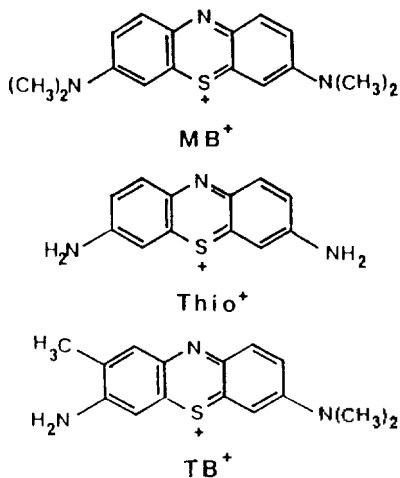


Table 1. Absorption Characteristics of 1.0×10^{-6} MB⁺ and 1.0×10^{-5} M TPB⁻ in various Solvents and Specifications of the Solvents

solvent	dielectric constant ^a	refractive index ^a	λ_{max} nm	$R_{m/s}^b$	$E_A(30)^c$ Kcal/mol	π^*d
1. CH ₂ Cl ₂	8.93	1.42115	663	2.33	41.1	0.80
2. DCE	10.36	1.4421	656	2.71	41.9	0.81
3. Pyridine	12.3	1.50745	663	2.14	40.2	0.87
4. 1-propanol	20.33	1.3837	656	2.40	50.7	0.51
5. acetone	20.70	1.3588 ^e	654	2.12	42.2	0.72
6. ethanol	24.55	1.3594	653	2.34	51.9	0.54
7. methanol	32.70	1.3265	653	2.14	55.5	0.60
8. DMF	36.71	1.4282	664	2.15	43.8	0.88
9. acetonitrile	37.5	1.34163	654	2.27	46.0	0.85
10. DMSO	46.68	1.4773	668	2.22	45.0	1.00
11. H ₂ O	78.54 ^e	1.331 ^e	666	1.08	63.1	1.09
12. formamide	111.0 ^e	1.44682	662	2.33	56.6	0.98
13. NMP	172.2	1.4345	662	2.36	—	—
14. NMF	182.4	1.4300	662	2.23	54.1	—

^a J. A. Riddick and W. B. Bunger, "Organic Solvents", Wiley, New York, 1970. ^b $R_{m/s}$ is the absorbance ratio of the maximum to the shoulder. ^c reference 10. ^d reference 11. ^e values at 20°C. Others at 25°C.

Contrary to MB⁺, the mixed aqueous solutions of Thio⁺ and TPB⁻ or TB⁺ and TPB⁻ did not exhibit characteristic absorption to the red of the absorption maximum of dye cation but showed essentially equal absorption spectrum with that corresponding to dye cation. The addition of 1,4-dioxane to Thio⁺-TPB⁻ or TB⁺-TPB⁻ mixed solutions produced neither spectral shift except a slight hyperchromic change nor a new absorption peak.

This different behaviour of Thio⁺ and TB⁺ from MB⁺ may be interpreted in terms of the capability of hydrogen bond formation of the dye cations with water. That is, since the hydrogen atoms on amino groups in Thio⁺ and TB⁺ can form hydrogen bond with water molecules, the hydrophobicity of dye cations is drastically lowered and consequently the hydrophobic interaction with TPB⁻ is completely eliminated.

Effect of Organic Solvent. It would be interesting to observe if the hydrophobic interaction between MB⁺ and TPB⁻ exist in other organic solvents. Absorption spectra of MB⁺ and TPB⁻ in a number of organic solvents over a wide range of dielectric constant were obtained and the results are summarized in Table 1.

Neither new absorption nor spectral change as can be judged from a relative constancy in $R_{m/s}$ was observed, reflecting no new absorbing species is formed in any of these solvents except water, where $R_{m/s}$ is the absorbance ratio of the maximum to the shoulder. However, the $R_{m/s}$ in water is conspicuously different from others. Water is probably the unique solvent showing such a hydrophobic interaction.

The absorption spectrum in the visible region is originated from a $\pi \rightarrow \pi^*$ transition and the transition is known to show a bathochromic shift with the increase of solvent polarity. The effect of solvent polarity has been theoretically treated by Bayliss, McRae, and later by Suppan.⁸ The solvent effects on the position of spectral maxima (Table 1) is not considerable reaching only from 668 nm in DMSO and to 653 nm in ethanol and methanol. Nevertheless, the variation

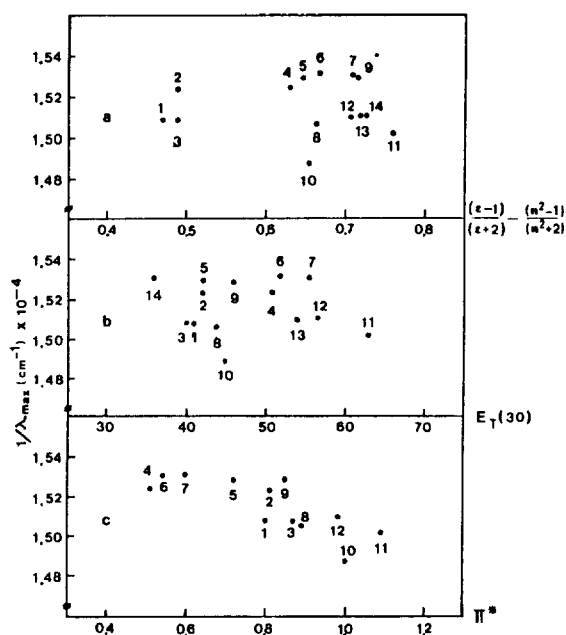


Figure 5. Plots of $1/\lambda_{\max}$ for the MB^+ and TPB^- in various solvents vs. $[(\epsilon-1)(\epsilon+2)^{-1} - (n^2-1)(n^2+2)^{-1}]$ (a), $E_T(30)$ -scale (b), and π^* -scale (c). The numbers correspond to the solvents in Table 1.

of $1/\lambda_{\max}$ is plotted in Figure 5(a) as a function of $[(\epsilon-1)(\epsilon+2)^{-1} - (n^2-1)(n^2+2)^{-1}]$ proposed by McRae⁹ to get an information on the nature of solvation, where ϵ is the dielectric constant and n is the solvent refractive index. This plot appears to show significant deviation of observed solvent shifts from predicted by the function, implying that more pronounced solvent-solute interactions are involved.

Because of difficulties in assessing the complex nature of solvent-solute interactions, an extensive number of empirical parameters of solvent polarity are frequently employed.¹⁰ The most comprehensive solvent scale is the $E_T(30)$ -scale. It might be considered suitable to apply the $E_T(30)$ -scale for an explanation of the spectral shifts in Table 1 since the $E_T(30)$ -scale is based on a $\pi\pi^* \rightarrow \pi^*$ transition of the cationic dye, 2,6-diphenyl-4(2,4,6-triphenyl-1-pyridinio)phenolate.¹⁰ As seen in Figure 5(b), the $E_T(30)$ -scale shows no better correla-

tion than the function used to obtain Figure 5(a). At last, the π^* -scale of solvent polarity, another widely known, was utilized to plot Figure 5(c). It appears that the π^* -scale¹¹ fits relatively well with the shifts of the present system. This is probably because hydrogen bond effect is minimized in establishing the scale.¹⁰ Incidentally, no hydrogen bond formation is expected between MB^+ and the organic solvents studied here. Based on these application of theoretical and empirical solvent polarities the π^* -scale apparently provides the best empirical parameters of solvent polarity to the MB^+ and TPB^- system. More experimental information using different types of dyes and a wide range of organic solvents will be needed to establish a firm conclusion on the solvent polarity.

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References

1. K. J. Yoon and K.-J. Kim, *Bull. Korean Chem. Soc.*, **6**, 149 (1985).
2. K. Bergmann and C.T. O'Konski, *J. Phys. Chem.*, **67**, 2169 (1963).
3. R.M. Diamond, *J. Phys. Chem.*, **67**, 2513 (1963).
4. H.-S. Song, Y.J. Park, and K.-J. Kim, *J. Korean Chem. Soc.*, **28**, 355 (1984).
5. C. A. Krauss and R. M. Fouss, *J. Am. Chem. Soc.*, **55**, 21 (1933).
6. C. H. Jenson and R. M. Diamond, *J. Phys. Chem.*, **75**, 79 (1971).
7. P. Mukerjee and A. K. Ghosh, *J. Phys. Chem.*, **67**, 193 (1962).
8. R. P. T. Tomkins and O. Popovych, "Nonaqueous Solution Chemistry", Wiley, New York, 1981, p320 and references therein.
9. E. G. McRae, *J. Phys. Chem.*, **31**, 562 (1957).
10. H. Ratajczak and W. J. Orville-Thomas, eds, "Molecular Interactions", vol. 3, Wiley, 1982, p 249.
11. M. J. Kamlet, J. L. M. Abboud, and R. W. Taft, *Prog. Phys. Org. Chem.*, **13**, 485 (1980).