

# Double Ion-Pair Formation in Aqueous Solutions of Methylene Blue and Tetraphenylborate

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Spectrophotometric and spectrofluorimetric methods of analysis were conducted in dilute aqueous solutions of methylene blue and tetraphenylborate. The formation of double ion-pair was confirmed and its overall formation constant,  $\Delta H^\circ$ , and  $\Delta S^\circ$  were obtained. The irradiation with wavelengths over visible region resulted in bleaching the mixed solution. The bleaching reaction was also proceeded at 55°C. The reactions of the double ion-pair were briefly discussed.

## Introduction

The determination of micro amounts of boron is very important in the fields of nuclear reactor and cladding materials, industry metallurgy materials, pharmacy, and agriculture<sup>1</sup>. Among several sensitive spectrophotometric methods for boron up to date, the method using the extraction of tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) with methylene blue is widely used. The methylene blue cation (MB<sup>+</sup>) reacts with BF<sub>4</sub><sup>-</sup> to form an ion-pair in the aqueous solution<sup>2</sup>. Ion-pairs have become widely used for the separation of ions by extraction, flotation and partition chromatography. Solvent extraction is one of the most important and useful separation procedures since the extract may be determined subsequently by various analytical techniques. In the extraction-spectrophotometric determination of boron, however, hydrofluoric acid is necessary for the formation of BF<sub>4</sub><sup>-</sup> and a long time is consumed. Besides, the absorbance of the blank is relatively large due to the interference by the presence of HF<sub>2</sub><sup>-</sup> in the solution<sup>3</sup>. It was therefore thought that the substitution of tetraphenylborate ion (TPB<sup>-</sup>) for tetrafluoroborate would lead to enhancement of the extraction and subject to less interferences because of more hydrophobicity of the former. The use of TPB<sup>-</sup> has primarily been concerned with the formation of insoluble salts with ions such as NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> for gravimetric determination. However, less importantly, TPB<sup>-</sup> has also been investigated as an agent of extraction for the separation of alkali metal ions<sup>4</sup>.

The extraction of boron with TPB<sup>-</sup> was improved over that with BF<sub>4</sub><sup>-</sup> as predicted<sup>3</sup>. Unexpectedly, however, the authors obtained a rather unusual spectral change, especially at long wavelengths, in visible absorption spectra of the MB<sup>+</sup> and TPB<sup>-</sup> mixed solutions, and a double ion-pair, (MB-TPB)<sub>2</sub> was attributed to the large absorption at longer wavelengths where MB<sup>+</sup> did not absorb<sup>5</sup>. The new absorption behavior could be clearly differentiated from the well-studied metachromatic effects in methylene blue both in solutions of pure MB<sup>+</sup> of varying concentrations and in systems where the dye is adsorbed on solid surfaces<sup>6</sup>. They consist of a shift of the long wavelength peak to a shorter wavelength. The metachromacy of aqueous MB<sup>+</sup> solutions can be related to the formation of dimer, (MB<sup>+</sup>)<sub>2</sub><sup>6-8</sup>.

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 to maximize the water-water bounding<sup>9</sup>. The opposite charges on the anion and cation facilitate the association. The ion-pair can be associated further to produce a double ion-pair again by the water structure as suggested recently<sup>5</sup>. In this work, the absorption and fluorescence emission behaviors of the mixed solution as functions of temperature and irradiation time are reported for the purpose of confirming and characterizing the double ion-pair.

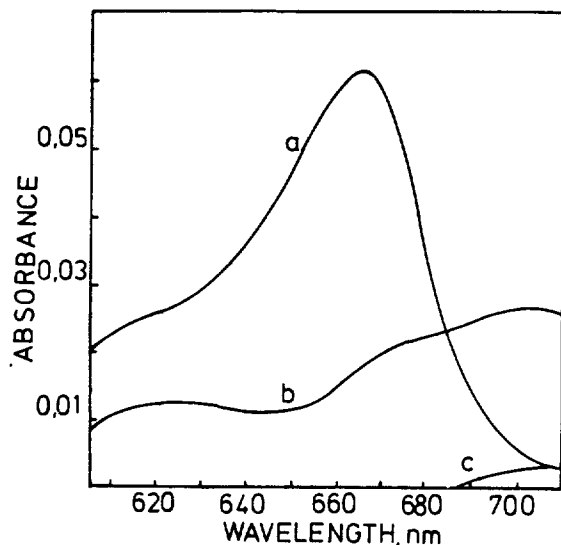
## Experimental

**Chemicals.** Methylene blue (Merck, GR) was used as a cationic, MB<sup>+</sup> source. Sodium tetraphenylborate (MCB, GR) as a boron complex anion, TPB<sup>-</sup> was dissolved in distilled water and stored in polyethylene bottles to prevent contamination from glasswares containing boron.

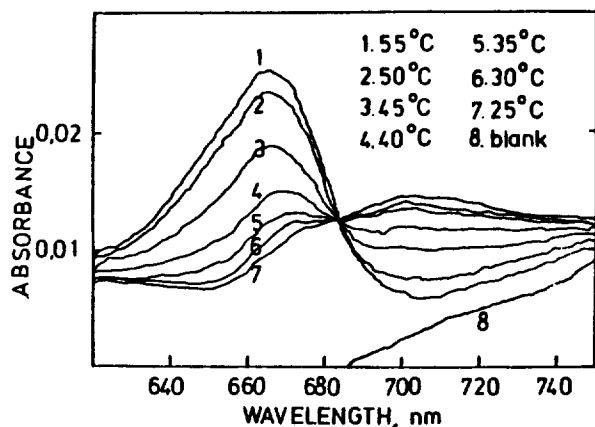
**Methods.** Ultraviolet-visible spectra were made on a Cary 17D spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Hitachi 650-60 spectrofluorimeter. The spectrofluorimeter equipped with a 150W Xe lamp was also utilized for irradiation. Solutions were temperature-controlled to  $\pm 1^\circ\text{C}$ . Since even room light caused spectral changes in the mixed solutions of MB<sup>+</sup> and TPB<sup>-</sup>, all experiments were carried out under the darkness unless specified.

## Results and Discussion

Figure 1 shows a typical absorption spectra of  $1.0 \times 10^{-6} M$  MB<sup>+</sup> and of a mixed solution of  $1.0 \times 10^{-6} M$  MB<sup>+</sup> and  $1.0 \times 10^{-5} M$  TPB<sup>-</sup>. Compared with a MB<sup>+</sup> solution, the mixed solution reveals a rather broad absorption structure. In particular, it has a considerable absorbance around 700nm and there exists a significant contribution near 620nm in the light of the decrease of MB<sup>+</sup> at the absorption maximum, 664nm. The species responsible for the spectral change in the mixed solution was recently attributed to a double ion-pair, (MB-TPB)<sub>2</sub><sup>5</sup>. This suggestion was further investigated by studying the effects of temperature and irradiation on the absorption and fluorescence emission spectra of the mixed solutions and relevant thermodynamic properties were evaluated.



**Figure 1.** Absorption spectra of  $\text{MB}^+$  (a) and of  $\text{MB}^+$  and  $\text{TPB}^-$  mixed (b) solutions. Concentration:  $1.0 \times 10^{-6} \text{M}$   $\text{MB}^+$ ;  $1.0 \times 10^{-5} \text{M}$   $\text{TPB}^-$ . (c) is the baseline.



**Figure 2.** Variation of absorption spectra of a  $1.0 \times 10^{-6} \text{M}$   $\text{MB}^+$  and  $1.0 \times 10^{-5} \text{M}$   $\text{TPB}^-$  mixed solution depending on temperature.

**Temperature Effect.** Contrary to  $\text{MB}^+$  solutions, the absorption spectra of the mixed solutions under the dark condition exhibit a remarkable temperature dependence as illustrated in Figure 2. The presence of an isosbestic point implies that there exist two absorbing species in the mixed solution. Increase in temperature appears to lead to liberation of  $\text{MB}^+$  and hinders the formation of the double ion-pair. As mentioned above we are inclined to assume the new species being the double ion-pair. In order to see the stability of the double ion-pair absorption spectra were run against time at  $55^\circ\text{C}$  in the dark. We found that the absorbance at  $664\text{nm}$  where  $\text{MB}^+$  absorbed significantly was decreased monotonically and reduced by almost half of the initial intensity after 90 min, whereas that of the double ion-pair near  $710\text{nm}$  remained nearly constant. Observation of such a result implies a bleaching process has been occurring through the double ion-pair in a steady state. However, on standing the mixed solution for 2 hours in the dark at room temperature caused no change in absorbance. Thus it appears that thermal energy presumably accelerates the irreversible bleaching reaction.

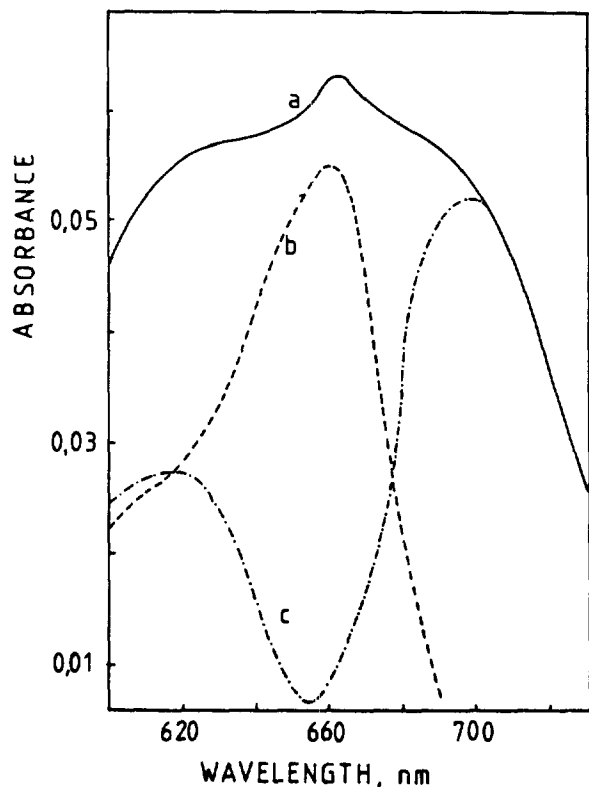
**Effect of Irradiation.** When an excess of  $\text{TPB}^-$  is added to a  $\text{MB}^+$  solution one observes by naked eyes the characteristic blue color to be gradually faded out under room light and at

room temperature, which indicates that the bleaching reaction is influenced by radiation. When a mixed solution was irradiated at  $710\text{nm}$  cumulatively at  $25^\circ\text{C}$  both of the absorbances at  $664\text{nm}$  and  $710\text{nm}$  showed steady decrease. The radiation of  $710\text{nm}$  was not unique to proceed the bleaching reaction. In fact, the effective irradiation wavelength was not selective but a wide range of wavelength in the visible region between  $400\text{--}700\text{nm}$  turned out to be active to have the mixed solution decolorized.

**Spectral Characteristics.** In order to characterize the fluorimetric behavior of the double ion-pair, a mixed solution of  $1.0 \times 10^{-6} \text{M}$   $\text{MB}^+$  and  $1.0 \times 10^{-5} \text{M}$   $\text{TPB}^-$  was excited at  $710$ ,  $713$ , and  $715\text{nm}$  at which the double ion-pair only absorbed. There was no measurable fluorescence emission observed. It means that the double ion-pair is non-fluorescent<sup>10</sup>.

A fact to be considered here is the presence of an intermediate species,  $\text{MB-TPB}$ , in the course of forming the double ion-pair. Prior to calculating the thermodynamic properties related to  $(\text{MB-TPB})_2$ , spectral behaviors of  $\text{MB-TPB}$  should be found. If the fluorimetric behavior of  $\text{MB-TPB}$  is not identical to that of  $\text{MB}^+$ , the fluorescence emission spectrum of the mixed solution will probably produce an intensity change and/or will be distorted relative to that of the  $\text{MB}^+$  only solution under the same condition since the  $(\text{MB-TPB})_2$  is found to be non-fluorescent. This was verified experimentally by observing almost complete overlap of fluorescence excitation and emission spectra of the  $\text{MB}^+$  solution with the respective spectrum of the mixed solution. We also have another reason to assume that the absorption spectrum of  $\text{MB-TPB}$  should be the same as that of  $\text{MB}^+$ . As shown in Figure 2, there seem to exist two absorbing species in the mixed solution.  $\text{MB}^+$  is the one and  $(\text{MB-TPB})_2$  the other. The assumption is further supported by the fact that the absorption spectra of  $\text{MB}^+$  with a few counter anions were identical in aqueous or in 1,2-dichloroethane even though ion-pairs were present<sup>3</sup>. Although it may be difficult to be true to extrapolate the experimental results obtained for smaller ions directly to a large hydrophobic anion such as  $\text{TPB}^-$ , we can at least assume that the interaction between  $\text{MB}^+$  and  $\text{TPB}^-$  is not strong enough to cause a noticeable absorption spectral change in Figure 2 or that the spectral change is not significant for our purpose if any. We may thus fairly conclude that the spectral behaviors of  $\text{MB}^+$  and  $\text{MB-TPB}$  are identical.

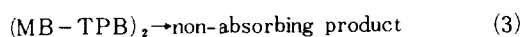
The facts that  $(\text{MB-TPB})_2$  is non-fluorescent and that absorptive and fluorescent spectral behavior of  $\text{MB-TPB}$  should be identical to those of  $\text{MB}^+$  enable us to determine the concentrations of  $(\text{MB-TPB})_2$  and of remaining species which contain  $\text{MB}^+$  in a mixed solution by making use of spectrofluorimetry together with spectrophotometry. That is, the sum of concentrations of  $\text{MB}^+$  and  $\text{MB-TPB}$  can be obtained from the fluorescence emission spectrum for a mixed solution, and their contribution can be subtracted from the absorption spectrum of the mixed solution to result in the calculated absorption spectrum of  $(\text{MB-TPB})_2$  only. A typical result is presented in Figure 3. The molar absorptivity of  $(\text{MB-TPB})_2$  at  $710\text{nm}$  attained through abovementioned procedure was calculated to be  $5.08 \times 10^4 \text{M}^{-1}\text{cm}^{-1}$  which was in good agreement with the value obtained in this laboratory<sup>11</sup>.



**Figure 3.** Absorption spectrum of a  $5.0 \times 10^{-5} M$  MB<sup>+</sup> and  $1.0 \times 10^{-5} M$  TPB<sup>-</sup> mixed solution (a), calculated absorption spectrum of the solution without the contribution of (MB-TPB)<sub>2</sub> (b), the difference spectrum (c).

A careful inspection of Figure 3 reveals the most powerful information that provides a conceptual framework for the double ion-pair. We note that there are two peaks in the absorption spectrum of (MB-TPB)<sub>2</sub> separated by nearly equal energy gap, 1060 and 980 cm<sup>-1</sup>, with respect to the main peak of MB<sup>+</sup>. The splitting between the two peaks amounts to be 2040 cm<sup>-1</sup> which agrees well with 2000 cm<sup>-1</sup> obtained with limited data<sup>5</sup>. The physical phenomenon of this peak splitting in a symmetrical fashion with respect to the maximum absorbing wavelength of MB<sup>+</sup>, reflects characteristically the presence of a dimer<sup>12</sup>, the double ion-pair in the present system. When the monomers of a dimer are close enough to interact electronically and the interactions are weak so that the individual monomers retain their identities, each monomer is perturbed by the electronic field of the other and the perturbation splits the excited state of the dimer into two states<sup>12,13</sup>. As a result one may observe normally a spectral shift depending on their relative orientations in space<sup>12</sup>. The reason for showing two absorption bands of considerable intensities in the present case can be explained in terms of multiple orientations of MB<sup>+</sup> in the double ion-pair due to the bulkiness of the (MB-TPB)<sub>2</sub> rather than of a single preferred orientation.

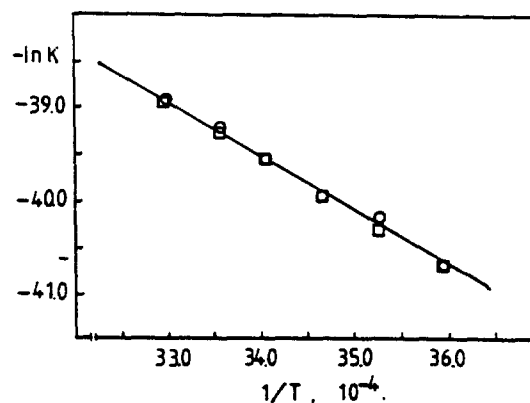
**Formation Constant.** Now, the reactions occurring in the mixed solution of MB<sup>+</sup> and TPB<sup>-</sup> may be written as follows.



The overall formation constant of (MB-TPB)<sub>2</sub>, K' is given by

**TABLE 1: Overall Formation Constants of (MB-TPB)<sub>2</sub> in Units of 10<sup>17</sup>M<sup>-3</sup> at various Formal Concentrations of TPB<sup>-</sup> and Temperatures. C<sub>MB<sup>+</sup></sub> = 1.0 × 10<sup>-5</sup>M**

Temp., K	C <sub>TPB<sup>-</sup></sub> , 10 <sup>-5</sup> M			
	1.5	2.0	2.5	3.0
278	4.8	3.6	5.2	4.7
283	2.8	3.4	3.3	2.8
288	2.3	2.6	2.9	2.8
293	1.5	1.5	1.6	1.6
298	1.1	1.4	1.2	1.2
303	0.82	0.84	0.86	0.85



**Figure 4.** Plot of  $-\ln K$  vs.  $1/T$  for the formation of (MB-TPB)<sub>2</sub> at  $1.0 \times 10^{-5} M$  MB<sup>+</sup> with  $1.5 \times 10^{-5} M$  (O) and  $2.5 \times 10^{-5} M$  (□) TPB<sup>-</sup> respectively.

$$K = K_1^2 K_2 = [(\text{MB-TPB})_2] / [\text{MB}^+]^2 [\text{TPB}^-]^2 \quad (4)$$

To evaluate the overall formation constant the concentrations of MB<sup>+</sup> and MB-TPB are also known. To do this we have two mass balance equations of

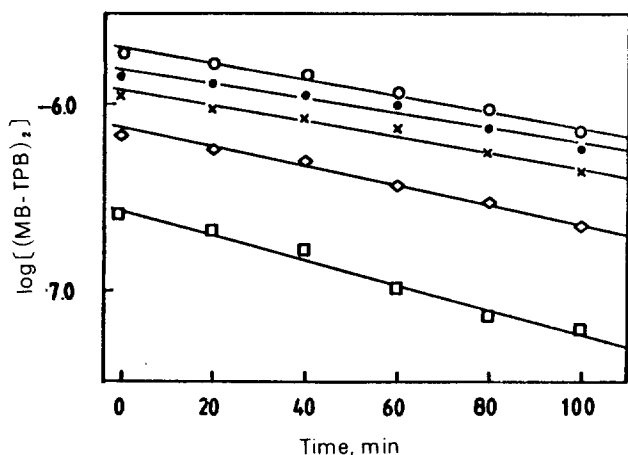
$$C_{\text{MB}^+} = [\text{MB}^+] + [\text{MB-TPB}] + 2[(\text{MB-TPB})_2] \quad (5)$$

and a similar equation for C<sub>TPB<sup>-</sup></sub>—where C<sub>MB<sup>+</sup></sub> and C<sub>TPB<sup>-</sup></sub> are the formal concentrations MB<sup>+</sup> and TPB<sup>-</sup>, respectively. In addition, from the temperature dependence of the formation constant,  $-\ln K = (\Delta H^\circ/RT) - (\Delta S^\circ/R)$  one can be sure the formation of (MB-TPB)<sub>2</sub> to be acceptable under the dark conditions as described by above equations.

By varying a range of temperature and concentration a large collection of absorption and fluorescence emission spectra were obtained. According to the procedures above the concentrations of the double ion-pair were determined and the overall formation constants are listed in Table 1. A plot of  $-\ln K$  versus  $1/T$  can be represented by a single straight line as shown in Figure 4 for four different concentrations of TPB<sup>-</sup>, which supports that the proposed mechanism is reasonable to accept if equilibrium is established in the dark. From the plot, we obtain  $\Delta H^\circ = -47.1 \text{ kJ} \cdot \text{mol}^{-1}$  and  $\Delta S^\circ = 170 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

The free energy change of the double ion-pairing consisted of approximately equal contributions from enthalpy and entropy. That the enthalpy change was not large accounts for the weak association.

Since both MB<sup>+</sup> and TPB<sup>-</sup>, large and hydrophobic, contribute to tightening up to their surrounding water, there would be a tendency for the water structure to force the ions into a single



**Figure 5.** Plot of  $\log [(MB-TPB)_2]$  vs. irradiation time at  $1.0 \times 10^{-5} M$   $TPB^-$  with  $1.0 \times 10^{-6}$ ,  $2.0 \times 10^{-6}$ ,  $3.0 \times 10^{-6}$ ,  $5.0 \times 10^{-6} M$   $MB^+$  from bottom to top, respectively.

**TABLE 2: Effect of Irradiation Time on the Concentration of  $(MB-TPB)_2$  in Units  $10^{-6} M$  at Various Formal Concentrations of  $MB^+$  and at  $25^\circ C$ .  $C_{TPB^-} = 1.0 \times 10^{-5} M$**

Irradiation Time, min	$C_{MB^+}, 10^{-6} M$				
	5.0	4.0	3.0	2.0	1.0
0	1.9	1.4	1.1	0.64	0.25
20	1.7	1.3	0.93	0.55	0.21
40	1.4	1.1	0.84	0.48	0.16
60	1.2	0.87	0.68	0.37	0.10
80	0.93	0.73	0.54	0.30	0.07
100	0.66	0.57	0.44	0.22	0.06

cavity in order to minimize disturbance of the water structure<sup>9</sup>. This type of ion-pairing would be extended to form a double ion-pair whose most stable structure would be a sandwich type rather than a linear chain type, that is, the opposite charges face each other to maximize the coulombic attraction. A series of this type of association would result in a large positive entropy change obtained above. This entropy effect supports the origin of the association between  $MB^+$  and  $TPB^-$  caused not to disturb the water structure.

We cannot exclude the possibility of higher aggregates involving more than two ion-pairs in concentrated solutions. There could be a set of equilibria among several polymers of the ion-pair represented by<sup>14</sup>



The proportions of the several molecular species will depend on the component concentrations.

**Reaction of  $(MB-TPB)_2$ .** Finally a great deal of effort has been directed toward confirming the reaction (3) to be a pseudo first order reaction. As mentioned previously the mixed solution did not show any changes at all in the absorption spec-

trum under the darkness for a long time, but irradiation caused rapid reduction in absorbance over the entire spectral range suggesting all species were being depleted. To be specific, the absorption and the fluorescence emission spectra were recorded against irradiation time at 710nm in the dark. The concentrations of  $(MB-TPB)_2$  were calculated as before and listed in Table 2. Logarithm of the concentration is plotted against irradiation time in Figure 5. The figure clearly indicates straight lines at five different formal concentrations of  $MB^+$  implying that the reaction (3) apparently proceeds via a pseudo first order under irradiation.

The reaction mixture was surveyed by a gas chromatograph to find any products containing simple aromatic hydrocarbons which could be produced if it was a decomposition reaction. However, no such products were detected.

Detail mechanism beyond  $(MB-TPB)_2$  has not been pursued further due to lack of any convenient analytical methods, but a reasonable consequence of the reaction seems to produce higher aggregates of  $MB-TPB$ , such as trimer, tetramer, etc.<sup>14</sup> The aggregation can apparently be produced by heat, radiation, and high concentration of either component of  $MB-TPB$ .

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