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Kinetic Study of the reaction of Leuco Methylene Blue with 2,6-Dimethyl-*p*-benzoquinone  
in a Reverse Micellar System

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**Abstract**

The kinetics of the reaction of leuco methylene blue (MBH) with 2,6-dimethyl-*p*-benzoquinone (DMBQ) were studied in a heptane/ bis (2-ethylhexyl)sulfo-succinate (AOT)/water reverse micellar system. The pseudo-first-order rate constant ( $k_{\text{obsd}}$ ) obtained in the presence of excess of DMBQ was found to be proportional to the initial concentration of DMBQ for  $W_0 = 3, 5, 10, 15,$  and  $20$  ( $W_0 = [\text{H}_2\text{O}] / [\text{AOT}]$ ). The second order rate constant ( $k_2 = k_{\text{obsd}} / [\text{DMBQ}]_0$ ) increased with an increase in the  $W_0$ -value, but was almost independent of the concentration of the water pool. A mechanism involving the distribution of DMBQ between the reverse micellar interface and bulk organic solvent was proposed to explain these findings.

*Keywords:* Reverse micelle; AOT; Oxidation of Leuco methylene blue; Kinetics;

Water pool;

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**1. Introduction**

Reverse micelles consist of micropools of water lined by a monolayer of a surfactant, all dispersed in a nonpolar solvent [1, 2]. The reverse micellar system is optically transparent and a change in the system can be followed by some spectroscopic methods. The physical characteristics of water microdroplets differ from those of bulk water

(mobility, polarity, and properties affected by its high ionic strength and by the electronic influence of the charged surfactant head groups) [2-6].

In principle, reverse micellar system can affect reaction rates by two main processes shown below [7-10]. They can increase or diminish the energy of the transition state of the reaction. This is called the medium effect, and it takes into account all of the properties of the interface such as micropolarity, microviscosity, ionic strength, charge density, etc. The other effect that can change the reaction location is called the solubilization effect. In the case of bimolecular reactions, solubilization of both reactants in the interfacial region can significantly accelerate reactions due to “concentration effect”, while reactions of segregated reactants may be retarded [11-13].

Previously, we studied the kinetics of the oxidation of leuco methylene blue (MBH) by some benzoquinones and the  $\text{Fe}^{3+}$  ion spectrophotometrically by means of the stopped-flow technique [14, 15]. Since MBH was known to be easily oxidized with dissolved oxygen, kinetic studies on the reactions of this compound with  $\pi$ -acceptors were not previously reported. In those studies, leuco methylene blue was produced by photoreduction of methylene blue ( $\text{MB}^+$ ) with triethylamine in ethanol and ascorbic acid (AA) in aqueous solution in the drive syringe of the stopped-flow apparatus and the solutions were used as it is in the measurement of the oxidation rate. A combination of the formation of unstable species by photoreduction in the closed system and the spectroscopic measurement under deaerated conditions provides the useful method for kinetic studies of reactions of species which are easily oxidized with dissolved oxygen.

The reagents present in the medium may be separated into different microscopic phases or may share the same phase in reverse micelles, and the kinetics of their reactions will reflect their various distributions. Further, in the heptane/bis (2-ethylhexyl)-sulfosuccinate (AOT)/water reverse micellar system, which can contain large quantities of water, the size of the water pool can be controlled by the water/AOT ratio.

Since  $\text{MB}^+$  and AA are soluble in water, but not soluble in non-polar solvents, MBH

must be formed by the photoreduction of  $\text{MB}^+$  with AA in water pools in the reverse micellar system. On the other hand, 2, 6-dimethyl-*p*-benzoquinone (DMBQ) is soluble in non-polar solvents. Therefore, MBH with DMBQ are present separately in the reverse micelles. The reaction of  $\text{MB}^+$  with DMBQ must occur only at the interface between heptane and water pool. We were interested in the mechanism of the reaction of MBH with DMBQ in the reverse micellar system, and examined the dependence of the rate of the reaction of MBH with DMBQ in the heptane/AOT/water reverse micelles on the DMBQ concentration and the size and the concentration of the water pool.

## 2. Experimental

Materials: All of the reagents were purchased from commercial sources (reagent grade).  $\text{MB}^+$  and DMBQ were purchased from Aldrich and were used as received. Ascorbic acid (AA) and heptane were obtained from Wako Pure Chemicals Industries and were used without further purification. Sodium bis (2-ethylhexyl) sulfosuccinate (aerosol OT, AOT) from Tokyo Chemical Industry was used as received.

Procedures: A  $0.2 \text{ mol dm}^{-3}$  stock solution of AOT was prepared by dissolving the necessary amount of AOT in heptane. Optically clear solutions were obtained by agitation in a sonicating bath. The stock solutions were dried with Molecular sieves 5A, and were filtered just before use. The appropriate amount of stock solution was transferred into a volumetric flask, and an aqueous solution of  $\text{MB}^+$  and AA was added with a microsyringe. The amount of water present in the system is expressed as the molar ratio between water and AOT ( $W_0 = [\text{H}_2\text{O}]/[\text{AOT}]$ ).

Kinetic measurements: The typical kinetic procedures were as follows. The cuvette which contained  $\text{MB}^+$  and AA reverse micellar solution was capped with a rubber septum. Inlet and outlet needles were attached, and nitrogen (99.999%) was bubbled through the solution for at least 10 min. MBH solution in the reverse micelle was prepared by irradiation of  $\text{MB}^+$  and AA solutions in a cuvette with visible light supplied by a 650 W

projector lamp. Upon irradiation, the solution changed from blue to colorless immediately. This indicates that MBH was formed. The cuvette was placed in a cell holder and thermostated. To start the reaction, the appropriate amount of previously deoxygenated DMBQ stock solution in heptane was injected with a microsyringe into the cuvette containing MBH in the reverse micellar system. Reactions were followed spectrophotometrically at 25 °C by monitoring the increase of the absorbance of MB<sup>+</sup> at 655 nm with a Shimadzu MUltiSpec-1500 photodiode-array spectrophotometer. In every case, first-order plots were obtained under the condition of excess DMBQ.

### 3. Results

Figure 1 shows the absorption spectra of MB<sup>+</sup> taken before and after the photoreduction and the spectrum of a mixture of MBH and DMBQ in the reverse micelle system. Figure 1 can be explained by the formation of MBH by photoreduction and reproduction of MB<sup>+</sup> by oxidation with DMBQ. MB<sup>+</sup> was almost quantitatively reproduced by the oxidation.

Figure 2 shows the time dependence of absorption of MB<sup>+</sup> at 655 nm after mixing a MBH solution with DMBQ solutions in a reverse micellar system ( $W_0 = 5$ ). The absorbances at 655 nm increased rapidly and reached a constant value after mixing of the MBH solution with DMBQ solutions of several concentrations.

The rates of formation of MB<sup>+</sup> in the presence of excess DMBQ obeyed pseudo-first-order kinetics (Fig. 3). The apparent first-order rate constants ( $k_{\text{obsd}}$ ) were estimated for several concentrations of DMBQ. The linear relationships between  $k_{\text{obsd}}$  and  $[\text{DMBQ}]_0$  were obtained for different  $W_0$  (Fig. 4). Second-order rate constants ( $k_2$ ) were obtained from slopes of the straight lines shown in Fig. 4 for  $W_0 = 3, 5, 10, 15,$  and  $20$ .

Since we used a large excess of AA as a reducing agent, it is necessary to examine the influence of AA on the rate of the oxidation of MBH. Table 1 shows the  $k_{\text{obsd}}$ -value obtained with various amounts of AA. As can be seen,  $k_{\text{obsd}}$  is independent of the

concentration of AA.

The dependence of  $k_2$  on  $W_0$ , keeping the AOT concentration constant, is shown in Fig. 5. As shown in Fig. 5, the  $k_2$ -value increases as  $W_0$  increases.

The kinetics of the reaction was studied while varying [AOT], keeping the other experimental conditions fixed. Figure 6 shows the  $k_2$ -values as a function of the concentration of the water pool ([WP]) at  $W_0 = 3$  and 10. [WP] is given by

$$[\text{WP}] = \frac{[\text{AOT}]}{n_{\text{agg}}} \quad (1)$$

where [AOT] and  $n_{\text{agg}}$  are the concentration of AOT molecules and the aggregation number. The values of  $n_{\text{agg}}$  for water pools with various sizes were estimated from the data shown by Casado et al. ( $n_{\text{agg}} = 34$  ( $W_0 = 3$ ), 55 ( $W_0 = 5$ ), 120 ( $W_0 = 10$ ), 200 ( $W_0 = 15$ ), and 310 ( $W_0 = 20$ )) [16]. As shown in Fig. 6, the  $k_2$ -values are almost independent of [WP] at  $W_0 = 3$  and  $W_0 = 10$ .

#### 4. Discussion

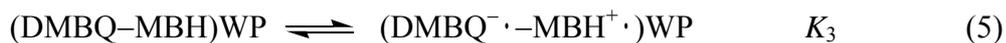
Since  $\text{MB}^+$  and AA are soluble in water and not soluble in heptane, MBH is produced in the water pool. On the other hand, since DMBQ is soluble in heptane and not soluble in water, it is mainly present in heptane.

The initial concentration of  $\text{MB}^+$  is smaller than that of the water pool for the present experimental conditions ( $[\text{MB}^+]_0 = 1.30 \times 10^{-5} \text{ mol dm}^{-3}$  and  $[\text{WP}] = 55.0$  ( $W_0=3$ ), 16.0 ( $W_0=5$ ), 6.1 ( $W_0=10$ ), 3.2 ( $W_0=15$ ), and  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$  ( $W_0=20$ ) are obtained from  $[\text{AOT}]_0 = 0.187 \text{ mol dm}^{-3}$  and the aggregation numbers of AOT molecules for water pools of various sizes shown above. Therefore,  $\text{MB}^+$  (and MBH produced by photoreduction of  $\text{MB}^+$ ) is accommodated singly in the water pool.

Considering these aspects, the reaction between MBH and DMBQ can only occur at the reverse micellar interface. Therefore, in the kinetic model, we considered for DMBQ only the equilibrium partitioning between the organic phase and the reverse micellar interface.

Considering only two pseudophases, the interface and the bulk organic solvent for

DMBQ, and taking into account the DMBQ distribution between these two environments, the following mechanism can be proposed (assuming MBH is located in water pool):



where (MBH)WP denotes the water pool which accommodates MBH,  $K_1$  is the distribution constant for DMBQ between the organic phase and micellar pseudophase. The reaction occurs only in the micellar interior of the water pool, which accommodates both DMBQ and MBH. Reactions (4)-(7) were proposed for the hydride-transfer reaction between DMBQ and MBH in ethanol in a previous study [14]. According to the reaction mechanism proposed, the reactants DMBQ and MBH are in rapid equilibrium with a charge-transfer complex ((DMBQ-MBH)WP) which is also in rapid equilibrium with the radical ion pair (DMBQ<sup>·-</sup>-MBH<sup>·+</sup>) formed by the reversible electron transfer from MBH to DMBQ in the complex (reactions (4) and (5)). This reversible electron transfer is followed by the irreversible proton transfer from MBH<sup>·+</sup> to DMBQ<sup>·-</sup> in the radical ion pair and the subsequent electron transfer to form MB<sup>+</sup> and DMBQH<sup>-</sup> (reactions (6) and (7)).

The rate of the formation of MB<sup>+</sup> can be expressed by (see Appendix)

$$\begin{aligned} \frac{d[\text{MB}^+]}{dt} &= -\frac{d[\text{MBH}]}{dt} = k[(\text{DMBQ}^{\cdot-}-\text{MBH}^{\cdot+})\text{WP}] \\ &= \frac{kK[\text{DMBQ}]_0}{1 + K_1[\text{WP}]_t} [\text{MBH}] \end{aligned} \quad (8)$$

If  $[\text{DMBQ}]_0$  and  $[\text{WP}]_t$   $[\text{MBH}]_0$ , pseudo-first-order behavior for the kinetics of the reaction can be assumed.

As mentioned above, the rate of the formation of MB<sup>+</sup> in the presence of an excess of DMBQ obeyed pseudo-first-order kinetics for  $W_0 = 3, 5, 10, 15$ , and 20 (see Fig. 3). These findings indicate that equation (8) holds for the conditions of present study. The apparent-first-order rate constant ( $k_{\text{obsd}}$ ) is expressed by the following equation:

$$k_{\text{obsd}} = \frac{kK[\text{DMBQ}]_0}{1 + K_1[\text{WP}]_t} \quad (9)$$

As mentioned above, MBH was assumed to be present in the water pool during the reaction. If MBH exudes to organic solvent before or during the reaction, the reaction rate must be dependent on the standing period of MBH solution after the formation of MBH in the reverse micelle. Table 2 shows the  $k_{\text{obsd}}$ -value obtained for various standing periods. As can be seen,  $k_{\text{obsd}}$  is independent of the standing period. This indicates that MBH stays in the water pool at least during the reaction. In order to examine whether MBH exists is only in water phase or not, solvent extraction of MBH from water phase to heptane phase was done. A solution of DMBQ in heptane was added to heptane phase which was shaken with the aqueous solution of MBH produced by photo-reduction of  $\text{MB}^+$ . The color of heptane phase did not change to blue but the water phase became gradually to be blue by this procedure, indicating an appreciable amount of MBH was not transferred from water phase to heptane phase.

As mentioned above, the values of  $k_2$  were obtained from the slopes of the straight lines between  $k_{\text{obsd}}$  and  $[\text{DMBQ}]_0$  shown in Fig. 4. The equation for  $k_2$  is expressed as follows:

$$k_2 = \frac{kK}{1 + K_1[\text{WP}]_t} \quad (10)$$

As mentioned above,  $k_2$  was found to be almost independent of  $[\text{WP}]_t$ , but it increased with increasing  $W_0$ . If  $K_1[\text{WP}]_t \ll 1$ ,  $k_2$  can be changed to

$$k_2 = kK \quad (11)$$

This equation shows that  $k_2$  is independent of  $[\text{WP}]_t$ . This is consistent with the observation shown in Fig. 6. The condition of  $K_1[\text{WP}]_t \ll 1$  shows that the concentration of DMBQ at the reverse micellar interface is low (may be lower than that of MBH in water pool). However, the concentration of DMBQ at the reverse micellar interface must be constant during the disappearance of MBH by the fast distribution equilibrium for DMBQ between the organic phase and micellar pseudophase. Therefore, pseudo-first-order behavior for the kinetics of the disappearance of MBH was observed even under the condition of  $K_1[\text{WP}]_t \ll 1$ .

1.

As mentioned above,  $k_2$  increased with increasing  $W_0$  (Fig. 5). In order to examine the dependence of  $k_2$  on the size of the water pool in detail,  $k_2$  was plotted against the

square of the radius ( $r$ ) of the water pool in Fig. 7 (the values of  $r$  for  $W_0 = 3, 5, 10, 15,$  and  $20$  were obtained from the data in Ref, (15)). As shown in Fig. 7,  $k_2$  is proportional to  $r^2$ . Since  $K_2$  and  $K_3$  are thought to be independent of  $W_0$ , this indicates that the distribution constant ( $K_1$ ) can be assumed to be proportional to the surface area of the water pool (the distribution constant per unit area of the water pool is independent of  $W_0$ ).

## 5. Conclusion

The kinetics of the oxidation of MBH with DMBQ was studied in a heptane/AOT/water reverse micelle. MBH was produced by the photoreduction of  $MB^+$  with AA in water pool. The pseudo-first order rate constant ( $k_{obsd}$ ) for the formation of  $MB^+$  was obtained in the presence of excess of DMBQ. The second-order rate constant ( $k_2$ ) was calculated from the slopes of straight lines between  $k_{obsd}$  and  $[DMBQ]_0$  for various  $W_0$ . The  $k_2$  value increased with increasing  $W_0$ -value. It was found that  $k_2$  is proportional to the square of radius of the water pool. In order to explain the findings, a mechanism involving the distribution of DMBQ between heptane and the interface of the reverse micelle was proposed. The distribution constant of DMBQ was found to be proportional to the surface area of the water pool.

## 6. Appendix

The distribution constant of DMBQ can be expressed by the equation

$$K_1 = \frac{[(DMBQ)WP]}{[DMBQ][WP]} \quad (A-1)$$

A simple mass balance using the distribution constant  $K_1$  and the analytical concentration of DMBQ ( $[DMBQ]_0$ ), allows the calculation of  $[(DMBQ)WP]$  (by assuming that the concentrations of the charge-transfer complex and the radical ion-pair can be neglected):

$$[(DMBQ)WP] = \frac{K_1[WP]_t[DMBQ]_0}{1 + K_1[WP]_t} \quad (A-2)$$

In this equation,  $[WP]$  was assumed to be equal to total concentration of the water pool

(this assumption is valid, if the distribution constant is small). Since MBH is assumed to be accommodated singly in a water pool, the proportion ( $f$ ) of the water pool which accommodates MBH to total water pool can be expressed by

$$f = \frac{[(\text{MBH})\text{WP}]}{[\text{WP}]} = \frac{[\text{MBH}]}{[\text{WP}]_t} \quad (\text{A-3})$$

Therefore, the concentration of the water pool which accommodates both DMBQ and MBH is expressed as follows:

$$\begin{aligned} [(\text{DMBQ}/\text{MBH})\text{WP}] &= f[(\text{DMBQ})\text{WP}] \\ &= \frac{K_1[\text{DMBQ}]_0[\text{MBH}]}{1 + K_1[\text{WP}]_t} \end{aligned} \quad (\text{A-4})$$

The equilibrium constants among the reactants, the charge-transfer complex and the radical ion-pair are expressed by

$$K_2 = \frac{[(\text{DMBQ} - \text{MBH})\text{WP}]}{[(\text{DMBQ}/\text{MBH})\text{WP}]} \quad (\text{A-5})$$

$$K_3 = \frac{[(\text{DMBQ}^{\cdot-} - \text{MBH}^{\cdot+})\text{WP}]}{[(\text{DMBQ} - \text{MBH})\text{WP}]} \quad (\text{A-6})$$

Therefore,  $[(\text{DMBQ}^{\cdot-} - \text{MBH}^{\cdot+})\text{WP}]$  is expressed as follows:

$$\begin{aligned} [(\text{DMBQ}^{\cdot-} - \text{MBH}^{\cdot+})\text{WP}] &= K_2 K_3 [(\text{DMBQ}/\text{MBH})\text{WP}] \\ &= \frac{K_1 K_2 K_3 [\text{DMBQ}]_0 [\text{MBH}]}{1 + K_1 [\text{WP}]_t} \\ &= \frac{K [\text{DMBQ}]_0 [\text{MBH}]}{1 + K_1 [\text{WP}]_t} \end{aligned} \quad (\text{A-7})$$

where  $K = K_1 K_2 K_3$ .

The rate of the formation of  $\text{MB}^+$  becomes

$$\begin{aligned} \frac{d[\text{MB}^+]}{dt} &= - \frac{d[\text{MBH}]}{dt} = k [(\text{DMBQ}^{\cdot-} - \text{MBH}^{\cdot+})\text{WP}] \\ &= \frac{kK [\text{DMBQ}]_0 [\text{MBH}]}{1 + K_1 [\text{WP}]_t} \end{aligned} \quad (\text{A-8})$$

If  $[\text{DMBQ}]_0$   $[\text{MBH}]_0$ , pseudo-first-order behavior for the kinetics of the reaction can be assumed.

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Table 1. Dependence of the concentration of AA on the apparent rate constant for the reaction of MBH with DMBQ in the reverse micelle

$10^4[\text{AA}] / \text{mol dm}^{-3}$	0.61	1.21	1.82	2.42	3.03
$10k_{\text{obsd}} / \text{s}^{-1}$	3.8	3.4	3.7	3.8	4.1

$W_0 = 10, [\text{DMBQ}]_0 = 2.02 \times 10^{-4} \text{ mol dm}^{-3}, [\text{MB}]_0 = 1.31 \times 10^{-5} \text{ mol dm}^{-3}.$

Table 2. Dependence of the standing period of the MBH solution on the apparent rate constant for the reaction of MBH with DMBQ in the reverse micelle

$t / \text{s}$	0	30	60	180	300	400
$10k_{\text{obsd}} / \text{s}^{-1}$	3.2	3.5	3.1	3.2	3.5	3.5

$W_0 = 10, [\text{DMBQ}]_0 = 1.96 \times 10^{-4} \text{ mol dm}^{-3}, [\text{MB}]_0 = 1.44 \times 10^{-5} \text{ mol dm}^{-3}.$

Figure captions

- Fig. 1. Absorption spectra of  $\text{MB}^+$  taken (1) before and (2) after photoreduction, and (3) that of the reaction mixture of MBH and DMBQ in the heptane/AOT/water system.
- Fig. 2 Time dependence of absorbance at 655 nm after mixing MBH solution ( $[\text{MBH}]_0 = 1.30 \times 10^{-5} \text{ mol dm}^{-3}$ ) with DMBQ solutions ( $[\text{DMBQ}]_0 = 1.33$  (1), 1.88 (2), 2.52 (3), 3.13 (4), and  $3.76 \times 10^{-4} \text{ mol dm}^{-3}$  (5)) at  $W_0 = 5$ .
- Fig. 3. Pseudo first-order plots of the reaction of MBH with DMBQ in the heptane/AOT/water system.  $[\text{MBH}]_0 = 1.30 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $[\text{DMBQ}]_0 = 1.33$  ( $\circ$ ), 1.88 ( $\bullet$ ), 2.52 ( $\square$ ), 3.13 ( $\blacktriangle$ ), and  $3.76 \times 10^{-4} \text{ mol dm}^{-3}$  ( $\square$ ) at  $W_0 = 5$ .
- Fig. 4. Plots of  $k_{\text{obsd}}$  vs.  $[\text{DMBQ}]_0$  for the reaction of MBH with DMBQ in heptane/AOT/water system for various  $W_0$  ( $W_0 = 3$  ( $\circ$ ), 5 ( $\bullet$ ), 10 ( $\square$ ), 15 ( $\blacksquare$ ), and 20 ( $\square$ )).
- Fig. 5. Plots of  $k_2$  vs.  $W_0$  for the reaction of MBH with DMBQ in the heptane/AOT/water system.
- Fig. 6. Plots of  $k_2$  vs.  $[\text{WP}]$  for  $W_0 = 3$  (1) and 10 (2) in the reaction of MBH with DMBQ in the heptane/AOT/water system.
- Fig. 7. Plots of  $k_2$  vs. square of the radius of water pool for the reaction of MBH with DMBQ in the heptane/AOT/water system.

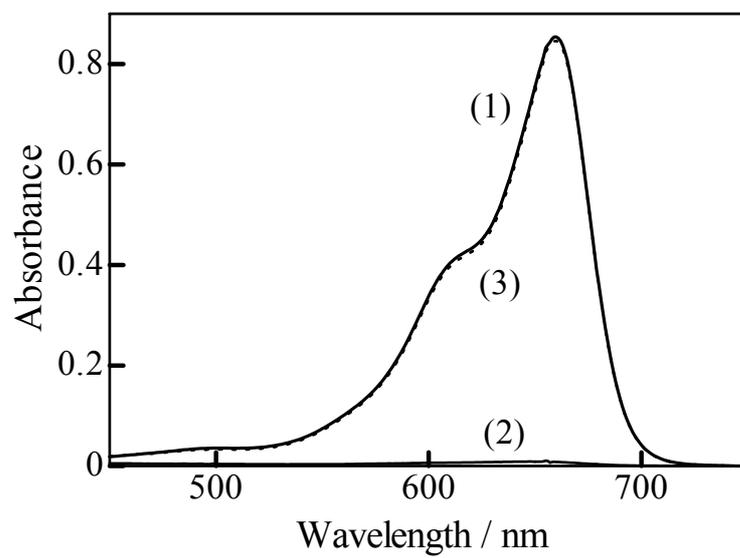


Fig. 1.

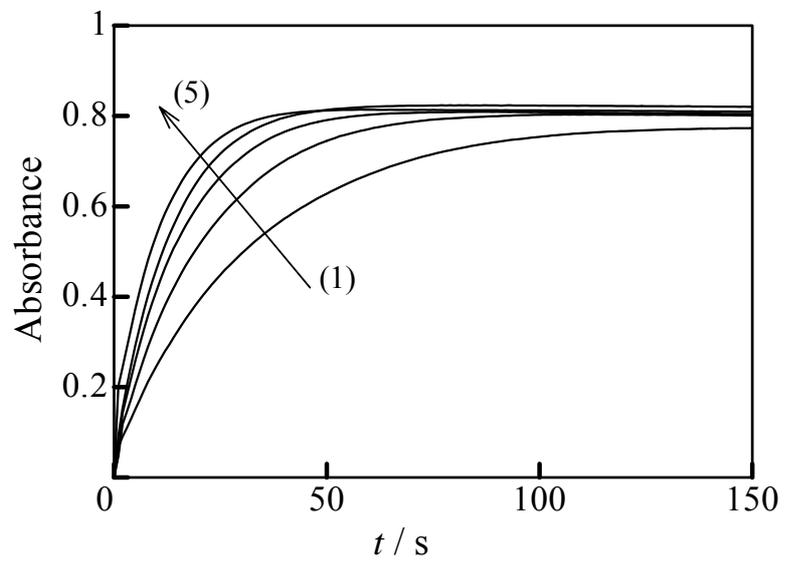


Fig. 2.

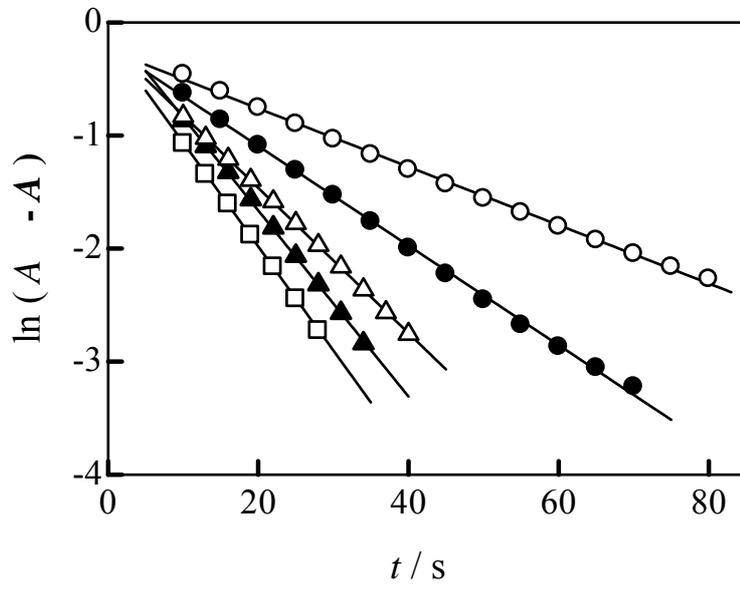


Fig. 3.

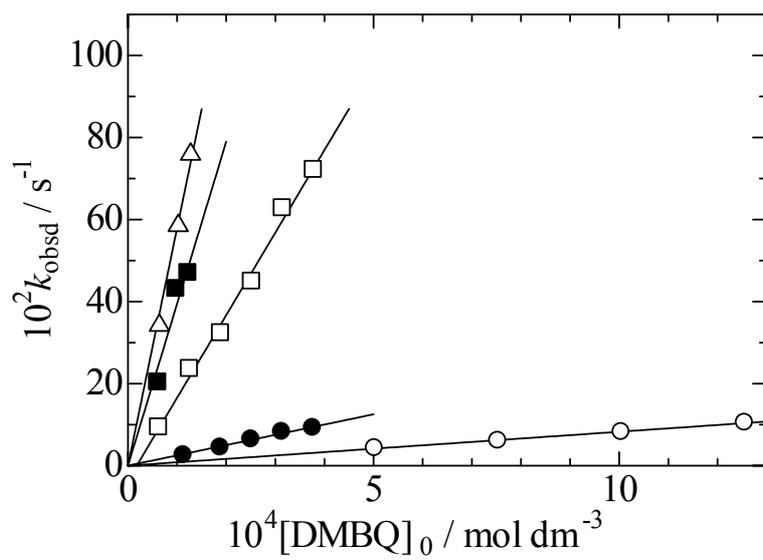


Fig. 4.

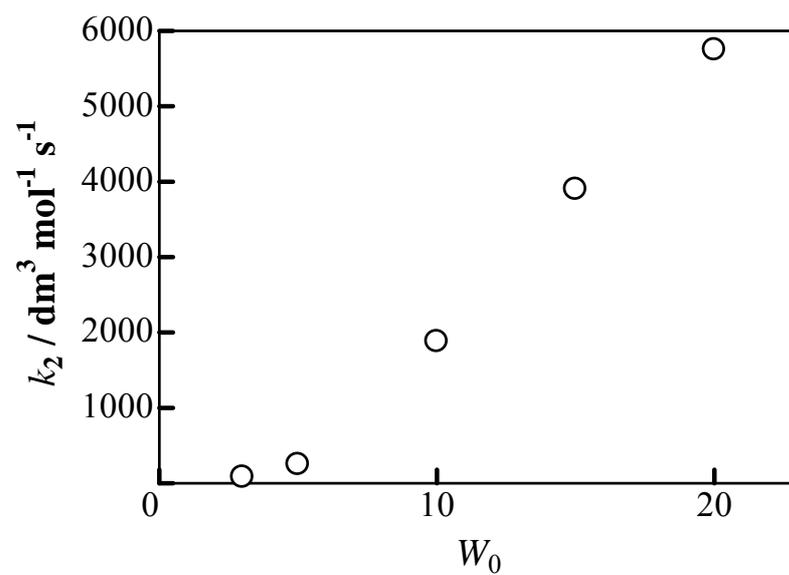


Fig. 5.

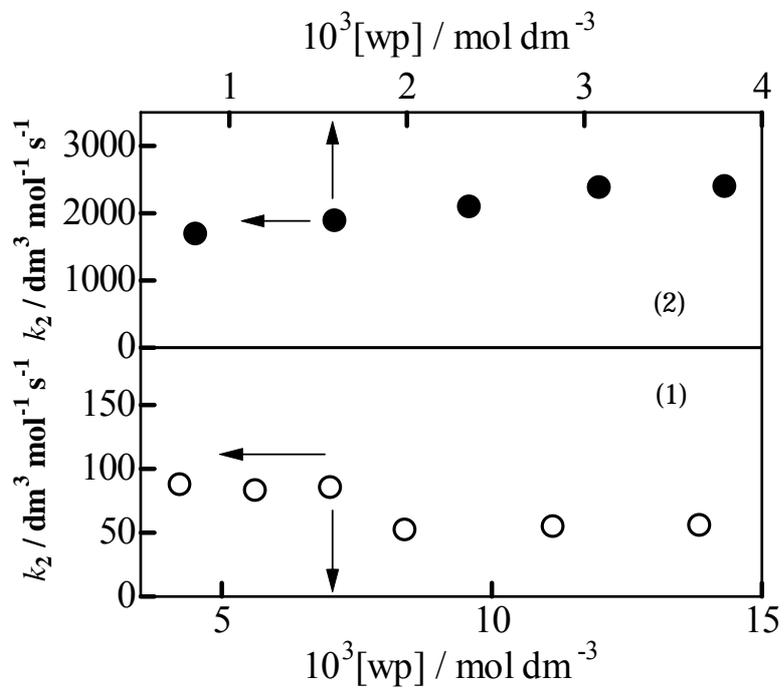


Fig. 6.

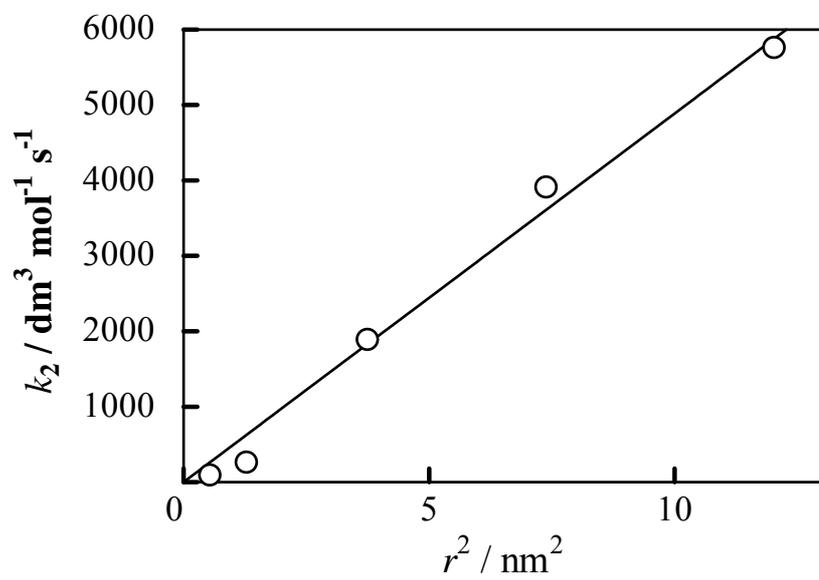


Fig. 7.