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Acid–Base and Monomer–Dimer Equilibria of Methylene Blue in Dip-Coated Thin Films

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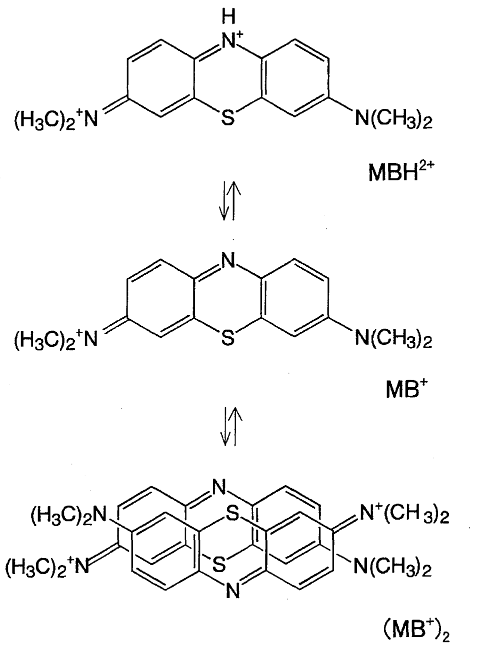
Thin films including Methylene Blue (MB) have been prepared. They were dip-coated using the sol–gel reaction of tetraethyl orthosilicate (TEOS). The absorption spectra of the individual thin films have been observed as a function of time after preparation of the films. The relative contributions of the monomer (MB^+), dimer ($(MB^+)_2$), and protonated species (MBH^{2+}) existing in the individual thin films to the total absorption spectra were obtained. The acidity in each film was estimated from the relative abundance of the MBH^{2+}. In the case of the system including a large amount of HCl as a catalyst, MB formed MBH^{2+} in addition to MB^+ and $(MB^+)_2$ just after preparation of the films. However, MBH^{2+} in every film disappeared 5—10 min after the preparation. The formation of MBH^{2+} indicates the very high acidity around MB molecules. In each film just after the preparation, the rate of the hydrolysis became slower and the concentration of the released proton remarkably increased because the polycondensation rapidly proceeded with the contraction in volume. Although growing –SiOSi– networks prevent the evaporation of the acid together with water and ethanol, the decrease of MBH^{2+} indicates the lowering of acidity in the films due to the evaporation.

The sol–gel method,[1—3] which has enabled us to encapsulate organic dyes in an inorganic solid, is useful to synthesize new organic–inorganic hybrid functional materials for applications such as devices for photonics and photoelectronics.[4,5] The photo-physicochemical properties of the dye molecules which are encapsulated in a solid matrix are influenced by the microchemical environment around the dye. Although the reaction during the sol–gel process consists of only hydrolysis and polycondensation, the changes are very complicated and not well known. In order to design the materials, it is important to clarify the change in the photo-physicochemical properties of the dye with the change in physicochemical environment around dye molecules in the sol–gel reaction system. The electronic spectra are a useful probe for an understanding of the changes.[4—16]

We have previously prepared thin sol–gel films including rhodamine B (RB)[17] which were dip-coated[2,3,18] using the sol–gel reaction of tetraethyl orthosilicate (TEOS) as a function of time after mixing of the reaction systems. The relative contributions of the monomer, H-dimer, and J-dimer of RB existing in the individual thin films to the total absorption and fluorescence spectra of the individual samples were obtained as a function of time after the preparation. In the fluid sol, RB existed as the monomer until the gelation occurred. On the other hand, in the dip-coated films, two types of dimers (H and J types) of RB were associated just after dip-coating until the –SiOSi– networks were almost formed. With the progress of the sol–gel reaction in the fluid sol, dimerization in the prepared film was gradually prevented and the monomer RB became the preferential species. These results indicate that prestructures of the pores including RB molecules were formed long before the gelation point.

A reductive dye, Methylene Blue (MB), is used as a redox indicator and for medicines. MB and the related substances are applicable to areas such as electrochromic materials and sensitizers of a solar cell.[19] MB exists as a monomer (MB^+) in neutral or low acidic solvents and forms a dimer ($(MB^+)_2$) with an increase of the concentration in aqueous solvents.[20—29] In the solutions containing highly concentrated acid, MB forms protonated species (MBH^{2+}).[21a,26d] The molecular forms of three chemical species of MB are illustrated in Scheme 1. MB forms only non-fluorescent H-dimer, whereas RB forms non-fluorescent H-dimer and fluorescent J-dimer. However, the change in the molecular and spectral structure of RB with acidity is very small.[17,30—33] On the other hand, the molecular structure and electronic spectra of MB are drastically changed by the protonation at nitrogen atom in phenothiazine skeleton. The value of pK_a for MB is very small compared with the value for RB. Therefore, MB is useful as a probe of the sol–gel reaction system at a different viewpoint from the case of RB. Although there are some reports on the spectroscopic properties of MB and the related substances adsorbed on the surface of the solid,[19,23,34,35] there are no reports on those doped in the sol–gel reaction system.

In this paper, we report the details of the absorption spectra of MB in dip-coated thin films prepared as a function of time after mixing of the HCl- and H_2SO_4-catalyzed sol–gel reaction systems, in order to clarify the chemical species



Scheme 1. Molecular forms of three chemical species of Methylene Blue (MB).

of MB ($\mathrm{MB^+}$, $(\mathrm{MB^+})_2$, and $\mathrm{MBH^{2+}}$) and the microscopic environment around the dye molecule in the films.

Experimental

Materials. MB, ethanol, TEOS, hydrochloric acid, and sulfuric acid (Wako Chemicals, JIS S grade) were used without further purification. The water was deionized and distilled. Slide glasses for use as the substrate (Matsunami S-1126) were washed with neutral detergents, soaked in 0.1 M ($\mathrm{M = mol\,dm^{-3}}$) aqueous HCl solution for 1 h, washed with water, and finally dried at room temperature.

Sample Preparation. In order to investigate the acidity dependence of the absorption spectra of MB, aqueous HCl solutions were prepared in a concentration range from 1.0×10^{-2} to 2.2 M, in which MB was dissolved at 1.0×10^{-5} M.

MB was dissolved in ethanol at 1.0×10^{-2} M for the sol–gel reaction. The starting solutions of the sol–gel systems contained 10.0 ml of MB in ethanol solution, 10.0 ml of TEOS, and 3.0 ml of a catalyst. The catalysts used were 1 M (System X-1), 0.1 M (System X-01), and 0.01 M (System X-001) aqueous HCl solutions, and 0.083 M aqueous $\mathrm{H_2SO_4}$ solutions (System Y-01). Concentration of $\mathrm{H_2SO_4}$ in the System Y-01 was adjusted to the same acidity as the System X-01. The solutions were stirred during the addition, stirred thoroughly for an additional 30 min, and then poured into individual polypropylene vials (50 ml). The vials were covered with a cap having a hole of 5 mm diameter and kept in a thermostat at 35 °C. The dipping substrates were withdrawn vertically from the sol–gel solution in the vial at a speed of 10 $\mathrm{mm\,min^{-1}}$ at room temperature. The dip-coated thin films were made as a function of reaction time of the prepared solutions. The prepared films were kept at room temperature.

Spectral Measurements. The absorption spectra were observed using a Hitachi U-3210 or a Shimadzu UV-2500PC recording spectrophotometer. The data were transferred to an NEC PC-9801 personal computer and recorded. The spectra were obtained using quartz cells of 1.0, 0.1, and 0.01 cm path lengths. The spectra in highly concentrated solutions were obtained by interposing the solution between two slide glasses. Plastic tape was wound around the two overlapped slide glasses to prevent evaporation of the solvent. The absorption spectra of the prepared thin films were observed as a function of time after the preparation. All spectral measurements were performed at room temperature (25 °C). The spectral data of the dip-coated thin films given in the Figures are the typical results for three to five different experiments.

Results and Discussion

Resolved Absorption Spectra of Three Chemical Species of MB in Aqueous Solvents. There have been some reports on the absorption spectra and the monomer–dimer equilibrium of MB in aqueous solvents.[20—29] However, the acid–base equilibrium of MB is not well investigated[21a,26d] and there is no report on the resolved absorption spectra of the three chemical species of MB. In order to clarify the relationship between the molecular forms and their corresponding absorption spectra in solvents and in the dip-coated thin films, we have investigated the dependence of the spectra on the concentration of MB and the acidity of aqueous solvents.

According to the concentration dependence of absorption spectra of MB in water, the value of the monomer–dimer ($\mathrm{MB^+}$–$(\mathrm{MB^+})_2$) equilibrium constant K_d = 5.81×10^3 $\mathrm{dm^3\,mol^{-1}}$ was obtained. This constant K_d corresponds to the values in the literature.[23,29] These spectra of MB in ethanol are almost independent of the concentration, indicating that MB can not dimerize much in ethanol at room temperature.[20,22]

$\mathrm{MB^+}$ is protonated and transforms to $\mathrm{MBH^{2+}}$ in very highly acidic solution. Hammett's acidity function H_+ is used as the degree of acidity and is defined as follows:[36,37]

$$\mathrm{MBH^{2+}} \overset{K_\mathrm{a}}{\rightleftharpoons} \mathrm{MB^+} + \mathrm{H^+}, \tag{1}$$

$$\mathrm{p}K_\mathrm{a} = H_+ + \log\left([\mathrm{MBH^{2+}}]/[\mathrm{MB^+}]\right), \tag{2}$$

$$\mathrm{p}K_\mathrm{a} = H_+ + \log\{(\varepsilon - \varepsilon_{\mathrm{MB+}})/(\varepsilon_{\mathrm{MBH2+}} - \varepsilon)\}, \tag{3}$$

where K_a is an acid dissociation constant, ε is an apparent molar absorption coefficient of the individual solutions, and $\varepsilon_{\mathrm{MB+}}$ and $\varepsilon_{\mathrm{MBH2+}}$ are actual molar absorption coefficients of $\mathrm{MB^+}$ and $\mathrm{MBH^{2+}}$, respectively. The value of H_+ increases as the degree of acidity decreases. According to ε observed at 745 nm of MB in aqueous HCl solutions in various values of H_+ and Eq. 3, it was estimated that the value of $\mathrm{p}K_\mathrm{a}$ is -0.258 ± 0.003. This value of $\mathrm{p}K_\mathrm{a}$ corresponds to the value in the literature.[26d] The absorption spectra of MB in 5 M aqueous HCl solution were not changed with the dye concentration, indicating that $\mathrm{MBH^{2+}}$ is unlikely to form the dimer $(\mathrm{MBH^{2+}})_2$.[20,21a]

Using the monomer–dimer equilibrium constant K_d = 5.81×10^3 $\mathrm{dm^3\,mol^{-1}}$ and the acid–base equilibrium constant $K_\mathrm{a} = 1.81$ $\mathrm{mol\,dm^{-3}}$ ($\mathrm{p}K_\mathrm{a} = -0.258$), we obtained the resolved absorption spectra of $\mathrm{MB^+}$, $(\mathrm{MB^+})_2$, and $\mathrm{MBH^{2+}}$ in water. The results are shown in Fig. 1. The peak wavelength and molar absorption coefficient of the components are 664 nm and 83400 $\mathrm{dm^3\,cm^{-1}\,mol^{-1}}$ for $\mathrm{MB^+}$, 605 nm and 59500

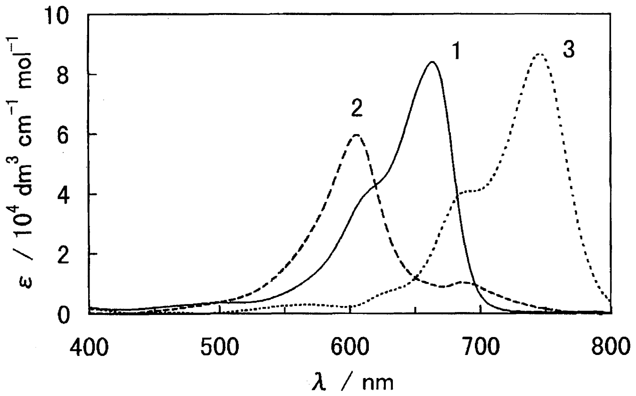


Fig. 1. Resolved absorption spectra for the three chemical species of Methylene Blue (MB) in aqueous solvent. (1) MB^+, (2) $(MB^+)_2$, and (3) MBH^{2+}.

$dm^3\,cm^{-1}\,mol^{-1}$ and 685 nm and 10300 $dm^3\,cm^{-1}\,mol^{-1}$ for $(MB^+)_2$, and 746 nm and 82900 $dm^3\,cm^{-1}\,mol^{-1}$ for MBH^{2+}, respectively. These values for MB^+ and $(MB^+)_2$ correspond to the spectral data in the literature.[21,23,24,27,29] According to the exciton theory,[38] the relative intensity of the dimer spectrum against the monomer's is reasonable, because the transition moment for the dimer (a unit composed of two molecules) is summed from the two constituent monomer transition moments. The resulting average transition moment for each molecule constituting the dimer is nearly equal to that of the monomer.

The resolved absorption spectra of the three chemical species of MB in aqueous solvents can be used in order to estimate those relative abundances in the dip-coated thin films. The relative abundance of MB^+ to that of MBH^{2+} can be the measure of the acidity in the environment around MB using Eq. 2. In applying to the measurement of the acidity in the dip-coated thin film, we assumed that the proportion of MB^+ to MBH^{2+} is not changed with the dye concentration under a certain acidity condition while the amount of $(MB^+)_2$ increases.

Absorption Spectra of MB in the Fluid Sol–Gel Reaction System of TEOS and in Dip-Coated Thin Films (System X-01). Figure 2 shows the absorption spectra of MB (A) in the fluid sol–gel reaction System X-01 along with the progress of the sol–gel reaction until gelation occurred and (B) in the dip-coated thin films withdrawn from the system. The spectra of the individual films were observed just after the preparation. It took 210 h for gelation in this system. It is interesting to clarify the change in the physicochemical environment around MB molecules in the fluid sol–gel reaction system and the dip-coated films. Based on the resolved absorption spectra in aqueous solvents shown in Fig. 1, we estimated the relative abundance of the three chemical species of MB in each film using the Simplex method.[39,40] Figure 3 shows the relative contribution of the three chemical species of MB to the total absorption spectra of (A) the fluid sol–gel reaction System X-01 and (B) the dip-coated thin films withdrawn from the system, corresponding to Figs. 2A and 2B, respectively. The abscissa indicates the reaction time of the sol–gel solution at which the thin films were prepared.

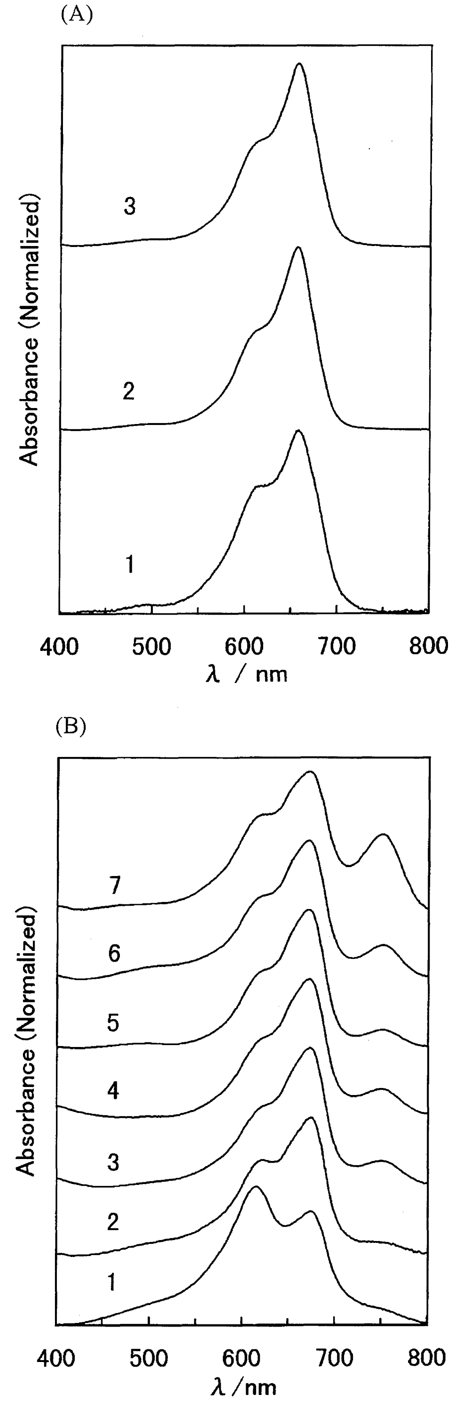


Fig. 2. Absorption spectra of Methylene Blue (A) in the fluid sol–gel reaction System X-01, observed at (1) 2 h, (2) 92 h, and (3) 185 h after start of the sol–gel reaction, and (B) in the dip-coated thin films withdrawn from the system at (1) 2 h, (2) 29 h, (3) 68 h, (4) 92 h, (5) 119 h, (6) 146 h, and (7) 185 h after start of the sol–gel reaction. The spectra of the individual films were observed just after the preparation.

There was a little change in the spectra of the fluid sol–gel system having a peak at 655 nm (Fig. 2A) as well as the spectra in ethanol, where most (73—92%) of MB molecules exists as monomers MB^+ (Fig. 3A), because the sol–gel re-

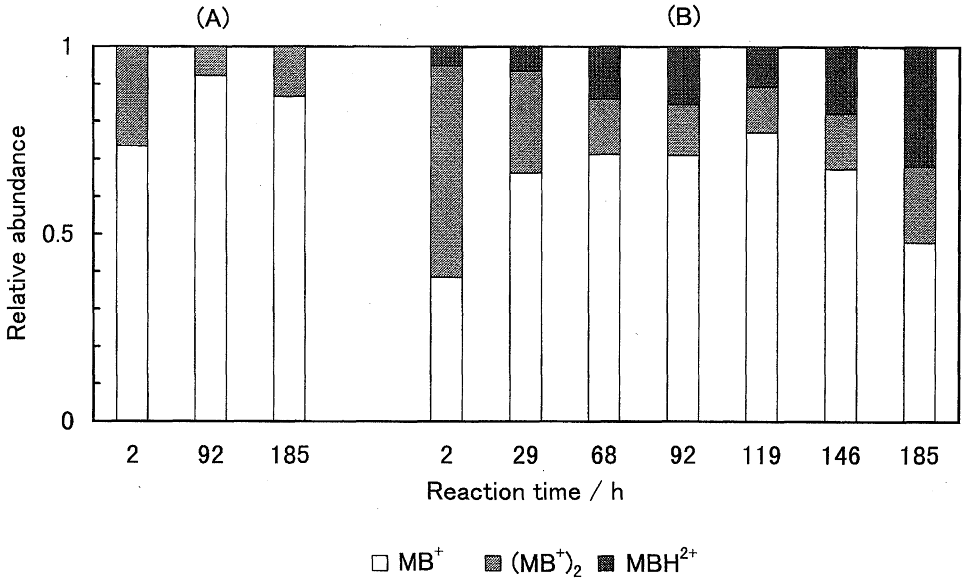


Fig. 3. The relative contribution of the three chemical species of Methylene Blue to the total absorption spectra of (A) the fluid sol–gel reaction System X-01 and (B) the dip-coated thin films withdrawn from the system. The inserted numbers and experimental condition are the same as that shown in Fig. 2.

action system contains a large amount of ethanol as solvent. The change in net-concentration of the dye during sol to gel transition under the present experimental conditions is not very large.[17] Since the existence of MBH^{2+} was hard to observe, the acidity in the matrix during the reaction corresponds to $H_+ > 2.0$ in water based on Eq. 2. The effective pH value of the sol–gel reaction systems was examined by using the absorption spectrum of Thymol Blue ($pK_a = 1.65$ and 9.20 in water, and 5.35 and 15.2 in ethanol).[15,41] Based on the estimated effective pH value, it is concluded that the value does not change much during the whole sol–gel–xerogel transitions. Consequently, the pH change has little influence on the molecular forms of MB ($pK_a = -0.258$ in water) during the present reaction. The same statements are true for using 1 M (System X-1) and 0.01 M (System X-001) aqueous HCl solution as a catalyst. In these systems the gelation occurred at 120 and 190 h, respectively.

The spectrum of the film prepared at the first stage of the sol–gel reaction (prepared at 2 h after mixing of the sol–gel reaction system, Fig. 2B-spectrum 1) contains the absorption bands at around 610—620 nm, 670—680 nm, and 750 nm, which are assigned to $(MB^+)_2$, MB^+, and MBH^{2+}, respectively, according to Fig. 1. These results indicate that $(MB^+)_2$ and MBH^{2+} were formed in the dip-coated film just after the preparation, although MB^+ was the preferential species in fluid sol (Figs. 2A and 3A). The relative abundances of MB^+, $(MB^+)_2$, and MBH^{2+} in the film prepared at 2 h were 38, 57, and 5%, respectively (Fig. 3B). Since the relative abundance of MBH^{2+} to the sum of MB^+ and MBH^{2+} (*RP*) is 12%, the acidity in this film, which can be estimated from Eq. 2, corresponds to $H_+ = 0.62$ in water. These results indicate that the acidity quickly became higher in the film just after preparation, in spite of low acidity ($H_+ > 2.0$) in the fluid sol–gel reaction system.

With the progress of the sol–gel reaction in the fluid system, the relative abundances of MB^+ and MBH^{2+} existing in the prepared film increased until about half time of the gelation point (92 h). The relative abundance of $(MB^+)_2$ decreased during this period. In the film prepared at 92 h, the relative abundances of MB^+, $(MB^+)_2$, and MBH^{2+} were 71, 14, and 15%, respectively. The *RP* is 18% and the acidity in this film corresponds to about $H_+ = 0.40$ in water. The change in relative abundance of MB^+ and $(MB^+)_2$ indicates that separation of MB molecules gradually proceed along with the progress of the polycondensation in the fluid system because of growing –SiOSi– networks around MB molecules. These phenomena are similar to the RB system reported in the preliminary papers.[17] On the other hand, the increase of MBH^{2+} reflects the progress of the hydrolysis reaction of TEOS in the fluid system.[15] The reasons of the increase are discussed later.

As the reaction in the fluid system proceeded further, the amount of MBH^{2+} decreased and then increased, while that of $(MB^+)_2$ was approximately constant. This decrease of MBH^{2+} reflects the progress of the polycondensation reaction of –SiOH and/or –SiOR in the fluid system.[15] The reasons of this decrease and the sequential increase of MBH^{2+} are described later. In the film prepared at 185 h after mixing of the system, the relative abundances of MB^+, $(MB^+)_2$, and MBH^{2+} were 48, 20, and 32%, respectively. The *RP* in this film is 40%, which corresponds to about $H_+ = -0.08$ in water. Although the increase, sequential decrease, and final increase of MBH^{2+} along with the progress of the sol–gel reaction are peculiar, these results have been reproduced in the five experiments.

In order to make clear the effect of HCl on the acidity in the dip-coated thin films, the acidity H_+ in the films prepared as a function of time after mixing of the Systems X-1, X-01, and X-001 are listed in Table 1. The data were obtained just after the preparation of the films. The degree of acidity was

Table 1. The Values Corresponding to Hammett's Acidity Function H_+ in Water Estimated from the Relative Contribution of the Monomer (MB^+) and the Protonated Species (MBH^{2+}) of Methylene Blue to the Total Absorption Spectra, Which Were Observed Just after the Films Were Made

Each film was prepared along with progress of the sol–gel reaction of Systems X-1, X-01, and X-001.

X-1		X-01		X-001	
Reaction time/h	H_+	Reaction time/h	H_+	Reaction time/h	H_+
2	0.32	2	0.62	2	>2.0
12	−0.26	29	0.75	21	>2.0
24	−0.07	68	0.45	57	>2.0
36	0.16	92	0.40	92	>2.0
46	0.11	119	0.60	119	>2.0
71	−0.13	146	0.32	146	>2.0
95	−0.37	185	−0.08	167	>2.0

obviously higher in the films prepared using a larger amount of HCl as a catalyst, although the acidity depends on the reaction time at which the films were prepared.

Change in Acidity of MB in Dip-Coated Thin Films after Preparation of the Films (System X-01). In order to clarify the change in the acidity in the dip-coated films, we observed the change in the absorption spectra of MB in the films along with the elapse of time after the preparation. As shown in Fig. 4, the results of MB in the dip-coated thin film prepared at 200 h after mixing of the System X-01 indicate the decrease of the MBH^{2+} band at around 750 nm. This fresh sol–gel reaction system shown in Fig. 4 was same composition as that in Figs. 2 and 3. It took 240 h for gelation in this system. The relative contribution of MBH^{2+} to the total absorption spectra of the films, which were prepared at 2, 100, and 200 h after mixing of the System X-01, was obtained as a function of time after preparation of the individual films. The results are shown in Fig. 5. In every film, MBH^{2+} was quickly formed just after the preparation (at 0 min) in spite of no MBH^{2+} in the fluid system (Figs. 2A and 3A). The relative abundance of MBH^{2+} decreased and disappeared within 5—10 min in every film, indicating that the acidity in the film became higher just after the preparation and then became lower immediately. In every film, the ratio of the amount of MB^+ to that of $(MB^+)_2$ was not largely changed along with the elapse of time.

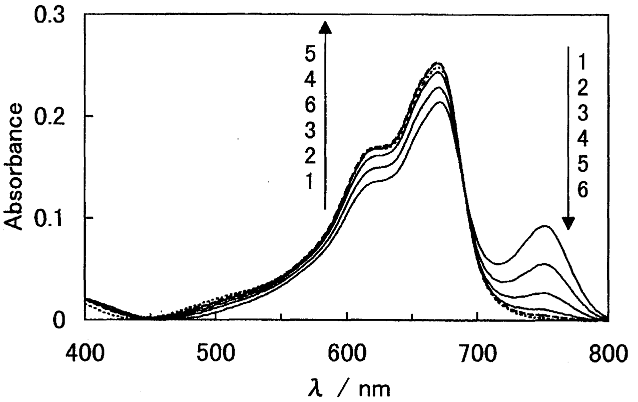


Fig. 4. Absorption spectra of Methylene Blue in the dip-coated thin film prepared at 200 h after mixing of the sol–gel reaction System X-01, observed at (1) 0 min, (2) 2 min, (3) 4 min, (4) 6 min, (5) 8 min, and (6) 13 min after the film was made.

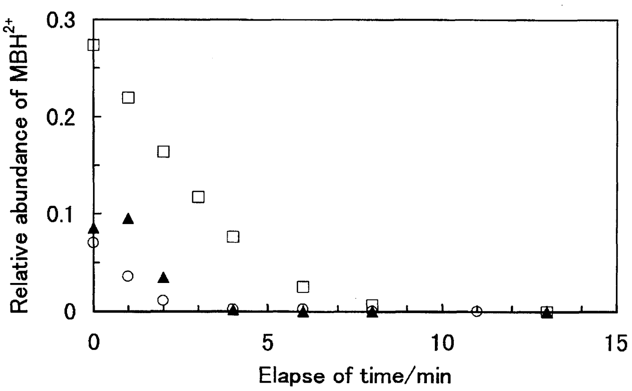


Fig. 5. The relative contribution of the protonated species of Methylene Blue (MBH^{2+}) to the total absorption spectra observed as a function of time after the films were made. Each film was prepared at 2 h (▲), 100 h (○), and 200 h (□) after mixing of the sol–gel reaction System X-01.

The cause for the increase of the acidity is that the rate of the hydrolysis became slower, the polycondensation of –SiOH and/or –SiOR occurred remarkably for a short time and the released proton became large enough to hydrolyze –SiOR. On the other hand, the decreasing of the acidity is due to the evaporation of HCl together with water and ethanol. The acidity in the film just after the preparation would be closely related to the rate of the polycondensation against that of the evaporation of HCl, which reflects the progress of the sol–gel reactions in the fluid system. As the polycondensation becomes faster, the evaporation of HCl becomes slower. The reason is that growing –SiOSi– networks due to the polycondensation prevent the evaporation of HCl together with water and ethanol. In order to investigate the effect of the sol–gel reaction, MB molecules were adsorbed on slide glasses using the same constituent solutions as the Systems X-1, X-01, and X-001 without TEOS. MB did not form MBH^{2+} because the evaporation of HCl merely occurs together with water and ethanol.

The progress of the hydrolysis in the fluid system promotes the polycondensation in the film, and the progress of the polycondensation in the fluid system causes a little polycondensation in the film. Primarily, the hydrolysis becomes

Table 2. Existence Time of the Protonated Species of Methylene Blue (MBH^{2+}) in the Dip-Coated Thin Films Prepared along with Progress of the Sol–Gel Reaction Systems X-01 and Y-01

X-01		Y-01	
Reaction time/h	Existnece time of MBH^{2+}	Reaction time/h	Existence time of MBH^{2+}
2	5—6 min	2	100—110 min
100	7—8 min	85	80—90 min
200	8—10 min	168	10 d

preferential process in the fluid system,[15] so that the rate of the polycondensation becomes faster in the prepared film. Next, the polycondensation becomes preferential process in the fluid system,[15] so that the rate of the polycondensation becomes slower in the prepared film. These phenomena cause the increase and sequential decrease of the amount of MBH^{2+} formed in the film until the middle stage of the sol–gel reaction (at 119 h after mixing of the reaction system), which are seen in Fig. 3B. The increase of MBH^{2+} just before the gelation indicates that the rate of the evaporation became slower because the thickness of the film increased with growing –SiOSi– networks and an increase of the viscosity of the fluid system.

The Case of Using H_2SO_4 as a Catalyst (System Y-01). The thin films were prepared using non-volatile H_2SO_4 as a catalyst in order to compare with volatile HCl. The films were prepared at 2, 85, and 168 h after mixing of the sol–gel reaction System Y-01 until gelation occurred, 180 h in this system. The decrease in the amount of MBH^{2+} were also observed in the prepared films in the same way as the System X-01. Table 2 compares the time at which MBH^{2+} disappeared in the films prepared along with progress of the sol–gel reaction Systems X-01 and Y-01. In every film prepared using the System Y-01, the existence of MBH^{2+} was observed for a longer time compared with the system containing HCl (System X-01). In the film prepared at 168 h, the amount of MBH^{2+} decreased quite slowly and at last it disappeared at 10 d after the preparation.

The existence of MBH^{2+} indicates that a large amount of H_2SO_4 remains in the thin films because of the non-volatility, whereas most HCl in the films evaporates for a short time after preparation of the films. As the sol–gel reaction proceeded, MBH^{2+} persisted for a remarkably long time in the prepared film because the –SiOSi– networks prevent the evaporation of H_2SO_4. In the case of adsorption on slide glasses using the same constituent solutions as the System Y-01 except for absence of TEOS, MB quickly formed MBH^{2+}, but this almost disappeared within 60 min because of the evaporation of H_2SO_4. The reason is that there is no hindrance of the evaporation of H_2SO_4 such as the –SiOSi– networks formed in the sol–gel reaction systems.

Conclusions

In the films made from the sol–gel reaction system including a certain amount of HCl, MB formed MBH^{2+} in addition to MB^+ and $(MB^+)_2$ just after preparation of the films, although MB^+ was the preferential species in the fluid system. The abundance of MBH^{2+} formed in the film increased with the concentration of acid in the system. The acidity in these films corresponds to that in highly concentrated aqueous HCl solutions. However, MBH^{2+} in every film disappeared at 5—10 min after the preparation. In the case of using non-volatile acid H_2SO_4, compared with the case of using volatile acid HCl, more MBH^{2+} was formed and persisted for a long time in the films. In the film just after the preparation, the rate of the hydrolysis became slower and the concentration of the released proton remarkably increased because the polycondensation rapidly proceeded with the contraction in volume. The decrease of MBH^{2+} indicates the lowering of acidity in the films, which is due to the evaporation of acid together with water and ethanol. On the other hand, growing –SiOSi– networks prevent such evaporation.

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