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Journal of Photochemistry and Photobiology A: Chemistry 183 (2006) 53–58
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Chelation of spironaphthoxazine with zinc ions during the sol–gel–xerogel transitions in silicon alkoxide systems

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Received 8 November 2005; received in revised form 13 February 2006; accepted 18 February 2006
Available online 6 March 2006

Abstract

Chelation of spironaphthoxazine (SNO) with zinc ions in the course of the sol–gel–xerogel transitions in the tetraethylorthosilicate (TEOS) systems has been investigated by monitoring the fluorescence and excitation spectra as a function of time. A fluorescence spectrum was observed at around 430 nm, just after the mixing SNO with zinc ions in TEOS, which was similar to that of SNO observed in protic high-polar solvents due to the existence of the considerable amounts of ethanol content in the TEOS systems. The fluorescence maxima were gradually red shifted to around 450 nm with the progress of the sol–gel reaction. This result indicates that SNO (ring-closed form) can interact by hydrogen bonding with SiOH groups generated by the hydrolysis of TEOS. Some of these SNO molecules formed the non-planar zwitterion as the C─O bond was cleaved. A spectrum originating from the zinc complex of the SNO-derivative, merocyanine (MC, ring-open form), also appeared at around 540 nm near the gelation point. This complexation occurred because SNO molecules and zinc ions were concentrated in the prestructural pores and easily interact with each other. The hydrogen-bonding species and the chelate species decreased during the drying process of the wet gel due to growth of the silica networks including zinc along with the condensation of SiOH groups. As the gel converted to the xerogel, the SNO molecules were more strongly adsorbed on the surface of the pores in the xerogel than in the wet gel due to the evaporation of solvent and a contraction of the space. The SNO molecules, therefore, form not only the MC–Zn complex again, but also the MC–SiOH complex. The photochromic behavior including the ring opening and association of the MC–Zn or MC–SiOH complex, and its dissociation and ring-closure were observed by UV and visible light irradiations in the xerogel systems.

Keywords: Chelation; Spironaphthoxazine; Fluorescence; Sol–gel method; Photochromism

1. Introduction

Some organometallic compounds efficiently emit visible light, even if their organic ligands can emit only weak blue fluorescence [1,2]. The metal complexes of organic compounds such as Alq_3 (Al complex of 8-hydroxyquinoline) are used as materials for organic electroluminescence [3–5]. A technique to control the absorption and/or fluorescence spectra of materials can contribute to the development of photo-memory and -switching functions [6–9]. Importantly, here, their spectroscopic properties have to be controlled on a molecular level in order to create the ultimate quantum computer. This technique would be realized by the photo-induced association and dissociation of such metal complexes.

Spirooxazines (SOs), well-known photochromic compounds, exhibit a photo-induced interconversion between the original colorless form and the colored merocyanine (MC) form [7,9]. The MC easily coordinates to specific metal ions (M: e.g., Zn^{2+}) in solution, and forms fluorescent and non-fluorescent MC–M complexes, the former is stable but the latter is unstable to heat and visible light [10,11]. In order to develop the photofunctional materials, a technique enabling reversible interconversion between the SO and MC–M complex by changing the incident-light wavelengths is needed.

We previously reported the details of the fluorescence and excitation spectra of an SO in various solvents [12]. It was found in the study that two types of fluorescent intermediate species are intervened between SO and MC by the cleavage of the spiro

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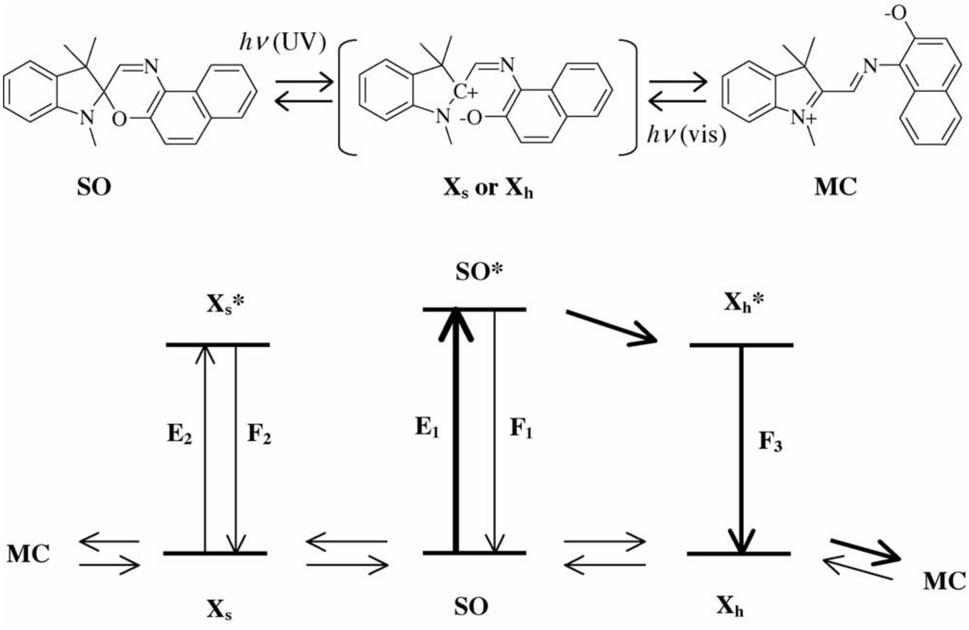
doi:10.1016/j.jphotochem.2006.02.021



Scheme 1. Molecular forms and fluorescence processes of SNO species in solvents.

C–O bond, as shown in Scheme 1. In low-polar solvents such as benzene, upon the excitation (denoted by E1) of SO from the ground state to the excited states (SO^*), the 390 nm fluorescence (F1) was normally emitted from SO^*. In aprotic polar solvents, such as acetonitrile, the SO molecules, in part, are transformed into a non-planar, strongly solvated species (X_s). The transition from species X_s to X_s^* (E2) is followed by a 440 nm fluorescent emission (F2). The structure of X_s or X_s^* is suggested to be a non-planar zwitterion formed by the bond cleavage. However, in protic polar solvents such as ethanol and water, the SO molecules, in part, are excited to SO^* (E1) to produce the hydrogen-bonded species (X_h^*), accompanied by the C–O bond cleavage in the excited states, and to emit the 440 nm fluorescence, leading to X_h (F3). The transient species X_h was immediately transformed into SO or MC in the ground state. The structure of X_s or X_s^* is suggested to be like that of X_h or X_h^*, except the form of interaction with the solvent molecules, resulting in the close values of their spectral peaks.

It is reasonable that the fluorescence peaks of X_s or X_h and MC–M are located at around 440 and 540 nm, respectively, since the iminonaphtholate moiety of the zwitterionic structure and its metal complex participate in the fluorescence emission. The fluorescence of MC–M is stronger than that of X_s or X_h because the metal ion occupies the unshared electron pair on the imine N which quenches the iminonaphtholate fluorescence [11].

The photochromic behavior of SOs in heterogeneous solid systems, e.g., polymers [13–18], self-assembled films [19–22], and clays [23,24], have been well studied by a number of the researches [13–24]. It is of great importance to investigate fluorescent and photoreaction properties of such SO species, including the metal complexes, in solid matrices and on solid surfaces in order to provide new light-emitting materials. In our other study, we observed a fluorescent behavior of photochromic materials, which involved the photo-induced interconversion between SO and the MC–Zn complex in the hydrophobic interlayers of montmorillonite clay modified by organic surfactants [23].

The sol–gel method is utilized for preparing the functional solid materials containing the organic and/or organometallic compounds at low temperature as well as the intercalation into the clay. There are many reports concerning the investigation of the photochromic behavior of SOs in the sol–gel reaction systems [25–30]. The microscopic change in such a system is, however, so complex, in which the physicochemical properties are investigated by in situ spectroscopic measurements using a molecular probe [31–37]. In present study, the silicon alkoxide systems including spironaphthoxazine (SNO) and Zn^{2+} were prepared in order to examine a possible chelation between the species. The changes in the fluorescence properties of SNO were observed during the sol–gel–xerogel transitions of the systems. We investigated the influence of the physicochemical properties, such as polarity and proton affinity, in the silicon alkoxide systems on the isomerization and Zn chelation by SNO. The present paper also describes the photochromic phenomena observed by UV and visible light irradiations of the xerogel systems.

2. Experimental

SNO was synthesized and purified according to a procedure described elsewhere [38]. Ethanol (S-grade), tetraethylorthosilicate (TEOS) (S-grade), zinc chloride (S-grade), and 5.0 mol dm^{-3} hydrochloric acid (for volumetric analysis), purchased from Wako Pure Chemicals, were used without further purification. Deionized and distilled water was used for preparing the solutions.

The sol–gel reaction systems of TEOS were prepared in the following compositions: the systems consisted of 0.50 cm^3 of an SNO ethanol solution (1.0×10^{-3} mol dm^{-3}), 9.50 cm^3 of a zinc chloride ethanol solution (0, 5.26×10^{-5}, 5.26×10^{-4}, or 5.26×10^{-3} mol dm^{-3}), 10.0 cm^3 of TEOS, and 3.30 cm^3 of hydrochloric acid (1.0×10^{-5} mol dm^{-3}). Since the molar ratios of SNO to Zn included in these solutions are 1/0, 1/1, 1/10, and 1/100, they are abbreviated as systems Z0, Z1, Z10, and Z100, respectively. Each solution was stirred for 5 min using a magnetic stirrer. The fluorescence and excitation spectra were measured as a function of the time along with the sol–gel–xerogel transitions using a Shimadzu RF-5300PC fluorescence spectrophotometer. After the xerogel formation of the samples, the changes in the fluorescence spectra by UV (350 ± 10 nm) and visible (450 ± 10 nm) light irradiations were observed to study the photochromic behavior.

3. Results and discussion

3.1. Measurements of fluorescence and excitation spectra as a function of reaction time

Fig. 1 shows the fluorescence and excitation spectra for system Z100 observed during the sol–gel–xerogel transitions. The excitation wavelengths for the fluorescence spectra (λ_{ex}) are 370 and 450 nm and the emission wavelength for the excitation spectra (λ_{em}) is 500 nm. Immediately after the sample preparation (on day 0), the fluorescence ((a)-1) and excitation ((c)-1) spectra are located at around 430 and 350 nm, respectively, which are similar to those of SNO in ethanol. Therefore, the fluorescence is concluded to be assigned to the hydrogen-bonded species X_h^* [12]. In the course of the hydrolysis of the silicon alkoxides, the fluorescence peak was red shifted because of an increase in the amount of the SiOH groups [32,33,37]. The gelation of this system occurred on the 5th day, when the bands assigned to the MC–Zn complex appeared at around 540 and 460 nm in the fluorescence ((a)-2, (b)-2) and excitation ((c)-2) spectra, respectively [27,30]. As the reaction further proceeded, the intensity of the complex bands decreased with the progress of the evaporation of the solvents in the gel pores ((a)-3, (b)-3, and (c)-3), and the bands of the species strongly encapsulated by the sol–gel matrix, like a solvated species X_s^*, appeared ((c)-4) [12] because the dehydrated condensation of the SiOH groups proceeded to form the –SiOSi– networks, accompanied by weakening these hydrogen bonding. These results reflect the fact that the band at around 370–380 nm appeared in the excitation spectra instead of the X_h^* band ((c)-4). After 20 days, the intensity of the 540 nm band ((b)-4) increased and the peak was blue shifted to 530 nm ((b)-7) with the lapse of reaction time. The assignment of this band will be described later.

The spectral changes in system Z0 are shown in Fig. 2. The λ_{ex} are 370 and 450 nm, and the λ_{em} are 420 and 500 nm. The spectral characteristics were similar to those of the system with Zn, but the following points were newly noted: in this system, no complex band was found around the gelation time because no Zn was present. However, after 300 days, the complex-like bands appeared in the fluorescence spectrum (around 520–530 nm) obtained by the 450 nm light-excitation ((a)-6) and the excitation spectrum (around 450 nm) observed at 500 nm ((b)-6).

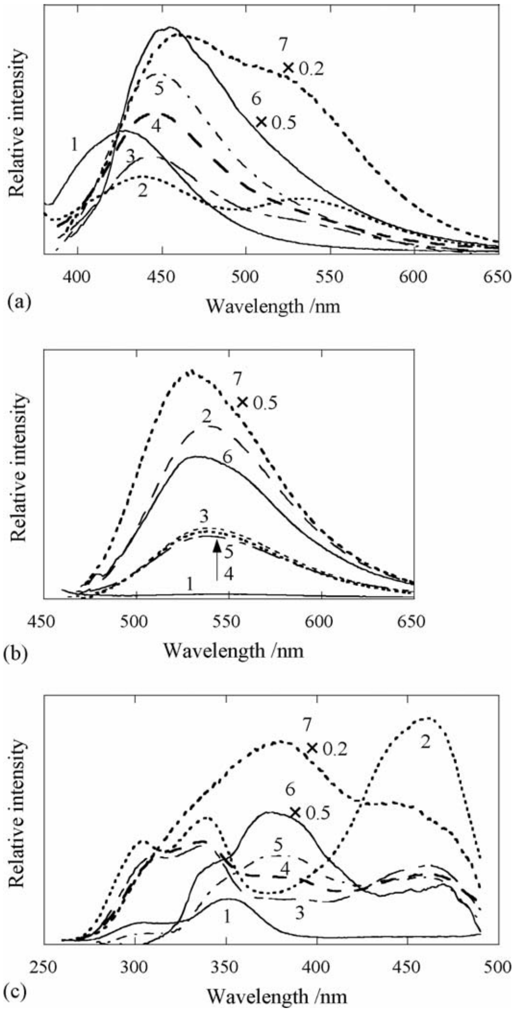


Fig. 1. Changes in (a and b) fluorescence and (c) excitation spectra for system Z100 during the sol–gel–xerogel transitions. These spectra were observed (1) just after and (2) 5, (3) 13, (4) 20, (5) 30, (6) 69, and (7) 300 days after the sample preparation. The fluorescence spectra were observed upon excitation at (a) 370 and (b) 450 nm. The excitation spectra were observed at 500 nm.

These spectra were assigned to the MC–SiOH complex like the MC–M because there are many SiOH groups on the surface of the gel pores in which the organic molecules are encapsulated [25,27,30,37].

Fig. 3 shows the dependences of the Zn content on the fluorescence spectra observed at the gelation point (on 5th day) and after the formation of the xerogel (on 300th day). The intensities of the complex band at around 530–540 nm are higher in the systems including a larger amount of Zn in the both the gel and xerogel states. This band observed at the gelation point may be assigned to the one attributable to the MC–Zn complex, while the formation of the MC–SiOH complex is unlikely, judging from the absence of the band in the system Z0 ((a)-1). On the other hand, both MC–Zn and MC–SiOH complexes are formed in the xerogel including Zn^{2+} ((b)-2, -3, and -4). According to the Zn-content dependence of the spectra observed in the xerogel, the MC induced from SNO interacts with Zn more preferentially than the SiOH groups.

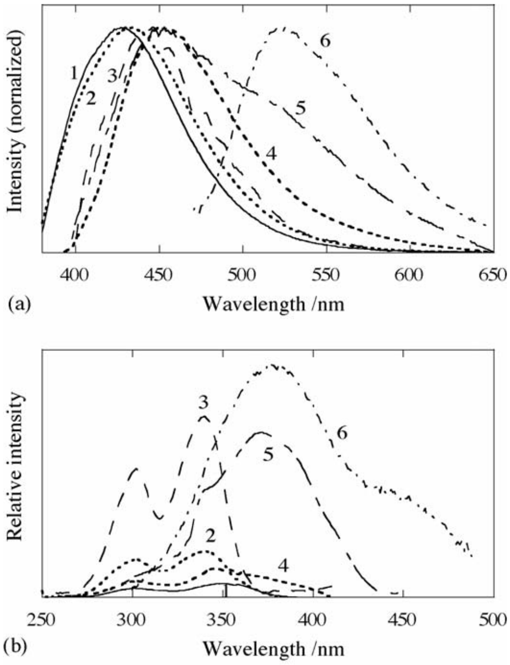


Fig. 2. Changes in (a) fluorescence and (b) excitation spectra for system Z0 during the sol–gel–xerogel transitions. The fluorescence spectra were observed upon excitation at (1–5) 370 and (6) 450 nm, (1) just after and (2) 5, (3) 20, (4) 69, and (5 and 6) 300 days after the preparation. The excitation spectra were observed at (1–4) 420 and (5 and 6) 500 nm, (1) just after and (2) 5, (3) 20, (4 and 5) 69, and (6) 300 days after the preparation.

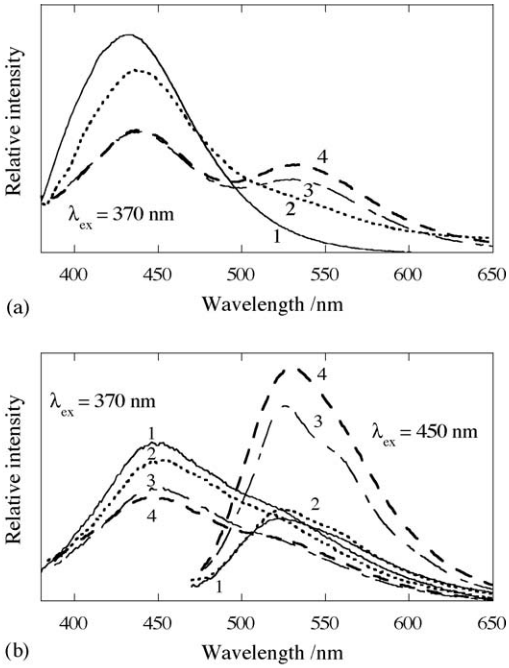


Fig. 3. Zn-content dependences of fluorescence spectra for TEOS systems (1) Z0, (2) Z1, (3) Z10, and (4) Z100 observed (a) at gelation point (5 days after) and (b) after formation of xerogel (300 days after). The spectra were observed upon excitation at 370 and 450 nm.

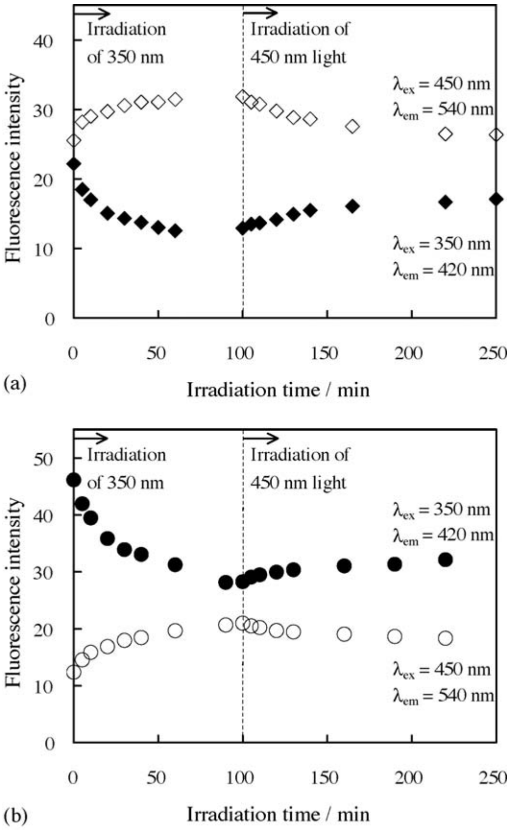


Fig. 4. Changes in fluorescence intensities of X_s and MC–Zn/MC–SiOH complexes in systems (a) Z100 and (b) Z0 during the UV or visible light irradiation.

3.2. Observation of spectral changes by light irradiation

The changes in the fluorescence spectra by UV and visible light irradiation were studied in order to examine the influence of Zn on the photochromic behavior in the xerogel samples. The results for systems Z100 and Z0 are shown in Fig. 4, where λ_{ex} is 350 and 450 nm, λ_{em} is 420 and 540 nm.

The changes in the fluorescence intensities of X_s ($\lambda_{ex} = 350$ nm, $\lambda_{em} = 420$ nm) and MC–Zn and/or MC–SiOH ($\lambda_{ex} = 450$ nm, $\lambda_{em} = 540$ nm) were plotted versus the irradiation time of 350 and 450 nm lights. As a result, the intensity of SNO decreased and that of the complex increased with an increase in the irradiation time of the 350 nm light, and the reverse process occurred with the 450 nm light irradiation. This behavior was seen in all our systems. The photo-induced interconversion between X_s and the MC–Zn/MC–SiOH complexes can be observed in these xerogel systems. However, this reversible reaction did not occur in the sol or wet gel.

It can be assumed that the interconversion between X_s and MC, regarded as the ring-opening and -closure reactions of SNO in this case, are the rate-determining steps of the chelation of SNO with Zn^{2+} during the UV and visible light irradiations, because the formation of the MC–Zn complex in solvents and the sol–gel matrices was found to be a quasi first-order reaction in previous studies [10,26,27,29]. Based on this assumption, the changes in the fluorescence intensities of X_s and the MC–Zn/MC–SiOH complexes were investigated against the

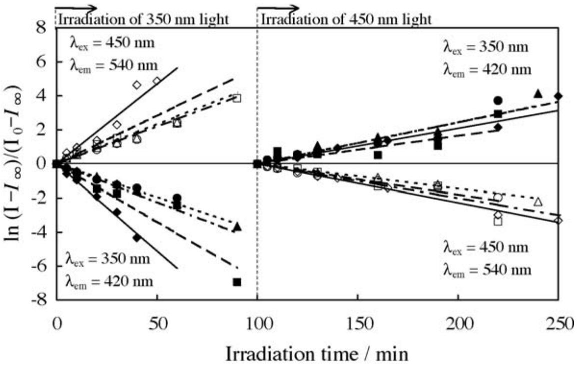


Fig. 5. First-order rate plots of changes in fluorescence intensities (I) of X_s and MC–Zn/MC–SiOH complexes for systems Z0, Z1, Z10, and Z100 during UV and visible light irradiations. The fluorescence data for X_s species in systems Z0 (●), Z1, (▲), Z10 (■), and Z100 (◆) were obtained by excitation at 350 nm and observation at 420 nm. The fluorescence data for the MC-Zn and/or MC-SiOH complex in systems Z0 (○), Z1, (△), Z10 (□), and Z100 (◇) were obtained by excitation at 450 nm and observation at 540 nm. I_0 and I_∞ are the fluorescence intensities at 0 and ∞ min, respectively.

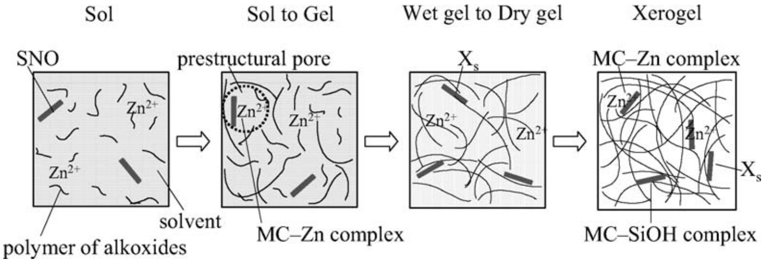
Table 1
Rate constants of formation and consumption of X_s and MC–Zn/MC–SiOH complexes in TEOS systems during light irradiation at 350 and 450 nm

SO/Zn	Rate constant (min^{-1})	
	350 nm irradiation	450 nm irradiation
X_s (λ_{ex} = 350 nm, λ_{em} = 420 nm)		
1/0	−0.045	0.024
1/1	−0.039	0.024
1/10	−0.068	0.016
1/100	−0.102	0.021
MC–Zn and/or MC–SiOH (λ_{ex} = 450 nm, λ_{em} = 540 nm)		
1/0	0.044	−0.020
1/1	0.047	−0.014
1/10	0.057	−0.018
1/100	0.094	−0.023

irradiation time of the UV and visible lights. The logarithmic plots of these values were confirmed to obey first-order kinetics, as shown in Fig. 5. The resulting apparent-rate constants of X_s and the MC–Zn/MC–SiOH are summarized in Table 1. The positive and negative slopes denote the formation and the consumption rates of these species, respectively. The absolute values of the formation and the consumption rates for each light irradiation are not significantly different. The rate constants of the X_s consumption and the MC–Zn/MC–SiOH formation by 350 nm light irradiation tend to increase with increasing in Zn content. The typical values are ca. 0.04 min^{-1} and ca. 0.10 min^{-1} for systems Z0 and Z100, respectively. On the other hand, the rate constants of the reverse processes by 450 nm light irradiation do not significantly depend on the Zn content, the values of which are scattered within 0.014–0.024 min^{-1}. These results indicate that Zn^{2+} tends to promote the ring-opening reaction and thus to accelerate the formation of the MC–Zn complex, whereas the reverse reaction is hardly affected by the Zn^{2+}. The apparent-rate constants of the ring-opening reaction, therefore, can be comparable among the four systems.

3.3. Schematic model of chelation of SNO with zinc ions during the sol–gel–xerogel transition

Scheme 2 shows a model of the chelation of SNO with Zn^{2+} during the sol–gel–xerogel transitions [37,39,40]. In the sol state, SNO and Zn^{2+} are similarly dispersed in the solvents. In the course of the sol–gel transition, polymerization of the silicon alkoxides was accelerated to form the prestructural pores of the sol matrices. Since SNO and Zn^{2+} are encapsulated with solvent and concentrated in such spaces, they are favorable for the formation of the MC–Zn complex. As the solvent evaporated and at the same time the amounts of the SiOH groups decreased with the progress of the polymerization, the MC–Zn complex was dissociated into SNO (X_s) and Zn^{2+} in the pores of the gel matrices. This is because SNO was adsorbed on the pore surface and Zn^{2+} was thought to be cross-linked in the silica networks by isomorphous replacement of Si by Zn. During the dry gel to xerogel transition, the MC–Zn complex was formed again by the concentration in the decreased pore volume. The MC–SiOH complex was also formed in the TEOS systems regardless of the presence or the absence of Zn^{2+}. The cross-linked Zn^{2+} especially plays an important role in the reversible photochromic reaction. The electrophilicity of Zn^{2+} is weakened by the incorporation in silica network. The Zn^{2+} is thought to appropriately interact with the excited species $X_s{}^*$, promotes the ring-opening reaction to produce MC, and then forms the complex with the resulting MC. Furthermore, the dissociation of the complex and the ring-closure reaction of the resulting MC also can proceed during the visible light irradiation and hardly depend on the Zn content. This is because X_s or MC interacts with the cross-linked Zn^{2+} more weakly than Zn^{2+} dissolved in a solvent, which exhibits the uncontrollable chelation. It is suggested that the activate energy for the ring-closure reaction is enough low and independent of the Zn content because the chelate bond is enough weak.



Scheme 2. Illustration of changes in configurational relationships among SNO, Zn and –SiOSi– polymers during the sol–gel–xerogel transitions in the TEOS systems.

4. Conclusions

Just after preparation of the sol–gel reaction systems, SNO and Zn^{2+} were homogeneously dispersed in the systems and the fluorescence originated from the hydrogen-bonded species (X_h^*) similar to that in ethanol. The fluorescence peak was red shifted with the progress of the hydrolysis of the silicon alkoxides due to the increases in the amount of the SiOH groups and in the proton-donating ability of the system. As the polymers of the silicon alkoxides grew to some extent, SNO and Zn^{2+} were encapsulated with solvent molecules in the prestructural pores near the gelation time. A grater amount of the MC–Zn complex was formed in the system that included a larger amount of Zn. The species X_s was gradually formed after the gelation time due to the decrease in the proton-donating ability of the pore surface during the polymerization of the SiOH groups. The MC–Zn complex was dissociated into SNO (X_s) and Zn^{2+} during the drying process of the wet gel because SNO was absorbed on the pore surface and Zn^{2+} was cross-linked to the silica networks during the evaporation of the solvent. During the dry gel to xerogel transition, both the MC–Zn complex and the MC–SiOH complex were formed because of contraction in volume of the pore in the systems. Furthermore, a photo-induced interconversion between the X_s and the MC–Zn or MC–SiOH complex was observed by UV and visible light irradiations in the xerogel systems, whereas it was difficult to control in the solvents.

Acknowledgment

This work was supported by a grant-in-aid from the Foundation of Nagano Prefecture for Promoting Science.

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