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Fluorescence Spectra of 1-Naphthol During the Sol-Gel Process of a Mixed Aluminum-Silicon Alkoxide (Si : Al=94 : 6)

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The fluorescence and fluorescence-excitation spectra of 1-naphthol during sol to gel to xerogel transitions of a mixed solution comprising silicon and aluminum alkoxides (Si : Al=94 : 6) catalyzed by a small amount of NaOH aqueous solution have been observed as a function of time. During the reaction of the system, the spectrum shifted to the red in the first stage and shifted to the blue in the next stage. This behavior reflects the changes of polarity and microviscosity of the matrix surrounding the doped 1-naphthol molecules during the sol to gel to xerogel transitions of the mixed metal alkoxide. The gelation occurred at 10 d. On the other hand, the most remarkable red-shift in the fluorescence spectrum was observed at 9 d. Comparing the fluorescence and fluorescence-excitation spectra of 1-naphthol in typical solvents with those of the sol-gel process, it has become apparent that a part of the doped 1-naphthol molecules in the ground state form a contact ion pair on the surface in cages of the prepared gel.

The application of the sol–gel process as a synthesis technique is a potential method for creating functionalized materials such as glasses, ceramic powders, films, and fibers.[1–10] The sol–gel method offers a low-temperature synthesis technique for the encapsulation of luminescent organic molecules in inorganic matrices on a molecular level.[11–31] Such organic molecules exhibit poor thermal stability and cannot be incorporated into traditional inorganic hosts materials. Therefore, the process is also a potential method for new applications to solid-state laser,[12,16,18,23,24,29] solar light guides,[17] and photodevices using photochromism[14,20,22,25] or photochemical hole burning.[15,19]

Although composite materials comprising inorganic matrices and organic luminescent molecules have been synthesized, little is known about the structural, chemical, and physical properties of the sol–gel matrices surrounding doped luminescent molecules on the molecular level, or the chemical nature of the interaction between the encapsulated luminescent molecules and the solid host matrix. The chemical and physical properties of the matrix during the first reaction stage or wet-gel stage are not especially revealed. Pyrene and other compounds have become useful fluorescence probes used in the sol–gel process.[13,21,26–28,30,31] Mackenzie has pointed out that the most serious problem in any application of the sol–gel process is the present lack of a scientific understanding of the many complexities associated with the process.[7]

Recently, Shizuka et al. studied the fluorescence spectra of the 1-naphthol–aliphatic amine hydrogen-bonded system in nonpolar rigid matrices at 77 K.[32] By means of nanosecond time-resolved emission spectroscopy, they have revealed that the total fluorescence spectra of 1-naphthol can be resolved into a two-component spectra ascribable to contact ion-pair species (e.g. $\sigma^{\max}=25300\ \mathrm{cm}^{-1}$ ($\lambda^{\max}=395$ nm)) and separated ion pairs (e.g. $\sigma^{\max}=23800\ \mathrm{cm}^{-1}$ ($\lambda^{\max}=419$ nm)). In our preceding papers we showed that observing the fluorescence spectra of 1-naphthol is a useful photophysical probe on a molecular level for studying the sol–gel process of tetraethyl orthosilicate ($Si(OC_2H_5)_4$, TEOS).[30] We report here on the use of the multiple fluorescent molecule, 1-naphthol, as a photophysical probe for investigating structural development, changes in the polar character, and changes in the microviscosity of the surrounding matrices around the doped photoprobe molecules, along with the sol to gel to xerogel transitions of an aluminum–silicon alkoxide (Si : Al=ca. 94 : 6) by NaOH catalyst. The fluorescence and fluorescence-excitation spectra were observed as a function of the excitation wavenumbers and monitored wavenumbers, respectively. The use of a NaOH catalyst for the sol–gel reaction of pure TEOS frequently results in the formation of opaque and white gels, which are unsuitable for spectroscopic measurements. In the present composite system, the prepared gels were transparent. The results are compared with the fluorescence spectra of 1-naphthol in typical solvents and during the sol to gel to xerogel transitions of a mixed alkoxide composed of Si : Al=90 : 10 system catalyzed by HCl,[33] in which system the gelation occurred at 4 d and the most remarkable red shift in the fluorescence spectrum was observed at 7 d. In addition to this, the ground- and excited-state species during the sol to gel to xerogel transitions will be discussed based on the experimental results.

Experimental

1-Naphthol (Wako, JIS S grade) was purified by repeated recrystallizations from ethanol, and then sublimed in vacuo. Cyclohexane, ethanol, acetic acid, TEOS, HCl, and NaOH were purchased from Wako and diisobuthoxyaluminium triethyl silicate ($(OBu^i)_2Al–O–Si(OEt)_3$), SAE) from Dynamit

Nobel, and were used without further purification. Water was deionized and distilled.

1-Naphthol was dissolved in ethanol at 2.24×10^{-4} M (1 M=1 mol dm^{-3}). The starting solution of the reaction system contained 2.55 ml of 1-naphthol in an ethanol solution, 0.9396 g of TEOS, 0.1074 g of SAE, and one drop of 1.0 M NaOH-aqueous solution as the catalyst. Therefore, the Si-to-Al ratio in the sample was ca. 94 : 6. The mixture was thoroughly stirred for 5 min and then poured into a plastic cell. This cell was covered by a thin polymer film with several pinholes and allowed to undergo a sol to gel to xerogel reaction at room temperature under dark conditions. We defined the gelation of the sample by the absence of fluidity in the solution-containing cell.[6,10,34,35] The gel, thus obtained, was transparent. The emission spectra were observed using a Shimadzu RF-5000 fluorescence spectrophotometer by the surface-emission method at room temperature. The measurement of the sample weight was carried out using a Sartorius R-200D semimicrobalance.

Results and Discussion

Fluorescence and Fluorescence-Excitation Spectra of 1-Naphthol in Typical Solvents. In order to clarify the ground- and excited-state species and characterize their fluorescence spectra of 1-naphthol during the sol to gel to xerogel transitions of the reaction system, the fluorescence and fluorescence-excitation spectra of 1-naphthol in some typical solvents have been observed from the stand point of the elucidation of the relation of chemical species between in the ground and excited states. The results of the nanosecond time-resolved emission of 1-naphthol in nonpolar rigid matrices[32] also indicate that the ground- and excited-state species of 1-naphthol are still not fully explained.

Figure 1 shows the fluorescence spectrum of 1-naphthol in cyclohexane, ethanol, 0.35 M acetic acid, H_2O, and 0.1 M NaOH aqueous solutions, respectively. There was no excitation wavelength dependence in these spectra. The spectrum observed in cyclohexane shows a vibrational fine structure and is located at higher wavenumber regions. 1-Naphthol shows a broad, less structured fluorescence spectrum in ethanol, and its peak wavenumber is located at around 27900 cm^{-1}. On the other hand, the fluorescence spectrum observed in 0.35 M acetic acid shows two broad, structureless fluorescence bands; their peak wavenumbers are observed at 26200 and 21500 cm^{-1}, respectively. The fluorescence spectrum observed in H_2O (line 4) has almost the same spectral features as that observed in a 0.1 M NaOH aqueous solution (line 5). The fluorescence spectra observed in H_2O and a 0.1 M NaOH aqueous solution show a broad, structureless band; its peak is located at 21200 cm^{-1}. Although the spectra observed in 0.1 M HCl and 1% NH_3 are not shown in Fig. 1, the spectral features of the spectra can be summarized as follows. The spectrum observed in 0.1 M HCl shows two broad, structureless bands which have similar features and spectral positions as those observed in a 0.35 M acetic acid solution. The spectrum observed in 1% NH_3 shows one broad, structureless band which resembles those observed in H_2O and a 0.1 M NaOH solution.

The fluorescence-excitation spectra of 1-naphthol in cyclohexane, ethanol, 0.35 M acetic acid, H_2O, and 0.1 M NaOH solutions are shown in Fig. 2. There was no emission wavelength dependence in the individual spectra. They comprise two characteristic spectra: One is observed in cyclohexane, and the other is observed in a 0.1 M NaOH aqueous solution. The spectrum observed in cyclohexane is assigned to the absorption spectrum of

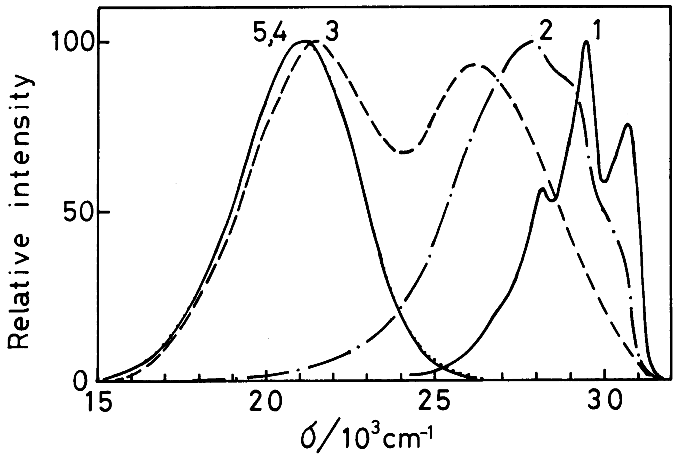

Fig. 1. Fluorescence spectra of 1-naphthol in (1) cyclohexane (—), (2) ethanol (—·), (3) 0.35 M acetic acid (- - -), (4) H_2O (·····), and (5) 0.1 M NaOH (—). It is noted that spectrum (5) agrees very closely with that of spectrum (4). Excitation wavenumber: 33670 cm^{-1} (297 nm) for (1), (2), (3), and (4) and 28990 cm^{-1} (345 nm) for (5), respectively.

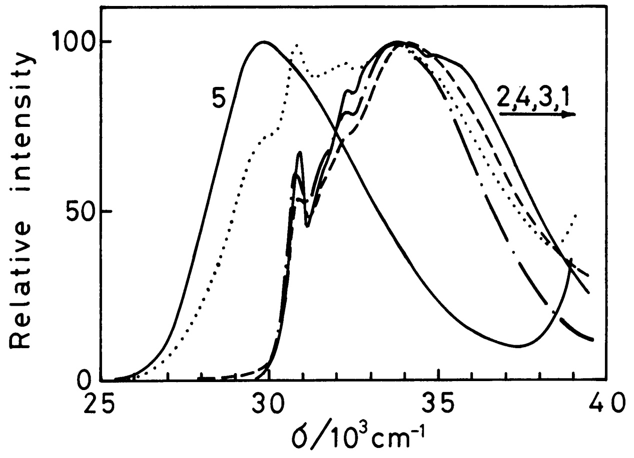

Fig. 2. Fluorescence-excitation spectra of 1-naphthol in (1) cyclohexane (—), (2) ethanol (—·), (3) 0.35 M acetic acid (- - -), (4) H_2O (·····), and (5) 0.1 M NaOH (—). Emission wavenumber: 27780 cm^{-1} (360 nm) for (1) and (2), 23530 cm^{-1} (425 nm) for (3) and (4), 22220 cm^{-1} (450 nm) for (5), respectively.

1-naphthol molecules, and the 0–0 band is located at 31100 cm^{-1}. This spectrum is attributable to an excitation of the neutral form of 1-naphthol molecules. On the other hand, the spectrum observed in 0.1 M NaOH shows a broad peak at 29700 cm^{-1}. This spectrum is attributed to excitation of the contact ion pairs which are formed from 1-naphthols in the excited state and even in the ground state.[32] Although there is a slight red shift, the spectrum observed in ethanol essentially shows the same spectral feature as observed in cyclohexane. The spectrum observed in 1% NH_3 is almost the same as that observed in 0.1 M NaOH. The spectrum observed in an acetic acid solution shows a contribution of the contact ion pairs at around 29500 cm^{-1}. The spectra observed in the 0.1 M HCl solution is similar to that observed in 0.35 M acetic acid. The contribution of the contact ion pairs in H_2O is larger than that in 0.35 M acetic acid. Although the fluorescence spectrum observed in H_2O is almost the same as those observed in 0.1 M NaOH and 1% NH_3 solutions, it is noted that its excitation spectrum shows that the main ground state species in H_2O are neutral molecules.

1-Naphthol has two electronic states, ^1L_b and ^1L_a, in the regions of their lowest absorption band.[36] These states lie close to each other. In free molecules and in nonpolar solvents, the fluorescent state is relatively structured ^1L_b. In polar solvents, the interaction between the dipole of excited 1-naphthol molecules and their surrounding solvent molecules lowers the energy of the ^1L_a state below that of the ^1L_b state in their equilibrium configuration. Under these conditios, the fluorescent state of 1-naphthol molecules is broad and structureless ^1L_a.[37,38]

1-Naphthol forms a hydrogen-bonded complex with suitable proton-accepting molecules. The hydrogen bonding between 1-naphthol and the proton-accepting molecules results in a change in the state of the fluorescence of 1-naphthol from the ^1L_b to the ^1L_a state. In relatively mild solvents regarding polarity, such as ethanol, the interaction between 1-naphthol and ethanol is mild, resulting in a lowering of the energy of the ^1L_a state below that of the ^1L_b state in the equilibrium configuration. Under these conditions the fluorescence shows a broad, structureless spectrum from the ^1L_a state.

The ground- and excited-state pK_a values for 1-naphthol are 9.2[39] and 0.4,[40,41] respectively. In the excited state of a hydrogen-bonded complex of 1-naphthol with suitable proton-accepting molecules, the oxygen of the naphthols becomes more positive than in the ground state.[42–46] Then, the formation of a complex of the contact ion pair and the separated ion pair in the excited state equilibrium configuration occurs in a methylcyclohexane and isopentane (3 : 1 v/v) mixed solution and in polyethylene film at 77 K.[32,47] The former and latter species show a broad, structureless band at around 25320 cm^{-1} (395 nm) and 23870 cm^{-1} (419 nm), respectively. The hydrogen bonding between 1-naphthol and proton-accepting molecules results in a change in the state of the fluorescence of 1-naphthol from the ^1L_b to the ^1L_a state. It has been reported that the 0–0 band in the absorption spectrum of the hydrogen-bonded complex between the 1-naphthol molecule and dioxane is observed at 30960 cm^{-1}.[48] In the case of the hydrogen-bonded complex between 1-naphthol and triethylamine, the 0–0 band of its absorption spectrum is located almost at the same position.[42] Upon excitation of the hydrogen-bonded complex, a proton transfer takes place to yield a contact ion pair within the lifetime of the excited singlet state; the fluorescence originates in the contact ion pair from its S_1 state, which can be assigned to the ^1L_a state; its peak is observed at around 24000 cm^{-1}.[42,43] On the other hand, the peak wavenumber of the fluorescence spectrum of the 1-naphtholate ion is located at 21000 cm^{-1} in a 0.1 M NaOH aqueous solution, 20600 cm^{-1} in EAA (ether, ethyl alcohol, ammonia (10 : 9 : 1) solution at room temperature.[49] In contrast to this, the peak in the EAA rigid matrix at 77 K appeared at 23900 cm^{-1}.[49] The good coincidence in the peak wavenumbers of the spectra observed in the EAA glass matrix at 77 K and in triethylamine indicates that the fluorescence spectra with a peak at around 24000 to 26000 cm^{-1} might be assigned to fluorescence originated from the S_1 state of the contact ion pair of 1-naphthol, and the fluorescence spectra with a peak at around 21000 cm^{-1}, from the fluorescence from 1-naphtholate ion,[49] respectively.

The fluorescence spectrum observed in 0.1 M NaOH shows a peak at 21000 cm^{-1}. The spectra observed in triethylamine and 0.35 M acetic acid show a peak at ca. 24000 cm^{-1}. On the other hand, the fluorescence-excitation spectra observed in a 0.1 M NaOH aqueous solution and in 0.35 M acetic acid show a peak at ca. 29500 cm^{-1}, though weak in 0.35 M acetic acid: that observed in a 0.2 M triethylamine solution in hydrocarbons shows a peak at 30960 cm^{-1}. This disagreement in the wavenumbers of the fluorescence-excitation spectra indicates that proton dissociation in the S_1 state takes place from either a contact ion pair or a separated ion pair to yield an ionic species (naphtholate ion) within the lifetime of the excited singlet state; the fluorescence with a peak at around 21000 cm^{-1} is emission arising from the naphtholate ion in 0.1 M NaOH, H_2O, and 0.35 M acetic acid solutions. Such phenomena are expected to occur because of the difference in pK_a values in the ground state and first excited singlet state of 1-naphthol.[40,41,44] Thus, the four fluorescent bands shown in Fig. 1 can be assigned to emission from the ^1L_b state of 1-naphthol in cyclohexane (with vibrational structure and located at higher wavenumber side).[37,38] The ^1L_a state of 1-naphthol in ethanol or suitable polar solvents being formed in hydrogen bonded species (broad and structureless band peaked at ca. 27900 cm^{-1}).[37,38] The ^1L_a state of a contact ion pair and/or a separated ion pair (broad, structureless band with peaked at ca. 24000 to 26000 cm^{-1}),[42,43] and 1-naphtholate ion (broad, structureless band with a peak at ca. 21000 cm^{-1}),[49] respectively.

Fluorescence and Fluorescence-Excitation Spectra During Sol to Gel to Xerogel Transition. Figure 3 shows the fluorescence spectra of 1-naphthol excited at 33670 cm^{-1} (297 nm, absorption peak of ^1L_a) during sol to gel to xerogel transitions of the sample as a function of time. Just after mixing, the fluorescence spectrum showed a broad, poorly structured spectrum similar to that observed in an ethanol solution. In this stage, the fluorescence state of 1-naphthol is essentially the ^1L_a state. We find that the spectrum shifted to the red and that the emission component with fine structure (fluorescence originated from ^1L_b state) became weaker during the time of the first reaction stage. Gelation occurred at 10 d. It is noted that the spectrum observed at 10 d showed a somewhat large relative intensity at around 29200 cm^{-1}, compared to that observed at 9 d in this reaction system. After gelation, the relative intensity at around 29200 cm^{-1} became large and somewhat structured. On the other hand, the direction of the spectral shift observed after 16 and 18 d turned to blue and emission with fine structure gradually became stronger. The spectrum observed after 32 and 50 d resembles that observed in cyclohexane, and the main fluorescent state during this stage can be assigned to the ^1L_b state.

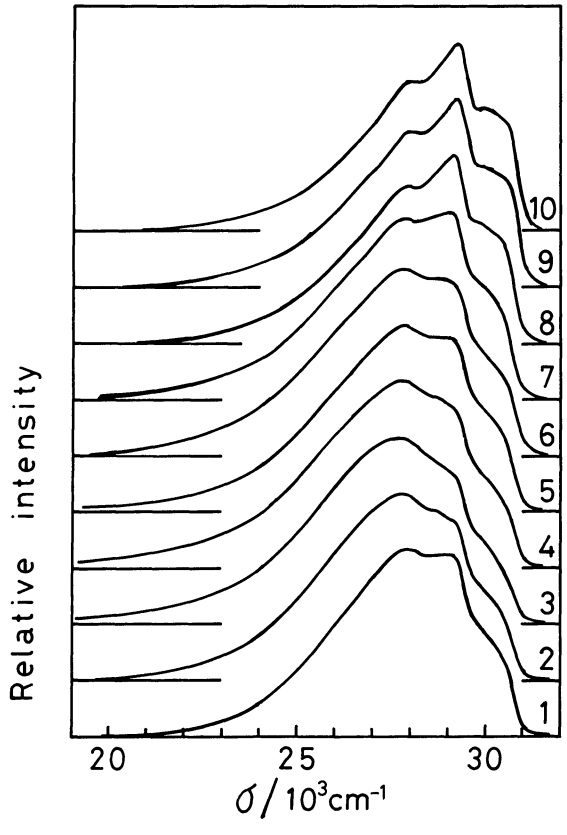

Fig. 3. Fluorescence spectra of 1-naphthol in the TEOS and SAE mixed solution (Si:Al=94:6) during the sol to gel to xerogel transitions: after 1 h (1), 5 d (2), 9 d (3), 10 d (4), 11 d (5), 12 d (6), 16 d (7), 18 d (8), 32 d (9), and 50 d (10). Excitation wavenumber is 33670 cm^{-1} (297 nm).

Figure 4 shows the fluorescence spectra of 1-naphthol excited at 28990 cm^{-1} (345 nm) during the sol to gel to xerogel transitions of the reaction system as a function of time. It is noted that the spectra show structureless emission during the transition, and that the peak wavenumber is located at around 25300 cm^{-1} at 0 day and 26000 cm^{-1} at 50 d. These wavenumbers agree well to that observed for the contact ion pair.[32] Although the intensity is very weak, it is noted that this broad fluorescence was observed even just after stirring the sample preparation.

The fluorescence spctrum of 1-naphthol in the Si–Al system of the present case closely resembles the corresponding spectra of the contact ion pair regarding in shape.[32,42,43] However, the peak wavenumber of the Si–Al system shifts to the blue by about 1300 to 2000 cm^{-1}, compared with that in triethylamine solution, since the excited species in the hydrogen-bonded complex with triethylamine is the separated ion pair.

Figure 5 shows the fluorescence-excitation spectra of 1-naphthol observed at 25000 cm^{-1} during the sol to gel to xerogel transitions of the reaction system as a function of time. Although the relative intensity of the 0–0 band of the ^1L_b (30800 cm^{-1}) to the intensity of the ^1L_a (at around 33000 cm^{-1}) changes during the transition, the spectral

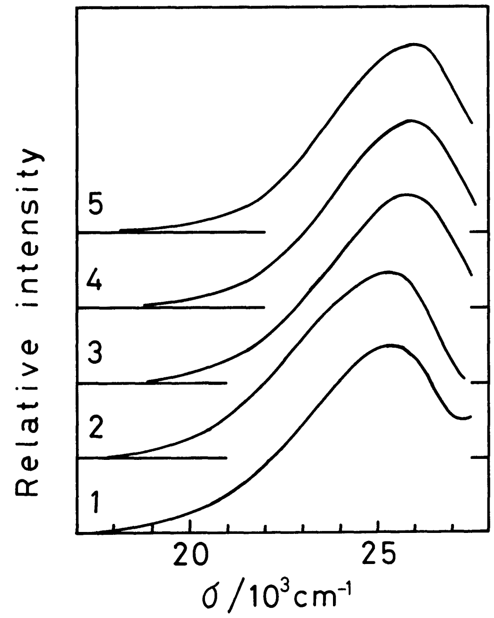

Fig. 4. Fluorescence spectra of 1-naphthol in the TEOS and SAE mixed solution (Si:Al=94:6) during the sol to gel to xerogel transitions: after 1 h (1), 10 d (2), 18 d (3), 33 d (4), and 50 d (5). Excitation wavenumber is 28990 cm^{-1} (345 nm).

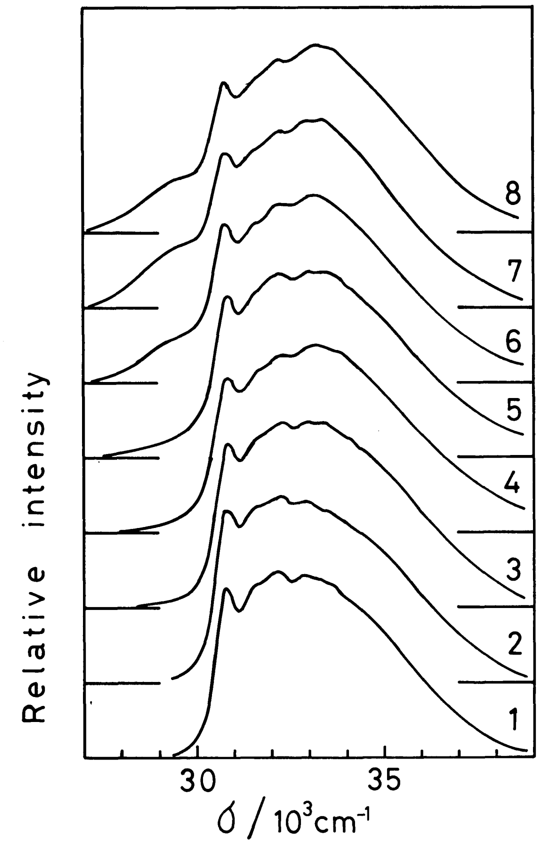

Fig. 5. Fluorescence-excitation spectra of 1-naphthol in the TEOS and SAE mixed solution (Si: Al=94: 6) during the sol to gel to xerogel transitions: after 1 h (1), 5 d (2), 10 d (3), 12 d (4), 16 d (5), 18 d (6), 32 d (7), and 50 d (8). Emission wavenumber is 25000 cm^{-1}.

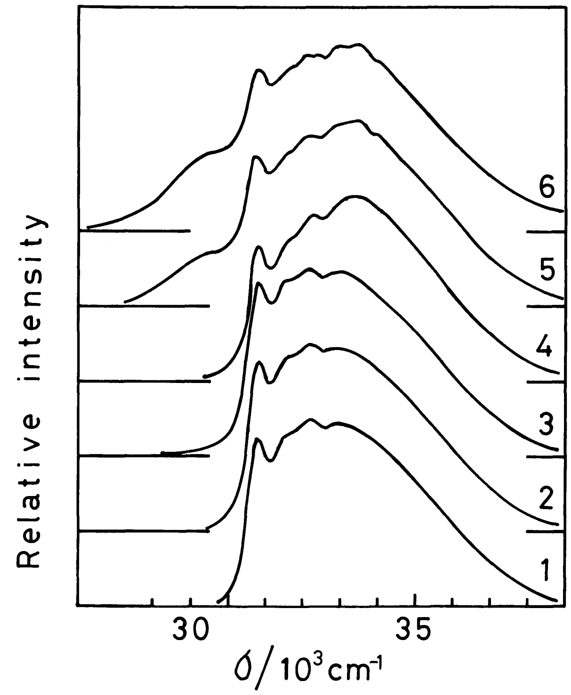

Fig. 6. Fluorescence-excitation spectra of 1-naphthol in the TEOS and SAE mixed solution (Si: Al=94: 6). (1), (2), and (3): observed after 1 h, (4), (5), and (6): observed after 50 d. Emission wavenumber are as follows, 28010 cm^{-1} (357 nm) for (1) and (4), 25000 cm^{-1} (400 nm) for (2) and (5), 23530 cm^{-1} (425 nm) for (3) and (6).

feature remains unchanged during the sol to gel to xerogel transition of this system, except for the pronounced appearance of a band at around 29500 cm^{-1}. The relative intensity of the band appearing at around 29500 cm^{-1} increases along with the progress of the reaction, especially after 18 d.

Figure 6 shows the observation-wavenumber dependence of the excitation spectra of 1-naphthol at 0 day and 50 d. There is a slight observation-wavenumber dependence when the spectra were observed just after stirring the reaction system. When the spectra were observed at 28010 cm^{-1} (357 nm), no significant spectral change was observed during the sol to gel to xerogel transition of the sample. On the other hand, when the spectra were observed at 25000 cm^{-1} (400 nm) and 23530 cm^{-1} (425 nm), a band at around ca. 29500 cm^{-1} had a remarkable change in intensity after 50 d. The results shown in Figs. 5 and 6 indicate that the fluorescent band around 25000 cm^{-1} increases in intensity along with the reaction.

The results shown in Figs. 1 to 6 reveal that there are two absorbing and emitting species in the xerogel state. The fluorescent species with a fine structure can be assigned to the ^1L_b state originating from neutral 1-naphthol molecules. On the other hand, the fluorescent species with a broad, structureless band with a peak located at around 25300 to 26000 cm^{-1} can be assigned to the ^1L_a state originating from the contact ion pair between doped 1-naphthol molecules and the surrounding matrix.

Possible Geometries of the Interacting Species between 1-Naphthol and the Prepared Gel Surface. Silica–alumina is a well-known and important acid catalyst.[50–56] The surface structure of silica–alumina and zeolites has been discussed from the stand points of surface acidity and reactions. The chemical reactions which occur on the silica–alumina surfaces are characterized by a silicon-to-aluminium composition.[51] It is concluded that dehydrated aluminum-on-silica contains only Lewis-acid sites, and that dehydrated alumina-in-silica contains only Brønsted acid sites. The former comprises tricoordinated aluminum atoms. The latter comprises tetracoordinate aluminum atoms. A proton linked to an oxygen interconnection SiO_4 and AlO_4 tetrahedral in silica–alumina is a very strong acid. In the present reaction system, the surface chemical structure of prepared gels may be essentially identical with that of the silica–alumina and zeolites catalysis. Some typical surface species comprising of silicon and

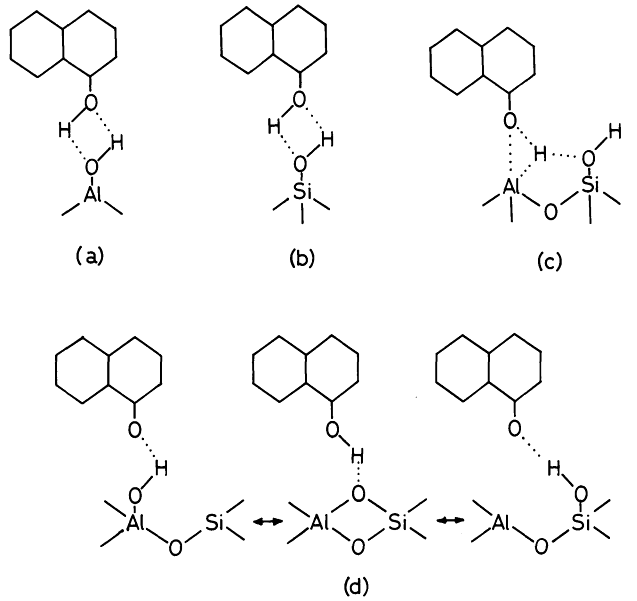

Fig. 7. Some geometries of typical interaction species formed between 1-naphthol molecules and the sites on the silica-aluminum gel surface. (a) and (b) illustrate hydrogen-bonded complexes. (c) and (d) illustrate ionpairs.

aluminium have been given in the literature.50–56) Figure 7 illustrates some possible geometries of the interacting species, such as hydrogen-bonded forms and contact ion-pair forms, which are formed between 1-naphthol molecules and the sites of pore surfaces of the prepared gels.

Differences of Photophysics and Photochemistry of 1-Naphthol in Solutions and during Sol to Gel to Xerogel Reaction. The fluorescence-excitation spectra of 1-naphthol shown in Figs. 2, 5, and 6 revealed that 1-naphtholate ions are generated by excitation in solvents such as H_2O, 0.1 M NaOH and 0.35 M acetic aicd. The spectral peak is located at ca. 29500 cm^{-1}. In contrast to this, the contact ion pair, which has the fluorescence-excitation peak at ca. 29500 cm^{-1}, shows a fluorescence peak at 25300 to 26000 cm^{-1}. The agreement of the spectral peak observed in the fluorescence-excitation spectra and the disagreement regarding the spectral peak observed in their fluorescence spectra can be attributable to the solid-matrix effect, especially in the xerogel state. In the xerogel state, 1-naphthol molecules are doped in cages of the prepared gel. Therefore, a large movement of the individual constituent atoms is completely prevented due to encapsulation of 1-naphthol molecules in cages of the prepared gel. Complete proton dissociation after photo-excitation of the contact ion pair is hindered along with the advance of the sol–gel reaction. Under these reaction conditions, the emission species in the xerogel state is still the contact ion pair. On the other hand, the relative movement of individual constituent atoms in solutions is probably larger than that in the doped state. Therefore, the excited 1-naphtholate ions in solutions are probably present in the contact ion pairs, due to the coincidence of the fluorescence-excitation spectra in solutions and in the xerogel state, though small amounts of 1-naphthol molecules are already in the contact ion pair. Figures 2 to 6, as well as the results reported by Shizuka et al., indicate that the excited separated ion pair and excited 1-naphtholate ion are generated by a large geometrical relaxation from the contact ion pair.

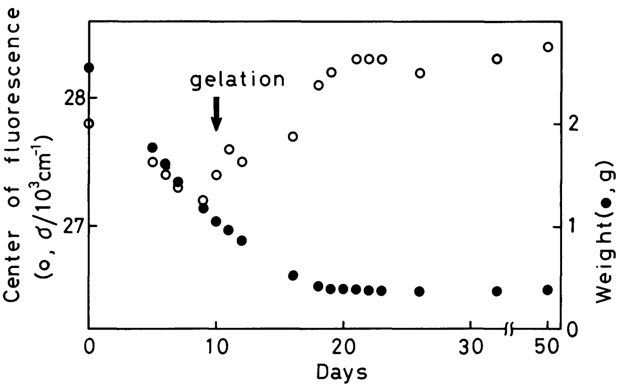

Fig. 8. Central wavenumber (○) of the fluorescence spectrum of 1-naphthol and the net weight (●) of the reaction system in the TEOS and SAE mixed system during the sol to gel to xerogel transitions.

Spectral Shift of the Reaction System. To clarify the spectral shift of 1-naphthol during the sol to gel to xerogel transitions, the mean (or center) wavenumber of the fluorescence spectra of 1-naphthol during the transitions is also plotted in Fig. 8, together with the net weight change of the reaction system during the sol–gel process. It can be seen from Fig. 8 that the net weight of the sample decreased both smoothly and gradually. The most striking aspect of the present results is that the fluorescence spectrum of 1-naphthol gradually shifts to the red during the first stage of the sol to gel reaction; in the next stage the spectrum gradually shifts to the blue. Since the net weight of the sample showed no accidental increase or decrease during the measurement, this red shift of the fluorescence spectrum of 1-naphthol indicates an increase in the polar nature of the matrix surrounding the doped or encapsulated 1-naphthol molecules in the prepared material.

No red shift was observed in a previous pure TEOS system,30) but also observed in the Si : Al=90 : 10 reaction system by HCl catalyst.33) This red shift reflects an increase in the polarity of the matrix surrounding the doped 1-naphthol molecules. The increase in the polar nature of the matrix is attributable to a substitution of an –OR group by an –OH in TEOS and SAE. This increase in the polar nature is similar to the polar nature of methanol, which is constructed by substitution of an –H group with an –OH for methane.

The emitting molecules is exposed to the influence of the surrounding matrix, which can produce significant changes in its photophysical properties. The blue shift shown in Figs. 3 and 4 indicates that the excited-state electronic relaxation process, including the surrounding matrix, which leads to an equilibrium excited configuration from a Frank–Condon excited configuration during the excited state lifetime, is gradually prevented on a molecular level and, hence, the fluorescence originating from the ^1L_b state become a major component. Therefore, the blue shift reflects an increase in the microviscosity of the matrix around the doped, or encapsulated, 1-naphthol molecules. The polymerization reaction, drying, densification, and rigidification of the gel matrix is attributable to an increased microviscosity around the doped 1-naphthol molecules and the blue shift.

Comparison of Si : Al=90 : 10 and 94 : 6 Systems. It is noted that the most red-shifted fluorescence spectrum was observed after 9 d, and that gelation of the present system occurred 10 d after starting the reaction. In contrast, a reverse time relation between the gelation time and the most red-shifted fluorescence was observed for a sytem comprising Si : Al=ca. 90 : 10 catalyzed by HCl.[33] In a system comprising Si : Al=ca. 90 : 10, it was found that gelation occurred at 4 d and that the most remarkable red-shift in this fluorescence spectrum was observed 6 d after mixing the solution. Both the gelation time and the time of the most remarkable red-shift in the fluorescence of the reaction system might be affected by the composition, catalyst, and temperature in the reaction system. It is probable that there is a certain difference in the polymerization reaction, drying, densification, and rigidification of the gel matrices, and that they affect the photophysical processes of encapsulated molecules during the sol to gel to xerogel transition of the mixed reaction systems of alkoxides. In our previous report for the Si : Al=90 : 10 system, the fluorescence and fluorescence-excitation spectra of 1-naphthol were observed at one excitation wavenumber and one observation wavenumber. In this study, we observed the spectra at several wavenumbers. It was found that part of 1-naphthol molecules are doped in the contact ion pair in the cage of the prepared gel. This finding regarding the present system suggests that there is also a possibility for the existence of ion pairs in the Si : Al=90 : 10 reaction system by an HCl catalyst. At this stage of study, we wish to elucidate what factors govern the sol to gel to xerogel reaction of metal alkoxides. A study of the detailed effect of the components of the reaction system and catalyst on the fluorescence spectra of 1-naphthol during the sol to gel to xerogel transition at constant temperature is in progress.

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