The Absorption Spectra of pH Indicator Dyes Doped in Silica Thin Films Prepared by the Method of Liquid Phase Deposition and the Spectroscopic Estimation of Effective Acidity of Internal Hydroxyl Groups of Silica

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The method of liquid phase deposition (LPD) is a wet process forming hard and transparent silica thin films on glass surfaces and has interesting features, such as some organic molecules can be directly doped inside silica phases. The pH indicator dyes methyl yellow and methyl orange were doped in silica thin films by the LPD method and the absorption spectra of the samples were observed. The comparison with the corresponding spectra of the pH indicator dyes in pH-controlled buffer solutions leads to the conclusion that the doped organic dye molecules in the LPD silica solid phase are in an acidic environment equivalent to pH=3.7. The acidity of the interior of LPD silica is high compared with surface acidity of other silicas such as silica gel. The origin of the high acidity of LPD silica has been attributed to the existence of Si–F bonds inducing an electron-attracting tendency.

The method of liquid phase deposition(1—5) (LPD) is a wet process forming silica thin films on substrates such as glass plates. The process has the following advantages.

1) The process forms hard and transparent silica thin films. The etching rates of LPD silica films as a measure of film resistance, which are measured by using P-etch solutions,(6) are equivalent to the corresponding rates of silica films prepared by the thermal oxidation method and an order of magnitude better than the ones prepared by the sol–gel method.

2) The process forms almost pure amorphous silica films with very low impurity concentrations. The XPS data indicate that the LPD silica films are mainly composed of Si and O and the atomic ratio of Si to O is very close to 1 : 2.(3) The fluorine content is exceptionally high compared with other contaminants and was found to be 5 to 8×10^{-2} g cm^{-3}, depending on preparation conditions.(4)

3) Some kinds of organic molecules can be directly doped into the LPD films.(7—9) Ino et al.(9) measured the dye elution out of LPD silica phases into water and ethanol. The absorbance of rhodamine 6G doped in LPD silica films decreases to about 90% after 100 h in 60 °C water and after that the decrease in absorbance is very small. The absorbance of rhodamine 6G doped in sol–gel films disappeared after 100 h at the same temperature. The results indicate that the LPD films are dense compared with sol–gel films and rhodamine 6G is directly doped inside the silica phases by using LPD procedures.

4) The process proceeds at ordinary temperatures. The process needs no baking or calcination, so that doped organic dyes can be doped into silica thin layers without thermal decomposition.

The doping ability of organic molecules(7—9) is the most interesting features of this method. Due to this feature, the process has the probability of forming organic–inorganic functional composite materials. The environment of organic molecules doped in silica phases is a kind of extreme condition for organic substances and the study of electronic states of doped organic molecules may contribute to the development of new functional composite materials.

To evaluate the acid strength of a solid surface, the color change of adsorbed indicator dyes has been observed and has widely used to measure the acid strength of surfaces in the field of catalytic chemistry.(10—12) The absorption spectra of pH indicator dyes adsorbed on solid surfaces are known to be a good measure of the proton-donating ability of the surface where dye

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molecules are adsorbed. The absorption spectra of pH indicator dyes doped in solid phases also seem to reflect the effective acidity of the environment for organic compounds.

Suzuki et al. observed the fluorescence spectra of acridine adsorbed on activated silica gel.[13)] They concluded that the dominant emitting species of acridine on silica gel are protonated ones and the fluorescence decay data suggest that hydrogen-bonded species also exist on the silica gel surface. The spectroscopic evidence of electronic states may provide some useful information on the acidity of the surface and interior of silica.

This paper reports the measurements of absorption spectra of pH-indicator dye molecules doped in silica thin films prepared by the liquid phase deposition process and the estimation of effective acidity of inorganic solid phase surrounding organic dye molecules, by comparing the corresponding spectra of pH-controlled aqueous buffer solutions. As far as we know, this is the first report which has experimentally measured the proton donating ability of the interior of the silica phase.

Experimental

Silica thin films in which organic dye molecules are doped can be prepared by the following LPD procedures. SiO_2 saturated aqueous solutions of hexafluorosilicic acid are prepared. Organic dye molecules are dissolved in the solutions and aluminum powder is then added in them. The solutions thus prepared are used as dipping solutions for the formation of organic-dye doped silica thin films. Glass plates of commercial slide glass are used as a substrate for deposition. They are dipped into the solutions and are kept quietly for some time at an appropriate constant temperature.

The equilibrium in the aqueous solution of hexafluorosilicic acid can be expressed as follows.

$$H_2SiF_6 + 2H_2O \longleftrightarrow SiO_2 + 6HF \qquad (1)$$

When some amount of Al is added to the solution, Al reacts with HF and generates gaseous hydrogen.

$$Al + 6HF \longleftrightarrow 3H^+ + AlF_6{}^{3-} + 3/2H_2 \qquad (2)$$

This reduces the concentration of HF in dipping solutions and shifts the equilibrium to the right in reaction 1. Addition of Al powder shifts the equilibrium to the deposition of silica on glass substrates.

The amount of Al powder, the temperature of the dipping bath solutions, and the time for dipping are very sensitive in order to make transparent films, so that these factors affecting the smoothness and transparency of formed films need to be adjusted appropriately.

The SiO_2 saturated aqueous solution of hexafluorosilicic acid the concentration of which is 4 $mol\,dm^{-3}$ was used in this study. Methyl yellow and methyl orange were dissolved in the solutions at a concentration of 4.1×10^{-4} and 1.2×10^{-3} $mol\,dm^{-3}$, respectively. Al powder of 0.7 g was added to the 250 cm^3 dipping solution. The temperature of 30 °C and dipping time of 30 h were proved to be mostly appropriate and the conditions of 30 °C and 30 h were used throughout these experiments.

After the glass plates coated with silica thin films were washed and dried, the absorption spectra of the samples were recorded on Hitachi U-3200 recording spectrophotometer. The data were stored on floppy diskettes on a personal computer through an RS-232C interface bus and were ready for any data processing.

Results and Discussion

The absorption spectrum of methyl yellow doped in silica thin films prepared by the LPD method is shown in Fig. 1. Because the concentration of doped dye molecules cannot be measured exactly, the spectra are plotted against the wavenumber such that the maximum absorbances are normalized to 1. Methyl yellow has a broad absorption band with a maximum at 22000 cm^{-1}. Figure 1 also includes the absorption spectrum of methyl yellow dissolved in dipping solutions for LPD procedures. The absorption spectrum in the dipping solutions is largely shifted to the red compared with the one in silica films.

Figure 2 shows the pH dependence of the absorption spectra of methyl yellow in pH-controlled buffer solutions. In a buffer solution of pH=2, the absorption spectrum of methyl yellow shows a band with a shoulder on the lower wavenumber side and has a maximum at the wavenumber of 19500 cm^{-1}. The absorption band is displaced to the blue with the increase in pH of buffer solutions and changes to one with a peak at the wavenumber of 22000 cm^{-1} above pH=4.

Comparison of the absorption spectra of methyl yellow doped in LPD silica films with those in buffer solutions shows that the spectral shape and position of the absorption band in LPD silica films roughly correspond to that in buffer solutions of pH=3. The best fit

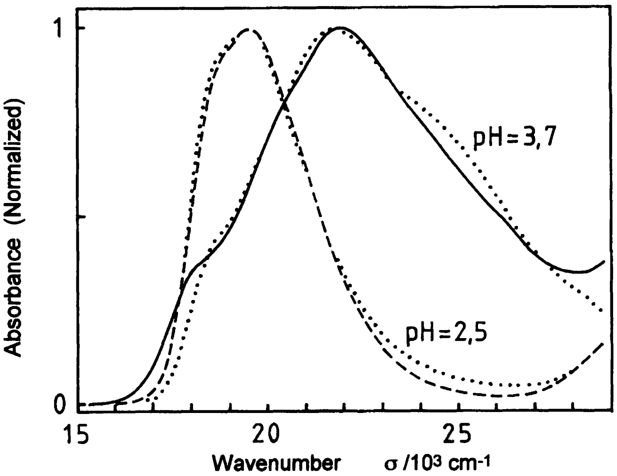

Fig. 1. The absorption spectra of methyl yellow doped in LPD silica films (—) and in dipping solutions (- - -). As for the ordinate, see the text. The absorption spectra of methyl yellow in buffer solutions corresponding closely to those in LPD films and in dipping solutions are included in the figure for ease of comparison. (a) pH=3.7; (b) pH=2.5.

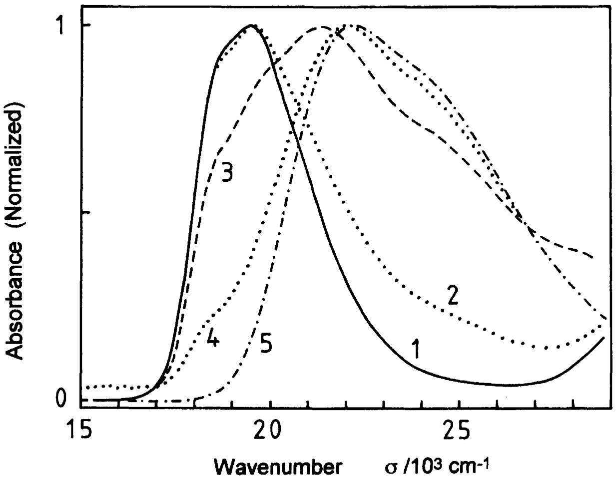

Fig. 2. The absorption spectra of methyl yellow in aqueous buffer solutions of various pH. (1) pH=2.0; (2) pH=3.0; (3) pH=3.5; (4) pH=4.0; (5) pH=12.0.

of the absorption band in buffer solutions with that in LPD silica films is obtained at pH=3.7. The absorption spectrum in the buffer solution of pH=3.7 is included in Fig. 1 with a dotted line. Analogous comparison of the absorption band of methyl yellow in dipping solutions leads to the result that the absorption spectrum in dipping solutions corresponds to that in the buffer solution of pH=2.5. The absorption spectrum of methyl yellow in the buffer solution of pH=2.5 is also included in Fig. 1.

These experimental findings indicate that the solid environment of LPD silica films surrounding methyl yellow corresponds to an acidic environment equivalent to pH=3.7. The pH of dipping solutions is 2.5 and is more acidic than that in LPD silica films. The environment of doped organic dyes in LPD silica films is considerably less acidic than in dipping solutions out of which silica films are deposited, but is still strongly acidic for ordinary conditions of organic molecules.

Figure 3 plots the absorption spectrum of methyl orange doped in LPD silica films as well as the one in dipping solutions. Because of low concentration of doped methyl orange in silica films, the spectrum in LPD silica films has a low signal-to-noise ratio. Methyl orange in an LPD film and in a dipping solution shows broad absorption bands with a maximum at about 20000 cm^{-1}. The spectral shape in the LPD film is broadened at the higher wavenumber side compared with that in the dipping solution. The absorption spectra of methyl orange in pH-controlled buffer solutions are given in Fig. 4. At a pH of 2.0, the peak of the absorption band lies slightly below 20000 cm^{-1}. On the increase in pH of buffer solutions, the peaks of absorption bands of methyl orange are displaced to the blue.

An analogous comparison to methyl yellow case leads to the conclusion that the best fit absorption spectrum in buffer solutions to the one in silica films is obtained at a pH of 3.5. The data are somewhat less reliable because of a lower signal-to-noise ratio than those of methyl yellow, but the result is consistent with that of methyl yellow. The absorption spectrum of methyl orange in a dipping solution corresponds to the one in buffer solution of pH=2.8. The best fit absorption spectra in buffer solutions are also included in Fig. 3. The data indicate that the effective acidity of LPD films is pH=3.5 and is consistent with the result obtained from the spectroscopic data of methyl yellow. The pH of dipping solutions obtained from the data of methyl orange is 2.8 and the result is also consistent with that of methyl yellow.

From the spectral data of methyl yellow and methyl

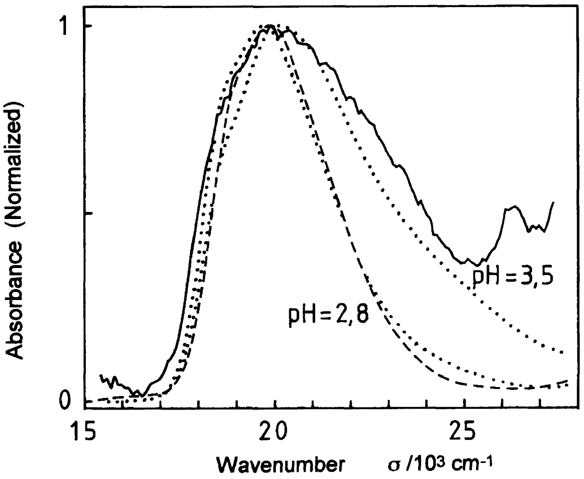

Fig. 3. The absorption spectra of methyl orange doped in LPD silica films (—) and in dipping solutions (- - -). The absorption spectra of methyl orange in buffer solutions corresponding closely to those in LPD films and in dipping solutions are included in the figure for ease of comparison. (a) pH=3.5; (b) pH=2.8.

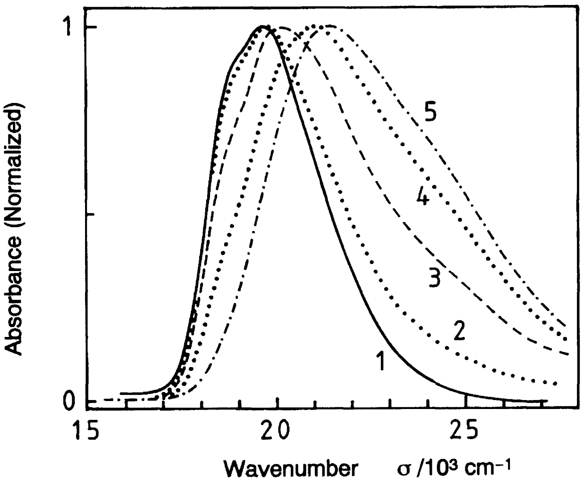

Fig. 4. The absorption spectra of methyl orange in aqueous buffer solutions of various pH. (1) pH=2.0; (2) pH=3.0; (3) pH=3.5; (4) pH=4.0; (5) pH=5.0—12.0.

orange doped in LPD silica films we conclude that the effective acidity inside the LPD silica evaluated by the coloring of pH indicator dyes is equivalent to $\mathrm{pH}=3.7$.

It is well accepted that silica or silica gel has hydroxyl groups (silanol groups) on their surface, which are attributed to the appearance of proton-donating ability.[14,15] The proton donating ability of the silica gel surface can be estimated from experimental findings on some appropriate properties of adsorbed species, such as coloring of pH indicator dyes adsorbed on the silica gel surface.[10—12] Strazhenko et al.[16] measured the $\mathrm{p}K_\mathrm{a}$ of surface hydroxyl groups to be 7.1 ± 0.5, by titrating the hydroxyl groups with several kinds of bases. Hair and Hertle[17] also concluded that the surface acidity was equivalent to $\mathrm{p}K_\mathrm{a}=7.1$, based on the frequency shifts of the OH stretching band of adsorbed phenol on silica gel. Such a proton-donating tendency of silica gel surfaces does not basically depend on the method of preparation, however, the $\mathrm{p}K_\mathrm{a}$ values largely depend on the existence of impurities.

A silica surface prepared by heat treatment at high temperatures is originally hydrophobic by nature. Surface hydroxyl groups introduced by activation treatment modify the affinity of silica surface and give hydrophilicity to the surface.[18,19] The modification of the silica gel surface introduces proton donating ability and, as the result of this, adsorbing ability of basic or polar molecules. This is the reason that activated silica gel is widely used as an adsorbent.

The results of this study show that the proton-donating ability of internal hydroxyl groups inside the LPD silica phases is extremely strong compared with those of surface hydroxyl groups of other kinds of silica. The strong proton-donating ability of LPD silica can be attributed to the electron-attracting tendency of Si–F bonds the existence of which is confirmed by the vibrational spectra of LPD silica.

As is described in the introduction, silica films prepared by the LPD method contain some fluorine elements. Hishinuma et al.[3] observed the infrared transmission spectra of LPD silica films deposited on silicon. The main features of the spectrum consist of those of amorphous $\mathrm{SiO_2}$, except for the following two bands. A weak absorption band near 3300—3700 $\mathrm{cm^{-1}}$ is assigned to the Si–O–H stretching mode and a weak but clearly distinct band near 950 $\mathrm{cm^{-1}}$ to the Si–F stretching mode. This suggests that a considerable amount of Si–F bonds are formed in the LPD process.

Chapman and Hair[20] reported that strongly acidic sites of the Brønsted type are generated on porous glass treated with ammonium fluoride. They proposed the mechanism of the appearance of the strong acidity, which involves the replacement of a hydroxyl group by a fluorine atom and the electron attraction to the substituted fluorine atom (Chart 1).

The Si–F bonds are considered to be formed in the process of silica deposition from an aqueous solution of hexafluorosilicic acid for the LPD process. The Si–F bonds of the type proposed by Chapman and Hair may be formed in the deposition process, but the following type of Si–F bonds is more favorably formed in the process. This type of Si–F bonds is produced only from geminal silanol groups on the silica gel surface, but there is no restriction of Si–F bond formation of this type in the LPD process (Chart 2).

The electron attraction to a fluorine atom is more direct in this scheme than in the one proposed by Chapman and Hair. The origin of the strong proton-donating ability of internal hydroxyl groups inside LPD silica films can be satisfactorily explained by a mechanism analogous to that proposed by Chapman and Hair.

It is known that activated silica gel has hydroxyl groups not only on the surface but in the bulk, and the hydroxyl groups show weak proton-donating ability.[21,22] The properties of internal hydroxyl groups are expected to relate closely to the tendency of incorporating hetero-molecules into the bulk, as well as those of surface hydroxyl groups, to decide the affinity with other various compounds. Proton donating ability of internal hydroxyl groups is, therefore, supposed to relate closely to the solubility of various organic molecules in LPD silica layers. For the reason that internal hydroxyl groups lie inside the bulk and cannot interact directly with probe molecules, direct experimental evidence is hard to obtain on the proton-donating ability of the interior of silica phases. As far as we know, no papers that experimentally measured the proton-donating ability of hydroxyl groups inside the bulk have been published. By using the dissolving ability of organic molecules in LPD silica layers, pH indicator dyes can be dissolved in LPD silica layers as a probe molecule inside the bulk; This study directly measured the proton-donating ability of internal hydroxyl groups for the first time, of course only in the special case of LPD silica.

In conclusion, the environment surrounding organic dye molecules doped in silica thin films prepared by the method of liquid phase deposition has an effective acidity equivalent to $\mathrm{pH}=3.7$. The origin of the strong

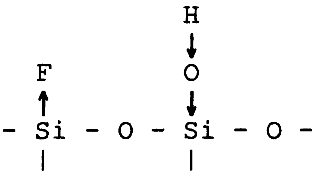

Chart 1.

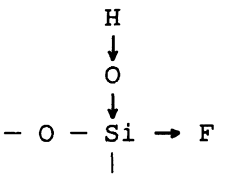

Chart 2.

proton-donating ability of the internal silanol groups of LPD silica can be satisfactorily explained by the mechanism involving Si–F bonds. Organic molecules that can be doped in LPD silica films are very limited in species and criteria for being doped in LPD silica films for organic compounds have not been established. The acidic conditions of the environment of LPD silica phases surrounding doped organic molecules may be an important factor affecting the doping ability of organic compounds into LPD silica thin films.

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