

Fluidity of Adsorbed Water in Alumina Gels as Studied
by ESR of Copper(II) Complex Probe

Shuji IKOMA,* Koichi KAWAKITA, Fusaji OZAWA, and Hiroshi YOKOI

Department of Applied Chemistry, Faculty of Engineering,
Shizuoka University, Hamamatsu 432

A kind of fluidity for adsorbed water in alumina gels prepared by the sol-gel method has been revealed by ESR-monitoring of the molecular motion of water-soluble polyamine copper(II) complexes as dopants; the complex molecules are almost free in tumbling motion at room temperature in air, but the motion stops when the gels are dried at 50 °C or in a desiccator.

Recently, there has been a considerable interest in oxide gels and glasses prepared by the sol-gel method, from the viewpoint of materials science.^{1,2)} Alumina and silica are representative ones. So far, however, much is not known about the structural details of the gels, although a few precise studies on the structures have been undertaken.³⁾ It is well known that adsorbed water in the gels plays an important role in determining their properties. In the present work, we report on the basis of the molecular motion of water-soluble copper(II) complexes as dopants that the adsorbed water of alumina gels unexpectedly shows a kind of fluidity. It may be noted that there have been almost no papers on the incorporation of impurities as metal complexes in alumina gels.

Alumina gels were prepared from aluminum isopropoxide according to the sol-gel method,¹⁾ where stable sols were obtained with a molar portion of 0.035 HCl. The gels were doped with (1,4,8,11-tetraazacyclotetradecane)copper(II) chloride and [N,N'-bis(2-aminoethyl)-1,3-propanediamine]copper(II) chloride (abbreviated as Cu-cyclam and Cu-2,3,2-tet, respectively, the structures being schematically shown in Fig. 1) in the molar ratio of Cu-cyclam/Al(OC₃H₇)₃ of 1/1000 by adding concentrated aqueous solutions of these complexes into transparent alumina sols before gelation

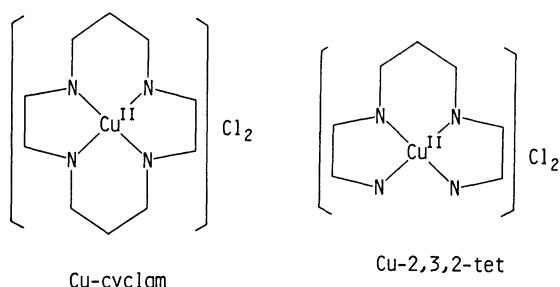


Fig. 1. Structures of copper(II) complexes doped in alumina gels and their abbreviations.

process. ESR spectra were recorded at room temperature and at the temperature of liquid nitrogen (77 K) with a JEOL JES-FE1XG ESR spectrometer. The samples were powdered alumina gels doped with the above complexes and 5 mM aqueous solutions of the complexes before doping.

Figure 2 shows two observed ESR spectra of Cu-cyclam in aqueous solutions, one having a line shape of the fluid solution type (A) and the other, that of the frozen solution type (B).⁴⁾ The A-type ESR line shape is determined by the almost complete averaging of anisotropies in g and hyperfine interaction, because individual copper(II) complex molecules are in rapid tumbling motion. On the other hand, the B-type line shape reflects the direct appearance of the anisotropies, because the complex molecules trapped in rigid solvent cages at 77 K are no longer mobile. Therefore, the B-type ESR signals are observed in wider magnetic field ranges than the A-type ones.

Figure 3 shows the observed ESR spectra of alumina gels doped with Cu-cyclam in various states. The alumina gels left in air at room temperature after preparation show quite different ESR spectra at room temperature (Fig. 3A) and at 77 K (Fig. 3B). This temperature dependence of ESR spectra is reversible, and quite

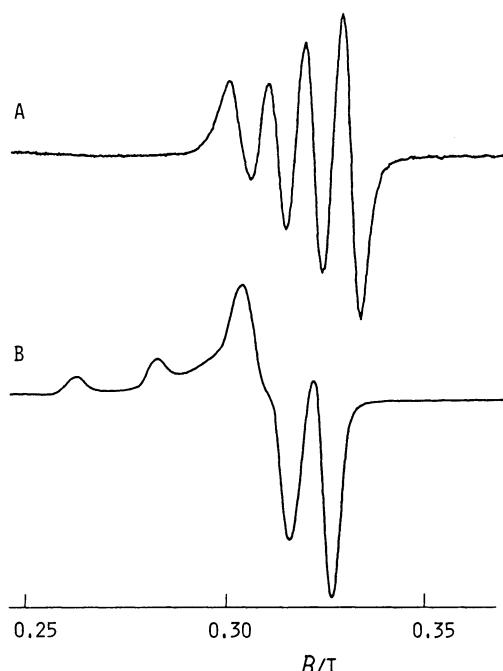


Fig. 2. ESR spectra of Cu-cyclam in aqueous solutions ([Cu-cyclam] = 5 mM (M = mol dm⁻³); [NaNO₃] = 0.20 M; pH ≈ 9): A, observed at room temperature (ν = 9.416 GHz; $g_{\text{O}} = 2.095$; $|A_{\text{O}}| = 0.0090 \text{ cm}^{-1}$); B, observed at 77 K (ν = 9.126 GHz; $g_{\parallel} = 2.182$; $|A_{\parallel}| = 0.0206 \text{ cm}^{-1}$).

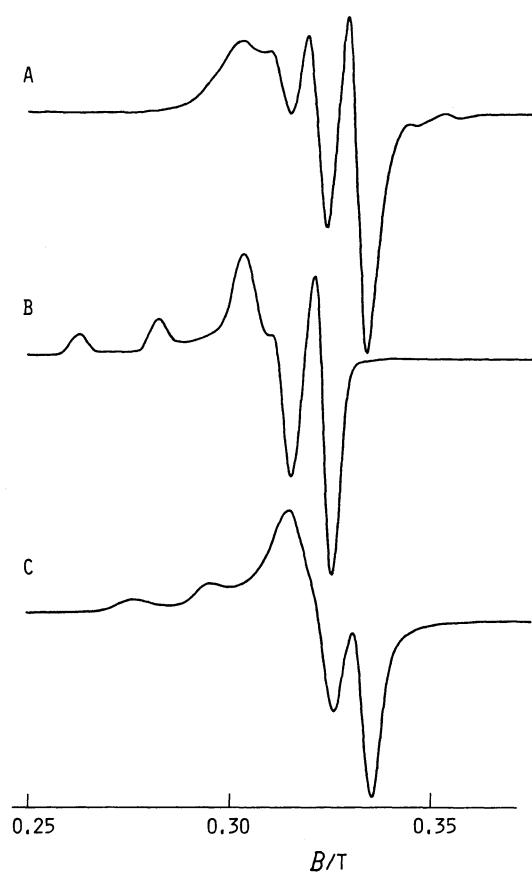


Fig. 3. ESR spectra of alumina gels doped with Cu-cyclam in the molar ratio of 1/1000: A, observed at room temperature ($\nu = 9.438$ GHz); B, observed at 77 K ($\nu = 9.128$ GHz; $g_{\parallel} = 2.187$; $|A_{\parallel}| = 0.0206$ cm^{-1}); C, observed at room temperature after heating at 50 °C for a week ($\nu = 9.432$ GHz).

resembles the ESR spectral patterns of the complex in aqueous solutions at room temperature and at 77 K in Fig. 2. The spectrum of Fig. 3B is identical with that of Fig. 2B, and the spectra of Figs. 3A and 2A are also the same, in view of both belonging to the A-type spectra. However, there is a slight difference in line shape between Figs. 2A and 3A, as is clearly shown, and an analytical study of this difference is now in progress. In conclusion, the above ESR result indicates that the Cu-cyclam molecules doped in alumina gels at room temperature are free in tumbling motion to almost the same extent as those in fluid aqueous solutions.

Thermal analyses have revealed that heating of these alumina gels at 50 °C in air evaporates a large quantity of adsorbed water, resulting in a weight loss of about 8%. The alumina gels thus dried showed the room-temperature ESR spectrum of Fig. 3C, whose line shape is rather close to the B-type one. When these gels were again allowed to stand in air at room temperature for a day or so, there was a weight gain of 2 – 3% by moisture absorption. Interestingly, this moisturized sample again showed the same ESR spectrum as Fig. 3A. Furthermore, it has been found that the same reversible interconversion in ESR spectra between Figs. 3A and

^{3C} can also be realized on drying with a desiccator. These experimental results indicate that a limited amount of adsorbed water in the gels functions as a solvent in which the Cu-cyclam molecules are almost free in tumbling motion, as in usual aqueous solutions. The word of "fluidity" often used here is just in this sense. The stop of tumbling motion of the incorporated molecules by evaporation of the adsorbed water may be possibly due to an adsorptive interaction of the molecules with some active sites on alumina interior walls. There was a close analogy between Cu-2,3,2-tet and Cu-cyclam in respect of behavior as dopants in alumina gels.

This work has first thrown light on an important property of adsorbed water in alumina gels such as fluidity. However, it is quite interesting that such a property could not be found for adsorbed water in silica gels at all,⁵⁾ suggesting that there are quite large differences in structure and function between alumina and silica gels.

References

- 1) S. Sakka and K. Kamiya, *J. Non-Cryst. Solids*, 42, 403 (1980); J. D. Mackenzie, *ibid.*, 48, 1 (1982); H. Dislich, *ibid.*, 57, 371 (1983).
- 2) D. Avnir, D. Levy, and R. Reisfeld, *J. Phys. Chem.*, 88, 5956 (1984); D. Avnir, V. K. Kaufman, and R. Reisfeld, *J. Non-Cryst. Solids*, 75, 395 (1985); V. R. Kaufman, D. Levy, and D. Avnir, *ibid.*, 82, 103 (1986); A. Makishima and T. Tani, *J. Am. Ceram. Soc.*, 69, C72 (1986).
- 3) A. C. Pierre and D. R. Uhlmann, *J. Non-Cryst. Solids*, 82, 271 (1986); J. C. Pouuxviel, J. P. Boilot, J. C. Beloeil, and J. Y. Lallemand, *ibid.*, 89, 345 (1987); B. Himmel, Th. Gerber, and H. Burger, *ibid.*, 91, 122 (1987).
- 4) G. F. Kokoszka and G. Gordon, "Technique of Inorganic Chemistry," ed by H. B. Jonassen and A. Weissberger, Interscience Publ., New York (1967), Vol. VII, p. 151; T. Vanngard and R. Aasa, "Paramagnetic Resonance," ed by W. Low, Academic Press, New York (1963), Vol. II, p. 509; R. Wilson and D. Kivelson, *J. Chem. Phys.*, 44, 4445 (1966).
- 5) H. Yokoi, S. Takano, F. Ozawa, and S. Ikoma, to be published.

(Received November 28, 1987)