A Magnetic Study of the Iron(III) Complexes of Polyols and Sugars in Aqueous Solution

Hiroshi Yokoi,* Yasuyoshi Mori, Tsuyoshi Mitani, and Satoshi Kawata†
Department of Applied Chemistry, Faculty of Engineering,
Shizuoka University, Hamamatsu 432
† Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
Hachioji-shi, Tokyo 192-03

(Received November 18, 1991)

Plots of the effective magnetic moment (μ_{eff}) of the iron(III) ion against pH for aqueous iron(III) ion solutions of 1,2-ethanediol, 1,3-propanediol, glycerol, D-glucitol, D-fructose, two oligo-sugars, poly(vinyl alcohol) (PVA), and methyl cellulose at various concentration ratios of polyols or sugars to the iron(III) ion ([iron(III) ion]=10.0 mM) at room temperature were obtained by the Gouy method. At low concentraion ratios, precipitation resulted at around neutral pH, where the concentration of polymers is expressed in terms of the monomeric residues. The pH range for precipitation became narrower as the ratio increased. However, the precipitates, once formed for the case of the former two diols, remained unchanged at any alkaline pH. During the course of the change in pH from 1 to 13, the μ_{eff} value in units of B.M. was initially ca. 6, but steeply decreased at around pH 2, and then leveled off at a constant value of ca. 3.6 in the pH range 3 to 10. It gradually rose to a value of 5—6 beyond pH 10 for the cases of glycerol, D-glucitol, and sugars. This fact, together with the ESR data obtained here, indicates that iron(III) ions exist as usual hydrated ions at pH 1—2, as some cluster like $Fe(OH)_3$ at pH 3—10, and mostly as mononuclear ions coordinated to the alcoholic OH groups at a stronger base pH.

Hydrated iron(III) ions are hydrolyzed at pH>2.5 to form a reddish-brown precipitate of $Fe(OH)_3$ or its analogue.[1] In the presence of poly(vinyl alcohol) (PVA), however, the solution of iron(III) ions similarly turns reddish-brown at the same pH, but remains transparent.[2-4] We have recently revealed that, in the above reddish-brown and transparent solution, ultrafine particles of $Fe(OH)_3$ or its analogue are solubilized by PVA, probably through a hydrophobic interaction,[3,4] as well as those of $Cu(OH)_2$ in transparent and green solutions of copper(II) ions and PVA.[4,5] On the other hand, it has been reported that iron(III) ions interact with excess sugars at the neutral or base pH to form soluble complexes,[6,7] in spite of the general belief that the alcoholic OH group has no ability to coordinate to metal ions in such a pH range.

The purpose of this work was to investigate the interaction of iron(III) ions with various polyols and sugars in aqueous or aqueous colloidal solutions in the pH range 1 to 13, mainly by magnetic susceptibility measurements at room temperature. Data concerning the conditions under which precipitates are formed in the above-mentioned solutions are also important in understanding the interaction.

Experimental

The polyols and sugars used were 1,2-ethanediol (ethyleneglycol), 1,3-propanediol, 1,2,3-propanetriol (glycerol), D-glucitol (D-sorbitol), D-fructose, two oligo-sugars (described below in detail), PVA (av. mol wt, 22000; the degree of saponification, ca. 98%), and methyl cellulose (viscosity, 80—120 cP (1 cP=10^{-3} Pa s) for 2% aqueous solutions at 20 °C). These reagents, except for the oligo-sugars, and various inorganic salts were of the highest grade and were used as received. The two oligo-sugars, which were a gift from Sanwa Denpun Kogyo Co., were mixtures of G_2, G_3, G_4, etc. synthesized by the enzymatic hydrolysis of starch; G_n expresses an oligo-saccharide consisting of n glucose units. Oligo-sugars A and B were 94.5 and 74.1% in the total content of G_n ($n \geqq 4$), and 20—40 and less than 10 cP in viscosity for 30% aqueous solutions at 30 °C, respectively.

Sample solutions for magnetic susceptibility, ESR, and optical absorption measurements were prepared by mixing aqueous solutions of $FeCl_3$ and polyol or sugar at various concentration ratios, and then adjusting the pH with NaOH or HCl without any buffer. R=[polyol]/[iron(III) ion] is defined here as being an experssion of the above-mentioned concentration ratio, although the concentration of oligo- and poly-saccharides and PVA is expressed in terms of the monomeric residues. [iron(III) ion] was 10.0 mM (1 M= 1 mol dm^{-3}) throughout this work, unless otherwise noted. Magnetic susceptibility measurements for aqueous solutions at room temperature were carried out by the Gouy method,[8] where the effective magnetic moments in units of B.M. were determined with an accuracy of better than 0.03. Frozen-solution ESR spectra were recorded at the temperature of liquid nitrogen with a JEOL JES-FE1XG ESR spectrometer.

Results and Discussion

Figure 1 shows plots of the effective magnetic moment (μ_{eff}) in units of B.M. against pH for typical PVA- and methyl cellulose–iron(III) ion systems. This figure also shows the same plot for the system of iron(III) ion alone, which becomes colloidal in the pH range 2.0 to 2.5, and forms a precipitate at pH>2.5; it is difficult to measure the magnetic susceptibility for inhomogeneous systems, such as precipitate-containing solutions. We succeeded in the magnetic susceptibility measurement of a $Cu(OH)_2$-precipitate slurry by the Gouy method.[9] The key to this measurement is to pack the slurry sample into a Gouy-balance sample tube homogeneously and accurately.

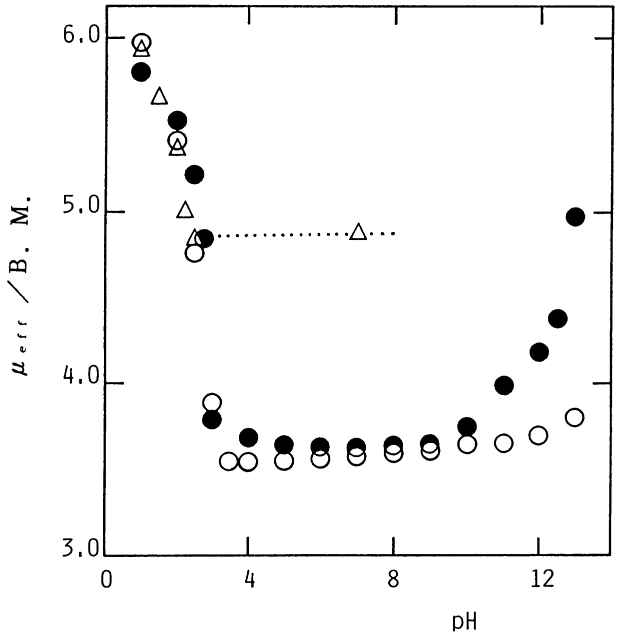

Fig. 1. Plots of μ_{eff} against pH for the aqueous iron(III) ion solutions of PVA at $R=20$ (○), of methyl cellulose at $R=10$ (●) and an aqueous solution of iron(III) ion alone (△). The last solution becomes colloidal at pH 2—2.5 and forms a precipitate at pH $\geqq 3$. The experimental point at pH 7 was obtained for a slurry of the precipitate prepared at the pH.

According to this method, we have measured the magnetic susceptibility for a $Fe(OH)_3$-precipitate slurry prepared at pH 7. The μ_{eff} value was thus determined as the average of four experiments; it is plotted at pH 7.0 in Fig. 1. This μ_{eff} value is very close to that of 4.73 reported by Au-Yeung et al. for a $Fe(OH)_3$ powder.[10] Interestingly, the μ_{eff} values at pH 2.5 and 7.0 in the figure are almost equal, suggesting that iron(III) ions in both states may be in almost the same magnetic and, hence, physico-chemical circumstances.

In Fig. 1, the system of iron(III) ion alone is similar to the other systems in the descending mode in the pH range 1 to 2.5. The latter system exhibit an almost constant μ_{eff} value (ca. 3.6) in the pH range 3 to 10. The μ_{eff} value expected for hydrated iron(III) ions at around pH 1 is close to a spin-only theoretical value of 5.92. In general, polynuclear high-spin iron(III) complexes with oxo, hydroxo, or alkoxo bridges have much smaller μ_{eff} values than 5.9, owing only to antiferromagnetic pairwise interactions between the iron(III) ions in the complexes.[11] All these facts strongly suggest that iron(III) ions in the PVA- and methyl cellulose-iron(III) ion systems form some aggregate, like $Fe(OH)_3$, in the pH range 3 to 10, as described in the introduction.[3,4]

Figure 2 shows plots of μ_{eff} against pH for D-sorbitol-iron(III) ion systems at three different R values, and the D-fructose-iron(III) ion system at $R=20$. This figure clearly demonstrates that, in the former systems, the pH range for precipitation becomes narrower as R increases. This tendency was observed for many other polyols and sugars. On the other hand, at the same R value (20), the pH range for precipitation is narrower for D-fructose than for D-sorbitol. This fact is consistent with the datum obtained by Charley et al.[6] concerning the relative ability for sugars to form complexes with iron(III) ion; D-fructose>D-sorbitol. Furthermore, the figure indicates that μ_{eff} is dependent to some degree upon R. This R dependence of μ_{eff} for D-sorbitol is summarized in Fig. 3 by plotting μ_{eff} against R at three different pH values.

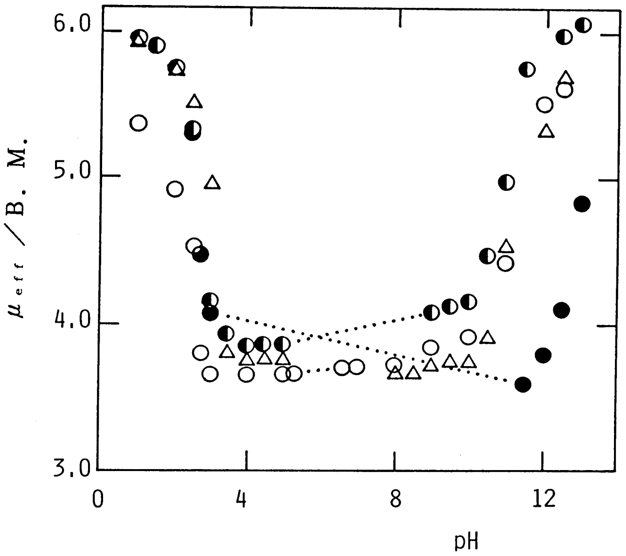

Fig. 2. Plots of μ_{eff} against pH for the aqueous iron(III) ion solutions of D-sorbitol (○, $R=150$; ◐, $R=20$; ●, $R=0.5$) and of D-fructose at $R=20$ (△). The dotted line in every plot for the D-sorbitol-iron(III) ion systems expresses the pH range in which precipitation results.

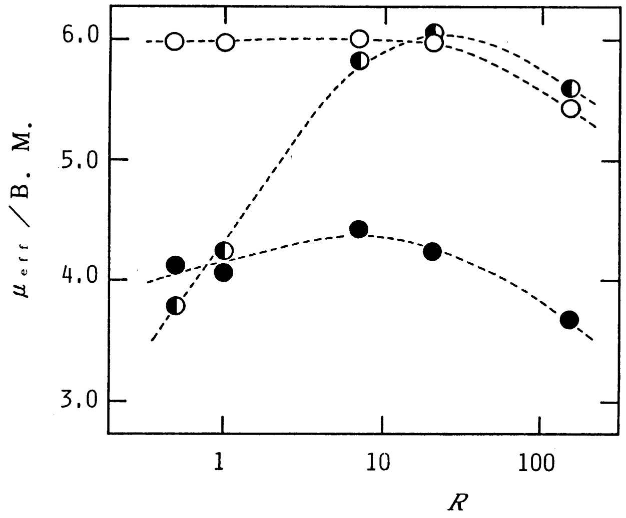

Fig. 3. R dependence of μ_{eff} for the aqueous solutions of iron(III) ion and D-sorbitol at three different pH values (○, pH 1; ●, pH 3; ◐, pH 12).

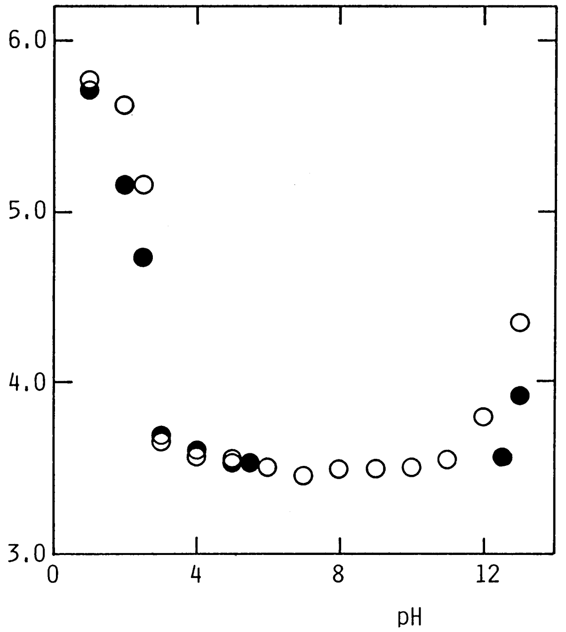

Fig. 4. Plots of μ_{eff} against pH for the aqueous iron(III) ion solutions of oligo-sugar A (○) and B (●) at R=20. In the case of oligo-sugar B, a precipitation is formed at pH $\gtrless$6, but redissolved at pH$>$12.

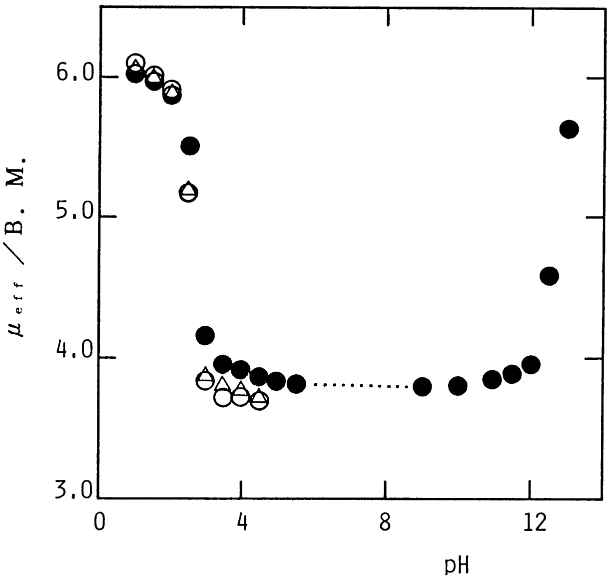

Fig. 5. Plots of μ_{eff} against pH for the aqueous iron(III) ion solutions of ethylene glycol (○), 1,3-propanediol (△), and glycerol (●) at R=100. The dotted line in the figure has the same meaning as those in Fig. 2.

The differences in μ_{eff} must reflect some difference in the structural circumstances of the iron(III) ion. Therefore, a change in μ_{eff} means the formation of another complex. At the present stage, however, there are no means for obtaining detailed structural information on complexes from only μ_{eff} data obtained at room temperature.

Plots of μ_{eff} against pH for oligo-sugar–iron(III) ion systems are shown in Fig. 4. Oligo-sugar B is smaller regarding the average degree of polymerization than is oligo-sugar A. No precipitation reaction occurred in any pH range for the system of oligo-sugar A at $R\geqq5$; precipitation resulted at pH$\gtrsim$6 for that of oligo-sugar B, even at R=20, even though this precipitate was dissolved at pH$>$12. These facts indicate that the ability of an oligo-sugar to form soluble complexes with iron(III) ion becomes higher with an increase in the degree of polymerization. Interestingly, the order of this ability for the oligo-sugars is in agreement with the order of strength in the adsorptive interaction with precipitated $Fe(OH)_3$.[12]

Figure 5 shows similar plots for ethylene glycol, 1,3-propanediol, and glycerol. For the former two diols, precipitates were produced at pH$>$5, even at a large R value of 100, and were never dissolved at pH$>$10. On the other hand, for glycerol at R=100, a precipitate was formed at pH$\gtrsim$6, but redissolved at pH$\geqq$9, accompanied by a remarkable increase in μ_{eff} at pH$\gtrsim$12. This difference between these diols and triol is of important significance, since all of the polyols or sugars which form soluble complexes at pH$>$10 formally have three neighboring OH groups, and are analogous to glycerol in this respect. For these polyols and sugars, except for PVA, μ_{eff} gradually increases with an increase in the pH beyond 10, as shown in Figs. 1, 2, 4, and 5. For certain polyols and sugars, the final μ_{eff} values at pH 13 reached to ca. 6, indicating that some kind of mononuclear high-spin iron(III) complexes are formed in these solutions, because an μ_{eff} value of ca. 6 is characteristic of almost all mononuclear high-spin iron(III) complexes and hydrated iron(III) ion.[13] ESR evidence has also been given regarding the formation of such mononuclear complexes, as is described below.

Frozen-solution ESR spectra have been measured for all of the systems mentioned above at various pH values. Their pH dependence was essentially the same, except for ethylene glycol, 1,3-propanediol, and PVA. The ESR spectra observed for the system of D-sorbitol at pH 1, 3, 10, 11, and 12 are shown as typical examples in Figs. 6A, B, C, D, and E, respectively. Such a spectral line-shape with an intense absorption at $g\cong4.2$ (Fig. 6 A) is very commonly observed for high-spin iron(III) ions in aqueous solutions with or without weak ligands.[14] This intense absorption is characteristic of the ^6S ground state of the iron(III) ion in a rhombic field, since absorption at ca. 0.15 T is expected by solving a spin Hamiltonian with the two zero-field splitting parameters D and E, if $E/D\cong1/3$ and $D>0.23\ cm^{-1}$. This intense absorption decreased in intensity with an increase in pH, and gradually changed to Fig. 6B at pH 3. Figures 6B and C show extremely broad ESR spectra, as if there were no ESR signals. This type of spectra are quite common for clusters of paramagnetic metal ions, between which there exists a strong pairwise spin-exchange interacton.[15]

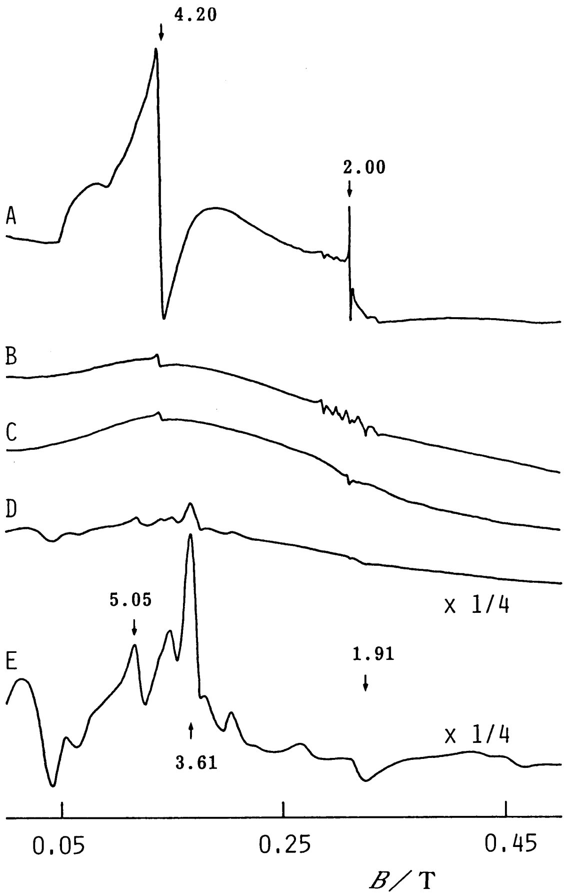

Fig. 6. Frozen-solution ESR spectra for the aqueous iron(III) ion solutions of D-sorbitol at R=20 at various pH values (measured at 77 K): A, pH 1; B, pH 3; C, pH 10; D, pH 11; E, pH 12. All of the spectra were observed at almost the same amplification degree of the spectrometer. The numbers in the figure express the g values at the spectral positions shown by arrows.

This ESR result at pH 3 and 10 is consistent with the above-mentioned μ_{eff} result; some iron(III) cluster is formed in this pH range. On the other hand, Figure 6 E is a very complicated ESR spectrum, probably due to two or more different iron(III) complex species, mainly comprising mononuclear high-spin iron(III) complexes.[16] The re-formation of mononuclear high-spin iron(III) complexes at pH≧12 for the system of D-sorbitol is strongly supported by the fact that $\mu_{\text{eff}} \geqq 5.9$ (Fig. 2). In general, however, the complete interpretation of such a complicated spectrum is very difficult at present.[16] Furthermore, ESR measurements at the temperature of liquid helium for this kind of sample system will be necessary for obtaining more accurate ESR information.

It is reasonably considered that, at pH>12, iron(III) ion directly coordinates to the alcoholic OH groups of polyols or sugars, similarly to the case of copper(II) ion.[17] For PVA, however, μ_{eff} remained almost unchanged at pH>10, indicating that the iron(III) ions in this system exist more stably as clusters than as mononuclear complexes, quite different from the case of copper(II) ions.[18] This propensity of the iron(III) ion is closely associated with the fact that 1,3-propanediol and ethylene glyocol do not form soluble complexes with the iron(III) ion at pH>10. In the interaction mode with the iron(III) ion at high pH, the above-mentioned two diols and PVA are clearly different from sugars and sugar alcohols.

A change in μ_{eff} for the iron(III) ion in solution indicates a structural change of its iron(III) complex, or in a shift in the equilibrium between iron(III) complexes with different μ_{eff} values; the structural details concerning these complexes are difficult to estimate from only the μ_{eff} data observed at room temperature. However, a plot of μ_{eff} against pH in an aqueous solution can be considered to be a sort of magnetic susceptibility titration curve, and, therefore, is a very useful to obtain new information concerning complex formation over a wide pH range, as shown in this work.

Thanks are given to Messrs. T. Takatani and H. Fujii for their assistance in the experimental work.

References

1) C. M. Flynn, Jr., *Chem. Rev.*, **84**, 31 (1984).

2) H. Shirai, Y. Nio, A. Kurose, S. Hayashi, and N. Hojo, *Nippon Kagaku Kaishi*, **1978**, 117.

3) H. Yokoi, K. Yagishita, Y. Mori, H. Matsumura, Y. Fujise, S. Kawata, and H. Sugiyama, *Macromolecules*, to be published.

4) H. Yokoi, "Kobunshi Sakutai (Dynamic Interactions and Electronic Processes of Macromolecular Complexes)," ed by E. Tsuchida, Japan Scientific Society Press, Tokyo (1991), p. 181.

5) H. Yokoi, S. Kawata, and M. Iwaizumi, *J. Am. Chem. Soc.*, **108**, 3358 (1986).

6) P. J. Charley, B. Sarkar, C. F. Stitt, and P. Saltman, *Biochim. Biophys. Acta*, **69**, 313 (1963).

7) L. Nagy, K. Burger, J. Kürti, M. A. Mostafa, L. Korecz, and I. Kiricsi, *Inorg. Chim. Acta*, **124**, 55 (1986).

8) R. L. Martin and A. Whitley, *J. Chem. Soc.*, **1958**, 1934.

9) H. Yokoi, S. Kawai, A. Kadowaki, and S. Ikoma, *Nippon Kagaku Kaishi*, **1989**, 872.

10) S. C. F. Au-Yeung, G. Dénès, J. E. Greedan, D. R. Eaton, and T. Birchall, *Inorg. Chem.*, **23**, 1513 (1984).

11) D. F. Harvey, C. A. Christmas, J. K. McCusker, P. M. Hagen, R. K. Chadha, and D. N. Hendrickson, *Angew. Chem., Int. Ed. Engl.*, **30**, 598 (1991), and references cited therein.

12) H. Yokoi, T. Tsutsui, Y. Mori, and T. Mitani, *Chem. Lett.*, **1991**, 2231.

13) E. König, "Magnetic Properties of Coordination and Organo-Metallic Transition Metal Compounds," Landolt-Börnstein Tables, New Series Group II, Vol. II, Springer-Verlag, Berlin (1966).

14) R. Aasa, B. G. Malmström, P. Saltman, and T. Vänngård, *Biochim. Biophys. Acta*, **88**, 430 (1964); P. Aisen, R. Aasa, B. G. Malmström, and T. Vänngård, *J. Biol. Chem.*, **242**, 2484 (1967); T. Caster, Jr., G. S. Newell, W. C. Holton, and C. P. Slichter, *J. Chem. Phys.*, **32**, 668 (1960); H. H. Wickman, M. P. Klein, and D. A. Shirley, *ibid.*, **42**, 2113 (1965); R. D.

Dowsing and J. F. Gibson, *ibid.,* **50**, 294 (1969).

15) E. A. Pinheiro, P. P. de Abreu Filho, F. Galembeck, E. C. da Silva, and H. Vargas, *Langmuir,* **3**, 445 (1987); G. Vierke, *J. Chem. Soc., Faraday Trans. 1,* **69**, 1523 (1973); L. Yarmus and A. A. Harkavy, *Phys. Rev.,* **173**, 427 (1968); T. G. Spiro, S. E. Allerton, J. Renner, A. Terzis, R. Bils, and P. Saltman, *J. Am. Chem. Soc.,* **88**, 2721 (1966).

16) D. Collison and A. K. Powell, *Inorg. Chem.,* **29**, 4735 (1990); E. A. Zhilinskaya, V. N. Lazukin, E. A. Bychkov, and I. L. Likholit, *J. Non-Cryst. Solids,* **119**, 263 (1990).

17) Y. H. Chao and D. R. Kearns, *J. Am. Chem. Soc.,* **99**, 6425 (1977); R. E. Reeves, *Adv. Carbohydr. Chem.,* **6**, 107 (1971).

18) H. Yokoi and A. Kadowaki, *Nippon Kagaku Kaishi,* **1988**, 209.