Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

Effect of Molecular Cage Size on the Motion and Coordination of Copper(2+) in Cross-Linked Poly(vinyl alcohol) and Poly(ethylene oxide) Gels: Electron Spin Echo and Electron Spin Resonance Studies

DARBHA SURYANARAYANA, P. A. NARAYANA, and LARRY KEVAN*

Received August 10, 1982

The structures of Cu^{2+}–water complexes in poly(vinyl alcohol) (PVA) and in poly(ethylene oxide) (PEO) gels with varying molecular cage sizes have been studied by electron spin resonance (ESR) and electron spin echo (ESE) modulation techniques. The ESE deuterium modulation of D_2O ligands of Cu^{2+} in PVA gels was analyzed with use of a Fourier transform technique combined with direct simulation of the echo modulation. The analysis indicates that the Cu^{2+} ion is coordinated to six D_2O ligands in PVA gels containing a relatively large molecular cage of an average diameter of 1.5 nm. The twelve deuterons surrounding the copper ion have an average distance of 0.30 nm with a hyperfine coupling of a_{iso} = 0.2 MHz. In PVA gels containing smaller molecular cages of 0.6-nm average diameter, Cu^{2+} is coordinated to only four D_2O ligands. Among these eight deuterons, four deuterons are at a distance of 0.30 nm with a_{iso} = 0.3 MHz, while the remaining four deuterons are at a distance of 0.35 nm with a_{iso} = 0.0 MHz. The ESE spectra for the smaller molecular cages of 0.6 nm normally show proton in addition to deuterium modulation. The proton modulation together with the reduction in the number of deuterons in the copper ligands suggests that Cu^{2+} is weakly bound to the PVA gel surface via hydroxyl groups in the smaller molecular cages. Two OH groups of PVA are suggested to be coordinated to the copper. The ESR spectra reveal that the Cu^{2+} is rapidly rotating in the 1.5 nm diameter cage, whereas its motion is hindered in the 0.6 nm diameter cage, even at room temperature. In addition to this, the four hyperfine components of the Cu^{2+} $a_{\|}$ feature in the ESR spectrum at 77 K reveal superhyperfine structure due to PVA gel protons for 0.6 nm diameter cages. However, for larger cage diameters, the ESR spectra at 77 K did not reveal such additional proton interactions. ESE studies of the Cu^{2+} ion in poly(ethylene oxide) (PEO) gels show results similar to those obtained in the PVA gels. Since there are no hydroxyl protons in the PEO gels, this indicates that the D_2O ligands attached to copper cause the ESE deuteron modulation. This suggests that the hydroxyl groups of PVA, even if partially deuterated by D_2O, do not contribute to the ESE modulation significantly.

Introduction

Zeolites are cage compounds that are among the most important sorbents and catalysts for a wide variety of chemical reactions. The catalytic properties of cation-exchanged zeolites are dependent on the nature, location, and hydration structure of the cations in the zeolite cages.[1] The general effect of molecular cage size on ion hydration geometry has been little studied on a molecular basis. We have recently shown that this question can be probed by using a VO^{2+} paramagnetic probe in polymeric molecular cages of variable size.[2] High-energy irradiation of polymers causes physical and chemical changes in their molecular structure, resulting in degradation as well as cross-linking.[3,4] The effect of cross-linking of poly(vinyl alcohol) (PVA) in H_2O brings about "gel" formation.[5] The polymer gel structure is considered to be made up of cubic cells or cages with an average edge $\bar{l}$. The average cage dimension $\bar{l}$ is taken as the average distance between nearest cross-links. By the assumption of random cross-linking and infinitely long chains of PVA the dimension may be calculated from

$$\bar{l}\ (\mathrm{nm}) = 0.25[(5.1 \times 10^8 + 1.37 \times 10^8 C)/R]^{1/2} \quad (1)$$

where C is the concentration of PVA in g/100 mL of H_2O and R is the total γ-irradiation dose in rads.[5] Thus, by controlling C and R it is possible to prepare PVA gels with various average cage dimensions. The distribution of $\bar{l}$ is estimated as ±15%, but it increases for smaller $\bar{l}$.[5]

It has been shown that metal ions and nitroxides can be doped in the molecular cages of PVA gels.[6–9] Thus, this is an attractive system for studying the effect of molecular cage size on ion hydration geometry. The PVA gel system also provides an approach for studying polymer–metal ion interactions. Numerous electron spin resonance (ESR) studies in this area have been reported,[10,11] but little detailed structural information has been obtained. To study the hydration structure or matrix interactions of a paramagnetic ion by ESR requires detection of very weak hyperfine interactions. ESR alone does not provide such information due to broad line widths. However, by the electron spin echo modulation (ESEM) technique,[12,13] it is possible to determine much weaker hyperfine interactions than is possible by ordinary ESR. The number of interacting nuclei and their distances from the paramagnetic center can be determined by ESEM.

In an electron spin echo experiment the spin system is subjected to a suitable microwave pulse sequence so that the individual spins dephase and rephase to form a burst of microwave energy called an echo. In a two-pulse experiment 90 and 180° pulses are applied separated by a time τ.[13] The echo appears at time 2τ after the first pulse and decays as a function of increasing τ. Often the echo decay is modulated when there are nearby interacting magnetic nuclei present in the system. Analysis of the modulation allows determination of the number (n), distance (r), and isotropic hyperfine splitting (a_{iso}) of the nearest nuclei.[13]

In the last several years, this technique has been applied to determine the solvation structure of trapped electrons, anions, cations, and atoms in frozen solutions.[14] Also this method has been successfully employed to study the location and ad-

---

(1) J. A. Rabo, Ed. "Zeolite Chemistry and Catalysis", ACS Monogr. No. 171, American Chemical Society, Washington, DC, 1976.

(2) D. Suryanarayana, P. A. Narayana, and L. Kevan, *J. Phys. Chem.*, **86**, 4579 (1982).

(3) B. Ranby and J. F. Rabek, "ESR Spectroscopy in Polymer Research", Springer-Verlag, New York, 1977.

(4) M. Dole, *J. Macromol. Sci., Chem.*, **A15**, 1403 (1981).

(5) A. Danno, *J. Phys. Soc. Jpn.*, **13**, 609, 614, 722 (1958).

(6) S. Fujiwara, K. Nagashima, H. Morita, and Y. Kanaoka, *Bull. Chem. Soc. Jpn.*, **50**, 2851 (1977).

(7) S. Fujiwara, S. Katasumata, and T. Seki, *J. Phys. Chem.*, **71**, 115 (1967).

(8) S. Fujiwara and Y. Fujiwara, *J. Phys. Soc. Jpn.*, **17**, 405 (1962).

(9) T. Watanabe, T. Yahagi, and S. Fujiwara, *J. Am. Chem. Soc.*, **102**, 5187 (1980).

(10) O. Sumita, A. Fukuda, and E. Kuze, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1801 (1978).

(11) A. K. St. Clair and L. T. Taylor, *J. Macromol. Sci., Chem.*, **A16**, 95 (1981).

(12) W. B. Mims in "Electron Paramagnetic Resonance", S. Geschwind, Ed., Plenum Press, New York, 1972, Chapter 4.

(13) (a) L. Kevan in "Time Domain Electron Spin Resonance", L. Kevan and R. N. Schwartz, Eds., Wiley-Interscience, New York, 1979, Chapter 8. (b) T. Ichikawa, L. Kevan, M. K. Bowman, S. A. Dikanov, and Yu. D. Tsevtkov, *J. Chem. Phys.*, **71**, 1167 (1979).

(14) L. Kevan, *J. Phys. Chem.*, **85**, 1628 (1981).

0020-1669/83/1322-0474$01.50/0

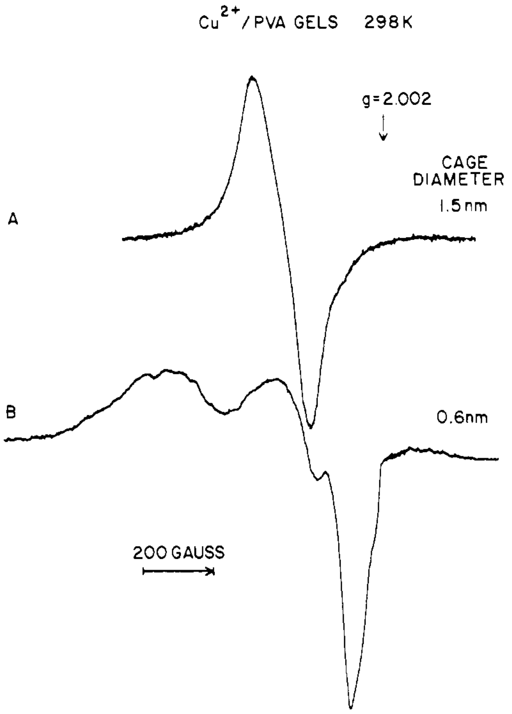


Figure 1. Room-temperature ESR spectra of the hydrated Cu^{2+} complex formed in PVA gels having molecular cage diameters of (A) 1.5 and (B) 0.6 nm.

sorbate interactions of paramagnetic probe ions on catalytic oxide surfaces[15,16] and the location of photoionized solubilized molecules in micelles.[17]

In the present investigation our previous studies of VO^{2+} in PVA gels[2] are extended to Cu^{2+} as a probe that has different water coordination numbers than VO^{2+}. Results are also presented for Cu^{2+} in poly(ethylene oxide) (PEO) gels. The PEO gel is of interest because it does not have the hydroxyl groups present in PVA gels and allows a test of the influence of hydroxyl groups on the motion of the hydrated Cu^{2+} in the molecular polymeric cages.

Experimental Section

Powdered PVA and PEO were obtained from Aldrich Chemical Co. Samples were prepared by dissolving 20 g of polymer in 100 mL of hot water. These samples were γ irradiated at room temperature in a Gammacell 220 containing ^{60}Co at a dose rate of 1.8 Mrd h^{-1}. PVA gels with average molecular cage diameters of 1.5–0.6 nm were prepared by varying the radiation dose from 5 to 100 Mrd. PEO gels were prepared similarly. Equation 1 does not apply quantitatively to PEO, but increasing the radiation dose will still decrease the average molecular cage size in PEO gels. Both PVA and PEO gel samples were soaked in 0.01 M aqueous solutions of $CuSO_4{\cdot}5H_2O$ overnight. The gel samples were thoroughly washed with distilled water and dried to remove surface moisture. The sample was then inserted into 4.0 mm o.d. Suprasil quartz tubes for ESR and ESE measurements.

ESR measurements were done on a Varian E-4 spectrometer. ESE spectra were recorded at 4.2 K with use of a home-built spectrometer.[18] In order to observe deuterium modulation in the ESE spectra, deuterated PVA and PEO gels were also prepared by radiation cross-linking of the polymers in D_2O followed by soaking in a deuterated solution of $CuSO_4{\cdot}5H_2O$. Both two-pulse and three-pulse ESE spectra[13] were recorded. The ESE spectra were stored on magnetic tape and were processed and simulated with use of a Tektronix 4052 minicomputer interfaced to a Honeywell 66/60 computer.

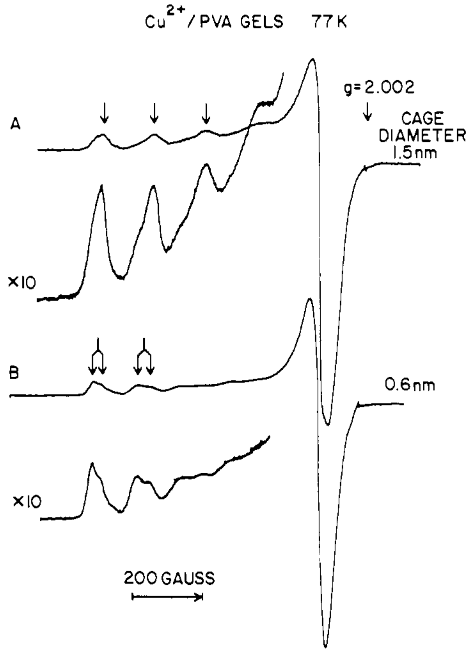


Figure 2. Liquid-nitrogen ESR spectra of the hydrated Cu^{2+} complex formed in PVA gels of cage diameters (A) 1.5 and (B) 0.6 nm. The vertical arrows indicate the positions of the $g_{\parallel}$ copper hyperfine lines.

Results

A. ESR Spectra of Cu^{2+} in PVA Gels. Room-temperature ESR spectra of Cu^{2+} in PVA gels with average cage diameters of 1.5 and 0.6 nm are given in Figure 1. The gel sample with a 1.5-nm cage shows a broad single line with a peak-to-peak separation of about 200 G and a nearly isotropic g value. In the gel sample with 0.6-nm cages, the ESR spectrum at room temperature is more complex and spreads over 1000 G. These spectra are attributed to cupric ion undergoing relatively "free" motion in the larger cage (1.5 nm) and being relatively "hindered" in the smaller cage (0.6 nm).

In Figure 2, we show the ESR spectra of 0.6 and 1.5 nm cage diameter deuterated PVA gel samples at 77 K. These spectra exhibit nearly the same line shapes with characteristic $g_{\parallel}$ and $g_{\perp}$ copper components. However, at higher sensitivity, the ESR spectrum of the 0.6 nm cage sample exhibits at least "doublet" splittings on the four hyperfine lines of the Cu^{2+} (see Figure 2B). In contrast, in the 1.5 nm cage sample the same Cu^{2+} hyperfine lines in the $g_{\parallel}$ region do not show any additional splitting (see Figure 2A). This suggests that the Cu^{2+} environment is much different in PVA gels with these two different cage sizes. In the smaller cages, one expects that the polymer chains are closer to Cu^{2+} than in the larger cages and a "metal–polymer" interaction becomes more probable. Hence we believe that the apparent "doublet" splittings of $\sim$20 G seen in Figure 2B can be interpreted as due to proton superhyperfine splitting originating from the OH groups of the polymer. The apparent doublet splitting is not well enough resolved to determine whether the interaction is to more than one matrix proton. Since the samples were prepared in D_2O, it appears that the hydroxyl protons in PVA gels are not easily exchangeable.

B. Electron Spin Echo Modulation of Cu^{2+} in PVA Gels. The experimental two-pulse ESE spectrum of Cu^{2+} in the PVA gel of 1.5 nm cage diameter, measured at 4.2 K, is given in Figure 3, where the echo intensity is plotted against the interpulse time. The spectrum exhibits deep modulation arising from nearby water deuterons in this gel sample. For a disordered system such as a glassy matrix or a polycrystal, the total modulation is obtained by averaging over all the angular orientations. The mathematical expressions for the two-pulse

---

(15) M. Narayana and L. Kevan, *J. Chem. Phys.*, **75**, 3269 (1981).
(16) T. Ichikawa and L. Kevan, *J. Am. Chem. Soc.* **103**, 5355 (1981).
(17) P. A. Narayana, A. S. W. Li, and L. Kevan, *J. Am. Chem. Soc.*, **103**, 3603 (1981).
(18) T. Ichikawa, L. Kevan, and P. A. Narayana, *J. Phys. Chem.*, **83**, 3378 (1979).

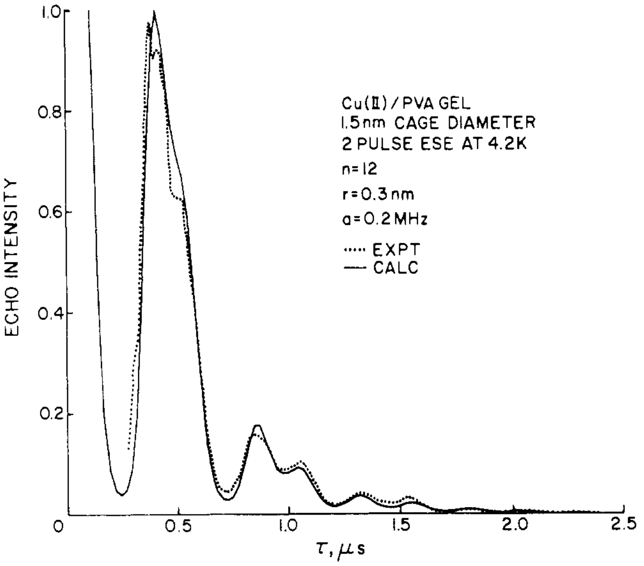


Figure 3. Comparison of the experimental (···) and simulated (—) two-pulse ESE deuterium modulation for Cu^{2+} in PVA gel, with a cage diameter of 1.5 nm. The experimental data were recorded at 4.2 K. For a direct comparison of the simulated and experimental data, the calculated normalized modulation is multiplied by the decay function: $\exp(3.23 - 3.03\tau + 0.20\tau^2)$.

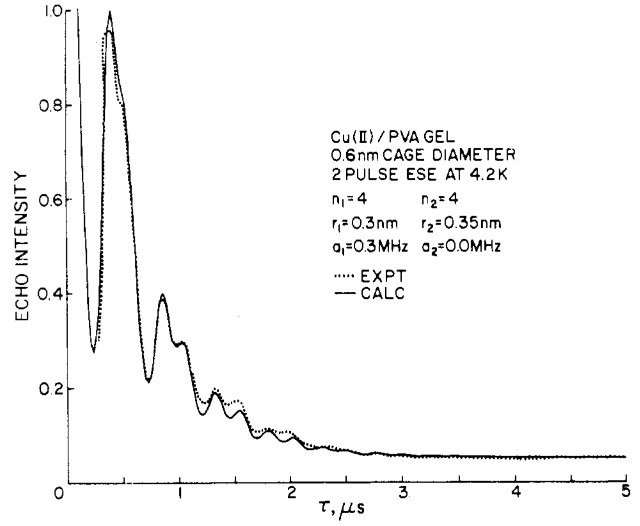


Figure 4. Comparison of the experimental (···) and simulated (~) two-pulse ESE deuterium modulation for Cu^{2+} in PVA gel having a cage diameter of 0.6 nm. The data were measured at 4.2 K. The simulated deuterium modulations were obtained with use of a two-shell model. For a direct comparison of the simulated and experimental data the calculated normalized modulation is multiplied by the decay function: $\exp(3.1 - 1.5\tau + 0.05\tau^2)$.

ESEM for $S = {}^1/_2$ and $I = 1$ have been reported earlier.[12,13] Simulations are made as a function of n equivalent nuclei at distance r and with isotropic hyperfine coupling a. The parameter n is constrained to be integral and can then be determined uniquely up to about $n = 10$ and to ±1 above that. The other parameters can be determined to better than 10%. Various two-pulse ESE simulations were performed by varying the parameters r, a, and n over a physically reasonable range. To facilitate direct comparison with the experimental modulation, we multiplied the simulated, normalized modulation by the decay function

$$V_{\mathrm{decay}} = \sum_{i=0}^{3} \exp(A_i \tau^i) \qquad (2)$$

where the A_i coefficients are given in the figure captions.

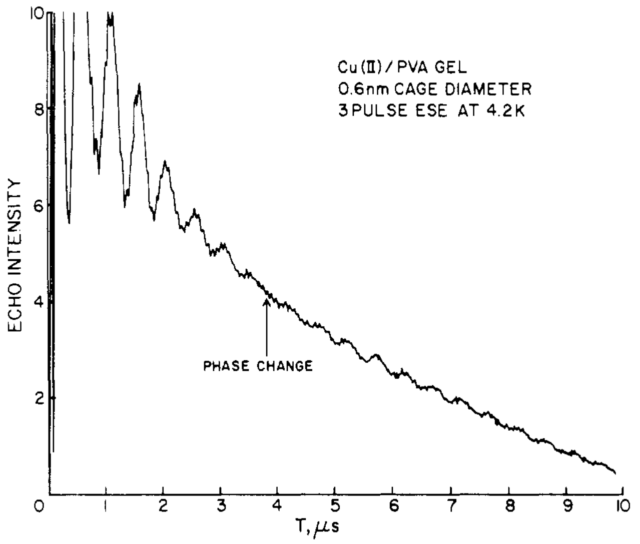


Figure 5. Three-pulse ESE deuterium modulation of Cu^{2+} in PVA gel having a cage diameter of 0.6 nm. The vertical arrow indicates the point where the phase change in the deuterium modulation is observed.

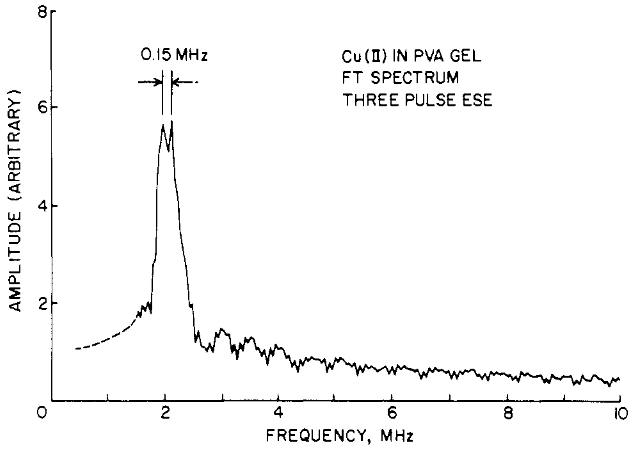


Figure 6. Fourier transform (FT) spectrum of the three-pulse ESE deuterium modulation of Figure 5. A decay function, $\exp(2.000 - 0.08\tau)$, is used to subtract the dc component in the FT spectral analysis.

The best fit shown in Figure 3 is obtained for 12 deuterons at 0.3 nm with an isotropic hyperfine coupling of 0.2 MHz. This implies six first-solvation-shell waters around Cu^{2+} if we make the reasonable assumption that the negative end of the water dipole is oriented toward Cu^{2+} so that the two water deuterons per molecule are at the same distance. Six waters indicates full solvation of Cu^{2+} as in bulk solution. Thus, in the relatively large 1.5 nm diameter molecular cages the Cu^{2+} is fully solvated.

In Figure 4, we give the two-pulse ESE spectrum of Cu^{2+} in a PVA gel of 0.6-nm cage diameter. Note that the deuteron modulation is not as deep and that the ESE signal decays more slowly than in Figure 3. This implies that the Cu^{2+} environment is significantly different in the smaller cage. A one-shell structural model will not fit the two-pulse ESEM results in Figure 4. Therefore, additional three-pulse ESE experiments[13] have been carried out. In a three-pulse ESE experiment the time between the first order pulses is held constant and the echo intensity is plotted against the time between the second and third pulses, T. A three-pulse ESE spectrum is shown in Figure 5. The three-pulse ESE spectrum shows a phase change at $T_p = 3.8$ μs. Narayana and Kevan[19] have earlier

---

(19) P. A. Narayana and L. Kevan, *J. Magn. Reson.*, **23**, 385 (1976).

shown that the phase change in the three-pulse ESEM is related to the distance to remote nuclei by

$$r\ (\text{nm}) = 0.1[10.7(T_p + \tau\ (\mu s))]^{1/3} \qquad (3)$$

We have recorded three-pulse echo envelopes for various values of τ in the range $0.3 \le \tau \le 0.7$ μs, and we have observed phase reversals in the range of 3.8–4.0 μs. When the appropriate values are put into eq 3, we obtain r = 0.34–0.36 nm. Simulations show that nuclei located at such a distance are too far to give rise to the deep modulation observed in the two-pulse echo envelope of Figure 4.

To gain information on closer nuclei, we have Fourier transformed[20] (FT) the three-pulse ESEM of Figure 5. The Fourier-transform spectrum shown in Figure 6 reveals a prominent peak centered at 2.20 MHz, which corresponds to the free precession frequency of deuterons. This corresponds to the distant deuterons with zero isotropic hyperfine coupling. The second peak occurs at 2.05 MHz; this is assigned to a closer set of deuterium nuclei with a small isotropic hyperfine coupling. For small isotropic hyperfine coupling one expects to see two peaks at $\omega_I \pm (a/2)$ in the FT spectrum, where ω_I is the free nuclear frequency. However, at short distances, typically less than 0.3 nm, only one peak is observed close to $\omega_I - (a/2)$. We therefore interpret the peak at 2.05 MHz as arising from closer deuterium nuclei with an isotropic hyperfine coupling of ~0.3 MHz.

Since the three-pulse ESE spectra indicate deuterium nuclei at two different distances, we have used a two-shell model to simulate the two-pulse ESE spectrum in Figure 4. With use of the far-deuteron distance and the close-deuteron isotropic hyperfine constant from the three-pulse ESE data the best fit of the two-pulse ESE data is found for $n_1 = 4$, $r_1 = 0.30$ nm, and $a_1 = 0.30$ MHz for the first shell and $n_2 = 4$, $R_2 = 0.35$ nm, and $a_2 = 0.0$ MHz for the second shell. The total of only eight deuterons in the first solvation shell indicates that Cu^{2+} is not fully solvated in the smaller 0.6 nm diameter molecular cage.

C. ESE Studies of Cu^{2+} in Poly(ethylene oxide) Gels. Poly(ethylene oxide) (PEO) with the formula $(-CH_2-CH_2-O-)_n$ also forms a gel after irradiation in aqueous solution. Although the molecular cage size has not been calibrated with respect to radiation dose as in PVA, it is clear from the ESR results that the qualitative dose dependences of PVA and PEO gels are similar. Thus "large" and "small" molecular cages in PEO gels can be prepared with the same doses used for PVA gels, but the actual magnitude of the average molecular cage diameter is uncertain.

In "large" PEO cages the ESR spectrum of Cu^{2+} is the same as in 1.5 nm diameter cages in PVA as shown in Figures 1 and 2. The two-pulse ESE spectrum is also the same as in Figure 3, which indicates a fully solvated cupric ion.

In "small" PEO cages the ESR spectrum of Cu^{2+} is similar to that in 0.6 nm diameter cages in PVA gels *except* that no multiplet structure is observed on the copper $g_\parallel$ hyperfine components. The two-pulse ESE spectrum of Cu^{2+} in small PEO cages is given in Figure 7. With use of the same procedure used in PVA the modulation pattern is best simulated by a two-shell model with the parameters given in Figure 7.

Discussion

Cupric ion in PVA gels has been studied previously by ESR.[6-9] In that work larger cage sizes of 10–2-nm diameter were investigated. In these quite large cages it was concluded that as many as eight hydrated copper ions occupied the same cage, giving rise to strong electron spin–electron spin dipolar interactions. As the cage size was reduced, the dipolar interactions decreased and the line widths narrowed.

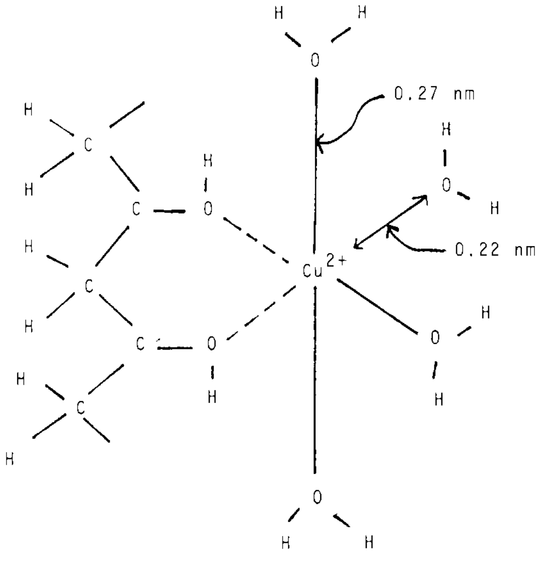
In the present study on molecular cages only large enough to contain one hydrated cupric ion, the focus is on the detailed cupric ion solvation structure. This is only possible by using the power of ESE modulation analysis. In the PVA gels with 1.5 nm diameter cages the ESE modulation results show that Cu^{2+} is solvated by six waters as in bulk aqueous solution. The broad isotropic ESR spectrum at room temperature indicates that this solvated ion is rotating more or less freely. However, at 77 K the anisotropic spectrum shows that this rotation is greatly hindered or stopped.

The ESE results give a Cu^{2+} to water deuteron distance of 0.30 nm. Assuming the geometry of molecular water and a water molecular dipole orientation toward Cu^{2+}, we obtain a Cu^{2+}–$O(H_2O)$ distance of 0.22 nm. This is slightly larger than the typical 0.20 nm found for Cu^{2+}–O distances in various complexes.[21]

In the smaller molecular cages of PVA with 0.6-nm diameter the ESR and ESE results are of even more interest. The room-temperature ESR spectra in Figure 1 show some anisotropy, indicating hindered rotation of solvated Cu^{2+} in this small cage. This is even more pronounced at 77 K in Figure 2. However, the most interesting observation is the multiplet splitting observed on the $g_\parallel$ hyperfine lines. This is interpreted as superhyperfine splitting due to hydroxyl protons on the PVA chains and suggests that Cu^{2+} may be coordinated in part to oxygens on PVA chains. Note that this superhyperfine splitting is not observed for Cu^{2+} in the larger 1.5 nm diameter cages (see Figure 2).

Nishide and Tsuchida[22] have very recently reported ligand superhyperfine ESR splitting for Cu^{2+} complexes in poly(4-vinylpyridine) resins for certain metal ion–ligand compositions. However, they could not determine a detailed structure from these data alone.

By using ESE modulation analysis, we can propose a detailed structure for Cu^{2+} in the small PVA cages. The results in Figure 4 indicate that Cu^{2+} interacts with two sets of four deuterons at different distances. This suggests that only four waters are coordinated to Cu^{2+} in the small cages in contrast to six in the large cages. The two different distances for the four waters argue against a square-planar or tetrahedral configuration, and the proton superhyperfine interactions indicate partial coordination to the PVA chains. Thus we suggest structure I in which two "axial" waters on a line



I

---

[20] P. A. Narayana and L. Kevan, *J. Magn. Reson.*, **46**, 84 (1982).

[21] B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

[22] H. Nishide and E. Tsuchida, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 835 (1981).

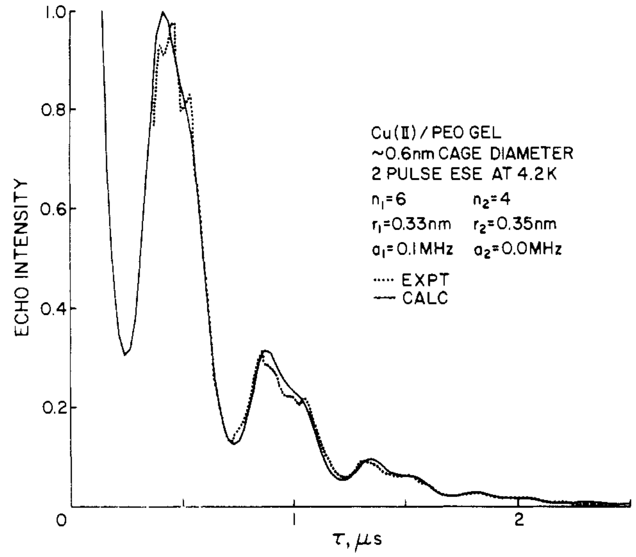
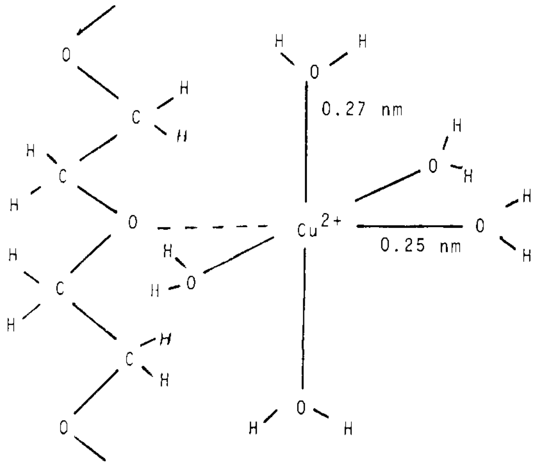


Figure 7. Comparison of the experimental (···) and simulated (—) two-pulse ESE deuterium modulation of Cu^{2+} in poly(ethylene oxide) (PEO) gel having a roughly estimated 0.6-nm cage diameter. The ESE experimental data were measured at 4.2 K. The deuteron modulation was analyzed with use of a two-shell model. A decay function, $\exp(3.46 - 2.4\tau + 0.05\tau^2)$, is used to directly compare with experiment.

perpendicular to the PVA chain have the larger coordination distance. Structure I has also recently been suggested qualitatively from ESR data alone.[23,24]

The ESR and ESE results on Cu^{2+} in PEO gels suggest a structural picture similar to that in the PVA gels. In "large" cages Cu^{2+} is coordinated to six waters at approximately equivalent distances and appears to be freely tumbling or rotating at room temperature but not at 77 K. In "small" cages Cu^{2+} is coordinated to only five waters, three with a Cu^{2+}–$O(H_2O)$ distance of 0.25 nm and two at a Cu^{2+}–$O(H_2O)$ distance of 0.27 nm. This distance difference is on the border line of experimental uncertainty. It is particularly significant that the ESR spectra at 77 K do not show any proton superhyperfine structure on the Cu^{2+} $g_\parallel$ components. This is expected since PEO has no hydroxyl groups. We suggest structure II for Cu^{2+} in small PEO molecular cages. Note that Cu^{2+} is expected to coordinate to only one oxygen on the PEO chain because two oxygens are not situated close enough for coordination to the same copper. This is consistent with our ESE result that five waters are coordinated to Cu^{2+}. This contrasts with structure I in PVA where two hydroxyl oxygens on the PVA chains are situated close enough for coordination to the same copper. In the PVA case the ESE results indicate Cu^{2+} coordination to only four waters. It appears that the ESR and ESE results are nicely self-consistent with the molecular structure of the PVA and PEO gels. It seems clear that cupric ion–polymer matrix coordination does occur if the molecular cages in the polymer matrices are small enough.



II

Acknowledgment. We thank the National Science Foundation and the Robert A. Welch Foundation for support of this research.

Registry No. Cu, 7440-50-8; PVA, 9002-89-5; PEO, 25322-68-3.

---

(23) O. Sumita, A. Fukuda, and E. Kuze, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1801 (1978).

(24) M. Takeishi, M. Veda, and S. Hayama, *Makromol. Chem., Rapid Commun.*, **2**, 167 (1981).