Solvation Structure of Manganese(II) Ion in Water-*N*,*N*-Dimethylformamide and Water-1,1,3,3-Tetramethylurea Mixed Solvents

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Abstract

The solvation structure of manganese(II) ion in water-*N*,*N*-dimethylformamide (DMF) and water-1,1,3,3-tetramethylurea (TMU) solvent mixtures has been studied by the extended X-ray absorption fine structure (EXAFS) method. It has been revealed that manganese(II) ion has a six-coordinate structure with the Mn-O length of 217(2) pm in water-DMF mixed solvents. In neat TMU, the coordination number of Mn(II) ion is five and the Mn-O length is 210(1) pm due to the bulkiness of a TMU molecule. Therefore, it is expected that the coordination number decreases from 6 to 5 with increasing TMU contents in water-TMU mixed solvents. Result of the EXAFS analysis indicates that the decrease of the coordination number with increasing mole fractions of TMU corresponds to the shortening of the Mn-O distance.

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1. Introduction

In two component solvent mixtures, an ion is solvated with two different kinds of solvent molecules. The solvent composition in the first coordination sphere of the ion may usually not be the same as that in the bulk. Such preferential solvation phenomena affect the reactivity of ion. When the solvation structure of a metal ion is discussed, knowledge on the total average coordination structure is necessary. EXAFS method is one of the most useful tools for the analysis of the first coordination sphere of metal ion in solution. By the EXAFS analysis, the solvation structure of Mn(II) in various solvents have been investigated, for example, water, DMF, *N*,*N*-dimethylacetoamide,[1] TMU,[2] methanol, ethanol, dimethyl sulfoxide,[3] acetonitrile, propionitrile,[4] hexamethylphosphoric triamide[5] and so on. Although a number of oxygen or nitrogen donor solvents form a six-coordination structure with manganese(II) ion in solution, the coordination number in TMU is five due to the bulky shape of TMU molecule. In this paper, results of XAFS study for the solvation structure of Mn(II) ion in water-DMF and water-TMU mixed solvents are discussed.

2. Experimental

Preparation of Sample Solutions

Manganese(II) perchlorate hydrate was prepared by dissolving the manganese carbonate in dilute perchloric acid and then recrystallized from water. Manganese(II) perchlorate DMF solvate was prepared by dissolving manganese(II) perchlorate hexahydrate crystals in DMF and recrystallized from DMF. The obtained crystals were dried at 40°C in a vacuum oven for several days and kept in a vacuum desiccator over P_2O_5. Manganese(II) perchlorate TMU solvates were prepared by the same method as the DMF solvates. The concentrations of Mn(II) ion in water-DMF and -TMU systems including neat DMF are 0.3 mol dm^{-3} while that in neat TMU is 0.1 mol dm^{-3}.

EXAFS Measurements and Data Analysis

EXAFS spectra of water-DMF solutions were measured around the Mn K-edge in the transmission mode using BL-4 at the SR center of the Ritsumeikan University. X-Rays were monochromatized by a Ge(220) double crystal monochromator. The measurements of water-TMU solutions were performed at BL-3 with a Si(220) monochromator.

The incident X-ray intensity, I_0, and the transmitted intensity, I, were simultaneously measured by the ionization chambers with lengths of 4.5 and 31 cm, filled with 85% N_2 + 15% Ar mixed gas and with 50% N_2 + 50% Ar gas, respectively.

A glass fiber filter was immersed to sample solutions and then sealed in a polyethylene bag in order to prevent evaporation of solvents. An effective jump at the absorption edge was obtained by changing the number of filters.

The normalized EXAFS oscillation function, $\chi_{\text{obsd}}(k)$, was Fourier transformed, and the structure parameters were determined using the radial distribution function. The model EXAFS oscillation function, $\chi_{\text{calc}}(k)$, is given as[6]

$$\chi_{\text{calc}}(k)=\sum_j S_0^2 n_j \frac{F_j(k)}{kr_j^2}\sin\bigl(2r_jk+\delta_j(k)\bigr)\exp\left(-2k^2\sigma_j^2-\frac{2r_j}{\lambda_j(k)}\right)$$

where $F_j(k)$ is the backscattering amplitude from each of n_j scatterers j at distance r_j from the X-ray absorbing atom, $\delta_{\square}(k)$ is the central- and backscattering-atom phase shift, σ_j^2 is the mean square fluctuation in r_j, $\lambda_j(k)$ is the mean free path of the photoelectron ejected, and S_0^2 is the overall amplitude reduction factor. The value of $F_j(k)$, $\delta_j(k)$, and $\lambda_j(k)$ were estimated using the FEFF program[7] by assuming the hypothetical cluster with a metal atom and six oxygen atoms. The vales of n_j, r_j, and σ_j^2 were optimized by fitting the model function to the observed curves in r-space using the ARTEMIS program.[8]

3. Results and Discussion

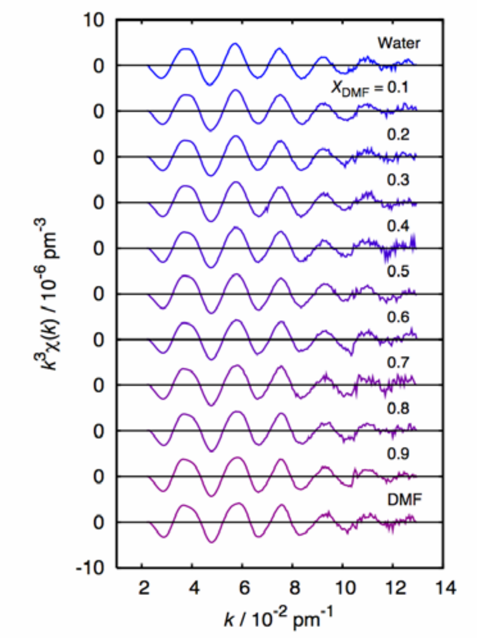

Fig. 1 The extracted EXAFS oscillations in the form of $k^3\chi(k)$ for Mn(II) ion in water-DMF solvents.

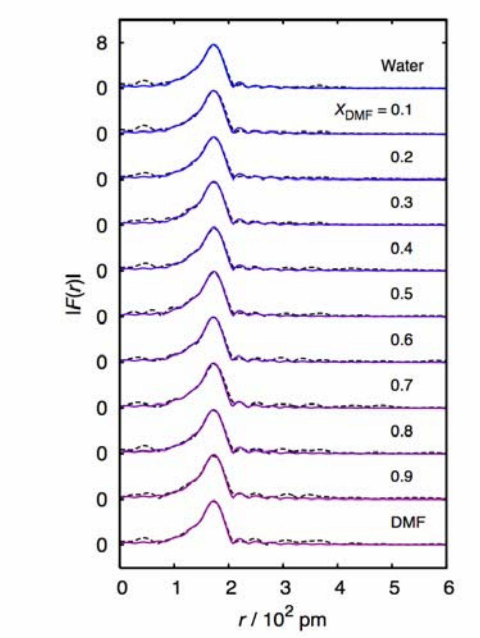

Fig. 2 The radial structure functions |$F(r)$| for Mn(II) ion in water-DMF solvents, phase shift uncorrected. The dashed lines are obtained experimentally, and the solid lines are calculated.

The extracted EXAFS oscillations of Mn(II) in the water-DMF solvents are shown in Fig. 1. The phase and amplitude of each curve are similar, although the shape at k = 3 to 6 × 10^{-2} pm^{-1} slightly differs. Figure 2 shows the radial structure functions obtained by Fourier transforming the curves in Fig. 1. The shape and position of the first intense peaks are similar and other distinct peaks are not observed. The structural parameters determined for the first coordination shell are listed in Table 1. The obtained n and r values show that the solvated structure of Mn(II) ion in water-DMF mixtures is six-coordinate and the Mn-O distance is 217(2) pm on average at all mole fractions.

Table 1 Structural parameters for Mn(II) in water-DMF mixtures[a]

	n	r / pm	σ^2 / 10 pm^2
Water	6[b]	217(1)	6(1)
X_{DMF} = 0.1	5.9(0.4)	216(1)	6(1)
0.2	5.9(0.5)	217(1)	6(1)
0.3	5.9(0.5)	217(1)	6(1)
0.4	5.8(0.5)	217(1)	6(1)
0.5	6.0(0.4)	217(1)	6(1)
0.6	5.7(0.3)	216(1)	5(1)
0.7	5.8(0.4)	216(1)	5(1)
0.8	5.9(0.4)	216(1)	6(1)
0.9	5.9(0.5)	216(1)	6(1)
DMF	5.7(0.4)	216(1)	6(1)

[a] The standard deviations are given in parentheses.

[b] The value was kept constant during the least-squares calculations.

The normalized X-ray absorption near edge structure (XANES) spectra for the water-TMU solutions are shown in Fig. 3. The background absorption in a raw spectrum of manganese was estimated by fitting the Victoreen formula in the pre-edge region and was subtracted from the total absorption by extrapolation. Then, the obtained absorption spectrum was normalized by dividing by the absorbance value at 7000 eV. Figure 4 shows a plot of the normalized absorbance at 6550.6 eV against mole fraction, which indicates the solvation environment of Mn(II) ion differs at a high X_{TMU} region. The EXAFS spectra

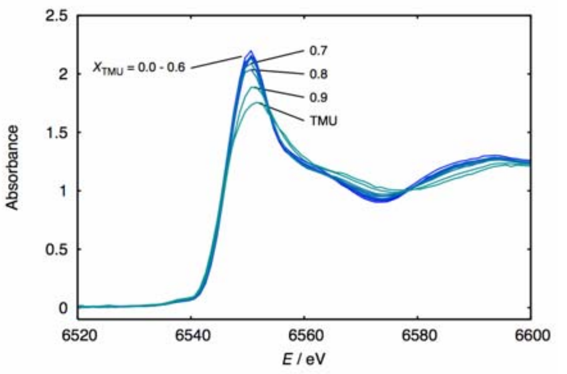

Fig. 3 The normalized XANES spectra of Mn(II) ion in water-TMU solvents.

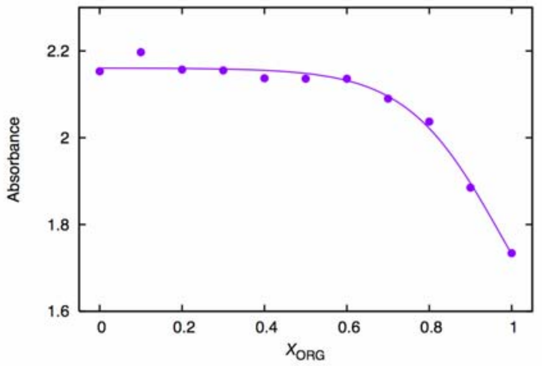

Fig. 4 The change of absorbance at 6550.6 eV of the absorbance shown in Fig. 3.

weighted by k^3 of the water-TMU system and their Fourier transforms are shown in Figs. 5 and 6, respectively. The structure parameters are listed in Table 2, and the coordination numbers and the Mn-O distances are plotted in Figs. 7 and 8, respectively.

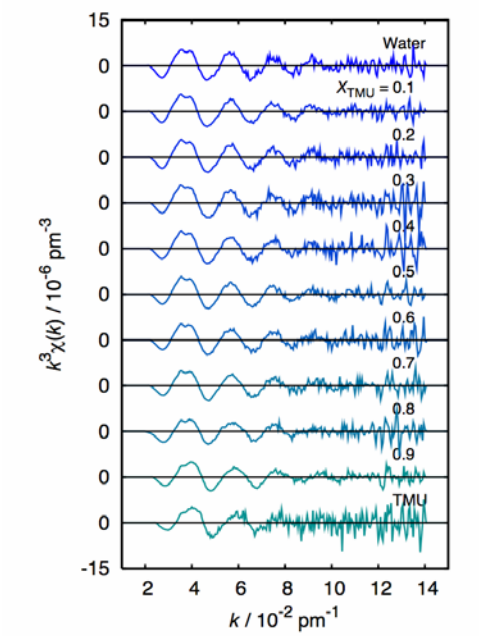

Fig. 5 The extracted EXAFS oscillations in the form of $k^3\chi(k)$ for Mn(II) ion in water-TMU solvents.

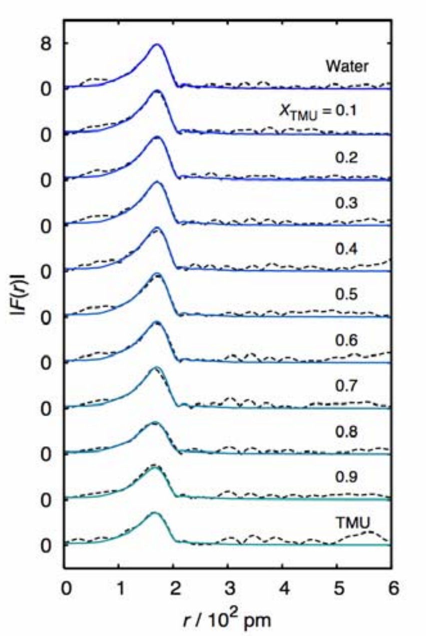

Fig. 6 The radial structure functions $|F(r)|$ for Mn(II) ion in water-TMU solvents, phase shift uncorrected. The dashed lines are experimentally obtained ones, and the solid lines are calculated ones.

Table 2 Structural parameters for Mn(II) in water-TMU mixtures[a]

	n	r / pm	σ^2 / 10 pm^2
Water	6[b]	217.6(0.3)	8.9(0.4)
X_{TMU} = 0.1	6.0(0.2)	217.8(0.2)	9.4(0.5)
0.2	6.1(0.3)	217.7(0.3)	9.3(0.6)
0.3	6.1(0.3)	217.8(0.2)	8.9(0.6)
0.4	6.1(0.3)	217.7(0.3)	9.6(0.7)
0.5	5.9(0.3)	217.5(0.2)	9.3(0.6)
0.6	5.8(0.4)	217.2(0.4)	9.4(0.9)
0.7	5.6(0.3)	216.2(0.3)	9.9(0.8)
0.8	5.3(0.5)	215.7(0.5)	11.7(1.3)
0.9	5.0(0.5)	212.4(0.5)	10.0(1.2)
TMU	4.8(0.7)	210.4(0.8)	10.5(2.1)

[a] The standard deviations are given in parentheses.

[b] The value was kept constant during the least-squares calculations.

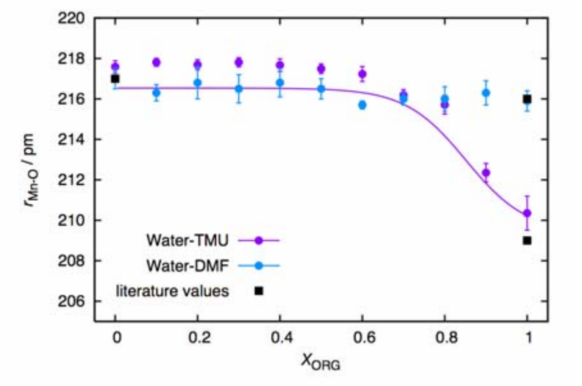

Fig. 7 The Mn-O distances obtained by EXAFS analysis. Filled squares show the values from refs. 1 and 2.

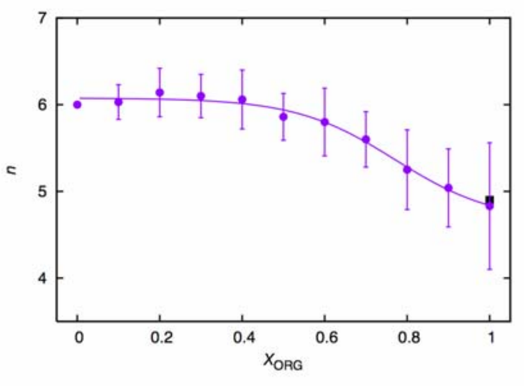

Fig. 8 The coordination number of Mn(II) in the water-TMU solutions. Filled square shows the value from ref. 2.

The Mn-O distance and the coordination number show that Mn(II) ion has a six-coordination structure from X_{TMU} = 0.1 to 0.6 as seen in Fig. 7. Over the TMU mole fraction of 0.7, the Mn-O distance gradually shortens to 210 pm at X_{TMU} = 1.0. This tendency fairly well correspond to that of the coordination number (Fig. 8) and the obtained XANES spectra (Fig. 4).

In conclusion, the solvation structure of Mn(II) ion in water-DMF solution is kept to be six-coordination with the Mn-O distance of 217(2) pm. In water-TMU solution, the coordination number of Mn(II) begins to decrease around at X_{TMU} = 0.7 and finally becomes five in the TMU solution.

References

(1) K. Ozutsumi, M. Koide, H. Suzuki, and S. Ishiguro, *J. Phys. Chem.*, **1993**, *97*, 500.

(2) Y. Inada, K. Sugimoto, K. Ozutsumi, and S. Funahashi, *Inorg. Chem.*, **1994**, *33*, 1875.

(3) Y. Inada, H. Hayashi, K. Sugimoto, and S. Funahashi, *J. Phys. Chem. A*, **1999**, *103*, 1401.

(4) Y. Inada, T. Sugato, K. Ozutsumi, and S. Funahashi, *Inorg. Chem.*, **1998**, *37*, 1886.

(5) K. Ozutsumi, Y. Abe, R. Takahashi, and S. Ishiguro, *J. Phys. Chem.*, **1994**, *98*, 9894.

(6) J. J. Rehr, R. C. Albers, *Rev. Mod. Phys.*, **2000**, *72*, 621.

(7) S. I. Zabinsky, J. J. Rehr, A. Ankudinov, R. C. Albers, and M. J. Eller, *Phys. Rev. B*, **1995**, *52*, 2995.

(8) B. Ravel and M. Newville, *J. Synchrotron Radiat.*, **2005**, *12*, 537.