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An X-Ray Diffraction Investigation of the Coordination Structure of Mn(II) Ions in Highly Concentrated Aqueous $MnBr_2$ and $MnCl_2$ Solutions

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The solute structures of highly concentrated aqueous 5.087 and 2.744 mol dm^{-3} $MnBr_2$, and 4.744 and 2.732 mol dm^{-3} $MnCl_2$ solutions were determined by the analysis of the radial-distribution function curves of X-ray diffraction experiments. Mixed-ligand aquahalogenomanganese(II) complexes were found to be present in these solutions, holding a distorted octahedral geometry. The interatomic distances of the aquabromo complex are 2.178—2.184 Å for Mn-OH_2 and 2.596—2.643 Å for Mn-Br; those of the aquachloro complex are 2.183—2.185 Å for Mn-OH_2 and 2.492—2.496 Å for Mn-Cl. The interatomic distances of Mn-OH_2 are shorter than those of the $MnBr_2\cdot 4H_2O$ and $MnCl_2\cdot 4H_2O$ crystals and are consistent with those of the $Mn(OH_2)_6(NO_3)_2$ crystal. The length of the Mn-Cl bond here determined is practically the same as that within the $MnCl_2\cdot 4H_2O$ crystal, but the Mn-Br bond found is shorter than that within the $MnBr_2\cdot 4H_2O$ crystal. The average coordination number of the Mn-Br contact per Mn(II) increased from 1.104 to 1.212 with an increase in the Br/Mn ratio from 2.076 to 3.269, while the number of the Mn-Cl contact per Mn(II) increased from 1.259 to 1.501 with an increase in the Cl/Mn ratio from 2.000 to 3.352. In all solutions, the aquamonohalogeno and aquadihalogeno complexes exist as the main species, but the aquadihalogeno complex is more dominant in the $MnCl_2$ solution than in the $MnBr_2$ solution.

The aquahalogenomanganese(II) complex in octahedral environments has a very characteristic visible spectrum which gives rise only to spin-forbidden d-d transitions. As its most striking feature is the extreme weakness of the bands, spectroscopic investigations of solution equilibria must be done in highly concentrated solutions, although the solutions may be more or less contaminated by impurities.[1,2] Therefore, the equilibrium constants, e.g., K_1, range from 0.14—3.89 mol^{-1} dm^3 for the aqueous ca. 1 mol dm^{-3} $MnCl_2$ solution and from 0.08—1.86 mol^{-1} dm^3 for the aqueous ca. 1 mol dm^{-3} $MnBr_2$ solution.[5] Thus, a "hard" element, manganese, is placed at different positions in the order of hardness by different investigations.[6]

The results of the X-ray crystal structural analysis of $MnCl_2\cdot 4H_2O$ and $MnBr_2\cdot 4H_2O$ show that manganese(II) in the crystals exists as a *cis*-dihalogenotetraaqua complex. In this paper, in oder to determine the structures of aquahalogeno complexes of the manganese(II) ion and the coordination number of manganese(II), and also in order to show the difference in the structures with different bases, such as Br and Cl, an X-ray diffraction investigation has been carried out in highly concentrated aqueous $MnBr_2$ and $MnCl_2$ solutions.

Experimental

All the reagents were of a reagent-grade and were obtained from Wako Pure Chemical Industries.

Aqueous Manganese(II) Bromide Solutions. Manganese(II) bromide was prepared by crystallizing the Mn(II) bromide obtained by dissolving $MnCO_3$ with a purified aqueous hydrobromic acid solution. The Br-1 sample solution was prepared by dissolving the manganese(II) bromide in degasified distilled water. The Br-2 sample solution was prepared by dissolving the manganese(II) bromide in a purified aqueous hydrobromic acid solution and by then diluting the solution with degasified distilled water.

Table 1. Solution Composition (mol dm^{-3}) and the Stoichiometric Volume V per Manganese Atom in Solutions

Solution	Br-1	Br-2	Cl-1	Cl-2
Mn	5.087	2.744	4.744	2.732
X	10.56	8.971	9.488	9.157
H_2O	42.19	44.52	46.08	46.64
ρ/g cm^{-3}	1.859	1.673	1.445	1.319
μ/cm^{-1}	76.68	63.40	13.90	9.923
V/Å^3	326.4	605.2	350.0	607.9

ρ: Density; μ: linear absorption coefficient of the solutions for Mo $K\alpha$ radiation.

Aqueous Manganese(II) Chloride Solutions. The Cl-1 and Cl-2 sample solutions were prepared in ways similar to those described in the preceding section.

The results obtained in the manganese(II) bromide system were compared with those of Fe(II) and Co(II) systems reported in our previous paper.[9] Furthermore, Br-1 and Cl-1 solutions are saturated solutions; thus, the coordination structures of the Mn(II) complexes in the solution may be compared with those in the $MnBr_2\cdot 4H_2O$ and $MnCl_2\cdot 4H_2O$ crystals respectively.

The concentrations of manganese(II) and halide ions in the solutions were determined by EDTA titration and the Volhard method respectively. The composition of the sample solutions is shown in Table 1.

X-Ray Diffraction Measurements and Data Treatments. X-Ray diffraction measurements were carried out under an N_2 atmosphere; the N_2 gas was purified by passing it through an alkaline pyrogallol.[9] The scattered intensities were measured at every 0.5° from θ=70° to 36°, at every

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0.25° from 36° to 18°, and at every 0.1° from 18° to 0.5°; 2θ was the scattering angle. The time required for accumulating 40000 counts was recorded for the Br-2 and Cl-2 solutions, and that for accumulating 80000 counts, for the Br-1 and Cl-1 solutions. The measurements and the treatment of the diffraction intensity data were carried out in the same way described in a previous paper.[10]

The radial distribution function $D(r)$ is given in Eq. 1;

$$D(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^{15} s\cdot i(s)\cdot M(s)\cdot \sin(r\cdot s)\cdot \mathrm{d}s, \tag{1}$$

where ρ_0 is the average scattering density of the sample solution and is given in the electron unit, and where s is equal to $4\pi\sin\theta/\lambda (\lambda=0.7107\,\text{Å})$. The modification function, $M(s)$, was the same as that employed previously. The intensities due to the interatomic interactions were:

$$i(s)_{\text{calcd}} = \sum_i \sum_j^{i\neq j} n_{ij}\cdot f_i(s)\cdot f_j(s)\frac{\sin(r_{ij}\cdot s)}{r_{ij}\cdot s}\exp(-b_{ij}\cdot s^2), \tag{2}$$

where $f_i(s)$ and $f_j(s)$ are the atomic scattering factors of the i and j atoms; n_{ij}, r_{ij}, and b_{ij} are, respectively, the frequency factor, the distance, and the temperature factor of the interaction between the i and j atoms.

In order to attain more precisely the structure parameter values, the above parameter values were refined by the least-squares refinement so as to minimize the difference between $i(s)_{\text{calcd}}$ and observed $i(s)$.

Results

Aqueous Manganese(II) Bromide Solutions. The radial-distribution function curves, $D(r)$ and $D(r)$-$4\pi r^2\rho_0$ of the Br-1 and Br-2 solutions are shown in Figs. 1 and 2. The radial distribution curve of the Br-1 solution and that of each atom-pair in it are depicted in Fig. 3. Four peaks are seen in the curves at ca. 1.0, 2.2, 2.7, and 3.5 Å; these are probably closely connected with intra- and inter-molecular atomic interactions of the solute complex and solvent H_2O molecules. The distance of the first peak at 1.0 Å is consistent with that of the O–H bond in water molecules.[11] The second peak at 2.2 Å can be ascribed to the Mn–O interaction in the solute complexes, the distance having been reported in the aqueous solution of 2.612 mol dm^{-3} $Mn(ClO_4)_2$.[12] The peak at 2.7 Å may be attributed to the Mn–Br interaction, because the distance is very close to the sum of the ionic radii of Mn^{2+} and Br^-, i.e., 2.79 Å {=0.970 Å(Mn^{2+})+1.82 Å(Br^-)};[13] the distance is also close to the values of 2.802 and 2.913 Å in the $MnBr_2\cdot 4H_2O$ crystal.[8]

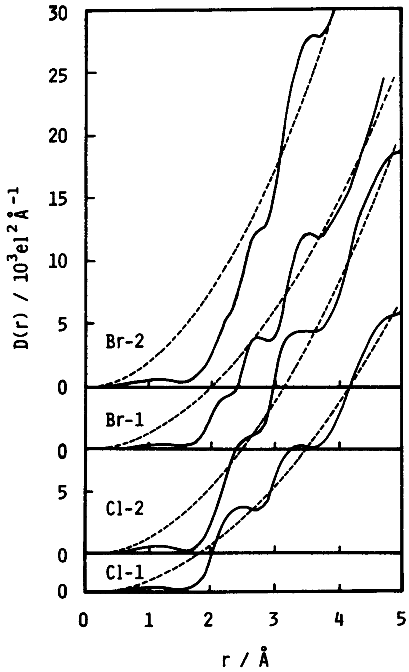

Fig. 1. The radial distribution curves, $D(r)$, for Br-1, Br-2, Cl-1, and Cl-2 solutions. The curves of $4\pi r^2\rho_0$ are shown by dashed lines.

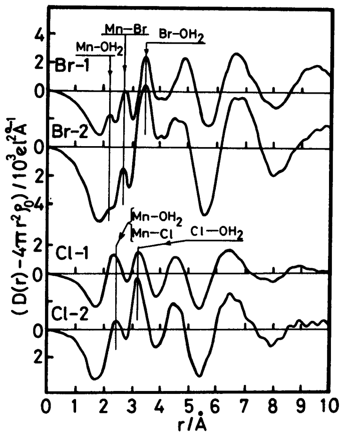

Fig. 2. The $D(r)$-$4\pi r^2\rho_0$ curves of Br-1, Br-2, Cl-1, and Cl-2 solutions.

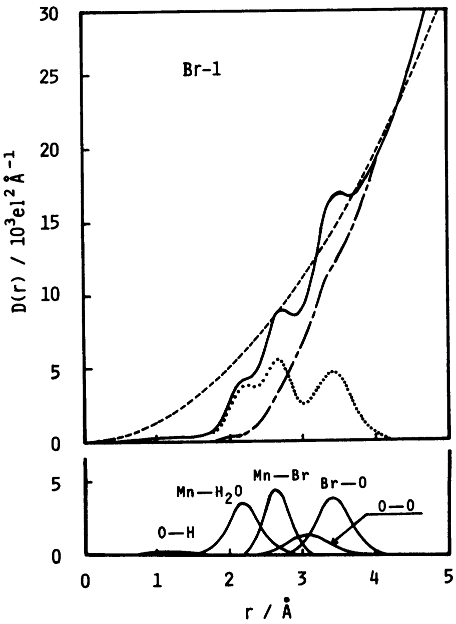

Fig. 3. The residual (——–) $D(r)$ curves obtained by subtracting calculated $D(r)$ curves (······) from observed $D(r)$ curve (——) for solution Br-1.

The peak at 3.5 Å can be attributed to the Br–OH_2 interaction, because no comparable peak in this region on the radial-distribution curves is observed for the aqueous 2.612 mol dm^{-3} $Mn(ClO_4)_2$ solution, while a clear peak due to the Br–OH_2 interaction is observed at 3.4 Å for the aqueous 2.5 mol kg^{-1} LiBr solution.[14)]

Aqueous Manganese(II) Chloride Solutions. The radial-distribution function curves, $D(r)$ and $D(r)-4\pi r^2\rho_0$, of the Cl-1 and Cl-2 solutions are shown in Figs. 1 and 2. The radial-distribution curve of the Cl-1 solution and that of each atom-pair are shown in Fig. 4. Three peaks are seen in these curves at ca. 1.0, 2.5, and 3.3 Å. The first peak is also consistent with that of the O–H bond in water molecules.[11)] The second peak at 2.5 Å may include the Mn–OH_2 and Mn–Cl interactions, because this peak shifted to longer distance with an increase in the concentration of chloride ions, and the position of this peak is close to the sum of the ionic radii of Mn^{2+} and Cl^-, i.e., 2.64 Å{=0.97 Å(Mn^{2+})+1.67 Å(Cl^-)},[13)] and it is close to the values of 2.475 and 2.500 Å of Mn–Cl in the $MnCl_2 \cdot 4H_2O$ crystal.[7)] The Mn–OH_2 interaction observed in the aqueous 2.612 mol dm^{-3} $Mn(ClO_4)_2$ solution at 2.20 Å[12)] also appears in the $MnCl_2 \cdot 4H_2O$ crystal at 2.22—2.19 Å. Therefore, the peak at 2.5 Å may tentatively be ascribed to the sum of those of the Mn–Cl and Mn–OH_2 interactions.

The peak at 3.3 Å can be ascribed to the Cl–OH_2 interaction, because no comparable peak in this region on the $D(r)$ curve is observed for the aqueous 2.612 mol dm^{-3} $Mn(ClO_4)_2$ solution,[12)] but a clear peak due to the Cl–OH_2 interaction is observed at 3.2 Å for the aqueous LiCl solution (mole ratio H_2O: LiCl=3).[15)]

From the above considerations, the parameter values on the interatomic distances and frequency and temperature factors of these interactions have been refined. The final parameters are listed in Table 2.

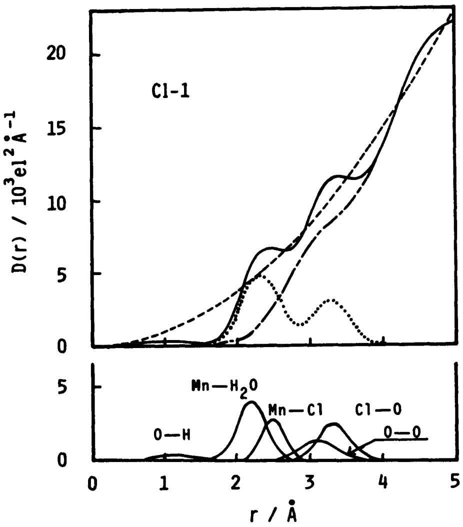

Fig. 4. The residual (– – –) $D(r)$ curve obtained by subtracting calculated $D(r)$ curve (······) from observed $D(r)$ curve (——) for solution Cl-1.

Discussion

Figures 5 and 6 show that the $s \cdot i(s)$ curves calculated from these final data are in good agreement with the observed $s \cdot i(s)$ curves in the region above $s > 5$ Å^{-1}. Calculations for the $s \cdot i(s)$ curves made by taking into consideration the Br(Cl)–Br(Cl) or Br(Cl)–H_2O interactions within the *cis*- or *trans*-dihalogeno complexes of manganese(II) did not appreciably improve the results. However, the final data for intramolecular interactions are, we believe, reliable enough, because we obtained smooth background curves in the radial-distribution curves of Br-1 and Cl-1 in the $r < 3$ Å region; the disagreement found in the $s \cdot i(s)$ curves of the sample solutions at $s < 5$ Å^{-1} is, therefore, due to long-range interactions which we did not take into account in the present calculation.

Aqueous Manganese(II) Bromide Solutions. Since the frequency factors, that is, the mean coordination numbers, n, of Br^- to Mn(II) for Br-1 and Br-2 solutions of Table 2 are 1.104 and 1.212 respectively, not only the monobromoaqua complex but also higher-

Table 2. Results of the Least-Squares Refinement of Solutions

Interaction	Parameter	Br-1	Br-2	Cl-1	Cl-2
Mn–O	r	2.178	2.184	2.185	2.183
	b	0.0045	0.0051	0.0049	0.0047
	n	4.986	4.809	4.654	4.444
Mn–X	r	2.643	2.596	2.492	2.496
	b	0.0050	0.0055	0.0052	0.0049
	n	1.104	1.212	1.259	1.501

X: Br, Cl; r: bond distance, Å; b: temperature factor, Å^2; n: frequency factor.

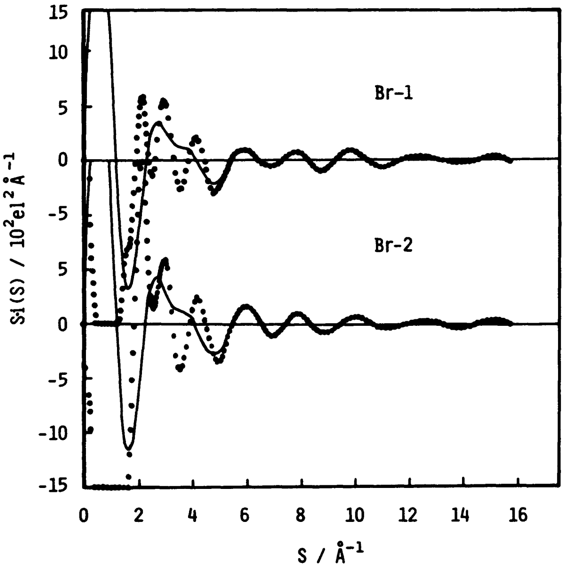

Fig. 5. Observed (ooooooo) and calculated (——) $s \cdot i(s)$ curves for solutions Br-1 and Br-2.

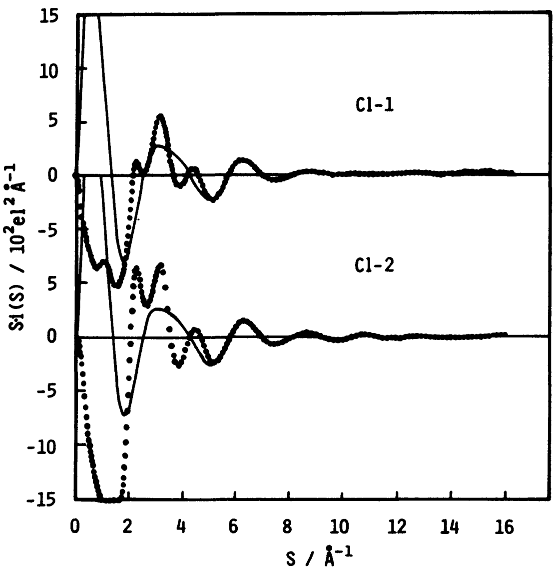

Fig. 6. Observed (∘∘∘∘∘∘) and calculated (——) $s \cdot i(s)$ curves for solutions Cl-1 and Cl-2.

bromoaqua complexes should be formed in these solutions. From a visible-spectrum investigation of the aqueous 4.5 mol dm^{-3} $MnBr_2$ solution, Ito[2] determined the equilibrium constants, K_1 and K_2, to be $K_1=K_2=$ 1.1 mol^{-1} dm^3. Libuš et al.[3,4] also reported the formation constant, K_1, of an aqueous 3.0 mol kg^{-1} $MnBr_2$ solution to be 0.19 mol^{-1} kg. If the K_3 and K_4 of our Br-1 solution are equal to zero, the mean coordination number is calculated as $n=1.46$ from these constant values;[2] this is close to the value obtained for the bromide solution by the X-ray diffraction experiment, if we take into consideration the different experimental conditions. From the present n value, we can conclude that the monobromoaqua complex is the predominant one in the solution, but that a small amount of the dibromoaqua complex may coexist. Little of the tri- and tetrabromo complexes presumably exist. The coordination numbers of the manganese(II) bromide solutions and those of the iron(II), cobalt(II), nickel(II), and copper(II) bromide solutions[9] suggest that the tendency of metal ions to form bromo complexes is in this order; Cu(II)>Mn(II)>Fe(II)>Co(II)>Ni(II).

Aqueous Manganese(II) Chloride Solutions. Since the mean coordination numbers, n, of Mn(II) with Cl^- in Cl-1 and Cl-2 solutions given in Table 2 are 1.259 and 1.501 respectively, some higher-chloroaqua complexes should exist besides the monochloroaqua complex in these solutions. The equilibrium constants of Mn(II) and Cl^- were determined by Ito[2] to be $K_1=3.6$ mol^{-1} dm^3 and $K_2=2.4$ mol^{-1} dm^3. The average coordination number in the Cl-1 solution calculated from these constants is 1.96, which is not too greatly different from the value obtained by the X-ray diffraction experiment. From the n-value results, the predominant solute species in the chloride solutions can be said to be the monochloroaqua complex, as a small amount of the dichloroaqua complex is also present. The concentrations of the tri- and tetrachloro complexes are presumably negligible in these solutions.

X-Ray diffraction measurements at different concentrations of solutions showed that the average coordination number of the Mn–X (X=Br,Cl) contact per Mn(II) increased slightly with an increase in the X/Mn ratios.

Since we could not prepare appropriate solutions for the structural analysis of the dihalogeno complexes because of the lack of reliable stability constants, we employed two saturated solutions, Br-1 and Cl-1, in order to determine the structure of the dihalogeno complexes in these solutions. However, we could not conclude whether the structure of the dihalogeno complexes in the solutions has a *cis*- or *trans*-geometry for the configuration of halogen, since calculated $s \cdot i(s)$ curves from both models of the *cis*- and *trans*-geometries of halogen agreed with the observed curves over the same s regions.

The $Mn-OH_2$ bond distances are 2.178 and 2.184 Å for the Br-1 and Br-2 solutions respectively, and 2.185 and 2.183 Å for the Cl-1 and Cl-2 solutions respectively. They are well consistent with those within the $Mn(H_2O)_6(NO_3)_2$ crystal[16] (2.157—2.211 Å) (average, 2.181 Å), and are shorter than those of the $MnBr_2 \cdot 4H_2O$ crystal[8] (2.221—2.475 Å) and the $MnCl_2 \cdot 4H_2O$ crystal[7] (2.185—2.224 Å) (average, 2.206 Å). The shortening of the $Mn-OH_2$ bond distances in these solutions may be understood by the explanation that the water molecules of the $Mn-OH_2$ bonds are attracted by other water molecules or halide ions less strongly in the solutions than in $MnX_2 \cdot 4H_2O$ crystals. The Mn–X bond distances are 2.643 and 2.596 Å for the Br-1 and Br-2 solutions respectively, and 2.492 and 2.496 Å for the Cl-1 and Cl-2 solutions respectively. The Mn–Cl bond distances are well consistent with those of the $MnCl_2 \cdot 4H_2O$ crystal, 2.475 and 2.500 Å. However, the Mn–Br bond in solution is appreciably shorter than those in the $MnBr_2 \cdot 4H_2O$ crystal (2.802 and 2.913 Å). The shortening of the Mn–Br bond distances in $MnBr_2$ solutions may also be understood by the explanation that the attraction between the bromine atoms of the Mn–Br bonds and water molecules coordinated to other Mn(II) bonds is less strong in the solutions than in the $MnBr_2 \cdot 4H_2O$ crystal, but in the case of the chlorine atoms of the Mn–Cl bonds, the analogous attractions in $MnCl_2$ solutions and in the $MnCl_2 \cdot 4H_2O$ crystal are nearly equal in strength.

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