

On the Movement of Paramagnetic Ions in an Inhomogeneous Magnetic Field

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The movement of transition-metal ions was observed in an inhomogeneous magnetic field. The solution containing Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} ions was spotted on a silica gel support and exposed to a magnetic field of $410 \text{ kOe}^2 \text{ cm}^{-1}$ intensity \times gradient. The distribution of the metal ions was measured, and the frictional coefficient of the movement was analyzed in relation to the susceptibility and concentration of the metal ions as well as to the size of the silica gel particles. When the concentration is higher, the metal ions move farther toward the maximum field. It is shown that a large group of metal ions and water molecules moves in a magnetic field.

1. Introduction

Recently the separation of transition-metal ions has been investigated in an inhomogeneous magnetic field.¹ When a solution containing Cu^{2+} (susceptibility $\chi = 1500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)² and Ag^+ ($\chi = -24 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)³ ions was spotted on a silica gel support and exposed to a magnetic field of $410 \text{ kOe}^2 \text{ cm}^{-1}$ intensity \times gradient, the Cu^{2+} ions were drawn toward the maximum field but the Ag^+ ions stayed at the spot position. It has been suggested that some flow of the solution occurs in the movement of the Cu^{2+} ions since the drift velocity of a single Cu^{2+} ion is too small to explain the large movement observed for the Cu^{2+} ions.

The present paper deals with the mechanism of the movement of paramagnetic ions. The analysis of the frictional coefficient clarifies the dependence of the movement on the susceptibility and concentration of paramagnetic ions as well as on the size of silica gel particles. The observation shows that the larger concentration induces the larger movement, indicating that paramagnetic ions move in a large group, not as a single particle.

2. Theory

The magnetic field is inhomogeneous. The intensity $H(z)$ and intensity \times gradient $H(z)\partial H(z)/\partial z$ depend on the position z from the field center along the magnet bore (Figure 1 of ref 1). The intensity reaches its maximum at the field center ($z = 0 \text{ mm}$), and the intensity \times gradient takes its highest (positive) and lowest (negative) values at -65 and $+65 \text{ mm}$ ($z = -65$ and $+65 \text{ mm}$), respectively, from the field center.

Suppose that metal ions with mole number n and molar susceptibility χ are placed at the position z in the magnetic field. The magnetic force $F(z)$ acting on the metal ions is expressed by

$$F(z) = \chi n H(z) \partial H(z) / \partial z \quad (1)$$

If the metal ions are paramagnetic ($\chi > 0$), the magnetic force works in the direction where the field intensity increases. The metal ions are attracted to move toward the maximum field.

The movement of the n metal ions is described as the drift motion of a group composed of the metal ions and water molecules. The drift velocity $v(z)$ is related to the magnetic force $F(z)$ by

$$v(z) = F(z)/f \quad (2)$$

where f is the frictional coefficient that the metal ion–water molecule group experiences against a bulk water atmosphere or silica gel support.

Now it must be recalled that the position z of the n metal ions is an implicit function of time t . The metal ions start from the position $z = z_0$ at time $t = t_0$ and go across the position $z = z_1$ at time $t = t_1$. The distance $z_1 - z_0$ on which the metal ions move in the time interval $t_1 - t_0$ is given by

$$z_1 - z_0 = \int_{t_0}^{t_1} v(z) dt \quad (3)$$

which is rewritten from eqs 1 and 2 as

$$z_1 - z_0 = (\chi n / f) \int_{t_0}^{t_1} [H(z) \partial H(z) / \partial z] dt \quad (4)$$

Then, the distance $z_1 - z_0$ is calculated by numerical integration of eq 4. The parameter $f/\chi n$ is the only one involved in eq 4 and determined by comparison with the observation.

The group consisting of the metal ions and water molecules is assumed to be a sphere of hydrodynamic radius R in which the metal ions are contained with molar concentration c . The frictional coefficient f is expressed by the Stokes' relation of

$$f = 6\pi\eta R \quad (5)$$

where η is the viscosity of the medium. The mole number n is related to the molar concentration c by

$$n = (4\pi/3)R^3 c \quad (6)$$

The parameter $f/\chi n$ in eq 4 is written from eqs 5 and 6 in the form of

$$f/\chi n = 9\eta/2\chi R^2 c \quad (7)$$

The right side of eq 7 involves explicitly the molar susceptibility

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χ and molar concentration c of the metal ions and enables one to estimate the radius R of the metal ion–water molecule group from the parameter $f/\chi n$.

3. Experimental Section

The magnetic fields up to $410 \text{ kOe}^2 \text{ cm}^{-1}$ intensity \times gradient were applied with a superconducting magnet (Oxford Spectromag 1000), in which the field direction was horizontal.

As the transition-metal salts, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (Wako, >99%), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Wako, >99%), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Wako, >99%), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (Wako, >98%), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Wako, >99%) were used. The metal ion solution ($0.2\text{--}3.0 \text{ mol dm}^{-3}$) was prepared from the corresponding metal salt and deionized water. As the silica gel supports, Wakogel C-300 ($45\text{--}75 \mu\text{m}$), C-200 ($75\text{--}150 \mu\text{m}$), C-100 ($150\text{--}425 \mu\text{m}$), and G ($300\text{--}600 \mu\text{m}$) were used. The silica gel support (35 g) was saturated with deionized water (57, 48, 49, and 28 cm^3 for C-300, C-200, C-100, and G, respectively) and laid in a glass vessel ($390 \times 40 \times 10 \text{ mm}^3$). The metal ion solution (50 mm^3) was spotted on the silica gel support at 100 mm from the field center. The glass vessel was placed in the magnet bore ($374 \times \phi 50.4 \text{ mm}$), allowed to stand at 295 K for 14 h, and then taken out of the magnet bore.

The Cr^{3+} ions were colored green ($\text{Cr}(\text{OH})_3$) and the Co^{2+} , Ni^{2+} , and Cu^{2+} ions blue ($[\text{Co}(\text{NH}_3)_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$, and $[\text{Cu}(\text{NH}_3)_4]^{2+}$) by a spray of ammonia solution (Kanto, 28–30%). The Mn^{2+} ions had a yellow color, which was deepened ($\text{Mn}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 2\text{H}_2\text{O}$) by a spray of ethanol solution containing 1% 8-hydroxyquinoline (Wako, >99%). The movement of the metal ions was recorded (Nikon Nikomat FTN) on a photograph, which was scanned (Epson GT-5000ART) into a personal computer (Apple 7600/132). The color-density profile of the metal ions was analyzed with an image-processing program (NIH Image 1.55).

4. Results and Discussion

4.1. Dependence of the Movement on the Susceptibility of Paramagnetic Ions. The movement in the magnetic field was observed for Mn^{2+} ($\chi = 14200 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$),² Co^{2+} ($\chi = 9500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$),² Cr^{3+} ($\chi = 6200 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$),² Ni^{2+} ($\chi = 4200 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$),² and Cu^{2+} ($\chi = 1500 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$)² ions. The solution containing the metal ions (1.0 mol dm^{-3}) was spotted on the silica gel support ($75\text{--}150 \mu\text{m}$) at 100 mm from the field center ($z' = z + 100 \text{ mm} = 0 \text{ mm}$), and exposed to the magnetic field of $100 \text{ kOe}^2 \text{ cm}^{-1}$. In Figures 1 and 2 is shown the distribution of the metal ions, measured along the distance (z') from the spot position of the solution. The Mn^{2+} , Co^{2+} , Cr^{3+} , Ni^{2+} , and Cu^{2+} ions move toward the maximum field by 81, 76, 63, 37, and 14 mm, respectively ($z' \approx 81, 76, 63, 37, \text{ and } 14 \text{ mm}$). It is clear that the larger movement ($\text{Mn}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+}$) corresponds to the larger susceptibility ($\text{Mn}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Ni}^{2+} > \text{Cu}^{2+}$) for the metal ions.

The movement was observed in the magnetic fields of $25\text{--}410 \text{ kOe}^2 \text{ cm}^{-1}$. The distribution of the metal ions was measured, and the distance on which the metal ions moved was determined at the peak position of the distribution. The parameter $f/\chi n$ is calculated numerically with eq 4, and plotted logarithmically in Figure 3 as a function of the molar susceptibility χ of the metal ions. The parameter $f/\chi n$ is the ratio of the frictional coefficient f to the product of the molar susceptibility χ and mole number n for the metal ions. The observed points are fitted with a line of slope of -1.11 ± 0.11 . Clearly, the parameter $f/\chi n$ is inversely proportional to the molar susceptibility χ . This

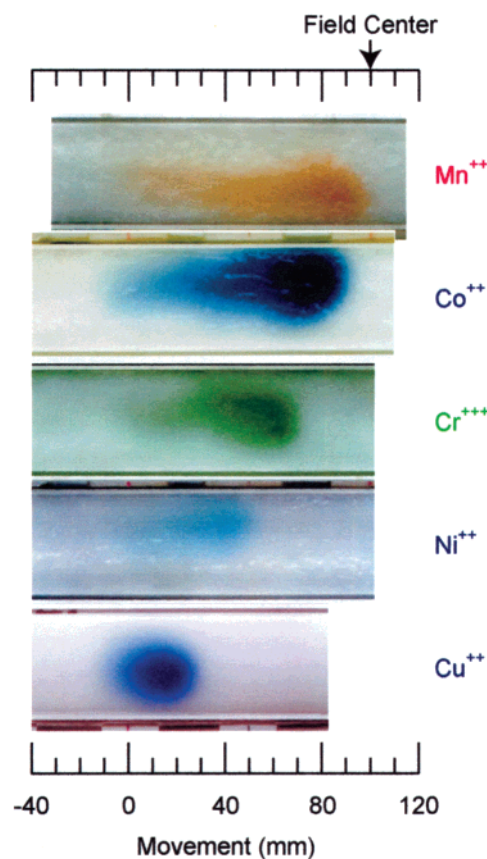


Figure 1. Movement of transition-metal ions on silica gel support. The metal ion solutions were spotted at the 0-mm position that was 100 mm from the field center.

means that the driving force of the movement is the magnetic force acting on the metal ions, as given in eq 1.

4.2. Dependence of the Movement on the Concentration of Paramagnetic Ions. The movement was examined for various concentrations of the Cu^{2+} ions. The Cu^{2+} ion solution was spotted on the silica gel support ($75\text{--}150 \mu\text{m}$) and exposed to the magnetic fields of $100\text{--}410 \text{ kOe}^2 \text{ cm}^{-1}$. When the concentration of the Cu^{2+} ions is higher, they move farther. The parameter $f/\chi n$ is plotted logarithmically in Figure 4 against the concentration c of the Cu^{2+} ions. After the solution was spotted, the Cu^{2+} ions diffused and the initial concentration decreased. Thus, the estimation is made for the concentration of the Cu^{2+} ions in the area of the diffusion on the silica gel support, under the assumption that the concentration is inversely proportional to the area of the diffusion at zero field. The concentration is estimated in Figure 4 at 0 (initial concentration), 1, and 2 h from the spot time of the solution. The initial concentration at 0 h decreases immediately and does not give an estimate of the concentration during the movement of the Cu^{2+} ions. After 1 h, the concentration reduces slowly, leading to a similar shift to the left direction in Figure 4 for all the initial concentrations. The observed points are fitted linearly with slopes of -0.83 ± 0.04 , -1.02 ± 0.05 , and -1.01 ± 0.03 for 0, 1, and 2 h, respectively. It is seen, from the slopes for 1 and 2 h, that the parameter $f/\chi n$ is inversely proportional to the concentration c .

The movement of transition-metal ions is discussed from the possible point of view of the drift motion of a single metal ion. If a single Cu^{2+} ion ($1/n = 6.022 \times 10^{23} \text{ mol}^{-1}$, $2R = 0.40 \text{ nm}$) is assumed to move in a water atmosphere ($\eta = 1.0 \text{ mPa s}$), the frictional coefficient f is calculated to be $3.8 \times 10^{-12} \text{ kg s}^{-1}$ from the Stokes' relation in eq 5. The parameter $f/\chi n$ is

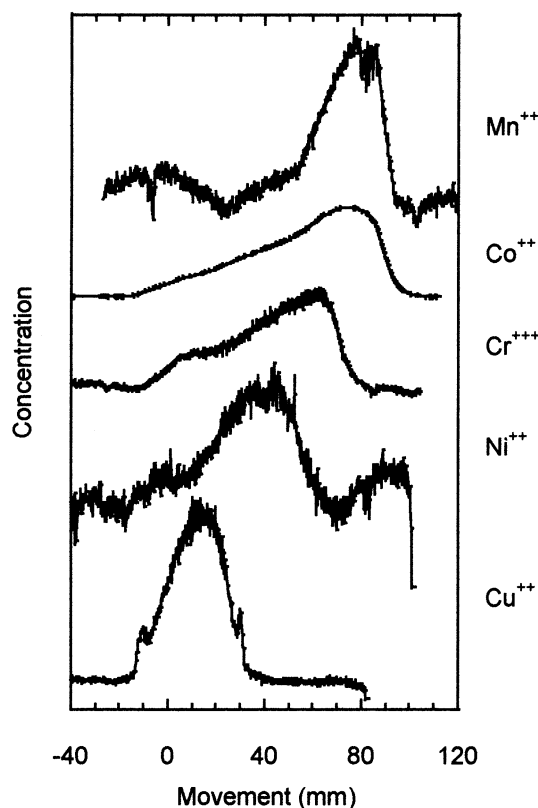


Figure 2. Distribution of transition-metal ions on silica gel support. The metal ion solutions were spotted at the 0-mm position that was 100 mm from the field center.

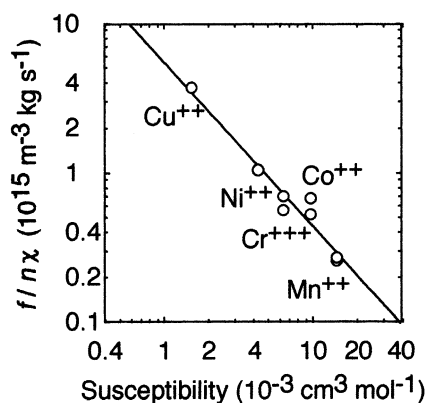


Figure 3. Dependence of the movement on the susceptibility of paramagnetic ions. The ordinate ($f/n\chi$) is the ratio of the frictional coefficient (f) to the product of the molar susceptibility (χ) and mole number (n) for paramagnetic ions.

predicted to be $1.5 \times 10^{21} \text{ m}^{-3} \text{ kg s}^{-1}$, which is independent of the concentration c of the Cu^{2+} ions. This is in conflict with the observation in Figure 4, denying the movement of a single metal ion.

The movement of transition-metal ions is discussed on the model of the drift motion of a group composed of metal ions and water molecules. If the sphere of a metal ion–water molecule group moves in a water atmosphere ($\eta = 1.0 \text{ mPa s}$), the mole number n is proportional to the concentration c for the metal ions in the group, as given in eq 6. Then, the parameter $f/n\chi$ is inversely proportional to the concentration c , as in eq 7. From the slope for 1 h in Figure 4, the diameter $2R$ is estimated to be $2.4 \text{ }\mu\text{m}$ and the frictional coefficient f is predicted to be $2.3 \times 10^{-8} \text{ kg s}^{-1}$ for the Cu^{2+} ion– H_2O molecule group. A large group with $2.4 \text{ }\mu\text{m}$ diameter moves in a water atmosphere.

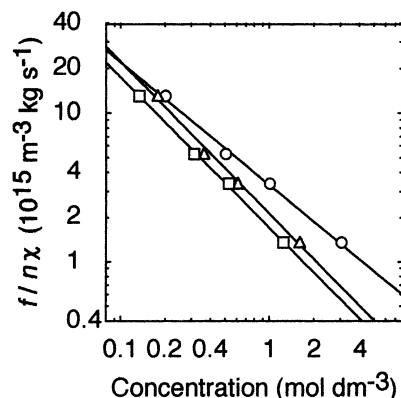


Figure 4. Dependence of the movement on the concentration of Cu^{2+} ions. The concentration is given as a value at 0 (○), 1 (△), and 2 (□) h from the spot time of the solution.

In the above discussion of the movement of a group of metal ions and water molecules, the friction has been assumed to arise from a water atmosphere. However, the friction may be caused by a silica gel support, and the group may be subject to a loss of its mobility. If a metal ion–water molecule group moves against a silica gel support, the nominal “viscosity” η of a silica gel support must be estimated to be larger, due to a decrease in the mobility of the group, than that of a water atmosphere. The diameter $2R$ must be larger, and the frictional coefficient f must be larger for the metal ion–water molecule group.

Since the phenomenon is interpreted as the motion of a group of metal ions and water molecules in a certain size unit, one can expect that cosolutes will be transported together with the metal ions. Then, the experiment was made for a check on this expectation. A mixture of two kinds of metal ion solutions was prepared from the Cr^{3+} , Mn^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} ion solutions. It was spotted on the silica gel support and exposed to the magnetic fields. The result shows that, although the susceptibility is different between the component metal ions, the mixture of the metal ions moves in a body without giving any separate distribution for them. (The separation of different kinds of metal ions is not possible in this case, but it is possible in case that the adsorption on silica gel particles is different between component metal ions.)⁴ The observation of the inseparable movement of the metal ion mixture suggests the validity of the model of the motion of a metal ion–water molecule group.

4.3. Dependence of the Movement on the Size of Silica Gel Particles. The movement of the Cu^{2+} ions was examined for various sizes of silica gel particles. The Cu^{2+} ion solution (1.0 mol dm^{-3}) was spotted on the silica gel support and exposed to the magnetic fields of $100\text{--}410 \text{ kOe}^2 \text{ cm}^{-1}$. When the silica gel particles have a larger diameter, the Cu^{2+} ions move into a larger distance. The logarithmic plot of the parameter $f/n\chi$ vs the diameter L of the silica gel particles is given in Figure 5. As the diameter L , the mean value is used for the silica gel particles. A linear fitting results in a slope of -1.01 ± 0.09 . It is found that the parameter $f/n\chi$ is inversely proportional to the diameter L .

The relationship of the parameter $f/n\chi$ to the diameter L is discussed in terms of the total surface area NS for the silica gel particles (the product NS of the number N of particles and the surface area S of one particle).⁵ Since the total surface area NS is inversely proportional to the diameter L for the silica gel particles in a fixed volume, i.e., in a fixed weight, the parameter $f/n\chi$ is proportional to the total surface area NS . It is possible

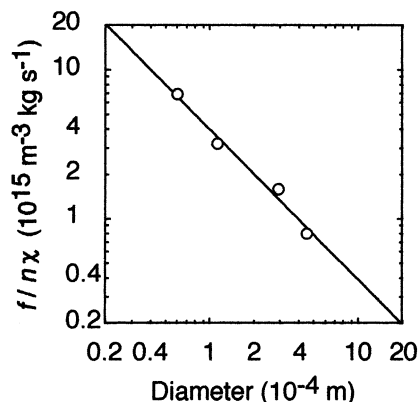


Figure 5. Dependence of the movement of Cu^{2+} ions on the size of silica gel particles.

that the frictional coefficient f is proportional to the total surface area NS .

However, this discussion does not consider the diffusion on the silica gel particles. A decrease in the frictional coefficient f for the silica gel particles of large diameter L induces the diffusion of the metal ions, which causes a decrease in the concentration of the metal ions, leading to a reduction of the movement, as mentioned in section 4.2. The effect of the diffusion of the metal ions, or of the adsorption on the silica gel particles, is not resolved at present, but must be clarified soon.

5. Conclusion

The movement of transition-metal ions in an inhomogeneous magnetic field has been analyzed. The parameter $f/\chi n$ depends on the susceptibility χ and concentration c of the metal ions as well as on the diameter L of the silica gel particles, where f is the frictional coefficient and n is the mole number for the metal ions in motion. The inverse proportionality of the parameter $f/\chi n$ to the concentration c shows that a large group of metal ions and water molecules moves in a magnetic field.

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References and Notes

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- (4) Chie, K.; Fujiwara, M.; Fujiwara, Y.; Tanimoto, Y. *J. Phys. Chem. B* **2003**, *107*, 14374.
- (5) The surface area S is at the square of the diameter L for one silica gel particle ($S \sim L^2$). The volume V is at the cube of the diameter L for one silica gel particle ($V \sim L^3$), and the number N included in a fixed volume decreases at the inverse cube of the diameter L for silica gel particles ($N \sim L^{-3}$). Thus, the total surface area NS is in inverse proportion to the diameter L for silica gel particles in a fixed volume ($NS \sim L^{-1}$).