Determination of the Diffusion Coefficients of 
CuCl₂, FeCl₃, CuSO₄, and Fe₂(SO₄)₃ in Aqueous Solutions

By Zhi-chun Wu*,†, Yasuhiro Awakura*, Satoru Ando**, and Hiroshi Majima*

The diffusion coefficients of CuCl₂, FeCl₃, and Fe₂(SO₄)₃ in acidic aqueous solutions were measured at 298 K using a diaphragm-cell method. Also the diffusion coefficients of CuCl₂ in water were determined at the same temperature. The data obtained are listed as a function of the molar concentrations of the solutes. The diffusion coefficients of CuCl₂ in water are larger than those of CuSO₄. The concentration dependency of the diffusion coefficients for CuCl₂ in water could be explained in terms of the changes in the mean activity coefficients of CuCl₂ and in the viscosity of the solutions. The diffusion coefficients of CuCl₂ in aqueous HCl solutions are larger than those of FeCl₃. The presence of HCl has a significant influence on the diffusion of CuCl₂ and FeCl₃, and it decreases their diffusion coefficients. On the other hand, the diffusion coefficients of CuSO₄ in aqueous H₂SO₄ solutions are larger than those of Fe₂(SO₄)₃. However, the presence of H₂SO₄ have no significant effect on the diffusion coefficients of Fe₂(SO₄)₃. The effect of HCl and H₂SO₄ on the diffusion coefficients of CuCl₂, FeCl₃ and Fe₂(SO₄)₃ were discussed based on the predominant diffusing species and the diffusion potential due to the H⁺ ions migration.

(Received July 26, 1990)

Keywords: diffusion coefficient, CuCl₂, FeCl₃, CuSO₄, Fe₂(SO₄)₃, diffusion potential, diaphragm-cell method

I. Introduction

CuCl₂, FeCl₃, CuSO₄, and Fe₂(SO₄)₃ are important electrolytes, which are often treated in hydrometallurgy. Thus, the activities of water and solutes in the acidic aqueous solutions of these electrolytes were determined at 298 K in the authors’ laboratory and reported elsewhere. Despite the importance of these electrolytes in hydrometallurgy, the other fundamental data available to these electrolytes are not necessarily sufficient. For example, the diffusion coefficients of these electrolytes in aqueous solutions must be known to discuss the transport process of these electrolytes in aqueous solutions. However, only the diffusion coefficient values at infinite dilution are known at present, except for those of CuSO₄, which were determined previously in the authors’ laboratory.

This work was done as a part of a systematic study on the determination of the kinematic properties of various electrolytes in aqueous solutions. In this study, diffusion coefficients of CuCl₂, FeCl₃, and Fe₂(SO₄)₃ in aqueous solutions were determined at 298 K by a diaphragm-cell method, as a function of acid and metal salt concentrations. The results obtained, including the previously reported data on CuSO₄, were compared with each other to analyse the controlling factors of diffusion coefficients of these aqueous solution systems.

II. Experimental Procedures

A diaphragm-cell method, which is applicable to the determination of diffusion coefficients in a solution system of mixed electrolytes, was employed for the determination of the diffusion coefficients in this work. The diffusion coefficients of CuCl₂ in water and aqueous acid solutions were measured, while those of FeCl₃ and Fe₂(SO₄)₃ were determined in aqueous acid solutions, both at 298 ± 0.1 K.

The experimental apparatus and procedures are the same as those described in a previous paper. The brief descriptions about them are as follows; Fig. 1 shows schematically the arrangement of a porous diaphragm-cell which are made of Pyrex, with each end having a volume of about 50 ml. The diaphragm is of No. 4 porosity (average pore size = 15 μm), 40 mm in diameter and 3 mm thick. It is essential in this method that the solution in the compartment of the either side must be maintained at a uniform concentration during diffusion experiment. Then, each compartment contains a stirrer which is rotated in the vicinity of the diaphragm by a motor-driven permanent magnet mounted around the cell. The upper compartment was filled with deionized water or aqueous acid solution of a definite concentration, and the lower with the test solution. The cell was then set in a thermostated-water bath to commence the diffusion experiment. After a definite duration, the sample solution was withdrawn from the upper compartment to analyze the concentration of diffusing solute. The concentrations of Cu²⁺ and Fe³⁺ ions were determined by EDTA titration.

The integral diffusion coefficient $D$ of solute electrolyte can be calculated from the results of the diaphragm-cell...
The kinematic viscosity and density of aqueous CuCl₂ solutions were also measured at 298 K using a Cannon-Fenske viscometer and a picnometer, respectively. All of the chemicals used in this study were of reagent grade. The solutions were prepared with deionized water with resistivity above $5 \times 10^6$ ohm m.

III. Experimental Results

The diffusion coefficients of CuCl₂ in water and in aqueous HCl solutions determined at 298 K are listed in Table 1. Those of FeCl₃ in aqueous HCl solutions and Fe₂(SO₄)₃ in aqueous H₂SO₄ solutions are shown in Tables 2 and 3, respectively, as a function of concentrations of acid and metal salt. The diffusion coefficients of FeCl₃ and Fe₂(SO₄)₃ in water could not be measured because of the hydrolysis of these metal salts.

Measured values of the kinematic viscosity and density of aqueous CuCl₂ solutions, which will be used later in the discussion of experimental results, are tabulated in Table 4.

IV. Discussion

1. A Comparison of the diffusion coefficients of MCl₂ and MSO₄ in water

Figure 2 shows the diffusion coefficients of CuCl₂ in water. For comparison, the diffusion coefficients of

$$D = \bar{D} + \frac{\sqrt{C}}{2} \frac{d\bar{D}}{d\sqrt{C}}$$ (2)

experiment based upon the following equation (6):

$$\bar{D} = \frac{1}{B t} \ln \frac{C_1 - C_2}{C_3 - C_4}$$ (1)

where $t$ is the diffusion time and $B$ is the cell constant. The terms $C_1$ and $C_2$ denote the concentrations (kmol m⁻³) of a diffusing solute at the beginning of the experiment for the lower and upper compartments, respectively, and the terms $C_3$ and $C_4$ those at the end of the experiment. The initial concentrations $C_1$ and $C_3$ are known. If the final concentration $C_4$ in the upper compartment is determined by chemical analysis, the final concentration $C_3$ in the lower compartment can be calculated from $C_1$, $C_2$, $C_4$, and the volumes of the cell compartments, since the total amount of diffusing solute is kept constant. The volume of each compartment of the cell was measured in a preliminary experiment by weighing the cell with the various parts filled in turn with deionized water. The cell calibration to determine $B$ was carried out using an aqueous potassium chloride solution at 298 K, the diffusion coefficient of which is known as a function of concentration.

The diffusion coefficient $D$ at various values of $C$ is calculated from a set of $\bar{D}$ values obtained directly in experiments based on the following equation (6).

Table 1. Diffusion coefficients of CuCl₂ in the aqueous solution systems of CuCl₂-HCl at 298 K.

<table>
<thead>
<tr>
<th>$C$(CuCl₂) (kmol m⁻³)</th>
<th>$C$(HCl) (kmol m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>12.6*</td>
</tr>
<tr>
<td>0.1</td>
<td>10.7</td>
</tr>
<tr>
<td>0.2</td>
<td>10.5</td>
</tr>
<tr>
<td>0.3</td>
<td>10.5</td>
</tr>
<tr>
<td>0.4</td>
<td>10.5</td>
</tr>
<tr>
<td>0.5</td>
<td>10.5</td>
</tr>
<tr>
<td>0.6</td>
<td>10.6</td>
</tr>
<tr>
<td>0.7</td>
<td>10.6</td>
</tr>
<tr>
<td>0.8</td>
<td>10.5</td>
</tr>
<tr>
<td>0.9</td>
<td>10.5</td>
</tr>
<tr>
<td>1.0</td>
<td>10.5</td>
</tr>
<tr>
<td>1.1</td>
<td>10.4</td>
</tr>
<tr>
<td>1.2</td>
<td>10.3</td>
</tr>
<tr>
<td>1.3</td>
<td>10.2</td>
</tr>
<tr>
<td>1.4</td>
<td>10.1</td>
</tr>
<tr>
<td>1.5</td>
<td>10.0</td>
</tr>
<tr>
<td>1.6</td>
<td>9.94</td>
</tr>
<tr>
<td>1.7</td>
<td>9.84</td>
</tr>
<tr>
<td>1.8</td>
<td>9.73</td>
</tr>
<tr>
<td>1.9</td>
<td>9.63</td>
</tr>
<tr>
<td>2.0</td>
<td>9.52</td>
</tr>
</tbody>
</table>

Unit of diffusion coefficient: $10^{-10}$ m² s⁻¹

* Value calculated from the equivalent ionic conductivity at infinite dilution.
Table 2  Diffusion coefficients of FeCl₃ in aqueous solution systems of FeCl₃–HCl at 298 K.

<table>
<thead>
<tr>
<th>C(FeCl₃) (kmol m⁻³)</th>
<th>C(HCl) (kmol m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>0.0</td>
<td>12.8*</td>
</tr>
<tr>
<td>0.1</td>
<td>6.94</td>
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<tr>
<td>0.2</td>
<td>7.41</td>
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<tr>
<td>0.3</td>
<td>7.68</td>
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<tr>
<td>0.4</td>
<td>7.86</td>
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<tr>
<td>0.5</td>
<td>7.98</td>
</tr>
<tr>
<td>0.6</td>
<td>8.06</td>
</tr>
<tr>
<td>0.7</td>
<td>8.12</td>
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<tr>
<td>0.8</td>
<td>8.15</td>
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<tr>
<td>0.9</td>
<td>8.17</td>
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<tr>
<td>1.0</td>
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<td>8.11</td>
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<td>1.7</td>
<td>8.06</td>
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<td>1.8</td>
<td>8.03</td>
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<tr>
<td>1.9</td>
<td>8.00</td>
</tr>
<tr>
<td>2.0</td>
<td>7.97</td>
</tr>
</tbody>
</table>

Unit of diffusion coefficient: 10⁻¹⁰ m² s⁻¹
* Value calculated from the equivalent ionic conductivity at infinite dilution.

Table 3  Diffusion coefficients of Fe₃(SO₄)₂ in aqueous solution systems of Fe₃(SO₄)₂–H₂SO₄ at 298 K.

<table>
<thead>
<tr>
<th>C(Fe₃(SO₄)₂) (kmol m⁻³)</th>
<th>C(H₂SO₄) (kmol m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>0.0</td>
<td>8.15*</td>
</tr>
<tr>
<td>0.1</td>
<td>4.52</td>
</tr>
<tr>
<td>0.2</td>
<td>4.25</td>
</tr>
<tr>
<td>0.3</td>
<td>4.11</td>
</tr>
<tr>
<td>0.4</td>
<td>4.03</td>
</tr>
<tr>
<td>0.5</td>
<td>3.97</td>
</tr>
<tr>
<td>0.6</td>
<td>3.94</td>
</tr>
<tr>
<td>0.7</td>
<td>3.92</td>
</tr>
<tr>
<td>0.8</td>
<td>3.90</td>
</tr>
<tr>
<td>0.9</td>
<td>3.89</td>
</tr>
<tr>
<td>1.0</td>
<td>3.87</td>
</tr>
</tbody>
</table>

Unit of diffusion coefficient: 10⁻¹⁰ m² s⁻¹
* Value calculated from the equivalent ionic conductivity at infinite dilution.

Table 4  Kinematic viscosity and density of aqueous CuCl₂ solutions at 298 K.

<table>
<thead>
<tr>
<th>C(CuCl₂) (kmol m⁻³)</th>
<th>Kinematic viscosity (10⁻⁴ m² s⁻¹)</th>
<th>Density (10⁵ kg m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.9215</td>
<td>1.0094</td>
</tr>
<tr>
<td>0.2</td>
<td>0.9572</td>
<td>1.0217</td>
</tr>
<tr>
<td>0.5</td>
<td>1.0126</td>
<td>1.0577</td>
</tr>
<tr>
<td>1.0</td>
<td>1.1479</td>
<td>1.1154</td>
</tr>
<tr>
<td>1.5</td>
<td>1.2738</td>
<td>1.1714</td>
</tr>
<tr>
<td>2.0</td>
<td>1.4315</td>
<td>1.2252</td>
</tr>
</tbody>
</table>

Fig. 2  The concentration dependency of the diffusion coefficients of CuCl₂ and CuSO₄ in water at 298 K.

NiCl₂, CdCl₂, NiSO₄, CuSO₄, and ZnSO₄, which were previously determined by the authors(10,11), are also shown in the same figure. It is apparent that the diffusion coefficients of metal chlorides in water show quite different concentration dependency. The values of the CuCl₂ diffusion coefficients are close to those of NiCl₂ at low concentrations, decreasing sharply with an increase in concentration. However, a further increase in CuCl₂ concentration causes a gradual decrease in the diffusion coefficient of CuCl₂, which locates between those of NiCl₂ and CdCl₂.

In contrast, all the diffusion coefficients of MSO₄ show similar trends in concentration dependency. The values decrease sharply with a slight increase in sulfate concentration up to 0.2 kmol m⁻³ MSO₄ and then decrease to a lesser extent with further increases in concentration.

It should be noted that the diffusion coefficients of CuCl₂ in water are 2 or 3 times larger than those of CuSO₄. The order of the decreasing sequence of diffusion coefficients of these chlorides may be attributed to the order of the formation of strong chloro-complexes.

Previously, the authors analyzed the concentration dependency of the diffusion coefficients of NiCl₂ and CdCl₂ as well as that of CuSO₄ in water(10,11) according to the method proposed by Wishaw and Stokes(10).

The diffusion coefficient, D, of a 2–1 type electrolyte of a non-complexing metal such as NiCl₂ in water, can be expressed as

\[
D = \left( 1 + \frac{d \ln y_s}{d \ln C} \right) \left( D^0 + \Delta_1 + \Delta_2 \right) \frac{\eta^o}{\eta}
\]

where \( D^0 \) is the Nernst limiting diffusion coefficient of the solute, and C and \( y_s \) are the molarity and the mean
activity coefficient of the diffusing solute on the molar scale, respectively. The terms $\Delta_1$ and $\Delta_2$ are both small concentration dependent corrections to take into account the electrophoretic effect. The term $\eta^0/\eta$ is the reciprocal value of relative viscosity of the solution; $\eta^0$ and $\eta$ are the viscosities of the infinitely diluted solution and the aqueous solution, respectively. From the analysis based on eq. (3), it was concluded in a previous paper\(^{30}\) that the concentration dependency of the diffusion coefficients of NiCl$_2$ in water can be explained by the changes in the chemical potential and in the viscosity of the solution\(^{31}\). In contrast, the expression, corresponding to eq. (3), for the diffusion coefficients of CdCl$_2$ in water is more complicated, since Cd(II) reacts with Cl$^-$ ions to form chloro-complexes\(^{36}\). However, assuming that the absolute mobility of CdCl$^+$ is almost equal to that of CdCl$_2$, it was theoretically derived that the change in the diffusion coefficients of CdCl$_2$ with concentration is due to the chemical potential of CdCl$_2$ and the solution viscosity. The analysis, which is similar to that in the case of NiCl$_2$ and is based on the mean activity coefficient of CdCl$_2$ and the solution viscosity determined experimentally, also supported it\(^{39}\).

Cu(II) also reacts with Cl$^-$ to form chloro-complexes\(^{30}\), and the calculation of equilibrium concentration of Cu(II) species for aqueous CuCl$_2$ solutions shows that the predominant species of Cu(II) are Cu$^{2+}$ and CuCl$^-$. Therefore, the expression of the diffusion coefficient, corresponding to eq. (3), cannot be derived simply, but assuming that the absolute mobilities of Cu$^{2+}$ and CuCl$^-$ are almost the same, it could be shown in the following manner that the concentration dependency of the CuCl$_2$ diffusion coefficients is due to the chemical potential term and the solution viscosity term.

Figure 3 illustrates the concentration dependencies of the parameter $(1 + d \log y_{\infty} / d \log C) \eta/\eta_1$ for the metal chlorides as well as the metal sulfates, shown in Fig. 1, in single electrolyte solutions. The comparison of Figs. 2 and 3 clearly shows that the concentration dependencies of the diffusion coefficients of CuCl$_2$ and of the parameter, $(1 + d \log y_{\infty} / d \log C) \eta/\eta_1$, are quite similar. Thus, the concentration dependency of the diffusion coefficient of CuCl$_2$ in water can be explained by the change in the chemical potential of the solute and in the viscosity of the solution. Similar agreements are observed for the metal sulfates\(^{40}\).

2. Diffusion coefficients of CuCl$_2$ and FeCl$_3$ in aqueous HCl solutions and those of CuSO$_4$ and Fe$_2$(SO$_4$)$_3$ in aqueous H$_2$SO$_4$ solutions

1) A comparison of diffusion coefficients

Figure 4 shows the values of diffusion coefficients of CuCl$_2$ and FeCl$_3$ in 0.1 kmol m$^{-3}$ HCl solutions and those of CuSO$_4$ and Fe$_2$(SO$_4$)$_3$ in 0.1 kmol m$^{-3}$ H$_2$SO$_4$. For comparison, those of other metal chlorides and metal sulfates determined in previous studies\(^{10}\),\(^{36}\) are also demonstrated in the same figure. For sulfate systems, the diffusion coefficients of 2-2 type sulfates demonstrated in this figure are almost the same, while those of Fe$_2$(SO$_4$)$_3$ are smaller than those of the other sulfates, but its concentration dependency is essentially similar to the other sulfates investigated.

The diffusion coefficient of FeCl$_3$ increases gradually with an increase in FeCl$_3$ concentration up to 0.5 kmol m$^{-3}$. However, it remains almost constant with a further increase in FeCl$_3$ concentration. On the other hand, the diffusion coefficients of metal chlorides in 0.1 kmol m$^{-3}$ HCl solutions greatly differ from each other. Diffusion coefficient of ZnCl$_2$ in aqueous HCl solution increases with the increase in ZnCl$_2$ concentration, while that of CdCl$_2$ exhibits a decreasing tendency\(^{39}\). In contrast, the diffusion coefficient of CuCl$_2$ or NiCl$_2$ shows the maximum value around 1.0 kmol m$^{-3}$ MCl$_2$. It should be noted that the diffusion coefficients of FeCl$_3$ in HCl solution are smaller than those of CuCl$_2$ over the wide concentration range studied.

Figure 5 shows the concentration dependencies of CuCl$_2$ and FeCl$_3$ in 1.0 kmol m$^{-3}$ HCl solution and those of CuSO$_4$ and Fe$_2$(SO$_4$)$_3$ in 1.0 kmol m$^{-3}$ H$_2$SO$_4$ solution. For comparison, those of other metal chlorides and metal sulfates are also depicted in the same figure\(^{10}(\text{ii})\). As compared with the results for 0.1 kmol m$^{-3}$ HCl, the diffusion coefficients of CuCl$_2$ and FeCl$_3$ are smaller over the whole MCl$_2$ concentration range studied. The change in the diffusion coefficients of MCl$_2$ with concentration in 1.0 kmol m$^{-3}$ HCl solutions is also smaller than in 0.1 kmol m$^{-3}$ HCl solutions. Furthermore, it should be noted that the difference among the diffusion coefficients of MCl$_2$ except for ZnCl$_2$ becomes smaller in 1.0 kmol m$^{-3}$ HCl solutions than in 0.1 kmol m$^{-3}$ HCl solutions. On the other hand, in 1.0 kmol m$^{-3}$ H$_2$SO$_4$ solutions, the diffusion coefficients of CuSO$_4$ are larger than those of Fe$_2$(SO$_4$)$_3$, but their concentration dependencies are...
Figure 4: The concentration dependency of the diffusion coefficients of CuCl₂ and FeCl₃ in aqueous 0.1 kmol m⁻³ HCl solution and those of CuSO₄ and Fe₂(SO₄)₃ in aqueous 0.1 kmol m⁻³ H₂SO₄ solutions at 298 K.

Figure 5: The concentration dependency of the diffusion coefficients of CuCl₂ and FeCl₃ in aqueous 1.0 kmol m⁻³ HCl solution and those of CuSO₄ and Fe₂(SO₄)₃ in aqueous 1.0 kmol m⁻³ H₂SO₄ solutions at 298 K.

Similar to each other.

(2) Concentration dependencies of the diffusion coefficients of CuCl₂ and FeCl₃ in aqueous HCl solutions
Since there are several ways to satisfy electrical neutrality during the diffusion process of metal chloride, MClₓ, in aqueous HCl solutions, it is impossible to rigorously apply the same analytic method as that for the diffusion coefficients of MClₓ in water. However, it was concluded in a previous paper that the presence of HCl in the solution affects the diffusion coefficients by modifying the diffusion potential as well as the mean activity coefficients of MClₓ and the solution viscosity. That is, even when the concentration of HCl is uniform over the upper and lower compartments of the diaphragm-cell, the activity values of HCl, a(HCl) in the lower compartment containing MClₓ, is higher than that of the upper one without MClₓ. This means that HCl diffuses through the diaphragm from the lower compartment to the upper one, and this results in the development of a diffusion potential toward the upper compartment because the H⁺ ions have a greater mobility than any other ions. On the other hand, the diffusion of MClₓ in water generates a diffusion potential in the reverse direction, as expected from the mobilities of metal aquo-ions and chloride ions. The diffusion potential in aqueous HCl–MClₓ solutions reduces the diffusion coefficients of MClₓ if the predominant diffusing species are cations. This effect should be more substantial at higher concentrations of HCl.

As shown in Figs. 2, 4, and 5, the presence of HCl or the increase in HCl concentration reduces the diffusion coefficients of CuCl₂, FeCl₃, and NiCl₂. In contrast, the effects of HCl through the diffusion potential on the diffusion coefficients of ZnCl₂ seems to be small, but as reported in a previous paper, the presence of 2 kmol m⁻³ HCl increases the diffusion coefficient of ZnCl₂. On the other hand, the diffusion coefficient of CdCl₂ increases slightly with the increase in HCl concentration.

In regard to this, the authors pointed out in a previous paper that the difference among the diffusion coefficients of different chlorides in aqueous HCl solutions is closely related to what are the predominant diffusing species in the solution. Particularly, the most reasonable explanation for the difference is due to the difference in the valence of predominant diffusing species. Therefore, the equilibrium concentrations of chemical species in the aqueous HCl–MClₓ solutions were calculated by using the values of formation constants of chloro-complexes, which are given in Table 5.

Figures 6 and 7 show the distribution diagram of the various chemical species calculated for aqueous MClₓ solutions containing 0.1 and 1.0 kmol m⁻³ HCl, respectively. As is clear in these figures, the predominant species in aqueous HCl solution containing CuCl₂, FeCl₃, and NiCl₂, respectively, are cations. In aqueous CdCl₂–0.1 kmol m⁻³ HCl solutions, the predominant Cd(II) species are CdCl₂²⁻ and CdCl₄⁻. The addition of 1.0 kmol m⁻³ HCl to the solutions causes an increase in CdCl₄⁻ concentration and a decrease in the CdCl₂²⁻ concentration, respectively. On the other hand, the predominant Zn(II) species in aqueous ZnCl₂–0.1 kmol m⁻³ HCl solutions are dependent on the concentration of ZnCl₂; Zn²⁺ and ZnCl⁺ ions are predominant in dilute ZnCl₂ solutions, but Zn²⁺ ions become less significant with increasing
Table 5  Formation constants of chloro-complexes of Cu(II), Fe(III), Cd(II), and Zn(II) at zero ionic strength and 298 K.10

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log ( k_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+}) + Cl(^-) = CuCl(^+)</td>
<td>0.4</td>
</tr>
<tr>
<td>Fe(^{3+}) + Cl(^-) = FeCl(^{2+})</td>
<td>1.48</td>
</tr>
<tr>
<td>FeCl(^+_2) + Cl(^-) = FeCl(^{2+})</td>
<td>0.65</td>
</tr>
<tr>
<td>Cd(^{2+}) + Cl(^-) = CdCl(^+)</td>
<td>1.98</td>
</tr>
<tr>
<td>CdCl(^{+2}) + Cl(^-) = CdCl(^{2+})</td>
<td>0.62</td>
</tr>
<tr>
<td>CdCl(^{1+}) + Cl(^-) = CdCl(^{2+})</td>
<td>-0.20</td>
</tr>
<tr>
<td>CdCl(^{2+}) + Cl(^-) = CdCl(^{3+})</td>
<td>-0.70</td>
</tr>
<tr>
<td>Zn(^{2+}) + Cl(^-) = ZnCl(^{2+})</td>
<td>0.43</td>
</tr>
<tr>
<td>ZnCl(^{2+}) + Cl(^-) = ZnCl(^{3+})</td>
<td>-0.43</td>
</tr>
<tr>
<td>ZnCl(^{1+}) + Cl(^-) = ZnCl(^{2+})</td>
<td>0.50</td>
</tr>
<tr>
<td>ZnCl(^{2+}) + Cl(^-) = ZnCl(^{3+})</td>
<td>-0.30</td>
</tr>
</tbody>
</table>

ZnCl\(^2\) concentration, while ZnCl\(^{3+}\) ions increase in importance. The increase in the HCl concentration results in the increase in the ZnCl\(^2\)\(^-\) and ZnCl\(^{3+}\) concentrations independent of the ZnCl\(^2\) concentration. In aqueous ZnCl\(^2\)-1.0 kmol m\(^{-3}\) HCl solutions, the predominant Zn(II) species are ZnCl\(^{3+}\) and ZnCl\(^{3+}\).

When metal chloride diffuses in aqueous HCl solution, diffusion of the cationic species among various chloro-complexes present in the solution are suppressed by the diffusion potential generated due to the diffusion of protons. In contrast, the diffusion of anionic species is enhanced. As a whole, it can be said that the concentration dependency of diffusion coefficients of metal chloride in aqueous HCl solution greatly depends on the identity of diffusing species, their valencies and distribu-

Table 6  Formation constants of sulfato-complexes of Cu(II) and Fe(III) at zero ionic strength and 298 K.10

<table>
<thead>
<tr>
<th>Reaction</th>
<th>log ( k_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(^{2+}) + SO(^{2-}) = CuSO(^{3+})</td>
<td>2.36</td>
</tr>
<tr>
<td>Fe(^{3+}) + SO(^{2-}) = FeSO(^{3+})</td>
<td>4.04</td>
</tr>
<tr>
<td>FeSO(^{3+}) + SO(^{2-}) = FeSO(^{4-})</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Fig. 6  Distribution diagram of Ni(II), Cu(II), Fe(III), Cd(II), and Zn(II) species in respective aqueous solutions of MCl\(^-\)-0.1 kmol m\(^{-3}\) HCl at 298 K.

Fig. 7  Distribution diagram of Ni(II), Cu(II), Fe(III), Cd(II), and Zn(II) species in respective aqueous solutions of MCl\(^-\)-1.0 kmol m\(^{-3}\) HCl at 298 K.
tion beside the chemical potential gradient of metal chloride and the viscosity of the solution.

(3) Concentration dependency of the diffusion coefficients of CuSO₄ and Fe₂(SO₄)₃ in aqueous H₂SO₄ solutions

Figure 8 shows the distribution diagram of Cu(II) and Fe(III) species in aqueous CuSO₄ and Fe₂(SO₄)₃ solutions containing H₂SO₄, which were constructed using the data of formation constants of sulfato-complexes as shown in Table 6[8]. As can be seen from this figure, the electrically neutral CuSO₄₂⁻ is the predominant Cu(II) species in aqueous CuSO₄–H₂SO₄ solutions. Therefore, H₂SO₄ affects the diffusion coefficients of CuSO₄ only through both the chemical potential and the viscosity of the solution, which were studied in a previous paper[9]. On the other hand, the FeSO₄⁺ and Fe(SO₄)₂⁻ are the predominant Fe(III) species in aqueous Fe₂(SO₄)₃–0.1 kmol m⁻³ H₂SO₄ solutions. The increase in H₂SO₄ concentration from 0.1 to 1.0 kmol m⁻³ results in the increase in Fe(SO₄)₂⁻ concentration and the decrease in FeSO₄⁺ concentration. The activity of H₂SO₄ in the lower compartment of a diaphragm-containing Fe₂(SO₄)₃ is higher than that of the upper compartment without Fe₂(SO₄)₃. This means that a diffusion potential due to the H⁺ ion migration is developed similar to the case of acidic chloride solutions. Thus, it is expected that compared with 0.1 kmol m⁻³ H₂SO₄, the diffusion coefficients of Fe₂(SO₄)₃ become larger in aqueous 1.0 kmol m⁻³ solutions because of large concentration ratio of negative species, Fe(SO₄)₂⁻ to positive species, FeSO₄⁺. However, it should be noted that the addition of H₂SO₄ to the solution increases the solution viscosity.

V. Conclusions

The diffusion coefficients of CuCl₂, FeCl₃, and Fe₂(SO₄)₃ in acidic solutions and those of CuCl₂ in water were measured at 298 K using a diaphragm-cell method. The diffusion coefficients of CuCl₂ in water are larger than those of CuSO₄ in water. The concentration dependency of the diffusion coefficients for CuCl₂ differs substantially from those of other chlorides such as NiCl₂ and CdCl₂. This observation is completely different from that the diffusion coefficients of CuSO₄, NiSO₄, and ZnSO₄ show almost the same concentration dependency. The concentration dependency of the diffusion coefficients of CuCl₂ in water was rationalized in terms of the chemical potential gradient of CuCl₂ and the viscosity of the solution.

The diffusion coefficients of CuCl₂ in aqueous HCl solutions are larger than those of FeCl₃. The presence of HCl has a significant influence on the diffusion of CuCl₂ and FeCl₃ and decreases their diffusion coefficients. The distribution diagrams of Cu(II) and Fe(II), which were constructed using the data of chloro-complexes, showed that the predominant species in acidic solutions are cationic species. The effect of HCl on the diffusion coefficients of CuCl₂ and FeCl₃ in aqueous HCl solutions could be qualitatively explained based upon both the predominant diffusion species and the diffusion potential due to the migration of H⁺ ions. On the other hand, the diffusion coefficients of CuSO₄ in aqueous H₂SO₄ solutions are larger than those of Fe₂(SO₄)₃. The presence of H₂SO₄ has no significant effect on the diffusion coefficients of Fe₂(SO₄)₃.

REFERENCES