Solubility of Cl₂ Gas in Aqueous Chloride Solution*

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The electrowinning of zinc is currently practiced using acidic sulfate solutions. This process is characterized by a large anodic overvoltage, required to discharge oxygen at a lead anode. If acidic zinc chloride solution can be used in the electrowinning, the dimensional stable anodes originally developed for the chloroalkali industry may find further application. These anodes discharge chlorine with the operation of low overvoltages and high current densities, permitting energy savings and an increase in plant productivity.

For this reason, a fundamental study was undertaken to establish the solubility of chlorine gas in various chloride solutions at 298 K. The solubility of chlorine gas in aqueous HCl solutions decreases drastically with increasing HCl concentration up to 0.2 kmol·m⁻³, and then it increases gradually with a further increase in HCl concentration. In aqueous HCl solutions containing MCl₂ (M: Na, K, Ca, Ba, Mg, Ni, Co, Zn, and Fe(III)), the solubility of chlorine gas decreases steadily with increasing MCl₂ concentration. Chlorine exists as Cl₂(aq), HClO, and ClO⁻ in aqueous solutions. Based on the speciation of chlorine in aqueous solutions, it was found that the decrease in solubility of chlorine in aqueous HCl solutions in the concentration range of 0-0.2 kmol·m⁻³ is due to a decrease in HClO and that the gradual increase in solubility with further additions of HCl is due to an increase in ClO⁻. Moreover, the addition of MCl₂ in aqueous solutions decreases the solubility in response to a decrease in Cl₂(aq).

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I. Introduction

The electrowinning of zinc is currently practiced using acidic sulfate solutions. This process is characterized by a large anodic overvoltage, required to discharge oxygen at a lead anode. Consequently, the cell voltage is unavoidably high. If acidic zinc chloride solution can be used in the electrowinning, the dimensional stable anodes originally developed in the chloroalkali industry may find further application. These type of anodes discharge chlorine with the operation of low overvoltages and high current densities, permitting energy savings and an increase in plant productivity⁷⁸.)

However, a part of chlorine gas evolved at the anode dissolves in the electrolyte. This dissolved chlorine gas is also reduced at the cathode, which may lower the current efficiency. Therefore, if a diaphragm is installed between the anode and cathode as a preventative measure, the advantage of using chloride electrolyte will be lost due to the potential drop within the diaphragm.

The present authors measured solubilities of Cl₂ gas in aqueous HCl solutions as well as aqueous solutions of HCl–ZnCl₂ to obtain fundamental data for the electrowinning of zinc chloride without the use of a diaphragm cage. Also the cathodic reduction of dissolved chlorine was studied, the results of which are reported elsewhere⁹.

Although chlorine gas dissolves as molecular chlorine, Cl₂(aq), in aqueous solutions, it reacts with H₂O and Cl⁻ to form HClO and ClO⁻, respectively⁶. The solubility and the reactivity of Cl₂ gas may be affected by the composition of aqueous solutions, but no data have been reported. Therefore, the solubility of Cl₂ gas in aqueous solutions containing metal chloride alone and mixed aqueous solutions of HCl–MCl₂ (M: Na, K, Ca, Ba, Mg, Ni, Co, Zn, and Fe(III)) were determined at 298 K in this study.

II. Experimental Procedures

Figure 1 shows schematically the apparatus used in this study for the determination of Cl₂ solubility. Cl₂ gas supplied from a gas cylinder (A) passed through a flowmeter (C) and a pre-saturator (E) which contains an aqueous solution with the same composition as a test solution in a saturator (F). The Cl₂ gas was dissolved in a test solution contained in a saturator (F) with an inner volume of 1.4×10⁻⁴ m³. Excess Cl₂ gas flowed out from the saturator and was absorbed in 1 kmol·m⁻³ KI–1 kmol·m⁻³ Na₂SO₃ solution⁵ in Cl₂ gas absorbers, (I) and (J).

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Throughout the experiments, the pre-saturator (E) and the saturator (F) were maintained at constant temperature in a water bath (K). The test solution in the saturator was agitated by means of a magnetic stirrer (G). After Cl\(_2\) gas was blown into the saturator for a pre-determined period, all the valves connected to the saturator were released to achieve an equilibrium between the test solution and 1 atm Cl\(_2\) gas. Then an aliquot of test solution was quickly withdrawn and added to a 2 kmol·m\(^{-3}\) KI-0.02 kmol·m\(^{-3}\) HCl solution by means of pressurized N\(_2\) gas from the cylinder, (B), to determine the concentration of dissolved chlorine. In acidified KI solution, dissolved Cl\(_2\) is reduced to chloride ions, Cl\(^-\), by I\(^-\) ions forming I\(_2\) ion. The stable I\(_2\) ions formed were titrated with 0.1 N Na\(_2\)S\(_2\)O\(_3\) solution\(^{(5)}\). Unless otherwise stated, all solubility measurements were conducted at 298 K, and by blowing Cl\(_2\) gas at 3.3 × 10\(^{-3}\) m\(^3\)·s\(^{-1}\) for 1800 s.

The chemicals used in this study were all reagent grade supplied commercially. De-ionized water with a specific conductivity greater than 5 × 10\(^4\) Ω·m was used to prepare the aqueous solutions.

In order to express the solubility of Cl\(_2\) gas in units of mol (kg·H\(_2\)O\(^{-1}\)), the density value, \(\rho\), of a mixed electrolyte solution was required. To estimate the density of the mixed electrolyte solution from the density data of single-electrolyte solutions, eq. (1) was employed\(^{(6)}\):

\[
\rho = \frac{\sum Q_i C_i \rho_i}{\sum Q_i C_i}
\]

where \(\rho\) is the density of the mixed aqueous solution, \(\rho_i\) is the density of a solution of electrolyte \(i\), at the same ionic strength (on the molar scale) as the mixed solution, and the term \(C_i\) is the molarity of electrolyte \(i\) in the mixed solution. The factor \(Q_i\) takes on the values 1, 3, 4, or 6 when \(i\) is a 1-1, 2-1, 2-2, or 3-1 electrolyte, respectively. Density data of aqueous single-electrolyte solutions necessary for the calculation are cited in the literature\(^{(7)}\).

### III. Experimental Results

#### 1. Dissolution rate of Cl\(_2\) gas

Prior to the determination of Cl\(_2\) gas solubility, the blowing time of Cl\(_2\) gas necessary to reach equilibrium was determined experimentally. Figure 2 shows the relationship between the gas-blowing time and the Cl\(_2\) concentration in aqueous solutions at a blowing rate of 3.3 × 10\(^{-3}\) m\(^3\)·s\(^{-1}\). As is clear in the figure, the equilibrium state seems to be established after blowing of Cl\(_2\) for 600 s with both pure water and 1.0 kmol·m\(^{-3}\) HCl-1.0 kmol·m\(^{-3}\) ZnCl\(_2\) solution. Therefore, all solubility measurements in this work were performed after blowing of Cl\(_2\) at the same rate for 1800 s. The saturated concentration of dissolved Cl\(_2\) in pure water, thus determined, agrees well with those reported in the literature\(^{(8)-(10)}\) within experimental error.

![Fig. 2] Dissolved chlorine concentration as a function of time in water and in an acid chloride solutions of zinc.

![Fig. 3] Effect of HCl concentration on the solubility of chlorine gas in aqueous HCl solutions.

#### 2. Solubility of Cl\(_2\) gas in aqueous HCl solution

Figure 3 depicts the effect of HCl concentration on the solubility of Cl\(_2\) gas in aqueous HCl solutions. The solubility of Cl\(_2\) gas decreases sharply with increasing HCl concentration up to 0.2 kmol·m\(^{-3}\) and then increases slightly with further increases in HCl concentration.

#### 3. Solubility of Cl\(_2\) gas in aqueous MC\(_i\) solutions

Figure 4 shows the solubilities of Cl\(_2\) gas in aqueous NaCl and KCl solutions as a function of chloride concentration. By increasing the NaCl or KCl concentration form 0 to 0.5 kmol·m\(^{-3}\), the solubility of Cl\(_2\) gas decreases considerably; however, further increases in chloride concentration result in a slightly linear decrease in Cl\(_2\) solubility.

Figure 5 illustrates the effect of MC\(_i\) concentration on the solubility of Cl\(_2\) gas in aqueous MC\(_i\) (M: Ca, Ba, Mg, Ni and Co) solutions. As is clear in this figure, the solubility of Cl\(_2\) gas in these chloride solutions decreases with increasing MC\(_i\) concentration, and does not differ significantly among salts.
Solubility of Cl₂ Gas in Aqueous Chloride Solution

4. Solubility of Cl₂ gas in aqueous HCl-MCl₃ solutions

Figure 6 shows the effect of NaCl concentration on the solubility of Cl₂ gas in aqueous solutions of HCl-NaCl. At constant HCl concentration, the solubility of Cl₂ gas decreases with increasing NaCl concentration. The effect of NaCl concentration on the solubility is almost identical to that of aqueous NaCl solutions above 0.5 kmol·m⁻³. No significant change in the solubility dependence on NaCl concentration was detected when the concentration of HCl was changed. A similar tendency was observed for the solution systems of HCl-MgCl₂, HCl-ZnCl₂, and HCl-FeCl₃.

Figure 7 shows the effect of MCl₃ (M: Na, Mg, Zn, and Fe(III)) concentration on the solubility of chlorine gas in aqueous HCl-MCl₃ solutions. The chlorides MCl₃ include NaCl, MgCl₂, ZnCl₂, and FeCl₃. The solubility of Cl₂ gas in these aqueous solutions decreases with increasing MCl₃ concentration, and the degree of decreasing the Cl₂ solubility follows the order of ZnCl₂ < NaCl < MgCl₂ < FeCl₃.

IV. Discussion

Reported values on the solubility of Cl₂ gas in acidified aqueous chloride solutions are rather limited. As can be understood from the experimental results in this work, the solubility of Cl₂ gas decreases in the presence of metal chloride in aqueous HCl solutions. Figures 3 to 5 show that the effect of chloride concentration on the solubility of Cl₂ gas is different for the aqueous HCl solution and the aqueous MCl₃ solutions. The solubility of Cl₂ gas in aqueous HCl solution, shown in Fig. 3, decreases sharply with an increase in HCl concentration in the low concentration range, and it shows a slightly increasing trend at higher HCl concentrations. In contrast, the solubility of Cl₂ gas in aqueous MCl₃ solutions, as shown in Figs. 4 and 5, decreases steadily with increasing MCl₃ concentration. Further consideration on the effects of electrolyte concentration on the solubility of Cl₂ gas in aqueous HCl solution and aqueous MCl₃ solution is given below.

When Cl₂ gas dissolves in an aqueous solution, in addition to dissolved molecular chlorine, Cl₂(aq), HClO and Cl⁻ are formed by the rapid hydrolysis reaction of Cl₂(aq) and the reaction between Cl₂(aq) and Cl⁻, respectively. The equilibrium relations of these three chemical species are given by the following equations:  

\[
\text{Cl}_2(g) = \text{Cl}_2(aq) \quad K_c(298) = 6.2 \times 10^{-3} \quad (2)
\]

\[
\text{Cl}_2(aq) + H_2O = HClO + H^+ + Cl^- \quad K_c(298) = 3.94 \times 10^{-4} \quad (3)
\]

\[
\text{Cl}_2(aq) + Cl^- = Cl_2^- \quad K_c(298) = 1.95 \times 10^{-1} \quad (4)
\]
The solubilities of Cl$_2$ gas in aqueous solutions containing various chlorides can be calculated using these equilibrium relations. However, the equilibrium constant given in eq. (2) is that of pure water, which is not applicable for mixed concentrated solutions, mainly because the activity of water in the solutions is less than unity. Therefore, the concentrations of Cl$_2$(aq), HClO and Cl$_2^-$ in aqueous solutions of HCl–NaCl, HCl–MgCl$_2$ and HCl–ZnCl$_2$ were calculated by using our observed results on the solubility of Cl$_2$ gas, $K_b$, $K_m$, mass balance equations, and an electrical neutrality equation. The data for the formation constants of zinc chloro-complex ions were also included in the calculation of aqueous HCl–ZnCl$_2$ solutions.

The calculation procedures are exemplified by the aqueous HCl–ZnCl$_2$ system, which is the most complicated system studied in this work. The terms $C_1$, $C_2$, and $C_3$ (kmol·m$^{-3}$) denote the analytical concentrations of HCl, ZnCl$_2$ and the saturated concentration of Cl$_2$ in solution, respectively. In this solution system, there are 10 unknown variables which include the concentrations, [Cl$_2$(aq)], [HClO], [Cl$_2^-$], [Cl$^-$], [H$^+$], [Zn$^{2+}$], [ZnCl$^+$], [ZnCl$_2$], [ZnCl$^-$], and [ZnCl$_3^-$]. On the other hand, six equilibrium relations, three mass balance equations and one electrical neutrality equation are available to define this system.

**Equilibria:**

$$K_b = \frac{[\text{HClO}] [\text{H}^+] [\text{Cl}^-]}{[\text{Cl}_2(\text{aq})]} \quad (3')$$

$$K_c = \frac{[\text{ZnCl}_2]}{[\text{Cl}_2(\text{aq})] [\text{Cl}^-]} \quad (4')$$

$$k_1 = \frac{[\text{ZnCl}^+]}{[\text{Zn}^{2+}] [\text{Cl}^-]} \quad (5)$$

$$k_2 = \frac{[\text{ZnCl}_2]}{[\text{ZnCl}^+] [\text{Cl}^-]} \quad (6)$$

$$k_3 = \frac{[\text{ZnCl}_3^-]}{[\text{ZnCl}_2] [\text{Cl}^-]} \quad (7)$$

$$k_4 = \frac{[\text{ZnCl}^-]}{[\text{ZnCl}_2] [\text{Cl}^-]} \quad (8)$$

**Mass balances:**

$$\text{H:} \quad C_1 = [\text{H}^+] - [\text{HClO}] \quad (9)$$

$$\text{Zn:} \quad C_2 = [\text{Zn}^{2+}] + [\text{ZnCl}^+] + [\text{ZnCl}_2] + [\text{ZnCl}^-] + [\text{ZnCl}_3^-] \quad (10)$$

$$\text{Cl}_2: \quad C_3 = [\text{Cl}_2(\text{aq})] + [\text{HClO}] + [\text{Cl}_2^-] \quad (11)$$

**Electrical neutrality:**

$$[\text{H}^+] + 2[\text{Zn}^{2+}] + [\text{ZnCl}^+]$$

$$= [\text{ZnCl}_2] + 2[\text{ZnCl}_2^-] + [\text{Cl}^-] + [\text{Cl}_2^-] \quad (12)$$

From these equations, eqs. (13) through (15) are obtained.

$$[\text{Zn}^{2+}] = C_2 / \left( 1 + k_1 [\text{Cl}^-] + k_2 k_3 [\text{Cl}^-]^2 + k_4 k_5 [\text{Cl}^-]^3 \right) \quad (13)$$

$$[\text{Cl}_2(\text{aq})] = \frac{C_3 + C_1 - (1 + K_c [\text{Cl}^-]) [\text{Cl}_2(\text{aq})]}{C_3 - (1 + K_c [\text{Cl}^-]) [\text{Cl}_2(\text{aq})]) [\text{Cl}^-] / K_b} \quad (14)$$

$$\{C_3 - (1 + K_c [\text{Cl}^-]) [\text{Cl}_2(\text{aq})]) [\text{Cl}^-] / K_b \} \quad (15)$$

These simultaneous equations can be solved by a successive approximation method using a micro computer. First, the concentration of Zn$^{2+}$, [Zn$^{2+}$], is calculated by substituting an appropriate initial value of [Cl$^-$] into eq. (13). Next, the concentration of dissolved molecular chlorine, [Cl$_2$(aq)], is calculated by substituting the [Zn$^{2+}$] value thus obtained and the initial value of [Cl$^-$] into eq. (14). Then, the values of [Zn$^{2+}$], [Cl$_2$(aq)], and [Cl$^-$] are introduced into eq. (15) to test whether the equation is satisfied with these concentrations or not. These calculations are repeated by changing [Cl$^-$] gradually until concentrations of [Zn$^{2+}$], [Cl$_2$(aq)], and [Cl$^-$] common to eqs. (13), (14), and (15) are found. Once these concentrations are obtained, the concentrations of the other seven species can be calculated easily. The successive formation constants of Zn(II) chloro-complexes used in the calculation are $k_1 = 10^{-0.3}$, $k_2 = 10^{-0.2}$, $k_3 = 10$ and $k_4 = 10^{-1}$ at 298 K and zero ionic strength.

Similar calculations were made for the aqueous solution systems of HCl, HCl–NaCl, and HCl–MgCl$_2$.

The calculated results for typical solution compositions of the solution systems mentioned above are given in Table 1. Also, the distribution diagrams of each chemical species in the aqueous solutions of HCl alone, HCl–NaCl and HCl–ZnCl$_2$ are illustrated in Figs. 8, 9, and 10, respectively.

Figure 8 shows the distribution of each chemical species in aqueous HCl solutions. It can be seen that the concentration of Cl$_2$(aq) remains almost constant despite the increase in HCl concentration, while the concentration of HClO decreases sharply. On the other hand, the concentration of Cl$_2^-$ increases with increasing HCl concentration. This result agrees qualitatively with the data on Cl$_2$ gas solubility in aqueous HCl solutions, shown in Fig. 3. Therefore, the decrease in solubility with increasing HCl concentration, below 0.2 kmol·m$^{-3}$ HCl, and the slight increase in solubility at higher HCl concentrations may be explained by a decrease in HClO concentration and an increase in Cl$_2^-$ concentration, respectively.

Figure 9 shows the distribution of each chemical species in aqueous HCl–NaCl solutions. In this solution system, the changes in the HClO and Cl$_2^-$ concentrations are similar to those in the aqueous HCl solutions. However, the Cl$_2$(aq) concentration decreases with increasing NaCl concentration. The solubility of chlorine gas in the solutions is primarily controlled by the concentration of Cl$_2$(aq), as expected from the figure. The solubility decreases gradually over the entire concentration range of NaCl. It should be noted that the curve corresponding to HClO concentration for the aqueous NaCl solution containing 1.0 kmol·m$^{-3}$ HCl is not visible because of its low concentration.
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<tr>
<th>Composition of solution, ( \text{C(MCl}_2\text{)} / \text{kmol} \cdot \text{m}^{-3} )</th>
<th>Solubility of chlorine gas, ( S(\text{Cl}_2) / 10^{-2} \text{ kmol} \cdot \text{m}^{-3} )</th>
<th>Concentration, ( \text{C(Cl}_2\text{)} / 10^{-3} \text{ kmol} \cdot \text{m}^{-3} )</th>
<th>Distribution (%)</th>
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Fig. 8 Speciation of dissolved chlorine in aqueous HCl solutions.

Fig. 9 Speciation of dissolved chlorine in aqueous HCl-NaCl solutions.
on solubility were examined. The main results are summarized as follows:

1. Solubility of Cl₂ gas in aqueous HCl solution decreases sharply with increasing HCl concentration, and then increases slightly above 0.2 kmol·m⁻³ HCl.

2. Solubility of Cl₂ gas in aqueous MCI, (M: Na, K, Ba, Ca, Mg, Ni, and Co) solution steadily decreases with an increase in MCI concentration. The solubility of Cl₂ gas in mixed aqueous solution of HCl–MCI, (M: Na, K, Ca, Ba, Mg, Ni, Co, and Fe(III)) decreases linearly with increasing MCI concentration, at constant HCl concentration.

3. Although Cl₂ gas in aqueous solution dissolves as a molecular chlorine, Cl₂(aq), it also forms HClO and Cl⁻, when reacting with H₂O and Cl⁺, respectively. The concentrations of these chemical species at equilibrium were calculated from the measured solubility of Cl₂ gas. The calculated concentrations indicate that the sharp decrease in Cl₂ gas solubility, in dilute HCl solution, can be attributed to a decrease in HClO concentration, and that the increase in Cl⁻ solubility, in concentrated HCl solution, is mainly caused by an increase in Cl⁻ concentration. Furthermore, the steady decrease in Cl₂ gas solubility in aqueous MCI solutions, as well as in aqueous HCl–MCI solutions, can be attributed to a salting-out effect by MCI.

REFERENCES


V. Conclusions

The solubilities of Cl₂ gas in aqueous solutions of HCl, MClₓ, and HCl–MCl were measured at 298 K in this work. Also, the effects of HCl and MCI concentrations...