

Experimental Determination of Equilibrium Constants of Copper Complexes in Aqueous Environment

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(Manuscript received 22 December, 2011; revised 19 March, 2012; accepted 19 April, 2012)

Abstract

The experimental determination of equilibrium constants is required to estimate concentrations of reagents and/or products in environmental chemical reactions. For an example, the choice of copper (Cu) complexation reactions was motivated by their fast kinetics and the ease of measurement of Cu by an ion-sensitive electrode. Each individual titrant of sulfate (SO_4^{2-}) and oxalate ($\text{C}_2\text{O}_4^{2-}$) was expected to have its own unique characteristics, depending on the bonding in Cu-ligands connected to the aqueous species. The complexation reaction of Cu with SO_4^{2-} somewhat fast reached equilibrium status compared with $\text{C}_2\text{O}_4^{2-}$. The experimental equilibrium constants (K_{eq}) of copper sulfate (CuSO_4) and copper oxalate (CuC_2O_4) were determined $10^{2.2}$ and $10^{3-4.3}$, respectively.

Key Words : Equilibrium constants, Copper (Cu), Complexation reaction, Cu-ligands, Sulfate (SO_4^{2-}), Oxalate ($\text{C}_2\text{O}_4^{2-}$)

1. Introduction

Equilibrium constants have been measured for metal complexes in water system due to their importance in environmental chemistry. In general, chemical reactions move towards a dynamic equilibrium in which both reactants and products are present but have no further tendency to undergo net change (Atkins and Paula, 2005). Due to this phenomenon, both reactants and products have the significant concentrations in the equilibrium mixture.

Equilibrium constants for chemical reactions can be computed from thermodynamic data. However, if thermodynamic data are unavailable for a particularly environmental chemical reaction, they can be estimated experimentally (Brewer and Baughman, 2004). Equilibrium constants can be determined by

different methods such as potentiometric titration, chromatography, ultrafiltration, equilibrium dialysis, ion specific electrodes (ISE), differential pulse anodic stripping voltametry (DPASV), fluorescence spectrometry, and modeling of scatchard method (Sparks, 2003).

Some metal ions in aquatic systems can pose a threat to public health and can damage drinking water systems, showing toxicity to humans in various forms. In some cases, toxicity is limited to certain chemical species and is measured by the total exposure to the metal. When a specific complex is toxic at low concentrations, an obvious problem exists. However, the higher the total metal concentration can be increased by the formation of complexes over what would be predicted by equilibrium concepts, the greater the problem is general. For an example, the copper sulfate is widely used to eliminate filamentous algae and phytoplankton in surface water (Chen and Lin, 2001; Haughey et al., 2000; Van Hullebusch et al., 2002). The toxicity of copper has been reported as 96-h LC_{50} (median lethal concentration) values

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when total copper concentrations are from 0.6 to 2.4 mg/L (Bambang et al., 1995; Chen and Lin, 2001; Guo and Liao, 1992). For simplicity, regulatory agencies typically specify standards for discharge of pollutants or drinking water quality based on the total metal concentration.

In this study, equilibrium constants under chemical reaction conditions in aqueous environment were experimentally estimated. This experiment helps researchers and/or students that study complexation reactions involving copper using the cupric ion-sensitive electrode and calculate the concentration of the copper in water when thermodynamic data are unavailable.

2. Materials and Methods

2.1. Equilibria of complexation reactions of copper

In this experiment, the cupric ion-sensitive electrode was used to determine the concentration of free cupric ions (Cu^{2+}). Sodium sulfate (Na_2SO_4) and sodium oxalate ($\text{Na}_2(\text{C}_2\text{O}_4)$) were also used as titrants. In the presence of complexing agents (SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$), the total Cu concentration ($C_{T,\text{Cu}}$) can be written as:

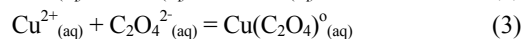
$$C_{T,\text{Cu}} = [\text{Cu}^{2+}] + [\text{CuSO}_4 \text{ or } \text{Cu}(\text{C}_2\text{O}_4)] \quad (1)$$

where CuSO_4 or $\text{Cu}(\text{C}_2\text{O}_4)$ denote copper complexed with ligands. In this experiment, a solution of known $C_{T,\text{Cu}}$ (10^{-3} M $\text{Cu}(\text{NO}_3)_2$) was titrated with the solutions with known ligand concentration such as 0.5 M Na_2SO_4 and 0.01 M $\text{Na}_2(\text{C}_2\text{O}_4)$.

Since $C_{T,\text{Cu}}$ was known, and $[\text{Cu}^{2+}]$ was measured by the electrode, the concentration of complexed Cu (i.e., $[\text{CuSO}_4]$ and $[\text{Cu}(\text{C}_2\text{O}_4)]$) was calculated by difference using the equation (1).

For this experiment, the two ligands were sulfate (SO_4^{2-}) and oxalate ($\text{C}_2\text{O}_4^{2-}$). According to the reaction, the SO_4^{2-} and the $\text{C}_2\text{O}_4^{2-}$ complexes with

copper are, respectively:



At equilibrium, the K_{eq} is related to the activities according to:

$$K_{\text{eq},\text{sulfate}} = \frac{\{\text{CuSO}_4^0_{(\text{aq})}\}}{\{\text{Cu}^{2+}\} \{\text{SO}_4^{2-}\}} \quad (4)$$

$$K_{\text{eq},\text{oxalate}} = \frac{\{\text{Cu}(\text{C}_2\text{O}_4)^0_{(\text{aq})}\}}{\{\text{Cu}^{2+}\} \{\text{C}_2\text{O}_4^{2-}\}} \quad (5)$$

$[\text{Cu}^{2+}]$ was measured, and $[\text{CuSO}_4^0]$ and $[\text{Cu}(\text{C}_2\text{O}_4)^0]$ were calculated by the equation (1). $[\text{SO}_4^{2-}]$ and $[\text{C}_2\text{O}_4^{2-}]$ were computed by the following equations.

For a given volume of titrant, the total concentrations of sulfate (C_{T,SO_4}) and oxalate ($C_{T,\text{C}_2\text{O}_4}$) can be calculated:

$$C_{T,\text{sulfate}} \text{ or } C_{T,\text{oxalate}} = \frac{V_t \times M}{V_t + V_o} \quad (6)$$

where V_t is the volume of titrant added (L), V_o is the original volume of the solution being titrated (L), and M is the molarity of sulfate or oxalate in the titrant. The total copper concentration must also be corrected for use in the equation (1).

$$C_{T,\text{Cu}} = \frac{V_o \times (C_{T,\text{Cu}})_o}{V_t + V_o} \quad (7)$$

where $(C_{T,\text{Cu}})_o$ is the original concentration of copper in the sample solution. Therefore, the concentration of SO_4^{2-} or $\text{C}_2\text{O}_4^{2-}$ can be calculated by the following mass balances, respectively:

$$C_{T,sulfate} = [SO_4^{2-}] + [CuSO_4^0(aq)] \quad (8)$$

$$C_{T,oxalate} = [C_2O_4^{2-}] + [CuC_2O_4^0(aq)] \quad (9)$$

Thus, for any titrant addition, the equilibrium constants for reactions (2) and (3) are estimated by measuring $[Cu^{2+}]$, estimating $[CuSO_4^0]$ and $[Cu(C_2O_4)^0]$ by the equation (1), and estimating $[SO_4^{2-}]$ or $[C_2O_4^{2-}]$ by the equations (8) and (9), respectively.

2.2. Experimental procedure

Five standard solutions with $Cu(NO_3)_2$ (ACS reagent, Sigma-Aldrich, U.S.A.) concentrations of 10^{-5} , 2.5×10^{-5} , 10^{-4} , 2.5×10^{-4} , and 10^{-3} M had been prepared. The mV readings of the five standard solutions were measured by pH meter (Eutech pH 700, Singapore) to construct a standard curve. The 100 mL solution of 10^{-3} M $Cu(NO_3)_2$ was titrated by 0.5 M Na_2SO_4 (ACS reagent, Sigma-Aldrich, U.S.A.), being adjusted to pH 5.5. 2 mL of ionic strength adjuster (ISA: 5 M $NaNO_3$; for trace analysis, Fluka, Swiss) was added to the solution of 10^{-3} M $Cu(NO_3)_2$ and the solution was titrated with the sulfate titrant, recording the mV reading. As the previous procedure of the titration was repeated by 0.01 M $Na_2(C_2O_4)$ (ACS reagent, Sigma-Aldrich, U.S.A.), the mV reading for a new solution of 10^{-3} M $Cu(NO_3)_2$ was recorded.

3. Results

The mV readings of the five standard solutions of $Cu(NO_3)_2$ were measured by the pH meter and presented in Table 1. Plotting the mV readings on the linear axis and the concentrations of standard

solutions on the logarithmic axis, the standard curve was constructed and the regression line with the equation ($\log[Cu^{2+}] = (0.035 \times \text{Electrical potential}) - 8.6128$) 8.613 , $r^2 = 99.8\%$) was created (Fig. 1).

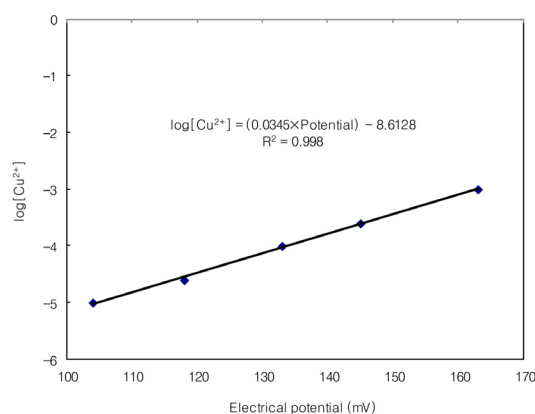


Fig. 1. The plot of electrical potential and standard solutions of $Cu(NO_3)_2$.

The mV readings of the solution of 10^{-3} M $Cu(NO_3)_2$ in response to the titrations by Na_2SO_4 and $Na_2(C_2O_4)$ were expressed in Table 2. The concentrations of Cu^{2+} ($[Cu^{2+}]$) with the addition of two titrants were calculated by the regression equation in Fig. 1. The concentrations of $C_{T,Cu}$ were determined by the equation (7) and also exhibited in Table 2, respectively. The molar concentrations of $[Cu^{2+}]$ and $C_{T,Cu}$ were plotted on y-axis and the volume of titrants of Na_2SO_4 and $Na_2(C_2O_4)$ added was on x-axis in order to draw the titration curves for each titrant, respectively (Figs. 2 and 3).

The activities of Cu^{2+} , the concentrations of its complexes ($CuSO_4^0(aq)$; $Cu(C_2O_4)^0(aq)$) and the free ligands (SO_4^{2-} ; $C_2O_4^{2-}$), and the values of each activity

Table 1. Concentrations and electrical potentials of standard solutions

Concentrations (mol $Cu(NO_3)_2/L$)	Standard solutions				
	1×10^{-5}	2.5×10^{-5}	1×10^{-4}	2.5×10^{-4}	1×10^{-3}
Electrical potentials (mV)	104	118	133	145	163

Table 2. The concentrations of cupric ion (Cu^{2+}) and total copper ($C_{\text{T,Cu}}$) with each addition of titrants of Na_2SO_4 and $\text{Na}_2(\text{C}_2\text{O}_4)$

Na_2SO_4				$\text{Na}_2(\text{C}_2\text{O}_4)$			
Addition (mL)	Potential (mV)	$[\text{Cu}^{2+}]^a$ (mol/L)	$C_{\text{T,Cu}}^b$ (mol/L)	Addition (mL)	Potential (mV)	$[\text{Cu}^{2+}]^a$ (mol/L)	$C_{\text{T,Cu}}^b$ (mol/L)
0	163	1.02×10^{-3}	1.02×10^{-3}	0	163	1.02×10^{-3}	1.02×10^{-3}
5	157	6.36×10^{-4}	9.72×10^{-4}	2	161	8.74×10^{-4}	1.00×10^{-3}
10	153	4.63×10^{-4}	9.29×10^{-4}	4	161	8.74×10^{-4}	9.82×10^{-4}
15	150	3.65×10^{-4}	8.89×10^{-4}	6	160	8.08×10^{-4}	9.63×10^{-4}
20	147	2.88×10^{-4}	8.53×10^{-4}	8	160	8.08×10^{-4}	9.46×10^{-4}
25	145	2.45×10^{-4}	8.19×10^{-4}	10	159	7.46×10^{-4}	9.29×10^{-4}
30	144	2.27×10^{-4}	7.88×10^{-4}	15	159	7.46×10^{-4}	8.89×10^{-4}
35	142	1.93×10^{-4}	7.59×10^{-4}	20	158	6.89×10^{-4}	8.53×10^{-4}
40	141	1.79×10^{-4}	7.33×10^{-4}	25	157	6.36×10^{-4}	8.19×10^{-4}
45	139	1.52×10^{-4}	7.08×10^{-4}	30	156	5.88×10^{-4}	7.88×10^{-4}
50	138	1.41×10^{-4}	6.84×10^{-4}	35	155	5.43×10^{-4}	7.59×10^{-4}
55	137	1.30×10^{-4}	6.63×10^{-4}	40	154	5.01×10^{-4}	7.33×10^{-4}
60	136	1.20×10^{-4}	6.42×10^{-4}	45	154	5.01×10^{-4}	7.08×10^{-4}
				50	153	4.63×10^{-4}	6.84×10^{-4}
				55	152	4.28×10^{-4}	6.63×10^{-4}
				60	151	3.95×10^{-4}	6.42×10^{-4}
				65	150	3.65×10^{-4}	6.23×10^{-4}
				70	149	3.37×10^{-4}	6.05×10^{-4}

$$^a[\text{Cu}^{2+}] = 10^{(0.0345 \times \text{Electrical potential}) - 8.6128}$$

^b $C_{\text{T,Cu}}$ was calculated by the equation (7)

Table 3. Concentrations, activities, activity coefficients, ion activity product (IAP), and the values of log (K) for sulfate titration

V_t (mL)	Potential (mV)	$[\text{CuSO}_4^0(\text{aq})]$ (M)	$C_{\text{T,SO}_4^{2-}}$ (M)	$[\text{SO}_4^{2-}]$ (M)	$\gamma_{\text{Cu}^{2+}}$ ^a	γ_{CuSO_4} ^a	$\gamma_{\text{SO}_4^{2-}}$ ^a	IAP	Log (K) ^b
0	163	0.00×10^{-0}	0.00×10^{-0}	0.00×10^{-0}	0.356	1.0	0.356	NA	NA
5	157	3.40×10^{-4}	2.38×10^{-2}	2.35×10^{-2}	0.356	1.0	0.356	$1.80 \times 10^{+2}$	2.254
10	153	4.69×10^{-4}	4.55×10^{-2}	4.50×10^{-2}	0.356	1.0	0.356	$1.77 \times 10^{+2}$	2.249
15	150	5.26×10^{-4}	6.52×10^{-2}	6.47×10^{-2}	0.356	1.0	0.356	$1.76 \times 10^{+2}$	2.245
20	147	5.67×10^{-4}	8.33×10^{-2}	8.28×10^{-2}	0.356	1.0	0.356	$1.88 \times 10^{+2}$	2.274
25	145	5.75×10^{-4}	1.00×10^{-1}	9.94×10^{-2}	0.356	1.0	0.356	$1.86 \times 10^{+2}$	2.269
30	144	5.62×10^{-4}	1.15×10^{-1}	1.15×10^{-1}	0.356	1.0	0.356	$1.70 \times 10^{+2}$	2.231
35	142	5.66×10^{-4}	1.30×10^{-1}	1.29×10^{-1}	0.356	1.0	0.356	$1.79 \times 10^{+2}$	2.253
40	141	5.54×10^{-4}	1.43×10^{-1}	1.42×10^{-1}	0.356	1.0	0.356	$1.72 \times 10^{+2}$	2.235
45	139	5.55×10^{-4}	1.55×10^{-1}	1.55×10^{-1}	0.356	1.0	0.356	$1.86 \times 10^{+2}$	2.269
50	138	5.43×10^{-4}	1.67×10^{-1}	1.66×10^{-1}	0.356	1.0	0.356	$1.83 \times 10^{+2}$	2.263
55	137	5.31×10^{-4}	1.77×10^{-1}	1.77×10^{-1}	0.356	1.0	0.356	$1.82 \times 10^{+2}$	2.261
60	136	5.21×10^{-4}	1.88×10^{-1}	1.87×10^{-1}	0.356	1.0	0.356	$1.83 \times 10^{+2}$	2.263

$$^a \log \gamma_i = -Az_i^2 \left(\frac{I^{0.5}}{1+I^{0.5}} - 0.2I \right)$$

where, I (ionic strength) = 0.1 M

A (constant) = 0.5085 at 25°C

Z = the number of equivalents per mole of compound

^b log (K) = log (IAP)

IAP = ion activity product

A = not available

Table 4. Concentrations, activities, activity coefficients, ion activity product (IAP), and the values of log (K) for oxalate titration

Vt (mL)	Potential (mV)	[Cu(C ₂ O ₄) ⁰ (aq)] (M)	C _{T,C₂O₄} (M)	[C ₂ O ₄ ²⁻] (M)	γ _{Cu²⁺} ^a	γ _{CuC₂O₄} ^a	γ _{C₂O₄²⁻} ^a	IAP	Log (K) ^b
0	163	0.00×10 ⁻⁰	0.00×10 ⁻⁰	0.00×10 ⁻⁰	0.356	1.0	0.356	NA	NA
2	161	1.30×10 ⁻⁴	1.96×10 ⁻⁴	6.56×10 ⁻⁵	0.356	1.0	0.356	1.79×10 ⁻⁴⁴	4.254
4	161	1.11×10 ⁻⁴	3.85×10 ⁻⁴	2.73×10 ⁻⁴	0.356	1.0	0.356	3.67×10 ⁻³³	3.564
6	160	1.59×10 ⁻⁴	5.66×10 ⁻⁴	4.07×10 ⁻⁴	0.356	1.0	0.356	3.83×10 ⁻³³	3.583
8	160	1.41×10 ⁻⁴	7.41×10 ⁻⁴	5.99×10 ⁻⁴	0.356	1.0	0.356	2.31×10 ⁻³³	3.363
10	159	1.86×10 ⁻⁴	9.09×10 ⁻⁴	7.23×10 ⁻⁴	0.356	1.0	0.356	2.72×10 ⁻³³	3.434
15	159	1.45×10 ⁻⁴	1.30×10 ⁻³	1.16×10 ⁻³	0.356	1.0	0.356	1.33×10 ⁻³³	3.123
20	158	1.65×10 ⁻⁴	1.67×10 ⁻³	1.50×10 ⁻³	0.356	1.0	0.356	1.26×10 ⁻³³	3.100
25	157	1.84×10 ⁻⁴	2.00×10 ⁻³	1.82×10 ⁻³	0.356	1.0	0.356	1.25×10 ⁻³³	3.098
30	156	2.01×10 ⁻⁴	2.31×10 ⁻³	2.11×10 ⁻³	0.356	1.0	0.356	1.28×10 ⁻³³	3.107
35	155	2.16×10 ⁻⁴	2.59×10 ⁻³	2.38×10 ⁻³	0.356	1.0	0.356	1.32×10 ⁻³³	3.122
40	154	2.31×10 ⁻⁴	2.86×10 ⁻³	2.63×10 ⁻³	0.356	1.0	0.356	1.38×10 ⁻³³	3.141
45	154	2.05×10 ⁻⁴	3.10×10 ⁻³	2.90×10 ⁻³	0.356	1.0	0.356	1.12×10 ⁻³³	3.047
50	153	2.20×10 ⁻⁴	3.33×10 ⁻³	3.11×10 ⁻³	0.356	1.0	0.356	1.20×10 ⁻³³	3.081
55	152	2.33×10 ⁻⁴	3.55×10 ⁻³	3.31×10 ⁻³	0.356	1.0	0.356	1.30×10 ⁻³³	3.114
60	151	2.45×10 ⁻⁴	3.75×10 ⁻³	3.50×10 ⁻³	0.356	1.0	0.356	1.40×10 ⁻³³	3.146
65	150	2.56×10 ⁻⁴	3.94×10 ⁻³	3.68×10 ⁻³	0.356	1.0	0.356	1.50×10 ⁻³³	3.177
70	149	2.66×10 ⁻⁴	4.12×10 ⁻³	3.85×10 ⁻³	0.356	1.0	0.356	1.62×10 ⁻³³	3.208

$$^a \log \gamma_i = -Az_i^2 \left(\frac{I^{0.5}}{1+I^{0.5}} - 0.2I \right)$$

where, I (ionic strength) = 0.1 M

A (constant) = 0.5085 at 25°C

Z = the number of equivalents per mole of compound

^b log (K) = log (IAP)

IAP = ion activity product

NA = not available

Table 5. The values of equilibrium constants (K_{eq}), and standard free energies (ΔG_{rxn}° , $(\Delta G_f^{\circ})_{CuSO_4(aq)}$, $(\Delta G_f^{\circ})_{Cu(C_2O_4)^{\circ}(aq)}$)

Titration Parameters	Sulfate	Oxalate
K _{eq} ^a	1.83 × 10 ³	1.26 × 10 ³
ΔG_{rxn}° (kcal/mol) ^b	-3.086	-4.229
$(\Delta G_f^{\circ})_{copper\ complexes}$ (kcal/mol) ^c	-165.236	-149.679

^aEquilibrium constant

^bFree energy of reaction at standard conditions

^cMolar free energy of formation

where, f = formation

^o = standard conditions (pressure = 1 atm, temperature = 298.15 K, activity =1)

⁻ = molar basis (per mole of chemical)

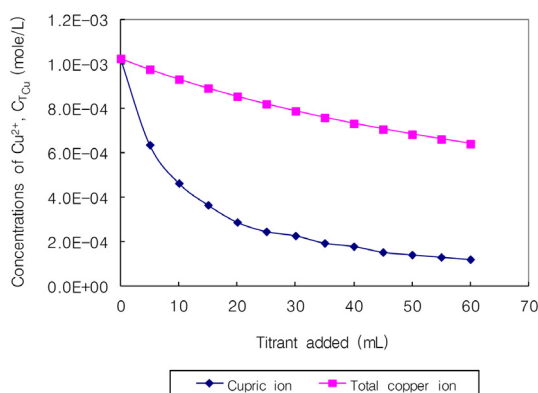


Fig. 2. Changes in the concentrations of Cu^{2+} and $C_{T,\text{Cu}}$ by the addition of Na_2SO_4 .

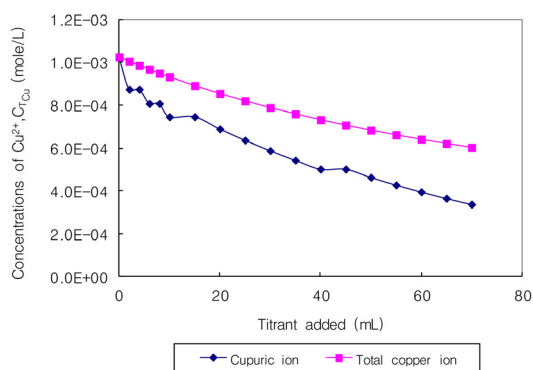


Fig. 3. Changes in the concentrations of Cu^{2+} and $C_{T,\text{Cu}}$ by the addition of $\text{Na}_2(\text{C}_2\text{O}_4)$.

coefficient ($\gamma_{\text{Cu}^{2+}}$; $\gamma_{\text{CuSO}_4(\text{aq})}$; $\gamma_{\text{Cu}(\text{C}_2\text{O}_4)(\text{aq})}$; $\gamma_{\text{SO}_4^{2-}}$; $\gamma_{\text{C}_2\text{O}_4^{2-}}$) according to each addition of titrants of SO_4^{2-} and $\text{C}_2\text{O}_4^{2-}$ were estimated by the equations and presented in Tables 3 and 4, respectively. The estimated values for the ion activity product (IAP) and $\log(K)$ were also shown in Tables 3 and 4.

In order to determine the values of K_{eq} in each titration, the volume of SO_4^{2-} added from 50 to 60 mL and that of oxalate added from 20 to 30 mL were selected from Tables 3 and 4, since those IAP values in the volume added by each titration were very close one another. For each experiment, the K_{eq} using the average IAP was 1.83×10^2 for sulfate titration and

1.26×10^3 for oxalate titration, respectively (Tables 3 and 4).

The standard free energies ($\Delta G_{\text{rxn}}^{\circ}$) of the reactions can be calculated by the following equation:

$$\Delta G_{\text{rxn}}^{\circ} = -RT \ln K_{\text{eq}} \quad (10)$$

where R is gas constant (1.987×10^{-3} kcal/mol·K) and T is temperature (298.15 K at standard condition). To estimate the standard free energies of the copper complexes, $\text{CuSO}_4^{\circ}(\text{aq})$ and $\text{Cu}(\text{C}_2\text{O}_4)^{\circ}(\text{aq})$, the standard free energies of copper (+15.65 kcal/mol), sulfate (-177.8 kcal/mol), and oxalate (-161.10 kcal/mol) are also required (Faure, 1998). With these values, the standard free energies of the copper complexes of $\text{CuSO}_4^{\circ}(\text{aq})$ and $\text{Cu}(\text{C}_2\text{O}_4)^{\circ}(\text{aq})$ were computed by the following equations and shown in Table 5:

$$\Delta G_{\text{rxn,sulfate}}^{\circ} = (\overline{\Delta G_f^{\circ}})_{\text{CuSO}_4(\text{aq})} - (\overline{\Delta G_f^{\circ}})_{\text{Cu}^{2+}(\text{aq})} - (\overline{\Delta G_f^{\circ}})_{\text{SO}_4^{2-}(\text{aq})} \quad (11)$$

$$\Delta G_{\text{rxn,oxalate}}^{\circ} = (\overline{\Delta G_f^{\circ}})_{\text{Cu}(\text{C}_2\text{O}_4)^{\circ}(\text{aq})} - (\overline{\Delta G_f^{\circ}})_{\text{Cu}^{2+}(\text{aq})} - (\overline{\Delta G_f^{\circ}})_{\text{C}_2\text{O}_4^{2-}(\text{aq})} \quad (12)$$

4. Discussion

The Cu^{2+} concentrations in the solution of 10^{-3} M $\text{Cu}(\text{NO}_3)_2$ with addition of the Na_2SO_4 and $\text{Na}_2(\text{C}_2\text{O}_4)$ titrants were computed by the standard curve and the regression equation of Fig. 1. The total copper concentrations were estimated by the equation (7). Initial concentrations of Cu^{2+} and $C_{T,\text{Cu}}$ with the addition of titrants began to be simultaneously diluted (Table 2). The dilution rates of the concentrations of Cu^{2+} and $C_{T,\text{Cu}}$ were different in the presence of complexing agents, indicating that the dilution rates of $[\text{Cu}^{2+}]$ are greater than those of $C_{T,\text{Cu}}$

(Figs. 2 and 3). In conjunction with this different dilution rate between $[\text{Cu}^{2+}]$ and $[\text{C}_{\text{T,Cu}}]$, even though the concentration of Cu^{2+} may be below the drinking water standard (5 $\mu\text{g/L}$ ~30 mg/L) in Europe, Canada and the USA (Health Canada, 1992; IPCS, 1998; US EPA, 1991; US NRC, 2000), the presence of complexed Cu can result in total Cu concentrations exceeding the standard.

The dilution rates of Cu^{2+} were also different, being dependent on the addition of the different titrants. The dilution rates of Cu^{2+} with the SO_4^{2-} titration were faster than those with the $\text{C}_2\text{O}_4^{2-}$ titration (Figs. 2 and 3). It implies that the complexation reaction with the addition of Na_2SO_4 is likely to somewhat quickly reach equilibrium compared with the addition of $\text{Na}_2\text{C}_2\text{O}_4$. This was examined by equilibrium constants of sulfate and oxalate titrants in Table 5.

The equation of Davies approximation was used to estimate the ion activity coefficients of $\text{Cu}^{2+}_{(\text{aq})}$, $\text{SO}_4^{2-}_{(\text{aq})}$, and $\text{CuSO}_4^0_{(\text{aq})}$, using the value of ionic strength ($I = 0.1 \text{ M}$). The $\log(K)$ values ($\log K_{\text{eq}}$ of $\text{CuSO}_4 = 2.2$; $\log K_{\text{eq}}$ of $\text{CuC}_2\text{O}_4 = 3.0$ ~ 4.3) of the experimentally computed stability constants were involved in the range of the theoretical values ($\log K_{\text{eq}}$ of $\text{CuSO}_4 = 0.5$ ~ 2.5 ; $\log K_{\text{eq}}$ of $\text{CuC}_2\text{O}_4 = 2$ ~ 6) (Faure, 1998). The experimental values were not independent of theoretical ranges.

These estimates of the equilibrium constants were used to determine the standard free energies of $\text{CuSO}_4^0_{(\text{aq})}$ and $\text{Cu}(\text{C}_2\text{O}_4)^0_{(\text{aq})}$. The calculated value of $(\Delta G_f^\circ)_{\text{CuSO}_4^0_{(\text{aq})}}$ was 165.2 kcal/mol (Table 5) and was very close to the thermodynamic data (165.3 kcal/mol) (Faure, 1998).

Stability constants can be conditionally impacted by some factors such as ionic strength of the solution, temperature, pH, method of analysis of the complex, and method of data manipulation and stability constant calculation (Borge and Madariaga, 1997;

Brewer and Baughman, 2004). I had adjusted two titrants solution to pH 5.5 prior to the titration, since the stability constants were slightly higher at pH 5.0 than at pH 3.5. This is probably due to the higher dissociation of functional groups at pH 5.0, H^+ and the metal ions competing for binding sites on the ligand, and the status of metal binding at the lower pH (Sparks, 2003).

5. Conclusion

In this analytical experiment, an ion-specific electrode was used to determine copper concentrations in aqueous solutions. The values of stability constants ($K_{\text{eq},\text{SO}_4^{2-}} = 1.83 \times 10^2$; $K_{\text{eq},\text{C}_2\text{O}_4^{2-}} = 1.26 \times 10^3$) for each titrant were experimentally estimated and the standard free energies of SO_4^{2-} (-3.086 kcal/mol), $\text{C}_2\text{O}_4^{2-}$ (-4.229 kcal/mol), $\text{CuSO}_4^0_{(\text{aq})}$ (-165.236 kcal/mol), and $\text{Cu}(\text{C}_2\text{O}_4)^0_{(\text{aq})}$ (-149.679 kcal/mol) for the complexation reactions were also calculated.

The values of stability constants are able to be determined experimentally in the case of the unavailability in the scientific literature. Their dependence on the total concentration of metal and ligand present in a given system reinforces the fact that there are valid for the environmental conditions under which they were determined. For this reason, using the average of stability constants determined under similar environmental conditions in this experiment was applied by the concept of equilibrium constants for metal-ligand complexes.

Acknowledgements

This work was experimentally supported by the Environmental Chemistry Laboratory in the Department of Civil and Environmental Engineering, Syracuse University, Syracuse, NY, USA. I appreciate the help of Dr. Chris E. Johnson in laboratory analyses and anonymous reviewers in

improvements of the manuscript. I also appreciate the financial help of Korea Maritime Institute (KMI) in the publication of this manuscript. KMI is a government sponsored research organization affiliated with the Prime Minister's office of the Republic of Korea.

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