

*The Conductance of Copper(II) Sulfate in Water at Various Temperatures**

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Abstract

The present investigation was undertaken to obtain the thermodynamic properties of ion association reactions. The electrolytic conductances of copper(II) sulfate in water at the temperatures ranging from 5° to 45° C were measured in order to study the effect of temperature on ion association constants. The data were analyzed using Shedlovsky's method based on the Onsager's limiting law and ion association constants K_A , equivalent conductances at infinite dilution Λ_0 were obtained. From the plot of $\log K_A$ vs. $1/T$ over the whole temperature range following values obtained; $\Delta H = 1.89$ kcal deg⁻¹ mol⁻¹, $\Delta G = -3.22$ kcal deg⁻¹ mol⁻¹, $\Delta S = 17.1$ cal mol⁻¹ at 25° C.

1 Introduction

With the high charge type electrolyte and the solvent of low dielectric constant the "ion association" become apparent due to the electrostatic interaction between ions.¹⁻⁵⁾

In the equilibrium between the free ion and the ion-pair,



the ion association constants K_A are shown by (2).

$$K_A = \frac{\{AX^{(m-n)+}\}}{\{A^{m+}\} \{X^{n-}\}} \quad (2)$$

where { } is represent activities. K_A 's calculated from the electrolytic conductance data of the dilute solution.

In the previous paper,^{6,7)} electrolytic conductances of copper(II) sulfate and *m*-benzendisulfonate have been measured in the methanol-water and dioxane-water mixtures to study the effect of solvents on ion association reactions in the solution of high charge type electrolyte.

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The present investigation was undertaken to obtain the thermodynamic properties of ion association reactions and the conductance of copper(II) sulfate in water have been measured at the temperatures ranging from 5° to 45° C.

2 Experimental

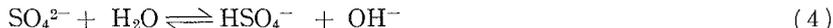
(1) *Materials and Methods*

The experimental methods were carried out with the apparatus previously described.^{6,7)} Copper(II) sulfate was recrystallized twice from the conductivity water and dried at 110° C to its monohydrate.

A Jones's type bridge (accurate to within $\pm 0.05\%$)⁸⁾ was used for the conductance measurements. It was operated with alternating current at 2 to 10 kcycles. The cells of flask type were used for the measurements, and the cell constants were determined as functions of the measured specific conductance by the potassium chloride solutions at each temperatures. The specific conductance of conductivity water was less than 10^{-6} moh. The equivalent conductance Λ ohm⁻¹ cm² equiv⁻¹ was measured in the range of concentration c from 10^{-4} to 10^{-3} mol liters⁻¹.

(2) *The hydrolysis correction for copper(II) sulfate solution by pH measurement*

It must be assumed that CuOH⁺ and HSO₄⁻ ions are produced from the complicated hydrolysis of copper(II) sulfate in water.



The measured specific conductance should be corrected for the presence of hydrolysis product. The contribution of ions other than Cu²⁺ and SO₄²⁻ ions to the specific conductance were estimated roughly and deducted from the observed specific conductance value of copper(II) sulfate solution.

The corrections were carried out as follows; the *pH* values of the conductivity water and copper(II) sulfate solution were measured at each temperature. Carbon dioxide absorbed from the air were assumed essentially constant. The specific conductance of solvent L_{water} , was assumed to be due to H⁺ and HCO₃⁻ ions produced from the ionization of the dissolved carbon dioxide, and a constant residual specific conductance ΔL , due to unknown impurities. And ΔL was deduced from (5).

$$10^3 L_{\text{water}} = \lambda_{\text{H}^+}[\text{H}^+] + \lambda_{\text{HCO}_3^-}[\text{HCO}_3^-] + 10^3 \Delta L \quad (5)$$

where λ 's are the ion equivalent conductance.

The ion concentration of CuOH⁺, HSO₄⁻ and HCO₃⁻ were calculated from the hydrogen ion concentration in copper(II) sulfate solution and dissociation constant of HSO₄⁻ and HCO₃⁻ with the relation of (6).

$$[\text{HCO}_3^-] + [\text{CuOH}^+] = [\text{H}^+] + [\text{HSO}_4^-] \quad (6)$$

As described above, the concentration $[\text{H}^+]$ and $[\text{HCO}_3^-]$ were calculated from

the pH values obtained at each temperatures.

Thus, the correction for the measured specific conductance Values ΔL_S in the copper(II) sulfate solution were given by (7).

$$10^3 \Delta L_S = \lambda_{H^+}[H^+] + \lambda_{HCO_3^-}[HCO_3^-] + 10_3 \Delta L \\ - [CuOH^+] (2\lambda_{Cu^{2+}} - \lambda_{CuOH^+}) \\ - [HSO_4^-] (2\lambda_{SO_4^{2-}} - \lambda_{HSO_4^-}) \quad (7)$$

Where the hydrolytic correction values were larger than 3%, the data were dropped for the all calculations of the association constant.

3 Results and Discussion

The corrected values of the equivalent conductances A of copper(II) sulfate and their plot against the square root of concentration $c^{1/2}$ are shown in Table 1 and Fig. 1, respectively.

Table 1 Measures equivalent conductance A of copper(II) sulfate solution in water

5°		15°		25°	
$10^4 c$	A	$10^4 c$	A	$10^4 c$	A
2.3935	71.78	3.7100	91.66	1.8959	121.92
3.6621	70.54	5.9287	88.38	2.4711	120.18
4.9297	68.80	9.1490	84.69	3.5858	117.34
7.8792	65.98	16.117	78.95	5.5247	113.46
14.460	61.40	27.206	73.01	10.466	106.16
35°		45°			
$10^4 c$	A	$10^4 c$	A		
2.3510	148.07	1.7344	180.71		
3.3261	144.81	2.4635	177.14		
4.7403	140.84	3.0914	174.58		
10.372	129.56	4.9629	167.46		
18.170	119.51	8.8257	157.14		

From the results of Table 1, the equivalent conductances at infinite dilution A_0 and ion association constants K_A were calculated by means of Shedlovsky's method based on the Onsager's limiting equation. The association equilibrium constant K_A is given by (8).

$$K_A = \frac{1-\alpha}{c\alpha^2 f_{\pm}^2} \quad (8)$$

where c is concentration (mol liter⁻¹), α is degree of dissociation and the activity

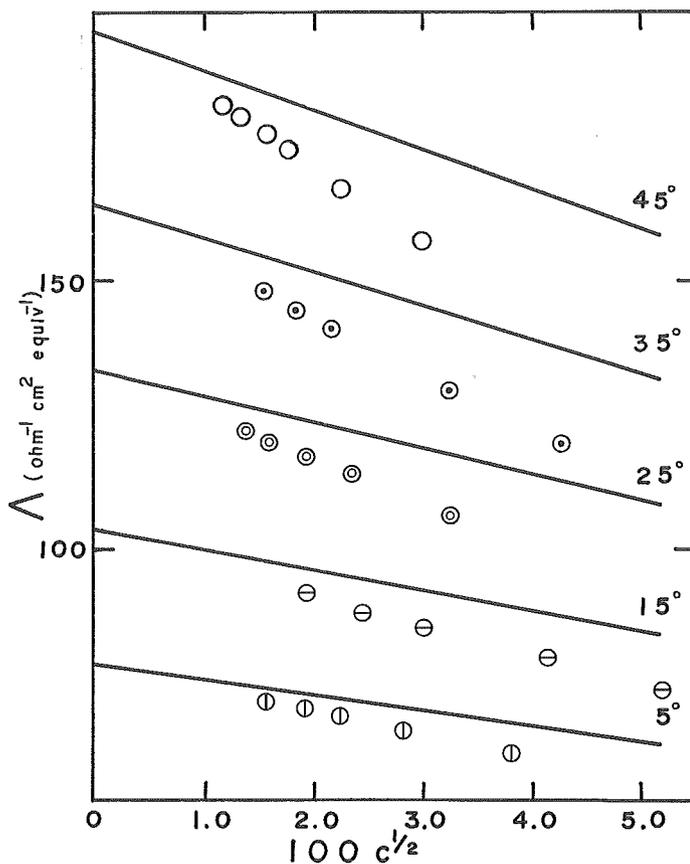


Fig. 1 Λ - $c^{1/2}$ plot of copper(II) sulfate in water.
 ○-45°, ⊙-35°, ⊗-25°, ⊖-15°, ⊕-5°,
 — limiting law.

coefficient f_{\pm} is given by Debye-Hückel equation (9).

$$-\log f_{\pm}^2 = A(c\alpha)^{1/2} \quad (9)$$

$$\alpha = \frac{AS}{A_0} \quad (10)$$

$$\text{where } S = \left\{ \frac{Z}{2} + \left[1 + \left(\frac{Z}{2} \right)^2 \right]^{1/2} \right\}^2 \quad (11)$$

$$\text{and } Z = \frac{(cA)^{1/2}}{A_0^{3/2}} (\alpha^* A_0 + \beta^*) \quad (12)$$

$(\alpha^* A_0 + \beta^*)$ is limiting slope.

First, a value of A_0 is estimated from the extrapolation of $\Lambda - c^{1/2}$ plot then

α 's calculated from equation (10). From combining equations (8) and (10).

$$\frac{1}{AS} = \frac{1}{A_0} + \frac{cASf_{\pm}^2 K_A}{A_0^2} \quad (13)$$

An extrapolation of $1/AS - cASf_{\pm}^2$ plot gives a better value of A_0 and K_A . The successive approximation gave final values of A_0 and K_A . The results are shown in Table 2.

Table 2 Summary of conductance parameters of copper(II) sulfate in water at various temperatures.

Temp. °C	D^*	A_0	K_A	$A_0\eta$
5	86.12	78.0	185	1.182
15	82.23	103.0	210	1.172
25	78.54	132.9	230	1.183
35	75.04	162.9	250	1.172
45	71.70	196.2	289	1.170

* Where D are the dielectric constants of solvent⁵³.

The Walden's product $A_0\eta$ were essentially constant as indicate in Table 2. The equivalent conductances at infinite dilution A_0 value at 25° C is in agreement with the value of OWEN, B. B. and GURRY, R. W.¹⁰ within the experimental error.

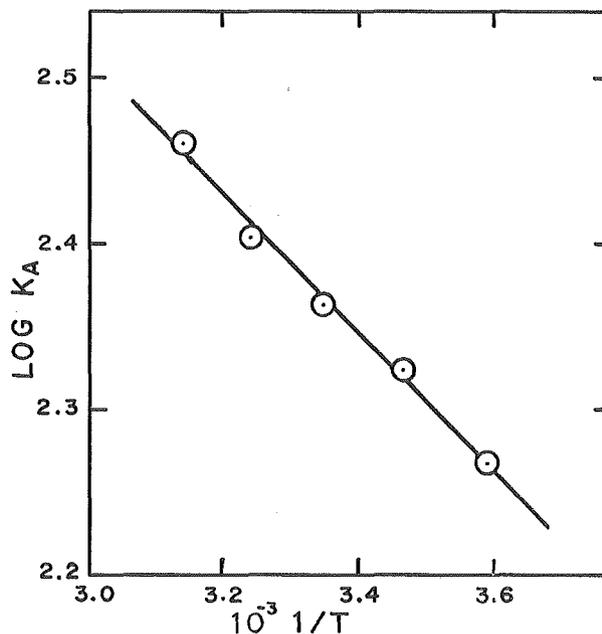


Fig. 2 $\log K_A - 1/T$ plot of copper(II) sulfate in water.

The $\log K_A - 1/T$ plot gives an straight line as shown in Fig. 2.

The heat ΔH and the entropy changes ΔS of the ion association reaction were calculated from (14) and (15).

$$\frac{d \ln K_A}{d(1/T)} = - \frac{\Delta H}{R} \quad (14)$$

$$- RT \ln K_A = \Delta H - T \Delta S \quad (15)$$

The best straight line for the $\log K_A - 1/T$ plot over the whole temperature range was obtained by least squares, $\Delta H = 1.89 \text{ kcal deg}^{-1} \text{ mol}^{-1}$, and equation (15) gives the values of $\Delta S = 17.1 \text{ cal mol}^{-1}$ at 25° C . The values are compared in with the data of calcium¹¹⁾ and magnesium¹²⁾ sulfates.

Table 3 Thermodynamic properties of ion association reaction in water at 25° C .

Reaction	K_{A298}	ΔH (kcal mol ⁻¹)	ΔG (Kcal mol ⁻¹)	ΔS (cal mol ⁻¹)	Ionic radius (Cation Å)
$\text{Cu}^{2+}, \text{SO}_4^{2-}$	230	1.89	- 3.22	17.1	0.96
$\text{Ca}^{2+}, \text{SO}_4^{2-}$	200	1.65	- 3.15	16.1	0.99
$\text{Mg}^{2+}, \text{SO}_4^{2-}$	234	4.55	- 3.22	26.1	0.65

As shown in Table 3, the ΔH values are positive, and the reaction is endothermic. The ΔS value of the association reaction of copper(II) sulfate and calcium sulfate are close, which might be due to a close resemblance of the ionic radius and also the hydration entropy of ions. The ΔS values of the reactions are positive. This reflects the decreased orientation of water molecules when the ion-pair forms.

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