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Potentiometric Studies on Sulfato Complex of Aluminium(III) in Aqueous Solution at Elevated Temperatures

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Equilibria in aluminium sulfate solutions with a 1 mol kg^{-1} KCl medium and low pH range have been investigated by means of acidity measurements with a hydrogen ion concentration cell from 25 to 125 °C. The results were treated with a nonlinear least squares computer program to analyze the equilibrium constants for aluminium complexes by using a single parameter type of Debye-Hückel equation. The log(K/mol^{-1} kg) values of the formation constant for the reaction, $Al^{3+}+SO_4^{2-} \rightleftarrows [AlSO_4]^+$ varied from 3.35 at 25 °C to 5.34 at 125 °C and were formulated as a function of temperature. The standard enthalpy and entropy of the complex formation computed from the variation of the formation constant with temperature are presented over the experimental temperature range. The species $[Al(SO_4)_2]^-$ was not detected under the present conditions.

Sulfate ion affects the hydrolysis and the precipitation of polyvalent metal ions considerably through complex formation at elevated temperatures and much evidence has been reported for the interaction of sulfate ion with metal ions such as aluminium(III)[1] and iron(III).[2]

Izatt et al. have reported a large number of formation constants for sulfato complexes at 25 °C as determined by calorimetry.[3] Those values become greater with the charge of metal ion.

However, those data are very limited even at moderate temperatures because the hydrolysis of metal ions is too complicated to allow satisfactory analysis of the equilibrium in the solution. Nikolaeva has measured the formation constants of sulfato complexes of bivalent metal ions up to 90 °C by the conductometric method.[4] With regards to tervalent metal ions, only Matijević et al. have investigated sulfato complexes of iron(III)[5] and aluminium(III)[6] ions up to 100 °C with respect to the preparation of monodispersed particles of the hydrous oxides of the metal ions.

At elevated temperatures, Marshall et al. studied the formation of $[MgSO_4]$[7] and $[CaSO_4]$[8] by solubility measurements.

Akitt and his co-workers have studied the complex formation in aqueous aluminium sulfate solution by aluminium-27 NMR spectroscopy.[9] The spectrum of aluminium sulfate solution contains two resonances, one due to the hexa-aqua cation and the other due to the inner sphere sulfato complex. This result showed direct evidence of the existence of sulfato complex of aluminium ion. Unfortunately, an increase in the temperature caused broadening of the two signals and prevented accurate measurements. In a previous study,[10] we have evaluated the second dissociation constant of sulfuric acid up to 200 °C using a hydrogen-ion concentration cell with a view to determining the formation constants for sulfato complexes of multivalent metal ions such as Al^{3+} and Fe^{3+}, because those values are especially important for quantitative analysis of the precipitation of nickel sulfide from the sulfate solutions and the removal of Fe^{3+} from the sulfate solutions at elevated temperatures.

The present study has been undertaken to determine the formation constant for sulfato complexes of aluminium ion in aluminium sulfate solutions using the hydrogen-ion concentration cell at elevated temperatures. It is favorable to study aluminium ion since the solubility of aluminium sulfate is relatively high even at elevated temperatures and aluminium hydrolysis products have been extensively studied.[11]

Experimental

Materials: All aluminium solutions were prepared by dissolving reagent grade aluminium chloride in dilute hydrochloric acid to suppress the hydrolysis of aluminium ion. The total concentration of aluminium ions was determined by back titration of an excess of EDTA with a standard Zn^{2+} solution. The total equivalent cation concentration was determined by using ion exchange resin Amberlite IR-120B(H) in the hydrogen form, followed by titration of the eluate with a 0.1 M (M=mol dm^{-3}) NaOH solution. A stock solution of a 0.1 M HCl was prepared from analytical grade hydrochloric acid diluted with doubly distilled water. Reagent grade KCl and K_2SO_4 were used without further purification. Ultrapure H_2 (99.99999%) was used.

Potentiometric Apparatus and Procedures: The hydrogen ion concentration cell is shown in Fig. 1. The apparatus and the procedure were first developed by Le Peintre[12] and later, Mesmer[13] and MacDonald[14] made similar measurements with some modifications. It consists of a titanium autoclave housing an outer glass beaker and an inner PTFE cup containing matched hydrogen electrodes. These two compartments were connected through the fluid phase by a porous PTFE disk,[10] and vapor space was interconnected via a 0.7 mm pin hole which allowed rapid pressure equilibration of hydrogen gas, yet was small enough to minimize the distillation of hydrochloric acid. The reversible hydrogen electrodes consisting of pure platinum were insulated from the autoclave body and were lightly platinized by electrolysis in a dilute solution of hexachloroplatinic acid before use. A porous PTFE disk (pore size, 0.2 μm; thickness 1 mm), which replaced air in the pores with a saturated KCl solution, was employed for the liquid junction. The treatment of the porous PTFE has been described previously.[10]

The cell representation is:

$$\mathrm{Pt,\ H_2}\left|\begin{array}{ll}\mathrm{AlCl_3} & (m_1)\\ \mathrm{HCl} & (m_2)\\ \mathrm{K_2SO_4} & (m_3)\\ \mathrm{KCl} & (m_5=1)\end{array}\right\|\begin{array}{ll}\mathrm{HCl} & (m_4=0.001)\\ \mathrm{KCl} & (m_5=1)\end{array}\left|\mathrm{H_2,\ Pt}\right. \qquad (\mathrm{I})$$

where m represents molality. The right hand (inner cup) of the cell (I) contains the reference electrode. Solution compositions in the test solutions are listed in Table 1. In order to suppress hydrolysis of aluminium ion, the test solutions were acidified (pH<3). The concentration of hydrochloric acid in the reference solution was 0.001 mol kg^{-1}. To minimize the liquid junction potential and to keep the ionic strength constant, KCl was added as a supporting electrolyte in both solutions (1 mol kg^{-1}).

After assembly the gas in the cell was exchanged by alternatively pressurizing it with hydrogen gas to 1.0 MPa and by venting it to an atmospheric pressure five times. Finally, the cell was pressurized to about 0.5 MPa with the hydrogen.

The entire autoclave was immersed in an oil bath. Potentials were measured successively from 25 to 125 °C at 25 °C intervals with a digital voltmeter and were recorded after they had reached a stable value within 0.1 mV for a few minutes.

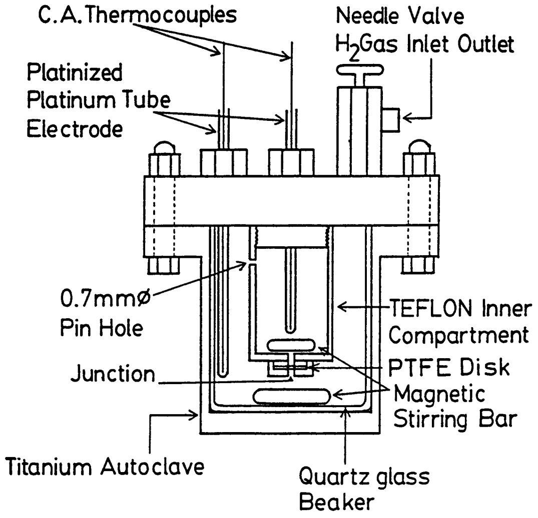

Fig. 1. E.M.F. apparatus for high temperature concentration cell.

Table 1. Initial Concentrations of Each Component at Various Runs

Run No.	$AlCl_3$	K_2SO_4	HCl
	mol kg^{-1}	mol kg^{-1}	mol kg^{-1}
1	0.020	0.020	0.016
2	0.020	0.020	0.018
3	0.020	0.020	0.022
4	0.020	0.020	0.025
5	0.020	0.020	0.027
6	0.020	0.030	0.030
7	0.020	0.032	0.032
8	0.020	0.034	0.034
9	0.020	0.036	0.036
10	0.020	0.038	0.038
11	0.020	0.040	0.040
12	0.020	0.020	0.020
13	0.022	0.022	0.022
14	0.020	0.027	0.027
15	0.030	0.027	0.027

1 mol kg^{-1} KCl as a supporting electrolyte.

Results and Discussion

The results of the potentiometric measurements are summarized in Table 2.

The potentials E (V) for the cell (I) are given by the expression:

$$E=(RT/F)\ln(a_{\mathrm{H^+},t}/a_{\mathrm{H^+},r})+E_j \qquad (1)$$

where $a_{\mathrm{H^+}}$ represents the activity of hydrogen ion and subscripts t and r denote the test and reference solutions, respectively. The second term in Eq. 1 represents the liquid junction potential, which can be estimated using the Henderson equation:[13]

$$E_j=-\sum D_i(m_{i,t}-m_{i,r}) \qquad (2)$$

$$D_i=(RT/F)(|Z_i|/Z_i)\lambda_i/\sum(|Z_i|\bar{m}_i\lambda_i) \qquad (3)$$

where $\bar{m}_i$ denotes the average concentration of species i in the two compartments, Z_i is the ionic charge, and λ_i is the limiting equivalent conductance of the i th ion. Values of λ_i have been reported by Quist and Marshall,[15] but that of Al^{3+} was calculated from the Stokes's law:

$$\lambda_i=0.820|z_i|r_s\eta \qquad (4)$$

where r_s is the "Stokes radius" taken as 3.95 Å for aluminium(III) ion[16] and η is the viscosity of water. Since the molal ratio of supporting electrolyte to total aluminium was large, the liquid junction term in Eq. 1 rarely exceeded 1 mV.

It has been recognized that the activity coefficients for uni- and bivalent[17–19] ionic species are expressed

Table 2. Electromotive Force (mV) of the Cell at Each Run

Run No.	Temperature/K				
	298	323	348	373	398
1	64.64	66.97	67.91	69.84	77.80
2	69.00	71.94	73.37	75.57	82.13
3	74.17	77.88	79.71	82.19	87.94
4	77.41	81.35	84.29	87.01	92.56
5	80.00	84.12	87.19	90.26	96.18
6	80.71	84.01	85.84	87.35	92.08
7	81.90	85.22	86.81	88.32	92.55
8	83.29	86.52	88.38	89.71	93.77
9	84.61	87.88	89.60	90.96	94.87
10	86.19	89.45	91.25	92.66	96.25
11	87.39	90.61	92.73	93.79	97.23
12	71.02	74.14	75.99	78.43	84.87
13	73.21	76.48	78.58	81.03	87.48
14	79.37	82.61	84.36	86.05	90.78
15	79.91	83.30	85.83	88.91	96.14

sufficiently to 1 molal 1-1 electrolyte solutions by the single parameter type of Debye-Hückel equation and to 5 molal solutions by the extended Debye-Hückel equation. Although those of the highly charged ions can be estimated only very poorly, Lietzke and Stoughton,[20] and Marshall and Slusher[21] have proved the efficacy of applying the equation to the extent of tervalent ion in the solubility measurement of lanthanum sulfate and samarium sulfate, respectively. Therefore, we used a Debye-Hückel equation to calculate the activity coefficients for ionic species at elevated temperatures:

$$\log \gamma_i = -Z_i{}^2 S\sqrt{I}/(1 + A\sqrt{I}) \qquad (5)$$

where I is the ionic strength and, S is the Debye-Hückel limiting slope given by:

$$S = 1.824 \times 10^6\ \rho^{1/2}/(\varepsilon T)^{3/2}\ (\mathrm{kg^{1/2}\ mol^{-1/2}}) \qquad (6)$$

Dielectric constant of water ε is available up to 640 K by Akerlof and Oshry[22] and ρ is the density of water. The adjustable parameter A was experimentally determined from the solubility measurements of various sulfates,[17-19] i.e. A varies from 1.5 at 25 °C to 1.6 at 125 °C.

The principal equilibrium reactions governing the thermodynamic behavior of aluminium sulfate solution at elevated temperatures are assumed to be:

$$Al^{3+} + SO_4^{2-} \rightleftharpoons [AlSO_4]^+ \qquad (7)$$

$$2Al^{3+} + 2H_2O \rightleftharpoons [Al_2(OH)_2]^{4+} + 2H^+ \qquad (8)$$

$$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-} \qquad (9)$$

$$K^+ + SO_4^{2-} \rightleftharpoons KSO_4^- \qquad (10)$$

Aluminium ion is extensively hydrolyzed at elevated temperatures and produces various hydroxo complexes.[23] Under the present conditions we assume only one hydrolyzed product, $[Al_2(OH)_2]^{4+}$, reported by MacDonald et al., because the present experimental conditions of hydrothermal hydrolysis (pH, ionic strength, and aluminium concentration) were similar to their ones.

Equilibrium constants for above reactions are expressed as follows:

$$K_f = a_{[AlSO_4]^+}/a_{Al^{3+}}\,a_{SO_4^{2-}} \qquad (11)$$

$$= (\gamma_{[AlSO_4]^+}/\gamma_{Al^{3+}}\,\gamma_{SO_4^{2-}})(m_{[AlSO_4]^+}/m_{Al^{3+}}\,m_{SO_4^{2-}}) \qquad (11')$$

$$K_h = a_{[Al_2(OH)_2]^{4+}}a_{H^+}^2/a_{Al^{3+}}^2 \qquad (12)$$

$$= (\gamma_{[Al_2(OH)_2]^{4+}}\gamma_{H^+}^2/\gamma_{Al^{3+}}^2)(m_{[Al_2(OH)_2]^{4+}}m_{H^+}^2/m_{Al^{3+}}^2) \qquad (12')$$

$$K_2 = a_{H^+}a_{SO_4^{2-}}/a_{HSO_4^-} \qquad (13)$$

$$= (\gamma_{H^+}\gamma_{SO_4^{2-}}/\gamma_{HSO_4^-})(m_{H^+}m_{SO_4^{2-}}/m_{HSO_4^-}) \qquad (13')$$

$$K_k = a_{KSO_4^-}/a_{K^+}\,a_{SO_4^{2-}} \qquad (14)$$

$$= (\gamma_{KSO_4^-}/\gamma_{K^+}\gamma_{SO_4^{2-}})(m_{KSO_4^-}/m_{K^+}m_{SO_4^{2-}}) \qquad (14')$$

The values of K_2 and K_k were determined previously at temperatures up to 200 °C.[10]

Total analytical concentrations of Al^{3+}, H^+, K^+, and SO_4^{2-} ions are given by:

$$m_{Al^{3+}} + m_{[AlSO_4]^+} + 2m_{[Al_2(OH)_2]^{4+}} = m_1 \qquad (15)$$

$$m_{H^+} + m_{HSO_4^-} - 2m_{[Al_2(OH)_2]^{4+}} = m_2 \qquad (16)$$

$$m_{K^+} + m_{KSO_4^-} = 2m_3 + m_5 \qquad (17)$$

$$m_{[AlSO_4]^+} + m_{HSO_4^-} + m_{KSO_4^-} + m_{SO_4^{2-}} = m_3 \qquad (18)$$

And the ionic charge balance in the solution is:

$$3m_{Al^{3+}} + m_{[AlSO_4]^+} + 4m_{[Al_2(OH)_2]^{4+}} + m_{H^+} + m_{K^+}$$
$$= 2m_{SO_4^{2-}} + m_{HSO_4^-} + m_{KSO_4^-} + m_{Cl^-} \qquad (19)$$

If a, h, and s are taken as the Al^{3+}, H^+, and SO_4^{2-} concentrations, the solution of Eqs. 11—19 can be obtained by the following simultaneous equations:

$$a + h + \gamma^{12}K_f as + \gamma^4 hs/K_2 - m_1 - m_2 = 0 \qquad (20)$$

$$s + \gamma^{12}K_f as + \gamma^4 hs/K_2$$
$$+ \gamma^4 K_k(1 + 2m_3)s/(1 + \gamma^4 K_k s) - m_2 = 0 \qquad (21)$$

$$h + 3a + \gamma^{12}K_f as + 4K_h a^2/h^2 - (1 + 3m_1 + m_2)$$
$$- \gamma^4 hs/K_2 - 2s + (1 + 2m_3)(1 - \gamma^4 K_k s)/$$
$$(1 + \gamma^4 K_k s) = 0 \qquad (22)$$

The computer program employed to carry out the calculation of K_f and K_h was described below. First, a preliminary value of ionic strength was assumed and was substituted into Eq. 5 to yield the activity coefficients. The concentrations of each ionic species was determined by simultaneous solution of Eqs. 20—22 by the Newton-Raphson method. The ionic strength of the solutions was calculated from the concentrations of each kind of ions and determined by the method of successive approximations. Thus, the activity of hydrogen ion, a_{H^+}, was determined and combined with Eq. 1, and the calculated value of potential was obtained. Then the experimental data were treated with a nonlinear least squares method to analyze the most appropriate set of K_f and K_k, i.e., to minimize the summation of the square difference of observed and calculated values of the potential. The computations were carried out for each system from 25 to 125 °C at 25 °C intervals. The formation constants of aluminium sulfate obtained by the above procedure are presented in Table 3 and illustrated in Fig. 2. Their change with temperature shows that the association of aluminium ion and sulfate ion increases strongly with temperature. Potentials measured at temperatures higher than 125 °C increased gradually, presumably due to the hydrolysis of aluminium ion, followed by precipitation. Therefore it was difficult to deter-

Table 3. Thermodynamic Quantities for the Formation of $AlSO_4^+$

T / K	log (K/mol^{-1}kg)	ΔG° / kJ mol^{-1}	ΔH° / kJ mol^{-1}	ΔS° / J mol^{-1} K^{-1}
298	3.35	−19.1	6.61	86.2
	3.01	−17.2	9.58	89.5[a]
323	3.59	−22.2	30.3	162
348	4.08	−27.2	50.9	224
373	4.66	−33.3	68.6	273
398	5.34	−40.7	83.3	312

a) Ref. 3.

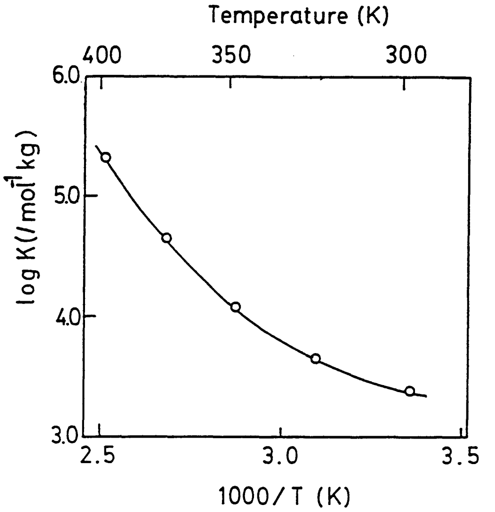

Fig. 2. The formation constant of $AlSO_4^+$ from 25 °C to 125 °C.

mine the association constant of the $[AlSO_4]^+$ ion pair at temperatures above 125 °C. The X-ray diffraction patterns of the precipitate showed that the major constituent was alunite, $KAl_3(SO_4)_2(OH)_6$. Lines assignable to aluminium oxides, hydroxides, and oxychlorides were not observed.

Essentially, the equilibrium constant obtained by the e.m.f. measurements is a sum of the equilibrium constants for the inner-sphere complex, $[Al(SO_4)(OH_2)_{6-x}]^+$ and the outer-sphere one, $[Al(OH_2)_6(SO_4)]^+$. These constants were determined by the pressure jump method up to 40 °C[25] and the inner-sphere complex occupies 17% at 25 °C. The NMR measurements of aluminium sulfate solutions show that the ratio of the inner-sphere complex to the outer one increases with an increase in temperature.[9]

Although the disulfato complex, $[Al(SO_4)_2]^-$, has been reported by other authors[3,6,26] we could not find evidence of its existence. It is supposed that the experimental conditions of both low pH level and small ratio of $[SO_4^{2-}]/[Al^{3+}]$ are unfavorable to the formation of the disulfato complex. If we take into account the precipitation of alunite above 125 °C, it seems that the disulfato or hydroxodisulfato complex may be formed at higher temperatures because aluminium ion in the crystal of alunite is hexa-coordinated with two oxygen atoms of SO_4^{2-} ions and four OH^- ions.[27]

From the formation constant obtained in this work, it is possible to compute the composition of the aluminium sulfate solutions. Some examples are shown in Table 4. As has been pointed out by Akitt et al.,[9] HCl suppresses the formation of $[AlSO_4]^+$, due to the formation of HSO_4^- over the pH range examined at all temperatures.

Table 4. Molalities of Various Species Present in a Solution Containing 0.020 *m* in $AlCl_3$ and 0.032 *m* in K_2SO_4, and 0.032 *m* in HCl at Various Temperatures

Species	Temperature		
	298 K	348 K	398 K
Al^{3+}	1.78×10^{-2}	1.61×10^{-2}	1.08×10^{-2}
$AlSO_4^+$	2.19×10^{-3}	3.87×10^{-3}	8.32×10^{-3}
$Al_2(OH)_2^{4+}$	—	—	4.53×10^{-4}
SO_4^{2-}	1.80×10^{-2}	1.14×10^{-2}	4.54×10^{-3}
HSO_4^-	6.51×10^{-3}	1.33×10^{-2}	1.77×10^{-2}
KSO_4^-	5.26×10^{-3}	3.44×10^{-3}	1.46×10^{-3}
H^+	2.55×10^{-2}	1.87×10^{-2}	1.52×10^{-2}

1 m=1 mol kg^{-1}.

On the assumption of the linear dependency of ΔC_p° over the temperature range of 25 to 125 °C, the present values of the formation constant were fitted by a method of least squares to yield the four-parameter equation as a function of temperature (K):

$$\log (K_f/\mathrm{mol^{-1}\,kg}) = -765.90 + 290.161 \log (T/\mathrm{K}) + 26255/(T/\mathrm{K}) - 0.1234(T/\mathrm{K}) \quad (23)$$

From the treatment of Eq. 23, thermodynamic functions for the standard Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were obtained from 25 to 125 °C. The values are given in Table 3. At 25 °C the values ΔG°, ΔH°, and ΔS° in this table were compared reasonably with those of Izatt et al.[3]

Another equation for $\log K_f$ was obtained by assuming that ΔC_p° varied as quadratic function of temperature. This equation is given as follows:

$$\log(K_f/\mathrm{mol^{-1}\,kg}) = -14847.75 + 6358.721 \log (T/\mathrm{K}) + 328608/(T/\mathrm{K}) - 7.75167(T/\mathrm{K}) + 3.66574\times10^{-3} (T/\mathrm{K})^2 \quad (24)$$

The thermodynamic quantities derived from Eq. 24 at 25 °C showed unreasonably low values. Therefore, the four-parameter equation (Eq. 23) is believed to yield a better description of the present equilibrium from 25 to 125 °C.

Because all of the test solutions were fairly acidic ($\mathrm{pH}<3$), hydrolysis of Al^{3+} ion at moderate temperatures was suppressed, and consequently, the formation constant for the hydrolyzed product, $[Al_2(OH)_2]^{4+}$, was ill-defined. The hydrolysis occurred with an increase in temperature, and $\log(K_h/\mathrm{mol\,kg^{-1}})=-3.0$ was determined for the formation of $[Al_2(OH)_2]^{4+}$ at 125 °C.

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