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Ionic Equilibria in Tri-Bivalent Salts at 35°C Aluminium Sulphate (Potash Alum)

S. N. JHA

Post Graduate Department of Chemistry, Bhagalpur University, Bhagalpur-812 007

and

P. N. JHA

Department of Chemistry, R. D. & D. J. College, Monghyr

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Dissociation constants of $Al(SO_4)_2^-$ and $AlSO_4^+$ were measured by Sharma and Prasad. They neglected the concentration of Hg_2^{2+} ion. Their values at 35° have been revised after taking the concentration of Hg_2^{2+} ion into account.

THE dissociation constants of $Al(SO_4)_2^- \rightleftharpoons AlSO_4^+ + SO_4^{2-}$ and $AlSO_4^+ \rightleftharpoons Al^{3+} + SO_4^{2-}$ were measured by Sharma and Prasad[1] using cells of the type :

$$\mathrm{Pt}\left|\begin{array}{l} Al_2(SO_4)_3(C_1) \\ Q.H. \\ H_2SO_4(C_2) \end{array}\right|\begin{array}{l} Al_2(SO_4)_3(C_1) \\ \\ H_2SO_4(C_2) \end{array}\left|\begin{array}{l} Al_2(SO_4)_3(C_1) \\ Hg_2SO_4 \\ H_2SO_4(C_2) \end{array}\right|\mathrm{Hg}$$

where Q.H. stands for quinhydrone. They neglected the concentration of Hg_2^{2+} which resulted in much higher values of dissociation constants. With their experimental values of e.m.f. (Stockholm convention) and stoichiometric concentrations of $Al_2(SO_4)_3$ and H_2SO_4, the values of the dissociation constants have been recalculated. All concentrations refer to 35° and are in gm mole/litre. Concentrations are indicated by [].

The e.m.f. of the cell given in para one and that of

$$\mathrm{Pt}\left|\begin{array}{l} H_2SO_4(C) \\ Q.H. \end{array}\right|\begin{array}{l} H_2SO_4(C) \\ \\ \end{array}\left|\begin{array}{l} H_2SO_4(C) \\ Hg_2SO_4 \end{array}\right|\mathrm{Hg}$$

are given by the same equation

$$E = E^\circ - \frac{2.3026\,RT}{2F}\log [H^+]^2 [SO_4^{2-}]$$

$$+\frac{2.3026\,RT}{F}\times 3A\sqrt{\mu} - \frac{2.3026\,RT}{2F}\times\beta\mu \quad \ldots \quad (1)$$

The values of E° (−.0880 abs.volt) molarity scale and β(3.87) were found from the cell given in this paragraph[2]. Sharma and Prasad's equations[3,4] corresponding to the dissociation $HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$ and solubtlity product of Hg_2SO_4 both at 35° are given below :

$$\log\frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$$

$$= \bar{3}.920 + 4\times 0.5190\sqrt{\mu} - 3.3334\,\mu \quad \ldots \quad (2)$$

where log K = $\bar{3}.920$

$$\log [Hg_2^{2+}][SO_4^{2-}] = \bar{7}.9410 + 8\times 0.5190\sqrt{\mu}$$

$$-3.3334\times 2\,\mu \quad \ldots \quad (3)$$

where log Ksp = $\bar{7}.9410$

The data concerning the dissociation of (i) $Al(SO_4)_2^- \rightleftharpoons AlSO_4^+ + SO_4^{2-}$ and (ii) $AlSO_4^+ \rightleftharpoons Al^{3+} + SO_4^{2-}$ are given in Table 1 and 2 respectively.

Discussion :

H_2SO_4 dissociates according to the following scheme :

$$\begin{array}{lll} H_2SO_4 & \xrightarrow[\text{complete}]{\text{1st step}} & H^+ + HSO_4^- \\ C_2 & & C_2 \quad (1-\alpha)C_2 \\ & & \qquad\quad \rightleftharpoons \\ & & \qquad\quad H^+ + SO_4^{2-} \\ & & \qquad\quad \alpha C_2 \;\; \alpha C_2 \end{array}$$

Hence for any mixture of $Al_2(SO_4)_3$ and H_2SO_4 ; $[H^+] = (1+\alpha)C_2$, $[HSO_4^-] = (1-\alpha)C_2$, where α is the degree of dissociation of HSO_4^- and C_2 is the stoichiometric concentration of H_2SO_4. An arbitrary value is assigned to μ. The value of $[H^+]^2 [SO_4^{2-}]$ is found from equation (1). For

TABLE 1—TEMPERATUER 35°±0.05°C
DISSOCIATION : $Al(SO_4)_2^- = AlSO_4^+ + SO_4^{2-}$
$C_1 = [Al_2(SO_4)_3]T$
$C_2 = [H_2SO_4]T$

$C_1 \times 10^3$	$C_2 \times 10^3$	E in abs. mv.	$[SO_4^{2-}] \times 10^4$	$[AlSO_4^+] \times 10^4$	$[Al(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_{1(A)} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
2.88	2.16	147.40	34.72	44.84	12.76	132.2	$\bar{3}.872$
5.76	4.32	128.75	42.29	70.92	44.28	197.1	$\bar{3}.575$
8.64	6.48	119.00	40.75	84.70	88.70	245.8	$\bar{3}.306$
11.52	8.64	111.50	44.27	105.60	124.80	303.2	$\bar{3}.266$
14.40	10.80	105.61	48.16	128.61	159.39	361.1	$\bar{3}.258$

TABLE 2—DISSOCIATION : $AlSO_4^+ = Al^{3+} + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs. mv.	$[SO_4^{2-}] \times 10^4$	$[Al^{3+}] \times 10^4$	$[AlSO_4^+] \times 10^4$	$\mu \times 10^4$	$\log K_{2(A)} - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$
11.52	8.64	174.09	22.52	0.56	18.83	83.78	$\bar{5}.272$
14.40	10.80	167.11	28.12	4.80	18.78	115.16	$\bar{4}.253$
17.28	12.96	161.50	34.08	9.63	17.85	150.06	$\bar{4}.585$
20.16	15.12	156.79	43.37	18.34	13.18	206.98	$\bar{3}.173$
23.04	17.28	152.86	47.01	20.90	13.92	229.05	$\bar{3}.030$

the same ionic strength the value of

$\frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$ is found from equation (2).

Dividing the value of $[H^+]^2[SO_4^{2-}]$ by that of $\frac{[H^+][SO_4^{2-}]}{[HSO_4^-]}$, we get $[H^+][HSO_4^-]$ i.e. $(1-\alpha^2)C_2^2$.

Since C_2 is known, α may be calculated and hence $[H^+]$ and $[HSO_4^-]$ corresponding to the assumed value of μ are found out. The corresponding value of $[SO_4^{2-}]$ is calculated by dividing the value of $[H^+]^2[SO_4^{2-}]$ by that of $[H^+]^2$. Knowing the value of $[SO_4^{2-}]$, the corresponding value of $[Hg_2^{2+}]$ is calculated from the equation (3). The corresponding values of $[Al^{3+}]$, $[AlSO_4^+]$ and $[Al(SO_4)_2^-]$ are found out from following equation :

$$[Al]_T = [Al^{3+}] + [AlSO_4^+] + [Al(SO_4)_2^-] \ldots\ldots\ldots (4) ;$$

π based on the conservation of matter and

$$3[Al^{3+}] + [H^+] + [AlSO_4^+] + 2[Hg_2^{2+}] = [Al(SO_4)_2^-] + 2[SO_4^{2-}] + [HSO_4^-] \quad \ldots \quad (5)$$

Based on electro-neutrality.

Sharma and Prasad had used the equation :—

$$3[Al^{3+}] + [H^+] + [AlSO_4^+] = [Al(SO_4)_2^-] + 2[SO_4^{2-}] + [HSO_4^-] \quad \ldots \quad (6)$$

instead of equation (5). Since the ionic concentration of Hg_2^{2+} ion is of the same order as that of Al^{3+} ion, the concentration of the former ion cannot be neglected.

On adding equations (4) and (5) we get,

$$2[Al^{3+}] - 2[Al(SO_4)_2^-] = 2[SO_4^{2-}] + [HSO_4^-] - [H^+] - [Al]_T - 2[Hg_2^{2+}] \quad \ldots \quad (7)$$

Similarly, multiplying equation (4) by three and then adding to equation (5) we get,

$$2[AlSO_4^+] = 3[Al]_T + [H^+] + 2[Hg_2^{2+}] - 2[SO_4^{2-}] - [HSO_4^-] - 4[Al(SO_4)_2^-] \quad \ldots \quad (8)$$

On feeding the values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$, $[Hg_2^{2+}]$ and $[Al]_T$ in equation (7), we get $2[Al^{3+}] - 2[Al(SO_4)_2^-]$. In a very dilute solution, if a preliminary assumption is made that $Al(SO_4)^{2-}$ ion is absent, we get the value of $[Al^{3+}]$.

In case of these solutions, the value of $[AlSO_4^+]$ is calculated from equation (8) assuming that $[Al(SO_4)_2^-] = 0$. We get a new value of ionic strength from the equation :

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[AlSO_4^+] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + 4.5[Al^{3+}]$$

This process is repeated till μ becomes constant upto the 4th place of decimal. When we increased the concentrations beyond a certain limit, we found that $[Al^{3+}]$ was almost zero. Hence it was decided to take concentrations slightly above this range and assume that $[Al^{3+}] = 0$.

At such high concentration values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$ and $[Hg_2^{2+}]$ for an arbitrary value of μ are determined as described earlier. These values are put in equation (7) and it is assumed that $[Al^{3+}] = 0$. So we get a value of $[Al(SO_4)_2^-]$. By feeding all these values in equation (8). we get a value of $[AlSO_4^+]$. A new value of ionic strength (μ) is found from the equation :

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[AlSO_4^+] + \tfrac{1}{2}[Al(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}].$$

This process is repeated till μ becomes constant upto four or five in the fifth place of decimal. The concentrations of the ionic species at this stage are assumed to be the exact concentrations and they are given in Table 1. Now, thermodynamic dissociation constant of Al $(SO_4)_2^-$,

$$K_1 = \frac{AlSO_4^{+}\,{}^{a}SO_4^{2-}}{{}^{a}Al(SO_4)_2^-}$$

$$= \frac{[AlSO_4^+][SO_4^{2-}]}{[Al(SO_4)_2^-]} \times \frac{f_{AlSO_4^+}.f_{SO_4^{2-}}}{f_{Al(SO_4)_2^-}} \quad \ldots \quad (9)$$

Equation (9) can be written as follows :

$$\log \frac{[AlSO_4^+]\,[SO_4^{2-}]}{[Al\,(SO_4)_2^-]} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_1 - b\,\mu \quad \ldots \quad (10)$$

where $b = b_{AlSO_4^+} + b_{SO_4^{2-}} - b_{Al(SO_4)_2^-}$

Taking a number of solutions with different ionic strengths (Table 1) and plotting L.H.S. of equation (10) against μ, we get a straight line. The straight line is drawn in such a manner that equal and least number of squares lie above and below the straight line. We get the values of K_1 and b from the plot. In this way the values of K_1 and b have been calculated at 35°.

In more dilute solution of $Al_2(SO_4)_3$ in H_2SO_4, the total Aluminium is present as Al^{3+}, $AlSO_4^+$ and Al $(SO_4)_2^-$ ions. By the process outlined below, the value of $[Al(SO_4)_2^-]$ need not be neglected while calculating $[Al^{3+}]$ as done by Sharma and Prasad[1].

At lower concentrations the values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$ and $[Hg_2^{2+}]$ corresponding to an arbitrary value of μ are calculated as done earlier. Now the values of $[SO_4^{2-}]$, K_1 and b are put in equation (10), when we get a ratio of $[AlSO_4^+]$ to $[Al(SO_4)_2^-]$. The values of $[Al^{3+}]$, $[AlSO_4^+]$ and $[Al\,(SO_4)_2^-]$ can be found out with the help of equations (7), (8) and (11), i.e.

$$\frac{[AlSO_4^+]}{[Al(SO_4)_2^-]} = K' \quad \ldots \quad (11)$$

where K′ is a known quantity. A new value of μ is now calculated from :

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[AlSO_4^+] + \tfrac{1}{2}[Al(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + [4.5]\,Al^{3+}$$

The whole process in repeated till the ionic strength is constant upto four or five in the sixth place of decimal. The ionic concentrations at this stage are assumed to be correct and are given in Table 2.

Now, thermodynamic dissociation constant of $AlSO_4^+$ i.e.

$$K_2 = \frac{a_{Al^{3+}}.a_{SO_4^{2-}}}{a_{AlSO_4^+}}$$

$$= \frac{[Al^{3+}][SO_4^{2-}]}{[AlSO_4^+]} \times \frac{f_{Al^{3+}}.\,f_{SO_4^{2-}}}{f_{AlSO_4^+}} \quad \ldots \quad (12)$$

Equation (12) reduces itself to

$$\log \frac{[Al^{3+}][SO_4^{2-}]}{[AlSO_4^+]} - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_2 - B\mu \quad \ldots \quad (13)$$

where $B = B_{AL^{3+}} + B_{SO_4^{2-}} - B_{AlSO_4^+}$

Taking a number of solutions of different ionic strengths (Table 2) and plotting the L.H.S. of equation (13) against μ, a straight line is obtained. The values of K_2 and B are found from 'Plot'.

The thermodynamic dissociation constants at 35°, thus found and those reported by Sharma and Prasad are given below :

	Sharma and Prasad's values	*Our values*
$K_1 \times 10^2$	8.9	1.32 ± 0.01
$K_2 \times 10^3$	8.3	0.0398 ± 0.00044

Our value of K_1 is of the same order as that[5] of $Cr(SO_4)_2^- = CrSO_4^+ + SO_4^{2-}$ and of[6].

In $(SO_4)_2^- =$ In $So_4^+ + SO_4^{2-}$. Similarly our value of K_2 is of the same order as that of[5] $CrSO_4^+ = Cr^{3+} + SO_4^{2-}$ and of[6] In $SO_4^+ = In^{3+} + SO_4^{2-}$.

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