Asian Journal of Chemistry Vol. 6, No. 3 (1994), 619–625

Ionic Equilibria in Tri-Bivalent Salts (Indium Alum) at 15°C.

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We have measured the dissociation constants of $In(SO_4)_2^-$ and $InSO_4^+$ at 15°C by E.M.F. method taking $[In_2(SO_4)_3]_T : [H_2SO_4]_T : 1 : 1$. Our values are of the same order as those of Jha and Prasad, who had taken $[In_2(SO_4)_3]_T : [H_2SO_4]_T : : 4 : 5$. The method of computation of result has been improved.

INTRODUCTION

A large number of workers have studied the dissociation constants of the salt indium sulphate using different methods[1–6]. Jha and Prasad[7] have also measured the thermodynamic dissociation constants (by e.m.f. method) of

$$In\,(SO_4)_2^- \rightleftarrows InSO_4^+ + SO_4^{2-}$$

$$In\,SO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$$

at 5°, 15°, 25°and 35°C taking indium sulphate and H_2SO_4 in the molar ratio 4 : 5. In the present work, we have taken $[In_2(SO_4)_3]_T : [H_2SO_4]_T : :1 : 1$ and calculated thermodynamic dissociation constants of $In(SO_4)_2^- \rightleftarrows InSO_4^+ + SO_4^{2-}$ and $InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$ at 15°C only. Our values of dissociation constants are of the same order as those reporded by Jha and Prasad[7].

EXPERIMENTAL

The dissociation constants of $In(SO_4)_2^-$ and $InSO_4^+$ have been determined at 15°C from the study of the cells of the type

		$H_2SO_4(C_1)$	$H_2SO_4(C_1)$	$H_2SO_4(C_1)$		
Pt	Q.H.				Hg_2SO_4	Hg
	Sat.	$In_2(SO_4)_3(C_2)$	$In_2(SO_4)_3(C_2)$	$In_2(SO_4)_3(C_2)$		

where Q.H. stands for quinhydrone. $In_2(SO_4)_3$ and H_2SO_4 were mixed in the ratio 1 : 1 and the cell was studied at 15°C for a number of concentrations of $In_2(SO_4)_3$ and H_2SO_4. Sulphuric acid (G.R. sample) and indium sulphate (Schuchardt Noncem) were used Quinhydrone of analytical grade (Ranalbuda

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Pest) was crystallised and dried before used, following the method of Harned and Wright[8]. The bridges were of the type suggested by Guggenheim[9] with slight modification.

The mercurous sulphate was prepared by electrolytic method devised by Hulett[10]. Stock solution of sulphuric acid (H_2SO_4) was prepared and standardised against lorex[11]. Stock solution of indium sulphate [$In_2(SO_4)_3$] in dilute sulphuric acid was prepared and indium was estimated gravimetrically as oxinate[12]. In order to know the total amount of sulphate in the stock solution, a definite quantity of stock solution of $In_2(SO_4)_3$ in dilute sulphuric acid was boiled with a known volume of standard Na_2CO_3 solution for about an hour, cooled and the excess of Na_2CO_3 was titrated with standard H_2SO_4 solution. All solutions were prepared at the experimental temperature, Presaturated nitrogen gas was used to remove oxygen from the solution used in the cells. The temperature of air thermostat was constant within ±0.05°C. E.M.F. measurements were made with a Tinsley vernier potentiometer Type 4363 make 1942 (Tinsley and Co. Ltd., Werndee Hall) using a Bajaj mirror Galvanometer, Type M.G.8 (Sensitivity 3.92×10^{-10} amps/m.m.). The e.m.f. values (absolute volt) given in Table 1 and 2 are mean of the duplicate experiments of two cells (four experiments), which generally differed from one another by less than 0.10 mv. Stockholm convention has been followed for standard electrode potentials.

RESULTS AND DISCUSSION

We have measured the dissociation constants of $In(SO_4)_2^- \rightleftarrows InSO_4^+ + SO_4^{2-}$ and $InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$ using cells of the type

Pt	Q.H.	$In_2(SO_4)_3(C_1)$ $H_2SO_4(C_2)$	$In_2(SO_4)_3(C_1)$ $H_2SO_4(C_2)$	$In_2(SO_4)_3(C_1)$ $H_2SO_4(C_2)$	Hg_2SO_4	Hg
					Cell(c–1)	

where Q.H. stands for quinhydrone. With our experimental values of e.m.f. (Strockholm convention) and stoichiometric concentration of $In_2(SO_4)_3$ and H_2SO_4 the values of the dissociation constants have been calculated at 15°C. All concentration terms are in mol dm^{-3}.

The e.m.f. of cells (C–1) and (C–2) are given in equation (1).

$$Pt \mid Q.H.\ H_2SO_4(C) \mid H_2SO_4(C) \mid H_2SO_4(C), Hg_2SO_4 \mid Hg \quad .. \quad (C\text{–}2)$$

$$E = E^\circ - \frac{2.3026RT}{2F} \log [H^+]^2[SO_4^{2-}] + \frac{2.3026RT}{F} \times 3A\sqrt{\mu} - \frac{2.3026RT}{2F} \beta\mu \qquad (1)$$

The values of E^o(–0.0857 abs. volt molarity scale) and β(3.99) were found from the cell given in this paragraph[13]. Sharma and Prasad's equation[14, 15] corresponding to the dissociation.

$HSO_4^- \rightleftarrows H^+ + SO_4^{2-}$ and solubility product of Hg_2SO_4 both at 15°C are given below.

$$\log \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = \bar{2}.200 + 2.0008\sqrt{\mu} - 3.41176\mu \qquad (2)$$

where $\log K = \bar{2}.200$

and $$\log [Hg_2^{2+}][SO_4^{2-}] = \bar{7}.87040 + 4.0016\sqrt{\mu} - 6.82352\mu \qquad (3)$$

where $\log K_{sp} = \bar{7}.87040$

The data concerning the dissociation of

(i) $In(SO_4)_2^- \rightleftarrows InSO_4^+ + SO_4^{2-}$ and

(ii) $InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$ are given in Tables 1 and 2 respectively.

H_2SO_4 dissociates according to the following scheme

$$\underset{(C_2)}{H_2SO_4} \xrightarrow[\text{complete}]{\text{Ist step}} \underset{(C_2)}{H^+} + \underset{(1-\alpha)C_2}{HSO_4^-}$$

$$\uparrow\downarrow$$

$$H^+ + SO_4^{2-}$$

$$\alpha C_2 \ \alpha C_2$$

Hence for any mixture of $In_2(SO_4)_3$ and H_2SO_4; $[H^+] = (1+\alpha)C_2$, $[HSO_4^-] = (1-\alpha)C_2$ whrer α is the degree of dissociation of HSO_4^- and C_2 is the stoichiometric concentration of H_2SO_4. A rough value is assigned to μ. The value of $[H^+]^2[SO_4^{2-}]$ is found from equation (1). For the same ionic strength the value of $[H^+][SO_4^{2-}] / [HSO_4^-]$ is found from equation (2). Dividing the value of $[H^+]^2[SO_4^{2-}]$ by that of $[H^+][SO_4^{2-}] / [HSO_4^-]$, 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 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 equation (3). The corresponding values of $[In^{3+}]$, $[InSO_4^+]$, and $[In(SO_4)_2^-]$ are found out from following equation

$$[In]_T = [In^{3+}] + [InSO_4^+] + [In(SO_4)_2^-] \qquad (4)$$

based on the conservation of matter and

$$3[In^{3+}] + [H^+] + [InSO_4^+] + 2[Hg_2^{2+}] = [In(SO_4)_2^-] + 2[SO_4^{2-}] + [HSO_4^-] \qquad (5)$$

based on electroneutrality.

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

$$2[In^{3+}] - 2[In(SO_4)_2^-] = 2[SO_4^{2-}] + [HSO_4^-] - [H^+] - [In]_T - 2[Hg_2^{2+}] \qquad (6)$$

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

$$2[InSO_4^+] = 3[In]_T + [H^+] + 2[Hg_2^{2+}] - 2[SO_4^{2-}] - [HSO_4^-] - 4[In(SO_4)_2^-] \qquad (7)$$

On feeding the values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$, $[Hg_2^{2+}]$ and $[In]_T$ in equation (6), we get $2[In^{3+}] - 2[In(SO_4)_2^-]$. In very dilute solution, if a preliminary assumption is made that $In(SO_4)_2^-$ ion is absent, we get value of $[In^{3+}]$.

In case of these solutions, the value of $[InSO_4^+]$ is calculated from equation (7), assuming that $[In(SO_4)_2^-] = 0$. We get a new value of ionic strength from the equation

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[InSO_4^+] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + 4.5[In^{3+}]$$

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

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 (6) and it is assumed that $[In^{3+}] = 0$. So we get a value of $[In(SO_4]_2^-]$. By feeding all these values in equation (7), we get a value of $[InSO_4^+]$. A new value of ionic strength (μ) is found from the equation

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[InSO_4^+] + \tfrac{1}{2}[In(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}]$$

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

TABLE-1

TEMPERATURE 15°C ± 0.05°C; DISSOCIATION: $In(SO_4)_2^- \rightleftarrows InSO_4^+ + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E in abs. m.V.	$[SO_4^{2-}] \times 10^4$	$[InSO_4^+] \times 10^4$	$[In(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_1(A) - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}}$
35.06	35.06	117.56	46.79	53.67	16.44	171.8	–2.048
42.08	42.08	112.47	52.46	62.85	21.31	196.6	–2.056
49.09	49.09	108.28	57.28	71.18	27.00	219.9	–2.079
63.12	63.12	101.32	68.26	90.26	35.98	268.8	–2.048
70.12	70.12	98.48	72.87	98.91	41.28	292.2	–2.049

to be the exact concentrations and they are given Table 1. Now, thermodynamic dissociation constant of $In(SO_4)_2^-$

$$K_1 = \frac{{}^aInSO_4^+ \cdot {}^aSO_4^{2-}}{{}^aIn(SO_4)_2^-}$$

$$= \frac{[InSO_4^+][SO_4^{2-}]}{[In(SO_4)_2^-]} \times \frac{{}^fInSO_4^+ \cdot {}^fSO_4^{2-}}{{}^fIn(SO_4)_2^-} \cdots \quad (8)$$

Equation (8) can be written as follows

$$\log \frac{[InSO_4^+][SO_4^{2-}]}{[In(SO_4)_2^-]} - \frac{4A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_1 - b\mu \ldots \quad (9)$$

where $b = {}^bInSO_4^+ + {}^bSO_4^2 - {}^bIn(SO_4)_2^-$

Taking a number of solutions with different ionic strengths (Table 1) and plotting L.H.S. of equation (9) 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 15°C.

In more dilute solution of $In_2(SO_4)_3$ in H_2SO_4, the total indium is present as In^{3+}, $InSO_4^+$ and $In(SO_4)_2^-$ ions. By the process outlined below, the value of $[In(SO_4)_2^-]$ need not be neglected while calculating $[In^{3+}]$ as done by Sharma and Prasad[16].

At lower concentrations the values of $[H^+]$, $[HSO_4^-]$, $[SO_4^{2-}]$ and $[Hg_2^{2+}]$ corresponding to a rough value of μ are calculated as done earlier. Now the values of $[SO_4^{2-}]$, K_1 and b are put in equation (9), when we get a ratio of $[InSO_4^+]$ to $[In(SO_4)_2^-]$. The values of $[In^{3+}]$, $[InSO_4^+]$ and $[In(SO_4)_2^-]$ can be found out with the help of equations (6), (7) and (10) *i.e.*

$$\frac{[InSO_4^+]}{[In(SO_4)_2^-]} = K^1 \quad (10)$$

where K^1 is a known quantity. A new value of μ is now calculated from

$$\mu = \tfrac{1}{2}[H^+] + \tfrac{1}{2}[HSO_4^-] + \tfrac{1}{2}[InSO_4^+] + \tfrac{1}{2}[In(SO_4)_2^-] + 2[SO_4^{2-}] + 2[Hg_2^{2+}] + 4.5[In^{3+}]$$

The whole process is repeated till the ionic strength becomes constant up to 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.

TABLE 2
TEMPERATURE 15°C ± 0.05°C; DISSOCIATION $InSO_4^+ \rightleftarrows In^{3+} + SO_4^{2-}$

$C_1 \times 10^4$	$C_2 \times 10^4$	E abs. m.V.	$[SO_4^{2-}] \times 10^4$	$[InSO_4^+] \times 10^4$	$[In^{3+}] \times 10^4$	$[In(SO_4)_2^-] \times 10^4$	$\mu \times 10^4$	$\log K_2(A) - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}}$
12.03	12.03	147.95	25.54	19.15	1.35	3.56	92.73	–4.271
14.03	14.03	143.56	27.58	22.48	1.10	4.48	99.38	–4.408
16.02	16.02	139.76	29.68	25.49	1.16	5.40	106.97	–4.434
18.02	18.02	136.15	33.45	26.83	2.96	6.25	125.01	–4.079
20.06	20.06	133.05	35.84	29.54	3.29	7.30	134.69	–4.023

Now thermodynamic dissociation constant of $InSO_4^+$ *i.e.*

$$K_2 = \frac{{}^aIn^{3+} \cdot {}^aSO_4^{2-}}{{}^aInSO_4^+}$$

$$= \frac{[In^{3+}][SO_4^{2-}]}{[InSO_4^+]} \times \frac{^fIn^{3+} \cdot {^fSO_4^{2-}}}{^fInSO_4^+} \qquad (11)$$

Equation (11) reduces itself to

$$\log \frac{[In^{3+}][SO_4^{2-}]}{[InSO_4^+]} - \frac{12A\sqrt{\mu}}{1+\sqrt{\mu}} = \log K_2 - B\mu \qquad (12)$$

where $B = {^BIn^{3+}} + {^BSO_4^{2-}} - {^BInSO_4^+}$

Taking a number of solutions of different ionic strengths (Table 2) and plotting the L.H.S. of equation (12) against μ, a straight line is obtained. The values of K_2 and B are found from plot.

The thermodynamic dissociation constants at 15°C, thus found are given below

	Value	Dissociation
K_1	9.55×10^{-3}	$In(SO_4)_2^- = InSO_4^+ + SO_4^{2-}$
K_2	3.47×10^{-6}	$InSO_4^+ = In^{3+} + SO_4^{2-}$

Our values of K_1 is of the same order as that[17–19] of

(i) $Al(SO_4)_2^- = AlSO_4^+ + SO_4^{2-}$

(ii) $Cr(SO_4)_2^- = CrSO_4^+ + SO_4^{2-}$

(iii) $In(SO_4)_2^- = InSO_4^+ + SO_4^{2-}$

Similarly our values of K_2 is of the same order as of[18]

$CrSO_4^+ = Cr^{3+} + SO_4^{2-}$ and of[19] $InSO_3^+ = In^{3+} + SO_4^{2-}$

ACKNOWLEDGEMENT

The authors are thankful to late Prof. Balbhadra Prasad for his valuable suggestions and constant encouragement and one of us (S.N.J) is grateful to U.G.C. and C.S.I.R. for granting financial help and to the authorities of Patnà University for laboratory and library facilities.

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(*Received*: 2 July 1993; *Accepted:* 4 October 1993) AJC-702