

## Studies on Ion Association Equilibria. Spectrophotometric Determination of the Thermodynamic Instability Constants of $AlSO_4^+$ , $GaSO_4^+$ and $InSO_4^+$

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### Summary

In the present work the instability constants of  $AlSO_4^+$ ,  $GaSO_4^+$ ,  $InSO_4^+$  ion-pairs have been determined by an indirect spectrophotometric method depending on the decrease in the absorbancy of  $CuSO_4$  solution at  $260\text{ m}\mu$  on adding the respective perchlorates. From a knowledge of the equilibrium constants of  $CuSO_4$  and  $H_2SO_4$ ,  $pH$  of the solution and the extinction coefficient of  $Cu^{++}$  ion and  $CuSO_4$ , the concentrations of the different ion species in solution have been calculated. The activity coefficients of species have been calculated using DAVIES'S empirical equation. The average thermodynamic instability constants of  $AlSO_4^+$ ,  $GaSO_4^+$  and  $InSO_4^+$  at 29 to  $30^\circ\text{C}$  are  $9.08 (\pm 0.44) \cdot 10^{-3}$ ,  $1.03 (\pm 0.05) \cdot 10^{-3}$  and  $1.80 (\pm 0.06) \cdot 10^{-4}$  respectively.

Sulphate ion is known to form complexes with many metal ions. A large number of such complexes, resulting from the association of sulphate ions with uni- and bivalent metal ions have been reported and their instability constants determined with sufficient accuracy. Only a few tripositive ion sulphates have, however, been studied. In the present investigations the instability constants of the ion pairs formed between the aluminium, gallium and indium ions with the sulphate ion have been determined. Of these, the only report, we have in literature, is the stability constant of  $InSO_4^{+1}$ . The sulphates of these three cations are colourless, and they do not have any characteristic absorption peak between 200 and  $400\text{ m}\mu$ . So the study of any

<sup>1</sup> Stability constants, Part II. Spl. Pub. No. 7; Chemical Society, London.

of these systems by a direct spectrophotometric method, either in the visible or in the ultraviolet region of the spectrum, is out of question. An indirect displacement method has, therefore, been adopted in the present investigation. Copper sulphate is known to absorb strongly around  $260\text{ m}\mu$  and it is found that the addition of aluminium perchlorate of comparable concentration to a solution of  $\text{CuSO}_4$  results in a sharp decrease of the absorbancy in this region, though both aluminium perchlorate and sulphate ions are found to be almost transparent at the said wave length. This is taken to indicate complex formation between  $\text{Al}^{3+}$  and  $\text{SO}_4^{--}$  ions. Similar observations are obtained on adding  $\text{Ga}(\text{ClO}_4)_3$  and  $\text{In}(\text{ClO}_4)_3$  to  $\text{CuSO}_4$  solution. So from the measured decrease in optical density and from a knowledge of the instability constants of  $\text{CuSO}_4$  and  $\text{HSO}_4^-$  ion, the instability constants of the ion pairs formed by the tripositive ions with the sulphate ion have been calculated.

### Experimental

Aluminium perchlorate was prepared by the method followed in our earlier work<sup>2</sup> and estimated as  $\text{Al}_2\text{O}_3$ . Gallium perchlorate was prepared by the method of FOSTER<sup>3</sup>, and estimated as  $\text{Ga}_2\text{O}_3$ . Indium perchlorate solution was prepared as follows. 99.9% pure Indium metal was dissolved in hydrochloric acid and the excess acid was boiled off. Indium hydroxide was precipitated from this solution and it was washed free from chloride. The hydroxide precipitate was dissolved in perchloric acid solution and the  $pH$  of this stock solution was maintained below  $pH$  2.0 to prevent hydrolysis. The indium content of the solution was estimated gravimetrically by precipitating and weighing as the oxide by the method of MOELLER<sup>4</sup>. Copper perchlorate solution was prepared by dissolving cupric carbonate in perchloric acid and then estimating the copper content iodometrically. Sodium sulphate solution used was prepared by mixing equivalent amounts of caustic soda and sulphuric acid solutions.

In order to determine the instability constants of the ion-aggregates formed between these trivalent metal ions and sulphate ions, solutions were prepared by mixing different amounts of copper perchlorate, sodium sulphate and the perchlorate of either aluminium,

<sup>2</sup> NANDA and ADITYA, J. Indian chem. Soc. **34** (1957) 577.

<sup>3</sup> FOSTER, J. Amer. chem. Soc. **61** (1939) 3122.

<sup>4</sup> MOELLER, J. Amer. chem. Soc. **62** (1940) 2444.

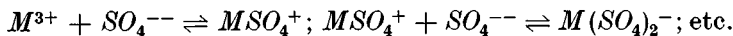
gallium or indium. In these solutions, the  $Cu^{++}$  ion concentration was comparable to the concentration of the trivalent ions present, whereas the concentration of the sulphate ion was much less. The  $pH$  of the solutions was maintained below 2.5 in accordance with the observations of MONK et al.<sup>5</sup>

All optical density measurements were made with Hilger-Watts 'UVISPEK' spectrophotometer model H 700/303, using matched fused silica cells of 1 cm. light path. To avoid errors creeping into these measurements, readings were taken by interchanging the cells. All measurements were carried out at room temperature varying between 29 and 30°C. All  $pH$  measurements were made with a Marconi, battery operated,  $pH$  meter model T.F. 511 D.

### Results

From the measured optical densities of the solution, the instability constants of the complexes were calculated in the following manner.

The equilibria representing the combination of the trivalent ions with the sulphate ion may be represented as:



From electrostatic considerations, the species  $MSO_4^+$  will be more stable than  $M(SO_4)_2^-$ . Further, in all our measurements the concentration of sulphate ion was much less in comparison with the concentration of  $Cu^{++}$  and  $M(III)$  ions. As such, the concentration of the species  $M(SO_4)_2^-$  will be negligible in comparison with that of  $MSO_4^+$ . So only the equilibrium,  $M^{3+} + SO_4^{--} \rightleftharpoons MSO_4^+$ , has been considered in the calculation of equilibrium constants.

In the mixed solution only  $CuSO_4$  and free  $Cu^{++}$  ions may be taken to show absorption at 250  $m\mu$ . The concentrations of  $CuSO_4$  and free  $Cu^{++}$  ion in solution have been obtained by a method of approximation. As a first step in the approximation procedure, it is assumed that  $CuSO_4$  is the only species absorbing at the wave length concerned. Therefore:

$$\text{Optical density (O.D.) of the solution} = \epsilon_2 [CuSO_4] \quad (1)$$

where  $\epsilon_2$  is the extinction coefficient of  $CuSO_4$ . From this equation an approximate value  $[CuSO_4]$  in the solution is obtained. The difference of this from the total copper perchlorate gives an approximate value

<sup>5</sup> MONK et al., Trans. Faraday Soc. 52 (1956) 816.

of free  $Cu^{++}$  ion in solution. A better value of  $[CuSO_4]$  and  $[Cu^{++}]_{free}$  is then obtained from the equation,

$$\text{O.D.} = [Cu^{++}]_{free} \cdot \varepsilon_1 + [CuSO_4] \cdot \varepsilon_2 \quad (2)$$

where  $\varepsilon_1 = 2.27$  and  $\varepsilon_2 = 151.5$ .

This process is repeated till fairly constant values for the concentration of  $CuSO_4$  and hence that of free  $Cu^{++}$  ion in solution are obtained. The instability constant  $K_1$ , of the  $CuSO_4$  species being known from the work of MONK et al.<sup>5</sup> the concentration of free sulphate ion in solution can be calculated from the equation:

$$[SO_4^{--}]_{free} = \frac{K_1 [CuSO_4] f_{CuSO_4}}{[Cu^{++}]_{free} \cdot f_{Cu^{++}} \cdot f_{SO_4^{--}}} \quad (3)$$

Knowing, therefore, the instability constant, ' $K_2$ ', of the  $HSO_4^-$  ion from the work of DAVIES, JONES and MONK<sup>6</sup> and the hydrogen ion activity  $a_{H^+}$  from the measured  $pH$  of the solution, the concentration of free  $HSO_4^-$  ion can be calculated from the equation:

$$[HSO_4^-]_{free} = \frac{a_{H^+} [SO_4^{--}]_{free} f_{SO_4^{--}}}{K_2 \cdot f_{HSO_4^-}} \quad (4)$$

Now the total sulphate ion in solution is made up of free sulphate ion,  $CuSO_4$ ,  $HSO_4^-$  and the complex ion  $MSO_4^+$ , the amount existing as  $NaSO_4^-$  is too small and is neglected. Therefore:

$$[SO_4^{--}]_{total} = [SO_4^{--}]_{free} + [HSO_4^-]_{free} + [CuSO_4] + [MSO_4^+] \quad (5)$$

$[MSO_4^+]$  which is the only unknown quantity in equation (5) can thus be calculated. The difference of this from  $[M^{3+}]_{total}$  gives  $[M^{3+}]_{free}$ .

It is clear from the above that an evaluation of the concentration of  $MSO_4^+$  requires a knowledge of activity coefficients of the respective species, for which we must know the ionic strength of the solution. The latter has been calculated by the method of successive approximation. To start with, we neglect the activity coefficient terms and using only the concentration terms, we get the approximate ionic strength of the solution. For this ionic strength, the activity coefficients are found. Substituting these in equations (3) and (4) we get more accurate concentrations of the different species. With these new values a more accurate ionic strength is calculated and the corresponding activity coefficients are used again in equations (3) and (4) to give better values

<sup>6</sup> DAVIES, JONES and MONK, Trans. Faraday Soc. 48 (1952) 421.

of the concentrations of the different species. This process is repeated till we have constant concentrations of the ions and hence a constant ionic strength. These values have been used to get the thermodynamic instability constant of the species  $MSO_4^+$  from the equation:

$$K_{MSO_4^+} = \frac{a_{SO_4^{--}} \cdot a_{M^{3+}}}{a_{MSO_4^+}} \quad (6)$$

Due to the lack of ionic radius data for the different species, the calculation of the activity coefficients from the ionic strength of the solution has not been done on the basis of DEBYE-HÜCKEL equation. Instead, a modified form of the same equation as suggested by DAVIES<sup>7</sup> has been used. The thermodynamic instability constants, calculated in the manner described above, of the  $AlSO_4^+$ ,  $GaSO_4^+$  and

Table 1

Total conc. of $Cu^{++} \cdot 10^2 M$	Total conc. of $Al^{3+} \cdot 10^2 M$	Total conc. of $SO_4^{--} \cdot 10^3 M$	$pH$	Optical density	Instability constant $\cdot 10^3$
1.0	1.0	7.5	2.0	0.2037	11.6
0.7	1.0	7.0	2.46	0.144	8.22
1.2	0.8	10.0	2.54	0.3195	9.84
1.0	0.8	5.0	2.46	0.1605	8.97
0.8	0.8	8.0	2.51	0.193	8.52
1.1	1.4	11.0	2.25	0.254	8.40
1.2	1.2	7.5	2.26	0.2127	8.01

Average value of  $K_{AlSO_4^+} = 9.08 (\pm 0.44) \cdot 10^{-3} M$ .

Table 2

Total conc. of $Cu^{++} \cdot 10^2 M$	Total conc. of $Ga^{3+} \cdot 10^2 M$	Total conc. of $SO_4^{--} \cdot 10^3 M$	$pH$	Optical density	Instability constant $\cdot 10^3$
1.0	1.188	7.5	1.84	0.131	0.863
0.7	0.9920	7.0	1.90	0.1005	0.847
1.2	0.9902	10.0	1.82	0.203	1.02
1.0	1.188	5.0	1.69	0.089	0.988
0.8	1.486	8.0	1.66	0.096	1.00
0.8	0.9902	6.0	1.81	0.0987	1.17
1.1	1.683	11.0	1.60	0.153	1.24
1.2	1.188	7.5	1.72	0.147	1.13

Average value of  $K_{GaSO_4^+} = 1.03 (\pm 0.05) \cdot 10^{-3} M$ .

Table 3

Total conc. of $Cu^{++} \cdot 10^2 M$	Total conc. of $In^{3+} \cdot 10^2 M$	Total conc. of $SO_4^{--} \cdot 10^3 M$	$pH$	Optical density	Instability constant $\cdot 10^4$
1.0	1.162	7.5	1.89	0.096	1.65
0.7	1.246	7.0	1.79	0.0635	1.95
1.2	0.9965	10.0	2.17	0.175	1.61
1.0	1.162	5.0	1.88	0.069	1.66
0.8	1.246	8.0	1.95	0.083	1.75
0.8	0.9965	6.0	2.44	0.084	2.08
1.1	1.662	11.0	1.63	0.116	1.89

Average value of  $K_{InSO_4^+} = 1.80 (\pm 0.06) \cdot 10^{-4} M$ .

$InSO_4^+$  complexes are given in the Tables 1, 2 and 3. The average values are  $9.08 (\pm 0.44) \cdot 10^{-3}$ ,  $1.03 (\pm 0.05) \cdot 10^{-3}$  and  $1.80 (\pm 0.06) \cdot 10^{-4}$  respectively.

### Discussion

The instability constant of  $InSO_4^+$  reported earlier<sup>1</sup> does not compare with the value obtained in the present work. The former ( $\log K_{inst.} = -1.78$ ) was measured in a 2 M sodium perchlorate solution while in the present case we have reported the thermodynamic value. The difference is clearly due to the effect of ionic strength (Cf. different stability constants given in ref. 1). FERNELIUS and coworkers<sup>8</sup> have determined the stability constants of acetylacetonate complexes of *Al*, *Ga* and *In*. They find that the order of stability is  $Ga > Al > In$ . In our work on<sup>9</sup> salicylate and sulpho-salicylate complexes we have also noted the same sequence as in acetylacetonates, which can be correlated simply by plotting  $\log K$  against ionisation potential or as has been done by ROSSOTTI<sup>10</sup> by plotting  $\log K$  against ALREED ROCHOW electronegativity<sup>11</sup>. But our results with sulphate complexes ( $In > Ga > Al$ ) do not agree with this sequence. Possibly that is due to the fact that the acetylacetonate, sulpho-salicylate or salicylate complexes are chelates whereas the sulphate complexes are BJERRUM type ion-pairs.

<sup>7</sup> DAVIES, J. chem. Soc. [London] 1938, 2093.

<sup>8</sup> IZATT, FERNELIUS and BLOCK, J. physic. Chem. 59 (1955) 170.

<sup>9</sup> NANDA, Ph. D. Thesis, Utkal University, India, 1961.

<sup>10</sup> ROSSOTTI, p. 43, Modern Co-ordination Chemistry, Ed. Lewis and Wilkins, Interscience Pub. 1960.

<sup>11</sup> ALREED and ROCHOW, J. Inorg. Nuclear Chem. 5 (1958) 264.

Although we have found no similarity in the values of the stability constants of the sulphate complexes of *Al*, *Ga* and *In* with those of the complexes of the same metals with other ligands, it is quite interesting to note that in the case of sulphates of *Gr IA* and *Gr IIA* metals similar reversal in the stability constants, as we find in the present work, has been reported. DAVIES<sup>12</sup> and WILLIAMS<sup>13</sup> have suggested that the reverse sequences occur with the outer sphere complexes, for which the reciprocal radius of the hydrated metal ion would be more suitable. The radii of the hydrated ions are not available and so it is not possible to test the correlation.

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<sup>12</sup> DAVIES, J. chem. Soc. [London] 1951, 1256.

<sup>13</sup> WILLIAMS, J. chem. Soc. [London] 1952, 3770.