Factors Affecting In(III)-hydroxysalt Precipitation and the Equilibria of In(III)-hydroxysalt in Sulfate Aqueous Solution*

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The present investigation was carried out to examine the chemical composition of precipitates produced during a titration of indium sulfate aqueous solution with sodium hydroxide, to obtain the standard free energy of formation of In(III)-hydroxysalt, and to determine the pH-dependence of its solubility at 333 K.

The results obtained are summarized as follows:

1. The hydrolysis proceeds via two steps. The precipitates produced in the first and the second step hydrolysis were identified to be \( \{Na_x{(H_2O)}_{1-x}\}In_3(SO_4)_2(OH)_6\), where the value of \( x \) varies with the composition of the solution, and \( In(OH)_3\), respectively. These hydrolysis reactions are represented by \( xNa^+ + 3In^{3+} + aSO_4^{2-} + \beta HSO_4^- + (7-x)H_2O = \{Na_x{(H_2O)}_{1-x}\}In_3(SO_4)_2(OH)_6 + (5+x+\beta)H^+ \), where \( \alpha + \beta = 2 \), and \( \{Na_{x_a}{(H_2O)}_{1-x_a}\}In_3(SO_4)_2(OH)_6 + (2+x)H_2O = 3In(OH)_3 + (x/2)Na_2SO_4 + ((4-x)/2)H_2SO_4 \).

2. The standard free energies of formation of \( \{Na_x{(H_2O)}_{1-x}\}In_3(SO_4)_2(OH)_6\) were obtained for the \( x \)-values of 0.26, 0.34, 0.64 and 0.85 at 333 K.

3. The pH-dependence of the solubility of \( \{Na_x{(H_2O)}_{1-x}\}In_3(SO_4)_2(OH)_6\) was determined for various choices of the parameter, which can be calculated from the composition of solutions immediately before the beginning of the first step hydrolysis.

Furthermore, several factors affecting the precipitation of In(III)-hydroxysalt were also studied systematically.

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I. Introduction

Ion activity-pH diagrams for the metal-H_2O system, which are often referred to as the background for precipitation operation, are not always useful for more complicated aqueous solution systems containing sulfate ions which have a strong tendency to form sulfato-complexes with metal ions. From this standpoint, the authors have made a series of investigations, particularly to elucidate the pH-dependence of the solubility of hydroxysalts of IIIb-metals which are, in recent years, of great importance as electronic materials.

The results for aluminium and gallium\(^{1)-(4)}\) have already been reported.

In this study on indium, investigations were carried out to examine the factors affecting the In(III)-hydroxysalt precipitation that occurs in the hydrolysis of indium sulfate aqueous solution with lithium carbonate and also to determine the chemical composition of the precipitates produced in the first step hydrolysis in the hydrolysis of indium sulfate aqueous solution with sodium hydroxide solution and its standard free energy of formation as well as the pH dependence of its solubility at 333 K.

II. Experimental

The apparatus used in this investigation is quite similar to that described in the previous papers\(^{1)-(6)}\).
1. Factors affecting In(III)-hydroxysalt precipitation

1 dm³ aqueous solution with the prescribed concentrations of In₂(SO₄)₃ and Na₂SO₄ and a desired value of pH was poured into a 2 dm³ flask with five arms to set up electrodes for the measurement of pH, an impeller, a thermometer, a Li₂CO₃ inlet, and so on. The solution was agitated by the impeller and temperature was maintained at 333 ± 0.5 K by means of a thermostated water bath. Lithium carbonate was used as an alkali for the hydrolysis, because it is known that lithium cannot be a metallic constituent of the alkali jarosite. Figure 1 shows an example of the change in pH of the solution with time after the addition of Li₂CO₃. The desired value of pH was achieved by repeating the addition of Li₂CO₃ several times. After a fixed period of time, the precipitate was taken, filtered, washed with double distilled water, dried at a temperature of around 323 K, and analyzed chemically (In(III), Na(I), and Li(I): atomic absorption spectrochemical analysis, (SO₄²⁻)ₜₒᵗ: BaSO₄-gravimetric analysis, where the subscript “Tot” is an abbreviation of “Total”) to determine its chemical composition. Furthermore, it was also identified qualitatively by X-ray diffraction analysis. For making the solutions, the ordinary laboratory double distilled water and the chemicals of reagent grade were used. The experimental conditions are summarized in Table 1. The agitation speed and reaction time as the physical conditions as well as the pH-value of the solution and In(III)- and Na(I)-concentrations as the chemical conditions were varied. The standard experimental conditions are underlined in the table. For example, in the case of examining the effect of the pH-value on the In(III)-hydroxysalt precipitation, only the pH-value was changed under a setting of the other conditions at the underlined values. Incidentally, the change in Na(I)-concentration also means a change in that of (SO₄²⁻)ₜₒᵗ since Na(I) is added as Na₂SO₄.

2. Thermodynamic behavior of In(III) in the hydrolysis

In order to obtain the desired pH-value and In(III)-concentration of the solution, sulfuric acid and indium sulfate were successively added to 1 dm³ of double distilled water in a 2 dm³ flask with five arms for installing electrodes for the measurement of the pH- and potential-values, the impeller, the thermometer, the NaOH-solution supplying tube, and so on. The solution was agitated at a constant rotational speed by the impeller and the temperature was maintained at 333 ± 0.5 K by using a thermostated water bath. Argon gas was injected into the solution at a flow rate of 5 × 10⁻⁶ m³·s⁻¹ for 3.6 ks to drive out the dissolved oxygen gas and was then allowed to flow over the solution at the same flow rate to maintain an inert atmosphere in the flask. Subsequently, a 2.5 kmol·m⁻³ NaOH-solution was added into the solution and the variation of the pH-value with time was measured and recorded. When the pH-value became constant, this value was taken as the equilibrium one. By repeating this procedure, titration curves were obtained. In each procedure, after the establishment of equilibrium, samples of

![Figure 1](image-url)
The solution and precipitates were taken and filtered. The precipitates were then washed with double distilled water until no sulfate ions were detected, then dried slowly at a temperature of around 323 K, and chemically analyzed for Na(I), In(III), and SO$_4^{2-}$. The precipitates were also identified qualitatively by X-ray diffraction analysis. Table 2 shows the initial composition of the solutions immediately before the beginning of the first step hydrolysis reaction (see section III.2).

All the chemicals used were of reagent grade.

### III. Experimental Results

#### 1. Factors affecting In(III)-hydroxysalt precipitation

Figure 2 shows the effect of rotational speed on the yield and chemical composition of the precipitates. The ordinate represents the molar ratio of Na(I) and In(III) to two moles of SO$_4^{2-}$ in the precipitates. Lithium was never detected in the precipitates. At the rotational speeds of 5 to 15 s$^{-1}$, no change in the chemical composition of the precipitates was recognized and the molar ratio represented by Na(I):In(III):SO$_4^{2-}$ was invariably close to 1:3:2. However, the molar ratio of Na(I) to two moles of SO$_4^{2-}$ was always somewhat smaller than unity. From the above molar ratios, the mass balance, and the electro-neutrality of the precipitates, regarding them as {Na$_x$ (H$_3$O)$_{1-x}$}In$_3$(SO$_4$)$_2$(OH)$_6$ (x=0–1, In(III)-hydroxysalt), the sum of the weight percentages of their constituents, %Na(I) + %H$_3$O(I) + %In(III) + %SO$_4^{2-}$ + %OH$^-$, results in a value of almost 100%. By the way, the question arose whether or not the chemical form of the precipitates was changed during the washing and drying operations. Therefore, the X-ray diffraction patterns of the precipitates collected directly from the solution were compared with those of the precipitates which were washed or dried after washing. There was no difference among their patterns. It is reasonable, therefore, to consider that the chemical form of the precipitates will not be changed by the washing and drying operations. The amount of the precipitates produced gradually increases with increasing rotational speed and reaches a constant value at the rotational speeds above 10 s$^{-1}$. In addition, at the rotational speed of 5 s$^{-1}$ the precipitates adhered strongly to the glass wall of the flask.

#### Table 2 Initial compositions of solutions.

| Run | In$_3$(SO$_4$)$_2$ | Na$_2$SO$_4$ |
|-----|-------------------|--------------|
| 1   | 0.182             | 0.250        |
| 2   | 0.028             | 0.930        |
| 3   | 0.0155            | 0.025        |
| 4   | 0.025             | 0.          |

Fig. 2 Effect of agitation speed on the amount of In(III)-hydroxysalt produced and its composition.

Fig. 3 Effect of reaction time on the composition of In(III)-hydroxysalt.
For these reasons, the rotational speed of 15 s\(^{-1}\) was chosen in the subsequent experiments. The reaction time does not essentially affect the molar ratios of Na(I) and In(III) to SO\(_{2}^{4-}\) as shown in Fig. 3. The mean value of \(x\) obtained in these experiments was 0.86.

The effects of the chemical factors, i.e., the pH-values and the initial concentrations of In(III), Na(I), and (SO\(_{2}^{4-}\))\(_{\text{Tot}}\) in the solution on the chemical composition of the precipitates are indicated in Figs. 4–8. As shown in...
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Fig. 4, the chemical composition of the precipitates produced at the pH-values of 2.5 and 3.0 were almost the same, while at the pH-value of 3.7 the molar ratio of In(III) to \( SO_4^{2-} \) increased and that of Na(I) decreased. In the latter case, In(OH)₃ was identified in addition to In(III)-hydroxysalt by X-ray diffraction analysis. From this, it can be considered that In(OH)₃ was partly produced, since the pH-value in the immediate vicinity of the Li₂CO₃ particles added rose to a value in the pH-region in which In(OH)₃ was thermodynamically stable. The thermodynamically stable hydrolysis reaction product at the pH-value of 3.7 is In(III)-hydroxysalt(see subsequent section). However, once In(OH)₃ is formed, the rate of the conversion of In(OH)₃ to In(III)-hydroxysalt(the rate of the backward reaction of eq. (3)) is extremely slow in comparison with that of the forward reaction. This is particularly remarkable after the completion of the conversion on the surface of the In(OH)₃ particles, since the backward reaction accompanies the incorporation of Na(I) and \( SO_4^{2-} \) into In(OH)₃\(^{[3][4]}\). As is obvious from Fig. 5, the initial concentration of In(III) does not affect the molar ratios of Na(I) and In(III) to \( SO_4^{2-} \) above 0.05 kmol·m⁻³. Below 0.05 kmol·m⁻³, some decrease in the Na(I)-content was recognized. At the initial concentration of Na(I) above 0.6 kmol·m⁻³, the chemical compositions of the precipitates remain unchanged (Fig. 6). However, below 0.2 kmol·m⁻³, the molar ratio of In(III) abruptly increases, while that of Na(I) decreases. Also, in this case, the formation of In(OH)₃ was confirmed by X-ray diffraction analysis. It was, therefore, examined how the production ratio of In(OH)₃ to In(III)-hydroxysalt varied with decreasing initial concentration of Na(I) in the solution. The results obtained are shown in Fig. 7. The ratio increases to a considerable extent at the low initial concentration of Na(I). It was also found that the Na(I)-content in In(III)-hydroxysalt gradually decreased with a decrease of the initial concentration of Na(I). When the solution contained no sodium, the production ratios of In(OH)₃ and In(III)-hydroxysalt were 76 and 24%, respectively. The In(III)-hydroxysalt produced under this condition is (H₂O)In₃(SO₄)₂(OH)₆. In the case of iron, it has been reported that the production ratio of (H₂O)Fe₃(SO₄)₂(OH)₆ was 100\(^{[5]}\) under a similar condition.

When the initial concentration of Na(I) in the solution is 0.2 kmol·m⁻³, the molar ratio of Na(I) to In(III) in the solution is 2.0 (Fig. 6), whereas, at the initial concentration of In(III) of 0.5 kmol·m⁻³ (Fig. 5), that of Na(I) to In(III) is only 1.2. In the latter case, however, neither the production of In(OH)₃ nor the decrease of the Na(I)-content in In(III)-hydroxysalt was recognized. Thus, with increasing In(III)-concentration in the solution, an In(III)-hydroxysalt of higher Na(I)-content is likely to be produced. The same tendency was also observed in the case of gallium\(^{[3][4]}\).

Figure 8 shows the effect of the initial concentration of \( SO_4^{2-} \)\(_{\text{tot}} \) in the solution on the chemical composition of the precipitates. The molar ratio of In(III) to \( SO_4^{2-} \) in In(III)-hydroxysalt remains invariably constant at 3:2 over the wide range of the molar ratios of \( (SO_4^{2-})_{\text{tot}}/\text{In(III)}=2~\sim~22 \) in the solution. In this way, the molar ratio (3:2) of In(III) to \( SO_4^{2-} \) in In(III)-hydroxysalt is invariant.

2. Thermodynamic behavior of In(III) in hydrolysis

(1) Titration curves and chemical composition of precipitate produced by hydrolysis

Neutralization of the solution proceeds in three steps, i.e., neutralization of the acid and the first and second step hydrolysies, as will be seen from the titration curves shown later. In the first and the second step hydrolysis, the pH-value of the solution gradually decreased with time after the addition of NaOH-solution and attained to the respective constant values in about 28 ks (8 h) in the former case and in about 48 ks (13 h) in the latter case. The values which remained constant over a period of 10.8 ks (3 h) for the first step hydrolysis and 18 ks (5 h) for the second step hydrolysis were adopted as the equilibrium ones.

Relations between the amounts of NaOH added and the equilibrium pH-values obtained in the above way are illustrated in Fig. 9. It can be seen from this figure that, as in the case of
aluminium\textsuperscript{(1)(2)} and gallium\textsuperscript{(3)(4)}, the hydrolysis reaction proceeds in two steps. The molar ratio of Na(I) and In(III) to two moles of SO\textsubscript{4}\textsuperscript{2-} in the precipitates taken after the completion of the first step hydrolysis were 0.26–0.85 and ca. 3, respectively, as tabulated in Table 3. From these molar ratios of the first step hydrolysis reaction products and, moreover, their mass balance and electro-neutrality, regarding them as \{Nax, (H\textsubscript{3}O)\textsubscript{1-x}\}In\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6} (x=0–1), the sum of the weight percentages of their constituents, i.e., %Na(I) + %H\textsubscript{2}O(1) + %In(III) + %SO\textsubscript{4}\textsuperscript{2-} + %OH\textsuperscript{-}, results again in more than 98\%. From these results, the first step hydrolysis reaction may be represented as,

\[ x\text{Na}^+ + 3\text{In}^{3+} + \alpha\text{SO}_4^{2-} + \beta\text{HSO}_4^- + (7 - x)\text{H}_2\text{O} = \{\text{Nax}, (\text{H}_3\text{O})_{1-x}\}\text{In}_3(\text{SO}_4)_2(\text{OH})_6 \]

\[ + (5 + x + \beta)\text{H}^+ \] (1)

where \( \alpha + \beta = 2. \)

The initial concentrations of Na(I) in the solutions in Runs 3 and 4 are below 0.2 kmol\textperiodcentered m\textsuperscript{-3}. Judging from Fig. 6, this corresponds to the condition under which In(OH)\textsubscript{3} is partly produced. However, in both experiments the formation of In(OH)\textsubscript{3} was not observed. In this manner, modes of the hydrolysis reaction seem to be different for the addition of Li\textsubscript{2}CO\textsubscript{3} solid particles and of NaOH-solution, when Na(I) does not exist in the solution enough to form only In(III)-hydroxysalt for the addition of Li\textsubscript{2}CO\textsubscript{3}.

Neither Na(I) nor SO\textsubscript{4}\textsuperscript{2-} was analytically detected from the second step hydrolysis reaction products, which were identified as In(OH)\textsubscript{3} by X-ray diffraction analysis (in the cases of aluminium and gallium, the second step hydrolysis products were Al(OH)\textsubscript{3}\textsuperscript{(1)(2)} and GaOOH\textsuperscript{(3)(4)}, respectively). From these facts, the second step hydrolysis reaction may be written as

\[ \{\text{Nax}, (\text{H}_3\text{O})_{1-x}\}\text{In}_3(\text{SO}_4)_2(\text{OH})_6 + (2 + x)\text{H}_2\text{O} = 3\text{In(OH)}_3 + \frac{x}{2}\text{Na}_2\text{SO}_4 + \frac{4-x}{2}\text{H}_2\text{SO}_4. \] (3)

In order to ascertain whether or not \{Nax, (H\textsubscript{3}O)\textsubscript{1-x}\}In\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6} and In(OH)\textsubscript{3} are thermodynamically stable, the same experiment as explained in Fig. 3 in the previous papers\textsuperscript{(3)(4)} was carried out. That is to say, the amount of 2.5 kmol\textperiodcentered m\textsuperscript{-3} NaOH-solution required only for completion of the first step hydrolysis reaction was added instantaneously into the indium sulfate aqueous solution to examine the conversion of In(OH)\textsubscript{3} to \{Nax, (H\textsubscript{3}O)\textsubscript{1-x}\}In\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6}. In this experiment, it was confirmed that In(OH)\textsubscript{3} was converted to \{Nax, (H\textsubscript{3}O)\textsubscript{1-x}\}In\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6} at a value in the pH-region in which \{Nax, (H\textsubscript{3}O)\textsubscript{1-x}\}In\textsubscript{3}(SO\textsubscript{4})\textsubscript{2}(OH)\textsubscript{6} was produced in the experiments conducted for obtaining the titration curves in Fig. 9. From this fact, it can be reasonably considered
that both \{\text{Na}_x, (\text{H}_3\text{O})_{1-x}\} \text{In}_3(\text{SO}_4)_2(O\text{H})_6 \text{ and In(OH)}_3 are thermodynamically stable in their corresponding pH-regions.

(2) **Backward phenomenon of the pH-value in the hydrolyses**

As seen in Fig. 9, a backward phenomenon of the pH-value was observed at the beginning stage of both the first and second step hydrolysis reactions. The reason is that the hydrolysis reactions expressed by eqs. (1) and (3) start to proceed only when NaOH exists in excess in the solution. This tendency was the strongest in the case of indium, followed by gallium\(^{(1)(2)}\), and was scarcely observed in the case of aluminium\(^{(3)(4)}\).

‡W. Discussion

For arguing on the total concentration of a metal dissolved in the solution, excluding the high alkali region, the first step hydrolysis usually comes into question. The following discussion is, therefore, focused exclusively on this aspect.

1. **Relation between the total indium concentration and pH-value in the solution**

From the equilibrium constant, \(K_1\), of eq. (1) and the dissociation equilibrium constant\(^{(1)(2)}\) of HSO\(_4^-\) ion at 333 K, one obtains the relation between the molarity of In\(^{3+}\) ion, \(C_{\text{In}^{3+}}\), and pH-value,

\[
\log C_{\text{In}^{3+}} = \left\{ -\log \gamma_{\text{In}^{3+}} - \frac{1}{3} \left( \log K_1 + x \log a_{\text{Na}^+} + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-} \right) \right\} \cdot \text{pH},
\]

since the molarity, \(C\), can be regarded as being nearly equal to the molality, \(m\), in the relatively low concentration region of the solutes. In eq. (4), \(a\) and \(\gamma\) are the molal activity and the activity coefficient, respectively.

According to the Stability Constants\(^{(6)}\), indium exists in the form of four different ionic species, i.e., In\(^{3+}\), InSO\(_4^+\), In(\text{SO}_4\)\(_2^-\), and In(\text{SO}_4\)\(_3^-\) in sulfate aqueous solutions. The stepwise formation constants, \(k_1\), \(k_2\) and \(k_3\) of In(III) sulfato-complexes,

\[
\text{In}^{3+} + \text{SO}_4^{2-} = \text{InSO}_4^+, \quad \frac{C_{\text{InSO}_4^+}}{C_{\text{In}^{3+}} \cdot C_{\text{SO}_4^{2-}}} = k_1
\]

are 70.8, 5.62 and 2.51, respectively, in NaClO\(_4\)-solution with an ionic strength of 1 at 298 K. Since the temperature dependence of \(k_1\), \(k_2\) and \(k_3\) is unknown, the above values of \(k_1\), \(k_2\) and \(k_3\) are also assumed to be valid at 333 K. Then, the total concentration, \(C_{\text{In}}\), of indium dissolved in sulfate aqueous solution may be represented as

\[
C_{\text{In}} = C_{\text{In}^{3+}} + C_{\text{InSO}_4^+} + C_{\text{In(\text{SO}_4\)\(_2^-)}\} + C_{\text{In(\text{SO}_4\)\(_3^-)}\} = (1 + k_1C_{\text{SO}_4^{2-}} + k_1k_2C_{\text{SO}_4^{2-}}^2 + k_1k_2k_3C_{\text{SO}_4^{2-}}^3) \cdot C_{\text{In}^{3+}}.
\]

Taking logarithm of eq. (8) and substituting eq. (4) into it gives

\[
\log C_{\text{In}} = \log (1 + k_1C_{\text{SO}_4^{2-}} + k_1k_2C_{\text{SO}_4^{2-}}^2 + k_1k_2k_3C_{\text{SO}_4^{2-}}^3) - \left\{ -\log \gamma_{\text{In}^{3+}} - \frac{1}{3} \left( \log K_1 + x \log a_{\text{Na}^+} + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-} \right) \right\} \cdot \text{pH},
\]

where \(\gamma_{\text{In}^{3+}}\) is the molal activity of In\(^{3+}\) ion.
Furthermore, assuming the sum of the terms not including pH in eq. (9) to be constant, one finally obtains

$$\log C^T_{\text{In}} = \text{const.} - \left[ \frac{5+x}{3} + \frac{2}{3[1+\exp\{2.303(pH-2.42)\}]^2} \right] \cdot \text{pH}. \quad (10)$$

Introducing the parameter, $\varepsilon$, defined by

$$\varepsilon = \log (1 + k_1C_{\text{SO}_2^-} + k_1k_2C_{\text{SO}_4}^{3-} + k_1k_2k_3C_{\text{SO}_4}^{6-})$$

$$- \left\{ \log \gamma_{\text{In}^{3+}} + \frac{1}{3} (x \log a_{\text{Na}^+} + \alpha \log a_{\text{SO}_4}^- + \beta \log a_{\text{HSO}_4}^-) \right\}. \quad (11)$$

the term "const." can be expressed as

$$\text{const.} = \varepsilon - \frac{1}{3} \log K_1 \quad (12)$$

which is a constant adjustable to suit the experimental data.

As shown in Table 3, four kinds of In(III)-hydroxysalts with the values of 0.26, 0.34, 0.64 and 0.85 for $x$ were found to be produced depending on the initial condition of the solution. For example, the relation between $\log C^T_{\text{In}}$ and pH-value at equilibrium of the first step hydrolysis reaction is shown in Fig. 10 for the In(III)-hydroxysalt with the $x$-value of 0.85, i.e. $\{\text{Na}_{0.85}(\text{H}_3\text{O})_{0.15}\} \text{In}_3(\text{SO}_4)_2(\text{OH})_6$. By most close fitting of eq. (10) on all the data points obtained experimentally, the value of const. was determined to be 3.38 with the standard deviation of 0.14. Such a small value of the standard deviation demonstrates the validity of the assumption made above that the sum of the terms not including pH in eq. (9) is constant. The relationship of eq. (10) having the value of const. of 3.38 is shown by a heavy solid line in Fig. 10. Since the value of const. has been determined in this way, if it is possible to estimate the value of $\varepsilon$, one can, then, obtain the value of the equilibrium constant, $K_1$, for the first step hydrolysis reaction of eq. (1). In order to estimate the value of $\varepsilon$, molalities and activity coefficients of $\text{SO}_4^{2-}$, $\text{HSO}_4^-$, and $\text{Na}^+$ ions, activity coefficient of $\text{In}^{3+}$ ion, and ionic strength of the solution are required to be known. This treatment is valid also for the other three kinds of In(III)-hydroxysalts.

2. Ionic strength of the solution and molalities of $\text{SO}_4^{2-}$, $\text{HSO}_4^-$, and $\text{Na}^+$ ions

Strictly speaking, $\text{H}_2\text{SO}_4$, $\text{NaOH}$, $\text{Na}_2\text{SO}_4$, and $\text{In}_2(\text{SO}_4)_3$ exist in the solution. However, the first step hydrolysis proceeds in the acidic pH region so that the existence of $\text{OH}^-$ ion is negligible. In this case, the ions existing in the solution may be considered to be $\text{H}^+$, $\text{HSO}_4^-$, $\text{SO}_4^{2-}$, $\text{Na}^+$, $\text{NaSO}_4^-$, $\text{In}^{3+}$, $\text{InSO}_4^+$, $\text{In}(\text{SO}_4)^{-2}$, and $\text{In}(\text{SO}_4)_3^{-3}$. Their molalities can be calculated from a combination of the following relations (A)-(H):

(A) Ionic strength, $I$

![Fig. 10 The pH dependence of the solubility of $\{\text{Na}_{0.85}(\text{H}_3\text{O})_{0.15}\} \text{In}_3(\text{SO}_4)_2(\text{OH})_6$ in indium sulfate aqueous solutions at 333 K.](image-url)
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$$I = \frac{1}{2} (m_{H^+} + m_{HSO_4^-} + 4m_{SO_4^{2-}} + m_{Na^+} + m_{NaSO_4^-} + 9m_{In^{3+}} + m_{InSO_4^2-} + m_{In(SO_4)_2^-} + 9m_{In(SO_4)_3^3-})$$  

(B) Dissociation quotient \( \frac{m_{H^+} \cdot m_{SO_4^{2-}}}{m_{HSO_4^-}} \) of HSO_4^- ion

$$\log \left( \frac{m_{H^+} \cdot m_{SO_4^{2-}}}{m_{HSO_4^-}} \right)_{333K} = -2.420 + \frac{2.188\sqrt{I}}{1 + 0.41\sqrt{I}}.$$  

(C) pH-value of the solution

$$\text{pH} = -\log a_{H^+} = -\log \gamma_{H^+} - \log m_{H^+}$$

$$\log \gamma_{H^+} = -\frac{0.5471\sqrt{I}}{1 + \sqrt{I}} + bI + c$$

$$b = -0.516m_{H_2SO_4}^{0.264} + 0.283$$

$$c = 0.683m_{H_2SO_4}^{0.593} + 0.144.$$  

(D) Mass balance of SO_4^{2-}

$$m_{HSO_4^-} + m_{SO_4^{2-}} + m_{NaSO_4^-} + m_{InSO_4^2-} + 2m_{In(SO_4)_2^-} + 3m_{In(SO_4)_3^3-} = m_T^{SO_4^-}$$

where \( m_T \) represents the total concentration and can be determined by chemical analysis.

(E) Mass balance of In(III)

$$m_{In^{3+}} + m_{InSO_4^2-} + m_{In(SO_4)_2^-} + m_{In(SO_4)_3^3-} = m_T^{In^{3+}}.$$  

(F) Mass balance of Na(I)

$$m_{Na^+} + m_{NaSO_4^-} = m_T^{Na^+}.$$  

(G) Stepwise formation constant of Na(I) sulfato-complex

$$Na^+ + SO_4^{2-} = NaSO_4^{-}, \quad \frac{m_{NaSO_4^-}}{m_{Na^+} \cdot m_{SO_4^{2-}}} = 5.25.$$  

(H) Stepwise formation constants of In(III) sulfato-complexes; eqs. (5)-(7) are used by approximating \( C \) to be nearly equal to \( m \).

3. Activity coefficients of HSO_4^- and SO_4^{2-} ions in the solution at 333 K used in this investigation

Awakura et al.\(^{(7)}\) have reported the activities of H^+, HSO_4^-, and SO_4^{2-} ions for the ternary system Na_2SO_4-H_2SO_4-H_2O at 298 K. The molalities of those ions can be obtained by considering ionic strength of the solution, dissociation equilibrium of HSO_4^- ion at 298 K, and mass balance of H_2SO_4 and Na_2SO_4\(^{(3)}\). Accordingly, the activity coefficients of those ions at 298 K can be calculated from both the activities and the molalities determined above.

The authors have analysed the activity coefficients of HSO_4^- and SO_4^{2-} ions obtained in this way as a function of ionic strength by using \( m_{H_2SO_4} \) as a parameter on the basis of the following equation\(^{(2)}\):

$$\text{log } \gamma = \frac{-Az_i^2\sqrt{I}}{1 + \sqrt{I}} + bI + c$$

where \( z_i \) is the electric charge on ion, \( i \), and \( A \) is equal to 0.5092\(^{(6)}\) at 298 K.

In calculation of the activity coefficients of HSO_4^- and SO_4^{2-} ions in the solutions at 333 K used in this investigation, the following assumptions were made.

(i) The solution used in this investigation may be assumed approximately as the ternary system Na_2SO_4-H_2SO_4-H_2O, since the concentration of indium is lower than that of sodium throughout the first step hydrolysis. Even in the case of Run 1, where the initial concentration of In(III) in the solution is the highest of all the solutions used, the value of \( c \) calculated for the solution with a high In(III)-concentration immediately after the beginning of the first step hydrolysis reaction agrees, within the range of 7%, with that of \( c \) calculated for the solution with extremely low In(III)-concentration just before the completion of the first step hydrolysis reaction.

(ii) The value of \( A \) in the Debye-Hückel expression depends only on temperature (\( A = 0.5471^{(6)} \) at 333 K), while the values of \( b \) and \( c \) are independent of temperature.

Under these assumptions, the activity coefficients of HSO_4^- and SO_4^{2-} ions of the solution at 333 K used in this investigation can be calculated from the following equations\(^{(2)}\):

$$\text{log } \gamma_{HSO_4^-} = \frac{-0.5471\sqrt{I}}{1 + \sqrt{I}} + 0.276I - 0.0823.$$  

$$\text{log } \gamma_{SO_4^{2-}} = \frac{-0.5471 \times 4\sqrt{I}}{1 + \sqrt{I}} + bI + c.$$
b = 0.0260m^0.976_{H_2SO_4} + 0.348. \quad (26)

c = -1.39m^0.686_{H_2SO_4} - 0.166. \quad (27)

4. Activity coefficients of the In^{3+} ion and activity of Na^+ ions

As mentioned in section IV.2, the solutions used in this investigation may be assumed to be the In_2(SO_4)_3·Na_2SO_4·H_2SO_4·H_2O system. By applying Meissner's empirical procedure\(^{(9)-(12)}\) to this system, the total mean activity coefficients\(^{(9)(13)}\) of In_2(SO_4)_3 and Na_2SO_4, and hence their activities can be estimated\(^*\). These activities, \(a_{In_2(SO_4)_3}\) and \(a_{Na_2SO_4}\), are related to the molalities, \(m_{In^{3+}}, m_{Na^+},\) and \(m_{SO_4^{2-}}\) as well as their free activity coefficients\(^{(9)(13)}\), \(\gamma_{In^{3+}}, \gamma_{Na^+},\) and \(\gamma_{SO_4^{2-}}\), by the equations,

\[
\gamma_{In_2(SO_4)_3} = \gamma_{In^{3+}} \cdot \gamma_{SO_4^{2-}} \cdot m_{In^{3+}} \cdot m_{SO_4^{2-}} \quad (28)
\]

and

\[
\gamma_{Na_2SO_4} = \gamma_{Na^+} \cdot \gamma_{SO_4^{2-}} \cdot m_{Na^+} \cdot m_{SO_4^{2-}} \quad (29)
\]

from which the values of \(\gamma_{In^{3+}}\) and \(\gamma_{Na^+}\) can be determined by calculating the values of \(m_{In^{3+}}, m_{Na^+},\) and \(m_{SO_4^{2-}}\) with the aid of the methods described in sections IV.2 and IV.3, respectively.

5. Standard free energies of formation of the In(III)-hydroxysalts and pH-dependence of their solubility in sulfate aqueous solution

The values of \(\alpha, \beta, \epsilon,\) and \(\log K_1\) can be calculated from the activity coefficients and/or molalities of \(H^+, HSO_4^-, SO_4^{2-}, In^{3+}\) and \(Na^+\) estimated in sections IV.2 to IV.4. By applying the values of \(\alpha\) and \(\beta\) to eq. (1), one can determine the standard free energies of formation of In(III)-hydroxysalts with different Na(I)-contents. The results obtained are listed in Table 4.

The value of const., as mentioned above, remains almost constant throughout the first step hydrolysis. Therefore, as long as the composition of the solution immediately before the beginning of the first step hydrolysis reaction is known, the value of const. can be estimated from one of the values of the standard free energies of formation of \(\{Na_x, (H_3O)^{1-x}\} In_2(SO_4)_3(OH)_6\) listed in Table 4. Accordingly, from Eqs. (10) and (12), one can determine the pH dependence of the solubility of \(\{Na_x, (H_3O)^{1-x}\} In_2(SO_4)_3(OH)_6\) with four different Na-contents in sulfate aqueous solutions by using values of const. as a parameter. As mentioned in section III.1, In(III)-hydroxysalts with the \(x\)-value smaller than 0.64 are produced only under limited conditions. Even in the case of the hydrolysis with Li_2CO_3, as long as the Na(I)-concentration in the solution is higher than 0.6 kmol·m^{-3}, an In(III)-hydroxysalt with the \(x\)-value of 0.86 is produced. In this sense, the pH dependence of the solubility of \([Na_{0.85}, (H_3O)^{0.15}] In_2(SO_4)_3(OH)_6\) only is shown with fine solid lines in Fig. 10. That is to say, if merely the composition of the solution immediately before the beginning of the first step hydrolysis reaction is given, it is possible to decide on the solubility line which should be used prior to the hydrolysis.

V. Conclusions

The investigation on the factors affecting In(III)-hydroxysalt precipitation in the hydrolysis by the addition of Li_2CO_3 of indium sulfate aqueous solution containing Na(I)-ions showed that (i) the In(III)-hydroxysalt is in the form of \(\{Na_x, (H_3O)^{1-x}\} In_2(SO_4)_3(OH)_6\) (\(x=0\sim 1\)) and the molar ratio of In(III) to SO_4^{2-} is invariably constant at 3 to 2, (ii) when the initial concentration of In(III) in the solution is above 0.1 kmol·m^{-3}, \(\{Na_{0.85}, (H_2O)^{0.15}\} In_2(SO_4)_3(OH)_6\) is produced as long as the

| \(\mu_{313K}^{\circ}/kJ\cdot mol^{-1}\) |
|----------------|
| \{Na_{0.76}, (H_2O)^{0.74}\} In_2(SO_4)_3(OH)_6 | -3366 ± 8 |
| \{Na_{0.54}, (H_2O)^{0.66}\} In_2(SO_4)_3(OH)_6 | -3363 ± 7 |
| \{Na_{0.64}, (H_2O)^{0.36}\} In_2(SO_4)_3(OH)_6 | -3374 ± 5 |
| \{Na_{0.85}, (H_2O)^{0.15}\} In_2(SO_4)_3(OH)_6 | -3379 ± 11 |

\(^*\) Terms proposed by R. M. Pytkowicz\(^{(13)}\). The total mean activity coefficient of an electrolyte refers to its mean ionic activity coefficient calculated by assuming the complete dissociation of electrolytes in mixed solutions, and a free activity coefficient to the activity coefficient of a free ion which is not in the form of ion pairs\(^{(13)}\).
molar ratio of Na(I) to In(III) in the solution is larger than 6, (iii) when this molar ratio becomes less than 2, the value of $x$ gradually decreases, and (iv) $\{Na_{0.85}, (H_2O)_{0.15}\}In_3(SO_4)_2(OH)_6$ is preferentially produced with increasing In(III)-concentration in the solution, even the molar ratio of Na(I) to In(III) is less than 2.

Furthermore, from the subsequent investigation on the thermodynamic behavior of indium in the hydrolysis at 333 K of indium sulfate aqueous solution containing less than 0.2 kmol·m$^{-3}$ of In$_2$(SO$_4$)$_3$ with sodium hydroxide solution, it was found that (i) the hydrolysis proceeds in two steps, (ii) Precipitates produced in the first and second step hydrolysers were $\{Na_x, (H_2O)_{1-x}\}In_3(SO_4)_2(OH)_6$ and In(OH)$_3$, respectively, (iii) the first and the second step hydrolysis reactions were represented by

$$xNa^+ + 3In^{3+} + \alpha SO_4^- + \beta HSO_4^- + (7-x)H_2O = \{Na_x, (H_2O)_{1-x}\}In_3(SO_4)_2(OH)_6 + (5+x+\beta)H^+$$

and

$$\{Na_x, (H_2O)_{1-x}\}In_3(SO_4)_2(OH)_6 + (2+x)H_2O = 3In(OH)_3 + (x/2)Na_2SO_4 + ((4-x)/2)H_2SO_4,$$

respectively, where $\alpha + \beta = 2$ and $x = 0 \sim 1$, (iv) the standard free energies of formation of $\{Na_{0.85}, (H_2O)_{0.15}\}In_3(SO_4)_2(OH)_6$ at 333 K were $-3366 \pm 8$, $-3363 \pm 7$, $-3374 \pm 5$, and $-3379 \pm 11$ kJ·mol$^{-1}$, respectively, for the $x$-values of 0.26, 0.34, 0.64, and 0.85. The pH dependence of the solubility of $\{Na_x, (H_2O)_{1-x}\}In_3(SO_4)_2(OH)_6$ was also determined.

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