[DEPARTMENT OF CHEMISTRY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY]

Indium Halide Complexes Studied By Ion-exchange Methods

BY JOSEPH A. SCHUFLE AND H. MORRIS EILAND

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The aqueous complex systems of indium with fluoride, chloride, bromide and iodide have been studied from their equilibria in the presence of an ion-exchange resin, Amberlite IR-120. The solutions were kept at a constant ionic strength of one with sodium perchlorate, and at a constant pH of 3.8. The distribution of indium between the solution and resin phase was followed by using 50-day In^{114} as the tracer. The data were analyzed by the method of Sture Fronaeus. This method makes allowances for the formation of complexes higher than the first complex, and for the adsorption of the first complex as well as the metal cation itself on the resin. The results indicate the existence of three complexes in the bromide system for bromide concentrations up to 0.2 mole/l.; in the chloride system for chloride concentrations up to 0.12 mole/l.; and in the fluoride system for fluoride concentrations up to 0.004 mole/l. Formation constants calculated are: In–Cl system: $\beta_1 = 26$; $\beta_2 = 170$; $\beta_3 = 1680$. In–Br system: $\beta_1 = 16$; $\beta_2 = 60$; $\beta_3 = 300$. In–I system: $\beta_1 = 2$. In–F system: $\beta_1 = 1000$; $\beta_2 = 6 \times 10^5$; $\beta_3 = 4 \times 10^8$. The concentrations at which the first two complexes in the chloride and bromide systems predominate are determined.

The aqueous indium halide system is interesting in that a regular series of complexes seems to be formed as predicted by Bjerrum.[1] Earlier work at high chloride concentrations[2] showed the possibility of $InCl_2^+$ and $InCl_4^-$ complexes existing. Work by Schubert[3] and Fronaeus,[4] among others, has shown that the ion-exchange method may be applied to the study of complex systems. Schubert's treatment is especially applicable where only the first complex is formed in appreciable amounts and it assumes that the adsorption of the complex cation on the resin is negligible.[5] Neither of these requirements is strictly met in the indium halide systems, since complexes higher than the monocomplex can be demonstrated and there is an appreciable adsorption of the first complex on the resin. Therefore the data were analyzed in the more general terms of Fronaeus.

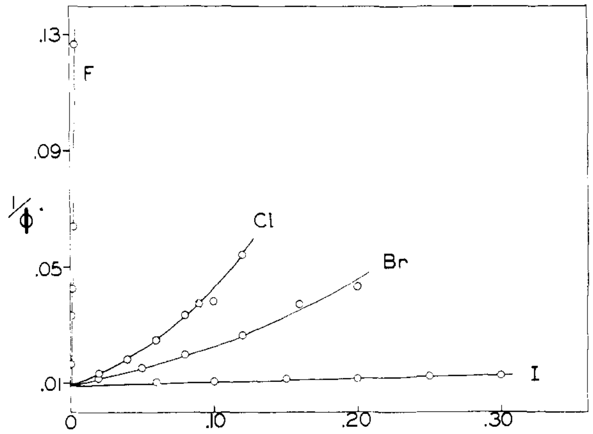

Fig. 1.

The following notation, largely that of Fronaeus and Bjerrum is used

$(M), (MA), (MA_2), \ldots (MA_N)$ = equil. concn. of metal ion and complex ions in soln.

C_M = total metal concn. in soln. in all forms

$(MR), (MAR)$ = equil. concn. of metal ion and complex ion in the resin

(A) = equilibrium concn. of halide ion in soln.

$$\phi = \text{distribution coefficient} = \frac{(MR) + (MAR)}{(M) + (MA) + (MA_2) + \ldots (MA_N)} = \frac{\%\ \text{activity in resin}}{\%\ \text{activity in soln.}} \times \frac{\text{vol. soln.}}{\text{mass resin}}$$

$$l_0 = \frac{(MR)}{(M)};\ l_1 = \frac{(MAR)}{(MA)};\ l = \frac{l_1\beta_1}{l_0}$$

$$\beta_n = \text{formation constant of the } n\text{th complex} = \frac{(MA_n)}{(M)(A)^n}$$

$$X = \sum_0^N \beta_n(A)^n;\ (\beta_0 = 1)$$

$$\phi_1 = (l_0/\phi - 1)/(A)$$

$$f = \frac{l_0/\phi\{(\beta_1 - l)(A) - 1\} + 1}{(A)^2}$$

$$a_n = \text{degree of formation of the } n\text{th complex} = \frac{(MA_n)}{C_M}$$

$$\bar{n} = \text{av. no. of ligands attached to } M = n + \frac{d \log a_n}{dp(A)}$$

Only the terms (MR) and (MAR) are shown in the numerator of ϕ as defined above since it has been shown that the adsorption of the MA_2^+ complex in such a tri-univalent system as this is probably negligible.[6] If the following equation for ϕ is deduced

$$\phi = \frac{l_0(1 + l(A))}{X} \qquad (1)$$

Fronaeus[7] has shown that equation 1 may be written in the alternate form

$$f = \beta_1\phi_1 - X_2 \qquad (2)$$

where

$$X_2 = \beta_2 + \beta_3(A) + \beta_4(A)^2 + \ldots\ldots \qquad (3)$$

Also from equation 1 and the definition of ϕ_1, one may show that the $\lim\limits_{(A)\to 0} \phi_1 = (\beta_1 - l)$.

By a graph of $1/\phi$ *vs.* (A) one obtains $1/l_0$ by extrapolation to zero concentration of (A) (Fig. 1). By a graph of ϕ_1 *vs.* (A) the quantity $(\beta_1 - l)$ is obtained by extrapolation. The function f may now be calculated for various values of (A), and X_2 evaluated from equation 2 for various values of (A).

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[1] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

[2] J. A. Schufle, M. F. Stubbs and R. E. Witman, THIS JOURNAL, **73**, 1013 (1951).

[3] J. Schubert, E. R. Russell and L. S. Myers, Jr., *J. Biol. Chem.*, **185**, 387 (1950).

[4] S. Fronaeus, *Acta Chem. Scand.*, **5**, 859 (1951).

[5] J. Schubert and A. Lindenbaum, THIS JOURNAL, **74**, 3529 (1952).

[6] S. Fronaeus, *Sartryck ur Svensk Kemisk Tidskrift*, **65**, 19 (1953).

[7] S. Fronaeus, *ibid.*, **64**, 317–324 (1952).

TABLE I

Sample no.	(A), mole/l.	In soln., %	ϕ, ml./g.	$1/\phi$, g./ml.	ϕ_1, l./mole	f, (l./mole)^2	Δf(A), (l./mole)^3	$\Delta\phi_1/$(A), (l./mole)^2	X_2, (l./mole)^2
				Indium Iodide System					
...	0	..	(110)	(0.009)	(1.2)				
1, 2	0.06	50.7	97.0	.0103	1.6				
3, 4	.10	51.4	94.6	.0106	1.3				
5, 6	.15	53.4	87.3	.0115	1.5				
7, 8	.20	53.8	86.0	.0116	1.2				
9, 10	.25	55.0	81.8	.0122	1.2				
11, 12	.30	56.0	78.6	.0127	1.2				
				Indium Bromide System					
...	0	..	(110)	(0.009)	(12.3)	(137)	..	...	(60)
1, 2	0.02	51.7	93.5	.0117	.....	..	..	...	...
3, 4	.05	60.4	65.5	.0153	13.6	142	100	26.0	70
5, 6	.08	66.5	50.4	.0199	14.8	151	175	31.3	80
7, 8	.12	72.6	37.8	.0265	15.9	166	242	30.0	90
9, 10	.16	78.8	26.9	.0372	19.5	194	356	43.8	110
11, 12	.20	81.2	23.1	.0432	18.8	199	310	32.5	100
				Indium Chloride System					
...	0	..	(110)	(0.009)	(21.0)	(360)	..	...	(180)
1, 2	0.02	57.4	76.0	.0132	23.1	380	1000	105	210
3, 4	.04	64.4	55.3	.0181	25.2	425	1625	105	220
5, 6	.06	71.4	40.1	.0250	29.7	480	2000	145	280
7, 8	.08	77.0	29.9	.0335	34.0	552	2400	163	320
9, 10	.09	79.0	26.5	.0377	35.0	580	2442	156	320
11, 12	.10	79.2	26.3	.0381	32.3	567	2070	113	260
13, 14	.12	84.5	18.4	.0545	42.1	709	2910	176	370
				Indium Fluoride System					
...	0	..	(110)	(0.009)	(550)	(0.5×10^5)	..	...	(6×10^5)
1, 2	0.88×10^{-3}	61.4	60.8	.0166	940	0.7×10^5	0.3×10^8	4.4×10^5	8.6×10^5
3, 4	1.76	76.8	30.2	.0331	1520	2.9	1.4	5.5	12.4
5, 6	2.20	81.0	23.5	.0426	1700	4.1	1.6	5.2	12.8
7, 8	2.64	86.0	15.6	.064	2300	6.0	2.1	6.7	17.2
9, 10	4.40	92.4	7.9	.13	3000	10.8	2.3	5.5	18.9

At low values of (A)

$$X_2 = \beta_2 + \beta_3(\mathrm{A}) \qquad (4)$$

and from equations 2 and 4 we obtain

$$\Delta f = \beta_1\Delta\phi_1 - \beta_3\Delta(\mathrm{A}) \qquad (5)$$

Thus, from a graph of $\Delta f/\Delta(\mathrm{A})$ *vs.* $\Delta\phi_1/\Delta(\mathrm{A})$, β_1 is obtained from the slope of the line and β_3 as the intercept.

From equation 4, a graph of X_2 *vs.* (A) should give a straight line of slope equal to β_3 and intercept equal to β_2.

Experimental Part

In^{114}, half-life 50 days, in solution as the perchlorate, was used. The indium concentration in the final equilibrium mixtures was $2.6\text{–}5.2 \times 10^{-5}$ mole/l. Probably because of the low concentration used, ϕ was not found to vary with metal ion concentration as Fronaeus found in his work. Indium showed appreciable amounts of adsorption on the walls of the flask at this concentration, and it was necessary to run blanks (no resin) with each system to correct for this adsorption. Distribution ratios (ϕ) were determined by radiochemical assay of the solutions after equilibrium was reached. One-milliliter portions of solution were evaporated in metal planchets one inch in diameter. Samples were counted with an end-window G–M counter at uniform (approximately 5%) geometry. Sample counts of the order of 1000 c.p.m. were obtained, with a background count of 15–20 c.p.m. The per cent. indium on the resin was obtained from the difference in activity between the original solution and the solution in equilibrium with the resin. Solution and resin were brought to equilibrium by mechanical shaking for one hour, followed by standing for 24 hours in a constant temperature bath at 25°. Studies on the time necessary for equilibrium to be reached showed no appreciable change in the system after 2 hours.

The resin used was Amberlite IR-120 A.G. (Rohm and Haas Co., Philadelphia) converted into the sodium form at *p*H 3.8, air-dried, screen size 28–60 meshes per inch, moisture content 12.68%. All values of ϕ were calculated on the basis of oven-dry resin (0% moisture). The resin had an exchange capacity of 3.8 meq. per gram of oven dry resin.

The *p*H of the solutions was maintained at 3.8, since $In(OH)_3$ precipitates at *p*H values slightly above this. A Beckman *p*H meter and glass electrode were used to measure *p*H. Distribution ratios (ϕ) were found to be constant when solution to resin ratio was changed, indicating absence of colloidal indium.

The ionic strength of all solutions was kept at one using sodium perchlorate as the added electrolyte.

Additional work has been done using carrier-free In^{115} as the tracer for radiochemical assay, and general confirmation of the work with In^{114} was obtained. However, the adsorption of In^{115} on the container walls at the carrier-free concentrations used (approximately 10^{-12} mole/l.) was a considerably greater factor than for the concentrations of 10^{-5} mole/l. used in the work with In^{114}. Therefore these results were considered less reliable and are not reported here.

The data obtained are given in Table I.

The data for the indium chloride system gave the most satisfactory values for β_1, β_2 and β_3. Values of $\Delta f/(\mathrm{A})$ were plotted against values of $\Delta\phi_1/(\mathrm{A})$ according to equation 5. From the slope of the line, $\beta_1 = 26$, and from the intercept, $\beta_3 = 1500$. From a graph of X_2 *vs.* (A) (equation 4), a more reliable value of $\beta_3 = 1680$ was obtained from the slope of the line, and $\beta_2 = 170$ as the intercept. An attempt to determine β_4 from equation 3 resulted in a negative value for β_4, indicating the data are insufficiently accurate for determination of β_4 at concentrations of chloride ion up to 0.12 mole/l., and that the amount of $InCl_4^-$ formed at these concentrations is probably very small. $(\beta_1 - l)$ obtained by extrapolation of ϕ_1 to (A) = 0 was 21.0. Thus $l = 5$, $l_1 = 0.021$ l./g. = (MAR)/(MA). The value of (NaR)/(Na) is (0.0038 mole/g.)/(1 mole/l.) = 0.0038 l./g. Thus the ratio (MAR)/(MA) is about five times the ratio (NaR)/(Na) showing an appreciable exchange of Na^+ for MA^{++} on the resin.

The data for the indium bromide system, treated in the same way as the data for indium chloride, gave formation constants as: $\beta_1 = 16$; $\beta_2 = 60$; $\beta_3 = 300$. $(\beta_1 - l)$ was found to be 12, and thus $l = 4$ and $l_1 = 0.028$ l./g.

The data for the indium iodide system did not justify estimation of formation constants higher than β_1. Appreciable formation of complexes higher than the first seems to be lacking in iodide concentrations up to 0.3 mole/l. In the iodide system, $(\beta_1 - l) = 1.2$. The average value of l_1 from the chloride and bromide systems is 0.02 l./g. If this value is used for the iodide system: $(\beta_1 - l) = \beta_1 - (l_1/l_0)\beta_1 = \beta_1 - (0.02)/(0.110)\beta_1$. Thus $\beta_1 = 2$.

In studying the indium fluoride system it was necessary to correct the concentration of added fluoride for the formation of HF. The fluoride concentration was calculated from the equation

$$(F^-) = \left(\frac{1}{(H)/K_{HF} + 1}\right)(A) \qquad (6)$$

where (A) is the concentration of added sodium fluoride. K_{HF} is 6.9×10^{-4} for low ionic strength.[8] The value of this constant would be approximately doubled for an ionic strength of one. Therefore a value of 1.4×10^{-3} was used for K_{HF}, and at pH 3.8 equation 6 becomes $(F^-) = 0.88(A)$. The data for the indium fluoride system gave $\beta_1 = 1000$. Values of $\beta_2 = 6 \times 10^5$ and $\beta_3 = 4 \times 10^8$ were found and are probably significant only as to order of magnitude.

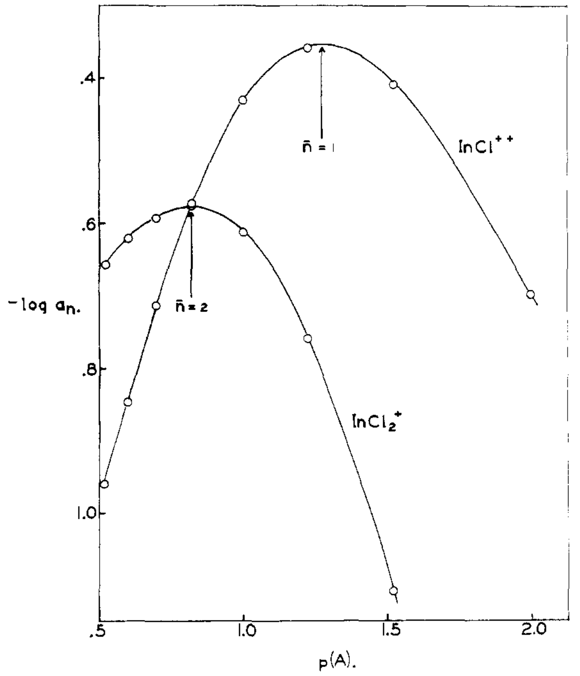

Fig. 2.

A consideration of the effect of the hydrolysis of indium on the formation of the halide complexes, as suggested by Hepler and Hugus,[9] indicates that the value of β_1 might be increased by about a factor of two by the presence of $InOH^{++}$ ion in solution, at pH 3.8. When an additional factor of approximately five is included to correct for differences in ionic strength, the total factor of ten brings the results of this work into reasonable agreement with the work of Hepler and Hugus.

The degree of formation of the individual complexes, a_n, may be calculated, once the formation constants are known, from the equation

$$a_n = \beta_n(A)^n/X \qquad (7)$$

Then from the relation given by Bjerrum[10]

$$\bar{n} = n + \frac{d \log a_n}{dp(A)} \qquad (8)$$

if log a_n is plotted against p(A), $\bar{n}$ will be equal to n where the slope of the curve is zero. Thus the data for the indium chloride system given in Table II, and Fig. 2, show the areas of chloride concentration in which the first two chloride complexes of indium predominate. $InCl^+$ is the predominant species at chloride concentrations of 0.05 mole/l., whereas $InCl_2^+$ is the predominant complex at 0.16 mole/l. A similar determination from the data for the indium bromide system shows that the $InBr^{++}$ and $InBr_2^+$ ions predominate at bromide ion concentrations of 0.08 and 0.3 mole/l., respectively

Summary.—The aqueous indium halide systems have been studied from their equilibria in the presence of an ion-exchange resin and the data analyzed by the method of Sture Fronaeus. Formation constants obtained are

In–Cl system: $\beta_1 = 26$; $\beta_2 = 170$; $\beta_3 = 1680$
In–Br system: $\beta_1 = 16$; $\beta_2 = 60$; $\beta_3 = 300$
In–I system: $\beta_1 = 2$
In–F system: $\beta_1 = 1000$; $\beta_2 = 6 \times 10^5$; $\beta_3 = 4 \times 10^8$

Halide concentrations at which the first two complexes in the chloride and bromide systems predominate are determined.

TABLE II

(A), mole/l.	p(A)	a_1	$-\log a_1$	a_2	$-\log a_2$
0.01	2.000	0.201	0.697	0.014	1.854
.03	1.523	.391	.408	.078	1.109
.06	1.222	.438	.358	.175	0.758
.10	1.000	.372	.430	.245	.611
.15	0.324	.268	.572	.266	.575
.20	.699	.194	.712	.256	.592
.25	.602	.145	.840	.240	.620
.30	.523	.111	.959	.221	.656

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(8) "International Critical Tables," Vol. 6, p. 260.

(9) L. G. Hepler and Z. Z. Hugus, Jr., THIS JOURNAL, **74**, 6115 (1952).

(10) J. Bjerrum, ref. 1, p. 22.