

Anion-Exchange Study

II. The Indium-Bromide System

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The indium-bromide complex system was investigated using the anion-exchange method given by Marcus and Coryell. The mononuclearity of the complexes was tested and confirmed for the range 3×10^{-5} – 3×10^{-4} M indium. The distribution of indium between the resin and the solution was determined in the range 0.1 M–9.3 M LiBr by the batch method using the tracer ^{114}In . A corrected distribution function was constructed showing the complexes from InBr_2^+ to InBr_6^{3-} , with the successive stepwise formation constants: $\log k_2 = 1.3$, $\log k_3 = 0.59$, $\log k_4 = -0.52$, $\log k_5 = -1.6$, and $\log k_6 = -2.2$. The values of k_2 and k_3 agree with published data.

The application of anion-exchange to quantitative investigations of complex systems, where the ligand is an anion, was introduced by Fronaeus¹. He showed that plots of the distribution coefficient *vs.* the ligand concentration gave information about the principal species of complexes in the aqueous phase. Marcus and Coryell² extended the application of the adsorption function to allow the determination of the complex formation constants. Marcus studied the systems $\text{Ag}-\text{Cl}$ ³, $\text{Cd}-\text{Cl}$ ⁴, $\text{Fe(III)}-\text{Cl}$ ⁵, $\text{Ag}-\text{S}_2\text{O}_3$ ⁶, and $\text{U(VI)}-\text{PO}_4$ ⁷ using the anion exchange method². The complex formation constants, obtained by the anion exchange method, were in agreement with data obtained by other physico-chemical methods.

The adsorption of indium into a bromide anion-exchange resin from HBr-solutions is strong ($D_{\text{max}} = \sim 4 \times 10^3$) in contrast to the adsorption of indium into a chloride anion-exchange resin from HCl-solutions ($D_{\text{max}} = \sim 20$)⁸. The system $\text{In}-\text{Br}$ was investigated more closely using the anion-exchange method. This method should be useful in evaluating the magnitude of the constants for the higher complexes, in particular the constants for InBr_3 and InBr_4^- , species with zero or unit charge². Table 1 lists the values of the consecutive formation constants of the $\text{In}-\text{Br}$ system obtained by earlier investigations together with the values obtained in this investigation. Spectrophotometry was used as a qualitative check of the interpretation of the ion exchange measurements.

Table 1.

Investigator	Method	Ionic strength	log k_1	log k_2	log k_3	log k_4	log k_5	log k_6
Hepler and Hugus ⁹	pH	vary	2.20					
Schufle and Eilnad ¹⁰	Ion-exchange	1.00	1.20	0.58	0.70			
DeSesa ¹¹	Potentiometric	vary	1.82					
Sundén ¹²	Potentiometric	2.00	1.98	0.58				
Sundén ¹³	Extraction		1.93	0.67				
Cozzi and Vivarelli ¹⁴	Polarography	2.00	3.80	1.00				
Carleson and Irving ¹⁵	Ion-exchange	0.691	2.01	1.09	0.18			
Irving and Rosotti ¹⁶	Extraction	1.00	2.06	1.28	0.36	-0.7		
Burns and Hume ¹⁷	Spectrophotometric	4.00	2.08	1.28	0.60	0.85		
This investigation	Anion-exchange	vary		1.3	0.59	-0.52	-1.6	-2.2

EXPERIMENTAL

The distribution coefficients were measured by the equilibration method¹⁸. The resin used, Dowex 1 \times 10, 200–400 mesh, chloride form, was converted to the bromide form with HBr. The resin was washed with distilled water and dried at 110°C. The capacity was 3.22 mequiv/g dry resin. The water content was 37.0 %.

The indium solutions were prepared from metallic indium, containing ¹¹⁴In as a radioactive tracer. The indium concentration was 3×10^{-5} – 3×10^{-4} M. The lithium bromide was prepared from Li₂CO₃ and HBr and recrystallized twice. Bromide was determined by AgNO₃-titration.

The batch samples contained 0.1–0.5 g resin and 5–10 ml lithium bromide solution. In order to repress hydrolysis, hydrobromic acid was added to the indium and lithium bromide solutions to give a final concentration of around 0.02 M HBr. The resin was shaken with the solution for 48 h at room temperature. The concentration of indium in the aqueous phase was determined using a well type scintillation counter.

The concentration of Li⁺ and Br⁻ in the resin phase was determined by a method given by Kraus and Moore¹⁹.

The spectrophotometric measurements were carried out with recording Cary 14 spectrophotometer using silica cells of 0.100 and 1.000 cm. lengths, wavelength: 200–300 m μ .

Table 2.

Concentration of ligand m_{LiBr} (mole/litre)	Indium-concentration $\times 10^{-4}$ M	Log of indium distribution coefficient log D .
0.44	0.3	1.20
0.44	1.5	1.15
0.44	3.0	1.20
1.12	0.3	1.76
1.12	1.5	1.75
1.12	3.0	1.78
4.53	0.3	3.78
4.53	1.5	3.80
4.53	3.0	3.74
5.14	0.3	3.97
5.14	1.5	4.01
5.14	3.0	3.98

Table 3. Effects of the variation of the LiBr-concentration.

LiBr-conc. (moles/litre)	Log of Br ⁻ activity function	Log of In-distribution coefficient
0.10	-1.10	0.40
0.21	-0.80	0.76
0.31	-0.63	0.98
0.44	-0.48	1.20
0.68	-0.29	1.52
0.87	-0.17	1.60
0.99	-0.10	1.70
1.18	0.00	1.81
1.38	0.09	2.00
1.58	0.18	2.10
1.97	0.30	2.38
2.46	0.46	2.50
2.95	0.60	3.00
3.44	0.76	3.20
3.80	0.86	3.45
4.72	1.13	3.90
5.24	1.28	4.06
5.66	1.40	4.20
6.16	1.54	4.35
6.56	1.66	4.48
7.08	1.81	4.60
7.50	1.94	4.75
8.03	2.10	4.84
8.44	2.22	4.93
8.88	2.36	4.97
9.35	2.52	4.97

RESULTS

The effect of variation in the indium concentration is shown in Table 2. The results show that the distribution coefficient is unaffected by changes in the indium concentration, indicating that the complexes are mononuclear in the range 3×10^{-5} — 3×10^{-4} M indium. Solvent extraction measurements of Irving and Rosotti¹⁸ were explained by dimerization of indium in aqueous bromide solutions. Johnson and Kraus²⁰, however, demonstrated by molecular weight measurements using an equilibrium ultracentrifuge that indium(III) in HBr exists only as mononuclear complexes. Table 3 shows the distribution of indium between the resin and the lithium bromide solutions in the range 0.1—9.3 M. The values of the activity function for the bromide ligand $a = m_{\text{LiBr}} \gamma_{\pm(\text{LiBr})}$ were obtained from Robinson and Stoke²¹. In Fig. 1 is plotted the logarithms of the distribution coefficient, D , vs. the logarithm of the ligand activity.

The spectrophotometric measurements show qualitatively that the complex formation in the system In—Br does not stop at a definite complex (*e.g.* InBr₃), but the complex formation is continued for increasing HBr concentrations.

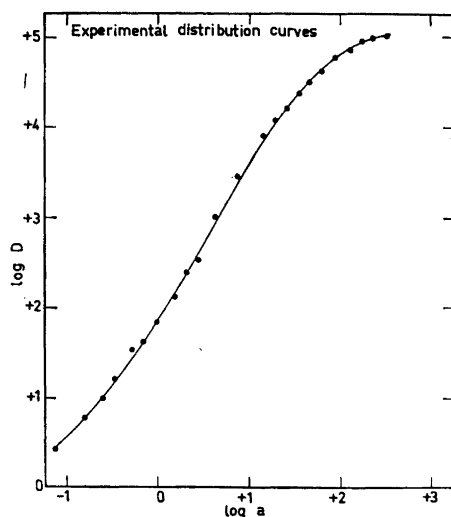
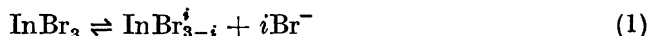


Fig. 1. The anion exchange distribution curve ($\log D$) plotted vs. the logarithm of the bromide activity function ($\log a = \log m_{\text{LiBr}} + \log \gamma_{\text{LiBr}}$) for the absorption of indium from lithium bromide by Dowex 1 bromide-anion exchange resin.

DISCUSSION

Using the terminology of Marcus and Coryell² the complexed species of indium may be considered to be formed in the reaction:



where i is the charge of the complex.

The thermodynamic equilibrium constant for the reaction (1) is:

$$\beta_i = (a_{\text{InBr}_{3-i}^i})(a_{\text{Br}})^i / (a_{\text{InBr}_3}) = m_i \cdot \gamma_i \cdot a^i \cdot a_0^{-1} \quad (2)$$

where m_i is the concentration of the i -th complex species, γ_i the activity coefficient, a is the ligand activity function and a_0 is the thermodynamic activity of the complex InBr_3 . The equation

$$\Sigma m_i = a_0 \Sigma \beta_i \gamma_i^{-1} a^{-i} \quad (3)$$

expresses the total concentration of indium in the aqueous phase. An equation analog to (3) expresses the series of complexes m in the resin phase. If $i = -p$ indicates the charge number of the principal species in the resin, the distribution coefficient D is defined by:

$$D = m_{-p} / \Sigma m_i = (\beta_{-p})(\gamma_{-p}^{-1})(a^{-p}) / \Sigma \beta_i \cdot \gamma_i^{-1} \cdot a^{-i} \quad (4)$$

as $a_0 = a_0$ at equilibrium.

Assuming that γ_i values are essentially independent of a , the activity of the ligand concentration, in the successive regions where the corresponding species InBr_{3-i}^i are predominant, and γ_{-p} is independent of a , the $\log D$ is expressed by

$$\log D = \log \beta^*_{-p} + p \log a - \log \Sigma \beta^*_i a^{-i} \quad (5)$$

when $\beta^*_i = \beta_i \gamma_i^{-1}$

As a Donnan equilibrium $a_{LiBr} = a_{LiBr}$ is proved to exist, the resin ligand activity function a can be expressed by the equation:

$$\log a = \log a + 1/2 (\log m_{Br} - \log m_{Li}) \quad (6)$$

If a^0 expresses the resin ligand activity function a at $a = 1$, a correction function F_a is defined as:

$$F_a = \log a - \log a^0 \quad (7)$$

The ideal or corrected distribution coefficient D^0 is defined by:

$$\log D^0 = \log D - p F_a = \log K_r - \log \Sigma \beta^*_i a^{-i} \quad (8)$$

in which $K_r = \beta_{-p} \cdot \gamma_{-p}^{-1} \cdot a^0$. According to eqn. (8) the ideal distribution coefficient D^0 should be a function of the complex formation in the aqueous solution only, for a given ion exchange resin.

The maximal co-ordination number of indium is 6. The ratio between the radius of the indium(III) ion and the radius of the bromide ion shows that the formation of an indium hexabromocomplex is geometrically possible. Woodward and Bill²² reported from a study of the Raman spectra of indium salts in the presence of a large excess of bromide, that no tetrahedral $InBr_4^-$ ion is present in the aqueous solution. Burns and Hume¹⁷ assumed that the indium tetrabromocomplex is $[In(H_2O)_2Br_4]^-$ with a structure as an octahedron, because indium frequently exhibits hexacoordination. The use of eqn. (8) combined with the assumption of the formation of a hexabromocomplex on the resin as R_3InBr_6 , results in values of the first complex formation constants in the system $In-Br$ in agreement with published data obtained by other methods (cation-exchange, extraction and spectrophotometry).

The correction function F_a was calculated by means of the activity values of the bromide ion, the concentration of the lithium ion and the concentration of the bromide ion in the resin phase. The reference point for a , as a^0 , at $a = 1$ is calculated like that $F_a = 0$ at this point; a^0 was determined to 0.46. It is known¹⁹ that the resin invasion is small at $a = 1$, but still accessible to reasonably accurate measurements. The values of the correction function F_a are shown in Fig. 2. The function F_a for the bromide system is nearly identical with the correction function for the chloride system reported by Marcus^{2,3}.

Using the values of F_a in Fig. 2, a corrected or ideal distribution coefficient D^0 is calculated by eqn. (8).

The average charge number \bar{i} and the average ligand number \bar{n} can be calculated from the slopes of the ideal distribution function:

$$\frac{d(\log D^0)}{d(\log a)} = \bar{i} = 3 - \bar{n}$$

since the parameters K_r and β^*_i are taken as constants.

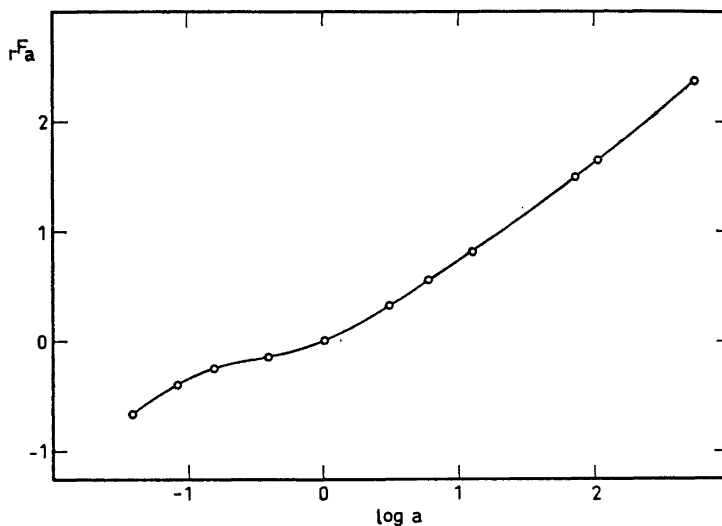


Fig. 2. The activity function r_a of bromide in the resin Dowex 1-bromide equilibrated with lithium bromide plotted as a function of the bromide activity function a in lithium bromide solutions (logarithmic scale).

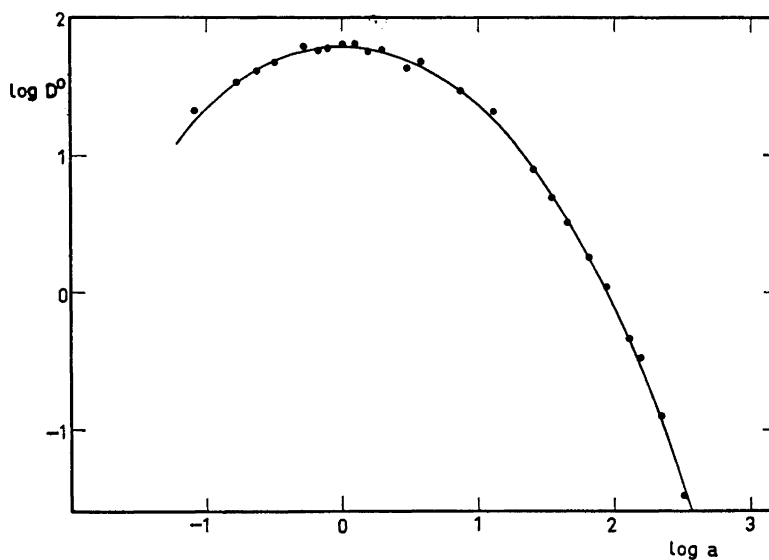


Fig. 3. The corrected distribution curve ($\log D^\circ$) using the parameter $p = 3$ for the predominant resin species R_3InBr_4 , plotted vs. the bromide activity function ($\log a$).

The curve has slopes ranging from approximately + 1.6 at the lowest concentration to exactly -3.00 at 9 M LiBr. The value + 1.6 refers to InBr_2^+ and the value -3.00 to InBr_6^{3-} .

The values of the successive formation constants k^* , were obtained by the Bjerrum's "half-integral i " method, where, to a first approximation:

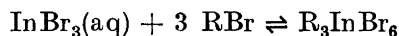
$$\log k^* = \log \beta^*_i / \beta^*_{i-1} = -\log a_{(\bar{i}-i-\frac{1}{2})}$$

The preliminary values, obtained by Bjerrum's method, were applied to calculate the formation constants by Sillen's "curve fitting" method²³. The values so obtained are: $\beta^*_2 = 1.2 \times 10^{-2}$; $\beta^*_1 = 0.26$; $\beta^*_{-1} = 0.30$; $\beta^*_{-2} = 7 \times 10^{-3}$; $\beta^*_{-3} = 5 \times 10^{-5}$. The values of the formation constants $k_n = (\text{InBr}_n^{3-n}) / (\text{InBr}_{n-1}^{3-(n-1)})(\text{Br}^-)$ were calculated: $\log k_2 = 1.3$; $\log k_3 = 0.59 \pm 0.08$; $\log k_4 = -0.52 \pm 0.07$; $\log k_5 = -1.6$ and $\log k_6 = \sim -2.2$. It is not possible to determine k_1 of the experimental results. $\log K$, is determined as 2.01 ± 0.04 .

The complex formation constants k_2 and k_3 found in the present work are seen to be in reasonable agreement with data obtained by other methods, Table 1. A determination of k_1 was carried out by spectrophotometric methods similar to that of Burns and Hume¹⁷. The value so obtained agrees with the value reported by Burns and Hume.

The value of k_4 agrees with the result of Irving and Rosotti¹⁶, but deviates from the value reported by Burns and Hume. The spectrophotometric measurements show that the complex formation in the system In-Br does not stop at a decided complex, but the complex formation is continued for increasing HBr-concentration. The value k_4 given by Burns and Hume was determined assuming that the complex InBr_4^- was the only absorbing species of higher complexes. Making a comparison with the complex formation constants of halogen complexes of the group Al, Ga, In, Tl²⁴ the published data show a marked tendency for the ratio $\log k_3/k_4 > 0$, as in the present work.

The parameter K , may be used to calculate the equilibrium constant for the reaction



by dividing K , with the 3rd power of a^0 ². This gives $\log K, -3a^0 = 2.01 - 1.38 = 0.63$ for the logarithm of this constant. A comparison between this value and the value for the corresponding reaction in the solution $\log \beta^*_{-3} = -4.3$ shows that the resin stabilizes the indium hexabromocomplex 10^5 -fold.

Acknowledgement. The authors are grateful to professor S. E. Rasmussen for his valuable advice and discussions.

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Received October 27, 1961.