The Extraction of Indium at Macro-concentrations from Hydrobromic Acid into iso*Butyl Methyl Ketone and Diethyl Ether.**

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Tracer studies of partition equilibria in the system indium bromide–hydrobromic acid–*iso*butyl methyl ketone have been extended to higher metal concentrations. The observed decrease in the distribution ratio is interpreted in terms of the formation of dinuclear indium–bromide complexes which are extracted to a negligible extent compared with the acido-complex $HInBr_4$,aq. With diethyl ether the distribution ratio increases with metal concentration and the acido-complex is shown by analysis to be extracted as the decahydrate.

It is well known that the partition of ferric iron between hydrochloric acid and diethyl or di*iso*propyl ether increasingly favours the organic phase as the concentration of metal is raised (Dodson, Forney, and Swift, *J. Amer. Chem. Soc.*, 1936, **58**, 2573). Tervalent gold (Mylius and Huttner, *Ber.*, 1911, **44**, 1315; McBryde and Yoe, *Analyt. Chem.*, 1948, **20**, 1094) and gallium (Nachtrieb and Fryxell, *J. Amer. Chem. Soc.*, 1949, **71**, 4035) behave in a similar manner in these solvents. The attempt to interpret such behaviour in terms of an increase in the activity of the metal halide species in the aqueous phase (Nachtrieb and Fryxell, *ibid.*, 1948, **70**, 3552) was disproved by its originators and it now appears to be accepted that the phenomenon results from some form of association of the species in the organic phase, or from a decrease in its activity due to this or other causes (cf. Myers, Metzler, and Swift, *ibid.*, 1950, **72**, 3767; Nachtrieb and Fryxell, *ibid.*, 1952, **74**, 897).

We have now found an example of the converse phenomenon. For, although tracer studies of partition equilibria in the system indium bromide–hydrobromic acid–*iso*butyl methyl ketone (Part III*) showed that the distribution ratio defined by

$$q = \frac{C_o}{C_w} = \frac{\text{total concentration of indium in organic phase}}{\text{total concentration of indium in aqueous phase}} \quad . \quad . \quad . \quad (1)$$

was independent of metal concentration up to $\sim 10^{-5}$M, yet, when the measurements were extended to higher concentrations of indium, the distribution ratio for any given constant concentration of hydrobromic acid was found to decrease.

Experimental

Materials.—Inactive indium bromide was prepared by dissolving a known weight of pure indium (Johnson Matthey, Ltd.) in the calculated quantity of 5N-hydrobromic acid, free from bromine. The solution was gently evaporated to small bulk and kept in a vacuum-desiccator over potassium hydroxide for some weeks. The composition of the pure white product was confirmed by gravimetric determination of indium as oxide (Moser and Siegmann, *Monatsh.*, 1930, **55**, 16) and of bromine as silver bromide; a stock solution of strength 0·2M was prepared. A $2{\cdot}5 \times 10^{-2}$M stock solution of radioactive indium bromide in N-hydrobromic acid was prepared from ^{114}In, and *iso*butyl methyl ketone was purified as described previously (Part III). Commercial diethyl ether was purified and freed from peroxides as described by Weissberger and Proskauer ("Organic Solvents," Oxford, 1935). "AnalaR" potassium nitrate was used to provide a salt background in some experiments.

Partition Experiments.—The distribution ratios of indium, as defined by equation (1), between *iso*butyl methyl ketone and hydrobromic acid were studied as a function of total indium concentration, C_{In}, at a number of different initial acid concentrations, N'. For a series of partition experiments solutions were made up identical in their content of hydrobromic acid and of radioactive indium bromide (10^{-5}—10^{-7}M) but which differed in their content of inactive indium (0—10^{-2}M). In some series of measurements the ionic strength was made up to 1·0M by

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* This forms Part IV of a group of papers of which Parts I, II, III are the preceding papers and Part V the following paper.

appropriate additions of potassium nitrate. Portions of these solutions (20 ml.) were equilibrated with equal volumes of *iso*butyl methyl ketone in 60-ml. Pyrex stoppered tubes by shaking for 5 min. in a horizontal position at 150 cycles per minute at room temperature (13° ± 3°). The phases were then allowed to separate with the tubes in a vertical position. With systems containing relatively high concentrations of indium ($\sim 10^{-2}$M) the ketonic layers were cloudy, and times up to 1 hr. had to be allowed before the phases had completely separated. The volumes V_o and V of the organic and the aqueous phase respectively after equilibration were measured, and radiometric determinations of indium were carried out as already described (Part III). The equilibrium acidity, N, was determined by titrating diluted aliquot portions of the aqueous phase with 0·1N-sodium hydroxide.

Results of the measurements are summarised in Tables 1 and 2, the symbols being those defined above. Unless the contrary is stated the equilibrium volumes $V_o = V = 20$ ml. within the limits of experimental error.

TABLE 1. *Variation in distribution ratio of indium between hydrobromic acid and* iso*butyl methyl ketone for different indium concentrations. (No added salts.)*

C_{In}	$-\log C_o$	$-\log C$	q	C_{In}	$-\log C_o$	$-\log C$	q
(a) $N' = N = 0{\cdot}20$N-HBr.							
$8{\cdot}008 \times 10^{-2}$	2·156	1·138	0·0956	$5{\cdot}145 \times 10^{-5}$	4·575	4·605	1·07
$1{\cdot}008 \times 10^{-2}$	3·029	2·039	0·102	$3{\cdot}168 \times 10^{-5}$	4·740	4·870	1·35
$1{\cdot}079 \times 10^{-3}$	3·670	3·063	0·247	$8{\cdot}33 \times 10^{-6}$	5·266	5·537	1·87
$4{\cdot}316 \times 10^{-4}$	3·932	3·502	0·372	$3{\cdot}168 \times 10^{-6}$	5·668	5·991	2·10
$7{\cdot}92 \times 10^{-5}$	4·436	4·371	0·862	$7{\cdot}92 \times 10^{-7}$	6·266	6·603	2·18
(b) $N' = 0{\cdot}40$N-HBr; $N = 0{\cdot}39$N-HBr; $V_o = 19{\cdot}5$ ml.; $V = 20{\cdot}5$ ml.							
$1{\cdot}00 \times 10^{-2}$	2·604	2·134	0·336	$5{\cdot}145 \times 10^{-5}$	4·346	5·148	6·34
$5{\cdot}50 \times 10^{-3}$	2·750	2·440	0·485	$6{\cdot}444 \times 10^{-6}$	5·222	6·242	10·5
$1{\cdot}001 \times 10^{-3}$	3·392	3·312	1·04	$5{\cdot}00 \times 10^{-6}$	5·325	6·429	12·7
$1{\cdot}011 \times 10^{-4}$	4·089	4·679	3·86	$2{\cdot}40 \times 10^{-6}$	5·647	6·707	11·5
$5{\cdot}377 \times 10^{-5}$	4·324	5·136	6·48	$6{\cdot}00 \times 10^{-7}$	6·245	7·349	12·7
(c) $N' = 1{\cdot}00$N-HBr; $N = 0{\cdot}975$N-HBr; $V_o = 19{\cdot}5$ ml.; $V = 20{\cdot}5$ ml.							
$2{\cdot}50 \times 10^{-2}$	1·682	2·332	4·46	$1{\cdot}111 \times 10^{-5}$	4·946	7·196	180
$2{\cdot}503 \times 10^{-3}$	2·626	3·726	12·6	$5{\cdot}00 \times 10^{-6}$	5·539	7·289	180
$2{\cdot}528 \times 10^{-4}$	3·596	5·286	49·4	$2{\cdot}50 \times 10^{-6}$	5·594	7·774	152
$5{\cdot}145 \times 10^{-5}$	4·283	6·363	119	$1{\cdot}00 \times 10^{-6}$	5·991	8·261	185
$2{\cdot}778 \times 10^{-5}$	4·560	6·629	114				

TABLE 2. *Variation of distribution ratio with indium concentration for extraction into* iso*butyl methyl ketone from hydrobromic acid in a medium of ionic strength* 1·0M.

C_{In}	$-\log C_o$	$-\log C$	q	C_{In}	$-\log C_o$	$-\log C$	q
(a) $N' = N = 0{\cdot}20$N-HBr.							
$8{\cdot}009 \times 10^{-2}$	2·416	1·118	0·0479	$7{\cdot}92 \times 10^{-5}$	4·951	4·168	0·165
$4{\cdot}004 \times 10^{-3}$	2·575	1·427	0·0712	$3{\cdot}168 \times 10^{-5}$	5·294	4·575	0·191
$8{\cdot}049 \times 10^{-3}$	3·175	2·132	0·0906	$7{\cdot}920 \times 10^{-5}$	5·859	5·184	0·212
$1{\cdot}079 \times 10^{-3}$	3·885	3·023	0·137	$3{\cdot}168 \times 10^{-6}$	6·246	5·585	0·218
$1{\cdot}079 \times 10^{-4}$	4·802	4·036	0·171				
(b) $N' = 0{\cdot}40$N-HBr; $N = 0{\cdot}375$N-HBr.							
$2{\cdot}50 \times 10^{-2}$	2·300	1·700	0·251	$2{\cdot}945 \times 10^{-5}$	4·730	4·966	1·72
$2{\cdot}505 \times 10^{-3}$	3·044	2·796	0·565	$5{\cdot}00 \times 10^{-6}$	5·502	5·733	1·70
$1{\cdot}002 \times 10^{-3}$	3·352	3·254	0·805	$5{\cdot}00 \times 10^{-7}$	6·500	6·736	1·73
$2{\cdot}545 \times 10^{-4}$	3·836	3·964	1·34				
(c) $N' = 0{\cdot}60$N-HBr; $N = 0{\cdot}563$N-HBr.							
$2{\cdot}00 \times 10^{-2}$	2·067	1·942	0·749	$2{\cdot}444 \times 10^{-5}$	4·665	5·551	7·68
$2{\cdot}004 \times 10^{-3}$	3·179	3·487	2·03	$5{\cdot}00 \times 10^{-6}$	5·355	6·237	7·61
$8{\cdot}016 \times 10^{-4}$	3·223	3·691	2·95	$5{\cdot}00 \times 10^{-7}$	6·355	7·237	7·60
$2{\cdot}044 \times 10^{-4}$	3·783	4·402	4·16				

Extraction of Indium from Hydrobromic Acid Solutions into Diethyl Ether.—A few experiments were performed to study the variation in distribution ratio with indium concentration. No alkali nitrate was added. Typical results are given in Table 3.

Analysis of the Organic Extracts.—A number of solutions in which the total indium concentration was of the order of 10^{-2}M were equilibrated with *iso*butyl methyl ketone or diethyl ether, and the organic phases analysed for hydrogen, indium, and bromine by the methods described by Irving and Rossotti (Part III). In these experiments, however, it was necessary to subtract a small blank from the titre of sodium hydroxide to allow for the amount of hydrobromic acid extracted in the absence of indium.

TABLE 3.

N'	N	C_{In}	q	C_{In}	q
2·0	1·80	10^{-5}	1·38	0·1	3·76
3·0	2·60	10^{-5}	11·9	0·05	32·4
4·0	3·24	10^{-5}	44·2	0·1	139

The diethyl ether extracts were also analysed for water co-extracted with the indium by the Karl Fischer method, using a micro-titration apparatus of the type described by Bonner (*Analyst*, **1946**, **71**, 483). Direct titrations were carried out in an atmosphere of nitrogen, the dead-stop end-point being used with the following modification. The indium content of an aliquot part of ethereal phase containing a conveniently measurable quantity of water being known from preliminary experiments, sufficient of a 0·5M-solution of 8-hydroxyquinoline in dry methanol to afford a tenfold excess was first titrated to the Karl Fischer end-point. The known volume of ethereal phase was then added, and the additional water titrated to the same end-point. Finally, the Karl Fischer reagent was standardised in the presence of the indium trisoxine complex. The amount of water present in diethyl ether after equilibration with hydrobromic acid of the desired concentration in the absence of indium was then determined and subtracted from the total concentration previously found. Diethyl ether was scrupulously freed from peroxides which react with the Karl Fischer reagent. The latter was of B.D.H. laboratory grade. Other materials were prepared as recommended by Mitchell and Smith (" Aquametry," Interscience Press, New York, 1948). The results are summarised in Table 4.

TABLE 4. *Analyses of organic extracts.*

(*a*) iso*Butyl methyl ketone.*

Composition of initial aqueous phase, moles/l.			Analytical ratios			
$InBr_3$	HBr	KNO_3	H_2O	H	In	Br
0·020	0·60	0·40	—	1·00	1·00	3·94
0·020	0·60	0·40	—	1·10	1·00	4·08
0·020	0·60	0·40	—	1·02	1·00	4·02
0·020	0·60	0·40	—	1·02	1·00	4·02
0·025	0·40	0·60	—	1·01	1·00	4·00
0·025	0·40	0·60	—	1·02	1·00	3·80
(*b*) *Diethyl ether.*						
0·10	2·0	—	10·0	0·92	1·00	3·96
0·05	3·0	—	10·0	1·00	1·00	4·16
0·10	4·0	—	9·45	1·12	1·00	4·10

Variation of Distribution Ratio with Metal Concentration in iso*Butyl Methyl Ketone Systems.*—Fig. 1, curve 1, shows how the distribution ratio, *q*, varies for the extraction of indium from an equilibrium concentration of 0·975M-hydrobromic acid at different total metal concentrations. The curves for extraction from equilibrium concentrations of 0·20 and 0·39M-hydrobromic acid (not reproduced here; data in Table 1) are strikingly similar and can be superimposed by a vertical displacement. Irrespective of the concentration of hydrobromic acid there is a range up to a total metal concentration of $C_{In} \sim 10^{-5}$M over which the distribution ratio is independent of metal concentration (cf. Part III). At higher metal concentrations the distribution ratio steadily decreases. In experiments at the lowest acidity (0·2M) a second region of almost constant distribution ratio is suggested by the experimental results. This may not be significant, for the addition of indium bromide in macro-concentration will have increased the concentration of free bromide ion and also the ionic strength. On the other hand, the possibility that a dinuclear indium–bromide complex is formed at high metal concentrations (see p. 1945) and has a small but significant partition coefficient cannot be excluded.

So long as indium is present only in small concentrations, the ionic strength in the aqueous phase is effectively that of the hydrobromic acid; hence, the activity coefficients remain constant (though different) in the three sets of experiments. Any attempt to explain the variations in q shown in Fig. 1 in terms of changes in the activity coefficient of the species extracted into the organic phase must explain why it is constant below 10^{-5}M, but increases markedly above this concentration. Not only is the magnitude of the change improbably large, but it is of opposite sign to that found in measurements of the activity of a similar solute, *viz.*, the ferric chloride–hydrochloric acid complex in *iso*propyl ether (Nachtrieb and Fryxell, *loc. cit.*). In the present paper we postulate that activity coefficients in the aqueous phase and (stoicheiometric) partition coefficients remain constant and explore the logical deductions which follow from an application of the law of mass action to the partition equilibria. Neglecting, then, any variations in activity in the organic phase, the observed variations in distribution ratio may be interpreted as arising from some form of association in the aqueous phase.

FIG. 1.

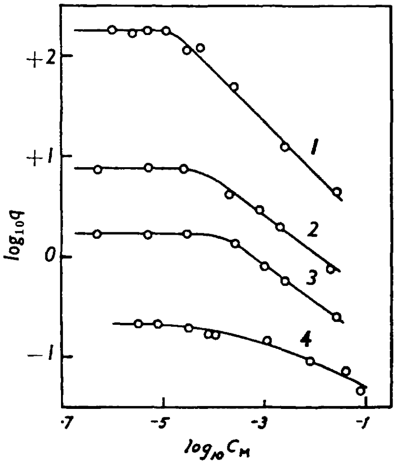

FIG. 2.

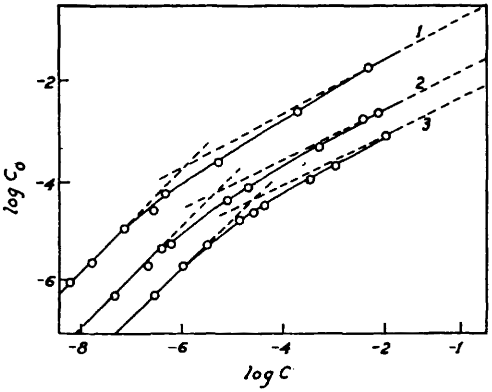

FIG. 1. *Dependence of distribution ratio upon total indium concentration for hydrobromic acid–*isobutyl *methyl ketone systems.*

Initial concns. of hydrobromic acid in the aqueous phase are 1·0, 0·6, 0·4, and 0·2N for curves 1, 2, 3, and 4 respectively. The ionic strength was made up to 1·0M with potassium nitrate for curves 2, 3, and 4.

FIG. 2. *Indium concentrations in* isobutyl *methyl ketone as a function of that in the aqueous phase.*

Initial concns. of hydrobromic acid in the aqueous phase are 1·0, 0·4, and 0·2N for curves 1, 2, and 3 respectively. No salt background was used in these equilibrations.

It has been shown that the value of the derivative $(\partial \log q/\partial \log [\mathrm{In}^{3+}])_{[\mathrm{HBr}]} = \bar{m} - \bar{m}$, where $\bar{m}$ is the average number of atoms of indium per molecule for all species in the organic phase and $\bar{m}$ is the corresponding ligand number for the aqueous phase (Part I). It will only be zero when both phases contain only species in the same degree of association. Under such conditions the derivative $(\partial \log q/\partial \log C_{\mathrm{In}})_{[\mathrm{HBr}]}$ should also be zero, and since this is found to be the case for indium concentrations less than $\sim 10^{-5}$M, it is reasonable to assume that all species are mononuclear there (cf. Part III). The negative value of the derivative at higher metal concentrations may then be taken as indicating a greater degree of association in the aqueous phase than in the organic phase. The experimental value of $-0{\cdot}5$ lies within the range, $0 \gg (\partial \log q/\partial \log [\mathrm{In}])_{[\mathrm{HBr}]} \gg -1$, which may be predicted where mononuclear and binuclear species coexist in the aqueous phase while only monomeric species are extracted. Were effectively the whole of the indium in the aqueous phase present as dimerised species, $C_o/\sqrt{C}$ would be constant so that

$$\log C_o = 0{\cdot}5 \log C + \text{constant} \quad . \; . \; . \; . \; . \; . \quad (2)$$

while if all species are monomeric in the aqueous phase

$$\log C_o = \log C + \log q \quad . \; . \; . \; . \; . \; . \; . \quad (2a)$$

Plots of log C_o against log C (Fig. 2) have unit slope at low metal concentrations, but the slope tends towards the value 0·5 at high concentrations suggesting that dimerisation is considerable in 0·1M-indium solutions. The nature of the dimerised species does not emerge from this oversimplified treatment, but if only one dimerised species predominated in the aqueous phase its probable composition can be deduced by the following treatment. First, it is desirable to consider whether the dimer might be a basic species containing, or bridged by, a hydroxyl group—especially as a similar type of phenomenon in the system zirconium–trifluorothenoylacetone–benzene has been interpreted by Connick and Reas (*J. Amer. Chem. Soc.*, 1951, **73**, 1171) as arising from the hydrolysis and polymerisation of zirconium. However, at metal concentrations less than 10^{-5}M we may estimate the ratio of concentrations of the first bromide-ion complex, $InBr^{++}$, to that of the first hydrolysis product, $InOH^{++}$, in solutions of hydrobromic acid of strengths 0·2—1·0N as of the order of 10^4—10^6 (cf. Part III). Consequently, the possibility that the dimer is a hydroxylated species at higher metal concentrations may be considered remote. Later we advance more decisive evidence. Assuming for the moment that one indium–bromide dimeric species predominates, we have :

$$C = [In^{3+}] + [InBr^{++}] + [InBr_2^{+}] + [InBr_3] + [InBr_4^{-}] + [HInBr_4] + 2[In_2Br_r^{6-r}] \quad . \quad (3)$$

it being assumed that $InBr_4^-$ is the highest mononuclear complex present. Thence

$$C = a[In^{3+}] + b[In^{3+}](1 + K^{H}[H^{+}]) + 2\beta_{2,r}[In^{3+}]^2[Br^{-}]^r \quad . \quad . \quad . \quad (4)$$

where $K^{H} = [HInBr_4]/[H^{+}][InBr_4^{-}]$, $\beta_{2,r} = [In_2Br_r^{6-r}]/[In^{3+}]^2[Br^{-}]^r$,

$$\beta_n = [InBr_n^{3-n}]/[In^{3+}][Br^{-}]^n,\ a = \sum_{n=0}^{n=3} \beta_n[Br^{-}]^n, \text{ and } b = \beta_4[Br^{-}]^4 \quad . \quad . \quad (5)$$

If now the sole species in the organic phase is the acido-complex, $HInBr_4$,

$$C_o = [HInBr_4]_o = p_4K^{H}b[H^{+}][In^{3+}] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $p_4 = [HInBr_4]_o/[HInBr_4]$. Substituting in equation (1) these values of C_o and C given by equations (4) and (6), and rearranging, we have

$$\frac{1}{q} = \frac{C}{C_o} = \frac{a + b(1 + K^{H}[H^{+}])}{p_4K^{H}b[H^{+}]} + \frac{2\beta_{2,r}[Br^{-}]^r\, C_o}{(p_4K^{H}b[H^{+}])^2} \quad . \quad . \quad . \quad . \quad (7)$$

If $1/q^o = \lim_{C_o \to 0} (1/q)$, rearrangement of equation (7) gives

$$\frac{1}{2C_o}\left(\frac{1}{q} - \frac{1}{q^o}\right) = \frac{\beta_{2,r}[Br^{-}]^r}{(p_4K^{H}b[H^{+}])^2} = j \text{ (say)} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Similarly, if indium tribromide were the only species in the organic phase,

$$C_o = p_3\beta_3[In^{3+}][Br^{-}]^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

where $p_3 = [InBr_3]_o/[InBr_3]$, and from equations (1), (4), and (6*a*)

$$j = \frac{1}{2C_o}\left(\frac{1}{q} - \frac{1}{q^o}\right) = \frac{\beta_{2r,}[Br^{-}]^{r-6}}{(p_3\beta_3)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8a)$$

Since j can readily be calculated from experimental data, its variation with $[Br^-]$ and $[H^+]$ according to equation (8) or (8*a*) will permit a decision as to the probable nature of the dimeric species in the aqueous phase—provided the composition of the extracted species is known. For this purpose we note that so long as the total concentration of indium is very much less than the concentrations of hydrobromic acid under consideration, $[H^+] =$

$[Br^-] = C_{HBr}$. Introducing into equation (8) the value of b from equation (5), and substituting C_{HBr} for $[H^+]$ and $[Br^-]$, we have

$$j(C_{HBr})^{10-r} = \beta_{2,r}/(p_4K^H\beta_4)^2 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

for the case where $HInBr_4$ is extracted. Similarly from equation (8*a*), we have

$$j(C_{HBr})^{6-r} = \beta_{2,r}/(p_3\beta_3)^2 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (9a)$$

for the case where $InBr_3$ is extracted. It will be apparent from the method of derivation that if the dinuclear species contains hydrogen in addition to bromine atoms (*i.e.*, if it has the composition $In_2Br_{t+s}H_s^{6-t}$) equations of exactly the same form will result, provided only that the index r is now taken to represent the total number of ligands (hydrogen and bromide ions) associated with each pair of indium ions, *i.e.*, provided $r = t + 2s$.

Experimental values of q^o, and values of j calculated by successive approximation which enable values of q calculated from equations (8) or (8*a*) to fit the experimental data most closely, were obtained from the measurements in 0·2, 0·39, and 0·975M-hydrobromic acid. From Table 5 it is clear that values of $j(C_{HBr})^4$ are almost the same for the three acid concentrations. Analyses of the organic phase at the highest metal concentrations used gave consistent values for $HInBr_4$ (cf. Table 4). Moreover, studies of partition equilibria at tracer concentrations (Part III) indicate that this acido-complex is the predominant species extracted from hydrobromic acid solutions. Assuming then that $HInBr_4$ is the sole extractable species, we have $10 - r = 4$, suggesting that the predominant dinuclear species formed in the aqueous phase is In_2Br_6.

TABLE 5. *Determination of the value of the index, r.*

C_{HBr}, M	q^o	j	jC_{HBr}	$j(C_{HBr})^2$	$j(C_{HBr})^3$	$j(C_{HBr})^4$	$j(C_{HBr})^5$
0·20	2·18	8000	1600	320	64·0	12·8	2·6
0·39	12·7	600	234	91·2	35·6	13·9	5·4
0·975	180	15	14·6	14·3	13·9	13·5	13·2

Systems with a Neutral Salt Background.—Although the ionic strength was constant in each series of experiments in 0·2, 0·39, and 0·975M-hydrobromic acid, it varied from one series to another. In order to examine the possible significance of this factor, the dependence of distribution ratio upon total metal concentration was remeasured for different concentrations of hydrobromic acid with a salt background of potassium nitrate to maintain an ionic strength of 1·0M throughout. It has been shown (Part III, *loc. cit.*) that indium nitrate does not pass by partition into *iso*butyl methyl ketone under these conditions, and that competitive complex-formation between bromide and nitrate ions is negligible.

The results (Fig. 1, curves 2, 3, and 4) for equilibrium acidities of 0·2, 0·375, and 0·563M-hydrobromic acid show the same general trend as those discussed above. Below indium concentrations of ~10^{-5}M, q is again constant; but it decreases at higher concentrations. Plots of log C_o against log C are found to have unit slope at low metal concentrations, and again the slope tends towards the value 0·5 at high metal concentrations. Comparison of measurements at similar acidities shows that the distribution ratios are lower in the presence of potassium nitrate. Whatever the origin of this salt effect may be, data obtained in the same medium are self-consistent, and since the possibility of competitive complex-formation had been eliminated, values of j were calculated as before. From Table 6 it appears that values of $j(C_{HBr})^3$ are most nearly constant, implying that the predominant dimeric species in the aqueous phase is $In_2Br_7^-$ in the presence of potassium nitrate as a background salt. As the method of calculation of the index r is based upon the simplifying assumptions that a single species, $HInBr_4$,

TABLE 6. *Determination of the index, r, in the presence of potassium nitrate at* $\mu = 1{\cdot}0$M.

C_{HBr}, M	q^o	j	jC_{HBr}	$j(C_{HBr})^2$	$j(C_{HBr})^3$	$j(C_{HBr})^4$
0·20	0·218	4000	800	160	32	6·4
0·375	1·72	581	218	82	30·8	11·5
0·563	7·63	160	90	50·7	28·6	16·1

predominates in the organic phase and that polymerisation in the aqueous phase is confined to a predominant dinuclear species $\text{In}_2\text{Br}_r^{6-r}$, the discrepancy between the values of r found in the two media is not unreasonable.

The hypothesis being accepted that the decrease in distribution ratio of indium between hydrobromic acid and *iso*butyl methyl ketone at metal concentrations above 10^{-5}M is due to the formation of species such as In_2Br_6 and In_2Br_7^- of low or negligible extractability when compared with that of the acido-complex HInBr_4, it is possible to estimate their stability. Irrespective of the salt medium and the precise value of β_4 which is assumed, the value of the product $p_4K^{\text{H}}\beta_4$ is found to be of the order 5×10^5 to 9×10^5 (cf. Part III). Hence, from equation (9) the equilibrium constant $\beta_{2,6}$ has the value 3×10^{12}—10^{13}. This leads to a value for the dimerisation constant of the reaction $2\text{InBr}_3 \rightleftharpoons \text{In}_2\text{Br}_6$ of the order of $\beta_{2,6}/(\beta_3)^2 = 5 \times 10^5$ to 4×10^6. Similarly, $\beta_{2,7} \sim 10^{13}$, and the equilibrium constant for the reaction $\text{InBr}_3 + \text{InBr}_4^- \rightleftharpoons \text{In}_2\text{Br}_7^-$ is $\beta_{2,7}/\beta_3\beta_4 \approx 10^7$.

We can now reconsider the possibility of the predominant dinuclear complex in the aqueous phase being a hydroxylated species, such as $\text{In}_2(\text{OH})_q$. Corresponding to equation (3) we have

$$C = [\text{In}^{3+}] + [\text{InBr}^{++}] + \ldots . [\text{InBr}_4^-] + [\text{HInBr}_4] + 2[\text{In}_2(\text{OH})_q] \quad . \quad (10)$$

Treating equation (10) in the same manner as equation (3), we find for the case where only the acido-complex, HInBr_4, is extracted into the organic phase

$$j(C_{\text{HBr}})^{10+q} = \beta_{2,q}K_w^{\,q}/(p_4K^{\text{H}}\beta_4)^2 \quad . \; . \; . \; . \; . \; . \quad (11)$$

where $\beta_{2,q} = [\text{In}_2(\text{OH})_q]/[\text{In}^{3+}]^2[\text{OH}^-]^q$, and K_w is the ion-product of water. Since from the experimental data summarised in Tables 5 and 6, the products $j(C_{\text{HBr}})^4$ and $j(C_{\text{HBr}})^3$ give the best agreement, we have $10 + q = 4$ or 3, whence $q = -6$ or -7. These are physically meaningless solutions which effectively dispose of the hypothesis that the dimer is a hydroxylated species.

Discussion.—Studies of partition equilibria at tracer concentrations of indium (Part III) and the macro-scale analyses now reported all indicate that the predominant species extracted from hydrobromic acid into *iso*butyl methyl ketone, diethyl ether, and many other solvents is the acido-complex HInBr_4. Analysis of the extracts in diethyl ether show that this species is associated with ten molecules of water. This degree of hydration does not appear unreasonable when comparison is made with the composition of the organic extract in other systems (cf. Table 7), although the very high hydration numbers reported in extraction by alcohols probably arise through some special hydroxyl mechanism; *initial* hydration numbers are often negative with alcohols. Preliminary experiments have shown that an ethereal extract containing HInBr_4 conducts electricity; so too does an ethereal solution of the similarly constituted salt NH_4GaCl_4 (Friedman and Taube, *J. Amer. Chem. Soc.*, 1950, **72**, 3362). Detailed experiments by Campbell (*loc. cit.*) show that $\text{HFeCl}_4,5\text{H}_2\text{O}$ behaves as a strong electrolyte when dissolved in *iso*propyl ether. The Raman spectrum of extracts from acid solutions of indium bromide into diethyl ether and *iso*butyl methyl ketone (Woodward and Bill, *J.*, 1955, 1699) proves to be that of the tetrahedral InBr_4^- ion and provides further evidence of ionisation. Now the unsolvated molecule of HInBr_4 has a somewhat improbable electronic structure, and if the hydrated

TABLE 7.

Species in organic phase	Solvent	Ref.
$\text{HFeCl}_4,4{\cdot}5\text{H}_2\text{O}$	2 : 2′-Dichlorodiethyl ether	*a*
$\text{HFeCl}_4,5\text{H}_2\text{O}$	Di*iso*propyl ether	*b, c*
$\text{Al(NO}_3)_3,9\text{H}_2\text{O}$	*n*-Hexanol	*d*
$\text{UO}_2(\text{NO}_3)_2,4\text{H}_2\text{O}$	Diethyl ether and other solvents	*e*
$\text{Co(ClO}_4)_2,14{\cdot}7\text{H}_2\text{O}$	Octan-2-ol	*f*
$\text{Ni(ClO}_4)_2,10\text{H}_2\text{O}$	Octan-2-ol	*f*

[a] Axelrod and Swift, *J. Amer. Chem. Soc.*, 1940, **62**, 33. [b] Nachtrieb and Conway, *ibid.*, 1948, **70**, 3547. [c] Campbell, A.E.C.U., 2313. [d] Templeton, *J. Phys. Coll. Chem.*, 1950, **54**, 1255. [e] McKay and Mathieson, *Trans. Faraday Soc.*, 1951, **47**, 428. [f] Yates, Laran, Williams, and Moore, *J. Amer. Chem. Soc.*, 1953, **75**, 2212.

complex, $HInBr_4$,aq., crosses the phase boundary, it probably does so in the form of the ion-pair $H_3O^+(H_2O)_nInBr_4^-$. In diethyl ether, $n = 9$; but it may have other values in different solvents.

Variations in distribution with total metal concentration may be interpreted in a number of ways. It may be postulated that activity coefficients are varying, that the presence of the extracted species has changed the solvent properties of the organic phase, or that changes in phase miscibility have altered the nature of both phases. For these, and for other reasons, stoicheiometric partition coefficients and stability constants may vary. At present it appears to be almost impossible to give quantitative expression to such hypotheses except for systems in which step-equilibrium may be neglected (Glueckauf, McKay, and Mathieson, *Trans. Faraday Soc.*, 1951, **47**, 437). The hydrobromic acid–*iso*butyl methyl ketone system was selected for detailed study after a survey of the partition of indium halides into a large number of solvents (Part V; *loc. cit.*) because variations in phase miscibility were negligible. From this it was inferred that changes in the solvent composition were negligible in both phases, so that the constancy of stoicheiometric partition coefficients and stability constants could be assumed. Activity coefficients have been controlled in the aqueous phase, and logical deductions made from the application of the law of mass action to the equilibria.

The hypothesis that the decrease in the distribution ratio of indium between hydrobromic acid and *iso*butyl methyl ketone at metal concentrations above 10^{-5}M is due to the formation of stable species such as In_2Br_6 and $In_2Br_7^-$ in the aqueous phase is supported by a growing body of evidence for the existence of polynuclear inorganic complexes in solution, and it is apparent that these occur more commonly than was formerly supposed. Thus dimeric halide species of the type M_2X_6 are well known in the vapour phase for indium (Brode, *Ann. Physik*, 1940, **37**, 344; Stevenson and Schomaker, *J. Amer. Chem. Soc.*, 1942, **64**, 2514) and for other tervalent metals, and have been demonstrated in solutions of iron and aluminium halides in non-associating organic solvents (Gmelin, " Handbuch der anorganische Chemie," Berlin, 1924). The addition of hydrobromic acid to a solution of Al_2Br_6 in benzene is known to give rise to the complex ion $Al_2Br_7^-$ (Dallinga, reported by van Eck, in Venanzi and Gamlen, *Chimia e l'Industria*, 1953, **35**, 926; cf. Brown and Pearsall, *J. Amer. Chem. Soc.*, 1952, **74**, 191). Although there is as yet less published information concerning dinuclear species in aqueous solution their presence has been established in mixtures of silver and chloride or bromide ions (Berne and Leden, *Svensk Kem. Tidskr.*, 1953, **65**, 88; *Z. Naturforsch.*, 1953, **11**, 719) and iodide or thiocyanate ions (Leden, personal communication). It is certain that the hydrolysis products of many ter- and quadri-valent aquo-cations, including indium, are extensively polymerised (Sillén, *Acta Chem. Scand.*, 1954, **8**, 299, 318; Mattock, *ibid.*, p. 777). The presence of polynuclear species in indium sulphate solutions has been reported by Sundén (*Svensk Kem. Tidskr.*, 1954, **66**, 20, 50) and may be inferred from his potentiometric data for other indium complexes. They have not been observed in measurements of the stability constants of indium halides with ion-exchange resins (Carleson and Irving, *J.*, 1954, 4390; Schufle and Eiland, *J. Amer. Chem. Soc.*, 1954, **76**, 960), doubtless owing to the low and small range of indium concentrations employed. Finally, the existence of dinuclear complexes of metals in different valency states bridged by hydroxyl or halide ions has been clearly established by studies of the kinetics of electron-transfer reactions (Amphlett, *Quart. Rev.*, 1954, **8**, 219, and refs. therein).

There is less evidence as to the stability of polynuclear complexes, though the values $[Fe_2(OH)_2{}^{4+}]/[Fe^{3+}]^2[OH^-]^2 \sim 10^{25}$ and $[Fe_2(OH)_2{}^{4+}]/[Fe(OH)^{2+}]^2 \sim 10^3$ (Hedström, *Arkiv Kemi*, 1953, **6**, 1) are suggestive. Independent confirmation of the existence and stability of indium–bromide ion complexes is clearly desirable and may be obtained potentiometrically.

Although the distribution ratio for indium between hydrobromic acid and *iso*butyl methyl ketone decreases with increasing metal concentration, yet with diethyl ether as solvent it increases, a result which is explicable if the degree of association in the organic phase is greater than in the aqueous phase. A similar situation obtains in the extraction of iron and gallium (Irvine, personal communication; cf. Dodson, Forney, and Swift, *J. Amer. Chem. Soc.*, 1936, **58**, 2573; Axelrod and Swift, *ibid.*, 1940, **62**, 33). With increasing metal concentration, extraction into 2 : 2′-dichlorodiethyl ether decreases, but into di*iso*propyl ether it increases. Such phenomena could be explained on the *ad hoc* hypothesis that dimeric species are extracted more readily than monomeric species into the aliphatic ethers, but considerably less readily into such solvents as *iso*butyl methyl ketone and chloro-ethers. If such were the case the extent of polymerisation of the extracted species should differ at different metal concentrations and also in the different classes of solvent. No such evidence has been advanced, however; on the contrary the absorption spectrum of the ferric chloride complex extracted into *iso*propyl ether obeys Beer's law over the range 10^{-2}—10^{-1}M (Nachtrieb and Conway, *ibid.*, 1948, **70**, 3547; Metzler and Myers, *ibid.*, 1950, **72**, 3776), and the extracts from indium bromide–hydrobromic acid mixtures into *iso*butyl methyl ketone and into diethyl ether have the same Raman spectra (Woodward and Bill, *loc. cit.*) and analytical composition (cf. Table 4). The apparent paradox could be explained if only monomeric species undergo partition, for their electrostatic association as ion-pairs, triplets, or even larger clusters will be favoured by solvents of very low dielectric constant (cf. Fuoss and Kraus, *ibid.*, 1933, **55**, 21) and would be greater in aliphatic ethers than in *iso*butyl methyl ketone or the chloro-ethers which have considerably larger dielectric constants. The effective degree of polymerisation of the metal in the aqueous phase may then become less than that prevailing in the organic phases composed of the former solvents, the difference increasing with the total metal concentration.

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