

**1161.** *Co-ordination Compounds of Indium. Part II.*<sup>1</sup> *Solvent Extraction Studies of Anionic Halogeno- and Cyano-Complexes of Indium(III).*

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The extraction of indium(III) from aqueous solutions of hydrofluoric, hydrochloric, hydrobromic, hydroiodic, and hydrocyanic acid into methyldiethylamine in chloroform has been investigated by tracer methods. There was no extraction from hydrofluoric acid; otherwise  $D_{in}$  increases in the order  $HCl < HBr < HI \approx HCN$ . Studies of the amine dependence of  $D_{in}$  show that singly, doubly, and triply charged anions are extracted. These conclusions are compared with previous work on the indium(III)-chloride system, and the nature of the aqueous phase species is discussed. The extracted indium(III)-cyanide anion has not been identified.

In the preceding paper,<sup>1</sup> evidence for four- and six-co-ordinate cationic and neutral indium(III) species was reviewed. Anionic complexes have been reported from halogen ligands,<sup>2</sup> and for sulphate<sup>3</sup> and oxalate.<sup>4</sup> With chloride and bromide, a number of crystalline complexes have been prepared,<sup>5-8</sup> with co-ordination numbers of 4 and 6 ( $NaInCl_4$ ,  $NH_4InCl_4$ ,  $K_3InCl_6$ ,  $K_3InBr_6$ ,  $Li_3InCl_6$ ,  $Rb_3InCl_6$ , and  $Cs_3InCl_6$ ). Inorganic complexes with five halide ions per indium atom are apparently hydrated, and on the basis of isomorphism with salts of  $[FeCl_5(H_2O)]^{2-}$ , are believed to be 6-co-ordinate.<sup>9</sup> Crystalline fluoride complexes appear to be 6-co-ordinate.<sup>10</sup> In addition to these compounds, Ekeley and Potratz<sup>11</sup> have

<sup>1</sup> Part I, Carty and Tuck, preceding paper.

<sup>2</sup> Sidgwick, "The Chemical Elements and their Compounds," O.U.P., 1950, vol. 1, p. 476.

<sup>3</sup> Pascal, "Nouveau Traité de Chimie Minérale," Masson, Paris, vol. 6, 1961, p. 870.

<sup>4</sup> Moeller, *J. Amer. Chem. Soc.*, 1940, **62**, 2444.

<sup>5</sup> Vovkogen and Fialkov, *J. Gen. Chem. (U.S.S.R.)*, 1945, **15**, 903.

<sup>6</sup> Meyer, *Annalen*, 1869, **150**, 148.

<sup>7</sup> "Gmelins Handbuch der Anorganische Chemie," vol. 37, Verlag, Berlin, 1936, pp. 109-115.

<sup>8</sup> Pascal, loc. cit., pp. 842-847.

<sup>9</sup> Wells, "Structural Inorganic Chemistry," O.U.P., 3rd edn., 1962, p. 367.

<sup>10</sup> Pascal, loc. cit., pp. 836-838.

<sup>11</sup> Ekeley and Potratz, *J. Amer. Chem. Soc.*, 1936, **58**, 907.

reported a series of double salts or complexes with substituted ammonium cations, ranging from  $M_4InX_7$  to  $M_2InX_5$  for  $X = Cl$ , and  $M_2InX_5$  and  $MInX_4$  for  $X = Br$ ; with trialkylsulfonium cations,  $MInI_4$  compounds were obtained.

A number of authors have discussed the solvent extraction of indium halide anionic species. Irving and Rossotti<sup>12</sup> found that with basic oxygenated solvents,  $D_{In}$  increases in the order chloride < bromide < iodide, and Woodward and his co-workers<sup>13</sup> showed that the species in the organic phase was  $H^+InX_4^-$  ( $X = Cl, Br$ ). Using amine extraction methods, White, Kelly, and Li<sup>14</sup> reported that the species extracted from aqueous hydrochloric acid was  $InCl_5^{2-}$ . While the present work was in progress, Maydan and Marcus<sup>15</sup> published results on amine extraction from hydrochloric acid, and more recently Good and Holland<sup>16</sup> have also discussed this system. We have studied the extraction of tracer amounts of indium(III) from aqueous hydrofluoric, hydrochloric, hydrobromic, hydriodic, and hydrocyanic acids into chloroform solutions of methyldiethylamine.

### EXPERIMENTAL

*Materials.*—The methyldiethylamine (MDOA) and chloroform were of the same quality as those used in previous work.<sup>17</sup> All reagents were AnalaR grade. Hydriodic acid was pretreated with tri-*n*-butyl phosphate to remove iodine and hydrogen tri-iodide.<sup>18</sup>

*Tracer Methods.*—Indium-114 (half-life 49 days) was obtained from A.E.R.E., Harwell. The neutron-bombarded metal (0.5 g.) was dissolved in 10M-hydrochloric acid and, for extraction studies in chloride media, the resultant solution diluted as required. For bromide and iodide studies, 5-ml. portions of the original hydrochloric acid solution were evaporated to dryness, and the residues dissolved in the minimum amount of 12M-hydrobromic or 7M-hydriodic acid. The resultant solutions were evaporated to dryness, and the evaporation-solution cycle repeated five times; the final solution was diluted as required for the measurement of distribution coefficients.

For work in fluoride or cyanide media, irradiated indium metal was dissolved in the minimum volume of 9M-nitric acid, and the resultant solution made up to 50 ml. Portions of this solution were dissolved in the appropriate hydrofluoric or hydrocyanic acid solution. The concentration of nitric acid in the experimental solutions was < 0.003M, and this cannot affect the results, since the indium(III) nitrate species is not extractable.<sup>19</sup> All work with hydrofluoric acid was carried out in Polythene vessels.

The indium concentration in the initial aqueous solutions in the distribution experiments was approx.  $10^{-3}M$ , and the activity  $\sim 10^{-4}$  c./min./ml. Samples (usually 100  $\lambda$ ) of both equilibrium phases were evaporated on to stainless-steel trays, and counted with an end-window Geiger counter provided with the usual electronic equipment. The counts give  $D_{In}$  = specific activity of the organic phase/specific activity of the aqueous phase, specific activity being measured in counts/min./ml. Duplicate determinations usually agreed to within 5%.

*Distribution Experiments.*—About 5 ml. of methyldiethylamine in chloroform were equilibrated with an equal volume of the appropriate hydrohalic acid, of such a strength as to give an equilibrium concentration in the aqueous phase equal to that used in the subsequent indium distribution experiment. The organic phase was removed after centrifugation, and 2 ml. of this phase equilibrated with an equal volume of tracer solution in hydrohalic acid. Check titrations showed that no change in aqueous acid concentration took place in this equilibration, which involved mechanical agitation in stoppered tubes for 15 min.

### RESULTS AND DISCUSSION

*Fluoride Media.*—No indium(III) was extracted by 0.4M-methyldiethylamine and up to 5M-hydrofluoric acid, and the addition of sodium fluoride as a salting-out agent was without effect. Nor was indium extracted by a 50% solution of tri-*n*-butyl phosphate in chloroform.

<sup>12</sup> Irving and Rossotti, *J.*, 1955, 1927, 1938, 1946.

<sup>13</sup> Woodward and Bill, *J.*, 1955, 1699; Woodward and Taylor, *J.*, 1960, 4473.

<sup>14</sup> White, Kelly, and Li, *J. Inorg. Nuclear Chem.*, 1961, **16**, 337.

<sup>15</sup> Maydan and Marcus, *J. Phys. Chem.*, 1963, **67**, 987.

<sup>16</sup> Good and Holland, *J. Inorg. Nuclear Chem.*, 1964, **26**, 321.

<sup>17</sup> Choi and Tuck, *Inorg. Chem.*, 1963, **2**, 780.

<sup>18</sup> Tuck, Walters, and Woodhouse, *Chem. and Ind.*, 1963, 1352.

<sup>19</sup> Tuck and Woodhouse, unpublished results.

These negative results may be due to an absence of anionic species in the aqueous phase, *e.g.*, predominant species  $\text{InF}_3(\text{H}_2\text{O})_3$ , or to the presence of anions, *e.g.*,  $[\text{InF}_4(\text{H}_2\text{O})_2]^-$ , for which the energetics of the desolvation process implicit in the extraction (see below) are unfavourable. The properties of hydrofluoric acid prevent investigation of this question by studies of ionic migration.

*Hydrochloric, Hydrobromic, Hydriodic, and Hydrocyanic Acid Media.*—In Fig. 1 we show the variation of  $D_{\text{In}}$  with acid concentration, up to 10M for hydrochloric and hydrobromic acids, 6M for hydriodic acid, and 4M for hydrocyanic acid. No extraction of indium

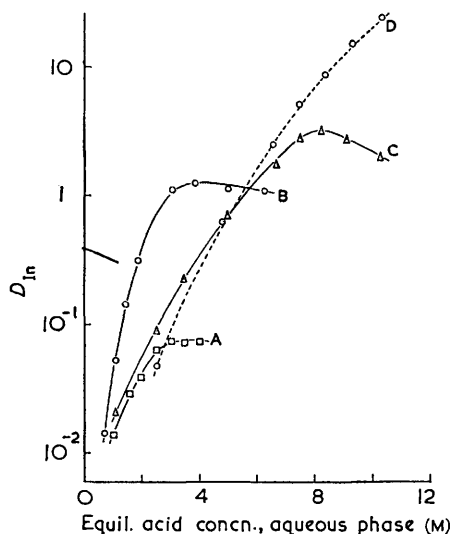
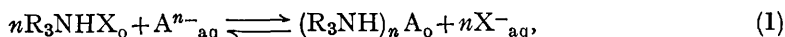


Fig. 1.  $D_{\text{In}}$  as a function of acid concentration:

curve A; HCN, 0.002M-MDOA;  
 B; HI, 0.00197M-MDOA;  
 C; HCl, 0.415M-MDOA;  
 D; HBr, 0.0195M-MDOA.

into chloroform alone could be detected at any of the acid concentrations studied. Different amine concentrations were used in these experiments, and from the results we estimate that, in comparable aqueous acid concentrations,  $D_{\text{In}}$  increases in the approximate order  $1:10^2:10^3:10^3$  for the chloride, bromide, iodide, and cyanide species. A similar increase for the extraction of halide anions into basic oxygenated solvents was reported by Irving and Rossotti.<sup>12</sup> This order is discussed below.

*Charge on the Extracted Species.*—It is well established that for an extraction process represented by

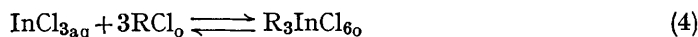
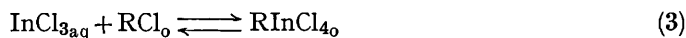


the charge on A can be found by measuring  $D_{\text{A}}$  as a function of amine concentration, since

$$\log D_{\text{A}} = n \log [\text{R}_3\text{N}] + \text{const.} \quad (2)$$

Following Maydan and Marcus,<sup>15</sup> we find that for chloride, bromide, and iodide systems  $n$  varies from 1 to 3 over the range of amine concentrations studied (see Figs. 2—4). The cyanide results are discussed below.

Maydan and Marcus<sup>15</sup> explained their chloride results on the basis of two extraction processes



although the postulate that  $\text{InX}_3$  is the only significant species in the aqueous phase does little to explain the extraction of  $\text{H}^+\text{InX}_4^-$  by basic oxygenated solvents.<sup>12,13</sup> We believe that there are significant concentrations of anionic indium(III) complexes at the acid concentrations in question,<sup>20</sup> and base our explanation on the existence of 6-co-ordinate species

<sup>20</sup> Celeda and Tuck, unpublished results.

in the aqueous phase. The evidence of the preparative work (Part I, and introduction to present paper) is that electronegative  $\sigma$ -bonding ligands favour 6-co-ordination around indium(II), and both  $\text{InX}_6^{3-}$  and  $[\text{InX}_5(\text{H}_2\text{O})]^{2-}$  anions are known. No salts of  $[\text{InX}_4(\text{F}_2\text{O})_2]^-$  have been prepared, but we have obtained the crystalline salt<sup>21</sup>  $(\text{Et}_4\text{N})[\text{nCl}_4\text{urea}]$ , and the isoelectronic tin(IV) compounds,  $\text{SnCl}_4\text{L}_2$  are well known.<sup>22</sup>

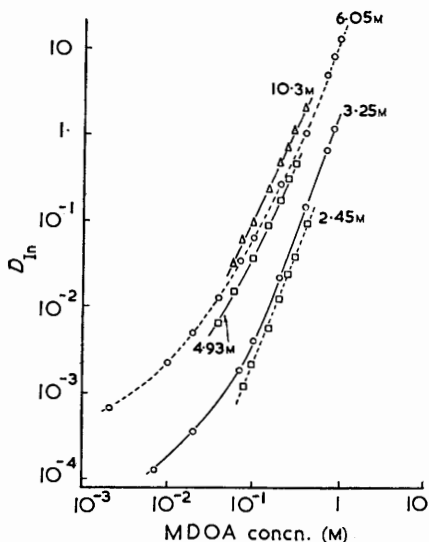


FIG. 2.  $D_{\text{In}}$  as a function of MDOA concentration in hydrochloric acid media; equilibrium aqueous phase hydrochloric acid concentrations as shown.

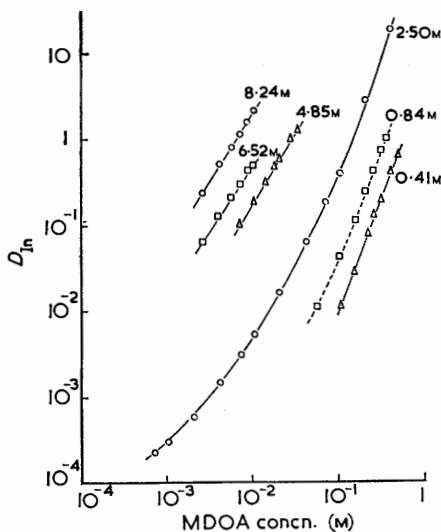


FIG. 3.  $D_{\text{In}}$  as a function of MDOA concentration in hydrobromic acid media; equilibrium aqueous phase hydrobromic acid concentrations as shown.

Equally, although  $\text{InI}_6^{3-}$  salts have not been reported,  $\text{SnI}_6^{2-}$  anions appear to be stable.<sup>23</sup>

There is an accumulation of evidence that hydrated anions are not extracted into basic solvents, even when such species exist in aqueous solution.<sup>24-26</sup> Thus in the extraction of indium(III) into basic oxygenated solvents, the organic phase anionic species is tetrahedral

<sup>21</sup> Tuck and Woodhouse, *Chem. and Ind.*, 1964, 1363.

<sup>22</sup> Beattie, *Quart. Rev.*, 1963, 17, 382.

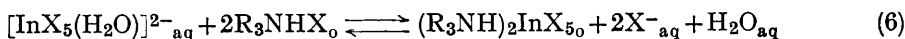
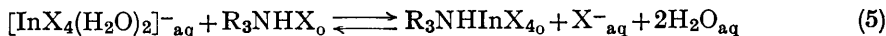
<sup>23</sup> Pascal, "Nouveau Traité de Chimie Minérale," Masson, Paris, vol. 8, 1963, p. 393.

<sup>24</sup> Tuck, *J.*, 1963, 2736; Tuck and Diamond, *J. Phys. Chem.*, 1961, 65, 193.

<sup>25</sup> Lindenbaum and Boyd, *J. Phys. Chem.*, 1963, 67, 1238.

<sup>26</sup> Creighton and Lippincott, *J.*, 1963, 5134.

$\text{InX}_4^-$  ( $X = \text{Cl}, \text{Br}$ ), although the evidence from Raman spectroscopy shows that there are no detectable amounts of this species in the aqueous solution. We therefore suggest that the dehydration of hydrated anions also occurs in the amine extraction system, and that the three equilibria involved are



with equilibrium constants  $K_5$ ,  $K_6$ , and  $K_7$ . Electrostatic hydration of the anions will increase with increasing charge density,<sup>27,28</sup> giving rise to the order  $K_5 > K_6 > K_7$ . There is also, however, the "chemical" hydration (*i.e.* the two bonded water molecules) in  $[\text{InX}_4(\text{H}_2\text{O})_2]^-$ ; we restrict the argument to this anion, since the behaviour of  $[\text{InX}_5(\text{H}_2\text{O})]^{2-}$

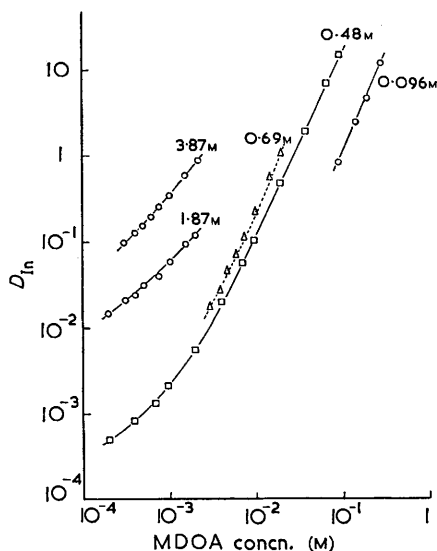
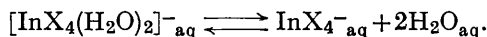


FIG. 4.  $D_{\text{In}}$  as a function of MDOA concentration in hydriodic acid media; equilibrium aqueous phase hydriodic acid concentrations as shown.

will presumably be in some way intermediate between  $[\text{InX}_4(\text{H}_2\text{O})_2]^-$  and  $[\text{InX}_6]^{3-}$ . The transfer of indium from aqueous to organic phase is then assumed to involve the intermediate step of dehydration of  $[\text{InX}_4(\text{H}_2\text{O})_2]^-$  (see above), which can be represented by the equilibrium



The Raman evidence for the absence of  $\text{InX}_4^-$  in the aqueous phase is not surprising, since this equilibrium presumably lies well to the left in the presence of large amounts of water. The energy needed to shift this equilibrium to the right so as to favour the formation of  $\text{InX}_4^-$  is difficult to estimate, but is probably quite small, especially if the  $[\text{InX}_4(\text{H}_2\text{O})_2]^-$  anion involved is the *cis*-isomer [cf. the arguments for this with the similar  $\text{SnCl}_4 \cdot 2(\text{dimethyl sulphoxide})$  compound<sup>22,29</sup>], since in this case little reorganization of the In-X bonds will be required. We therefore conclude that the order  $K_5 > K_6 > K_7$  is unlikely to be changed as a consequence of the dehydration processes in equations (5) and (6).

This order in the equilibrium constants explains the increase of  $n$  from 1 to 3 with increasing amine concentration, as observed by Maydon and Marcus,<sup>15</sup> and in the present work for chloride, bromide, and iodide media. We believe that White, Kelly, and Li<sup>14</sup> found

<sup>27</sup> Eley and Evans, *Trans. Faraday Soc.*, 1938, **34**, 1093.

<sup>28</sup> Diamond and Tuck, *Prog. Inorg. Chem.*, 1960, **2**, 109.

<sup>29</sup> Lappert and Smith, *J.*, 1961, 3226.

$n = 2$  by a fortuitous choice of a restricted range of conditions. A similar comment applies to the work of Good and Holland,<sup>16</sup> who reported that  $n$  (values 1—2) varied with the amine used and with the concentration of aqueous chloride. The latter workers only varied the amine concentration over less than two powers of 10, and Figs. 2—4 (and ref. 15) show that apparently constant values of  $n$  may arise within such a restricted range. The variation of  $n$  with the amine used presumably represents different average values of  $K_5$ ,  $K_6$ , and  $K_7$ .

The present theory explains the order iodide > bromide > chloride as being due to (a) size, and (b) the increasing ease of the six → four co-ordination change as the electronegativity of the ligand decreases (cf. Part I). The theory also suggests why, in ether and ketone extraction, the organic solvent only extracts  $H^+InX_4^-$  (Irving and Rossotti<sup>12</sup>); the

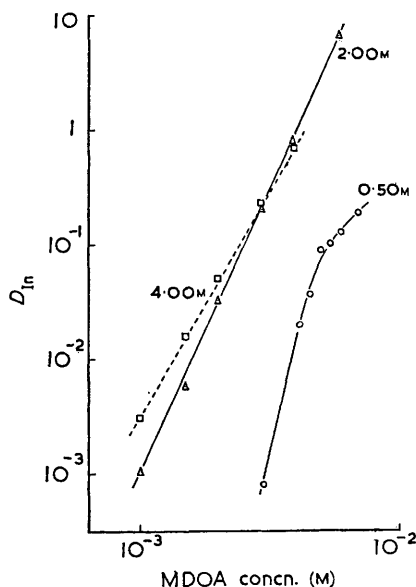


FIG. 5.  $D_{In}$  as a function of MDOA concentration in hydrocyanic acid media; equilibrium aqueous phase hydrocyanic acid concentrations as shown.

removal of the higher charged anions from the aqueous phase is energetically unfavourable, especially since extraction into such solvents does not involve ion-exchange transfer of  $X^-$  anions back into the aqueous phase, which does something to restore the energy balance. Equally, this argument explains the extraction of gallium(III) by amine extractants as  $GaCl_4^-$  from aqueous hydrochloric acid<sup>16</sup> as being the result of the strong tendency of Ga(III) to become 4-co-ordinate.

*Cyanide Media.*—Fig. 1 shows that indium(III) is efficiently extracted from aqueous hydrocyanic acid. Attempts to measure  $n$  as was done in the work on halides gave the results shown in Fig. 5, with  $n$  in the range 3—6. Two major difficulties prevent interpretation of these values: the unexplained nature of the organic ( $R_3NH \cdot CN$ ) phase,<sup>30</sup> and the possible polymerization of hydrogen cyanide in the aqueous phase. It seems clear that anionic indium(III)–cyanide species can exist; preparative work on this problem is in hand.

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<sup>30</sup> Bullock, Choi, Goodrick, Tuck, and Woodhouse, *J. Phys. Chem.*, 1964, **68**, 2687.