479. *The Extraction of Indium from Hydrobromic Acid into Mixed Organic Solvents.**

By H. IRVING and F. J. C. ROSSOTTI.

In agreement with theory, the logarithm of the distribution coefficient of indium between hydrobromic acid and mixtures of *iso*butyl methyl ketone with methyl *iso*propyl ketone, with *cyclo*hexane, and with benzene, is shown to be a linear function of the mole fraction of the second solvent.

ALTHOUGH tributyl phosphate has proved most valuable for the solvent extraction of certain inorganic salts,[1] for purposes of back-extraction it is generally necessary to reduce the very high value of the distribution ratio, q, either by adding an appropriate complex-forming agent to the aqueous phase, or by adding to the organic phase a diluent, *e.g.*, kerosene, for which q is smaller or negligible. The paucity of quantitative information on the extraction of inorganic solutes into mixtures of organic solvents prompted the following investigation.

The thermodynamic partition coefficient, $p^{\mathrm{T}}_{\mathrm{A}}$, the standard chemical potential, $\bar{\mathrm{G}}^{\circ}$, of a given solute in an aqueous phase (saturated with the slightly miscible organic solvent A), and the standard chemical potential, $\bar{\mathrm{G}}^{\circ}_{\mathrm{A}}$, in the organic solvent (saturated with water) are related by the equation:

$$RT \ln p^{\mathrm{T}}_{\mathrm{A}} = \bar{\mathrm{G}}^{\circ} - \bar{\mathrm{G}}^{\circ}_{\mathrm{A}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Changes in the extent of the mutual solubility of the phases caused by the addition to the aqueous phase of, *e.g.*, mineral acid or salts will affect both $\bar{\mathrm{G}}^{\circ}$ and $\bar{\mathrm{G}}^{\circ}_{\mathrm{A}}$, so that the value of the partition coefficient may vary with the composition and concentration of the partitionable solute and the salting-out medium. This introduces serious difficulties in the quantitative interpretation of the solvent extraction of inorganic salts [2] though these may be minimised by choosing an organic solvent such that the mutual solubility of the phases remains virtually unchanged as the concentrations of inorganic salts or of mineral acid are widely varied.[3,4]

Where conditions are such that the standard chemical potential, $\bar{\mathrm{G}}^{\circ}_{\mathrm{M}}$, in a mixture of two organic solvents, A and B, can be related to $\bar{\mathrm{G}}^{\circ}_{\mathrm{A}}$, $\bar{\mathrm{G}}^{\circ}_{\mathrm{B}}$, and to N_{B} the molar fraction of B, by the expression for a simple binary mixture:

$$\bar{\mathrm{G}}^{\circ}_{\mathrm{M}} = (1 - N_{\mathrm{B}})\bar{\mathrm{G}}^{\circ}_{\mathrm{A}} + N_{\mathrm{B}}\bar{\mathrm{G}}^{\circ}_{\mathrm{B}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

combination of equations (1) and (2) gives for the partition of a solute between mixed solvents and water

$$RT \ln p^{\mathrm{T}}_{\mathrm{M}} = (\bar{\mathrm{G}}^{\circ} - \bar{\mathrm{G}}^{\circ}_{\mathrm{A}}) - N_{\mathrm{B}}(\bar{\mathrm{G}}^{\circ}_{\mathrm{B}} - \bar{\mathrm{G}}^{\circ}_{\mathrm{A}}) \quad . \quad . \quad . \quad . \quad (3)$$

In the solvent extraction of metal halides from mineral acids it has been shown [2] that the experimentally measurable distribution ratio, defined by:

$$q = \frac{\text{(total concentration of metal in the organic phase)}}{\text{(total concentration of metal in the aqueous phase)}}$$

is a function of p^{T}, and the concentration of hydrogen ions, metal ions, and anions. If arbitrary values are assigned to these variables and the concentration of metal is sufficiently low, the function takes the simple form [cf. equation (5) of ref. 2]:

$$\log q = \log p + \text{Constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

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* Part VI of a group of papers of which Parts I—V appeared in *J.*, 1955, 1906, 1920, 1927, 1938, and 1946 respectively.

[1] Irving, *Quart. Rev.*, 1951, **5**, 200.

[2] Irving, Rossotti, and Williams, *J.*, 1955, 1906.

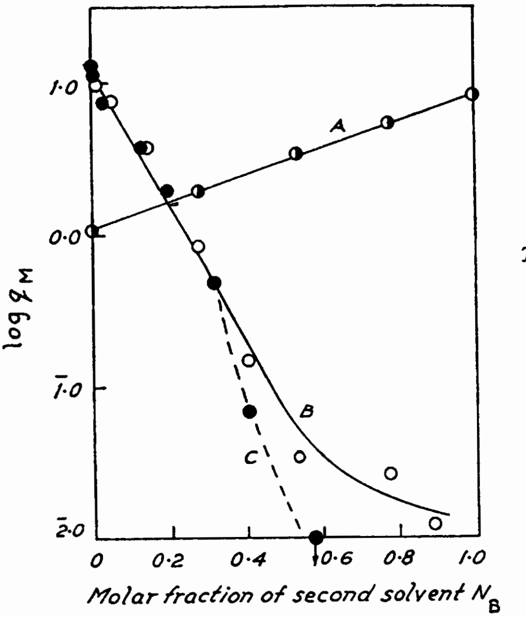
[3] Irving and Rossotti, *J.*, 1955, 1927.

[4] *Idem, J.*, 1955, 1946.

Finally, if the logarithm of the activity coefficient of the solute in the mixed organic solvents is proportional to the mole fraction, N_B,[5] a combination of the above equations leads to a linear relation of the form :

$$\log q_M = \log q_A - N_B(\log q_A - \log q_B) \quad . \quad . \quad . \quad . \quad . \quad . \quad , \qquad (5)$$

Equation (5) was tested by measuring the distribution ratio of indium at a constant tracer concentration from a fixed concentration of hydrobromic acid into *iso*butyl methyl ketone and its admixture with other solvents for which the partition was more, or was less, favourable. The results are shown in the Figure. At any given concentration of hydrobromic acid, q for methyl *iso*propyl ketone is greater than q for *iso*butyl methyl ketone; for mixtures, $\log q_M$ is an exactly linear function of the mole fraction of the former. *cyclo*-Hexane appears[4] to be incapable of extracting indium from hydrobromic acid ($q \approx 0$), and its addition to *iso*butyl methyl ketone reduces $\log q_M$ in proportion to the mole fraction of diluent over the whole range of values of distribution ratio which were experimentally significant. For benzene, q is also effectively zero,[4] and admixture with *iso*butyl methyl ketone again reduces $\log q_M$ in proportion to the mole fraction of diluent until it reaches 0·3—0·4; thereafter the rate of diminution of $\log q_M$ shows a marked increase. The departures from linearity are doubtless related, among other factors, to the decreased capacity of the *iso*butyl methyl ketone to solvate the partitioning species, $HInBr_4$, and emphasise the many simplifying assumptions made in deducing equation (5).



The extraction of indium from hydrobromic acid into mixtures of iso*butyl methyl ketone with*:
A, Methyl iso*propyl ketone.*
B, cyclo*Hexane.*
C, Benzene.

Since, from equation (5), $\partial \log q_M/\partial N_B = -(\log q_A - \log q_B)$, it is possible to estimate a value for q_B, the distribution ratio for indium between the diluent solvent and 0·5N-hydrobromic acid, from the measured slopes in the Figure and a knowledge of q_A for *iso*butyl methyl ketone. For benzene and *cyclo*hexane the value obtained is *ca.* 4×10^{-5}.

EXPERIMENTAL

Mixtures of organic solvents were prepared from $(20 - x)$ ml. of *iso*butyl methyl ketone and x ml. of methyl *iso*propyl ketone, *cyclo*hexane, or benzene. Within the limits of experimental error there were no volume changes on mixing, although the usual volume changes were observed

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[5] Scatchard, *J. Amer. Chem. Soc.*, 1925, **47**, 2098; 1927, **49**, 217; Akerlof, *ibid.*, 1930, **52**, 2353; Butler and Thomson, *Proc. Roy. Soc.*, 1933, *A*, **141**, 86.

on equilibration with an aqueous phase.[3,4] For each series of experiments a stock solution of ^{114}In, at a suitable level of activity for direct assay, was prepared in hydrobromic acid of the desired concentration. Equal volumes (20 ml.) of this indium bromide solution and of organic solvent were equilibrated for 5 min. and all measurements were carried out as described previously.[4] In the annexed Tables, q_M is the experimentally determined distribution ratio, and N_B the mole fraction of methyl *iso*propyl ketone, *cyclo*hexane, or benzene severally.

I. *Mixtures of* iso*butyl methyl ketone and methyl* iso*propyl ketone.* 5·14 × 10^{-5}M-*Indium in* 0·2N-HBr.

N_B	0·0	0·280	0·538	0·778	1·00
q_M	1·07	1·97	3·48	5·53	8·32

II. *Mixtures of* iso*butyl methyl ketone and* cyclo*hexane.* 5·14 × 10^{-5}M-*Indium in* 0·5N-HBr.

N_B	0·0	0·0344	0·0687	0·135	0·199	0·317	0·406	0·584	1·00
q_M	13·24	10·6	7·48	3·92	1·95	0·47	0·0665	0·0	0·0

III. *Mixtures of* iso*butyl methyl ketone with benzene.* 5 × 10^{-6}M-*Indium in* 0·5N-HBr.

N_B	0·0	0·0288	0·0574	0·142	0·278	0·410	0·536	0·776	0·891	1·00
q_M	12·7	9·85	7·75	3·85	0·854	0·151	0·034	0·0265	0·0118	0·0

INORGANIC CHEMISTRY LABORATORY,
SOUTH PARKS ROAD, OXFORD.

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