XLII.—*The Electro-deposition of Indium with the Dropping-mercury Cathode.*

By Seisi Takagi.

Numerous investigations with the dropping cathode have been carried out by J. Heyrovský and his collaborators (*Phil. Mag.*, 1923, **45**, 303; *Trans. Faraday Soc.*, 1924, **19**, 692; *Rec. trav. chim.*, 1925, **44**, 488—607). The method consists essentially in determining from the current-*E.M.F.* curves the cathode potential which corresponds to the deposition of metal (from a solution of a metallic salt) at the constantly renewed surface of the mercury cathode; in many cases this cathode potential is related to the metal-ion concentration in the simple reversible manner indicated by the classical Nernst logarithmic equation, and is thus, when reduced to normal concentration, characteristic of the particular ion. The method is described as being sensitive enough to detect many metals in a few c.c. of their aqueous solutions and at concentrations as low as $10^{-6}M$, and is obviously capable of many useful applications to qualitative and quantitative analysis, as indeed Heyrovský has already shown. The present investigation deals with the behaviour of acidified indium trichloride solutions when electrolysed with a dropping-mercury cathode, and with the qualitative and quantitative determination of indium by this method in the presence of zinc and gallium.

EXPERIMENTAL.

Preparation of the Indium Solutions.—The indium was obtained from Messrs. Adam Hilger, Ltd., and had been subjected to a detailed spectrographic analysis. Its composition was given as: In 99·5, Zn 0·4, Na 0·04, Si *ca.* 0·01, Pb 0·005, Sn *ca.* 0·001%, with traces of Ca, Al, and Mg.

The solutions were prepared by dissolving the metal in pure redistilled hydrochloric acid with the aid of a platinised platinum foil, the acid being used in excess to prevent hydrolysis of the indium trichloride and also to improve the electrical conductivity of the solution. The indium concentration was calculated from the known mass of metal dissolved.

Method and Apparatus.—The procedure described by Heyrovský and Shikata (*Rec. trav. chim.*, 1925, **44**, 496) was followed very closely. The current–potential curves were obtained by the photographic method, and by the use of a "polarograph" very kindly presented to this laboratory by Professor Heyrovský. The sensitivity of the galvanometer used was carefully determined, and kept constant throughout the measurements at $1{\cdot}5 \times 10^{-8}$ amp. per mm. scale deflexion, the scale being 1 m. distant from the mirror. In order to determine the metal deposition point, *i.e.*, the potential corresponding to the "turning point" of the current–voltage curve, the 45°-tangent was always used.

In the following tables, c denotes the concentration of the indium trichloride in mols. per litre, E the observed decomposition *E.M.F.*, π_0 the observed potential difference of the bottom mercury layer (anode) from a standard normal calomel electrode, π' the deposition potential of indium from the given solution ($\pi_0 - E = \pi'$) and π_N the normal deposition potential of indium, *i.e.*, the calculated potential at which the ions from a solution containing 1 g.-mol. of indium ion per litre would be deposited. Assuming reversible deposition and the validity of the Nernst equation, the calculation depends on the use of the equation

$$\pi_N - \pi' = RT/nF \,.\, \log C_N/C, \text{ where } C_N = 1 \text{ and } n = 3.$$

All the measurements described in this paper were carried out at room temperature (approx. 17°).

Indium Trichloride in 0·1M-*Hydrochloric Acid.*—The results of the electro-deposition in 0·1M-hydrochloric acid, but with various indium concentrations, are in Table I. For measuring the anode potentials, connexion with the normal calomel electrode was made by means of a saturated solution of potassium chloride. It was not necessary to use the Bjerrum extrapolation method, since the liquid junction potentials were small (1 millivolt or less). All potentials are given in volts.

TABLE I.

$c \times 10^5$.	E.	π_0.	π'.	π_N.
1140	0·5814	+0·0466	−0·5348	−0·498
1140	0·5862	+0·0466	−0·5396	−0·503
114	0·6056	+0·0494	−0·5562	−0·500
114	0·6080	+0·0496	−0·5588	−0·503
11·4	0·6261	+0·0480	−0·5781	−0·503
1·14	0·6397	+0·0476	−0·5921	−0·496
1310	0·5786	+0·0434	−0·5352	−0·499
131	0·5974	+0·0484	−0·5490	−0·494
13·1	0·6219	+0·0468	−0·5751	−0·501
13·1	0·6224	+0·0474	−0·5750	−0·501
1·31	0·6386	+0·0472	−0·5914	−0·499
1150	0·5856	+0·0484	−0·5372	−0·500
115	0·6055	+0·0488	−0·5567	−0·501
115	0·6035	+0·0474	−0·5561	−0·500
11·5	0·6176	+0·0486	−0·5690	−0·494
10·5	0·6230	+0·0454	−0·5776	−0·502
			Mean	−0·500

Table I shows that π_N, the calculated normal deposition potential of indium ions, remains sensibly constant, although c varies from $1{\cdot}14 \times 10^{-2}$ to $1{\cdot}31 \times 10^{-5}$. The mean value is −0·500 volt, reckoned from the normal calomel zero. These results agree very well with similar results obtained by Heyrovský in the case of many other metal kations. It was found in the present case that the turning point in the current–voltage curve almost disappeared when the concentration of indium trichloride fell to $10^{-6}M$.

Influence of Hydrochloric Acid Concentration.—The results given in Table II show that when in a dilute solution of indium trichloride the concentration of hydrochloric acid is decreased below $0{\cdot}1M$, the calculated value of π_N becomes less negative, and the turning point in the curve becomes indistinct and finally disappears. The effect of adding potassium chloride to the weakly acid solutions is to restore the turning point, although with diminishing concentration of potassium chloride the calculated value of π_N becomes increasingly more positive. The effect of diminishing the hydrochloric acid concentration cannot be attributed to hydrolysis of the indium salt, as this should make the deposition potential more, and not less, negative.

It appears from these results that both potassium chloride and hydrochloric acid, since they make the potential more negative, diminish the activity of the indium ions. The effect of higher concentrations of hydrochloric acid is shown in Table III. In

TABLE II.

Constant concentration of $InCl_3 = 1{\cdot}15 \times 10^{-4}$ *M*.

Solution.	*E*.	π_0.	π'.	π_N.
0·01 *M*-HCl	0·6521	+0·096	–0·556	–0·481
0·004*M*-HCl		Turning point indistinct.		
0·001*M*-HCl		No turning point observable.		
0·1 *M*-KCl 0·001*M*-HCl	0·6128	+0·0488	–0·564	–0·489
0·01 *M*-KCl 0·001*M*-HCl	0·6483	+0·098	–0·550	–0·475
0·05 *M*-KCl 0·001*M*-HCl	0·6445	+0·116	–0·529	–0·454
0·001*M*-KCl 0·001*M*-HCl		No turning point observable.		

these strongly acid solutions the liquid junction potential became of more importance. The results from which the calculated values of π_N are placed in col. *a* were obtained when a saturated potassium chloride solution was used in measuring the anode potential, whilst those carried into col. *b* were obtained by using saturated and half-saturated solutions and applying the Bjerrum extrapolation method.

TABLE III.

					π_N.	
$c \times 10^5$.	HCl, *N*.	*E*.	π_0.	π'.	*a*.	*b*.
105	0·3	0·5903	+0·0218	–0·5685	–0·512	—
			+0·0256	–0·5647	—	–0·508
11·5	0·4	0·5958	+0·0064	–0·5894	–0·515	—
			+0·0194	–0·5146	—	–0·502
11·5	0·5	0·6013	–0·0010	–0·6023	–0·528	—
1050	1	0·5509	–0·0288	–0·5797	–0·542	—
			–0·0192	–0·5701	—	–0·533
105	1	0·5684	–0·0290	–0·5974	–0·541	—
			–0·0208	–0·5892	—	–0·533
10·5	1	0·5846	–0·0370	–0·6216	–0·546	—
			–0·0330	–0·6176	—	–0·542
1·05	1	0·6068	–0·0394	–0·6462	–0·552	—
			–0·0338	–0·6406	—	–0·546
105	3	0·5193	–0·0954	–0·6147	–0·558	—
			–0·0758	–0·5951	—	–0·539
10·5	3	0·5385	–0·1060	–0·6445	–0·569	—
			–0·0904	–0·6289	—	–0·553
1·05	3	0·5594	–0·1028	–0·6622	–0·569	—
			–0·0852	–0·6446	—	–0·550

It will be seen from Table III that the effect of increasing the hydrochloric acid concentration is to make the value of the normal deposition potential more negative, *i.e.*, to decrease the activity of the indium ions. This is in agreement with the results obtained by diminishing the hydrochloric acid concentration (Table II). It is possible that the addition of hydrochloric acid (or of potassium chloride) to the indium trichloride solution tends to produce anionic complexes containing indium, and thus to reduce the concentration of the simple indium kations.

The Influence of Sulphate Ions.—Some experiments were made in the presence of zinc sulphate, in order to test the applicability of the present method to the detection of indium in metallic zinc. These results are shown in Table IV. It is noteworthy that in the presence of 0·045M-zinc sulphate and 0·01M-hydrochloric acid, the turning point entirely disappears from the polarisation curve of a 1·31 × $10^{-4}M$-indium chloride solution, but reappears when the hydrochloric acid concentration is increased to 0·1M. In the latter case the normal deposition potential agrees well with that found in a solution containing only 0·1M-hydrochloric acid (in addition to the indium chloride). It will also be observed from the table that potassium sulphate acts similarly to zinc sulphate. The disturbing effect is therefore due to the sulphate ion, which, in the presence of an insufficient concentration of hydrogen ions, appears to remove indium ions, probably in the form of a basic salt. In the 1·31 × 10^{-3} M-solution of indium chloride, however, the turning point was obtained even in the presence of 0·045M-zinc sulphate and 0·01M-hydrochloric acid, and the corresponding normal deposition potential agreed well with that of a solution of the same composition in the absence of zinc sulphate.

TABLE IV.

$\times 10^5$.	Solution.	E.	π_0.	π'.	π_N.
131	0·045M-$ZnSO_4$ 0·01 M-HCl	0·6377	+0·0986	−0·539	−0·484
13·1	0·05 M-$ZnSO_4$ 0·001M-HCl	No turning point for indium.			
13·1	0·045M-$ZnSO_4$ 0·01 M-HCl	No turning point for indium.			
13·1	0·045M-$ZnSO_4$ 0·1 M-HCl	0·6278	+0·0524	−0·575	−0·501
1·31	0·045M-$ZnSO_4$ 0·1 M-HCl	0·6437	+0·0532	−0·590	−0·497
11·5	0·05 M-K_2SO_4 0·001M-HCl	No turning point for indium.			
11·5	0·045M-K_2SO_4 0·01 M-HCl	No turning point for indium.			
11·5	0·045M-K_2SO_4 0·1 M-HCl	0·6274	+0·0534	−0·574	−0·500

Estimation of Indium in Metallic Gallium.—The sample of gallium was obtained from Messrs. Adam Hilger, Ltd. From the results of chemical and spectrographic analysis it was reported to contain 0·8% of indium. 0·1227 G. of this metallic gallium was dissolved in hydrochloric acid so as to yield 10 c.c. of a solution of the chloride in 0·1M-hydrochloric acid. When this solution was electrolysed with the dropping-mercury cathode, the turning points corresponding to the indium ion and the hydrogen ion were obtained on the current–voltage curves. Since the deposition potential of gallium is near to that of hydrogen, but more negative, no turning point due to gallium ion is observable in the acid solution. For the turning point due to the indium ion the results were as follows: $E = 0{\cdot}6167$ volt, $\pi_0 = +\ 0{\cdot}0402$ volt, $\pi' = -\ 0{\cdot}5765$ volt. From the equation given on p. 302, by substitution of $\pi_N = -\ 0{\cdot}500$ and $C_N = 1$, the molar concentration of indium in the solution was found to be 0·00094. Hence the indium content of the gallium metal was 0·88%.

Summary.

1. The electro-deposition of indium at the dropping-mercury cathode from solutions of the trichloride in $0{\cdot}1M$-hydrochloric acid was found to proceed reversibly in conformity with the Nernst logarithmic equation.
2. The normal deposition potential of the indium ion in the above solution was found to be —0·500 volt, with reference to the normal calomel electrode.
3. The normal deposition potential was found to depend on the concentration of the hydrochloric acid, being more negative the higher the concentration.
4. A remarkable effect on the deposition potential due to sulphate ion was observed and investigated.
5. The present method can be applied to the detection and estimation of indium in metallic zinc and gallium. For this purpose, the metals should be dissolved in hydrochloric acid and the free acid concentration should be $0{\cdot}1M$. The minimum concentration of indium chloride which can be detected and estimated in this manner is 10^{-5} mol. per litre.
6. The deposition potential of gallium cannot be determined in acid solutions.

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