

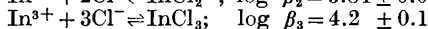
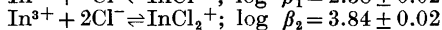
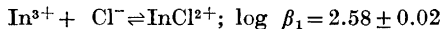
On the Complex Formation Equilibria Between Indium(III) and Chloride Ions

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The complex formation equilibria between indium(III) and chloride ions have been studied at 25°C by measuring with emf methods the $[\text{In}^{3+}]$ and the $[\text{Cl}^-]$ of solutions where the total molarity was kept at the 3 M level by the addition of NaClO_4 . The indium concentration of the test solution, B , was varied between 5×10^{-4} and 1.5×10^{-2} M, and for each level of B the chloride ion concentration, A , was increased stepwise to 0.3 M.

The $[\text{In}^{3+}] = f(A)_B$ as well as the $[\text{Cl}^-] = f(A)_B$ data can be explained by assuming the equilibria



No evidence has been found for the formation of indium bearing species containing more than three chloride ions.

Previously reported data on indium chloride complex formation equilibrium have been subjected to a critical examination.

This publication summarizes the first part of an investigation undertaken to ascertain the hydrolysis equilibria of the indium chloride complex species. The hydrolysis equilibria of the chloride complexes have been studied¹¹ by determining at a series of acidity levels the apparent chloride complex formation constants of the indium ion. In order to interpret these data in terms of true ionic species, the hydrolysis equilibria of the free (hydrated) In^{3+} ion, as well as the chloride complex formation equilibria at acidities where the hydrolysis is negligible must be known. The former have previously been examined¹ in this laboratory at 25°C in the ionic medium 3 M NaClO_4 , and it was decided that identical experimental conditions be used for the study of complex formation.

LIST OF SYMBOLS

$B = [\text{In(III)}] = \text{total indium concentration}$

$b = [\text{In}^{3+}] = \text{free indium ion concentration}$

$A = [\text{Cl}^-] + \sum n[\text{InCl}_n] = \text{total chloride concentration}$

$a = [\text{Cl}^-] = \text{free chloride ion concentration}$

$h = [\text{H}^+] = \text{hydrogen ion concentration at equilibrium}$

$Z = (A - a)/B = \text{average number of chloride ions bound per indium ion}$

$R = (B - b)/A = \text{average number of indium ions bound per chloride ion}$

METHOD OF INVESTIGATION

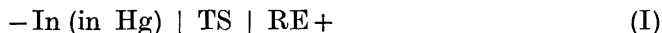
To study the complex formation the $[\text{In}^{3+}]$ and $[\text{Cl}^-]$ of a series of solutions were measured in which the total molarity was kept constant at 3 by the addition of NaClO_4 and the hydrogen ion concentration, h , was maintained at the 100 mM level. Thus all the test solutions had the general composition B mM In(III) , 100.0 mM H^+ , $(3000 - 3B - 100)$ mM Na^+ , A mM Cl^- , $(3000 - A)$ mM ClO_4^- ; this solution will be denoted in the following discussion by TS.

The value 100.0 mM was chosen for h to suppress the hydrolysis of In^{3+} without introducing the experimental complications associated with the decrease of the overpotential of hydrogen, which are inevitably encountered at substantially higher acidities.

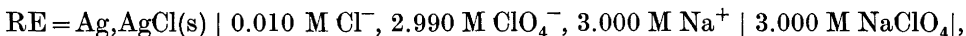
The B values studied have ranged from 5×10^{-4} to 1.5×10^{-2} M. The lower limit was set by the impurity concentration of the NaClO_4 solutions used and by the slowness of the electrode process $\text{In}^{3+} + 3e \rightleftharpoons \text{In}$ (in Hg). Because of these sources of error at $B = 0.1$ mM the indium amalgam half-cell potentials were found to drift and they were greatly influenced by the rate of stirring indicating that mixed potentials were measured. The higher limit $B = 15$ mM was chosen with the intention of avoiding an appreciable change in the activity factor of the In^{3+} ion.

Chloride concentrations up to 300 mM have been studied, the maximum value corresponds to a replacement of 10 % of the perchlorate ions by Cl^- . Data at chloride ion concentrations exceeding 100 mM were required to obtain a complete picture of the process of complex formation.

The equilibrium concentration of the indium ions, b , has been determined by measuring the emf of the cell

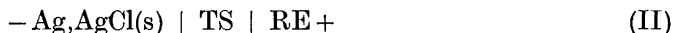


where RE is the symbol for the reference half-cell



and In (in Hg) denotes a dilute indium amalgam in which the indium concentration was kept constant throughout a series of measurements.

The chloride ion concentration at equilibrium, a , has been determined by measuring the emf of the cell



The emfs of the cells (I) and (II) at 25°C may be put into the forms

$$E_B = E_{0,B} - 19.72 \log b + E_j \quad (1)$$

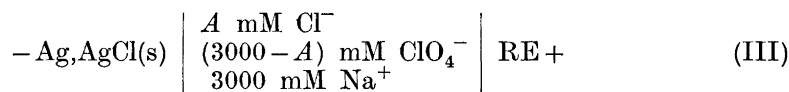
and

$$E_A = E_{0,A} + 59.16 \log a + E_j \quad (2)$$

In eqns. (1) and (2) $E_{0,B}$ and $E_{0,A}$ represent constants which have been evaluated by measuring E_B in chloride-free and E_A in indium-free solutions, and E_j is the symbol for the liquid junction potential arising between the test solutions and the 3 M NaClO₄ because of the replacement of ClO₄⁻ by Cl⁻ ions. As throughout this work h was maintained at 100.0 mM, the liquid junction potential due to hydrogen ions remains unchanged and can conveniently be incorporated into the constants $E_{0,B}$ and $E_{0,A}$. The influence of indium ions on the liquid junction potential has been supposed to be negligible for data of the present accuracy.

To test that no appreciable change in h had occurred in the series of measurements, which were carried out as potentiometric titrations, a glass electrode was also inserted into the test solution TS. In no case has a change in the glass electrode half-cell potential exceeding 0.2 mV been found.

The part of the liquid junction potential denoted by E_j was determined by measuring the emf of the cell



as a function of A in the range 10 to 500 mM.

The emf of cell (III) may be written

$$E_c = E_{0,c} + 59.16 \log A + E_j \quad (3)$$

where $E_{0,c}$ stands for a constant. This was evaluated by plotting $E_c - 59.16 \log A$ against A and extrapolating to $A = 0$. As the data could be approximated by a straight line no serious error is involved in the extrapolation. The $E_j = E_j(A)$ data have been found to fit the equation

$$E_j = -(3.8 \pm 0.2) A \text{ mV} \quad (4)$$

where A is expressed in M units. The fit is demonstrated in Fig. 1. Similar measurements previously made in this laboratory² up to $A = 0.1$ M are in complete agreement with the present data.

In each series of measurements B was kept constant while A was increased stepwise to an A/B value of at least 20. The $\log(Bb^{-1}) = f(A)_B$ and $(A - a)B^{-1} =$

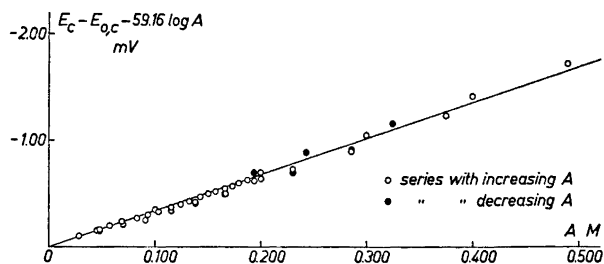


Fig. 1. The liquid junction potential (cf. eqn. 3) due to the replacement of the ClO₄⁻ by Cl⁻ ions. The data are represented by circles. The line represents the equation $-E_j = 3.80 A \text{ mV}$.

Table 1. Survey of the measurements.

The indium amalgam half-cell data

$B = 5.0 \times 10^{-4}$ M; $\log(B/b)$, $A \times 10^3$ M: 0.0675, 0.51; 0.1239, 0.99; 0.1818, 1.52; 0.2306, 2.00; 0.2742, 2.51; 0.3152, 3.00; 0.3545, 3.53; 0.3894, 3.99; 0.4226, 4.49; 0.4559, 5.01; 0.5170, 6.01; 0.5687, 6.99; 0.6198, 8.00; 0.6819, 9.36; 0.7078, 10.00; 0.7496, 10.99; 0.8182, 13.00; 0.9172, 16.00; 1.0298, 20.00; 1.1428, 24.79; 1.2519, 30.11; 1.3373, 35.01; 1.4157, 39.96; 1.4949, 45.30; 1.5654, 50.61; 1.6198, 54.97; 1.6990, 64.96; 1.8357, 74.95; 1.9282, 84.95; 2.0086, 94.96; 2.0969, 104.98; 2.1550, 115.37.

$B = 1.00 \times 10^{-3}$ M; $\log(B/b)$, $A \times 10^3$ M: 0.1225, 1.10; 0.2196, 2.09; 0.4461, 5.05, 0.6968, 10.00; 0.8827, 15.03; 0.9872, 19.88; 1.1367, 24.90; 1.2440, 30.08; 1.3373, 35.14; 1.4949, 45.21; 1.6270, 54.92; 1.7471, 65.52; 1.8447, 74.83; 1.9393, 84.92; 2.0270, 95.14; 2.1025, 105.06; 2.1741, 114.91; 2.2440, 125.02; 2.3098, 134.98; 2.3666, 144.94; 2.4203, 155.27; 2.4814, 165.10; 2.5302, 174.99; 2.5800, 184.98; 2.6270, 195.01; 2.6739, 205.01; 2.7167, 214.97; 2.7585, 225.01; 2.8013, 235.01; 2.8386, 245.00.

$B = 4.78 \times 10^{-3}$ M; $\log(B/b)$, $A \times 10^3$ M: 0.3014, 4.95; 0.5332, 9.55; 0.7277, 14.28; 1.4538, 47.84; 1.9630, 95.52; 2.0770, 109.98; 2.1741, 124.06; 2.2989, 144.28; 2.3766, 157.58; 2.4615, 172.00; 2.5329, 186.17; 2.5999, 200.63; 2.6617, 214.97; 2.7249, 229.20; 2.7760, 243.58; 2.8340, 257.87; 2.9009, 272.23; 2.9800, 300.89; 3.0770, 334.32.

$B = 4.85 \times 10^{-3}$ M; $\log(B/b)$, $A \times 10^3$ M: 0.1155, 2.00; 0.2287, 3.88; 0.3338, 5.70; 0.4270, 7.46; 0.5066, 9.11; 0.5791, 10.73; 0.6458, 12.28; 0.7543, 15.25; 0.8449, 18.05; 0.9191, 20.65; 0.9836, 23.10; 1.0647, 26.50; 1.1336, 29.63; 1.2248, 34.25; 1.3440, 41.20; 1.4152, 45.68; 1.4780, 50.00.

$B = 15.00 \times 10^{-3}$ M; $\log(B/b)$, $A \times 10^3$ M: 0.0363, 1.50; 0.0802, 3.18; 0.1219, 4.66; 0.1620, 6.03; 0.2287, 8.36; 0.2519, 8.94; 0.2993, 10.38; 0.3562, 12.10; 0.3988, 13.52; 0.4461, 14.94; 0.8780, 29.99; 1.1875, 45.12; 1.4165, 60.24; 1.5986, 74.83; 1.7578, 90.13; 1.8928, 104.93; 2.0145, 120.00; 2.1229, 135.04; 2.2219, 150.01; 2.3069, 165.01; 2.3908, 180.10; 2.4684, 195.12; 2.5426, 210.04; 2.6079, 224.97; 2.6709, 240.02; 2.7290, 255.05; 2.7959, 270.03; 2.8538, 284.98; 2.8973, 300.00; 2.9456, 315.02; 3.0000, 330.00.

The Ag,AgCl half-cell data

$B = 1.0 \times 10^{-3}$ M; Z , $-\log a$: 0.229, 3.113; 0.401, 2.796; 0.515, 2.605; 0.602, 2.469; 0.676, 2.364; 0.729, 2.278; 0.780, 2.206; 0.820, 2.144; 0.861, 2.090; 0.893, 2.041; 0.960, 1.957; 1.000, 1.921.

$B = 5.0 \times 10^{-3}$ M; Z , $-\log a$: 0.288, 2.974; 0.507, 2.608; 0.778, 2.214; 0.942, 1.988; 1.058, 1.832; 1.144, 1.715; 1.217, 1.621; 1.281, 1.544; 1.340, 1.478; 1.392, 1.420; 1.434, 1.368; 1.518, 1.281; 1.586, 1.207.

$B = 1.50 \times 10^{-2}$ M; Z , $-\log a$: 0.693, 2.336; 1.044, 1.844; 1.245, 1.580; 1.397, 1.409; 1.520, 1.277; 1.600, 1.181; 1.687, 1.099; 1.748, 1.028; 1.787, 0.966; 1.853, 0.913; 1.933, 0.821; 2.010, 1.745; 2.095, 0.680; 2.127, 0.623.

$f(\log a)_B$ data so obtained, which are collected in Table 1, will serve as the basis for the following discussion.

EXPERIMENTAL

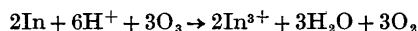
Reagents and analysis

The *indium perchlorate* stock solutions were prepared from indium metal of 99.95 % purity, kindly supplied and spectrographically examined by the Consolidated Mining and Smelting Company of Canada Ltd. Two methods were employed to prepare indium perchlorate solutions containing a small excess of perchloric acid.

In the first, previous experience¹ was followed. The metal was dissolved in 7 M HNO₃ (indium reacts very slowly with perchloric acid and at higher temperatures considerable amounts of Cl⁻ are formed), the excess of HNO₃ was removed by evaporation, and then the resulting wet material was transformed at 400°C to indium oxide, which finally was dissolved in the minimum amount of 6 M HClO₄ by heating.

The second method involved a quantitative dissolution of indium metal in a weighed amount of standardized perchloric acid, thus using this approach no analysis is needed.

A piece of indium serves as the anode in a cell which contains a platinum gauze cathode. About 1 M HClO₄ is placed in the cell vessel, and a vigorous stream of an ozone-oxygen gas mixture is passed through the solution. On passing a current of a few tenths of an ampere finely divided indium is deposited on the cathode which has proved to be oxidized rapidly by ozone:



At the end of the electrolysis the rate of this reaction steadily decreases because of the decrease in the hydrogen ion concentration, and so the current strength must be diminished. Ozone is passed through the solution until all the indium metal has dissolved, which is easy to ascertain by visual observation. In agreement with the reports of previous investigators,³ who have prepared ozone by electrolysis, no detectable amounts of platinum have been found to be dissolved in the final indium solution.

After this work had been completed, a still more rapid and convenient method was found for the quantitative synthesis of indium perchlorate solutions which is based on the reaction $\text{In} + 3\text{H}^+ + 3\text{I}^- \rightarrow \text{In(III)} + \frac{3}{2} \text{H}_2$ (in iodide solution) + $\frac{3}{2} \text{H}_2$. The procedure which can be applied to a large number of metals will be described in a forthcoming publication.⁴

The indium concentration of the stock solutions was determined gravimetrically, In³⁺ being transformed to In₂S₃. The technique recommended by Thiel and Luckmann⁵ was used in these determinations.

The perchloric acid concentration of the indium stock solutions was measured by potentiometry. An exactly known volume of a saturated solution of NaCl containing a few tenths of a mmol of hydrochloric acid was added to the test solution, so that the value of the ratio chloride per indium exceeded 10³. The resulting indium chloride solution was then titrated with a standardized NaHCO₃ solution; after each addition the hydrogen ion concentration was measured with a glass electrode. The equivalence point was calculated by a Gran-plot.⁶ In the presence of such a great excess of chloride ions the hydrolysis of In³⁺ becomes quite negligible for log *h* > -4, and consequently the equivalence point can be determined with a high accuracy. The hydrogen ion concentration of the slightly acid NaCl solution has been determined conveniently by coulometric alkalification in conjunction with a glass electrode.

NaHCO₃ solutions were prepared from chloride-free samples of Merck NaHCO₃, *p.a.* The solutions were analyzed by adding a small excess of hydrochloric acid, and then evaporating the solution slowly at 120°C. The resulting NaCl was freed of water before weighing by drying for several hours at 380°C.

HClO₄ solutions were prepared from Merck azeotropic perchloric acid of *p.a.* quality. The solutions, which were always tested for the presence of traces of iron(III), were standardized either by titration against purified samples of KHCO₃ or by coulometric analysis. The results have always been found to agree to within 0.1 %.

NaCl solutions, made from Merck sodium chloride *p.a.*, were found to contain less than 0.01 % of Br⁻ ions, as no Br⁻ ions were detectable by the eosin method.

NaClO₄ solutions were prepared and analyzed as usual in this laboratory.¹

Mercury was purified by distilling it twice at so low a partial pressure of oxygen that no HgO is formed. The oxides of the other metals present as impurities could be easily removed from the distillate by filtration. The second distillate has usually shown a completely bright surface.

Nitrogen was taken from a cylinder and freed from oxygen by passing it through activated copper. Acidic and basic impurities were removed by letting the gas slowly pass through 1 M NaOH and then a 1 M HClO₄ solution. Before introducing the gas into the test solution it was bubbled through water and 3 M NaClO₄ to attain the correct water vapour pressure.

Experimental details of the emf measurements

All the emf measurements were carried out using a paraffin oil bath maintained at $25.00 \pm 0.01^\circ\text{C}$; the bath was placed in a thermostat room kept at $25.0 \pm 0.1^\circ\text{C}$. The cell vessel described by Forsling, Hietanen and Sillén⁷ was employed. The E_B and E_A values were determined with a Dynamco Ltd. digital voltmeter, type DM2022, which has been found to have an input impedance quite sufficient for the present purpose. Both the amalgam and the silver cells were found to attain a few minutes after each addition of a reagent solution an emf value which remained constant for 24 h within the precision of the instrument, ± 0.02 mV.

Indium amalgams for the study of solutions containing more than 5 mM indium(III) could be prepared by electrolysis in the test solution itself.

A weighed amount of mercury was introduced into a vessel which was connected to both the reference half-cell RE and the anode compartment of an electrolysis cell. Next the test solution was added and was freed of oxygen by passing purified nitrogen through it for a few hours. Then the mercury pool was made the cathode of the electrolysis cell, and indium was deposited by a current of 1 mA, until the indium concentration in the amalgam attained 0.01 wt. %. The exact number of μF employed could be calculated from the duration of the electrolysis, as the current level was kept constant to within 0.01 % by an electronically regulated current supply. A glass electrode inserted into the test solution indicated that the current efficiency of the reduction of In^{3+} was 100.0 %. The amount of indium removed from the test solution has, of course, been taken into account when the functions $\log(B/b)$ and $(A-a)B^{-1}$ were calculated. The volume changes occurring due to electrolysis have been estimated to be negligible. In each series of measurements two amalgam pools were prepared, which always have been found to yield potentials not differing by more than 0.02 mV.

Unfortunately, a current efficiency of 100 % could not be obtained with reasonable current strengths in the most dilute indium solutions. In this case, an amalgam of 0.01 % indium was prepared by electrolysis in a vessel provided with a capillary tube. A portion of this amalgam was then rapidly introduced *via* the capillary into the test solution through an opening of the vessel, while a vigorous stream of nitrogen was made to issue from the same opening. The apparatus described by Aladjoff⁸ has also proved to be of value for the convenient transfer of amalgam.

Ag, AgCl electrodes have been prepared by electrolysis as recommended by Brown.⁹ They were often tested especially for reversibility by comparing emf data obtained with solutions in which the $[\text{Cl}^-]$ was successively decreased with data for solutions in which the $[\text{Cl}^-]$ was increased. The two sets of results agreed to within 0.02 mV. An important precaution is to work with oxygen-free solutions.

ASCERTAINMENT OF THE FORMATION CONSTANTS

The determination of the composition of the indium chloride complex species and the evaluation of the corresponding formation constants, which is the subject of the present section, is based mainly on the amalgam half-cell data, $\log b(A)_B$, summarized in Table 1. The main reason for this preference is that, as will be demonstrated below, the $\log b$ data may be directly compared with model functions. On the other hand, the $\log a(A)_B$ data can only be used for equilibrium analysis after they have been recalculated to the form $Z = (A-a)B^{-1} = Z(\log a)$, and in a considerable part of the A and the B ranges studied in this work $(A-a)$ has turned out to correspond to a small quantity. Consequently the Z data are of limited accuracy.

The calculations have been carried out in two steps. In the first preliminary values of the formation constants were estimated by a graphical method. These values were then employed as the starting point for a comprehensive numerical treatment of the experimental data.

Estimation of the formation constants by projection maps. This graphical approach, which has been previously¹² applied in this laboratory to interpret the redox potential measurements in thallium chloride solutions, was chosen as it enables us to compare the primary data with normalized¹⁰ model functions representing different hypotheses. Since the uncertainty in the primary data can be estimated reliably, we can decide whether the precision is sufficient for a given model, to be preferred. Another advantage of the method adopted is that the free ligand concentration need not be calculated explicitly.

It is assumed in the following computations that only *mononuclear* complex species are formed. The next report¹¹ will show, however, that, if necessary, polynuclear mechanisms can also be treated by the present method.

First the $\log b(A)_B$ data have been recalculated by graphical interpolation to the form $\log b = \text{function of } \log\{(B-b)b\}_R$ where the symbol R designates $(B-b)A^{-1}$, the average number of indium atoms bound per chloride ion. The result of this recalculation is illustrated in Fig. 2, (circles), for a

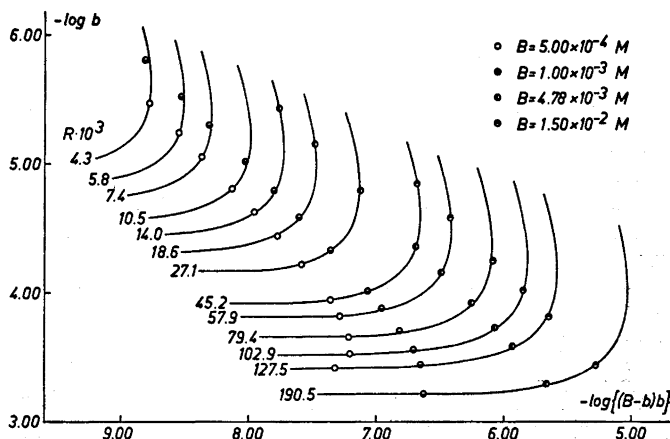


Fig. 2. Projection map of the amalgam half-cell measurements. The circles represent the data $\log b$ as a function of $\log\{(B-b)b\}$ for R levels ranging from 4.3×10^{-3} to 190.5×10^{-3} . The curves, $\log Y(\log X)_{R,\varrho}$, have been calculated with the set of the formation constants reported in the first row of Table 2.

series of R levels ranging from 0.1905 to 0.0043. Little, if any, loss of accuracy is introduced in the process of interpolation, as the experiments were designed to yield data at nearly the same R values.

The $\log b (\log\{(B-b)b\})_R$ data were then compared with model functions. These were calculated by starting from the material balance conditions

$$A = a + b \sum n \beta_n a^n \quad (5)$$

$$B = b + b \sum \beta_n a^n \quad (6)$$

where

$$\beta_n = \frac{[\text{InCl}_n^{(3-n)+}]}{b a^n}$$

denotes the formation constants of the species $\text{InCl}_n^{(3-n)+}$.

The function $R = R(a, b)$ can then be written

$$R = \frac{B-b}{A} = \frac{b \sum \beta_n a^{n-1}}{1 + b \sum n \beta_n a^{n-1}} \quad (7)$$

Let us now introduce the new variables u and v instead of b and a

$$u = \beta_1 b, \quad v = \beta_2 \beta_1^{-1} a \quad (8)$$

Making the further assumption that the maximum value of n is 3, *i.e.*, the concentration of negatively charged indium bearing species is negligible, introduction of the new variables u and v into eqns. (6) and (7) yields

$$R = \frac{u + uv + \rho uv^2}{1 + u + 2uv + 3\rho uv^2} \quad (9)$$

and

$$\log(B-b) + \log b = -\log \beta_2 + \log(u^2 v) + \log(1 + v + \rho v^2) \quad (10)$$

where ρ is the symbol for the initially unknown constant $\beta_3 \beta_1 \beta_2^{-2}$

Eqn. (9) shows that when R is kept constant and a value is chosen for the parameter ρ , then v becomes a function of u only, $v = v(u)_{R, \rho}$ which can be calculated by assuming a series of numerical values for u . Once $v = v(u)_{R, \rho}$ has been obtained, we can evaluate the appropriate model function $\log Y$ ($\log X$) $_{R, \rho}$ where

$$\log Y = \log u \quad \text{and} \quad \log X = \log(u^2 v) + \log(1 + v + \rho v^2) \quad (11)$$

Comparison of eqns. (11) with eqns. (10) and (8) shows that the family of curves $\log Y(\log X)_{R, \rho}$ differs from the set of $\log b(\log\{(B-b)b\})_R$ data only by the constants $\log \beta_1$ and $-\log \beta_2$. Hence on superimposing the $\log Y(\log X)_{R, \rho}$ curves on the data they can be made to coincide by vertical and lateral translations provided a correct value has been chosen for ρ . The probable values of $\log \beta_1$ and $\log \beta_2$ can be estimated by reading off the differences $\log Y - \log b$ and $\log X - \log\{(B-b)b\}$ in the position of the best fit.

The result of such a comparison is illustrated in Fig. 2 which shows the closest agreement that could be achieved. The family of $\log Y(\log X)_{R, \rho}$ curves in this figure was calculated with $\log \beta_1 = 2.58$, $\log \beta_2 = 3.81$, and $\log \beta_3 = 4.2$; these values may be regarded as the first estimates of the formation constants. The uncertainties in $\log \beta_1$ and $\log \beta_2$ given in the first row of Table 2 were obtained on the basis of the latitude of the translation which still yielded an acceptable agreement with the data represented by circles of a diameter corresponding to the experimental uncertainty ± 0.02 mV in E_B .

To assign an uncertainty to $\log \beta_3$ a great number of $\log Y(\log X)_{R, \rho}$ plots have been prepared in which $\log \rho$ has been varied in small steps. A difference of 0.1 unit in $\log \rho$ was found to give rise to a deviation exceeding by far the experimental uncertainty. Not much time was used, however, to calculate this series of curves since they could be easily calculated with a high speed digital computer.

Table 2. Survey of the values of the formation constants.

Method	$\log \beta_1$	$\log \beta_2$	$\log \beta_3$
Normalized projection maps	2.57 ± 0.02	3.81 ± 0.02	4.2 ± 0.1
Letagrop	2.58 ± 0.01	3.84 ± 0.01	4.25 ± 0.02
Proposed values	2.58 ± 0.02	3.84 ± 0.02	4.2 ± 0.1

LEAST SQUARE TREATMENT OF THE DATA BY LETAGROP

There are several reasons to test the validity of the conclusions reached by employing the projection maps with a powerful numerical method.

First it is difficult, though possible, in the graphical approach of the preceding section to take into account more than three reaction products. The hypothesis that in the most concentrated chloride solutions negatively charged indium bearing species might also be present in appreciable amounts, which consequently had been overlooked in the graphical treatment, must be tested.

Moreover, the uncertainty in the $\log b(A)_B$ data was assumed in the foregoing calculations to be due entirely to the uncertainty in the indium amalgam half-cell potential measurements, which was estimated to amount to ± 0.02 mV. A number of other sources of errors, however, such as slight analytical inconsistencies, accidental contamination of the test solutions and an eventual uncertainty in the $E_{0,B}$ determination must also be considered. The last of these seems especially important, as the $E_{0,B}$ value was calculated on the basis of a single emf determination.

The least square computations were performed using the most recent version of the Letagrop program described by Sillén and Warnqvist.¹² In each phase of the treatment reported below, the sum $U = \sum (E_{B,C} - E_B)^2$ has been minimized, where $E_{B,C}$ denotes an emf value for cell(I) calculated with a certain set of assumed formation constants and $E_{0,B}$ values.

In the first instance the results obtained with the projection maps have been checked by postulating the presence of InCl_2^{2+} , InCl_2^+ and InCl_3 as well as the correctness of the $E_{0,B}$ values. The $\log \beta_n$ values yielding a minimum for U have been found to agree to within 0.03 units with those derived graphically.

Next, a search was made for the species InCl_4^- . No positive value for β_4 could, however, be found which would furnish a U value smaller than the U_{minimum} obtainable with the three constants β_1 , β_2 , and β_3 . Thus the data of the present precision do not afford evidence for the formation of appreciable amounts of negatively charged complex species.

In the last step, in addition to the three formation constants the individual $E_{0,B}$ values were also taken as variables. The minimum error square sum

under these conditions has been found with the same set of the β_n 's as previously, but some of the $E_{0,B}$ values became adjusted. In no case has the correction for $E_{0,B}$ proved to exceed 0.2 mV. Since the corrections are negative they can probably be explained by accidental contamination of the starting solution yielding a $[\text{Cl}^-]$ of a few tenths of a μM .

The final results of the Letagrop computations are summarized in Table 2 and they are illustrated in Fig. 3. As Table 2 indicates the projection map and

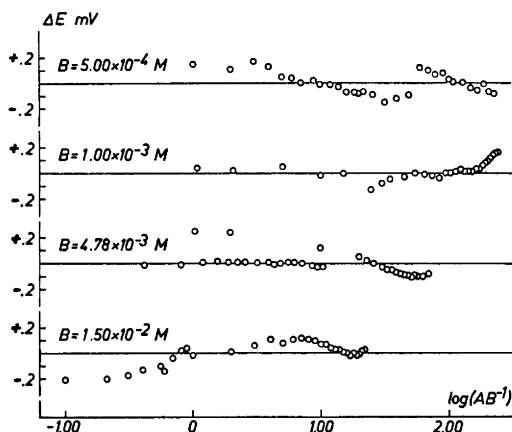


Fig. 3. The difference, ΔE , between the emf values calculated with the proposed set of the formation constants of Table 2 and the measured emf values as a function of the ratio $[\text{Cl}^-]_{\text{tot}} [\text{In(III)}]^{-1}$ for different levels of $[\text{In(III)}]$.

the least square calculations furnish practically coincident values for the formation constants. The uncertainties estimated graphically represent maximum errors, while the uncertainties given by the Letagrop refer to 99 % confidence limit.

The deviations between the emf data and the emf values calculated with the set of formation constants, and of the $E_{0,B}$ parameters giving the minimum error square sum, are graphically represented in Fig. 3. Of the 128 amalgam data, the deviation ($E_{B,C} - E_B$) is positive for 64 points, while for 53 points it is negative; the deviation for 11 points is less than 0.01 mV. The average positive deviation amounts to 0.07 mV which coincides with the average negative deviation. The magnitude of the average deviation does not significantly exceed the estimated experimental uncertainty of the $\log b$ determination corresponding to 0.04 mV.

We may thus conclude that the $\log b(A)_B$ data of Table 1 are quite satisfactorily explained with the formation constants given in Table 2.

Comparison of the $[\text{Cl}^-]$ measurements with the amalgam half-cell data. For the reasons set forth in the introductory part of this section the $\log a(A)_B$ data of Table 1 have not been employed for the evaluation of the formation constants. The main interest has instead been devoted to the question

to which extent the $[\text{Cl}^-]$ measurements agree with the conclusions derived from the amalgam data.

Fig. 4 shows the $\log a(A)_B$ data recalculated to the form $Z = (A - a)B^{-1} = Z(\log a)$ for each of the three B levels studied: 1, 5 and 15 mM. The uncertainty of the Z values – represented by the diameter of the circles of Fig. 4 – has

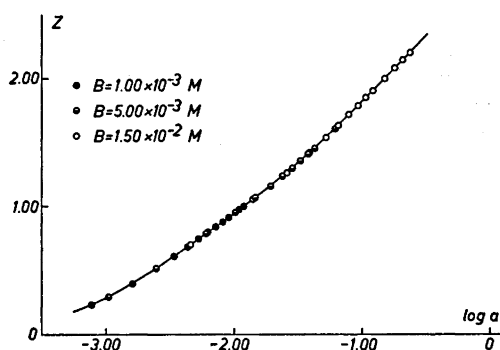


Fig. 4. Measurements with the Ag,AgCl half-cell. The average number of chloride ions bound per indium atom, Z , as a function of $\log[\text{Cl}^-]$. The data are represented by circles; the curve has been calculated with the proposed set of the formation constants of Table 2.

been estimated with the equation $dZ = a \times 10^{-3}/B$, by assuming the uncertainty of the E_A and $E_{0,A}$ determinations to amount to 0.03 mV. The full-drawn curve illustrates the $Z(\log a)$ function calculated with the proposed set of the constants in Table 2 which are based entirely on the amalgam measurements.

Fig. 4 demonstrates the excellent consistency of the two sets of independent data. It is worth emphasizing that this result could be achieved only by taking into account the quite considerable liquid junction potential term of eqn. (2) when calculating the value of a .

The consistency implies that no serious error was made by neglecting in eqn. (1) the variation of the activity factor of the In^{3+} ion, $f_{\text{In}^{3+}}$, due to the replacement of ClO_4^- by Cl^- . Since the chloride ion concentration was increased to 300 mM, while the chosen levels of $[\text{In(III)}]$ did not exceed 15 mM, the value of $f_{\text{In}^{3+}}$ might have been expected¹⁹ to be more affected than f_{Cl^-} . Probably the variation of both $f_{\text{In}^{3+}}$ and f_{Cl^-} are, under the present experimental conditions, negligible compared with the uncertainty of the measurements.

The agreement shown in Fig. 4 thus provides additional evidence for the great practical value of the ionic medium method.

COMPARISON WITH PREVIOUS INVESTIGATIONS

In the last twenty years the complex formation equilibria between indium and chloride ions have been studied by a number of investigators who have employed a variety of approaches.

The most comprehensive work on this subject was carried out by Sundén, who in 1954 published a series of reports¹³ giving closely agreeing values for the formation constants, valid at 20°C and in a 2 M NaClO₄ medium, derived on the basis of potentiometry, of a solvent extraction study and of an investigation of adsorption equilibria on a cation exchange resin. Sundén obtained the highest precision in his indium metal half-cell measurements, and he explained the emf data covering the *B* range 10 to 40 mM by assuming $\log \beta_1 = 2.15$ and $\log \beta_2 = 3.59$. Thus, in contrast to the results of the present work, Sundén found in his solutions, in which the chloride ion concentration was increased to 0.5 M, no evidence for the formation of the species InCl₃. This serious discrepancy led the present author to undertake a recalculation of Sundén's $\log b(A)_B$ data.

Comparison of these data with normalized projection maps of the type described in a previous section has clearly indicated, that in order not to exceed deviations greater than 0.3 mV (which is the precision of the emf measurements according to Sundén) the formation of the species InCl₃ must

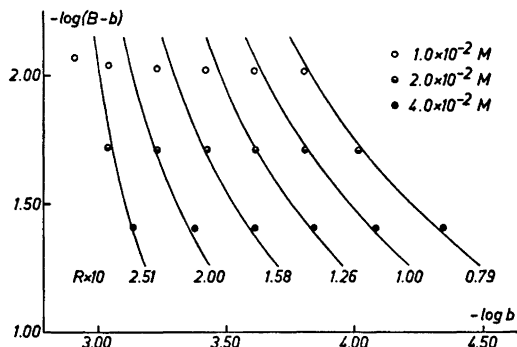


Fig. 5. Recalculation of Sundén's measurements with indium metal half-cells. The circles represent Sundén's data in the form $\log(B-b)$ as a function of $\log b$ at *R* levels ranging from 0.079 to 0.251. The curves, $\log Y(\log X)_{R,\rho}$ have been calculated assuming $\log \beta_1 = 2.43$, $\log \beta_2 = 3.43$, and $\log \beta_3 = 3.59$.

also be taken into account. The best agreement, which is illustrated in Fig. 5, has been attained by assuming the following values for the formation constants

$$\begin{aligned} \log \beta_1 &= 2.43 \pm 0.05, \quad \log \beta_2 = 3.4 \pm 0.1 \\ \log \beta_3 &= 3.6 \pm 0.2; \quad 20^\circ\text{C}, \quad 2 \text{ M NaClO}_4^- \end{aligned} \quad (12)$$

Using the constants of eqn. (12) the emf values were computed and they were compared with the data;¹³ it was found that the average deviation, $E_{\text{calc.}} - E_{\text{obs.}}$, amounts to 0.3 mV. Of the 32 points, 19 show negative deviations and 12 positive, the average of both is 0.3 mV. On the other hand assuming the values for the formation constants proposed by Sundén the average deviation was calculated to be as much as 1.4 mV.

The difference between the magnitudes of the constants of (12) and those of Table 2, may be ascribed to the difference in temperature and total molarity.

The recent work of Ryhl¹⁴ has shown the formation of indium chloride complex species to be an endothermic process, hence the $\log \beta$ values at 25°C must be higher than at 20°C.

Carleson and Irving's¹⁵ accurate study of cation exchange resin equilibria, made at 20°C and in a 0.7 M HClO₄ medium, has furnished the values $\log \beta_1 = 2.36$, $\log \beta_2 = 3.64$ and $\log \beta_3 = 3.95$. These are in quite satisfactory agreement with the present results. Evidently, if the experimental conditions are correctly chosen, their method is capable of providing a quantitative explanation for successive mononuclear equilibria.

Fridman *et al.*¹⁶, in connection with an investigation of mixed complex formation, employing polarography and indium amalgam half-cells, have also evaluated the chloride formation constants $\log \beta_1 = 2.26$, $\log \beta_2 = 2.50$, and $\log \beta_3 = 3.55$, which are valid in 4 M NaNO₃ medium at 25°C. Complex formation between indium and nitrate ions is likely to be the main reason for the considerable lower values found by these authors for the formation constants than those derived in the present work.

White *et al.*¹⁷ as well as Marcus and Maydan¹⁸ have studied distribution equilibria between indium chloride solutions and liquid ion exchangers. Marcus and Maydan have moreover also studied equilibria with a cation exchange resin. Although the main intention of both groups of investigators was to ascertain the composition of the negatively charged indium-bearing ions predominating in concentrated chloride solution, they have also derived equilibrium constants involving positively charged and neutral indium species. Their conclusions, however, deviate considerably from the present results. A satisfactory explanation for this discrepancy is made difficult by the lack of experimental details.

A careful investigation of the experimental conditions required to bring potentiometry and distribution methods to agreement would be of great service for the further development of equilibrium analysis.

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