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REVIEW

The electrochemistry of indium

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1. Nature of indium metal and its ions

Indium was discovered in 1863 by F. Reich and T. Richter; it does not occur in the native state. Indium is most frequently associated with zinc, and is recovered commercially from zinc residues and smelter slags. These by-products constitute the main commercial sources of indium. For preparative details the reader is referred elsewhere [1].

Indium is a silvery white metal with a brilliant metallic lustre, similar in colour to platinum. It is softer than lead and is malleable, ductile and crystalline. Indium is less volatile than zinc or cadmium, but sublimes when heated in hydrogen or in a vacuum. The molten metal wets clean glass.

Table 1 shows relevant properties.

Table 1. *General properties of indium [1]*

Crystal structure	Face-centred tetragonal $a_0 = 4{\cdot}583$ Å, $c_0 = 4{\cdot}936$ Å
Density at 293 K (g cc^{-1})	7·31
Specific heat at 293 K (cal g^{-1} K^{-1})	0·057
Melting point	429·5 K
Boiling point	2273 ± 10 K
Coefficient of linear expansion at 293 K	33×10^{-6} per K
Thermal conductivity (cal cm^{-2} cm^{-1} K^{-1} s^{-1})	0·057
Electrical resistivity (ohm-cm)	
3·38 K	Superconducting
293 K	9×10^{-6}
429·5 K (melting point)	29×10^{-6}
573 K	36×10^{-6}
873 K	44×10^{-6}
Temperature coefficient of resistance	0·00498 per K
Standard electrode potential (V)	~ −0·34
Magnetism	Diamagnetic

2. Chemical properties

The ionization potentials for the three valence electrons of indium are approximately 5·8 (5 p), 18·8 (5 s) and 27·9 (5 s) V. These values indicate that the trivalent form of indium is relatively covalent in its bond-forming character, which is borne out by the chemical and electrochemical behaviour of the element.

The standard potential of the reaction $In^{3+} + 3e = In$ is approximately −0·34 V. However the bonding characteristics of indium influence the apparent reactivity of the metal, for the relative slowness of chemical reactions involving indium make the metal appear less reactive than might be expected from free energy considerations.

Indium dissolves very slowly in cold dilute mineral acids and more rapidly in hot dilute or concentrated acid. It is not attacked by boiling water or alkalis. Finely divided indium reacts to form the hydroxide on contact with water.

Indium is resistant to corrosion in air at room temperature. It retains its bright appearance to a little above its melting point, but at higher temperatures it oxidizes to the trioxide.

Indium most nearly resembles tin in behaviour in aqueous acids; for example it is not very corrosion resistant, particularly in the presence of dissolved oxygen. Being very slightly amphoteric, however, the metal shows excellent resistance to the action of alkaline solutions.

Indium has been successfully electroplated onto a number of metals, including lead, zinc, copper, cadmium, tin, precious metals and iron. The most promising electrolytes are cyanide, sulphate, fluoborate and sulphamate. The metal can also be deposited on cold surfaces by vacuum evaporation.

The only ion stable in aqueous solution is the In(III) ion. However, univalent indium has been prepared but reacts to form In(III). The iodide is the most stable univalent indium species. There has been controversy about the existence of In(II) but up to the present time there is little concrete evidence for its existence.

3. Equilibrium studies

The In^{3+} ion in aqueous solution is hydrolysed to some extent. Seward [2], as a result of early pH measurements, concluded that indium sulphate solutions show a considerable degree of hydrolysis. Moeller [3, 4] calculated degrees of hydrolysis of the In^{3+} ion as high as 0·35 in 0·005 M $InCl_3$ solution and found that at pH 3·42 precipitation of a hydrated oxide (hydroxide) could be detected in solution. Just prior to precipitation solutions had a certain degree of colloidal character. Rossotti and Rossotti [5] have used a radioactive technique to determine the hydrolysis constants of the In^{3+} ion in aqueous solution. Values of hydrolysis constants

$$[InOH^{2+}]\,[H^+]/[In^{3+}] = 10^{-4{\cdot}4}$$

$$[InOH_2^+]\,[H^+]/[In^{3+}] = 10^{-8{\cdot}8}$$

were obtained, in good agreement with the earlier quantitative work of Biedermann [6]. Stepwise equilibria in complex solutions have been examined by Carleson and Irving [7]. As a result of experiments using radioactive indium the existenceof the complex species InA^{2+}, InA_2^+ and InA_3 were established (where A is Cl^-, Br^-, I^-). The stability constants ($K_1 > K_2 > K_3$) decreased in the order $Cl > Br > I$. Ferri [8] has recently critically studied the complex formation equilibria between In(III) and chloride ions by an e.m.f. method. In these experiments the total molarity was kept at the 3 M level with $NaClO_4$. The experimental data fitted the equilibria

$$In^{3+} + Cl^- \rightleftharpoons InCl^{2+}; \quad \log\beta_1 = 2{\cdot}58 \pm 0{\cdot}02$$

$$In^{3+} + 2Cl^- \rightleftharpoons InCl_2^+\,; \quad \log\beta_2 = 3{\cdot}84 \pm 0{\cdot}02$$

$$In^{3+} + 3Cl^- \rightleftharpoons InCl_3\,; \quad \log\beta_3 = 4{\cdot}2 \pm 0{\cdot}1.$$

Species containing more chloride ions than three were not detected.

The solution equilibria present when indium(III) salts are dissolved in water are therefore quite complex and the hydrolysis reactions of the type studied by Moeller [3, 4] are more complicated than originally assumed. Thus Biedermann *et al.* [9] have studied the hydrolysis equilibria of In(III) in 3 M chloride solution. The data fitted the equilibria

$$In^{3+} + H_2O \rightleftharpoons InOH^{2+} + H^+ \quad \log k_{a1} = -6{\cdot}9 \pm 0{\cdot}1$$

where k_{a1} is the equilibrium constant for the reaction

$$2In^{3+} + 2H_2O \rightleftharpoons In_2(OH)_2^{4+} + 2H^+;$$

$$\log\beta_{22} = -10{\cdot}1 \pm 0{\cdot}1.$$

The work, however, indicated that species denoted by '$InOH^{2+}$' and '$In_2(OH)_2^{4+}$' are in reality mixed $Cl^- - OH^-$ complexes. This is in agreement with the recent work of Ferri [10] who studied the hydrolysis equilibria of the indium chloride complex species, $InCl^{2+}$ and $InCl_2^+$ at 25°C, by measuring the $[In^{3+}]$ with the indium amalgam half-cell as a function of the chloride ion concentration, the measurements being made at a series of $\log[H^+]$ levels ranging from $-2{\cdot}69$ to $-3{\cdot}38$. Test solutions were made to contain a total molarity of 3 M by adding $NaClO_4$. The e.m.f. data, which indicated that only a small part of the indium chloride complexes could be transformed to hydrolysis products before precipitation occurs, were explained by assuming the equilibria

$$InCl^{2+} + In^{3+} + H_2O \rightleftharpoons In_2ClOH^{4+} + H^+;$$

$$\log x_{2,1,1} = -2{\cdot}3 \pm 0{\cdot}1$$

$$InCl^{2+} + H_2O \rightleftharpoons InClOH^+ + H^+;$$

$$\log x_{1,1,1} = -3{\cdot}9 \pm 0{\cdot}1$$

where the x's are corresponding equilibrium constants. On the basis of these equilibrium constants it was concluded that the main product of the hydrolysis was the species In_2ClOH^{4+}. No other mechanism involving only two chloride bearing hydrolysis products was found which would explain the data.

3.1. *The potential of the indium electrode*

The first reliable determination of the In^{3+}/In potential was that reported by Hakomori [11]. This was followed by the investigations of Hattox and De Vries [12], Kangro and Weingärtner [13], Lietzke and Stoughton [14], Covington *et al.* [15] and Hampson and Piercy [16]. The problem inherent in the determination of $E^{\ominus}$ is that at the low ionic concentration necessary for the extrapolation to zero concentration ($\gamma_{\pm} = 1$) the indium (III) ion suffers hydrolysis first to a colloidal particle and then to deposit $In(OH)_3$ (or oxide) in solution and at the electrode. Under certain conditions phase oxide at the electrode engenders an electrode of the second kind. Most of the authors [11–16] have realized this problem and ways of avoiding it generally follow Hakomori [11] in working at controlled pH. This necessarily involves a long extrapolation and ways of doing this have been discussed [16]. The final extrapolated $E^{\ominus}$ values are subject to a larger inherent error than those in most other systems [16] . A critical examination of the available data indicates preferred values for the electrode potential and other thermodynamic quantities as set out in Table 2.

Table 2. Summary of equilibrium potential data

Electrode	$E^{\ominus}$(mV)	$dE^{\ominus}/dT$(mVK^{-1})
$In^{3+} + 3e = In$	$-332{\cdot}9$	$1{\cdot}13$

The stability of lower oxidation states of indium in aqueous solution has been examined by Latimer and co-workers [17, 18]. Compounds such as InCl and $InCl_2$ or In_2Cl_4 exist. It was observed that if either of the lower oxidation state chlorides were reacted with water, a solution containing tripositive indium ions and a deposit of indium metal was obtained. This information leads one to expect that such species as In^+ and In^{2+} may exist in aqueous solutions at low concentration, even though they are unstable at high concentrations with respect to disproportionation to the metal and the In^{3+}(aq) ion. To account for these observations, Latimer [18] has taken the approximate potentials for the various indium couples to be

$$In^+ + e \rightarrow In \qquad E^{\ominus} = -0{\cdot}25\ V$$

$$In^{2+} + e \rightarrow In^+ \qquad E^{\ominus} = -0{\cdot}35\ V$$

$$In^{3+} + e \rightarrow In^{2+} \qquad E^{\ominus} = -0{\cdot}45\ V.$$

The equilibria between In^{3+}(aq) and In(m) have been investigated by Hepler *et al.* [17]. Equilibrium constants for the reactions: $2In(m) + In^{3+}(aq) = 3In^+(aq)$ and $In(m) + 2In^{3+}(aq) = 3In^{2+}(aq)$ were found to be $2{\cdot}4 \times 10^{-11}$ and $1{\cdot}9 \times 10^{-8}$, respectively. From these results the potentials were calculated:

$$In^+(aq) + e = In(m), \qquad E^{\ominus} = -0{\cdot}14\ V;$$

$$In^{2+}(aq) + e = In^+(aq), \qquad E^{\ominus} = -0{\cdot}40\ V;$$

$$In^{3+}(aq) + e = In^{2+}(aq), \qquad E^{\ominus} = -0{\cdot}49\ V.$$

Losev and co-workers [19, 20] have examined the participation of low valence ions in the equilibrium between indium and indium amalgam electrodes and aqueous indium salt solutions. Thus Losev and Pchel'nikov [20] have studied the dependence of the potential of the indium electrode on the concentration of $In(ClO_4)_3$ and of $HClO_4$. It was shown that for low acidities ($3 \times 10^{-3} - 1 \times 10^{-2}$ M $HClO_4$) the equilibrium potential followed the Nernst equation, whilst for more acid solutions, this relation was destroyed. A theoretical analysis of the origin of the potential was given for systems involving a number of successive electrochemical stages, considering unstable intermediate products capable of oxidation by the components of the solution. The results of this analysis were compared with experimental data for the indium electrode, and it was shown that unstable univalent ions apparently participate in setting up the equilibrium. For the amalgam electrode [19] a potentiostatic method was described for studying the applicability of the Nernst equation to electrodes in solution containing In^{3+} at very low concentrations. Here again, experimental data for the indium amalgam at low ion concentrations did not agree with the Nernst equation, possibly due to the participation of In^{+}.

3.2. *The double layer at the indium/aqueous solution interphase*

The double-layer capacity of indium amalgams was measured by Butler *et al.* [21] at 25°C in 0·1 M $HClO_4$ using a dropping electrode. Fourteen amalgams ranging from 0·001–64·4 mol % In were studied. Below 0·001% the capacity was identical to pure mercury; at higher concentrations, a pseudocapacity due to the dissolution of indium was observed at potentials more positive than the $In–In^{3+}$ equilibrium potential. As the concentration of indium was varied from 1–70%, the p.z.c. shifted 0·4 V more negative, the capacity-potential curve showing a corresponding shift. The capacity-surface charge curve for concentrated indium amalgams showed the same 'hump' near the e.c.m. as pure mercury. At a surface charge of $-10\,\mu C\,cm^{-2}$, the capacity varied from $15\,\mu F\,cm^{-2}$ for mercury to $20\,\mu F\,cm^{-2}$ for 64% indium amalgam. At a surface charge of $+10\,\mu C\,cm^{-2}$, the capacity of a 64% amalgam was approximately twice that of mercury at the same surface charge. The potential drop across the diffuse double layer was calculated. The influence of the diffuse double layer was found to be greater for concentrated amalgams than for mercury.

Sluyters and co-workers [22, 23] examined the double layer impedance of indium amalgams in contact with aqueous KCl and KSCN solutions. Here the specific aim of the work was to provide data for the Delahay [24, 25] – Reinmuth [22] model of charge separation for the case of specific adsorption of electroactive species. The specific adsorption of indium from 1 M KSCN followed a linear adsorption isotherm up to 0·4 m M. No specific adsorption of indium was detected from KCl solutions. The electrode reaction in 1 M KCl was not completely reversible: $K_{sh} = (6 \pm 2) \times 10^{-2}$ cm s^{-1} at the standard potential, supporting the hypothesis that adsorption of reactants makes the electrode reaction reversible. Minima in the In^{3+} limiting current were also studied. The faradaic impedance was negative at the potentials of the minima. These phenomena were explained qualitatively by a potential-dependent k_{sh}. It was proposed that k_{sh} depends exponentially on the specifically adsorbed charge, q^1, of the anions of the supporting electrolyte. This exponential dependence was verified for 0·4 m M In^{3+} in 1 M KCl at potentials near the half-wave potential.

Russian workers [26] have reported on the electrocapillary behaviour of indium amalgams containing from 0·1 to 57·5% by weight In and the adsorption of inorganic anions and surface-active organic substances on the surface of the amalgams was investigated. Introduction of indium into mercury displaced the maximum of the electrocapillary curves in the direction of negative potentials, the dependence of the maximum interfacial tension on the indium concentration passed through a minimum. With increasing negative potentials a transition occurred from positive adsorption of indium to negative adsorption.

Indium amalgam electrodes have been used to show that the rate of anion electroreduction is determined by the structure of the electrical double layer. Thus Yakovleva *et al.* [27] examined the differential capacitance of the electrical double layer on electrodes of 2% and 51% indium amalgam and calculated the surface charge densities and the potentials at the outer Helmholtz plane. It was shown that the Tafel plots corrected for the above effects for the reduction of $S_2O_8^{2-}$ and $Fe(CN)_6^{3-}$ agree well for different base-electrolyte concentrations and different amalgams.

For the case of solid indium, relatively few data have been reported. Levin and Rotinyan [28] reported a value for the p.z.c. of −0·67 ± 0·01 V (n.h.e.) obtained from capacitance minima in dilute, acidified Na_2SO_4 solution. Grigor'ev *et al.* [29] confirm that the p.z.c. lies in this region on the basis of similar measurements in NaF, $HClO_4$ and NaCl solutions. Piercy *et al.* [30] have attempted a more critical assessment of capacitance data, for KF, $NaClO_4$, KCl and Na_2SO_4 solutions, than the previous Russian workers. Of the systems studied, the indium/sodium sulphate system was the only one to show potential regions where the electrode-aqueous solution interphase was considered to be uncomplicated by adsorption or the formation of films. The p.z.c. for this system was estimated to be −0·95 ± 0·02 V (SCE). It was not possible to determine unequivocally the p.z.c. for indium in fluoride electrolytes, although a well-defined capacitance minimum occurred at −0·93 ± 0·02 V (SCE) in dilute fluoride solutions. For unacidified chloride and perchlorate electrolytes a well-defined capacitance minimum was not observed as the ionic concentration was lowered. In unacidified solutions of KF and $NaClO_4$ at high ionic concentrations, the anodic rise in electrode capacitance due to lattice oxidation was suppressed due to the irreversible formation of highly insoluble films at the electrode surface. A pseudocapacitance peak at −0·90 V (SCE) in KF solutions, −0·90 V (SCE) in $NaClO_4$ solutions and −0·95 V (SCE) in KCl solutions was concluded to be due to OH^- ion interaction with the indium electrode surface and subsequent dissolution of the metal lattice. The concentration of solution soluble indium species in equilibrium with the electrode at the capacitance peak was calculated to be $7 \cdot 0 \times 10^{-6}$ $mol\,l^{-1}$ for the fluoride system and $1 \cdot 7 \times 10^{-5}$ $mol\,l^{-1}$ for the chloride case (1 $mol\,l^{-1}$, unacidified solutions) at these peak potentials.

The indium/aqueous nitrate ion interphase is of great interest [31]. Oscillations of potential occur in the region −1·2 to −1·5 V (SCE). A number of mechanisms for this behaviour have been postulated [31], however there is no doubt that the reduction of NO_3^- to NO_2^- is involved.

4. The polarography of indium

The work of Heyrovsky [32], Takagi [33], Tomes [34] and Lingane [35] has formed the basis for the polarographic analysis of indium. Lingane [35] observed that the aquoindic ion present in perchloric acid solutions was irreversibly reduced to produce an extended wave (half-wave potential is −0·95 V versus SCE). The wave showed a pronounced maximum suppressed by methyl red or gelatin. When chloride or iodide was added, the wave shifted to a more positive value, becoming steeper and better-defined because of the formation of chloro-complex ions of the In^{3+} ion which are reduced more reversibly than the aquoindic ion. In 0·1 and 1 M potassium chloride the half-wave potentials were reported to be, respectively, −0·561 and −0·597 V versus SCE, and the slope at the foot of the wave corresponded closely to a reversible 3-electron reduction.

In 1 M potassium chloride the diffusion current is well-defined for about 0·3 V beyond the half-wave potential, then decreases markedly, exhibiting a minimum at about −1·4 V, and then rises to its initial value just before the final current rise. When methyl red is added the minimum is first decreased, but with larger amounts of the dye it becomes a maximum. Large concentrations of sulphate ion greatly suppress the diffusion current. The most satisfactory diffusion current is obtained in 0·1 M potassium chloride in the presence of a small amount of gelatin.

Salient data are summarized in the following table pertaining to the cathodic reduction.

Species	*Medium*	*$E_{\frac{1}{2}}/V$ (SCE)*
$In^{3+}.aq$	$HClO_4$; H_2SO_4; HNO_3	−1·0
$InCl_x^{(3-x)+}$	1 M KCl	−0·61
$InBr_x^{(3-x)+}$	1 M KBr	−0·579
$InI_x^{(3-x)+}$	1·3 M KI	−0·56

Other workers [36] have investigated the polarography of indium from which it is clear that anion effects, particularly in the cases of halide and thiocyanate, are important in the behaviour of the indium ion at the DME (see also Sections 4, 7 and 5·5). The reader is referred to the original papers [36]. For complexes of indium, Tuck *et al.* [37] conclude that the polarographic reduction takes place in successive one-electron steps. This is supported by Inai [38] who claimed that In^{2+} developed a well-defined reversible wave at −0·57 V (SCE) in 2 M acetic acid. At lower acetic acid concentration a second irreversible wave was obtained at −1·05 V. The reactions

$$In^{3+} + e = In^{2+} \qquad (1)$$

$$2In^{2+} = In^{3+} + In^{+} \qquad (2)$$

$$Hg + In^{+} + In^{2+} = In^{3+} + In(Hg) \qquad (3)$$

were invoked to explain the kinetics. The accelerating effect of Cl^- was apparent in Reactions 2 and 3. Russian workers [39] agree that the Cl^- ion has an accelerating effect upon the polarographic reaction of In^{3+} which displaces the polarographic waves to more negative potentials and sharply increases the height. Additional waves have been ascribed by other workers to basic salt formation [40] and also to the formation of complex ions. Thus in sulphuric acid solution Aksel'rud [41] found that the formation of complex ions accounted for the displacement of the reduction curve for In^{3+} in H_2SO_4 ($\sim -1{\cdot}0$ V). The ion involved was apparently $[In(SO_4)_2]^-$.

The influence of temperature on polarographic waves has been studied [42]. The temperature coefficients, $dE_{\frac{1}{2}}/dT$, for solutions containing indium chlorides, have been obtained. For indium $E_{\frac{1}{2}}$ ($-0{\cdot}615$ V) was found to have a temperature coefficient of 5×10^{-4} V K^{-1}. Diffusion currents become more prominent at higher temperature.

5. The mechanism of the exchange reaction at the indium electrode

The In^{3+}/In electrode reaction involves a 3-electron charge-transfer and this transfer is not likely to occur in 1-step. This is clear from the work of many groups. For example [43–45], for the electrochemical dissociation of In(Hg), Kozin *et al.* [43] have claimed that the limiting step of the process is the loss of the first electron and In^{3+} ions are formed as a result of a secondary disproportionation reaction involving the In^+ ions. For the metal, Kiss *et al.* [44, 45] found that the oxidation of indium at a rotating disc occurred in stages, the rate of the first process being larger than the succeeding processes. Later work with a ring-disc assembly indicated that the reduction of In^{3+} occurred in one-electron steps, the rate-determining reaction depending on the release of the second electron. These examples typify the complicated nature of the reaction, for convenience the reported work is reviewed by anion type.

In only relatively few electrolytes has the In^{3+}/In exchange been studied. Of these, perchlorate-supported electrolytes have formed the majority of the systems investigated for both solid and amalgam electrodes. To some extent the results of experiments with amalgam and solid electrodes are similar. However, in the interests of scholarship and completeness, the two types of electrode will be considered separately.

5.1. *Perchlorate electrolytes*

5.1.1. *Amalgam electrodes* Straumanis and Martin [46] reported that for the anodic dissolution of indium amalgams In(I) could not be found in the solution phase. However Budov and Losev [47] concluded, from a study of the electrode processes on an indium amalgam using a radioactive technique, that the anodic and cathodic processes were of a step-wise nature.

$$In \longrightarrow In^+ + e \qquad (4)$$

$$In^+ \longrightarrow In^{2+} + e \qquad (5)$$

$$In^{2+} \longrightarrow In^{3+} + e \qquad (6)$$

The most probable mechanism appeared to be that the stages involving the first and second electrons, Reactions 4 and 5, were equilibrium stages and the overall rate was determined by the rate of the last stage. This mechanism was based on a cathodic transfer coefficient $\alpha = 0{\cdot}91 \pm 0{\cdot}02$* and an anodic transfer coefficient $\beta = 2{\cdot}2 \pm 0{\cdot}07$. It was further shown [48] that, with the exception of F^-, the halide and the sulphates ions take a direct part in the anodic dissolution of indium. Recently [49] it has been shown, apparently unequivocally, that In^+ ions are participants in the anodic dissolution of indium. The effect of pH on the anodic dissolution of indium has also been examined by Losev and Molodov [50]. It was found that for the cathodic reduction of the hydrated indium ion, the rate was first order with respect to hydroxyl concentration. This was interpreted as indicating the involvement of cations $[In(H_2O)_5OH]^{2+}$ in the charge transfer step rather than the hexaquo cation. The slowness of the cathodic reduction of indium is therefore to be ascribed to the difficulty of removing a hydrogen ion from the bound hydration shell of the In^{3+} ion. Molodov and Losev [51] in a further investigation used a combined polarization and radiochemical method to study the formation of indium by cathodic reduction at a stationary electrode of indium amalgam in perchlorate solutions. Two parallel reduction processes were found: indium was formed either by direct discharge of the $In(H_2O)_6^{3+}$ ion, or by discharge of partially hydrolysed indium ions. The rate constant of the former process was about 10^5 times less than that of the latter. This latter process was found to be preceded by two consecutive chemical reactions – first the hydrolysis of $In(H_2O)_6^{3+}$ ions in the solution which limited the cathode process

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*See footnote p. 7.

at high pH and was independent of potential, and then the partial dehydration of $In(H_2O)_5OH^{2+}$ ions on the surface (this limited the rate of the second process at low pH and depended weakly on potential). The difficulty of dehydration of indium ions was emphasized by Chernom'orskii [52] and what amounts to the same suggestion is contained in other references by Russian workers [53, 54].

The transition between control of the electrochemical reaction by one rate process and another has been further studied in the case of indium by Molodov and Losev [55]. The dependence of the rule of the anodic processes and of the intensity of the exchange current on the concentration of the indium amalgam was measured in a solution of perchloric acid. It was found that at high concentrations of the amalgam the exchange current determined by the radiochemical method turned out to be lower than the exchange current determined by extrapolating the Tafel section of the curve to the equilibrium potential. A linear section with a slope ($2{\cdot}3\,RT/3\,F$) of 0·019 V appeared on the anodic current-voltage curve close to the equilibrium potential which corresponded to the limitation of the indium oxidation process by a subsequent chemical reaction [53]. At low concentrations of the amalgam this phenomenon was not observed – it was shown that by increasing the ratio of the concentration of indium in the solution to that in the amalgam a transition occurred from the region where the kinetics were determined by the limiting chemical reaction to the region where the kinetics were electrochemically controlled.

A very detailed review [56] by Losev summarizes some of the salient features of the indium exchange in perchlorate electrolyte from the mechanistic viewpoint. Losev [56] concludes that in the reaction only one of the electron transfers is rate-determining ($\alpha_a + \alpha_k = 3{\cdot}11$[*]) and that In^+ ions are in equilibrium with indium atoms in the amalgam.

5.1.2 *Solid electrodes* A number of investigations of the exchange at a solid indium electrode have been reported [57–68]. Pchel.nikov and Losev [59] established that the anodic dissolution reaction occurred with the formation of In(I) species which then reacted to form In(III) either chemically by reaction with H^+ in solution or by direct oxidation at the electrode. This caused the apparent valence from Faradaic charge calculations to differ from 3. Subsequently [60] the effect of NaI and NaCl on the reactions occurring at the indium electrode in perchlorate solution was studied. It was shown that these additives promoted the electrode reactions. A brownish-red deposit formed on the anode in the presence of NaI, the valence of the indium in this deposit being close to 1. This deposit was concluded to be InI, as confirmed by comparing the chemical properties of the deposit and those of InI synthesized from the elements at high temperature. A deposit of InI also formed reversibly on the electrode at NaI concentrations greater than 1×10^{-2} M, the indium metal functioning as a reversible electrode of the second kind under these conditions. Addition of Cl^- ions to perchlorate solutions increased the value of the apparent valency of dissolving indium in comparison with that for the perchlorate solutions, the reversible indium potential being determined by the concentration of the $InCl_2^+$ complex of trivalent indium. It is noteworthy that F^- has no effect on the In^{3+}/In exchange [61].

Similar conclusions about the participation of univalent indium species have been obtained by Visco and co-workers [62, 67]. In Visco's experiments [57, 67] the In(I) ion formed during anodization could be swept away from the electrode surface and detected polarographically in the bulk of the solution. The current efficiency in stirred solutions for In(I) production was about 2% in the case of dilute indium amalgams but for indium metal anodes, the current efficiency for In(I) production under the same conditions, was at least 75% and was dependent on anodic current density. The effects of mass transport conditions during electrochemical oxidation and of added complexing agents on the quantity of In(I) formed were also investigated. Based on overpotential decay curves, the polarographic behaviour of In(I) and In(III) and coulometric experiments, an electrochemical mechanism was proposed which postulates that the In(I)/In(O) couple is at equilibrium and that the interfacial concentration of In(I) is not

[*] In Losev's review [56], α_a and α_k refer to the anodic and cathodic transfer coefficients governing the overall potential-dependence of the rate of reaction and are related to the symmetry coefficients by the equations $\alpha_a = m - 1 + \beta_{a,m}$ and $\alpha_k = n - m + \beta_{k,m}$. n is the total number of electrons involved in the process and m is the ordinal number of the rate-determining step.

vanishingly small. An irreversible electrochemical step is associated with the further oxidation of In (I) to In(III). The rate constant of the formation of In^+ in the system has been reported [54] as $3{\cdot}2 \times 10^{-6}\ l\,m^2\,s^{-1}$.

In a later paper with Miller [62], Visco used the rotating disc-ring electrode technique to verify that the mechanism of the anodic dissolution of indium at a disc in 0·7 M $HClO_4$ was a rapid one-electron reaction to an In(I) species, sufficiently stable to be detected in theoretical amount at the ring. The Tafel behaviour of the disc reaction and the anodic and cathodic ring collection efficiencies were in accord with the above; the ring current-potential curves further showed that the slowness of the In(I)–In(III) reaction permits the thermodynamically less-favoured state to be formed in quantity.

Losev and Pchel'nikov [63], using a combination of radiochemical and electrochemical methods, have measured the exchange rate at a solid electrode. There was satisfactory agreement between exchange currents determined by the radiochemical method and by extrapolation of the anodic polarization curve to the equilibrium potential. The authors concluded that the exchange current increased with increasing In^{3+} ion concentration in the presence of added Cl^- ions and rose with increasing pH of the solution. The accelerating effect of halide ion is also noted in sections dealing with the polarography (Section 4), electrodeposition of indium (Section 7), and other aqueous electrolytes (Section 5.5). The kinetic parameters for the electrode reaction were determined from the relation between the exchange current and the $In(ClO_4)_3$ concentration, the values obtained being, for the anodic transfer coefficient*, $\beta = 1{\cdot}85$ and $i_0 = 2{\cdot}88 \times 10^{-3}\ A\,cm^{-2}$.

The cathodic process of discharge of indium ions on an indium electrode in perchlorate solutions in relation to potential and acidity of the medium was also investigated by Losev and Pchel'nikov [58]. With increase in acidity, on a solid indium electrode, in a similar manner to the indium amalgam case, a retardation of the cathodic process occurred, during which the rate of discharge of indium was almost independent of potential. In the presence of iodide ions the cathodic process was sharply accelerated and its rate began to be limited by diffusion. It was shown that the discharge of indium ions in perchlorate solutions was accompanied by preceding chemical reactions, during which, the ions taking part are not the $[In(H_2O)_6]^{3+}$ ions predominating in the solution but evidently the partially dehydrated hydrolysed ions of indium. This conclusion was verified in a more recent publication by the same authors [68] who investigated the influence of acidity and stirring on the cathodic reaction. It was found that the rate of indium discharge was inversely proportional to the acid concentration in the range studied ($3 \times 10^{-3} - 1$ M) and that the limiting current of the discharging indium ions was kinetic and not diffusional in nature. This is in general agreement with work using indicator electrodes [69] in which detection of hydrolysed $[In(OH)_2]^+$ ions confirmed the above suggested mechanism.

In dealing with the corrosion of indium in perchlorate media, Losev *et al.* [65] have formulated a stepwise corrosion mechanism for the metal in which the final corrosion product is formed by a complex electrochemical-chemical mechanism comprising the following steps: $M \rightarrow M^+ + e$; $M^+ \rightarrow M^{n+} + (n-1)e$; $M^+ + (n-1)O_x \rightarrow M^{n+} + (n-1)O_x^-$ and $O_x + e \rightarrow O_x^-$. A criterion of such a corrosion mechanism is the deviation of the experimental corrosion rate (i_c) from the reduction rate of oxidant O_x at the corrosion potential ($i_c^{extr.}$) found by extrapolation. Cathodic polarization curves on indium were measured and its corrosion rate was determined by a radiotracer method in aqueous $NaClO_4 + HClO_4$ solutions of varying acidity. i_c was considerably higher than $i_c^{extr.}$, the ratio $i_c/i_c^{extr.}$ approaching 3 with increasing acidity. In the same solutions containing 0·2 M NaCl, $i_c = i_c^{extr.}$, independent of acidity.

5.2. *Chloride electrolytes*

Markovac and Lovrecek [70] have investigated the kinetics of the reaction at a 0·3% In amalgam in chloride electrolyte. It was reported that the exchange reaction was fairly reversible up to a limit of 0·1 $A\,cm^{-2}$; however, when the current density was increased over this, the first step ($In^{3+} \rightarrow In^{2+}$) in the cathodic reaction was rate-determining. During anodic polarization, disproportionation reactions were thought likely to occur. The

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*See footnote p. 7.

quasi-reversibility of the reduction of indium at the D.M.E. was confirmed by the work of Jain and Gaur [71] who found k_s, the first-order standard rate constant, to be $\sim 10^{-4}$ cm s^{-1}. It was emphasized by these authors that the reduction is diffusion-controlled at the D.M.E. The reduction of In^{3+} was reported to be a 3-e reversible reaction on the basis of an a.c. polarographic study by Kopanskaya [72]. Losev [56] has pointed out, in connection with the reduction of indium in chloride solutions, that breaks in Tafel curves invoked by Lovrecek [70] to indicate mechanistic changes may, in the case of indium, indicate a reaction hindered by a preceding chemical reaction. In this case, this could be the hydrolysis of the hexaquo complex prior to the rate-determining charge-transfer step.

For the solid electrode in chloride solution, the dissolution reaction is accelerated. This acceleration was studied by Pchel'nikov *et al.* [73] who found that the reaction and the effect of chloride were consistent with a stepwise dissolution

$$In \rightleftharpoons In^{+} + e \qquad (7)$$

$$In^{+} \longrightarrow In^{3+} + 2e \qquad (8)$$

which was complicated by the reaction of the intermediate In^{+} with hydrogen ions

$$In^{+} + 2H^{+} \longrightarrow In^{3+} + H_2 \qquad (9)$$

The effect of chloride was specifically traced to the acceleration of Reaction 8.

5.3 *Sulphate electrolytes*

Lovrecek and Markovac [74, 75, 70] have studied the kinetics of the deposition and dissolution of indium (from indium amalgam) in indium sulphate solutions at pH 2·5 at a hanging drop of 0·3 mol % In amalgam, which was renewed for each pulse. Plots of the activation overpotential versus log current density showed good Tafel relations in both the cathodic and anodic regions. Analysis of these data showed the mechanism to consist of three consecutive electron transfer steps

$$In^{3+} \overset{e}{\rightleftharpoons} In^{2+} \overset{e}{\rightleftharpoons} In^{+} \overset{e}{\rightleftharpoons} In^{0}$$

The rate-determining step for both anodic and cathodic polarization was

$$In^{3+} \overset{e}{\rightleftharpoons} In^{2+}$$

for which the transfer coefficient α was determined to be approximately 0·83. At current densities higher than $2{\cdot}5 \times 10^{-3}$ A cm^{-2}, a change in the mechanism of the deposition and dissolution of indium was observed. Analysis of the experimental data obtained by cathodic polarization in indium sulphate solution at higher current densities indicated the reaction step $In^{3+} + 2e \rightarrow In^{+}$ to be rate-determining. For anodic polarization it was concluded that a disproportionation reaction occurred with increasing current density and that the first anodic reaction $In^{0} - e \rightarrow In^{+}$ became rate-determining. Some work on the catalytic effect of ionic species on the In(Hg) electrode has been reported by Loshkarev and Kazarev [76].

Russian workers [77] have examined the solid indium electrode reaction in sulphate electrolyte at 20, 40 and 50°C. It was found that at low temperatures the cathodic polarisation curves consisted of two regions and a plateau, indicating the occurrence of different cathodic processes. It was suggested that low-valence indium ions were formed at current densities corresponding to the first region of the curve; the cathodic and anodic current efficiencies were determined. Kozin and co-workers [78] have reported that the H_2O molecules in the diffusion layer have a limiting effect on the process of indium ionisation.

5.4. *Alkaline electrolytes*

Armstrong *et al.* [79] have studied the electrochemical behaviour of indium amalgams in alkaline solutions using potentiostatic and impedance techniques. It was found that the anodic dissolution followed a three-stage oxidation process, similar to the process in acidic solutions. This does not, however, agree with the later work of Leontovich [80] who suggested the limiting step $InOH^{2+} + e = InOH^{+}$ and this was claimed as similar to the mechanism in acid solution.

The anodic films produced on indium amalgams [79] were amorphous indium hydroxide. They were similar to anodic mercuric oxide and thallous chloride films in that those grown at very positive potentials were very thin whereas those grown at less positive potentials were much thicker. Anodic films formed on 1% amalgam in 0·1 M NaOH were found to be neither appreciably ionic nor electronic conductors.

The solid indium electrode [81–88] has attracted more attention than the amalgam mainly because of the metal's possible use in energy conversion devices. Boswell [82] has evaluated the potentialities of In, Bi–In and Pb–In alloys as energy-producing electrodes in small sealed cells. Bismuth is claimed to have value in promoting electrode reactivity at high current densities. The results indicated that indium could be stored in alkaline solutions without deterioration and function usefully after storage. It was concluded that these characteristics made indium a metal of potential interest in the energy conversion field.

Popova and Simonova [83] have shown that in alkaline solution passivation is due to an adsorbed monolayer. The behaviour is similar to that observed with all non-activating anions. With activating anions (Cl^-, ClO_4^-) the activating action is related to the displacement of adsorbed oxygen from the surface of the electrode, activation increasing with increased activator concentration. A more detailed investigation by Faizullin *et al.* [84] demonstrated that in the anodic polarisation of indium in solutions of potassium hydroxide under galvanostatic conditions, three anodic processes took place on an indium electrode, including the process of evolution of oxygen. The first anodic process was the transition of indium into the solution of alkali in the form of univalent ions, which, as a result of the disproportionation reaction, were oxidized to trivalent ions, forming indate ions (InO_2^-). In the second stage, indium undergoes anodic dissolution with direct formation of trivalent indium ions (InO_2^-). Both in the first and in the second stages of anodic polarisation, the phase oxide $In(OH)_3$ was formed on the indium surface. The anodic evolution of oxygen occurred on a passivated indium surface. In a further investigation [84], it was shown that the phase oxide film formed at the first two stages of the anodic polarization of indium was not the basic cause of the metal's passivation in alkaline solutions. Anodic passivation of indium occurred as a result of the formation of a second surface oxide film, situated directly on the metal under the phase oxide film. The passivating oxide film was identified as In_2O_3. The electrochemical parameters of the passivating oxide film were determined. By determining the type of conductivity, it was hypothesized that the passivating oxide film possessed a non-stoichiometric composition and contained an excess of In^{3+} cations. Work by Filippova and Kuzmin [85] and Lewis and Partridge [87] throws doubt on the work of Faizullin and Amirkhanova [84]. The main dissolution product at low current densities according to these authors [85, 87] is In(III).* Evidence for this was the relative dissolution current magnitudes at the In(I) and In(III) potentials.

Salem and Ismail [86] considered that the anodic polarization occurred in two stages: (i) the formation of indate ions, and (ii) the formation of indium hydroxide. The initial discharge of hydroxide ions governed the overall reaction rate, whilst the formation of InO_2^- on the electrode, it was suggested, was the rate-determining step. The number of electrons transferred from the electrode was 3.

Piercy *et al.* [88] agreed with previous workers that the anodic reaction conformed to passivation due to the progressive growth of a solid film on the electrode surface: under some conditions a precursor solution reaction may be observed. However, the polarisation behaviour was influenced by the semiconductor properties of oxide formed in the indium hydroxide layer.

Semiconductor effects of n-type indium oxides have also been investigated by Salem and Ismail [86] who demonstrated that the current/potential curves for the systems showed that the current multiplication factor was in the range 1·88–2·73, consistent with the material being a semiconductor.

5.5. *Other aqueous electrolytes*

Dom and Murray [89] have studied the adsorption of indium(III) at a mercury electrode from acid thiocyanate medium. Although In(III) gave no detectable adsorption from I^- or Br^- medium the In(III) surface excess passed through a maximum at 0·1–0·2 M thiocyanate. In a paper by Pospišil and De Levie [90] the slow step in the thiocyanate-catalysed electroreaction of indium(III) on Hg was identified as the surface reaction of In^{3+} with two adsorbed thiocyanate ions. This appeared to be the only reaction path available in thiocyanate solution when the pH was sufficiently low to prevent hydrolysis. The reaction rate was proportional to the square of the surface activity of adsorbed

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* The reader is referred to a recent paper presented at the 9th International Power Sources Symposium, Brighton, 1974. Paper 26 by R.D. Armstrong, T. Dickinson, B.A. MacFarlane and H.R. Thiusk indicates that this is the correct mechanism.

SCN^-. This work followed the recognition that during the polarographic reduction of In(III) in aqueous SCN^- a negative Warburg impedance may result from coupling between the diffusional and interfacial impedances [91, 92].

Brainina [93] has studied the reduction of the In(III) ion in the presence of a series of cations in chloride media. It was concluded that the mechanism was different at different potentials due to the alteration in the conditions of adsorption of the reducing particles. The electronic process was facilitated at potentials in the neighbourhood of the half-wave potential by the formation of 'anionic bridges', whilst a direct transfer of electrons from the electrode surface to the indium ions was observed at more negative potentials. Loshkarev *et al.* [94] have studied the polarographic separation and ionization waves of indium at amalgam and solid electrodes in various electrolytes. It was found that the polarization accompanying cathodic separation of indium was much higher than that accompanying anodic separation and varied with the nature of the anion in the sequence I^-, Br^-, $Cl^- < NO_3^- < SO_3NH_2^- < ClO_4^-$, SO_4^{2-}, $C_6H_4OHSO_3^- < BF_4^-$. In halide electrolytes, the ionisation of indium and the discharge of its ions were practically reversible. In sulphate electrolytes, the depolarizing action of the halide ions increased in the order Cl^-, Br^-, I^-, and increased with temperature and depolarizer concentration. On the basis of the potential dependence of halide-ion adsorption, the authors offered explanations of the occurrence of falling sections in the potential-current density curve for an In(Hg) electrode in mixed sulphate-chloride solutions and of the difference between the polarization curves for indium separating at solid and amalgam cathodes. Depolarizing action was also displayed by the CNS^- anion and certain organic compounds containing the $C = S$ group. The same authors in a later paper [95] followed the cathodic reduction and anodic ionization of indium on an amalgam electrode in electrolytes containing molecular and ionic organic compounds. It was established that the introduction of such compounds leads to an increase in the irreversibility of both reactions. In bromide, iodide and thiocyanate solutions with additives, the electrode processes were practically reversible. The influence of Cl^-, Br^-, I^- and CNS^- ions upon the polarization in the cathodic deposition of indium from a sulphuric acid electrolyte, containing organic additives, was studied quantitatively. The depolarizing action of the anions, increased in the series $Cl^- < Br^- < I^-$, CNS^- and increased with increasing temperature and concentration of the depolarizer.

5.6. *Non-aqueous electrolytes*

The anodic oxidation of indium in a number of electrolytes in liquid ammonia solution has been studied by McElroy *et al.* [96]. The results were erratic; initial valence numbers between 2 and 3 being obtained. With nitrate-bromide mixtures as electrolyte, the valence number did not appear to be a simple function of composition. The lower valent indium formed by electrolysis in ammonium bromide solution and assumed to be unipositive, was subject not only to oxidation by the electrolyte, but also to rapid disproportionation to the free metal and the tripositive ion.

Headridge and Pletcher [97] have produced In(I) solutions in acetonitrile.

Belitskaya *et al.* [98], studied the kinetics of cathodic deposition and anodic solution of indium from alkaline glycerin solutions of indium chloride at 85 ± 0·5°C. They suggested that indium was discharged from complex anions $[In(OH)_4]^-$. Discharge and ionization took place in steps via lower-valence ions; at low current densities, the slow stage of cathodic deposition and anodic solution of indium was attachment of a third electron in the cathode process and loss of a first electron in the anode process. This is similar to other work in acetamide [99] in which the metal was dissolved as the chloride. Alkali metal sulphates and chlorides were found to retard the indium dissolution.

The reduction of indium(III) ions in ethanolamines has also been reported [100].

6. The hydrogen evolution reaction on indium

Early work on the h.e.r. on indium was carried out by Theil [101], Bockris [102] and Rüetschi and Delahay [103]. Results were relatively unreliable and conflicting possibly due to lack of experimental control. Butler and co-workers [104, 105] provide the most reliable data. Butler and Makrides [104] measured the rate of the hydrogen evolution reaction at dropping indium amalgam electrodes (containing 0–65% indium) in 0·1 *M* $HClO_4$ at 25°C. The potential of zero charge was also determined for the same series of amalgams, and the Frumkin correction for the potential drop across the diffuse double layer was used to obtain the exchange current and transfer coefficient for each of the amalgams. The exchange current increased by approximately a factor of 10 as the composition was varied from 0 to 65% In. The transfer coefficient was 0·50 independent of composition within experimental error. The current at the zero-charge potential, which gave a measure of the free energy of activation for the discharge reaction, increased by a factor of 10^4 as the composition was changed from 0 to 65% In. The corresponding decrease in the free energy of activation was approximately 5 kcal, and was attributed primarily to a change in work function.

For the solid indium electrode, Butler and Dienst [105] made measurements of hydrogen overvoltage on indium electrodes in 0·1 M $HClO_4$ at temperatures from 21° to 59·5°C. The slow step in the hydrogen evolution reaction was thought to be discharge of a hydrogen ion, as indicated by the exchange current (10^{-11} A cm^{-2}), transfer coefficient (0·5), effect of added iodide ion and effect of acid concentration. The enthalpy of activation was found to be 14·1 ± 0·5 kcal mole^{-1} at the reversible hydrogen potential and 10·0 ± 0·2 kcal mole^{-1} at the zero-charge point. From these values, an estimate of 50 ± 10 kcal g atom^{-1} was obtained for the heat of adsorption of hydrogen atoms on indium. The reaction was very sensitive to traces of oxygen and the formation and removal of oxide films was discussed. Rotinyan *et al.* [106] have attempted to improve on the latter investigation [105]. It was established that on passing through the p.z.c., the hydrogen overpotential on indium showed a change in Tafel slope. The formation of InH_3 on the cathode surface can possibly affect the h.e.r. on solid indium, although further work is needed in this area [107].

7. Electrodeposition

Indium may be electroplated [108] successfully onto nearly all metals and alloys, such as rolled or cast iron, steel, stainless steel, cadmium, nickel, copper, tin, silver, lead. Indium plating is very simple, in contrast to that of many other metals such as chromium, for which there is only one method.

There have been proposed, and used to some extent commercially, some 6 different methods of plating indium. The best known baths are:

(a) Cyanide: prepared by adding excess sodium cyanide to a solution of indium chloride.
(b) Sulphate: consisting of indium sulphate with the addition of a small amount of sodium sulphate.
(c) Sulphamate: the main constituent of this bath is indium sulphamate.
(d) Alkaline: prepared by adding sufficient excess of sodium hydroxide to a solution of an indium salt so that the indium is kept in solution.
(e) Tartrate: this and similar baths are prepared in the following manner: ammonium hydroxide is added to a solution of indium chloride until precipitation begins. The precipitate is then dissolved with an excess of some weak organic acid, such as tartaric, formic, oxalic, citric, etc.

The most favoured electrolyte for the electrodeposition of indium is the sulphate solution. There are however difficulties which arise. Rakhmatullaev *et al.* [109] found that at low current densities in a stream of O_2 or air, O_2 was reduced and In 'self-dissolved'; at high current densities In was deposited in parallel with O_2 reduction. At high current densities the species $In(OH)_3$ was found to be involved in the deposition of the metal. Voronko *et al.* [110] have shown that passivation of the electrode surface could arise by an acid film $In_2(SO_4)_3.H_2SO_4.7H_2O$. This passivation was indicated by a minimum limiting current which depended on the constitution of the electrolyte. This observation is in agreement with the work of Garmute *et al.* [111] who found that during the electrodeposition of In from 0·1 M $In_2(SO_4)_3$ solution the insoluble compounds $In(OH)_3$ and $InOHSO_4$ were deposited on the cathode. It was suggested by these authors that such compounds arose as a consequence of pH increase due to the reaction of univalent indium with hydrogen ion.

$$In^+ + 2H^+ \longrightarrow In^{3+} + H_2.$$

An alternative explanation of the minimum in the limiting current has been advanced by Titov *et al.* [112]. Results showed that the limiting current decreased with increasing sulphate concentration and that the discharge of complex ions of the type $In(SO_4)_2^-$ took place. The best electrolysis conditions were reported to be pH > 1·6 with a current density below 1 A dm^{-2}.

The effect of halogen ions on the process of electrodeposition of the metal has been studied by Gershov and Purin [113]. Results indicated that some increase of reaction rate was obtained by the addition of the halide. In agreement with this, fluoridic electrolytes have been claimed as favourable in the plating of complex shapes, for example bearings. Martz [114] has described fluoroborate, fluosilicate and fluoride solutions which produce excellent coatings and give rise to corrosion resistant layers. A complicating factor in the electrodeposition of indium with supporting electrolyte (needed for improving throwing power) has been emphasized by Keseleva [115] who found that it was possible to introduce alkali metal atoms into the indium lattice. This should be avoidable using low current densities and high concentration indium solutions.

Of the large number of baths available, Rofalloff [116] recommends, on the basis of a radioactive investigation, the following deposition conditions for the simple and successful quantitative electrodeposition of indium: concentration in the range 10^{-1} -10^{-7} M: cathode-to-anode area ratio 1:3; sulphuric acid solution of pH 2; cathode current density 1·2–1·8 A cm^{-2}; temperature 50–60°C; addition of traces of gelatin as a colloid, and, when necessary, $(NH_4)_2SO_4$ as a conducting salt.

Indium may also be electrodeposited from non-aqueous systems. Thus Kakorev *et al.* [117] used polyethylene-polyamine electrolytes and established the feasibility of obtaining stable aqueous solutions of complexes of indium with amines forming part of the composition of polyethylene-polyamine, and their suitability for obtaining high-grade indium coatings by electrodeposition. The concentration ratios of indium salts, polyethylene-polyamine, and ammonium sulphate to obtain stable electrolytes with high throwing powers are given in their paper together with the pH and cathodic current density ranges which ensure the preparation of high-grade coatings. For further details the reader is directed towards their paper [117].

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