

Study on the Electroreduction of In(III) Ions at Gold from Acidic Bromide Solutions by the Rotating Ring-Disc Electrode Technique

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The mechanism of the indium electrodeposition on gold from acidic KBr solutions has been investigated by means of the rotating ring-disc electrode technique. The measurements showed that the overall electrode reaction $\text{In(III)} + 3 e \rightarrow \text{In}$ consists of two successive charge transfer steps, i.e. $\text{In(III)} + 2 e \rightarrow \text{In(I)}$ and $\text{In(I)} + e \rightarrow \text{In}$, with soluble monovalent indium as an intermediate. The current efficiency for In(I) generation under steady-state conditions is 100% in the case of low disc current densities. The disproportionation of In(I) in the bulk of solution occurs in slightly acidified solutions, $pH = 2$, in addition to the In(I) electrochemical reduction. Based on the ring current transients, it was established that the two-electron transfer step is preceded by the formation of a thin passive film of indium metal.

(Keywords: Electroreduction; Indium; Indous ion; Multi-step electrode reaction; Rotating ring-disc electrode)

Untersuchung der elektrochemischen Reduktion von In(III)-Ionen an Gold in sauren Bromidlösungen mit der rotierenden Ring-Scheiben-Elektrode

Mit Hilfe der rotierenden Ring-Scheiben-Elektrode wurde der Mechanismus der kathodischen Abscheidung von Indium auf Gold in sauren KBr-Lösungen untersucht. Aus den Messungen folgt, daß die Bruttoreaktion $\text{In(III)} + 3 e \rightarrow \text{In}$ über zwei aufeinanderfolgende Durchtrittsreaktionen, $\text{In(III)} + 2 e \rightarrow \text{In(I)}$ und $\text{In(I)} + e \rightarrow \text{In}$, mit löslichem einwertigem Indium als Zwischenprodukt abläuft. Bei kleinen Stromdichten werden die In(I)-Ionen mit 100%iger Stromausbeute erzeugt. In schwächer sauren Lösungen ($pH = 2$) konnte außer der elektrochemischen Reduktion von In(I) zusätzlich dessen Disproportionierung innerhalb der Lösung ermittelt werden. Auf Grund der Ringstrom-Zeit-Kurven wurde auch festgestellt, daß die Bildung von einer dünnen In-Metallschicht, die ein passives Verhalten aufweist, dem Zweielektronenübergang vorangegangen ist.

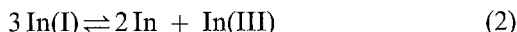
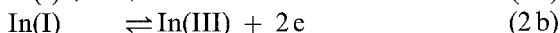
Introduction

The mechanism of the electrode reaction



in aqueous solutions was subject of numerous investigations at both solid and amalgam electrodes. A literature review concerning this problem has been given by *Piercy* and *Hampson*¹ as well as by *Losev* and *Molodov*^{2,3}. From the literature data, it appears that the reaction (1) proceeds in a step-wise manner. The indium(I) formed as an intermediate undergoes further electrochemical or chemical transformations.

In aqueous non-complexing media, the In(I) ion is unstable with respect to the disproportionation reaction which takes place as a combination of the coupled charge transfer steps

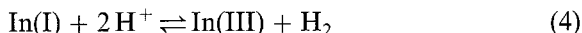


The equilibrium constant

$$K = c_{\text{In(III)}}/c_{\text{In(I)}}^3 \quad (3)$$

of this reaction in acidic perchlorate solutions is reported⁴ to be equal to about $10^{11} \text{ dm}^6 \text{ mol}^{-2}$ at 25 °C.

The In(I) ion is able to reduce hydrogen ions according to the reaction



In strongly acidified non-complexing solutions this reaction occurs at a relatively fast rate⁴⁻⁶. The side reaction (4) makes the process of indium electrodeposition or anodic dissolution very complex and provides an obstacle for the development of an exact mechanism of the In(III)/In electrode system.

In recent years, the most intensive studies to explain the multistep mechanism of the electrode reaction (1) were carried out in perchlorate⁷⁻¹², sulphate^{7,13} and chloride¹³⁻²⁰ media. However, this system was poorly investigated in bromide media^{21,22}.

The aim of the present work was to study the mechanism of the electroreduction of In(III) on gold from acidified KBr solutions. In the presence of bromide ions, indium(III) exists in the form of relatively weak complexes²³⁻²⁵ of the composition: InBr^{2+} , InBr_2^+ , InBr_3 and InBr_4^- . It is known that bromide ions accelerate the electroreduction of indium¹⁻³.

Our investigations were performed by means of the rotating ring-disc electrode (RRDE) which operates under well-defined mass transfer conditions. This technique is of a great utility in the study of multi-step

electrode reactions, since the amount of a soluble intermediate released by the disc can be quantitatively monitored at the ring electrode. Special attention was paid by us to the formation and disappearance of the In(I) species. Previous investigations^{26,27} of the equilibrium of the reaction (2) have shown an important increase of the stability of the In(I) ion in concentrated bromide solutions.

Experimental

The RRDE used in this investigation was constructed in our laboratory. Both the ring and disc were made from gold of high purity (99.99% Au). The disc radius was equal to $r_1 = 0.250$ cm, an inner ring radius $r_2 = 0.274$ cm, and an outer ring radius $r_3 = 0.374$ cm. The geometric area of the disc was $A = 0.196$ cm². The collection efficiency, N_0 , was determined experimentally with the Cu(II)/Cu(I) redox couple in chloride medium to be 0.42 ± 0.01 . The surface of the RRDE was initially prepared by coarse grinding with 600- and 800-grit silicon carbide paper followed by polishing with 1 000 and 1 200 alumina polishing powders on woollen cloth. After the mechanical pretreatment the RRDE was degreased with acetone, rinsed with triply distilled water and dried. The roughness factor of the disc was determined from measurement of the quantity of electrical charge required to form a layer of adsorbed oxygen on the electrode²⁸, and was found to be 2.0. The RRDE was driven with a synchronous motor and the rotation frequency was strictly controlled by means of a Zopan PFL-30 digital frequency meter.

All experiments were performed in a three-compartment electrochemical cell similar to that described by *Sonner et al.*²⁹. The main compartment held about 100 cm³ solution. A platinum wire spiral and a saturated calomel electrode (SCE) with KCl solution served as counter and reference electrodes and were isolated from the main cell compartment by fritted glass discs. All cell compartments were filled with the same solution. The reported potentials are given with respect to the SCE.

Constant current was supplied by a Radelkis OH-401/1 potentiostat galvanostat. Potentiostatic control of the ring electrode was maintained with an Elpan EP-20 fast-rise potentiostat having a current follower. The time dependence of the ring current was registered digitally using a Meratronik V-540 digital voltmeter connected with a RFT S-3291 numeric printer. For the synchronisation of measurements a quartz timer was employed.

Viscosities were determined with the aid of a Höppler viscometer.

All chemicals used were p.a. grade. Indium(III) bromide was prepared by dissolving metallic indium of high purity (99.999% In) in 40% HBr and then crystallizing from the solution. All solutions were prepared by dissolving a proper amount of substance in triply distilled water. Concentration of In(III) in stock solutions was checked by complexometric titration. Before electrochemical experiments the solutions were de-aerated by bubbling with pure argon. During the experiments, argon was passed over the solution.

All measurements were performed at 25 ± 0.2 °C.

Results and Discussion

The cathodic reduction of In(III) was performed on the disc under galvanostatic conditions at various values of the disc current, I_D . Each

current setting was made from open circuit. In certain specified experiments, a constant potential was maintained on the disc. After each cathodic run, the disc was potentiostated at +200 mV in order to dissolve the indium layer deposited. Then, the RRDE was refinished mechanically to minimize any effect of a changing electrode surface.

The In(I) formed as an intermediate on the disc electrode could escape to the ring where it was converted back to In(III). During the disc experiments, the ring electrode potential, E_R , was held constant at +200 mV, which value corresponds to the limiting current region of the anodic reaction: $\text{In(I)} = \text{In(III)} + 2e$. Therefore, the limiting ring current, $I_{R,L}$, could be used as a precise measure of the In(I) concentration on the disc surface.

Simultaneously with current measurements, we have carried out a visual observation of the disc surface since a change in its appearance might provide further significant informations about the process studied. The concentration of In(III) was usually either $5 \cdot 10^{-3}$ or 10^{-2} mol dm⁻³. Such high concentration was needed to improve the determination of the intermediate. As the background electrolyte, KBr solutions acidified with HBr (10^{-2} or 10^{-1} mol dm⁻³) to prevent hydrolysis of indium species were used. The total bromide concentrations investigated was 4 mol dm⁻³.

During the In(III) reduction on the disc, the limiting ring current was recorded as a function of the time of electrolysis, t . Figure 1 shows a typical $I_{R,L}$ vs. t curve obtained for a low disc current density. It should be noted that the ring current does not appear at the beginning of electrolysis on the disc but after a considerable period, indicated as t_1 , which is inversely proportional to the disc current. In this time, the disc surface is covered by a thin layer of indium metal which will be called a primary layer. After the primary indium layer is partially formed, the ring current begins to flow thus indicating that the In(I) ions are produced at the disc surface, and then transported into the bulk of solution. After some time the $I_{R,L}$ reaches a stationary value. During that time, the primary indium deposit is well observable on the disc surface.

In a certain range of the disc current, another type of the dependence of $I_{R,L}$ on time was observed, where the ring current passes through a maximum (Fig. 2).

On the basis of the $I_{R,L}$ vs. t curves registered at different disc currents and rotation velocities of the RRDE, plots of $I_{R,L}$ against I_D for the steady-state have been constructed. Fig. 3 presents some selected results for the solution containing $5 \cdot 10^{-3}$ M InBr₃, 0.1 M HBr and 3.885 M KBr. Nearly identical curves were obtained in the solution of lower acidity (10^{-2} M HBr).

As follows from Fig. 3, the dependence of $I_{R,L}$ on I_D for each rotation

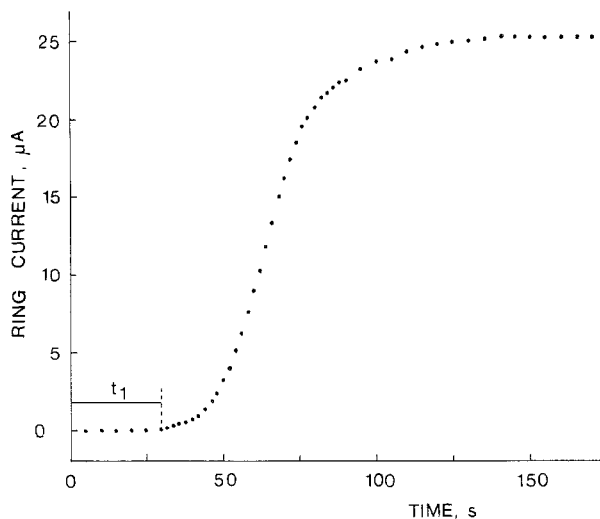


Fig. 1. The ring current response to a step of the disc current, $I_D = -60 \mu\text{A}$. Rotation frequency: 55 rps. Electrolyte: $5 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ InBr}_3$ in $10^{-2} \text{ mol dm}^{-3} \text{ HBr}$ and $3.975 \text{ mol dm}^{-3} \text{ KBr}$

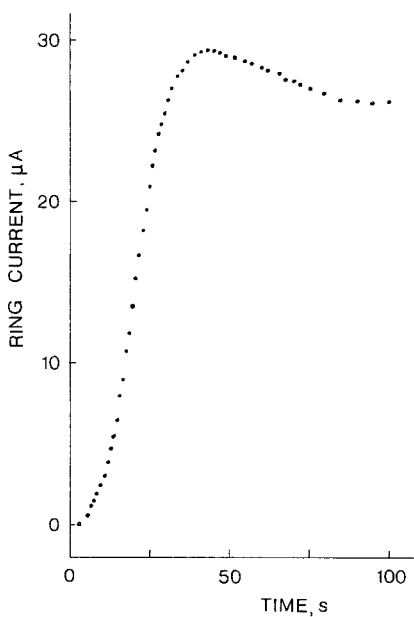


Fig. 2. The ring current response to a step of the disc current, $I_D = -160 \mu\text{A}$. Other experimental data as for Fig. 1

frequency consists of two parts with different slopes. In the region of low disc current densities, the stationary ring current increases linearly with the applied disc current, until a maximum is reached beyond which there is a decrease. The linear part of the plot has a slope of 0.42, which value is equal to the collection efficiency of the RRDE employed. Hence, the ring collection current satisfies the relation

$$I_{R,L} = N_0 |I_D| \quad (5)$$

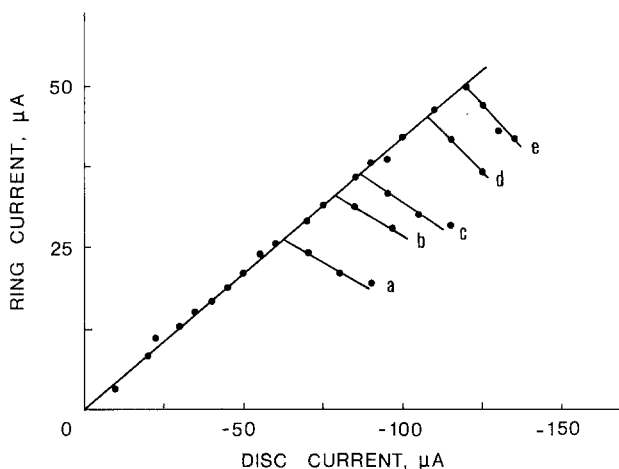


Fig. 3. Plots of the stationary ring current against the disc current for various rotation frequencies: *a* 8; *b* 15; *c* 25; *d* 40; *e* 55 rps. Electrolyte: $5 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ InBr}_3$ in $0.1 \text{ mol dm}^{-3} \text{ HBr}$ and $3.885 \text{ mol dm}^{-3} \text{ KBr}$

This result indicates clearly that all cathodic disc current is consumed by a reaction inverse to that occurring at the ring electrode, i.e.



One may observe that the straight line in Fig. 3 goes through the origin of the coordinate system. According to the theory³⁰, it follows from this fact explicitly that the electron transfer process (6) is not followed by any chemical reaction with components of the solution. Hence, the oxidation of In(I) by hydrogen ions which is described by eqn. (4) does not occur with an appreciable rate and can be neglected in the solutions investigated.

At higher disc current densities, a deviation from the linear $I_{R,L}$ vs. I_D relationship appears. If the applied disc current exceeds a critical value, $I_{D,cr}$, the ring current decreases considerably. This fact is due to further reduction of In(I) ions produced at the disc. Consequently, a secondary

indium layer is formed on the disc surface with $|I_D| > |I_{D,cr}|$. The deposit obtained appears to be less bright and smooth than the primary indium layer.

The characteristic fact is that the $I_{D,cr}$ value increases with an increase of the rotation velocity as well as the bulk concentration of In(I). These facts may suggest that the cathodic reduction of In(III) leads to the formation of the secondary indium layer when its concentration on the disc surface exceeds a value resulting from the equilibrium of reaction (2).

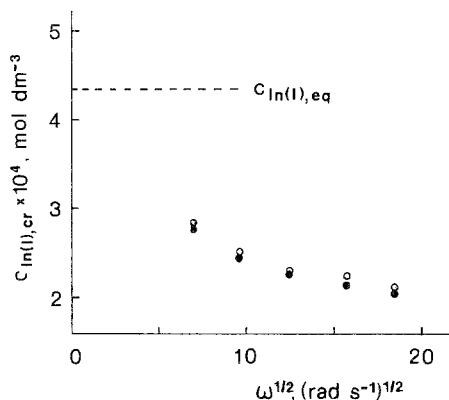


Fig. 4. Effect of rotation frequency on the critical In(I) concentration, $c_{In(I),cr}$, at the disc electrode surface. Electrolyte: (○) $5 \cdot 10^{-3}$ mol dm⁻³ InBr₃ in 0.1 mol dm⁻³ HBr and 3.875 mol dm⁻³ KBr; (●) $5 \cdot 10^{-3}$ mol dm⁻³ InBr₃ in 10^{-2} mol dm⁻³ HBr and 3.975 mol dm⁻³ KBr

Assuming that only the cathodic reaction (6) occurs, the surface concentration of In(I) corresponding to the applied disc current can be calculated by the use of the *Levich* equation, expressed in the following form:

$$c_{In(I)}^s = 1.61 n_D F^{-1} A^{-1} D_{In(I)}^{-2/3} \nu^{1/6} \omega^{-1/2} |I_D| \quad (7)$$

where n_D is the number of electrons involved in the electrode reaction, A the disc area, $D_{In(I)}$ the diffusion coefficient of In(I), ν the kinematic viscosity and ω the angular velocity of the RRDE. In this expression, the In(I) concentration in the bulk of solution is assumed to be zero.

Substituting the $I_{D,cr}$ values at different angular velocities into the equation, we have determined the corresponding critical concentrations of In(I) on the disc surface, $c_{In(I),cr}$. The data needed in eq. (7) were taken to be: $n_D = 2$, $A = 0.196$ cm², $\nu = 6.9 \cdot 10^{-3}$ cm² s⁻¹ and $D_{In(I)} = 1.35 \cdot 10^{-5}$ cm² s⁻¹. The former values was assumed to be equal to that of Tl(I) in 3.0 M KCl solution³¹.

The results obtained are presented in Fig. 4 and compared with the In(I) concentration concerning the equilibrium of the disproportionation reaction (2). The former value has been measured by us²⁷ separately for a solution of the same composition. A decrease of the In(III) concentration on the disc surface in relation to that in the bulk of solution was neglected. It seems to be permissible because the $I_{D,cr}$ values are rather low in comparison with the hypothetical limiting current of the reaction (6).

The data of Fig. 4 shows that the $c_{In(I),cr}$ values are about 2–3 times smaller than the In(I) equilibrium concentration. However, the critical concentration if In(I) shifts nonlinearly towards the $c_{In(I)}$ equilibrium value with decreasing $\omega^{1/2}$ but does not reach its in the attainable range of the rotation rate. This fact may be attributed to an irreversibility of the reaction (2) which consists of two complementary charge transfer steps, i.e. (2a) and (2b). It has been found²⁷ that the step (2b) is a rate determining one.

From the facts described above, one can assume that the secondary indium layer deposit is formed as a result of the electrochemical step



For the region of I_D somewhat exceeding the $I_{D,cr}$ value, transient ring current curves with a maximum are characteristic, particularly at high rotation rates. An example is given in Fig. 2. The decrease of $I_{R,L}$ with time up to a steady-state value can be explained by the In(I) supersaturation which is due to a slow electrocrystallization process.

Other possibilities of the indium(III) electroreduction mechanism than that described by eqns. (6) and (8) should be taken into consideration, too. Two problems are important here: (i) does In(I) disproportionate in the bulk of solution, particularly near the disc surface when its concentration reaches a sufficiently high value? (ii) are In(III) ions reduced directly to indium metal according to eqn. (1) parallel to the multistep electrode process? In order to explain these problems, we have applied the criteria reported in the theoretical consideration by *Damjanovic* et al.³² For this purpose, the electroreduction of In(III) was carried out at a constant disc potential. The experimental results have been plotted as $I_D/I_{R,L}$ vs. $\omega^{-1/2}$ for various disc potentials, E_D .

Fig. 5 shows some selected results obtained for $5 \cdot 10^{-3} M$ InBr₃ in 0.1 M HBr and 3.885 M KBr. At more positive potentials, the ratio $|I_D/I_{R,L}|$ is independent of the rotation frequency and exhibits a value equal to $1/N_0$ (curve a). According to the aforementioned theory this result confirms our earlier conclusion that the In(I) ions generated under similar conditions provide the final product of the cathodic reduction of In(III).

At sufficiently negative disc potentials, the dependence considered is given by straight lines intersecting the ordinate at the point of $1/N_0$ (curve c,

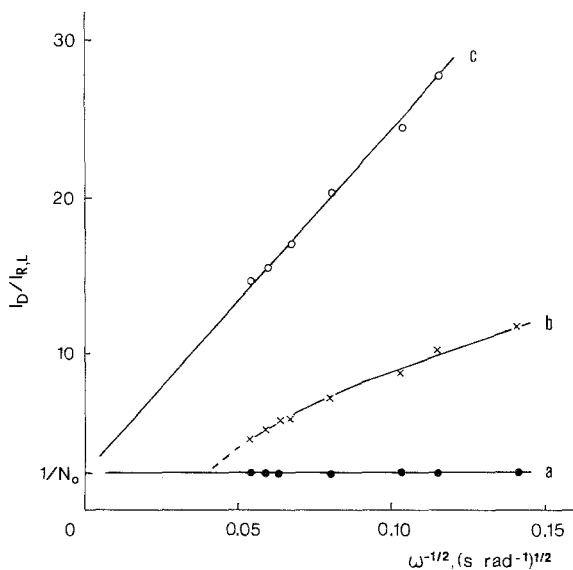


Fig. 5. Dependence of the ratio $I_D/I_{R,L}$ upon the reciprocal square root of angular velocity at different disc electrode potentials: *a* – 700; *b* – 720; *c* – 735 mV vs. SCE. Electrolyte: $5 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ InBr}_3$ in $0.1 \text{ mol dm}^{-3} \text{ HBr}$ and $3.885 \text{ mol dm}^{-3} \text{ KBr}$

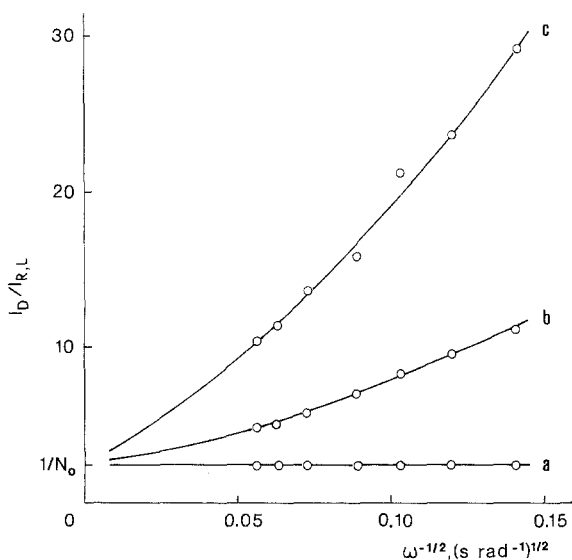


Fig. 6. Dependence of the ratio $I_D/I_{R,L}$ upon the reciprocal square root of angular velocity at different disc electrode potentials: *a* – 708; *b* – 732; *c* 739 mV vs. SCE. Electrolyte: $10^{-2} \text{ mol dm}^{-3} \text{ InBr}_3$ in $10^{-2} \text{ mol dm}^{-3} \text{ HBr}$ and $3.96 \text{ mol dm}^{-3} \text{ KBr}$

Fig. 5). In this potential range, the secondary indium layer forms on the disc surface. The graphical relationship obtained corresponds to that predicted by *Damjanovic* et al.³² for the electrode process consisting only of successive charge transfer steps. From these data, it is clear that the direct electroreduction of In(III) to the metal does not occur.

Curve b in Fig. 5 represents an example of a transitional behaviour. At lower rotation rates ($\omega^{-1/2} \rightarrow \infty$), the convective transport of In(I) ions from the disc surface into the bulk of solution is slow enough to facilitate their further electroreduction. In this case, a linear asymptote intersecting the $I_D/I_{R,L}$ axis at $1/N_0$ is obtained. Contrary to that, at higher rotation frequencies ($\omega^{-1/2} \rightarrow 0$), the surface concentration of In(I) on the disc is not sufficient to cause the occurrence of the next charge transfer step (8). As a result a deviation from the linearity of the $I_D/I_{R,L}$ vs. $\omega^{-1/2}$ plot is observed.

As follows from Fig. 6, the dependences of $I_D/I_{R,L}$ on $\omega^{-1/2}$ for the solution of lower acidity ($10^{-2} M$ HBr) are more complex as in the foregoing case. However, at potentials less reducing at which only the electron transfer reaction (6) takes place, the dependence considered is identical with the that for the solution containing $0.1 M$ HBr (curve a). As the disc potential becomes more negative that the $I_{D,cr}$ value is exceeded, a positive deviation from the linearity appears (curves b and c in Fig. 6). This results indicates that a part of the In(I) ions formed on the disc participates in a chemical reaction parallel to the charge transfer step (8). One can expect that it is the disproportionation of indium(I) which proceeds beyond the disc surface. This conclusion is supported by results of visual observation of both the RRDE and the solution during the electrolysis. Colloidal indium metal being a product of the reaction (2) deposits on the gap and the outer insulating part of the RRDE and becomes appreciable after a longer period of electrolysis. Simultaneously, some alteration of the colour of the solution was observed which turned pale blue. It should be pointed out that these effects did not appear in this solution at $|I_D| < |I_{D,cr}|$.

In order to examine features of the primary indium layer, some experiments at the open-circuited disc electrode were made. In these experiments, the ring collection transients were observed on open-circuiting the disc after a primary indium film has been formed completely. Curve a in Fig. 7 presents a typical example of such a transient. As shown in this Fig., the ring current at first falls rapidly and next decays gradually. It reaches zero after a relatively short time after the disc current was switched off. It should be emphasized that the layer investigated did not disappear nor did it change appreciably even at a very long duration of the contact with the electrolyte.

Contrary to that, the secondary indium layer exhibits a typical behaviour characteristic for an active metal surface. As follows from Fig. 7, curve b, after the disc electrode was open-circuited, the ring current rises rapidly to a stationary value. This $I_{R,L}$ value is determined by the corrosion rate of indium metal due to the inverse reaction of eqn. (2).

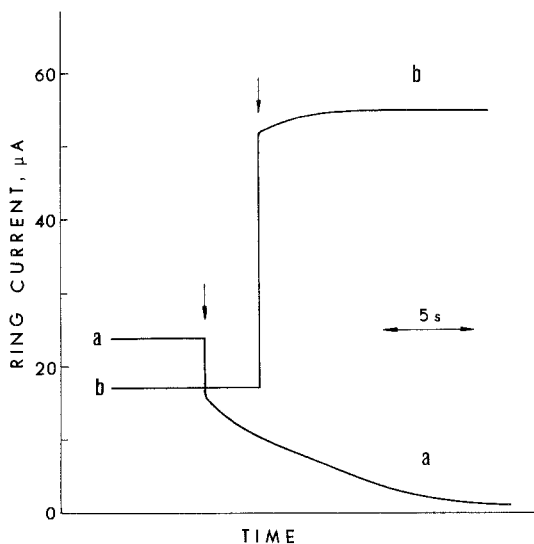


Fig. 7. Open-circuit transients of the ring current. Disc current: $a - 40$; $b - 300 \mu\text{A}$. Rotation frequency: 60 rps. Electrolyte: $5 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ InBr}_3$ in $10^{-2} \text{ mol dm}^{-3} \text{ HBr}$ and $3.975 \text{ mol dm}^{-3} \text{ KBr}$. Vertical arrows indicate the open-circuit time

Comparing the results mentioned above, it is clear that the primary film is a passive one. This observation led us³³ to study the kinetics of the electron transfer step (6) on the gold electrode covered with such a film. On the other hand, it seems impossible at this stage to propose a mechanism of inactivation; this requires some more experiments by different electrochemical techniques.

Referring to the transient $I_{R,L}$ curves again, we have estimated the thickness of the primary indium film. The film formation current, I_{ff} , is given by

$$|I_{ff}| = |I_D| - I_{R,L}/N_0 \quad (9)$$

The charge required to form a minimal part of the film on the gold surface prior to initiation of In(I) generation can be calculated simply as $Q_1 = I_D t_1$ (see Fig. 1). The calculations indicate that there is no ring

response to the cathodic disc current until more than 6.6 mC of indium per geometric cm^2 have been accumulated on the disc electrode surface. This charge proved to be practically independent of the solution acidity as well of both the disc current density and the rotation velocity. Since the roughness factor of the electrode employed was 2.0, our experimental value for the minimal amount of In(0) that must be deposited is 3.3 mC per real cm^2 . Using the indium atomic radius of 0.166 nm, we estimated that the charge obtained corresponds approximately to 8 close-packed monolayers.

The final thickness of the primary indium layer is much greater than the initial one. It can be deduced from the time dependence of I_{ff} during the transition period. Thus, integrating eqn. (9) and assuming $I_D = \text{const.}$ yields an expression for the charge consumed to form the primary layer of the steady-state thickness

$$Q_2 = |I_D t_2| - \frac{1}{N_0} \int_0^{t_2} I_{R,L} dt \quad (10)$$

where t_2 is the time required for the ring current to attain the stationary value.

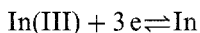
The average Q_2 value was calculated using eqn. (10) for some disc currents and found to be about 20 mC per cm^2 of geometric disc area. This implies that the complete primary indium film corresponds to about 25 monolayers. In contrast to the secondary indium deposit, this is probably a layer of a well-ordered structure.

During the last years, the underpotential deposition of thin metal layers on foreign solid electrodes was observed in many systems using different experimental techniques³⁴. The formation of such layers was stated as an initial process not only for electrocrystallization on a foreign substrate but also for cathodic electron transfer reactions, e.g. $\text{Cu(II)} + e \rightarrow \text{Cu(I)}$ on platinum in aqueous chloride solution³⁵. Consequently, the primary indium film formation on gold can now be considered as a regular step prior to the In(III)/In(I) electrode reaction.

Difficulties arise in the interpretation of the film thickness obtained. Nearly all the systems studied thus far show a coverage of the foreign substrate surface with one or two monolayers in the underpotential region. However, it must be noticed that those investigations were in general performed at low ($< 10^{-4} M$) depolarizer concentrations. Thus, one may expect that the formation of the much more thicker indium film on gold is connected with the use of more concentrated In(III) solutions in the course of this study.

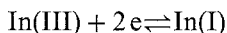
Conclusions

The measurements performed by means of a rotating ring-disc electrode strongly indicate that the mechanism of the overall electrode reaction



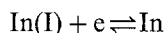
occurring at gold in acidic bromide media includes the following steps:

- (1) Formation of a primary indium inactive film on the gold surface.
- (2) Two-electron transfer step

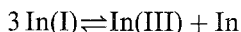


which proceeds on the primary film formed with the 100% current efficiency for generation of the In(I) soluble intermediate under certain experimental conditions.

(3) Formation of a secondary indium active deposit as a result of the further charge transfer step



(3 a) Disproportionation of the intermediate, In(I), in the bulk of solution



which is observed only in slightly acidified solutions, $pH = 2$, apart from the secondary film formation on the electrode surface.

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