Monatshefte für Chemie 126, 271–279 (1995)

Monatshefte für Chemie
Chemical Monthly

Redox Equilibria in the In(III)-In(I)-In System in Aqueous KBr Solutions II. A Rotating Ring–Disc Electrode Study

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Summary. The open-circuit behaviour of thick indium films formed onto gold by the electroreduction of In(III) has been investigated in acidified aqueous KBr solutions using the rotating ring–disc electrode technique. The spontaneous dissolution of indium metal immersed in the solution containing its own ions of higher valency yields In(I) ions. Information about the equilibrium and mechanism of the process studied was drawn from measurements of the limiting ring current and disc potential as a function of the electrode rotation rate. It was proved that the overall reaction $2\mathrm{In} + \mathrm{In(III)} \rightleftarrows 3\mathrm{In(I)}$ occurs as a coupling of two electrochemical steps: $\mathrm{In} \rightleftarrows \mathrm{In(I)} + e^-$, and $\mathrm{In(III)} + 2e^- \rightleftarrows \mathrm{In(I)}$. The cathodic half-reaction is the rate-determining step, whereas the anodic half-reaction is reversible.

Keywords. Bromide solutions; Indium(I); Reproportionation; Rotating ring–disc electrode.

Das Redox-Gleichgewicht im In(III)-In(I)-In-System in wäßrigen KBr-Lösungen, 2. Mitt. Untersuchungen mit der rotierenden Ring-Scheiben-Elektrode

Zusammenfassung. Die spontane Auflösung von Indium unter der Wirkung von eigenen Ionen (In(III)) wurde in sauren bromidhaltigen Lösungen mit Hilfe der rotierenden Ring-Scheiben-Elektrode untersucht. Die Angaben über das Gleichgewicht und den Mechanismus des untersuchten Prozesses wurden auf Grund der Abhängigkeit der Grenzströme an der Ring-Elektrode und der Elektrodepotentiale der Scheiben-Elektrode von der Umdrehungsgeschwindigkeit erreicht. Aus den Messungen folgt, daß die Bruttoreaktion $2\mathrm{In} + \mathrm{In(III)} \rightleftarrows 3\mathrm{In(I)}$ aus zwei überlagerten Durchtrittsreaktionen, $\mathrm{In} \rightleftarrows \mathrm{In(I)} + e^-$ und $\mathrm{In(III)} + 2e^- \rightleftarrows \mathrm{In(I)}$, besteht. Die kathodische Reaktion ist geschwindigkeitsbestimmend, während die anodische Teilreaktion reversibel abläuft.

Introduction

Indium(I) ions may be obtained in a reproportionation reaction in which In(III) is reduced by metallic indium according to

$$\mathrm{In(III)} + 2\mathrm{In} \rightleftarrows 3\mathrm{In(I)} \qquad 1$$

The reaction above can be considered as a corrosion process in which the In ion of higher oxidation state is the metal oxidant. Theoretically, such processes may occur according to a chemical or electrochemical mechanism [1]. In the latter case, the anodic half-reaction

$$\mathrm{In} \rightleftarrows \mathrm{In(I)} + e^- \qquad 2$$

should occur independently of the cathodic reaction

$$\mathrm{In(III)} + 2e^- \rightleftarrows \mathrm{In(I)} \qquad 3$$

In this scheme, the cathodic reaction is balanced by the anodic dissolution of metallic indium. Knowledge of the values of the equilibrium constant for reaction 1 is very important for the interpretation of the mechanism of the electrochemical reduction of In(III) to metallic indium. It should be noted that some controversy arose very recently, concerning the mechanism of this process [2].

Molodov and coworkers [3,4] have shown that the various types of reproportionation mechanisms can be readily distinguished by the use of the rotating ring–disc (RRDE) technique. This approach has been extensively applied by the same group to determine the mechanism of Cu(I) reproportionation in aqueous [5] and methanolic solutions [6,7] containing Cu(II) ions. However, these authors claimed that the results were not sufficiently reproducible to estimate the equilibrium constants of the reproportionation reaction.

Kiss and coworkers [8,9,10,11,12] have recommended a quite different theoretical approach to the use of the RRDE technique for the study of the spontaneous metal dissolution (for a review, see Ref. [13]). This theory is especially useful for the investigation of the kinetics of the mentioned processes. Using the RRDE technique, these authors have determined the equilibrium constants for copper(I) reproportionation in aqueous solutions in an indirect way from kinetic data [12].

It seems that, hitherto, the advantages of the RRDE technique have been little exploited concerning the equilibria of the spontaneous dissolution of metals caused by their own ions of higher oxidation state.

In our previous communication [14], the equilibrium of In(I) reproportionation in aqueous bromide solutions has been studied by potentiometric and coulometric techniques. In the present investigation, we used the RRDE technique to elucidate the mechanism of this reaction. The RRDE technique appeared to be a powerful tool for understanding the spontaneous indium dissolution, since the amount of indium(I) released by the disc can be quantitatively monitored by the ring electrode.

Results and Discussion

The electrochemical experiments consisted of two steps:

(i) *Deposition of an indium layer*
Indium metal was deposited electrochemically at a constant potential, in most cases at −750 mV *vs.* SCE, on the disc electrode from the solutions studied. The volume of tested solutions was so large that the electrolysis could not cause any substantial change in the In(III) bulk concentration.

(ii) *Spontaneous dissolution of the indium deposit*
When the desired quantity of indium had been plated, the disc electrode was disconnected from the electrical circuit. In order to quantitatively determine the soluble indium(I) produced at the disc, the ring electrode was held at a constant

potential 200 mV *vs.* SCE which corresponded to the limiting current plateau for the In(I) → In(III) oxidation. The current due to this reaction was measured as a function of time.

A series of experiments was conducted in which the concentration of the bromide ion was varied from 1.0 to 4.0 mol·dm^{-3}. A set of typical transients for the ring collection current, observed on the disc at open circuit after the formation of a thick indium layer, is shown in Fig. 1. After the time at which the disc had been open-circuited, the limiting ring current decreased slightly. The possible explanation of this is that a slow passivation of the metal film formed occurred. It seems that the irreproducibility of results reported by *Molodov* and coworkers [5, 7] was caused by a similar aging process of the deposited copper metal.

We calculated the average transition time, τ, required that the product formed at the disc is transferred across the gap between the two electrodes, according to

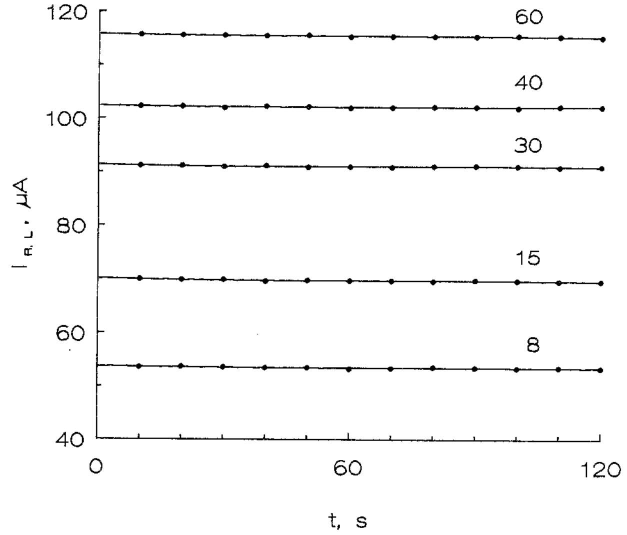

Fig. 1. Time dependence of the ring collection current recorded after open-circuiting of the disc electrode. The indium films were produced by potentiostating the disc at −750 mV *vs.* SCE. Electrolyte: 0.01 mol·dm^{-3} In Br$_3$, 0.01 mol^{-3} HBr, and 3.96 mol·dm^{-3} KBr. Rotation frequency of the RRDE in Hz is indicated at each curve; ring electrode potential: 200 mV

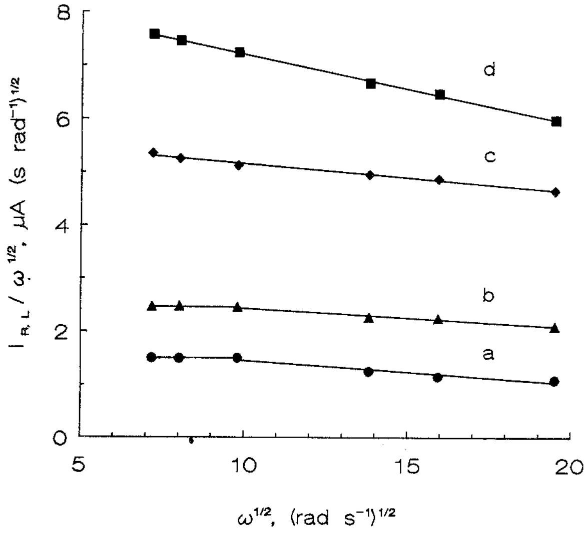

Fig. 2. Dependence of the ratio $I_{R,L}/\omega^{1/2}$ upon the square root of the angular rotation rate. The solutions contained 0.01 mol·dm^{-3} InBr$_3$, 0.01 mol·dm^{-3} HBr, and a suitable quantiy of KBr to obtain a total concentration of Br$^-$ equal to (a) 1.0, (b) 2.0, (c) 3.0, and (d) 4.0 mol·dm^{-3}

Bruckenstein and *Feldman* [16]. It follows from the calculations made for In(I) in the 4.0 mol·dm^{-3} solution that τ changed from 360 to 48 ms when the rotation frequency was varied from 8 to 60 Hz. Hence, its value was negligibly small compared to the time scale of the experiments.

Similar results were obtained for all solutions studied. In order to obtain reproducible values of the ring collection current for further calculations, we extrapolated the $I_{R,L}$ *vs.* t data to $t = 0$.

Simultaneously, the potential of the disc, E_D, at zero current was monitored at various rotation frequencies and in the quiescent solution. It should be noted that E_D, measured at a chosen rotation frequency, remained practically independent of the time. The disc potentials determined at the motionless electrode were employed as equilibrium potentials in the In(III)–In(I)-In system.

The effect of the mass transport on the rate of indium dissolution was studied by applying various rotation frequencies of the RRDE. The values of $I_{R,L}$ obtained at $t = 0$ were then plotted as $I_{R,L}/\omega^{1/2}$ *vs.* $\omega^{1/2}$ (ω is the angular rotation velocity), according to the proposal of *Galus* [17]. The flux of In(I) and the associated ring current will depend upon the rotation velocity, but depend linearly on $\omega^{1/2}$ only for a process controlled by the mass transport. Consequently, the value of $I_{R,L}/\omega^{1/2}$ should be independent of the rotation velocity. As can be seen from Fig. 2, the plots are independent of $\omega^{1/2}$ in a limited range of the rotation rate ($\omega \rightarrow 0$) only for the solutions containing 1.0 or 2.0 mol·dm^{-3} Br$^-$. At higher rotation rates, an essential decrease of the ratio $I_{R,L}/\omega^{1/2}$ occurs. In the case of more concentrated KBr solutions ($\geqslant 3$ mol·dm^{-3}), the said quotient decreases linearly with increasing $\omega^{1/2}$ in the whole range of the applied rotation frequency.

Analogously, the values of E_D were plotted against $\omega^{1/2}$ for the solutions studied (Fig. 3). In the case of solutions containing 1.0 or 2.0 mol·dm^{-3} Br$^-$, two regions can be clearly distinguished: (a) at $\omega \rightarrow 0$, the disc potential is practically not affected by the rotation rate and remains approximately equal to the equilibrium potential of the In(III)/In couple: (b) at higher rotation rates, E_D changes linearly towards negative values with increasing $\omega^{1/2}$.

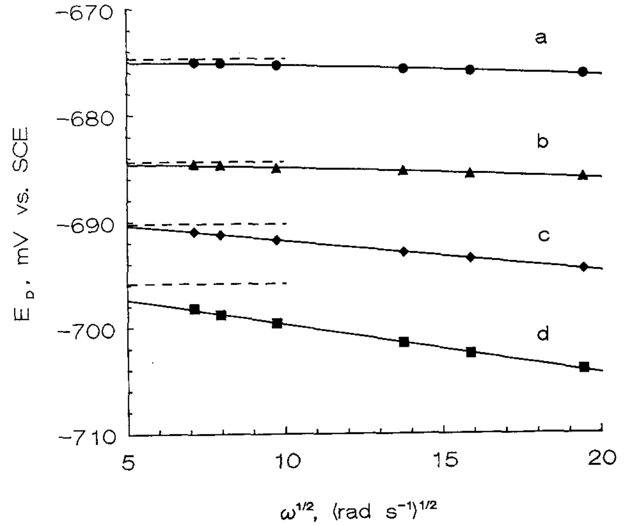

Fig. 3. Effect of the rotation rate on the potential of the open-circuited disc electrode. Experimental conditions as for Fig. 2. The horizontal dashed lines show the equilibrium potentials measured at the motionless electrode

According to the diagnostic criteria given by *Molodov* [4], this fact in connection with the non-linear relationship of $I_{\mathrm{R,L}}$ *vs.* $\omega^{1/2}$ clearly demonstrates that the mechanism of reaction 1 is not a chemical but an electrochemical one. Thus, reaction 2 is the electrochemical dissolution of indium metal to form In(I) ions in solution, whereas reaction 3 represents the electrochemical reduction of In(III) ions to form In(I). Moreover, the negative shift of E_{D} with the increasing rotation frequency suggests that the electron transfer reaction 3 is the rate determining step. Accordingly, reaction 2 behaves as a fast one.

From the experimental data presented above, it was possible to calculate the equilibrium constant of reaction 1

$$K_{\mathrm{r}} = \frac{(c_{\mathrm{In(I),eq}})^3}{c_{\mathrm{In(III),eq}}} \qquad 4$$

where $c_{\mathrm{In(I),eq}}$ are the equilibrium concentrations of In(I) and In(III) species, respectively.

If the process 1 is controlled by the rate of transport, $c_{\mathrm{In(I),eq}}$ is equal to the surface concenttation of In(I) at the disc electrode, $c_{\mathrm{In(I),s}}$, which may be calculated by the use of the *Nekrasov* equation [18]:

$$c_{\mathrm{In(I),s}} = \frac{1.61}{2FN_0AD_{\mathrm{In(I)}}^{2/3}\nu^{-1/6}} \cdot \frac{I_{\mathrm{R,L}}}{\omega^{1/2}} = kI_{\mathrm{R,L}}\omega^{-1/2} \qquad 5$$

In this equation, $D_{\mathrm{In(I)}}$ is the diffusion coefficient of the In(I) species, ν is the kinematic viscosity, and the other symbols have their usual meaning. In(I) is assumed to be absent in the bulk of solution.

The disc potential at open circuit can differ from the equilibrium potential since the spontaneous dissolution of indium causes the interfacial concentrations of solution species to deviate from their respective equilibrium values. As stated above, the process studied is kinetically controlled by the half-reaction 3 whereas the half-reaction 2 is a reversible one. Hence, according to the theory [4], the shift of the disc potential, $\Delta E_{\mathrm{D}} = E_{\mathrm{D}} - E_{\mathrm{D,eq}}$, is given by

$$\Delta E_{\mathrm{D}} = \frac{RT}{F} \ln\left(\frac{c_{\mathrm{In(I),s}}}{c_{\mathrm{In(I),eq}}}\right) \qquad 6$$

After substituting eqn. 5 into eqn. 6, the following expression for ΔE_{D} is obtained:

$$\Delta E_{\mathrm{D}} = \frac{RT}{F} \ln\left(\frac{kI_{\mathrm{R,L}}}{c_{\mathrm{In(I),eq}}\omega^{1/2}}\right) \qquad 7$$

A plot of $\log(I_{\mathrm{R,L}}/\omega^{1/2})$ *vs.* ΔE_{D} should be linear with a slope of $-2.303\,RT/F$. The intercept of this plot allows the determination of $c_{\mathrm{In(I),eq}}$.

If the reaction 1 occurs quasi-reversibly, we have simply determined the equilibrium concentration of In(I), $c_{\mathrm{In(I),eq}}$, from 5 (the *Nekrasov* equation) using the ratio of $I_{\mathrm{R,L}}/\omega^{1/2}$ at $\omega \to 0$. Under these conditions, the process is controlled exclusively by the rate of transport. The values of $D_{\mathrm{In(I)}}$ determined by us in the previous work [14] were employed in the calculations. The dynamic viscosity and density data for KBr solutions were taken from the literature [19].

However, some difficulty arises when the rate-determining step is fully irreversible, as for instance in the solution containing 4.0 mol·dm^{-3} Br$^-$. In such cases, we have applied eqn. 7. Accordingly, plots of $\log(I_{R,L}/\omega^{1/2})$ against ΔE_D were generated. A typical application of this procedure is illustrated in Fig. 4. The plots obtained yielded reasonable straight lines with slopes of 59 ± 3 mV/decade. The extrapolation of the plots to $\Delta E_D = 0$ allowed us to determine the equilibrium concentrations of In(I) at the disc surface. The data of Fig. 4 indicate that the reversibility of the reproportionation reaction is strongly influenced by the bulk concentration of depolarizer. The lower the concentration, the more irreversible is the process, as predicted by the theory of *Molodov* [4].

Subsequently, the equilibrium constants of reaction 1 were estimated using eqn. 4. It should be stressed that two thirds of the In(I) ions originate from the oxidation of indium metal, and one third results from the reduction of In(III) ions. Consequently, the calculations of K_r were made, if needed, with regard to the decreasing In(III) surface concentration compared with that in the bulk of solution.

Table 1 summarizes the values of $c_{\mathrm{In(I),eq}}$ as well as the corresponding equilibrium constants for the reproportionation reaction 1. The results obtained in this investigation are in good agreement with our previous study [14]. However, the present values of K_r were in general found to be slightly lower than those determined using the potentiometric and coulometric technique. To our opinion, these discrepancies lie within the limits of experimental error.

In order to complete our knowledge about the mechanism of reaction 1, we have undertaken experiments with solutions of different acidities (0.1 and 1.0 mol·dm^{-3}). The variation of hydrogen ion concentration was carried out using the appropriate amount of HBr instead of KBr to maintain the bromide ion concentration constant at 4.0 mol·dm^{-3}. Inspection of the data collected in Table 1 show that reaction 1 is essentially unaffected by the acidity of the solution in the concentration range of 0.01 to 1.0 mol·dm^{-3} hydrogen. We can conclude that, on the time scale of the RRDE experiments, the hydrogen evolution was not superimposed on the main cathodic reaction to release more In(I) during the concurrent anodic reaction 2.

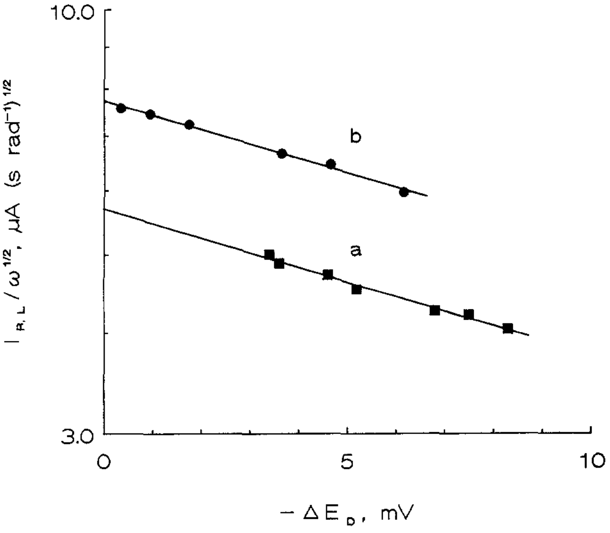

Fig. 4. Plot of the quotient $I_{R,L}/\omega^{1/2}$ (expressed in the logarithmic scale) against ΔE_D for solutions containing (a) 5×10^{-3} and (b) 1×10^{-2} mol·dm^{-3} InBr$_3$, respectively, and 0.01 mol·dm^{-3} HBr. Each solution contained an appropriate quantity of KBr to obtain a total concentration of Br$^-$ equal to 4.0 mol·dm^{-3}

Table 1. Equilibrium concentrations of In(I), $c_{\mathrm{In(I),eq}}$, and equilibrium constants, K_r, for reaction 1 at $T = 298\,\mathrm{K}$

Background electrolyte	Total bromide concentration	c_{HBr} ($\mathrm{mol \cdot dm^{-3}}$)	$c_{\mathrm{In(III)}}$ ($\mathrm{mol \cdot dm^{-3}}$)	$c_{\mathrm{In(I),eq}}$ ($\mathrm{mol \cdot dm^{-3}}$)	K_r (this work)	K_r (from Ref. [14])
KBr	1.0	0.01	0.01	1.03×10^{-4}	1.1×10^{-10}	$2.1 \times 10^{-10\,a}$
	2.0	0.01	0.01	1.68×10^{-4}	4.7×10^{-10}	$6.6 \times 10^{-10\,a}$
	3.0	0.01	0.01	3.5×10^{-4}	4.3×10^{-9}	$3.1 \times 10^{-9\,a}$
	4.0	0.01	0.005	3.7×10^{-4}	1.0×10^{-8}	1.6×10^{-8}
	4.0	0.01	0.01	5.0×10^{-4}	1.3×10^{-8}	1.8×10^{-8}
	4.0	0.1	0.01	4.5×10^{-4}	9.1×10^{-9}	
	4.0	1.0	0.005	3.6×10^{-4}	9.3×10^{-9}	
$MgBr_2$	4.0	0.01	0.01	8.2×10^{-4}	5.7×10^{-8}	
$CaBr_2$	4.0	0.01	0.01	7.6×10^{-4}	4.5×10^{-8}	

[a] measured at $c_{\mathrm{In(III)}} = 0.05\,\mathrm{mol \cdot dm^{-3}}$

To obtain more information concerning the medium effect on reaction 1, we have performed the RRDE measurements in solutions containing other bromides as background electrolytes: $MgBr_2$ and $CaCl_2$. The total concentration of bromide ions was maintained constant at $4.0\,\mathrm{mol \cdot dm^{-3}}$. The diffusion coefficients of In(I) in these solutions, required in eqn. 5, were calculated from the *Walden* product in the appropriate solution of KBr. The data needed were taken from our previous work [14]. we assumed that the *Walden* product would be practically unaffected by the nature of the background electrolyte cation because of the rather weak solvating power of water with respect to In(I) ions, as indicated by the *Gibbs* energy of hydration [20]. This assumption is also supported by the relatively high value of $D_{\mathrm{In(I)}}$ in concentrated KBr solutions, determined to be $1.8 \times 10^{-5}\,\mathrm{cm^2 \cdot s^{-1}}$ [14].

The values of K_r thus obtained are noticeably greater than that in the respective solution of KBr (see Table 1). The observed stabilization of the monovalent state relative to the trivalent one can be explained as a result of partial dehydration of mixed aquo-bromo complexes of In(III) in the solutions of $MgBr_2$ and $CaBr_2$. It is known from the literature that the electrolytes mentioned reveal low water activity and thus can act as dehydrating agents [21].

The major conclusions of the above investigations can be summarized as follows:

(1) The RRDE technique has been demonstrated to be a convenient tool for determining the equilibrium constants of reproportionation reactions under participation of metals as reactants. Two different electrochemical measuring techniques, coulometry and ring–disc voltammetry, give comparable results. Evidently, the RRDE technique allows to perform the suitable measurements in a rather short time. It appears that the principal source of the possible error may be the use of incorrect values of the diffusion coefficient for ions of the lower oxidation state in the computations.

(2) The experimental dependencies of disc potential and limiting ring current on the square root of rotation velocity indicate unequivocally that the reproportionation reaction of indium(I) occurs in aqueous bromide solutions according to the

electrochemical mechanism. The cathodic partial reaction 3 is the rate-determining step whereas the anodic partial reaction 2 is a reversible one.

Experimental

All chemicals were of p.a. grade. The solutions were prepared by dissolving a proper amount of substance in triply distilled water. The concentration of In(III) in stock solutions was checked by complexometric titration. The electrolytes were purged by high purity argon before each experiment.

The RRDE used in this investigation was constructed in our laboratory. Both the ring and the disc were made from gold of high purity (99.99% Au). The disc radius was equal to $r_1 = 0.250\,\mathrm{cm}$, the inner ring radius $r_2 = 0.274\,\mathrm{cm}$, and the outer ring radius $r_3 = 0.374\,\mathrm{cm}$. The geometric area of the disc was $A = 0.196\,\mathrm{cm}^2$. The collection efficiency, $N_0 = 0.42 \pm 0.02$, was determined experimentally with the Cu(II)/Cu(I) redox system in chloride medium. The value of N_0 calculated from the measured radii, using the digital simulation program supplied by *Penar* and *Sykut* [15], was equal to 0.435, in satisfactory agreement with the experiment. Before each set of experiments, the RRDE was cleaned by mechanical polishing with alumina powder (0.05 µm) and then by successive rinsing with water and acetone.

All electrochemical experiments were performed in a three-compartment glass cell. The capacity of the main compartment was approximately $100\,\mathrm{cm}^3$. This ensured that the accumulation of In(I) in the bulk of the solution was negligible during the course of a set of experiments.

The reference electrode, to which all potentials are referred, was a KCl-saturated calomel electrode (SCE). The counter electrode consisted of a spiral-shaped Pt wire of large area.

A Model 10.0.2 bipotentiostat (Institute of Chemistry, University of Lodz) was utilized to control both the disc and ring electrode. The dependencies of ring current and disc potential during the spontaneous dissolution of indium were recorded digitally using V-543 digital voltmeters (Meratronik) connected to an ERD-103 printer (Zootechnika Co-op) and a quartz timer.

Viscosities of the $MgBr_2$ and $CaBr_2$ solutions were measured with the use of an Ubbelohde viscometer.

All experiments were carried out at a temperature of 25 ± 0.2 °C.

Acknowledgements

The authors gratefully acknowledge financial support from the *State Committee for Scientific Research* (KBN) under grant No 1217/P3/92/02 (2 0007 91 01). Thanks also are due to Mrs. *M. Kaczor* for technical assistance in some of the experiments.

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Received April 8, 1994. Accepted (revised) November 21, 1994