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# Redox Equilibria in the In(III)–In(I)–In System in Aqueous KBr Solutions, I. Potentiometric and Coulometric Study

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**Summary.** The reproportionation of In(I) ions in acidic potassium bromide solutions was studied by means of the coulometric and potentiometric method. The formal potentials of the In(III)/In(I), In(III)/In and In(I)/In redox couples as well as the equilibrium constants of the reaction In(III) $+ 2\,\mathrm{In} = 3\,\mathrm{In(I)}$ were determined at a background electrolyte concentration ranging from 1 to $4\,\mathrm{mol\,dm^{-3}}$. Based on the experimental results, a scheme of the reproportionation reaction was proposed with regard to the participation of bromide ions. In addition, the diffusion coefficient of In(I) ions was determined using the chronopotentiometric technique.

**Keywords.** Bromide solutions; Diffusion coefficient; Indium(I); Potentiometry; Reproportionation equilibrium.

### Das Redox-Gleichgewicht im In(III)–In(I)–In-System in wäßrigen KBr-Lösungen, I. Potentiometrische und coulometrische Untersuchungen

**Zusammenfassung.** Die Reproportionierung von In(I)-Ionen in sauren Kalium-bromid-Lösungen wurde mittels der coulometrischen und potentiometrischen Meßmethode untersucht. Die Formal-Standardpotentiale der In(III)/In(I)-, In(III)/In- und In(I)/In-Redoxpaare sowie die Gleichgewichtskonstanten der Reaktion In(III) $+ 2$ In $= 3$ In(I) wurden im Konzentrationsbereich von 1–4 $\mathrm{mol\,dm^{-3}}$ ermittelt. Mit der Steigerung der KBr-Konzentration verschiebt sich das untersuchte Gleichgewicht erheblich zugunsten Indium(I). Aufgrund der potentiometrischen Meßergebnisse wurde ein Schema der Reproportionierung-Reaktion unter Berücksichtigung der Teilnahme von Bromidionen aufgestellt. Zusätzlich wurde der Diffusionskoeffizient von In(I)-Ionen mit Hife chronopotentiometrischer Messungen bestimmt.

## Introduction

Indium is a metal of growing practical importance, particularly in the technology of semiconducting materials. The knowledge of its electrochemical and corrosion behaviour is, therefore, of considerable interest. It is well known for a long time that the cathodic reduction of In(III) ions as well as the anodic dissolution of metal indium occurs in two consecutive charge-transfer steps and involves an In(I) species as intermediate [1]. Thus, the equilibrium of the reproportionation reaction

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

is of great importance for the understanding of the In(III)/In electrode mechanism. The equilibrium constant for this reaction can then be expressed by the equation

$$K_r = (c_{\mathrm{In(I)}})^3 / c_{\mathrm{In(III)}}. \tag{2}$$

The equilibrium of the reproportionation reaction (1) incorporates equilibria of single redox couples: In(III)/In(I), In(III)/In, and In(I)/In. The corresponding Nernst equations for these redox pairs can be expressed as follows:

$$E_{31} = E^{o\prime}_{31} + (RT/2F)\ln(c_{\mathrm{In(III)}}/c_{\mathrm{In(I)}}) \tag{3}$$

$$E_{30} = E^{o\prime}_{30} + (RT/3F)\ln c_{\mathrm{In(III)}} \tag{4}$$

$$E_{10} = E^{o\prime}_{10} + (RT/F)\ln c_{\mathrm{In(I)}}. \tag{5}$$

In these equations, $E^{o\prime}$ denotes the formal potential of the corresponding redox couple. The formal potentials listed above are mutually interrelated according to Luther's principle [2]:

$$E^{o\prime}_{10} = 3\,E^{o\prime}_{30} - 2\,E^{o\prime}_{31}. \tag{6}$$

When the equilibrium of reaction (1) is established, the reversible potentials which correspond to the individual redox systems become equal, i.e. $E_{31} = E_{30} = E_{10} = E_{eq}$. Consequently, the equilibrium constant of reaction (1) may be described using the formal potentials of individual redox couples, e.g.

$$\ln K_r = (6F/RT)(E^{o\prime}_{31} - E^{o\prime}_{30}). \tag{7}$$

In aqueous solutions, Eq. (1) significantly depends upon the nature and concentration of the background electrolyte. In the presence of non-complexing background electrolytes, e.g. perchlorates, indium(I) is very unstable with respect to In(III) and In(0). The equilibrium constant for reaction (1) in such media is reported in the literature [3, 4] to be equal to about $10^{-10}$ at 298 K.

The equilibrium above is markedly shifted to the right side in the solutions containing halides. The influence of bromides is particularly appreciable [5–7]. In spite of this fact the influence of bromide ion concentration on the equilibrium of indium(I) reproportionation reaction is rather not well recognized. Only Sheka and Kozin [6] studied this equilibrium in aqueous solutions containing 2.0, 5.0 and 8.0 mol dm$^{-3}$ $ZnBr_2$, at an elevated temperature (323 K). However, $ZnBr_2$ acts not only as a source of bromide anions but also as a strong dehydrating agent. It is known from the Ref. [8] that a decrease in water activity enhances the stability of In(I).

This paper is a continuation of our study on the medium effects on the electrochemical behaviour of the In(III)–In(I)–In system [9–11]. The purpose of the present work was to investigate the influence of bromide ions on the equilibrium of the In(I) reproportionation reaction. Coulometry and potentiometry have been used as main experimental techniques. To minimize the change of water activity with the increase in concentration of the background electrolyte, KBr was used as a source of the bromide ligand. It is known that this salt only slightly influences the water activity [12].

## Experimental Part

All chemical used were p.a. grade. Indium metal, obtained as wire or shot from Aluminium Works, Skawina, was of 99.999% purity. Indium(III) bromide was prepared by dissolving metallic indium in 40% HBr and subsequent crystallization from solution. All solutions were made with triply distilled water.

Potentials were measured and reported with respect to the external calomel reference electrode with saturated KCl solution (SCE). A small platinum disc with a geometric surface of 0.196 cm$^2$ was used as a working electrode in the chronopotentiometric measurements. The generating electrode in the coulometric titration was a large area platinum sheet. A Pt spiral served as a counter electrode. It was placed in a compartment separated by a fritted glass disc.

Constant current was supplied by a Radelkis OH-404/A potentiostat-galvanostat. In the coulometric work, an OH-404/B integrator was employed. Electrode potentials were measured using a Meratronik V-540 digital voltmeter. The chronopotentiometric curves were recorded digitally using a digital voltmeter fed to an ERD-103 printer (Zootechnika Co-op) and a quatz timer.

Before experiments, all solutions were de-aerated by bubbling with pure argon. During electrochemical measurements, argon was passed over the solution.

In(I) ions were produced in the solutions studied by their equilibration with metal indium. A wire of pure indium (99.999% In) was immersed into the solution investigated. The reproportionation reaction (1) was being conducted under stirring, sufficiently long to establish an equilibrium in the In(III)–In(I)–In system. The reaction advancement was checked through measurement of the potential difference between the indium and platinum electrode, $\Delta E = E_{30} - E_{31}$. After the equilibrium had been achieved, i.e. when $\Delta E = 0$, the stirring of the solution was interrputed and the potentials of the both electrodes were measured carefully against the SCE. Next, the chronopotentiometric measurements were made in order to determine the diffusion coefficients of In(I) ions. Finally, the indium electrode was removed from the solution, and the In(I) ion concentration was determined by coulometric titration with the anodically generated bromine.

All experiments were performed in a thermostated air box at 25 ± 2 °C (298.2 K).

## Results and Discussion

To prove that the indium(I) reproportionation reaction proceeds according to Scheme (1), the equilibrium concentration of In(I) was determined as a function of In(III) concentration. A series of experiments was conducted in which the $InBr_3$

**Table 1.** Equilibrium concentrations of In(I), electrode potentials, and equilibrium constants for the reaction (1) at various In(III) concentration in solutions containing 0.01 mol dm$^{-3}$ HBr and a suitable quantity of KBr to obtain a total concentration of Br$^-$ equal to 4.0 mol dm$^{-3}$; $T = 298$ K

| $c_{In(III)}$ mol dm$^{-3}$ | $c_{In(I)}$ mol dm$^{-3}$ | $E_{eq}$ mV vs. SCE | $K_r$ |
|---|---|---|---|
| 0.005 | $4.3 \cdot 10^{-4}$ | −706 | $1.6 \cdot 10^{-8}$ |
| 0.010 | $5.6 \cdot 10^{-4}$ | −698 | $1.8 \cdot 10^{-8}$ |
| 0.020 | $8.1 \cdot 10^{-4}$ | −689 | $2.7 \cdot 10^{-8}$ |
| 0.050 | $1.2 \cdot 10^{-3}$ | −682 | $3.5 \cdot 10^{-8}$ |
| 0.100 | $1.8 \cdot 10^{-3}$ | −676 | $5.8 \cdot 10^{-8}$ |

concentration ranged from 0.005 to 0.1 mol dm$^{-3}$ whilst the total concentration of bromide ions was maintained at 4.00 mol dm$^{-3}$. The results obtained are collected in Table 1. The reported data of the electrode potential were time-stable, and their reproducibility was better than 0.5 mV between extremes. It follows from these data that the electrode gives a Nernstian response to changes in the concentrations of In(III).

Figure 1 shows a plot of log $c_{\mathrm{In(I)}}$ vs. log $c_{\mathrm{In(III)}}$. A linear dependence with a slope of 0.48 was obtained, greater than that theoretically predicted value of 0.33. This deviation from the expected value can be due to the acid–base reaction between indium(I) and indium(III) which results in formation of In(I)·In(III) complexes

$$4\,\mathrm{In(III)} + 2\,\mathrm{In} \rightleftarrows 3\,\mathrm{In(I)\cdot In(III)}. \tag{8}$$

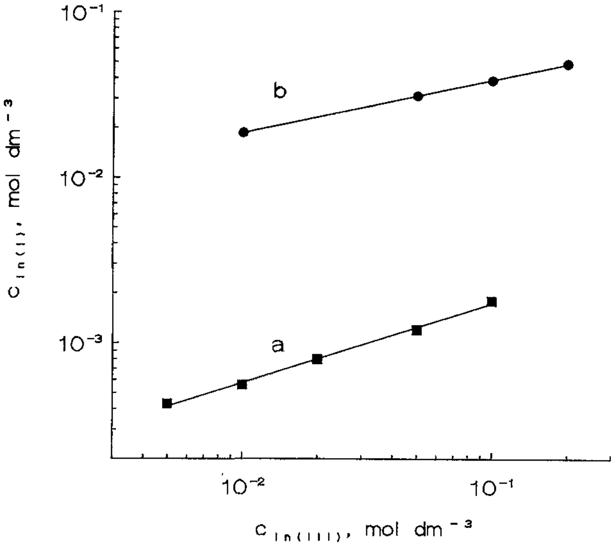

**Fig. 1.** Dependence of the In(I) equilibrium concentration on the concentration of In(III) in solutions containing (a) 4.0 mol dm$^{-3}$ KBr and 0.01 mol dm$^{-3}$ HBr at $T = 298$ K (this research); (b) 5 mol dm$^{-3}$ ZnBr$_2$ at $T = 323$ K (from Ref. [9]).

**Table 2.** The equilibrium concentrations of In(I), formal electrode potentials of the In(III)/In(I), In(III)/In and In(I)/In couples, referred to the SCE, equilibrium constants for the reaction (1), and diffusion coefficients of In(I) in aqueous KBr solutions of various concentration. Each solution contained 0.05 mol dm$^{-3}$ InBr$_3$ and 0.01 mol dm$^{-3}$ HBr

| Concentration of Br$^-$ ions mol dm$^{-3}$ | $c_{\mathrm{In(I)}}$ mol dm$^{-3}$ | $E^{0\prime}_{31}$ mV | $E^{0\prime}_{30}$ mV | $E^{0\prime}_{10}$ mV | $K_r$ | $10^5 D$ cm$^2$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 1.0 | $2.2 \cdot 10^{-4}$ | −728 | −633 | −441 | $2.1 \cdot 10^{-10}$ | 1.7 |
| 1.5 | $2.5 \cdot 10^{-4}$ | −734 | −641 | −453 | $3.2 \cdot 10^{-10}$ | |
| 2.0 | $3.2 \cdot 10^{-4}$ | −734 | −645 | −465 | $6.6 \cdot 10^{-10}$ | 1.7 |
| 3.0 | $5.2 \cdot 10^{-4}$ | −738 | −655 | −488 | $3.1 \cdot 10^{-9}$ | 1.8 |
| 4.0 | $1.2 \cdot 10^{-3}$ | −730 | −657 | −510 | $3.2 \cdot 10^{-8}$ | 1.8 |

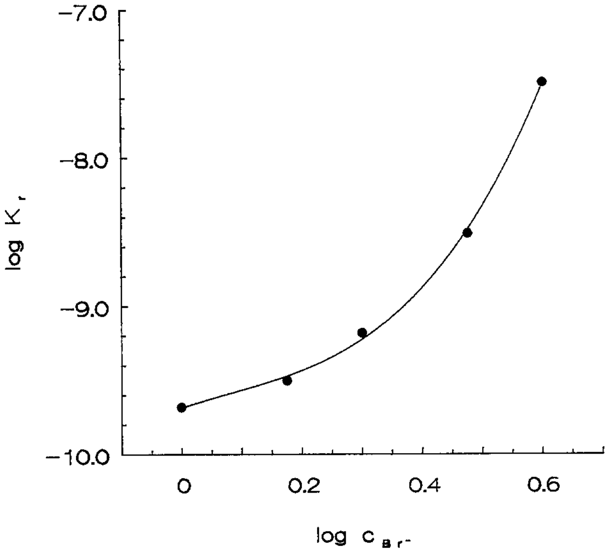

**Fig. 2.** Variation of the equilibrium constant for the In(I) reproportionation reaction (1) with the bromide ion concentration in solutions containing each 0.05 mol dm$^{-3}$ $InBr_3$ and 0.01 mol dm$^{-3}$ HBr, and an appropriate quantity of KBr

The solid state indium(I) compound having the composition $In^{I}In^{III}Br_4$ is known for some time [13].

The equilibrium constant of reaction (8) is given by the relation

$$K'_r = (c_{\mathrm{In(I)}\cdot\mathrm{In(III)}})^3/(c_{\mathrm{In(III)}})^4. \tag{9}$$

It follows that the dependence of $\log c_{\mathrm{In(I)}}$ on $\log c_{\mathrm{In(III)}}$ should be linear with a slope of 1.33. However, the experimental slope of the curve indicates that the contribution of reaction (8) is not very important. It should be noted that the analogous dependence obtained from data reported by Sheka and Kozin [6] for a 5 mol dm$^{-3}$ solution of $ZnBr_2$ at 323 K (Fig. 1, curve 2) exhibits a slope of 0.33.

Further investigations were perfomed at a constant concentration of In(III), equal to 0.05 mol dm$^{-3}$, whilst the total concentration of bromide ions ranged from 1.00 to 4.00 mol dm$^{-3}$. The results obtained are listed in Table 2.

As follows from the data presented (see also Fig. 2), $K_r$ rises about two orders of magnitude when the bromide concentration increases from 1 to 4 mol dm$^{-3}$. One can suppose that the observed important shift of the equilibrium (1) in favour of In(I) is due to the formation of strong complexes with bromide ions. Figure 3 represents plots of the formal potentials for the In(I)/In, In(III)/In and In(III)/In(I) redox couples against the logarithm of bromide ion concentration. One observes that the formal potentials of In(III)/In and In(I)/In pairs shift negative as the concentration of bromide increases. From the dependencies given in Fig. 3, the composition of In(III) and In(I) complexes with $Br^-$ can be determined. The plot for the In(III)/In couple is linear with a slope of −41 mV/log unit. This value corresponds to the average ligand number of 2.1, thus indicating the formation of $InBr_2^+$ as an In(III) species dominating in this concentration range. However, the plot of In(I)/In formal potential against the logarithm of bromide concentration is markedly curved. The slope of this plot changes from −68 mV/decade in the lower concentration range (at 1 mol dm$^{-3}$) to −176 mV/decade at very high concentrations, $c \to 4$ mol dm$^{-3}$. The former value is fairly close to that theoretically

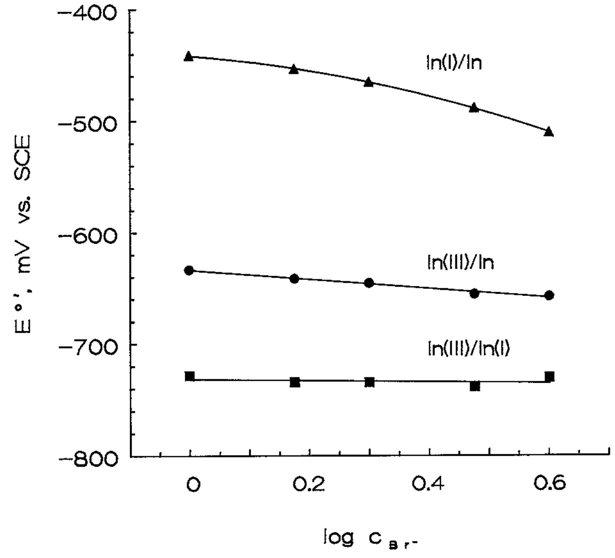

**Fig. 3.** Dependence of the formal potentials (expressed vs. SCE) for the In(I)/In, In(III)/In and In(III)/In(I) couples on the logarithm of the bromide ion concentration

expected for a ligand number equal three. The result obtained suggests that the complexes InBr, $InBr_2^-$ and $InBr_3^{2-}$ are formed in ratios dependent on bromide concentration. It is to note that the formation of $InBr_2^-$ has been reported by Redkin et al. [14] at concentrations of bromide ions below 1 mol dm$^{-3}$.

On the basis of the results obtained above, at higher bromide concentrations (close to 4 mol dm$^{-3}$) the following scheme for reaction (1) may be supposed with regard to the participation of bromide ions:

$$InBr_2^+ + 2\,In + 7\,Br^- \rightleftarrows 3\,InBr_3^{2-}. \qquad (10)$$

As mentioned in the Introduction, the equilibrium of reproportionation reaction (1) significanly affects the mechanism of the In(III)/In electrode process. Our study [9] on the electroreduction of In(III) at gold from acidic KBr solutions using the rotating ring-disc technique showed that the overall three-electron reaction proceeds in two successive steps

$$\mathrm{In(III)} + 2\,e^- \rightarrow \mathrm{In(I)} \qquad (11)$$

$$\mathrm{In(I)} + e^- \rightarrow \mathrm{In}. \qquad (12)$$

We have found that the intermediate In(I) ions can be generated with 100% current efficiency at low current densities, in spite of their low thermodynamic stability in this medium. Based on this finding, we have determined the kinetic parameters of the In(III)/In(I) electron transfer reaction in the solution of 4 mol dm$^{-3}$ bromides [10].

A much better stabilization of In(I) can be achieved in highly concentrated aqueous $ZnBr_2$ solutions, especially at elevated temperatures [6]. The voltammetric investigation carried out in our laboratory [11] showed that the reduction of In(III) on gold in this medium occurs in two well separated stages, according to the consecutive reactions (11) and (12), respectively, as the $ZnBr_2$ concentration exceeds 6 mol dm$^{-3}$. However, in this case, a high thermodynamic stability of In(I) ions results not only from their complexation by bromides but also from dehydration of In(III) upon drastical decreasing the water activity. In the present study, we have considerably avoided the mentioned complication by the use of KBr as the base electrolyte.

In addition, the diffusion coefficients of In(I) ions, $D_{\mathrm{In(I)}}$, were determined by means of the chronopotentiometric technique. The well-known Sand equation [15] was used in the calculations. The results are given in Table 2. As shown in this Table, the value of $D_{\mathrm{In(I)}}$ is practically independent of the background electrolyte concentration. This result is not surprising because the dynamic viscosity of aqueous KBr solutions changes insignificantly with the increase of salt concentration [16]. The comparable value of the diffusion coefficient, $1.8 \cdot 10^{-5}\,\mathrm{cm^2\,s^{-1}}$, has been obtained by Visco [3] for the hydrated In(I) ion in $0.7\,\mathrm{mol\,dm^{-3}}$ $HClO_4$ solution at 293 K.

Based on the diffusion coefficients determined, the ionic radius of the In(I) complex can be calculated under the assumption that the complex is regarded as a rigid sphere molecule, using the Einstein–Stokes relation in the form modified by McLaughlin [17]:

$$D = kT/4\pi\eta r. \tag{13}$$

The values of the dynamic viscosity, $\eta$, of KBr solutions needed for the calculations were interpolated from literature data [15]. A radius of about 0.22 nm for the In(I) species is obtained.

Further results concerning the reaction mechanism attained by the use of the rotating ring-disc electrode technique will be reported in a subsequent paper.

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