

# Mechanism and Kinetics of the Reduction of In(III) Ions at a Polycrystalline Gold Electrode from Highly Concentrated ZnCl<sub>2</sub> Solutions

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**Summary.** The mechanism of the cathodic reduction of In(III) at gold has been studied by rotating disc and ring-disc voltammetry in highly concentrated aqueous ZnCl<sub>2</sub> solutions. At concentration of the base electrolyte higher than 7 mol dm<sup>-3</sup>, the voltammetric curves recorded at the disc electrode split into two well-separated waves which correspond to the successive charge transfer reactions: In(III) + 2e<sup>-</sup> → In(I) and In(I) + e<sup>-</sup> → In. By the use of coulometric and potentiometric techniques, 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 reproporationation reaction In(III) + 2In ⇌ 3In(I) has been determined and discussed. The kinetic parameters of the In(III)/In(I) electrode reaction have been also evaluated and discussed.

**Keywords.** Electrode kinetics; Highly concentrated solutions; In(III) electroreduction; Multi-step electrode process; Rotating ring-disc electrode.

## Mechanismus und Kinetik der Reduktion von In(III)-Ionen an der Goldelektrode in hochkonzentrierten wäßrigen ZnCl<sub>2</sub>-Lösungen

**Zusammenfassung.** Es wird der Mechanismus der Reduktion von In(III)-Ionen in hochkonzentrierten ZnCl<sub>2</sub> Lösungen mittels der Scheiben- und Ring-Scheiben-Elektrode aus Gold untersucht. Wenn die Konzentration des Grundelektrolyten 7 mol dm<sup>-3</sup> übersteigt, verteilen sich die erhaltenen Stromspannungskurven auf zwei gut gestaltete Stufen, die den konsekutiven Durchtrittsreaktionen In(III) + 2e<sup>-</sup> → In(I) und In(I) + e<sup>-</sup> → In entsprechen. Aufgrund der coulometrischen und potentiometrischen Messungen werden die Formal-Standardpotentiale der In(III)/In(I)-, In(III)/In- und In(I)/In-Redoxpaare, die Gleichgewichtskonstanten der Reproportionierungsreaktion In(III) + 2In ⇌ 3In ermittelt. Die kinetischen Parameter der Durchtrittsreaktion In(III)/In(I) werden bestimmt und diskutiert.

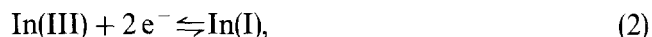
## Introduction

In our earlier work [1], the mechanism of the In(III) electroreduction on Au was investigated from highly concentrated aqueous ZnBr<sub>2</sub> solutions. An important feature of this medium is its ability to stabilize In(I) with respect to In(III) as illustrated by equilibrium (1). It is known that in non-complexing aqueous

solutions In(I) is unstable and disproportionates ( $K_d \approx 10^{11}$  [2, 3]), due to the strong hydration of In(III):



The mechanism of the In(III)/In electrode process in chloride media was intensively investigated [4–16], particularly by Russian workers (for a review see Ref. [17]). It was proved that the process studied is involved in two consecutive charge-transfer steps,



and that the intermediate In(I) ions does exist in measurable quantities. Kozin and co-workers [9, 11–13] demonstrated by means of the rotating ring-disc electrode technique (RRDE) that In(I) may be stabilized by using highly concentrated  $\text{ZnCl}_2$  solutions as the background electrolyte. Moreover, investigations were made on the equilibrium of the disproportionation/reproportionation reaction (1) in concentrated solutions of  $\text{CaCl}_2$  [18],  $\text{LiCl}$  [19],  $\text{ZnCl}_2$  [20] and other chlorides [21], mostly at elevated temperatures. Some physico-chemical properties of In(I) were also characterized in these media [8, 15]. Nevertheless, quite a few data of kinetic parameters for the electrode process considered in chloride media are reported in literature [5, 6]; all of them concern the overall electrode reaction In(III)/In.

This paper is a continuation of our study on the influence of highly concentrated background electrolytes on the electrochemical behaviour of the In(III)/In(I)/In system. In particular, we were interested in the kinetic data of the electron-transfer step (2). Zinc chloride was used as the background electrolyte because the hydrogen evolution reaction (HER) exhibits high overpotential on Au in its aqueous solutions, in comparison with other chlorides. In contrast, the In(III) reduction process is masked by the HER in concentrated  $\text{LiCl}$  and  $\text{CaCl}_2$  solutions.

## Experimental Part

All solutions were prepared from analytical grade reagents:  $\text{InCl}_3$  (Merck), 36%  $\text{HCl}$  (POCh, Poland) and  $\text{ZnCl}_2$  (Fluka), and triply distilled water. The stock solution of  $\text{ZnCl}_2$  was pre-treated by boiling with active charcoal (Merck) before use. Final solutions were acidified ( $0.1 \text{ mol dm}^{-3} \text{ HCl}$ ) to prevent complications due to hydrolysis of indium species.

A home made rotating ring-disc electrode (RRDE) was used. The apparatus consisted of an Au disc and a Pt ring. The dimensions of the RRDE were: disc radius  $r_1 = 0.250 \text{ cm}$ , inner ring radius  $r_2 = 0.275 \text{ cm}$  and outer ring radius  $r_3 = 0.375 \text{ cm}$ . The geometric area of the disc was  $A = 0.196 \text{ cm}^2$ . The collection efficiency,  $N_0$ , was determined by experiment with the  $\text{Cu(II)/Cu(I)}$  electrode reaction in the chloride medium to be  $0.42 \pm 0.01$ . In coulometric experiments, another rotating Au disc electrode with a geometric area of  $0.521 \text{ cm}^2$  was employed as the generating electrode.

The viscosities were measured at  $25 \pm 0.05^\circ \text{C}$  with a BH2 Höppler viscometer (Prüfgeräte-Werk Medingen), and the densities, required in this method, using a picnometer.

All other instrumentation and experimental arrangements were essentially as previously described [1].

All potentials were measured with respect to the saturated calomel electrode with  $\text{NaCl}$  solution, SCE( $\text{NaCl}$ ).

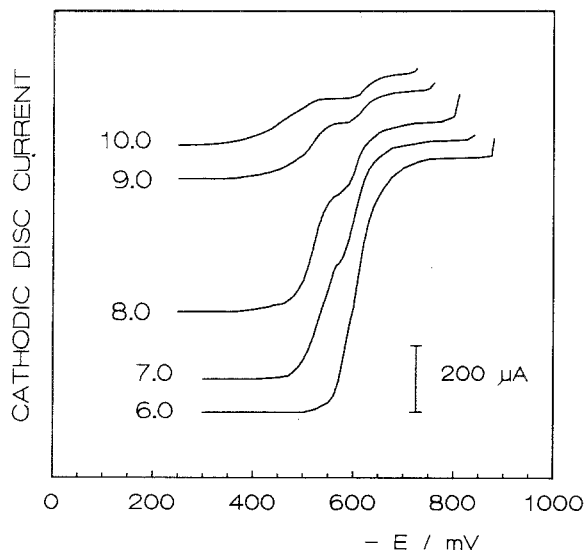
The electrochemical measurements were made at  $25 \pm 0.2^\circ \text{C}$  (298.2 K).

## Results

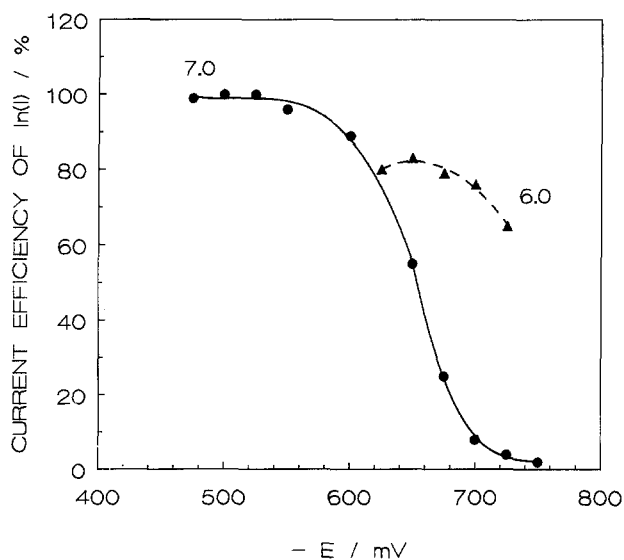
Figure 1 shows RDE voltammograms for the reduction of  $0.01 \text{ mol dm}^{-3}$  In(III) in the solution containing  $\text{ZnCl}_2$  of various concentration, as a background electrolyte. For the solution of  $6 \text{ mol dm}^{-3}$   $\text{ZnCl}_2$ , a single wave was obtained which can be attributed to the three-electron process In(III)/In. However, a weakly-shaped preliminary step is observed on this wave. An increase in the background concentrations makes this step more pronounced and higher. Finally, in the case of solutions containing  $8 \text{ mol dm}^{-3}$  or more  $\text{ZnCl}_2$ , the RDE voltammograms are split into two waves with the ratio of limiting currents equal to 2:1. This result suggests that the process studied occurs in the consecutive stages (2) and (3). A similar behaviour was observed before by us in the case of In(III) reduction on an Au-RDE from highly concentrated  $\text{ZnBr}_2$  solutions [1]. The wave due to the In(I) reduction in the solution containing  $11 \text{ mol dm}^{-3}$   $\text{ZnCl}_2$  was moved into the region of decomposition of the supporting electrolyte and became obscured.

The foregoing supposition was confirmed by experiments made with the rotating ring-disc electrode (RRDE). The disc current and ring current were measured step by step at various disc potentials during the reduction of In(III). The ring electrode was held at a constant potential which corresponded to the limiting current plateau for the anodic oxidation of In(I). The results obtained enabled us to calculate the current efficiency of the In(I) generation on the disc electrode. Two representative curves of the potential dependence of In(I) current efficiency are shown in Fig. 2, for the solutions containing  $6.0$  and  $7.0 \text{ mol dm}^{-3}$   $\text{ZnCl}_2$ , respectively. The plots in this figure confirm the assumption that electron-transfer reaction (2) may occur with 100% current efficiency when the  $\text{ZnCl}_2$  concentration is  $7 \text{ mol dm}^{-3}$  or more. Under these conditions, In(I) ions generated on the electrode surface become stable with respect to the disproportionation reaction.

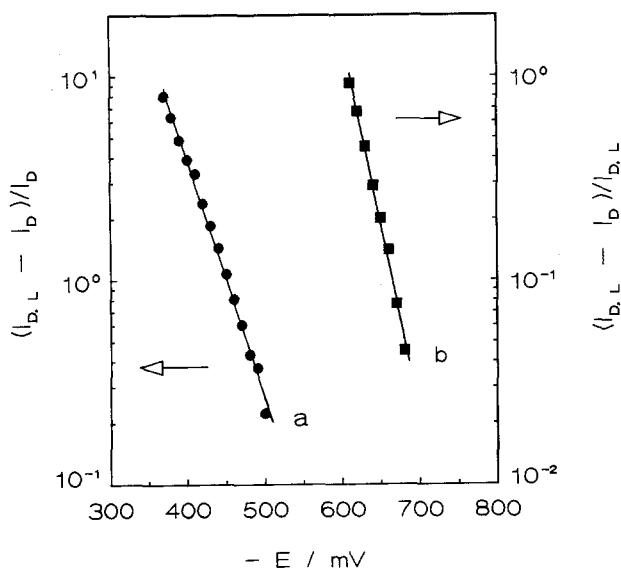
We have performed the semi-logarithmic analysis of the RDE voltammograms obtained for the solutions containing  $8.0 \text{ mol dm}^{-3}$  or more  $\text{ZnCl}_2$ . An example is



**Fig. 1.** RDE voltammograms recorded for the reduction of  $0.01 \text{ mol dm}^{-3}$  In(III) on Au from a solution containing  $0.1 \text{ mol dm}^{-3}$  HCl and various  $\text{ZnCl}_2$  concentrations (given at bottom of each curve). Rotation frequency 17 Hz; scan rate  $2 \text{ mV s}^{-1}$ .



**Fig. 2.** Potential dependence of the current efficiency for the generation of soluble In(I) at an Au disc electrode. Rotation frequency 8 Hz. The curves are labelled with molar concentration of  $\text{ZnCl}_2$



**Fig. 3.** Semi-logarithmic analysis of the first (curve *a*) and second wave (curve *b*) of In(III) electroreduction at a RDE. Electrolyte:  $0.01 \text{ mol dm}^{-3}$   $\text{InCl}_3$ ,  $0.1 \text{ mol dm}^{-3}$   $\text{HCl}$  and  $10.0 \text{ mol dm}^{-3}$   $\text{ZnCl}_2$ . Rotation frequency 50 Hz

presented in Fig. 3. For the first wave, plots of  $E$  vs.  $\log [(I_{D,L} - I_D)/I_D]$  are linear with reciprocal slopes of about  $90 \text{ mV}/\log$  unit indicating an irreversible electrode reaction.

In the case of the second wave, we applied the following equations,

$$E = E_{10}^{\circ} - (RT/F) \ln \chi_{\text{ox}} + (RT/F) \ln (I_{D,L} - I_D) \quad (4)$$

and

$$\chi_{\text{ox}} = 0.62 F A v^{-1/6} D_{\text{ox}} \omega^{1/2}, \quad (5)$$

in which  $E_{10}^{\circ}$  is the formal potential of the In(I)/In redox system,  $I_D$  is the disc current at the actual potential  $E$ ,  $I_{D,L}$  is the limiting disc current,  $A$  is the geometric

disc area,  $D_{ox}$  is the diffusion coefficient of the oxidized form of the reactant, while  $\nu$  and  $\omega$  denote the kinematic viscosity and the angular velocity of electrode, respectively. The symbols  $R$ ,  $T$  and  $F$  have their usual meaning. The above expressions are valid for the processes with formation of an insoluble product which covers the whole electrode surface. In our experiments, the above condition can be fulfilled because the voltammetric curves were recorded at a low potential sweep rate ( $2 \text{ mV s}^{-1}$ ).

In the case of a reversible electrode reaction, one obtains for  $I_D = 1/2 I_{D,L}$

$$E_{1/2r} = E_{10}' + (RT/F) \ln (c_{ox}/2), \quad (6)$$

where  $c_{ox}$  is the bulk concentration of the oxidized form of the reactant.

The semi-logarithmic analysis of the second wave was made in a normalized form by dividing the difference  $I_{D,L} - I_D$  by the limiting current (see curve b in Fig. 3). The plots obtained are linear with reciprocal slopes close to  $59 \text{ mV/decade}$  which is the theoretically expected value for a reversible one-electron process. The values of  $E_{10}'$  calculated using Eqs. (4) and (6) are reported in Table 1, except for the solution containing  $11 \text{ mol dm}^{-3} \text{ ZnCl}_2$ . In this solution, the limiting current plateau of the second wave was not attainable because of the earlier occurrence of zinc electrodeposition.

From the total limiting currents of the voltammograms recorded, the diffusion coefficients,  $D_{In(III)}$ , for the In(III) ions were evaluated using the Levich equation. Plots of the limiting current against the square root of the electrode rotation frequency were linear and passed through the origin of coordinates, indicating that the currents considered are controlled by the convective diffusion.

In order to determine the diffusion coefficients of the In(I) ion,  $D_{In(I)}$ , and the formal potentials of the In(III)/In(I) couple,  $E_{31}'$ , in the solutions containing from  $7.0$  to  $11.0 \text{ mol dm}^{-3} \text{ ZnCl}_2$ , the long-run electrolyses were carried out under coulometric control on the Au-RDE. The initial concentration of In(III) in the solutions investigated was  $0.01 \text{ mol dm}^{-3}$ . Details of the procedure were described earlier [1]. The values of diffusion coefficients for both In(I) and In(III) species are listed in Table 2.

By plotting the equilibrium potentials of the In(III)/In(I) couple against the logarithm of the  $c_{In(III)}/c_{In(I)}$  ratio, straight lines were obtained as shown in Fig. 4. The slopes of the plots are  $29 \pm 2 \text{ mV/decade}$  thus indicating that the In(III)/In(I)

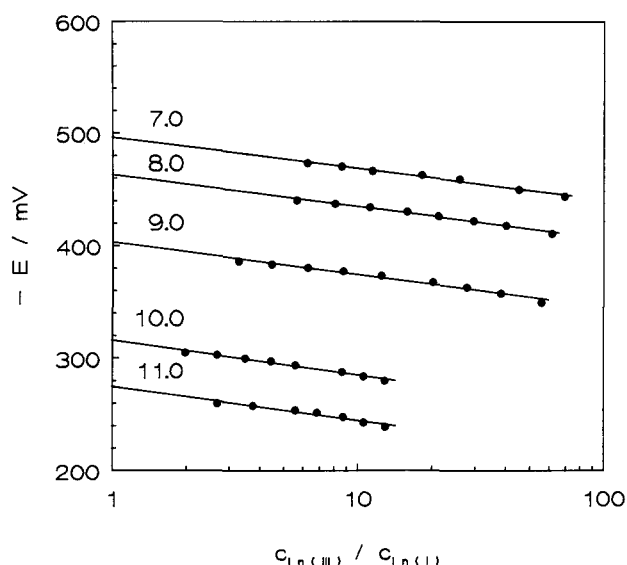
**Table 1.** Formal electrode potentials of the In(III)/In(I), In(III)/In and In(I)/In couples, and equilibrium constant of In(I) reproporationation

Concentration of $\text{ZnCl}_2$ , $\text{mol dm}^{-3}$	$E_{31}'$ , mV	$E_{30}'$ , mV	$E_{10}'$ , mV	$K_r$
7.0	-497			
8.0	-463	-467	-474	$2.5 \times 10^0$
9.0	-404	-431	-484	$5.0 \times 10^2$
10.0	-316	-377	-498	$1.4 \times 10^6$
11.0	-276			

**Table 2.** Kinetic parameters of the In(III)/In(I) system in aqueous ZnCl<sub>2</sub> solutions

Concentration of ZnCl <sub>2</sub> /mol dm <sup>-3</sup>	Viscosity 10 <sup>2</sup> η/g cm <sup>-1</sup> s <sup>-1</sup>	Diffusion coefficient 10 <sup>7</sup> D/cm <sup>2</sup> s <sup>-1</sup>		Formal rate constant 10 <sup>5</sup> k <sup>0</sup> /cm s <sup>-1</sup>	Cathodic transfer coefficient, α <sub>c</sub>
		In(I)	In(III)		
6.0	4.3		16.5		
7.0	7.1	21	12.2		
8.0	10.9	16	7.6	8.9 <sup>a</sup>	0.31
9.0	14.6	11.6	4.7	3.5	0.32
10.0	21.6	7.1	2.5	1.2	0.29
11.0	33.2	3.7	1.8	0.8	0.26

<sup>a</sup> Rate constant determined using the Jahn and Vielstich method



**Fig. 4.** Equilibrium electrode potentials of the In(III)/In(I) redox pair as a function of the concentration ratio in solutions containing 0.1 mol dm<sup>-3</sup> HCl and ZnCl<sub>2</sub> of the molar concentration indicated at each curve. Total concentration of In(III) and In(I) ions was 0.01 mol dm<sup>-3</sup>

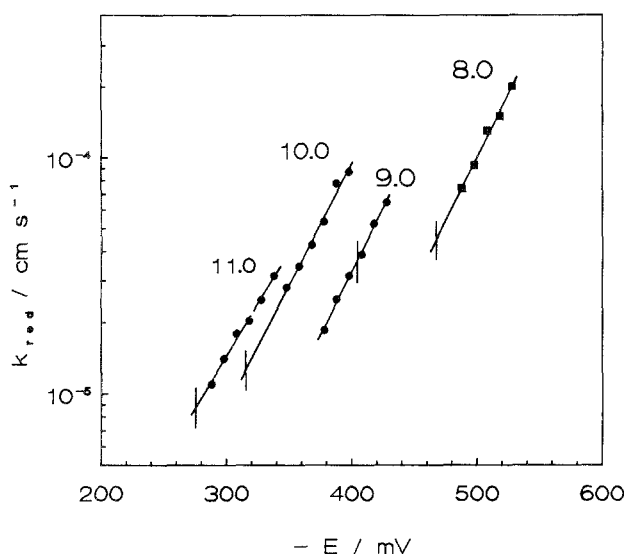
couple obeys the Nernst equation. The formal potentials  $E_{31}^{\circ'}$  were determined by extrapolation of these linear relationships to  $c_{\text{In(III)}}/c_{\text{In(I)}} = 1$ .

Once  $E_{10}^{\circ'}$  and  $E_{31}^{\circ'}$  were known, the formal potential  $E_{30}^{\circ'}$  of the In(III)/In couple could be calculated according to the Luther's rule,  $E_{30}^{\circ'} = (E_{10}^{\circ'} + 2 E_{31}^{\circ'})/3$ .

From the difference of the formal potentials for the In(III)/In and In(I)/In redox system, the approximate values of the equilibrium constant,  $K_r$ , for In(I) reproporation, i.e. for the reaction opposite to (1), were calculated according to the formula

$$\ln K_r = (2F/RT)(E_{31}^{\circ'} - E_{10}^{\circ'}). \quad (7)$$

The values of  $K_r$  and  $E^{\circ'}$  are summarized in Table 1.



**Fig. 5.** Potential dependence of the cathodic rate constant,  $k_{\text{red}}$ , for the In(III)/In(I) electron transfer reaction measured by means of the first (●) and second method (■). The lines are labelled with the molar concentration of  $\text{ZnCl}_2$ . The bars indicate the formal potentials

The rate constants of the electron transfer reaction In(III)/In(I) have been determined by means of the RDE technique in a manner similar to that used in polarography for quasi-reversible waves (Fig. 5). In order to evaluate the potential dependent cathodic rate constants,  $k_{\text{red}}$ , the voltammograms were analyzed by applying the relation derived by one of us [22]. For the solution containing  $7.0 \text{ mol dm}^{-3} \text{ ZnCl}_2$ , the kinetic parameters were evaluated by means of a modified version of the method of Jahn and Vielstich [23], as described elsewhere [24, 25]. The kinetic parameters determined for the system investigated are listed in Table 2.

## Discussion

The obtained values of  $K_r$  indicate that In(I) ions are stable, in terms of thermodynamics, in highly concentrated  $\text{ZnCl}_2$  solutions. The considerable alteration of this equilibrium is caused by two significant factors: complexation of In(I) (soft acid) by  $\text{Cl}^-$  anions, and dehydration of In(III) (hard acid).  $\text{ZnCl}_2$  is known as a strong dehydrating agent. The water activity, recalculated in the molar concentration scale from literature data [26], decreases from 0.42 to 0.049 as the  $\text{ZnCl}_2$  concentration increases from 6.0 to  $11.0 \text{ mol dm}^{-3}$ . In our opinion, the chloro-complex formation by In(III) may be treated as a less important factor. Thus, the progressive addition of  $\text{ZnCl}_2$  increases the  $\text{Cl}^-/\text{H}_2\text{O}$  ratio, which causes the displacement of equilibrium considered to the right-hand side.

On the other hand, the highly concentrated solutions of salts may be considered as a transition region when going from the "conventional" aqueous solutions to the molten salts (ionic liquids) [27]. Samoilov [28] stated that the structure of very concentrated aqueous solutions resembles the crystal hydrates, i.e. the ions approach a distribution characteristic of crystal hydrate.

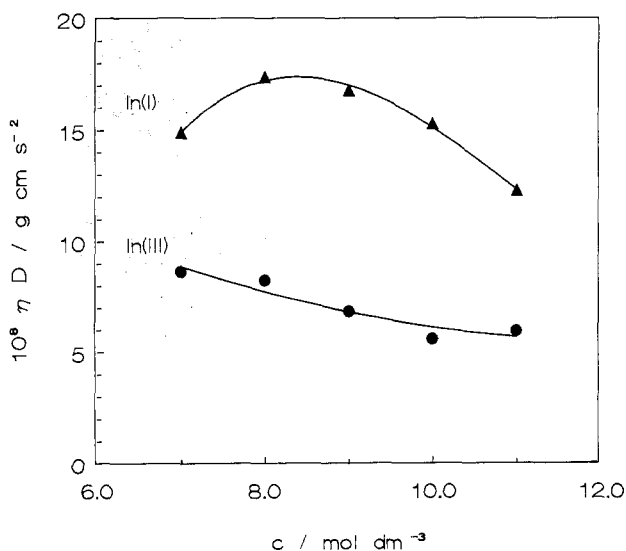
Besides low water activity, these media exhibit important changes in the dielectric permittivity. As follows from the data reported by Kaatze et al. [29], the contribution of the solvent water to the static dielectric permittivity of  $\text{ZnCl}_2$  solutions decreases from 68.0 to 41.3 with the increase of salt concentration from

0.48 to  $7.4 \text{ mol dm}^{-3}$ . Unfortunately, there are no data for the higher  $\text{ZnCl}_2$  concentrations.

In the case of aqueous  $\text{ZnCl}_2$  solutions of concentration higher than  $10 \text{ mol dm}^{-3}$ , Giaquinta and co-workers [30] postulated, on the basis of the Raman spectra, the formation of polynuclear aggregates typical of molten salts. It is interesting to note that the highly concentrated  $\text{ZnCl}_2$  solutions were included by Emons [27] to the low-temperature molten hydrates.

In this point, it should be mentioned that the  $\text{In(III)/In}$  electrochemical process occurs in fused  $\text{LiCl} + \text{KCl}$  [31, 32]  $\text{AlCl}_3 + \text{NaCl} + \text{KCl}$  [33] and  $\text{NaCl} + \text{KCl}$  melts [34] in two separated stages which corresponds to the  $\text{In(III)/In(I)}$  and  $\text{In(I)/In}$  electrode reactions, with formation of the thermodynamic stable  $\text{In(I)}$  species.

The viscosity of the solutions studied increases rapidly with increasing content of the background electrolyte, reaching a value of nearly 37 times greater than the viscosity of water, at  $11 \text{ mol dm}^{-3}$   $\text{ZnCl}_2$ . The diffusion coefficients of  $\text{In(III)}$  and  $\text{In(I)}$  decrease with the corresponding increase of viscosity of the solutions as expected, but not enough to hold the Walden product  $\eta D$  constant (Fig. 6). According to the Stokes-Einstein relation, the Walden product is inversely proportional to the radius of diffusing species. However, the interpretation of this relation is not straightforward since the diffusion coefficients also reflect changes in the structure of the electrolyte solution. Changes in the Walden product of  $\text{In(III)}$  with increasing  $\text{ZnCl}_2$  concentration may point out that the nearest environment of indium(III) undergoes enrichment in chloride ions. The observed decrease of  $\eta D_{\text{In(III)}}$  value may in some degree be due to the progressive replacement of water molecules by larger  $\text{Cl}^-$  anions in the coordination shell. In the case of  $\text{In(I)}$  ions, a more complicated relationship is observed between the value  $\eta D$  and the base electrolyte concentration. In the concentration range of background electrolyte close to  $8.5 \text{ mol dm}^{-3}$ , the Walden product passes through a maximum and thereafter becomes a steadily decreasing quantity. Such behaviour is not quite clear. In our opinion, the observed anomalies are attributable to



**Fig. 6.** Dependence of the Walden product,  $D\eta$ , for  $\text{In(I)}$  and  $\text{In(III)}$  ions on the molar concentration of  $\text{ZnCl}_2$



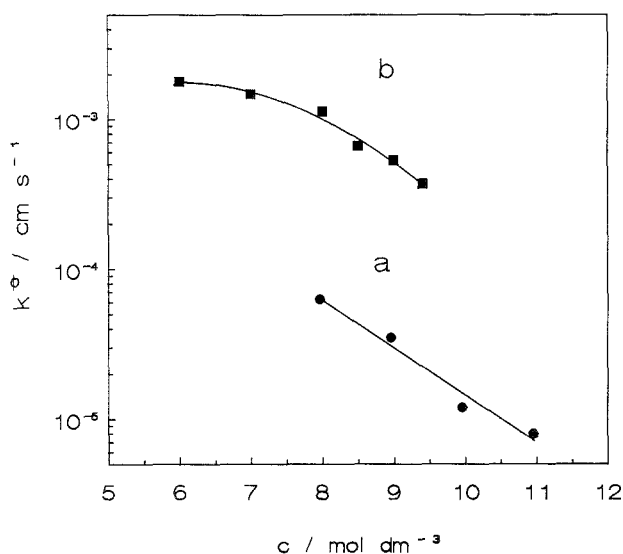


Fig. 7. Dependence of the formal rate constant for the In(III)/In(I) electrode reaction on the concentration of ZnCl<sub>2</sub> (curve a) and ZnBr<sub>2</sub> (curve b)

changes in the structure of the solution studied. It is known from literature that the thermodynamic, structural and transport properties of the ZnCl<sub>2</sub>-H<sub>2</sub>O system are essentially different of those of alkaline-earth halide aqueous solutions [ 29, 30, 35-37]. ZnCl<sub>2</sub> behaves as a normal 2:1 electrolyte with complete dissociation of ions only in dilute solutions. Conversely, the aqueous solutions of this salt consists, at higher concentrations, of several complexes as ZnCl<sup>+</sup>, ZnCl<sub>2</sub>, ZnCl<sub>3</sub><sup>-</sup> and ZnCl<sub>4</sub><sup>2-</sup> [36, 37]. On the other hand, the InCl compounds of various composition with ZnCl<sub>2</sub> are known in the solid state and ionic melts [38].

The formal rate constants determined are presented in Fig. 7 as a function of the concentration of background electrolyte, and compared with the data obtained in ZnBr<sub>2</sub> [1]. It is seen from this figure that the reaction In(III)/In(I) in ZnCl<sub>2</sub> is much slower (approximately one order of magnitude) than in ZnBr<sub>2</sub> solutions of the same concentrations.

The kinetic parameters for the electron-transfer reaction (2) were analyzed on the basis of the theory given by Bockris and Reddy [39]. The values of the cathodic transfer coefficient,  $\alpha_c$ , suggest that the rate determining step is transfer of the first electron to In(III),  $\text{In(III)} + e^- \rightarrow \text{In(II)}$ , while the second step is relatively fast. A similar result was obtained by us in the case of highly concentrated ZnBr<sub>2</sub> solutions [1].

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