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Electrochemical Reduction of Indium (III) in Molten Lithium Chloride — Potassium Chloride Eutectic

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The dependence of indium electrode potential vs. log. concentration of indium (III) is linear and the slopes determined are comparable with the slopes calculated from the Nernst equation, assuming $n = 3$. The potential of In/In(III) has been determined to be 0.805 ± 0.003 V with respect to $Pt/PtCl_2$ (1 M). At 693 K the free energy of formation of the indium(III) chloride in a 1 M solution is —325, 398 ± 500 J/mol.

A single chronopotentiometric wave is observed for the reduction of $InCl_3$ at —0.81 V vs the Pt(II)/Pt reference electrode. Based on analytical data $n = 3$, the diffusion coefficient was calculated to be 1.81×10^{-5} cm^2 s^{-1}. The values of αn_a and $k^o_{f,h}$ were calculated to be 0.6 and 3.25×10^{-3} cm s^{-1}.

Chronopotentiometry showed one step for the reduction of In_2O_3. The quarter wave potential was found to be —0.7 V vs. the Pt(II)/Pt reference electrode. The reduction was found not to be a diffusion controlled process over the time interval investigated. It was shown that In_2O_3 is not stable in the melt and enters in an acid-base reaction with the chloride melt.

Although there have been extensive electrochemical investigations of metal ions and metal ion complexes[1-5], the chlorides of indium have not been the subject of complete electrochemical investigation at elevated temperatures. The present work is concerned with thermodynamic properties of indium(III) chloride as well as with reduction of indium(III) compounds in molten LiCl—KCl eutectic. This investigation was made with cells of the type In/InCl₃, LiCl—KCl//LiCl—KCl, PtCl₂/Pt. Partial thermodynamic values were determined from 693 K to 800 K in the In(III) concentration range of 0.016 to 0.5 M. Indium(III) ions were therefore unimportant carriers of the current, and liquid junction potentials were consequently negligible.

EXPERIMENTAL

Solvent. — The eutectic mixture of potassium chloride (41 mole per cent (m/o) and lithium chloride (59 m/o) at 723 K was used a solvent system. The LiCl—KCl eutectic was obtained from Anderson Physics Laboratories, Incorporated, Champaign, Illinois. The method of purification has been described[6-8].

Electrolytic cell. — The cell used in this experiment has been previously described[9]. Within this and under an atmosphere of dry, oxygen-free argon, the solvent was allowed to collect into the fritted compartments which were used as experimental cells.

Electrodes. — The reference electrode was a platinum foil in contact with platinum (II) solution. This reference electrode has been shown to be reproducible and nonpolarizable over a long period of time.[10] The Pt indicator electrode used in this study has been previously described[6-8]. The carbon electrode which served as counterelectrode in all electrochemical investigations in the melt, was constructed as described by Propp[11]. Indium electrode potentials were measured against the platinum reference by a technique similar to that used by Laitinen and Liu[12]. Indium indicator electrode was prepared as follows; after a weighed addition of the anhydrous indium chloride into the fritted compartment, a tungsten electrode was immediately immersed in the solution and a small amount of indium was deposited. Such plated microelectrode then served as the indicator electrode for the measurement of potentials. The time required to deposit the metal and to measure the potential was usually less than ten minutes.

Chemicals. — All chemicals used in this study were reagent grade. Those chemicals containing water of hydration were vacuum dried at 383 K before being added to the melt. Solid chemicals were added to the melt by means of a small glass spoon. A blanket of argon was kept over the melt at all times to exclude oxygen and water vapor. The purification train used in purifying the argon has been described[6-8].

RESULTS

The present work was made with cells of the type In/InCl₃ LiCl—KCl// //LiCl—KCl, PtCl₂/Pt. The Pt electrode was used for convenience instead of measuring against the chlorine electrode directly. The precise data of Laitinen and Pankey (1) are available for the cell; Pt/PtCl₂ (1M) in LiCl— —KCl//LiCl—KCl/Cl₂. In Figure 1. indium electrode potentials are plotted vs. log. concentration of indium(III) for five temperatures. The dependence is linear and the slopes determined are compared in Table I with the slopes calculated from the Nernst equation, assuming $n = 3$. Using the equation:

$$E_{Pt/PCl_2//Cl^-/Cl_2} = -0.3223 + 0.00034 \, (t - 450) \tag{1}$$

determined by Laitinen and Pankey, indium electrode potentials with respect to the platinum reference electrode are normalized to the chlorine electrode, and the obtained values are numerically the same as the potential difference for the cell In/InCl₃, LiCl—KCl//LiCl—KCl/Cl₂. The reaction corresponding to this cell is the formation of indium(III) chloride in solution·

Using the relationships (2) to (4);

$$\Delta \overline{G} = -ZFE \tag{2}$$

$$\Delta \overline{S} = ZF \, (\partial E/\partial T)_p \tag{3}$$

$$\Delta H = \Delta G + T\Delta S \tag{4}$$

the partial thermodynamic quantities for the reaction were calculated from the data for these cells. Partial thermodynamic quantities for the formation of InCl₃ in molten LiCl—KCl were calculated and are listed in Table II.
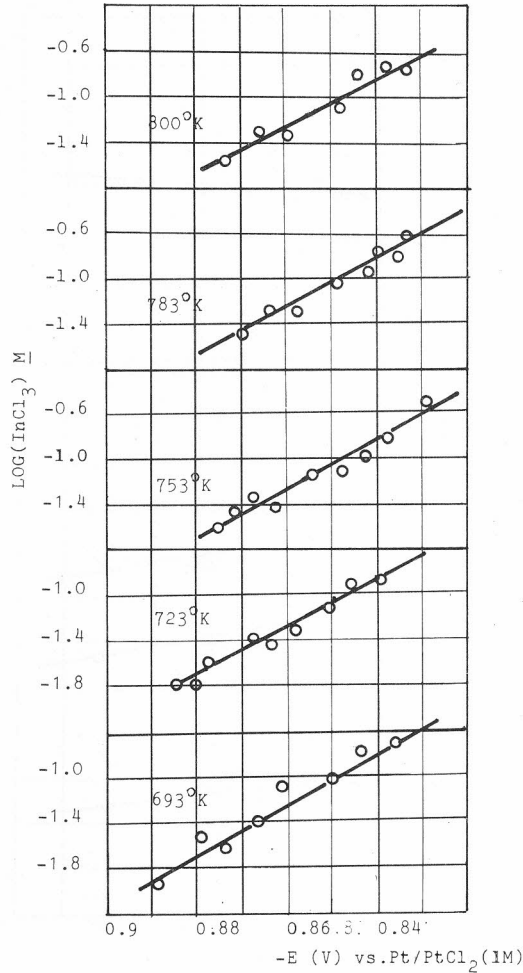
Figure 1. Potentials of indium electrodes with respect to the platinum reference electrode as a function of the concentration of $InCl_3$.

TABLE I

Nernst Behaviour of Indium Electrodes

Temperature/K	$(\partial E/\partial \log In^{3+})_T/V$	
	Calculated	Observed
693	0.0458	0.0490
723	0.0477	0.0450
753	0.0497	0.0468
783	0.0517	0.0481
800	0.0537	0.0522
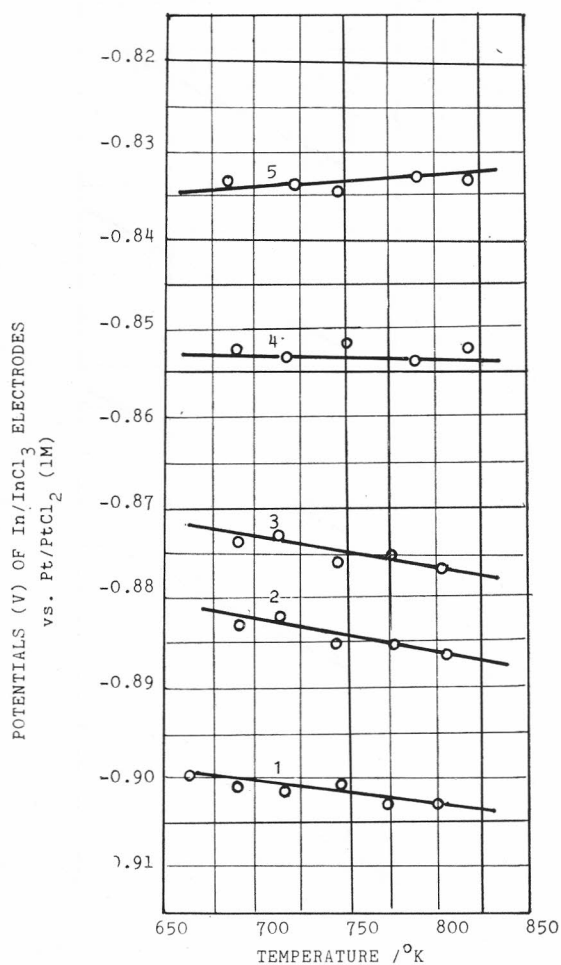
Figure 2. Potential of indium electrodes as a function of temperature.

1. $(InCl_3) = 0.0165$ M   4. $(InCl_3) = 0.1650$ M
2. $(InCl_3) = 0.0405$ M   5. $(InCl_3) = 0.5020$ M
3. $(InCl_3) = 0.0645$ M

TABLE II

Partial Thermodynamic Quantities for the Formation of $InCl_3$ in Molten LiCl—KCl

Concentration M	$\Delta \overline{G}$ J/mol 723 K	$\Delta \overline{S}$ J/K	$\Delta \overline{H}$ J/mol 723 K
0.0165	—349, 716 ± 500	95.53 ± 4	418, 784 ± 3500
0.0405	—344, 505	83.95	405, 784
0.0645	—342, 189	78.16	398, 698
0.1650	—336, 399	46.32	369, 888
0.5020	—330, 030	28.95	350, 960

The potential of indium electrode was plotted against temperature for fixed concentrations, Figure 2. and values of $(\partial E/\partial T)_p$ were found for each concentration. Using these values the partial molar entropy was calculated, as shown in Table II. Of interest are the partial free energies of the formation of $InCl_3$ at standard concentrations and at different temperatures. These are listed in Table III.

TABLE III

Partial Molar Free Energies of InCl₃ at Standard Concentration in LiCl—KCl

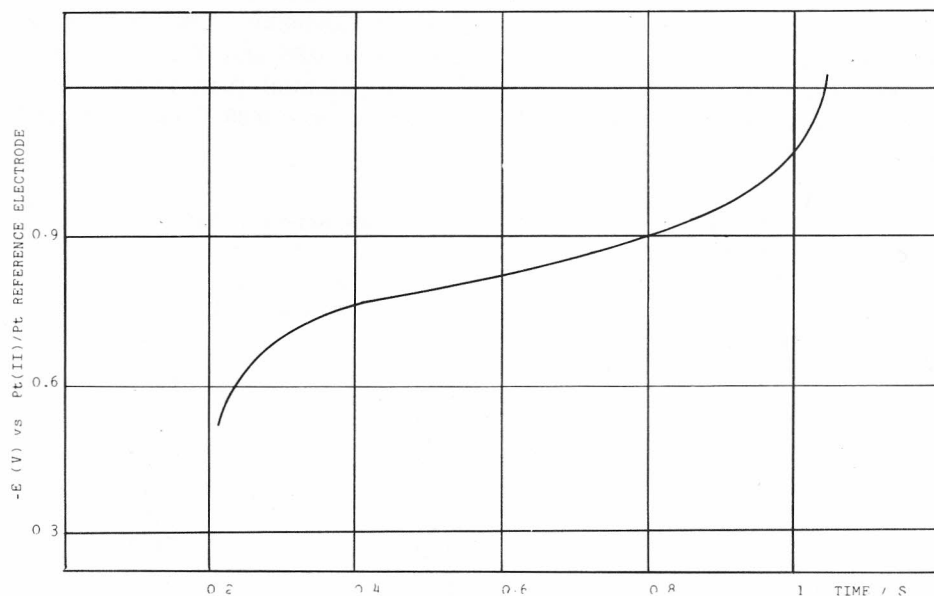| Temperature/K	$\Delta \overline{G}$ J/mol
693	—325, 398 ± 500
723	—324, 240
753	—323, 450
783	—324, 819
800	—323, 661

Figure 3. Potential — time curve for the reduction of $InCl_3$

Current density = 5×10^{-3} A/cm²
Concentration of In(III) = 7.46×10^{-3} M

Chronopotentiometry of $InCl_3$—LiCl—KCl system. After obtaining several chronopotentiograms of the melt, a known amount of $InCl_3$ was added to a fritted compartment. Chronopotentiograms of $In\,Cl_3$ in molten LiCl—KCl were found to depend on the concentration of $InCl_3$. A typical cathodic chronopotentiogram is shown in Figure 3. A single chronopotentiometric wave occurs at a quarter wave potential of —0.81 V vs the Pt(II)/Pt reference electrode. The Sand equation was tested at five different In(III) concentrations. The area of the electrode was measured to be 0.5 cm² in most cases.

The transition time constant in the Sand equation should be indipendent of the current or concentration for a diffusion controlled process. This constant has been calculated and is given in Table IV. The transition time constant is indipendent of I, indicating that the electrode process is diffusion controlled over the time interval investigated. The average value of the transition time constant is 545.48 A $s^{1/2}$ cm^3 mol^{-1}. Since the Sand equation permits only the determination of the product $nD^{1/2}$, either »n« or »D« must be obtained by an independent method. Based on analytical data $n = 3$, the diffusion coefficient was calculated to be 1.81×10^{-5} cm^2 s^{-1}. The potential-time curve for the reduction process at —0.8 V was analyzed in an attempt to obtain information concerning the kinetics of the electron transfer. If the electrode process is totally irreversible, the potential-time curve is described by Delahy-Berzins equation for the electrode process involving one rate determining step. The same form of the potential-time curve would be given by a reversible reaction leading to a solid reduction product of constant activity as it is obtained for the irreversible plot regardless of the solubility of the product. However, for a reversible reaction the slope would be different. Using the slope and intercept from the Delahay — Berzins equation, the values of αn_a and $k^0_{f,h}$ were calculated to be 0.65 and 3.25×10^{-4} cm s^{-1}. A more convinient and meaningful reference potential than Pt(II)/Pt is the potential at $t = 0$. In this regard, the value of $k_{f,h}$ at —0.08 V vs. the Pt(II)/Pt is 2.5×10^{-3} cm s^{-1}.

TABLE IV

Chronopotentiometric Data for the Reduction of $InCl_3$

C_{InCl_3} (M)	$I \times \tau^{1/2}$ ($Axs^{1/2}$) $\times 10^{-3}$	$I_o \times \tau^{1/2}/C$ $Axs^{1/2}$ cm^3 mol^{-1}
7.46×10^{-3}	3.99	534.8
	3.89	521.4
	4.08	538.8
1.65×10^{-2}	8.90	539.3
	8.82	534.5
	8.74	529.6
2.10×10^{-2}	11.45	542.2
	11.38	541.9
	11.35	540.4
3.35×10^{-2}	18.60	555.2
	18.09	540.4
	17.51	522.6
4.8×10^{-2}	26.90	560.4
	26.12	543.7
	25.81	537.5

In order to interpret the electrochemistry of $InCl_3$, information is needed on the chemical composition of the electrode deposit when $InCl_3$ is reduced and the current efficiency with which it is produced. Samples of electrode deposit were prepared by constant current electrolysis using low current densities. The electrode potential was monitored during electrolysis and it was never more negative than —0.8 V. The electrode deposit was found

dispersed into the melt, because indium is a liquid at temperatures at which the experiments were performed. The reduction product was analyzed by standard procedures and was found to be pure indium·

Chronopotentiometry of In_2O_3—LiCl—KCl. A single chronopotentiometric wave is observed for the reduction of In_2O_3 at —0.7 V vs. the Pt(II)/Pt reference electrode. This reduction was found not to be diffusion controlled over the time interval investigated. The transition time constant was calculated and was found to depend on the current density and concentration of In_2O_3. During the chronopotentiometric measurements it was observed that a volatile product evaporates from the melt, indicating that there is an acid-base reaction going on between In_2O_3 and chloride melt. In a nonprotonic solvent, such as alkali halide melt, acid-base reactions can be coveniently considered in terms of the Lewis acid-base concept. Since alkali metal ions have a relatively small ability to accept electrons, they will not ordinarily enter into acid-base reactions. On the other hand, because halide ions can donate a pair of electrons, they act as a leveling base upon most cations, forming metal halide complexes. The chronopotentiometric results of In_2O_3 reduction were checked for a preceding chemical reaction in order to determine if the acid-base reaction between In_2O_3 and chloride melt occurred completely before the electrolysis began. For a slow chemical reaction preceding the electrode process $I_o \times \tau^{1/2}/C$ decreases with increasing I_o. For this case the transition time is given by the Delahay-Berzins equation[13]:

$$I_o \tau_k^{1/2} = \pi^{1/2} nFC^oD^{1/2}/2 - \pi^{1/2} I_o/2K (k_f + k_b)^{1/2} \, \text{erf} \, [(k_f + k_b)^{1/2} \tau_k^{1/2}] \qquad (5)$$

where k_f and K_b are the forward and backward rate constants of the preceding chemical equilibrium and $K = k_f/k_b$ is the equilibrium constant. The first term on the right-hand side of Equation (5) is recognized as the diffusion-controlled term. The second term has two limiting forms; 1) For values of $(k_f + k_b)^{1/2} \tau_k^{1/2} > 2$ the error function is approximately unity and the quantity $I_o \tau_k^{1/2}$ is a linear function of I_o, with the intercept equal to the diffusion controlled value and the slope determined by the rate constants k_f and k_b. For a given set of values of k_f and k_b this condition is most closely obeyed at low current densities and correspondingly high values of τ. For values of $(k_f + k_b)^{1/2} \tau^{1/2} < 0.1$ the error function is adequately represented by the first two terms of the expansion and the Equation (5) becomes:

$$(I_o \tau_k^{1/2})_{I_o \to \infty} = nFC^o \pi^{1/2} D^{1/2}/2 \, (1 + 1/K) \qquad (6)$$

In this case the quantity $I_o \tau_k^{1/2}/C^o$ is once more independent of the applied current density but its value is less that the diffusion-controlled value by the factor $K/(1 + K)$. Thus, for the case of a slow preceding chemical reaction a plot of $I_o \tau_k^{1/2}$ against I_o will show first a linearly decreasing region and at high value of I_o it may show a constant region if the values of k_f and K are sufficiently small·

Experimentally, it was necessary to restrict the range of current densities that can be used at a given concentration and to limit the transition time to a range of 0.2 to 2.0 s to minimize the double layer effects and convection. The plot of $I_o \tau_k^{1/2}/C^o$ vs. I_o is shown in Figure 4. The fact that there is a discernible downward slope in Figure 4 may be used as evidence that the acid-
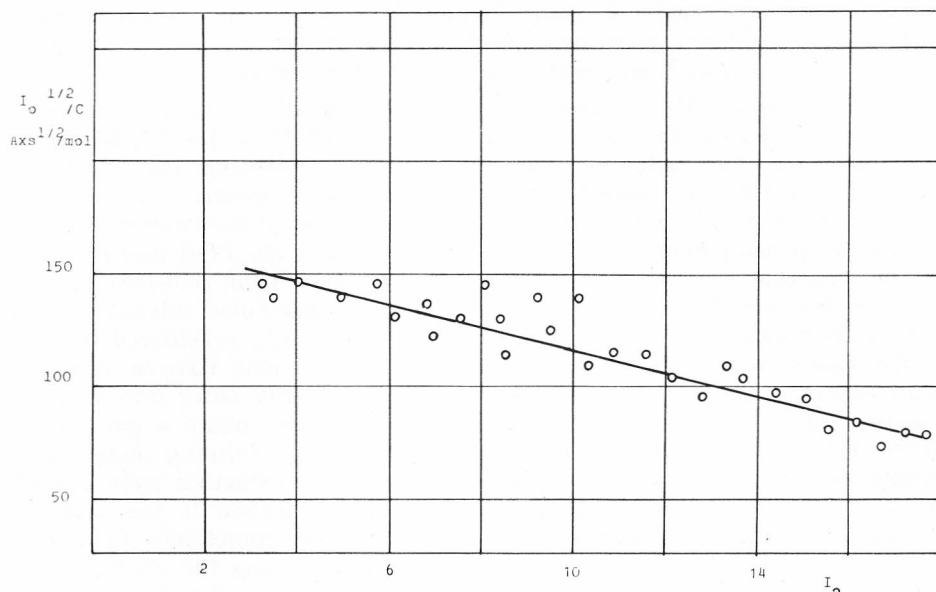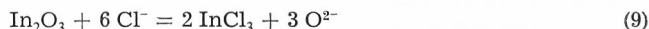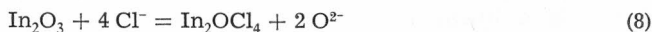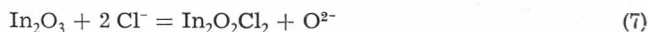
Figure 4. Variation of $I_o \tau^{1/2}$ with I_o for the reduction of In_2O_3.

-base reaction between In_2O_3 and chloride melt does not occur completely before the electrolysis begins. In order to account for the observed chrono-potentiometric results for In_2O_3 reduction, the following acid-base reactions were considered between In_2O_3 and chloride melt preceding the charge transfer:

$$In_2O_3 + 2\ Cl^- = In_2O_2Cl_2 + O^{2-} \tag{7}$$

$$In_2O_3 + 4\ Cl^- = In_2OCl_4 + 2\ O^{2-} \tag{8}$$

$$In_2O_3 + 6\ Cl^- = 2\ InCl_3 + 3\ O^{2-} \tag{9}$$

Samples of the electrode deposit were prepared by constant electrolysis. Examination of the cathode and melt solution did not show any reduction product. The platinum cathode became greyish, inflexible and breakable, indicating that the cathode had been destroyed reacting with the reduction product of In_2O_3. During electrolysis it was observed that a volatile product evaporates from the melt. The product was collected in the tube and was analyzed by standard methods. It was found to contain In and Cl^- but the sample weight cannot be completely accounted for in terms of the compound $InCl_3$, indicating that indium oxychloride is formed in the melt.

DISCUSSION

The dependence of indium electrode potential vs. log concentration of indium (III) is linear and the slopes determined are comparable with the slopes calculated from the Nernst equation, assuming $n = 3$. By extrapolation to the extent of 1 mol/l of indium chloride, the potential of In/In(III) has been determined to be 0.805 ± 0.003 V with respect to $Pt/PtCl_2$ (1 M). At 693 K the free energy of the formation of indium (III) chloride in a 1 M solution

is — $325,398 \pm 500$ J/mol. A negative value for the free energy of the formation means that the formation occurs spontaneously. Partial entropies as large as 95 J K/mol were obtained. Partial enthalpies, shown in Table II were determined according to relationship (4). The average deviation is based on the deviation on the free energies and entropy determinations.

A single chronopotentiometric wave is observed for the reduction of $InCl_3$ at — 0.81 V vs. the Pt(II)/Pt reference electrode. The transition time constant in the Sand equation is independent of I, indicating that the electrode process is diffusion controlled over the time interval investigated. Based on analytical data $n = 3$, the diffusion coefficient was calculated to be 1.81×10^{-5} cm^2 s^{-1}. The value of $k^o_{f,h}$ and αn_a were calculated to be 3.25×10^{-4} cm s^{-1} and 0.60. The value of $k^o_{f,h}$ at -0.8 V vs. the Pt(II)/Pt is 2.5×10^{-3} cm s^{-1}. Since the results indicate that the electrode reaction is irreversible, the potential of the indicator electrode is independent of the concentration of the reduced form. It is impossible, therefore, to obtain information on the chemical properties of the reduced species from an analysis of the potential-time behaviour. The reduction product of $InCl_3$ was analyzed by standard procedures and was found to be pure indium· The evidence provided by the film analysis and chronopotentiometric experiments indicates that the reduction of $InCl_3$ in pure LiCl—KCl eutectic proceeds through the reaction:

$$In^{3+} + 3\,e = In^0$$
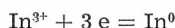
Chronopotentiometry has shown one step for the reduction of In_2O_3. The quarter wave potential was found to be -0.7 V vs. the Pt(II)/Pt reference electrode· This reduction was found not to be a diffusion controlled process over the time interval investigated. It was shown that In_2O_3 is not stable in the melt and enters in an acid-base reaction, which may be presented as $In_2O_3 + 2Cl^- = In_2O_2Cl_2 + O^{2-}$. Since there is a discernible downward slope in Figure 4, it may be used as evidence that the acid-base reaction between In_2O_3 and chloride melt does not occur completely before the electrolysis begins, indicating that the charge transfer process is complicated by a preceding chemical reaction. The scatter of the points in Figure 4 is probably accountable through the variation of the electrode area due to the reaction between the platinum cathode and the reduction product of the electroactive species in the melt. In spite of the fact that $In_2O_2Cl_2$ should not have been stable and should have an extremely high vapor pressure at 723 K, the results indicate that there is an interaction between $In_2O_2Cl_2$ and the chloride melt. The chloride melt probably stabilizes $In_2O_2Cl_2$ to an anion $In_2 O_2Cl_4^=$ in solution, which is further reduced at the Pt electrode.

REFERENCES

1. H. A. Laitinen and J. W. Pankey, *J. Am. Chem. Soc.* **81** (1959) 1053.
2. S. Senderoff and A. Brenner, *J. Electrochem. Soc.* **101** (1954) 16.
3. H. A. Laitinen and R. P. Tisher, *J. Electrochem. Soc.* **107** (1960) 546.
4. E. R. Van Artsdalen and I. S. Yaffe, *J. Phys. Chem.* **59** (1955) 118.
5. V. S. Lamb, *J. Electrochem. Soc.* **117** (1970) 1269.
6. B. N. Popov, *Ph. D. Thesis*, University of Zagreb (1972).
7. B. N. Popov and H. A. Laitinen, *J. Electrochem. Soc.* **117** (1970) 644.
8. B. N. Popov and H. A. Laitinen, *J. Electrochem. Soc.* **120** (1973) 1346.
9. B. N. Popov and H. A. Laitinen, *J. Electrochem. Soc.* **122** (1975) 1616.

10. H. A. L a i t i n e n and W. S. F e r g u s o n, *Anal. Chem.* **38** (1957) 644.
11. J. H. P r o p p and H. A. L a i t i n e n, *Anal. Chem.* **41** (1969) 645.
12. H. A. L a i t i n e n and C. H. L i u, *J. Am. Chem. Soc.* **80** (1958) 546.
13. P. D e l a h a y, *New Instrumental Methods in Electrochemistry,* Interscience Publishers, Inc., New York, 1966, p. 198—200.

SAŽETAK

Elektrokemijska redukcija indij(III)-iona u talinama eutektika litij-klorid/kalij-klorid

B. N. Popov i J. V. Ivshin

U elektrokemijskom članku In|InCl₃, LiCl—KCl||LiCl—KCl, PtCl₂|Pt određeni su termodinamički parametri u području temperatura 693 do 800 K i koncentracije iona In(III) od 0,016 do 0,500 mol dm⁻³. Mehanizam redukcije iona In(III) i redukcije In₂O₃ u talinama eutektika LiCl—KCl, kao i neki kinetički parametri, određeni su kronopotenciometrijskim mjerenjima.