

## Oscillopolarographic Behaviour of Lanthanide Ions in Potassium Iodide Solutions

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The oscillopolarographic depolarization effect of lanthanide ions in KI solutions was investigated using dropping (DME) and hanging-drop (HME) mercury electrodes. The lanthanide-ion incision depth in the  $dE/dt=f(E)$  curve, measured in a 1M KI solution (pH 3.65) with a DME, was found to be much deeper than that in a 1M KCl solution. The temperature coefficient was negative for the La and Sm incision depths in the temperature range from 25° to 50°C. The incision depths of the La (pH 4.0) and Sm (pH 4.5) ions in a solution with an ionic strength of 0.7 (KCl added) were found to depend on the  $I^-$  concentration. These facts seem to show that  $I^-$  is adsorbed on DME, and that the adsorbed  $I^-$  (at -1.4 V) promotes the electrode reaction of lanthanide ions.

Treindl<sup>1)</sup> has reported a study of the oscillopolarographic behaviour of La, Pr, Nd, and Sm ions in KI solutions. He has pointed out that, in a 0.2—1M KI (pH 6.4—6.8) solution, the position of the  $Q$  incision quotient of the  $dE/dt=f(E)$  curves are 0.66, and that a reversible incision is observed. However, no systematic study of the lanthanide ions has been reported. The present authors have noted previously that the lanthanide-ion incision<sup>2)</sup> depth measured in such supporting electrolytes as  $NaClO_4$ , KCl, KBr, and KSCN depends on the first ionization potential and the basicity of the lanthanides. In this study we investigated the oscillopolarographic behaviour of lanthanide ions in KI solutions; we found that their incision depths are much deeper than those in KCl solutions. This seems to indicate that the deeper incision depth is due to the  $I^-$  adsorption on the DME.

### Experimental

The preparation of 0.01M lanthanide-ion solutions has been described previously.<sup>2)</sup> All the other materials were of a reagent grade and were used without further purification. The KI solutions were prepared just before use. The pH values of the electrolyte solutions were adjusted by adding either a 0.01N HCl or 0.01N NaOH solution. All the experiments except for those shown in Figs. 6 and 7 were carried out in a constant temperature bath at  $25 \pm 0.1^\circ\text{C}$ . Dissolved oxygen was removed by passing nitrogen gas through.

The curves,  $dE/dt=f(E)$ , were recorded by a manual Heyrovsky-Forejt-type oscillopolarograph, as has been described previously.<sup>2)</sup> DME or HME was used as the polarizable electrode. The characteristics of the

DME and the HME were as follows. The value of  $m$  with a mercury height of 57.6 cm was 0.936 mg/sec; the dropping time was 1.7 sec (in the 1M KI solution), and the weight of a mercury drop was 0.0058 g. An alternating-current source provided 150 V at 50 cps; a 0.23 mA current (0.12 mA for the experiment in Fig. 2) was passed through the cell. The oscillopolarogram in Fig. 1 was photographically recorded by a Polaroid-Land camera using an Iwasaki UP-7 photo-oscilloscope unit. The incision positions and the depths of the  $dE/dt=f(E)$  curves were measured directly on the oscilloscope just before the mercury dropped. The values obtained are the averages of three measurements. The vertical-deflection sensitivity of the oscilloscope was 10.0 mV/cm

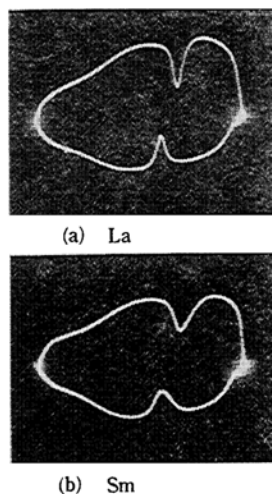


Fig. 1. Typical curves of the  $dE/dt=f(E)$  of the lanthanum and samarium ions in a deaerated M KI solution at pH 3.65. The concentration of lanthanide was 0.5 mM and the curves were obtained with a DME.

1) L. Treindl, *Chem. Listy*, **50**, 154 (1956).

2) A. Iwase and C. Yokoyama, *This Bulletin*, **42**, 2243 (1969).

when the DME was used and 5.5 mV/cm when the HME was used. The horizontal deflection sensitivity was 25 mV/mm.

### Results and Discussion

The  $dE/dt=f(E)$  curves of  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  are shown in Fig. 1. The solutions contained  $5 \times 10^{-4}\text{M}$   $\text{La}^{3+}$  (Curve a) or  $5 \times 10^{-4}\text{M}$   $\text{Sm}^{3+}$  (curve b) in  $\text{M KI}$  ( $\text{pH}=3.65 \pm 0.05$ ). The  $Q$  values of the cathodic and anodic incisions were 0.67 and 0.61 respectively. The values are shifted from the  $Q$  value, 0.66, of the reversible incision. The  $Q$  values for other lanthanide ions were the same as with the lanthanum. Figure 2 shows the incision

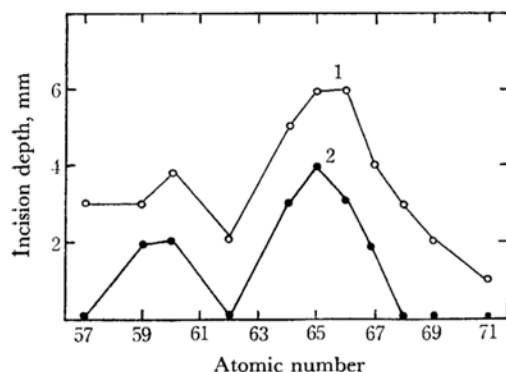


Fig. 2. Variation of the cathodic incision depth with the lanthanides in  $\text{M}$  (1)  $\text{KI}$  and (2)  $\text{KCl}$  solutions at  $\text{pH } 3.65 \pm 0.05$ . The concentration of lanthanides was 0.5  $\text{mM}$ .

depth of the  $5 \times 10^{-4}\text{M}$  lanthanide solution measured in  $\text{M KI}$  (curve 1) and in  $\text{M KCl}$  (curve 2) at  $\text{pH } 3.65$  plotted against the atomic number of the lanthanides. The vertical deflection sensitivity was 10 mV/cm for curve 1 and 2.5 mV/cm for curve 2. Curve 1 shows a deeper incision depth than does curve 2. Note that such ions as  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$ , and  $\text{Lu}^{3+}$ , which do not give any incision in  $\text{M KCl}$  ( $\text{pH } 3.65$ ), show a sharp incision in  $\text{M KI}$  ( $\text{pH } 3.65$ ). The difference between curves 1 and 2 can be definitely attributed to the presence of  $\text{I}^-$ .

Therefore, the depth of this incision depends on the concentration and a.c. frequency according to the following formula:<sup>3)</sup>

$$h = kc / (kc + 4C'\omega^{1/2})$$

$$k = n^2 F^2 D^{1/2} / RT$$

where  $C'$  denotes the differential capacity of the mercury, and  $\omega$ , the angular frequency. Moreover, the capacity-potential curves reported by Grahame<sup>4)</sup>

3) P. Zuman and I. M. Kolthoff, "Progress in Polarography," Vol. 2, Interscience Publishers, New York (1952), p. 453.

4) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York (1966), p. 123.

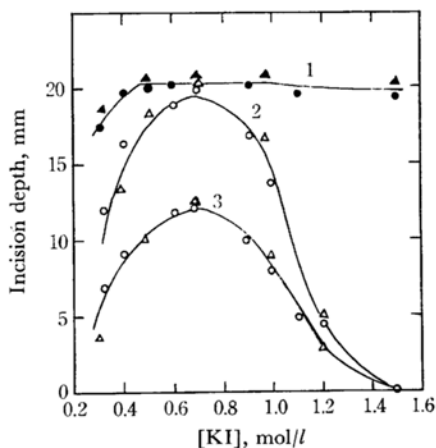


Fig. 3. Effect of potassium iodide concentration on incision depth of the lanthanum and samarium ions. The polarizable electrode used was a DME for (2) and (3) and a HME for (1).

were the same for mercury in  $\text{KI}$  and  $\text{KCl}$  (concentrations not stated) solutions except at potentials markedly were positive than the incision potential for the lanthanide ions. Consequently, it seems that the depth of incision in Fig. 2 is mainly a function of the electrode reaction rate.

The effect of the  $\text{KI}$  concentration on the electrode reaction of the  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  ions was investigated. Figure 3 shows the incision depths of a  $5 \times 10^{-4}\text{M}$  lanthanide ( $\text{La}$  or  $\text{Sm}$ ) solution of  $\text{pH } 3.65$  with  $\text{KI}$  concentrations from 0.3 to 1.5  $\text{M}$ . In this figure, curve 1 is a plot of the cathodic incision depth obtained using HME, while curves 2 and 3 are the plots of the cathodic and anodic incision depths respectively. In curve 1, the incision depth is almost constant over the  $\text{KI}$  concentration range from 0.4 to 1.0  $\text{M}$ . However, in curves 2 and 3, the incision depths show a maximum when the  $\text{KI}$  concentration is about 0.7  $\text{M}$ , and at a  $\text{KI}$  concentration of 1.5  $\text{M}$ , no incision depth was observed. On the contrary, at the  $\text{KI}$  concentrations, 1.5 and 0.7  $\text{M}$ , the incision depths in curve 1 are almost the same. It seems that  $\text{KI}$  promotes or retards the electrode reaction when the concentration is either lower or higher than 0.7  $\text{M}$  respectively. We interpret this as follows. In a 0.3–0.7  $\text{M KI}$  solution, the amount of  $\text{I}^-$  adsorbed on the electrode in the positively-polarized branch with respect to the electro-capillary maximum point, e.c.m., increases with an increase in the  $\text{I}^-$  concentration in the solution bulk. This results in an increase in the  $\text{I}^-$  remaining on the electrode surface in the desorption process in the negative polarization region, and it promotes the electrode reaction. In a 0.7–1.5  $\text{M KI}$  solution the electrode reaction rate decreases as the  $\text{KI}$  concentration increases. This effect may be attributed to the change in the potential,

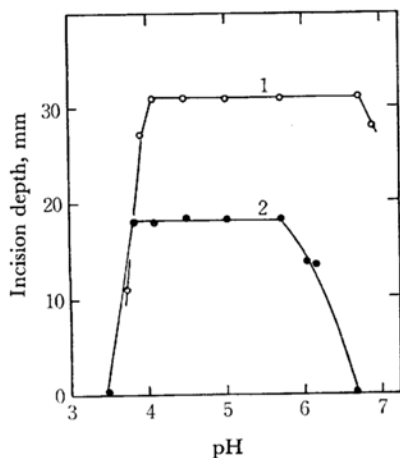


Fig. 4. Effect of pH on incision depth of (1) lanthanum and (2) samarium ions in M KI solution.

$\phi_2^{*1}$  (which becomes less negative). A similar phenomenon has been observed with Zn.<sup>5)</sup>

Figure 4 shows the effect of the pH on the incision depths of  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  ions. Both curves 1 (La) and 2 (Sm) were measured in solutions containing M KI and  $5 \times 10^{-4}$  M lanthanide ions, with pH values between 3.5 and 6.8. The incision depth was independent of the pH in the region between pH 4.0 and 6.7 for  $\text{La}^{3+}$  and between pH 3.8 and 5.7 for  $\text{Sm}^{3+}$ . At higher pH values the incision depth decreased due to the hydrolysis of  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  ions, and with a decrease in pH values in the lower pH region the incision depth decreased, eventually reaching zero at pH values of about 3.5. However, at pH 3.5, a fairly deep incision was observed with the HME. It seems that the cathodic incision of lanthanides is attributable to the reduction of  $\text{H}^+$  in hydrated water molecules<sup>6)</sup> and that the anodic incision is attributable to the oxidation of lanthanide-halogeno hydride complexes,<sup>7)</sup> which are formed by the hydride ions produced at the cathode. Consequently, the increase in the hydrogen-ion concentration on the electrode surface might suppress the formation of lanthanide-halogeno hydride complexes. The ratio of the incision depths of curves 1 and 2 at the plateaus is 1.7, and the depth is greater for  $\text{La}^{3+}$  than for  $\text{Sm}^{3+}$ . It is probably true that the larger the ionic size, the less the concentration of the ions in the

Helmholtz layers, since the Stokes radius<sup>8)</sup> of a  $\text{Sm}^{3+}$  ion is larger than that of a  $\text{La}^{3+}$  ion.

Figure 5 shows the relation between the incision depth and the concentrations of  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  ions. Curves 1 and 2 were measured using DME, while curves 3 and 4 were measured using HME in M KI solutions at pH 4.5. Curve 1 is linear in the range of  $\text{La}^{3+}$  concentrations ranging from 0.5 to  $3 \times 10^{-3}$  M, and curve 2 is linear in throughout the range measured. However, the plot of the ion concentration versus the incision depth shows

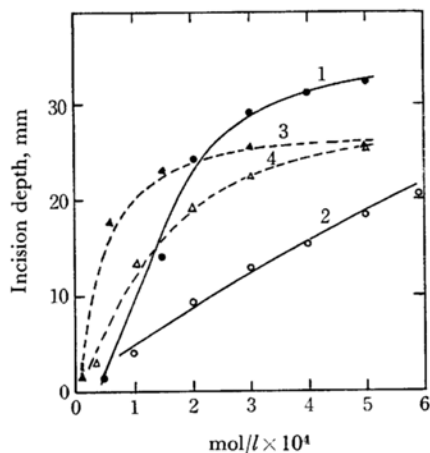


Fig. 5. Calibration curves of lanthanum and samarium ions in M KI solution at pH 4.5. The polarizable electrode used was a DME for 1 (La) and 2 (Sm) and a HME for 3 (La) and 4 (Sm).

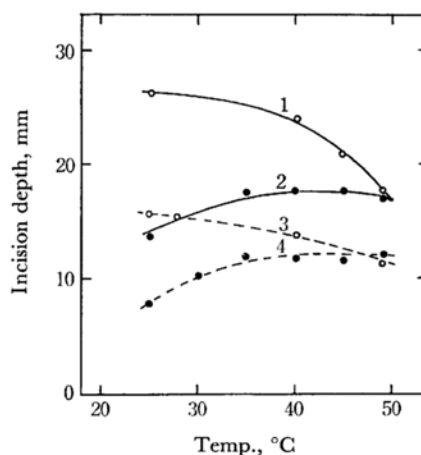


Fig. 6. Temperature dependence of incision depth of the lanthanum ion in KCl plus KI and KCl solutions at pH 4.4 (ionic strength, 0.7). Supporting electrolyte: curve 1 (cathodic) and 3 (anodic), 0.5M KI plus 0.2M KCl; curve 2 (cathodic) and 4 (anodic), 0.7M KCl.

\*1 Potential in outer plane of closest approach referred to the potential in the bulk of the solution outside the double layer.

5) T. Fujinaga and M. Maruyama, "Polarography," Vol. 3, Nankodo, Tokyo (1965), p. 201.

6) S. Misumi and Y. Ide, *Mem. Faculty Sci., Kyushu Univ., Ser. C, Chem.*, **3**, No. 3, 205 (1961).

7) J. Heyrovsky and R. Kalvoda, "Oszillographische Polarographie mit Wechselstrom," Akademie-Verlag, Berlin (1960), p. 106.

8) A. Iwase and T. Ito, *This Bulletin*, **42**, 2064 (1969).

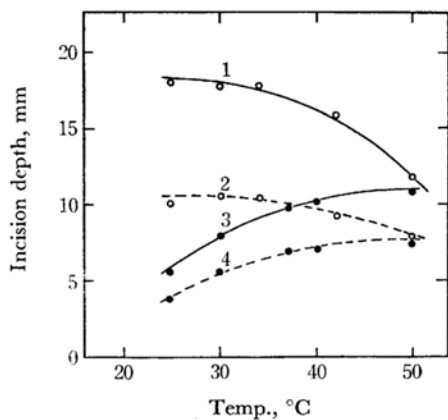


Fig. 7. Temperature dependence of incision depth of the samarium ion in KCl plus KI and KCl solutions at pH 4.4 (ionic strength, 0.7). Supporting electrolyte: curve 1 (cathodic) and 2 (anodic), 0.5M KI plus 0.2M KCl; curve 3 (cathodic) and 4 (anodic), 0.7M KCl.

saturated curves for  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$  when the HME is used.

The characteristic behaviour of KI, compared with that of other supporting electrolytes such as KCl or KBr, seems to be due to the adsorption of  $\text{I}^-$  on the electrode. Accordingly, we investigated the relative temperature dependence of  $\text{La}^{3+}$  and  $\text{Sm}^{3+}$ -ion incisions in the KCl and KI solutions. The results are shown in Figs. 6 ( $\text{La}^{3+}$ ) and 7 ( $\text{Sm}^{3+}$ ). In Fig. 6, curve 1 and curve 3 are the cathodic and anodic incisions, respectively, in 0.5M KI plus 0.2M KCl solutions, while curves 2 and 4 are the cathodic and anodic incisions respectively, in 0.7M KCl solutions. All the measurements shown in Fig. 6 were carried out at pH 4.4 in the temperature range from 25° to 50°C and with a  $5 \times 10^{-4}\text{M}$   $\text{La}^{3+}$  solution. The temperature coefficient of the incision depth in the KI solutions was found to be negative, whereas it was positive in the KCl solutions. The same result was obtained for  $\text{Sm}^{3+}$  ions (Fig. 7). The concentration dependence of the incision depth was further investigated at  $\text{I}^-$  concentrations from

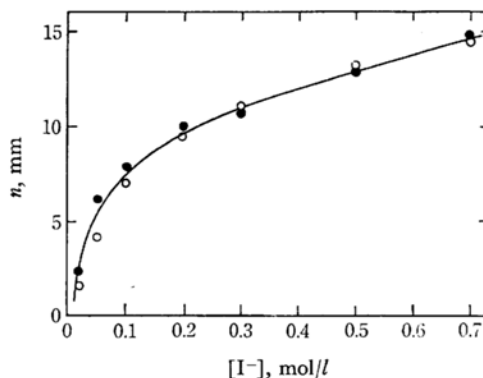
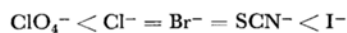


Fig. 8. Relation between the cathodic incision depth of La (pH 4.0) and Sm (pH 4.5) ions and the iodide concentration (ionic strength, 0.7).

0.02 to 0.7M, with the ionic strength kept at 0.7 with KCl. The results are shown in Fig. 8. In this figure,  $n$  is the increase in incision depth (in mm) on the addition of iodide ions. The  $n$  value increases sharply in the KI concentration range from 0.02 to 0.1M, and then it tends to slope gently above 0.1M. It may be supposed that the ionic adsorption of the  $\text{I}^-$  on the electrodes has a large effect on the electrode reaction of lanthanide ions, and that, therefore, the iodide complex is formed at the electrode surface. This assumption is also supported by the evidence of curve 1 in Fig. 2, which shows the dependence of the incision depth on the first ionization potential of lanthanides.

The incision depth of lanthanide ions increases with the following order of supporting electrolyte anions:



There is no experimental evidence that  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{SCN}^-$  ions remain on the electrode surface at a negative voltage ( $-1.4\text{ V}$ ). However, since these anions become strongly adsorbed at positive voltages, as is indicated by the above relation, some may remain as a lanthanide complex in the Helmholtz layer.