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Oscillopolarographic Behaviour of Lanthanide Ions at the Dropping and Hanging-drop Mercury Electrodes

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The oscillopolarographic behaviour of lanthanide ions at the dropping mercury electrode and hanging-drop mercury electrode was discussed. The variations of incision depth on the oscillopolarograms with a dropping mercury electrode in KSCN, KCl, KBr and $NaClO_4$ at pH 3.65 and 4.65 were found to depend on the first ionization potentials and the basicity of the lanthanide. On the basis of the results obtained it can therefore be presumed that the electrode reaction rate increases with the increase of the first ionization potentials.

It hat been reported[1,2] that the curves, $dE/dt=f(E)$, for the tervalent lanthanide ions, lanthanum, praseodymium and samarium in KI or KCl solutions, are affected by dissolved oxygen; the cathodic incision potential shifts in the negative direction and the anodic one in the positive direction and the incision depth decreases upon removal of the dissolved oxygen. This behaviour was attributed to the effect, as a catalyst, of hydroxide ions produced by the reduction of dissolved oxygen. However, little attention has been paid to the dependence of the incision depth on the characteristics of tervalent lanthanide ions.

The present investigation was undertaken to elucidate the relation between characteristics of the lanthanide ions, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Lu^{3+} and the incision depths in KSCN, KCl, KBr and $NaClO_4$ solutions. The data on the depolarization effect of the lanthanides reported herein indicate that the incision depths of the lanthanide ions are dependent on the first ionization potentials and the basicity.

Experimental

0.01 M solutions of lanthanide(III) chloride were prepared as follows: 99.9% lanthanide oxide was converted to the chloride and dissolved in diluted hydrochloric acid. Its concentration was standardized by a titration method[3] using an EDTA standard solution. Other reagents were all guaranteed grade and used without further purification. Adjustment of pH of the solution was done by adding 0.01 N hydrochloric acid or 0.01 N potassium hydroxide.

The curves, $dE/dt=f(E)$, were recorded with a manual Heyrovsky-Forejt type oscillopolarography constructed in this laboratory. A dropping mercury electrode (DME) and a hanging-drop mercury electrode (HME) were used as the polarizable electrode. The alternating current had a main frequency of 50 cps at 150 V. A direct current voltage in the range, -1.0 to -2.0 V, was superimposed on the alternating current. The alternating current intensities passing through the electrode were 0.12 mA for DME (surface area: 0.013 cm^2) and 0.23 mA for HME (surface area: 0.027 cm^2).

An Iwasaki SS-5051 synchroscope with WB-4 amplifier was employed and the photographs of the oscilloscope display were recorded with a Polaroid-Land camera and an Iwasaki UP-7 photo oscilloscope unit. The deflection sensitivities of the vertical axis were 3.5(DME) and 2.5 (HME) mV/cm except for Fig. 1. The positions of all incisions were measured directly on the oscilloscope and referred to a saturated calomel electrode by a comparative method[4] using the thallous or lead ions. The curves with the DME were photographed just before detachment of the mercury droplet when the surface area did not change appreciably with time. The capillary characteristics of DME used were an m value of 0.936 mg/sec and a drop time of 1.7 sec in an oxygen free 1 M potassium chloride solution for a mercury height of 57.6 cm. In order to ensure satisfactory reproducibility of the oscillopolarograms with HME, it was necessary to maintain a constant volume for the hanging-drop mercury. This was achieved by using a polarographic capillary with a mercury reservoir; after separation by means of gravitation, the mercury was caught on a glass spoon and attached to a silver wire by contact only. The weight of the mercury drop was 0.0058 g. For all experiments, the temperature was regulated at 25.0±0.1°C.

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[1] J. Heyrovsky and R. Kalvoda, "Oscillographische Polarographie mit Wechselstrome," Akademie Verlag, Berlin (1960), p. 107.

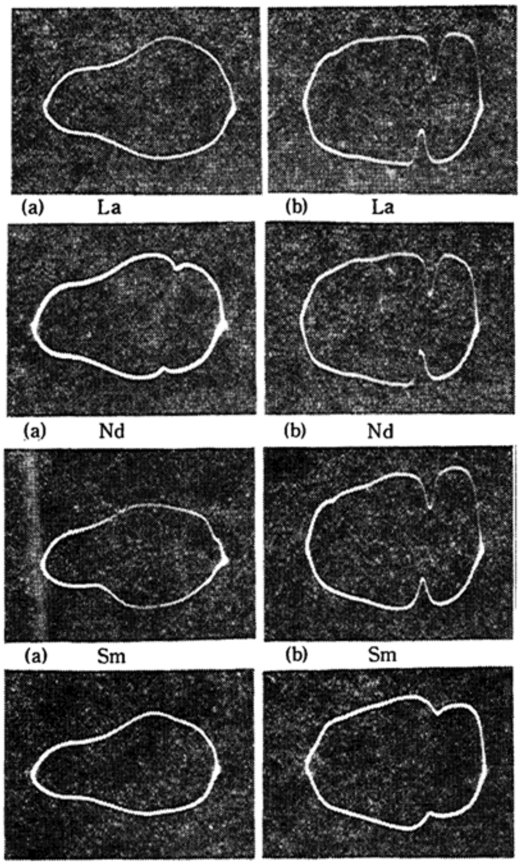
[2] S. Misumi and Y. Ide, *Mem. Faculty Sci., Kyushu Univ., Ser. C. Chem.*, **3**, 205 (1961).

[3] K. Ueno, "Chelatometric Titration," Nankodo, Tokyo (1964), p. 327.

[4] R. Kalvoda, "Techniques of Oscillographic Polarography," Elsevier, New York (1965), p. 168.

Results and Discussion

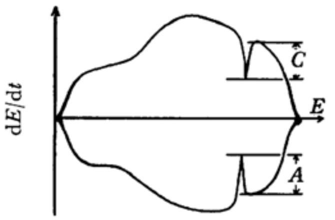
Oscillopolarographic Characteristics of Lanthanide Ions in Potassium Thiocyanate Solutions. The typical curves, dE/dt=$f(E)$, for 5×10^{-4}M lanthanide in a solution containing 1 M potassium thiocyanate at pH 3.65±0.05, are shown in Fig. 1. In this figure, curves (a) and (b) are the oscillopolarograms obtained with DME and with HME respectively. When DME was used the incision is observed for the Nd^{3+} ion only, whereas when HME was used the incision was observed for all ions in Fig. 1. It is obvious from comparison between the curves (a) and (b) that the incision depth is a function of the electrode reaction rate of the lanthanide ion. The oscillopolarographic characteristics of the lanthanide ions are shown in Tables 1[*1,*2] and 2.[*1,*2] In Table 1, the cathodic and anodic incision potentials obtained with DME were nearly constant and had a value of −1.41 and −1.40 V respectively. This is in agreement with the results reported by Dolezal1) for several lanthanide ions. The incision was negligible with the removal of the dissolved oxygen in studies of the lanthanum and samarium ions, but no measurable incision was formed with Er, Tm and Lu irrespective of the presence of dissolved oxygen at pH 3.65±0.05 in an unbuffered solution. Generally, the incision depth of these ions in presence of the dissolved oxygen was greater than that with removal of the dissolved oxygen, and constant for La^{3+}, Pr^{3+} and Nd^{3+}, but for other ions studied, no regularity was found.


(a) La (b) La

(a) Nd (b) Nd

(a) Sm (b) Sm

(a) Er (b) Er



(c) C, cathodic; A, anodic

Fig. 1. Typical curves of the dE/dt *versus* the potential, E, of the lanthanide ions in a deoxygenated 1 M KSCN solulion. The curves were obtained with (a) a dropping and (b) a hanging-drop mercury electrode; (c), shows the method of measuring the incision depth. The deflection sensitivities of vertical axis were 10.0 (DME) 10.0 (DME) and 5.5 (HME) mV/cm.

As shown in Table 2, for the dE/dt=$f(E)$ curves obtained with HME, the quotients Q agreed with those obtained with the dropping mercury electrode and the incision depths were constant in the series, lanthanum to gadolinium, and independent of the presence of dissolved oxygen. On the basis of these observation, it seems that the electrode reaction rate of the lanthanum and samarium ions is slower than that of the other lanthanide ions (for example; Pr^{3+}, Nd^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+} and Ho^{3+}). As for erbium, thulium and lutetium, it was very difficult to identify a well-defined incision both with DME and HME because these ions may be hydrolyzed at the electrode surface under the above conditions.

In Fig. 2, curve D shows the plot of the cathodic incision depth with DME (with removal of dissolved oxygen) against the atomic numbers. This curve has two maxima, each of which is coincident with a similar maximum in the curve of the first ionization potentials5) (curve E). As shown in Fig.3, the incision depth just before the detachment of the drop is dependent on the concentration of lanthanide ions. To determine the incision depths of neodymium, samarium and terbium, oscillopolarograms were measured on 0.5 to 5×10^{-4} M (HME), 0.5 to 5×10^{-3} M (DME, Nd^{3+}) and 0.5 to 3×10^{-3} M (DME, Tb^{3+}) lanthanide solutions containing 1 M KCl or 1 M KSCN at pH 3.65±

[*1] The quotient Q is equal to the ratio of the distance between the left limiting point and the peak of the incision to the distance between the two limiting points (Fig. 1-c).

[*2] Q values of the depolarization potential, incision depth and depolarization potential without removal of dissolved oxygen are shown in parentheses.

5) A. Cotton, "Progress in Inorganic Chemistry," Vol. 3, Interscience Publishers, New York (1962), p. 330.

Table 1. Depolarization potentials, incision depths and Q-quotients of lanthanides in 1 M potassium thiocyanate solutions with DME (pH: 3.65±0.05)

Lanthanide	Incision depth, mm				Q		Incition potential, V	
	C		A		C	A	C	A
La	disappear	(13.0)	disappear	(10.0)	(0.68)	(0.67)	(−1.41)	(−1.40)
Pr	1.0	(12.5)	1.0	(10.5)	0.69	0.67	−1.43	−1.40
Nd	2.0	(13.5)	2.0	(10.5)	0.69	0.67	−1.43	−1.40
Sm	disappear	(11.0)	disappear	(9.0)	(0.68)	(0.67)	(−1.41)	(−1.40)
Gd	4.5	(9.0)	4.0	(8.0)	0.68	0.67	−1.42	−1.40
Tb	6.0	(7.5)	4.0	(6.0)	0.68	0.67	−1.41	−1.40
Dy	4.0	(6.0)	3.5	(4.0)	0.68	0.67	−1.41	−1.40
Ho	2.0	(3.0)	1.0	(2.0)	0.68	0.67	−1.42	−1.40
Er Tm Lu	no measurable incision formed							

Table 2. Incision depths and Q-quotients of lanthanides in 1 M potassium thiocyanate solutions with HME (pH: 3.65±0.05)

Lanthanide	Incision depth, mm		Q	
	C	A	C	A
La	16.5 (17.0)	14.5 (15.0)	0.69	0.67
Pr	17.0 (16.5)	12.0 (12.0)	0.68	0.67
Nd	17.5 (17.0)	12.0 (12.0)	0.68	0.67
Sm	17.5 (17.0)	12.5 (12.0)	0.68	0.67
Gd	17.5 (17.0)	12.0 (12.0)	0.68	0.67
Tb	16.0 (14.5)	9.0 (10.0)	0.68	0.67
Dy	16.0 (13.5)	10.0 (9.0)	0.68	0.67
Ho	16.0 (10.0)	10.0 (6.5)	0.68	0.67
Er	3.5	2.0		
Tm	1.8			
Lu	no measurable incision formed			

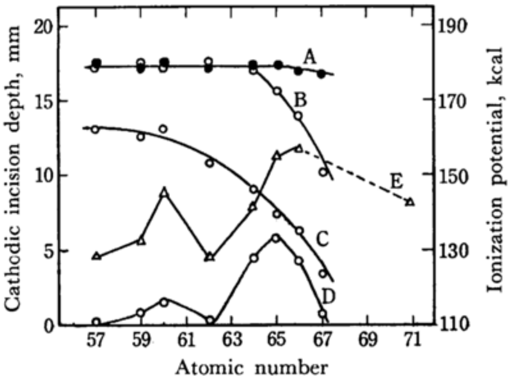


Fig. 2. Variation of cathodic incision depth with the lanthanides in 1 M KSCN solution at pH 3.65±0.05: curves A and B (without deaeration), with a HME; curve C (without deaeration) and D with a DME; curve E, the value of first ionization potential. The concentration of lanthanide added, A to D, was 0.0005 M.

0.05. As seen in Fig. 3, the incision depth increases proportionally to the lanthanide concentration for the range, 0.5 to 3×10^{-3}M (Tb^{3+}) and 0.5 to 5×10^{-3} M (Nd^{3+}) with the DME, and in the range, 0.5 to 2×10^{-4} M (Nd^{3+}, Sm^{3+} and Tb^{3+}) with HME.

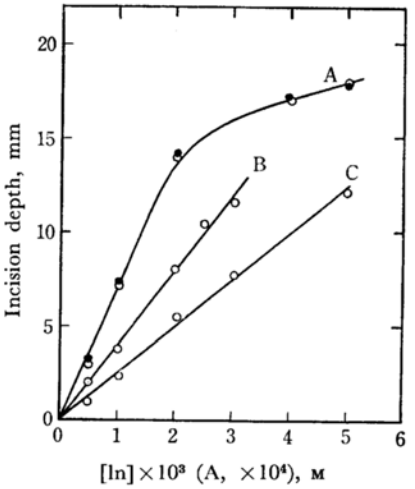


Fig. 3. Calibration curves of the lanthanides: curve A, with a HME (1 M KSCN and KCl; Tb, Sm and Nd); curves B and C, with a DME (1 M KCl; B, Tb; C, Nd).

Consequently, the variation of incision depth on curve D, Fig. 2, may be attributed to the difference in electrode reaction rate of each of the lanthanide ions.

Oscillopolarographic Characteristics of Lanthanide Ions in Potassium Chloride, Bromide and Perchlorate Solutions. The relation between the atomic number and the cathodic incision depth of the lanthanides at pH 3.65±0.05 are shown in Fig. 4 to 6. In Fig. 4, oscillopolarograms were recorded in the range of potassium chloride concentration, 0.5 to 2.0 M. These oscillopolarograms have tendencies similar to those of the potassium thiocyanate solutions which have cathodic and anodic potentials of incision equal to

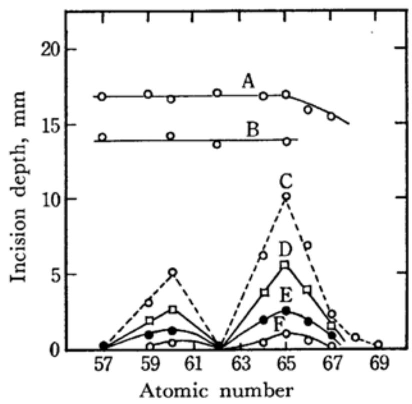


Fig. 4. Variation of the cathodic incision depth with the lanthanides in KCl solution at pH 3.65±0.05: the concentration of KCl added: A, B, C and E 1 M; D 0.5 M; F 2.0 M. The concentration of lanthanide added: A, D, E and F 0.0005; B 0.0002 M; C 0.0025 M. The kind of polarizable electrode used for A and B was a HME and C to F was a DME.

−1.42 and −1.40 V respectively. The curves C to F in Fig. 4 consist mainly of two peaks. This behaviour is also exhibited in the case of potassium thiocyanate solutions. Furthermore, the incision depths decrease to some extent as the concentration of potassium chloride increases. This effect may be attributed to the change of the potential ϕ_2[6] (which becomes less negative with increasing concentration). Curve A in Fig. 4, obtained with the HME, was similar to curve A in Fig. 2. The results measured at pH 4.65±0.05 in 1 M potassium chloride solutions are shown in Fig. 5.

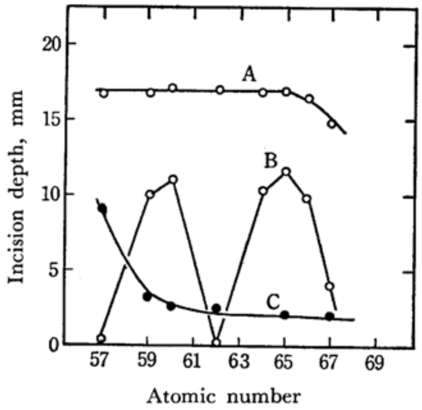


Fig. 5. Variation of the cathodic incision depth with lanthanide in 1 M KCl solution at pH 4.65±0.05. The concentration of lanthanide added was 0.0005 M and curve A was measured with a HME and curves B and C with a DME (C, without deaeration).

The value of the incision depth with HME in Fig. 5, 17.0±0.5 mm (La to Dy), was nearly equal to the value in the cases of 1 M potassium thiocyanate and of 1 M potassium chloride solutions at pH 3.65±0.05. The curve B in Fig. 5 shows the incision depths of lanthanide obtained with DME. These values were rather larger than those in the same supporting electrolyte at pH 3.65. It seems that the cathodic incision of lanthanides is attributable to the reduction of H^+ in hydrated water molecules[2] and that the anodic incision is attributable to the oxidation of lanthanide-halogeno hydride complexes,[1] which are formed by the hydride ions produced at the cathode. Consequently, the increase in the hydrogen ion concentration on the electrode surface might supress the formation of lanthanide-halogeno hydride complexes. Incision depths, without deaeration at pH 4.65, decreased with the decrease in the basicity and such behaviour may be caused by an increase of hydrolysis at the electrode surface. The incision potential was constant at −1.41±0.01 V *vs.* SCE.

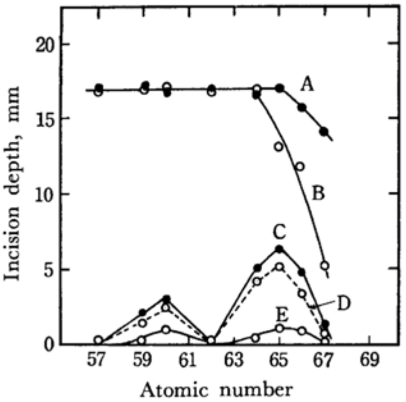


Fig. 6. Variation of the cathodic incision depth with lanthanide in 1 M KBr and $NaClO_4$ solution at pH 3.65±0.05. Supporting electrolyte: A and C, KBr; B, D (0.5 M) and E, $NaClO_4$. A and B, with HME; C to E, with DME.

In Fig. 6, curves A and B represent the results of analyses of the oscillopolarograms obtained on the solution containing 5×10^{-4} M lanthanide, 1 M potassium bromide, and 1 M sodium perchlorate, at pH 3.65±0.05 with HME. In curve B, the values of the incision depth from Tb to Ho are smaller than those of curve A. Curves C and E represent the results of analyses of the curves obtained on these solutions with DME. The values of the incision depth shown by curve C are larger than those by curve E (1 M sodium perchlorate). These results suggest the existence of halide and thiocyanato complexes of lanthanide at the electrode surface.

The authors are grateful to Professor M. Kobayashi for his interest in this work.

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[6] P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, New York (1966), p. 209.