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Polarographic Studies of Some Lanthanoids(III) in *N,N*-Dimethylacetamide

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Polarographic behaviour of some lanthanoids(III) has been studied in *N,N*-dimethylacetamide. La(III), Pr(III), and Nd(III) showed irreversible, three-electron reduction wave and the other lanthanoids(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Lu(III) except Sm(III), Eu(III), and Yb(III), gave irreversible, three-electron reduction wave with a pre-wave. The kinetic parameters for La(III), Pr(III), and Nd(III) were determined by means of Koutecky's method. Sm(III), Eu(III), and Yb(III) showed two-step reduction waves, the first wave being a reversible, one-electron reduction wave. These solvated lanthanoids(III) were investigated also by cyclic voltammetry.

The polarographic studies of Pb(II), Cd(II), *etc.*,[1] and alkali and alkaline earth metal[2] in *N,N*-dimethylacetamide (DMA) have been reported. However, lanthanoid(III) (Ln(III)) has not yet been investigated. It is interesting to compare the polarographic behaviour of each Ln(III), in particular the half-wave potential in DMA, with that in other non-aqueous solvents.

Important kinetic parameters for irreversible waves are transfer coefficient (α) and standard rate constant (k_s). There are few investigations of the rate constant of Ln(III) in non-aqueous solvents. Gaur and Zutshi[3] reported on the polarographic reduction of Eu(III) in formamide.

In this work polarographic and cyclic voltammetric studies and the kinetic parameters of some lanthanoids(III) in DMA are presented.

Experimental

Materials. DMA was fractionally distilled three times from calcium hydride *in vacuo* (10 mmHg) under nitrogen and finally distilled in the absence of calcium hydride. Moisture in DMA was determined by Karl-Fischer titration to be 0.04%. Lanthanoid(III) perchlorates were prepared by dissolving the oxides in perchloric acid and drying at 60°C *in vacuo*. Tetraethylammonium perchlorate (TEAP) was used as the supporting electrolyte. All other reagents were of extra pure grade.

Apparatus. The electrolysis cell consists of three electrodes.[4] The reference electrode was an SCE with a salt bridge:

$$\left(\frac{0.5\text{M TEAP}}{\text{DMA}}\middle|\frac{1\text{M NaClO}_4}{\text{H}_2\text{O}}\middle|\frac{1\text{M NaCl}}{\text{H}_2\text{O}}\middle|\frac{1\text{M KCl}}{\text{H}_2\text{O}}\right).$$

DME was used for DC polarography ($m^{2/3}t^{1/6}=1.25\ \text{mg}^{2/3}/$sec. in 0.1M TEAP-DMA medium at -2.4 V *vs.* SCE) and HDME (area of HDME; 0.051 cm^2) was used for cyclic voltammetry as thework ing electrode. Other apparatus were as described previously.[4]

Procedure. A sample solution of 0.1M TEAP-DMA containing 0.3~2.0 mM $\text{Ln(ClO}_4)_3$ of the final concentration was taken into a cell. After dried nitrogen gas was passed through it for 20 min., a polarogram was recorded. The junction potential was measured by using an SCE with a slowly flowing-type aqueous saturated KCl salt bridge and found to be 25 mV. All experiments were carried out at 25.0±0.1°C.

Results and Discussion

Polarograms of 0.3 mM Ln(III) except for Sm(III), Eu(III), and Yb(III) in DMA are shown in Fig. 1. Each reduction wave of La(III), Pr(III), and Nd(III) was single and irreversible in the concentration range 0.3~1.0 mM for Ln(III), whereas that of other lanthanoids(III) (Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), and Lu(III)) was single and irreversible with a pre-wave, the main wave becoming ill-defined with increasing concentration of Ln(III).

Polarographic data are shown in Table 1-1. The

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[1] S. Musha, T. Wasa, and K. Tani, *Rev. Polarog.* (Kyoto), **11**, 169 (1963).

[2] V. Gutmann, M. Michlmayr, and G. Peychal-Heiling, *Anal. Chem.*, **40**, 619 (1968). *J. Electroanal. Chem.*, **17**, 153 (1968).

[3] J. N. Gaur and K. Zutshi, *J. Electroanal. Chem.*, **11**, 390 (1966).

[4] S. Misumi and M. Aihara, *Talanta*, **19**, 549 (1972).

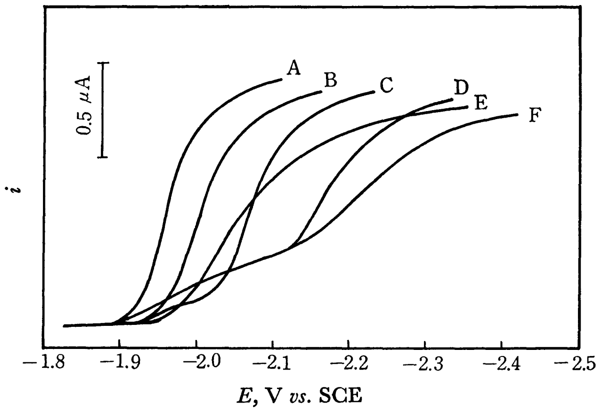

Fig. 1. Typical polarograms of 0.3 mM Ln(III) in DMA.
A: Pr(III), B: Nd(III), C: Gd(III), D: Er(III), E: La(III), F: Lu(III).

electrode reaction was found to be irreversible, of three-electron reduction and diffusion-controlled (Table 2-1). The diffusion current of the main wave decreased and the half-wave potential was shifted to a more negative value with decreasing ionic radius of Ln(III), the total wave height remaining nearly constant.

Table 1. Polarographic data for Ln(III) in 0.1 M TEAP in DMA

1-1 [Ln(III)]=0.30mM

	$-E_{1/2}$ V vs. SCE	I_d	reciprocal slope mV	α
La (III)	2.04_0	2.26	78	0.25
Pr (III)	1.95_6	2.84	37	0.52
Nd (III)	2.00_8	2.56	40	0.49
Gd (III)	2.09_2	2.36	48	0.41
Tb (III)	2.11_3	1.74	40	0.46
Dy (III)	2.13_0	2.02	43	0.46
Ho (III)	2.16_3	1.51	45	0.44
Er (III)	2.18_7	1.67	47	0.42
Tm (III)	2.18_1	1.13	45	0.44
Lu (III)	2.22_9	1.18	52	0.35

1-2 [Ln(III)]=1.00mM

Sm(III) (1st wave)	1.72_3	0.94	54	
(2nd wave)	2.10_6	0.77	38	
Eu(III) (1st wave)	0.53_8	0.89	59	
(2nd wave)	2.13_1	0.46	47	
Yb(III) (1st wave)	1.25_1	1.06	61	

Table 2. Dependence of limiting currents on the heights of mercury column

2-1 [Ln(III)]=0.30mM

Metal ion	$i_l/\sqrt{h_{corr.}}$	Metal ion	$i_l/\sqrt{h_{corr.}}$
La (III)	0.121±0.007	Dy (III)	0.113±0.002
Pr (III)	0.160±0.001	Ho (III)	0.082±0.004
Nd (III)	0.140±0.006	Er (III)	0.088±0.006
Gd (III)	0.124±0.009	Tm(III)	0.065±0.001
Tb (III)	0.102±0.003	Lu (III)	0.064±0.003

2-2 [Ln(III)]=1.00mM

Metal ion	$i_l/\sqrt{h_{corr.}}$		$i_l/\sqrt{h_{corr.}}$
Sm (III) (1st wave)	0.181±0.001	(2nd)	0.169~0.148[a]
Eu (III) (1st wave)	0.166±0.003	(2nd)	0.073~0.060[b]
Yb (III) (1st wave)	0.186±0.002		

a) Temperature coefficient: 5.5~9.5%.
b) Temperature coefficient: 6.5~9.0%.

The effect of increasing concentration of water to DMA on the reduction wave was investigated. Typical polarograms of Pr(III) and Er(III) in water-DMA medium are shown in Fig. 2. The values of half-wave potential and wave-height for Pr(III) did not change with addition of water, but the reduction wave for Er(III) became a single wave even with 1% addition of water. It was observed that the half-wave potential of this wave was shifted toward a more positive value with increasing concentration of water.

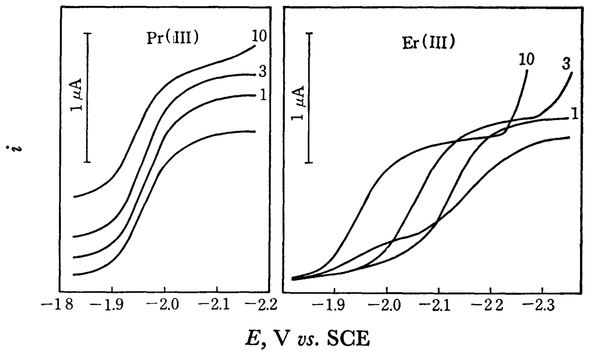

Fig. 2. Typical polarograms of 0.3 mM Pr(III) and Er(III) in water-DMA medium.
Numbers on curves refer to per-cent water added to the solution.

Cyclic voltammograms are shown in Fig. 3. No pre-wave was seen for La(III), Pr(III), and Nd(III) but one was observed for the other lanthanoids(III) such as Gd(III) and Tb(III). The height of the pre-wave also increased with decreasing radius of Ln(III). No anodic waves could be observed at this sweep rate because of the irreversibility of electrode reaction.

Polarograms for Sm(III), Eu(III), and Yb(III) are shown in Fig. 4. Sm(III) and Eu(III) showed two-step reduction waves but the second wave of Yb(III) was observed to overlap the residual current of the supporting electrolyte. Polarographic data are shown

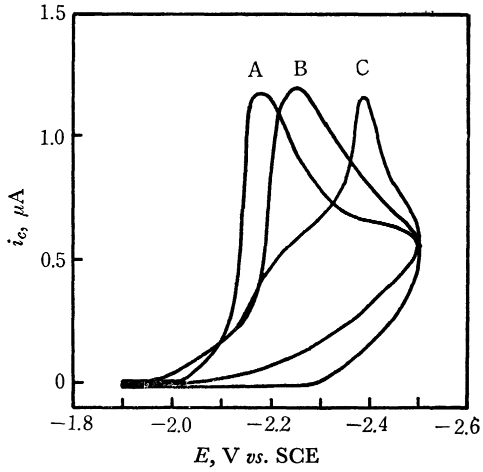

Fig. 3. Cyclic voltammograms of 0.3 mM Ln(III) in DMA.
A: Pr(III), B: Gd(III), C: Lu(III). Scan rate: 0.060 V/sec.

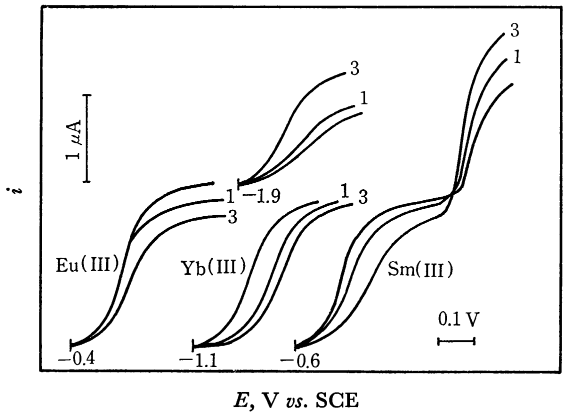

Fig. 4. Polarograms of 1.0 mM Sm(III), Eu(III) and Yb(III) in water-DMA medium.
Number on curves refer to per-cent water added to the solution.

in Table 1-2. The electrode reaction for the first wave is diffusion-controlled but the value of $i_l/\sqrt{h}_{\text{corr}}$. for the second wave decreased with increasing mercury pressure (Table 2-2). The value of temperature coefficient was in the range 5∼9%.

The value of reciprocal slope for the first wave is 54, 59, and 61 mV for Sm(III), Eu(III), and Yb(III), respectively. It was found that its electrode reaction is reversible and of one-electron reduction. The ratio of current for the first wave to that for the second wave is 0.84 for Sm(III) and 0.49 for Eu(III). The effect of water on the reduction wave is shown in Fig. 4. The half-wave potential for the first wave is shifted toward a more negative value and that for the second wave toward a more positive value with increasing concentration of water. The height of the second wave increases with the addition of water.

It is supposed that La(III), Pr(III), and Nd(III) would form a stable solvate species with DMA and these species would not be affected by the adidtion of water. The electrode reaction is assumed to be as follows.

$$[\text{Ln(DMA)}_x]^{3+} + y\text{H}_2\text{O} \rightleftharpoons [\text{Ln(DMA)}_{x-y}(\text{H}_2\text{O})_y]^{3+} + y(\text{DMA})$$

$$[\text{Ln(DMA)}_x]^{3+} + 3\text{e}^- \longrightarrow \text{Ln}^0 + x\text{DMA} \qquad (1)$$

$$[\text{Ln(DMA)}_{x-y}(\text{H}_2\text{O})_y]^{3+} + 3\text{e}^- \longrightarrow \text{Ln}^0 + (x-y)\text{DMA} + y\text{H}_2\text{O} \qquad (2)$$

Equations 1 and 2 correspond to the electrode reactions of the main wave and the pre-wave, respectively.

The half-wave potentials of the main waves corrected for the rubidium scale in three kinds of solvents (the donor numbers of DMA, *N,N*-dimethylformamide (DMF) and acetonitrile (AN) are 27.8, 26.6, and 14.1, respectively) are listed in Table 3. Values of the half-wave potentials are in the order AN[5]>DMF[6]>DMA. A comparison of these values shows that the half-wave potential is related to donor number and metal ion-solvent interaction depends on the polarographic over-voltage.

Table 3. Half-wave potential of Ln(III) in different solvents in volts *vs.* the half-wave potential of Rb^+

Ln (III)	Solvent DMA	DMF	AN
La	−0.09	−0.05	0.45
Pr	0.00	−0.05	0.45
Nd	−0.05	−0.05	0.45
Gd	−0.14	−0.14	0.45
Tb	−0.16	−0.14	
Dy	−0.18	−0.16	
Ho	−0.21	−0.18	
Er	−0.23	−0.19	
Tm	−0.23		
Lu	−0.27		

The half-wave potential of the first wave for Sm(III) and for Eu(III) in water[5] was more negative than that in DMA. This explains the negative shift of half-wave potential caused by the addition of water. The electrode reaction of the first wave is reversible and of one electron reduction, but that of the second wave differs from that in other solvents (*e.g.* Eu(II)→Eu(0) in acetonitrile[5]).

The kinetic parameters for the reduction of La(III), Pr(III), and Nd(III) were calculated by means of Koutecky's method[7] and the values of E_s (standard electrode potential) were obtained by Hale and Parson's method.[8]

For the reaction where $k_s \leq 5\times10^{-4}$ cm/sec, there is a region near the top of the wave in which $\exp\{nF(E\text{-}E_s)/RT\} \ll 1$. Under these conditions Koutecky's equations can be simplified as follows.

$$i/i_d = F(\chi) \qquad (3)$$

$$\chi = (12t/7D_0)^{1/2}k_f \qquad (4)$$

where $F(\chi)$[9] is a power series in the variable (χ) and k_f is the rate constant for the forward reaction. k_f is related to the standard rate constant by the equation.

$$(k_s): k_f = k_s e^{-\alpha nF(E-E_s)/RT} \qquad (5)$$

k_f and α can be determined from Eqs. (3), (4) ,and (5). When E equals E_s, $\exp\{nF(E-E_s)/RT\}$ becomes 1 and Koutecky's equations become

$$i/i_d = F(\chi)/2 \qquad (6)$$

$$\chi = 2(12t/7D_0)^{1/2}k_f \qquad (7)$$

By plotting $\log(F(\chi)/2)$ *vs.* $\log(\chi/2)$ and $\log(i/i_d)$ *vs.* $\log(12t/7D_0)^{1/2}k_f$, the intersection gives the point k_s.

$$k_f = k_s e^{-\alpha nF(E-E_s)/RT} = k_s$$

The values of α for La(III), Pr(III), and Nd(III) were determined also by plotting $\log\chi$ *vs.* E. The

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[6] G. Gritzner, V. Gutmann, and G. Schöber, *Mh. Chem.*, **96**, 1056 (1965).

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[8] J. M. Hale and R. Parsons, *ibid.*, **27**, 2444 (1962).

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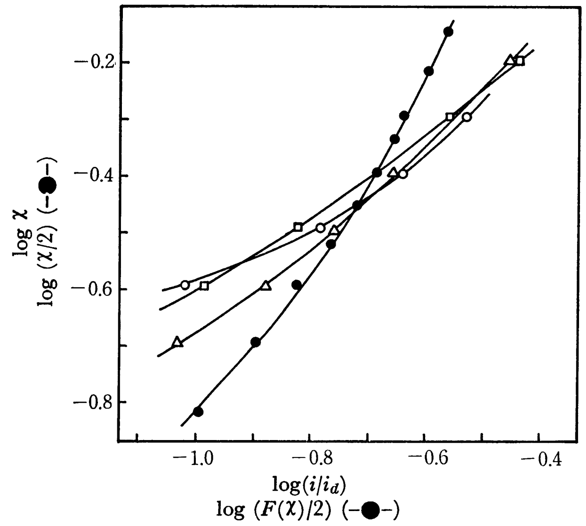

Fig. 5. Plot of log χ *vs.* log(i/i_d) and log$(\chi/2)$ *vs.* log$(F(\chi)/2)$. ○: La(III), △: Pr(III), □: Nd(III).

values were in agreement with those obtained by log-plot analysis. The results of the determination of $(k_s)_{ms}$ are given in Fig. 5 and kinetic parameters

Table 4. Data for parameters of reduction of La(III), Pr(III) and Nd(III) in DMA

	$(E_{1/2})_{irr}$ V *vs.* SCE	$(E_{1/2})_r$ V *vs.* SCE	$(\alpha_c)_{ms}$	$(k_s)_{ms}$ cm/sec
La	-2.04_0	-2.00_3	0.24	2.0×10^{-4}
Pr	-1.95_6	-1.93_7	0.49	2.2×10^{-4}
Nd	-2.00_8	-1.98_4	0.43	2.4×10^{-4}

in Table 4, where $(\alpha_c)_{ms}$ and $(k_f)_{ms}$ mean the parameters determined directly from the experimental data without any theoretical correction.

On the other hand, the value of k_f^0 (the forward rate constant of the electron transfer at zero volt *vs.* NHE) was obtained by cyclic voltammetry. The value of k_f^0 (5.3×10^{-27} cm/sec) for La(III) is nearly identical with that (3.0×10^{-27} cm/sec) obtained by using k_s, but in the case of Pr(III) and Nd(III) the values of k_f^0 do not coincide with those obtained by using k_s, because of very small values of k_f^0.

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