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# Stepwise Reduction of Samarium and Ytterbium in the Polarographic Reduction Process in the Presence of 1,4,7,10,13,16-Hexaoxacyclooctadecane[1)]

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Polarographic reduction of La, Pr, Nd, Sm, Gd, Dy, Er, and Yb was investigated in the aqueous solutions containing 1,4,7,10,13,16-hexaoxacyclooctadecane (18-CROWN-6). It is shown that Sm(III) and Yb(III) are reduced stepwisely *via* the divalent state in the presence of 18-CROWN-6. The divalent state is stabilized by the complex formation with 18-CROWN-6.

From the view point of f-series element chemistry, it is of great interest to investigate abnormal oxidation states. We are interested in low oxidation states found in aqueous solutions. For lanthanoids, Eu(II) and Yb(II) are farely stable in aqueous solutions. The findings of Sm(II) and Tm(II) were also reported[2,3)] but they are so unstable that they are rapidly oxidized in aqueous solutions. Because of this instability, the findings of Sm(II) and Tm(II) in aqueous solutions are not recognized widely.

Among many experimental techniques, polarographic reduction seems to be most promising for the investigation of low oxidation states of f-series elements in aqueous solutions. It affords useful information about the reduction process and we can inspect whether they are reduced directly to the metallic state or stepwisely *via* an intermediate lower oxidation state. In addition, it can be applied to the investigation of actinoids in tracer concentrations by the use of the radiopolarographic method.[4,5)]

1,4,7,10,13,16-Hexaoxacyclooctadecane(18-CROWN-6) has size selectivity for cations on complex formation.[6,7)] Taking into consideration the facts that the radii of some dipositive cations of lanthanoids($Ln^{2+}$) and actinoids($An^{2+}$) are very close to the radius of the ring of 18-CROWN-6, we expected that 18-CROWN-6 stabilizes $Ln^{2+}$ and $An^{2+}$ in aqueous solutions by complex formation.

In this report, we describe the stabilization of Sm(II) and Yb(II) by 18-CROWN-6 observed in stepwise reduction waves on a polarogram.

## Experimental

*Apparatus.* Yanagimoto PA-102 was used as a direct current polarograph. An ordinary polarographic cell was used and connected to the standard calomel electrode(SCE) through an agar gel bridge.

*Reagents.* 18-CROWN-6 produced by Nippon Soda Co., LTD was used without purification. After drying in a vacuum desiccator, 18-CROWN-6 was dissolved into pure water. A 1 M (1 M = 1 mol/dm$^3$) 18-CROWN-6 solution was used as a stock solution. Lanthanoid oxides of 99.99% purity were obtained from the Rare Earth Elements Purification Facility of our institute and converted to trichlorides before use.

*Procedures.* *Preparation of Sample Solutions*: Tetramethylammonium chloride(TMACl) was used as a supporting electrolyte in the concentration of 0.1 M. Because of the inertness of TMACl toward reduction, the reduction of Ln(II) can be investigated without disturbance by the discharge of the supporting electrolyte. The concentration of lanthanoids in the sample solutions was 4 mM. Sample solutions containing 18-CROWN-6 were prepared by the addition of the stock solution. Sample solutions of Ba(II) and Pb(II), which make stable complexes with 18-CROWN-6, were also prepared and the reduction behaviors were examined.

*Determination of Half Wave Potentials.* Direct current polarograms were obtained according to the ordinary method. Argon gas was bubbled into the sample solution for 10—15 min. in order to eliminate dissolved oxygen. The half wave potentials were determined after subtracting the back ground current induced by hydrogen discharge, which was observed at more positive potentials than the potentials for the reduction of Ln(II).

## Results and Discussion

*Reduction of Sm(III).* Several authors have reported the stepwise reduction of Sm(III) *via* a divalent state in weakly acidic solutions. Timnic reported the stepwise reduction under experimental conditions very similar to ours using tetramethylammonium iodide for the supporting electrolyte.[8)] However, the ratio of the

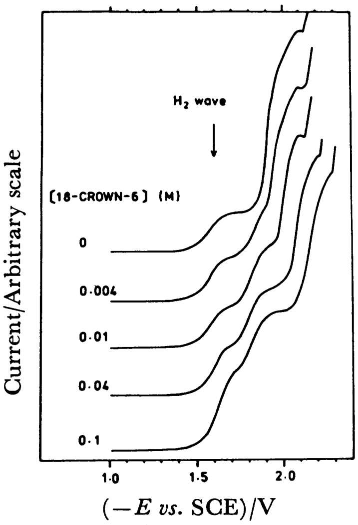

Fig. 1. Polarograms of Sm as a function of the concentration of 18-CROWN-6.

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diffusion current of the first wave to that of the second wave estimated from his data was not consistent with his conclusion. The ratio should be 1 : 2 for the reduction *via* the divalent state, while his data for the ratio varied with the concentration of Sm.

Polarograms of Sm are shown in Fig. 1. The small wave at about −1.55 V (*vs.* SCE) is the hydrogen discharge wave. The polarogram exhibits a deformed single wave at −1.8 V (*vs.* SCE) in the absence of 18-CROWN-6. We did not observe stepwise reduction with respect to the sample solutions without 18-CROWN-6. In contrast with this finding, the polarograms of Sm(III) in the presence of 18-CROWN-6 showed two well-defined reduction waves, as shown in Fig. 1. This fact was clearly observed as the splitting of a deformed single wave. The splitting was enhanced by the shift of the first wave to more positive potentials and the second wave to more negative potentials with the increase in the concentration of 18-CROWN-6. The ratio of the diffusion current of the two waves remained at 1 : 2. Therefore, it is quite reasonable to conclude that the first wave is due to a one-electron reduction of Sm(III) and the second wave is due to a two-electron reduction of Sm(II). And the direction of the shift of the second wave, along with the increase in the concentration of 18-CROWN-6, shows qualitatively the stabilization of Sm(II) by 18-CROWN-6.

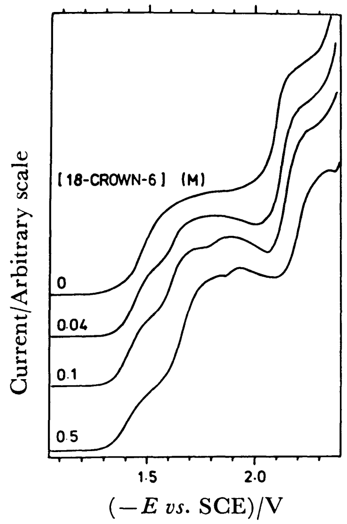

Fig. 2. Polarograms of Yb as a function of the concentration of 18-CROWN-6.

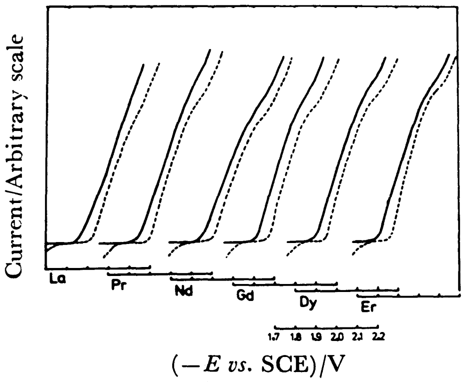

Fig. 3. Polarograms of some trivalent lanthanoids. Polarograms for the samples free from 18-CROWN-6 are shown by solid lines and for the samples of 0.48 M 18-CROWN-6 solutions by dotted lines.

*Reduction of Yb(III).* Polarograms of Yb are shown in Fig. 2. Yb(II) is more stable than Sm(II) in aqueous solutions. Two reduction waves were observed with respect to the solutions without 18-CROWN-6. The first wave, at about −1.4 V (*vs.* SCE), overlaps with the hydrogen discharge wave when the sample solution does not contain 18-CROWN-6. This wave shifts to more positive potentials with the increase in the concentration of 18-CROWN-6. The second wave, at about −2.1 V (*vs.* SCE), is attributable to the reduction of Yb(II) to Yb(0). The ratio of the diffusion currents of these two waves in the presence of 18-CROWN-6 is 1 : 2. Therefore, the first wave can be assigned to the reduction of Yb(III) to Yb(II). The other wave observed between the hydrogen discharge wave and the second wave seems to be a catalytic wave of hydrogen induced by the presence of 18-CROWN-6 in the sample solution.

*Reduction of La(III), Nd(III), Pr(III), Gd(III), Dy(III), and Er(III).* Divalent state of La, Nd, Pr, Gd, Dy, and Er are not yet known in aqueous solutions. For comparison to Sm and Yb, the reduction of these six elements were examined under the same condition. The polarograms are shown in Fig. 3. Only a single wave, due to the reduction of trivalent cation to the metallic state, was observed for every element. The presence of 18-CROWN-6 has little influence to the reduction wave. The results indicate that these six elements are reduced directly even in the presence of 18-CROWN-6. A small shift was observed but the magnitude of the shift did not exceed about 20 mV even in the sample solutions of 0.48 M 18-CROWN-6, the highest concentration used in this experiment.

*The Influence of 18-CROWN-6 to the Reduction of Ba(II) and Pb(II).* The influence of 18-CROWN-6 to the polarograms of Ba(II) and Pb(II) was examined in 0.1 M TMACl, pH 3.0 solutions. A well defined single reduction wave was observed. It was found that the addition of 18-CROWN-6 had no influence on the shape of the reduction wave. But the addition of 18-CROWN-6 induced a very large shift of the reduction wave to more negative potentials, which suggested a strong interaction between Ba(II) or Pb(II) and 18-CROWN-6.

*The Relation between the Shift of the Reduction Wave and the Concentration of 18-CROWN-6.* The stepwise reduction of the complex is represented by the following reactions.

1st reduction:

$$\mathrm{MX}_p^{m+} + r\mathrm{X} + (m-n)\mathrm{e}^- \longrightarrow \mathrm{MX}_q^{n+} + (p+r-p)\mathrm{X} \quad (1)$$

2nd reduction (reduction to metallic state in Hg phase):

$$\mathrm{MX}_q^n + n\mathrm{e}^- \longrightarrow \mathrm{M(Hg)} + q\mathrm{X} \quad (2)$$

In these expression, X represents a ligand, $p$ and $q$ are the coordination numbers, and $(m-n)$ and $n$ are the numbers of the electrons involved in the reduction. When complex formation proceeds reversibly and the electron transfer is rapid, the magnitude of the shift induced by the addition of X is expressed as follows for the second reduction.[9]

$$-\Delta E_{1/2} = (E_{1/2})_c - (E_{1/2})_s = \frac{RT}{nF}\cdot q\cdot \ln[X] + \frac{RT}{nF}\cdot \ln \beta_{MX_q} \qquad (3)$$

In this equation, $(E_{1/2})_c$ and $(E_{1/2})_s$ represent the half wave potentials of complex and hydrated cation, respectively. $\beta$ represents the formation constant of the complex. The value of $RT/F$ is 0.059 V under the present experimental condition. The shifts for Ba(II) and Pb(II) are also represented by Eq. 3.

The relation between the shift of the reduction waves and the logarithm of the concentration of 18-CROWN-6 is shown in Fig. 4 for the second waves of Sm and Yb. In the figure, the shifts of the waves of Pb and Ba are also shown. As shown in Fig. 4, an almost linear dependency between $-\Delta E_{1/2}$ and the logarithm of the concentration of 18-CROWN-6 was observed and the slope showed that $n$ was equal to $q$. Undoubtedly $n$ is equal to 2. Therefore, the coordination number was determined to be 2. Thus, the complex is probably of the sandwich type. From the intercepts, we estimated the values of log $\beta_{MX_2^{2+}}$ to be 3.8—4.3, 5.9—6.2, 6.3—6.9, and 4.1—4.9 for Yb(II), Pb(II), Sm(II), and Ba(II), respectively.

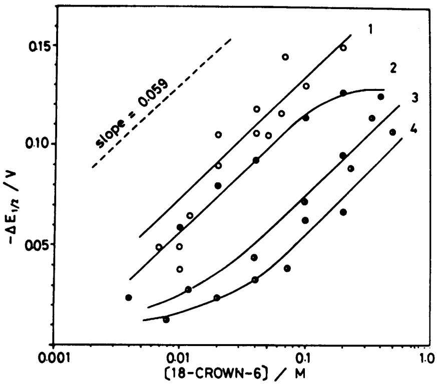

Fig. 4. $\Delta E_{1/2}$ vs. log [18-CROWN-6].
1: Sm(II), 2: Pb(II), 3: Ba(II), 4: Yb(II).

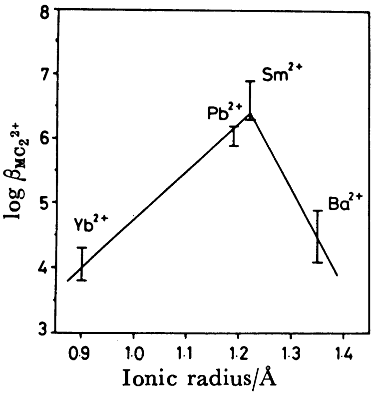

Fig. 5. Plot of log $\beta_{MX_2^{2+}}$ vs. cation crystal radius.

Considering that the formation constants of 18-CROWN-6 complexes exhibit a simple relation with the size of the central cations, we examined the dependence of log $\beta_{MX_2^{2+}}$ on the ionic radii of the four divalent cations We cited the ionic radii reported by Shanon.[10] The relation is shown in Fig. 5. A maximum of the stability is clearly observed at 1.2 Å. A similar tendency was reported by Izatt for 1 : 1 complexes of divalent cations.[6,7]

Consequently, we can say that Sm(III) and Yb(III) form stable complexes with 18-CROWN-6 and that Sm(III) is reduced stepwisely *via* divalent states in the presence of 18-CROWN-6.

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