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The Radiopolarography of Gadolinium, Ytterbium, and Californium

Yoshinobu SHIOKAWA* and Shin SUZUKI
The Research Institute for Iron, Steel, and Other Metals, Tohoku University, Katahira, Sendai 980
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The polarographic reduction of Gd, Yb, and Cf was investigated. It was found that the M(III)→Hg(M) reduction process in an aqueous solution, that cannot be detected by dc polarography, can be detected by radiopolarography. The polarographic behavior of Gd, Eu, Yb, and Cf in the presence of 1,4,7,10,13,16-hexaoxacyclooctadecane(18-crown-6) suggests that Cf(III) is reduced in two steps to Hg(Cf) in an aqueous solution.

The existence of divalent californium has been confirmed by the hydrogen reduction of CfI_3,[1] the polarographic reduction in an acetonitrile,[2] and the distribution between molten salts and liquid Bi.[3] However, concerning its existence in an aqueous solution there are conflicting observations. Musikas *et al.* observed through dc polarography and cyclic voltammetry that Cf(III) in 0.1 M $(CH_3)_4NI$ (1 M=1 mol dm^{-3}) was reduced in two steps.[4] On the other hand, David and Samhoun observed through radiopolarography Cf(III) in 0.1 M LiCl or 0.1 M $(CH_3)_4NClO_4$ was reduced in a single step.[5,6]

In the present work we wish to clarify the reduction process of Cf(III) in an aqueous solution. First, we performed the polarographic reduction of Gd(III) and Yb(III) in order to examine how the M(III)→Hg(M) process was observed by means of radiopolarography. Next, the reduction behavior of Gd, Eu, Yb, and Cf in the presence of 18-crown-6 was investigated.

Experimental

The ^{153}Gd, ^{169}Yd, and $^{250,252}Cf$ were purified by the standard ion exchange technique.[7,8] The tetramethylammonium iodide was used as a supporting electrolyte; in it Musikas *et al.* had observed the existence of Cf(II).[4] Aliquots of the gadolinium, ytterbium, or californium solution were evaporated to dryness and the residue was dissolved in 1 ml of 0.01 M H_2SO_4 and 5 ml of 0.2 M $(CH_3)_4NI$, and then the mixture was diluted to 10 ml. The pH value of the solution was adjusted by the use of 0.1 M H_2SO_4 or 0.1 M $(CH_3)_4NOH$.

In a conventional radiopolarographic cell, the aqueous solution examined is directly in contact with the insulating phase(CCl_4), in which the radioactive amalgam is accumulated. In such a cell, because of the direct contact with the organic solvent, the radiopolarographic reduction in an organic solvent or an aqueous solution which contains some soluble substance such as 18-crown-6 in the CCl_4, is difficult. In this experiment, however, we used a new radiopolarographic cell, shown in Fig. 1, in which the solution examined was not directly in contact with the CCl_4 phase. In this cell, the inner surface of the part of capillary E(inner diameter, 3 mm) below the stopcock F was treated with the vapor of dimethyldichlorosilane. The increased surface tension between the solution and the glass makes the solution hold above the argon phase.

The deoxidized CCl_4 and then the solution examined were introduced into the cell, and the tube connected to the needle valve I was filled with argon. A constant potential was imposed at the DME during 10 min, while the mercury drops were passed through the capillary E and the argon phase and then accumulated in the compartment on the stopcock G. Then, the stopcock F was closed and the needle valves I and J, and the stopcock G were opened. By the flow of CCl_4(J→G→I), the amalgam was rinsed in order to remove the radioactive solution adhered to it and falled into the compartment on the stopcock H. After the stopcock G was closed, the amalgam was taken out from cell with a small quantity of CCl_4. The dried amalgam was weighed, and then the amalgamated metal was extracted by shaking it with 1 ml of 0.5 M HCl or 0.5 M HNO_3 for 10 min. For the Gd and Yb runs, an aliquot of the extraction solution was determined by means of γ-ray spectrometry. For Cf, the sample, prepared by evaporating an aliquot of the solution on a dish of stainless steel, was determined by means of α-ray spectrometry.

There was no difference of more than 0.1 of the pH value between before and after experiments. The radiopolarographic cell was placed in a constant-temperature box with 25±1 °C. The polarograph and the DME knocker for obtaining a constant lifetime of a mercury drop were manufactured by ourselves. The DME knocker was used only in the dc polarography. The 18-crown-6 was a product of the Nippon Soda Co.,Ltd., and was dried by use of P_2O_5 in a vacuum desiccator with a liquid-nitrogen trap.

Results and Discussion

The dc polarogram of lanthanoid(III), except for

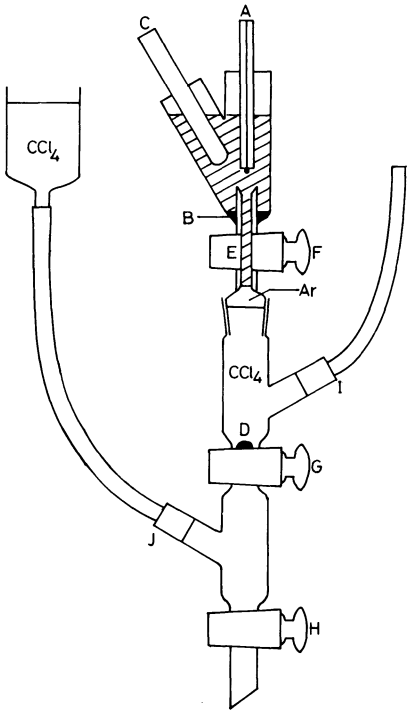

Fig. 1. Radiopolarographic cell.
A: dropping mercury electrode, B: mercury anode, C: reference electrode, D: amalgam, E: capillary, F, G and H: stopcocks, I and J: needle valves.

Eu(III) and Yb(III) in an aqueous solution, exhibits two waves, whose processes are not limited by the rate of diffusion, beyond the hydrogen discharge. According to Large and Timnick,[9] the first wave is attributed to the reduction of the hydrogen ions produced by the protolytic dissociation of the hydrated lanthanoid(III) at the electrode surface, while the second is due to the adsorption of the hydrolytic species of lanthanoid(III). Therefore, the reduction process of lanthanoid(III) cannot be detected by dc polarography.

In radiopolarography, the measured quantity is not the flux of electrons(current), but the amount of the amalgamated radioactive nuclide. That is, this quantity corresponds to the mass transfer associated by the electrode reaction and not to the electron transfer. Also, the concentration of the metal ions is much lower than that used in the dc polarography. It can, therefore, be expected that the reduction process of lanthanoid(III) in an aqueous solution can be detected by means of the radiopolarography.

Figure 2 shows the radio and dc polarograms of Yb(III). In the dc radiopolarogram, two waves due to the hydrogen discharge and reduction of Yb(III) to Yb(II) at about −1.5 V,[10] which, naturally, cannot be detected by the radiopolarography, are overlapped, while the wave at about −2.0 V is attributed to the reduction of Yb(II) to Hg(Yb). Its reciprocal of the slope of logarithmic analysis for the wave is 29—34 mV. On the other hand, the radiopolarographic wave is detected at about −2.0 V, and its reciprocal of the slope is 27—31 mv. Moreover, as is shown in Fig. 3, the limiting activity A_d, one at the plateaus of the radiopolarogram, is controlled by the rate of diffusion. Therefore, the radiopolarographic results are almost the same as the dc polarographic ones; nevertheless, the concentration of ytterbium on each solution examined differs by an order of four. The diffusion coefficient calculated from the limiting activity is 3—4×10^{-6} $cm^2 s^{-1}$, which is lower than that calculated from the limiting current. This may be attributed to desamalgamation in CCl_4.[5]

However, there is a little difference in the half-wave potentials, $E_{1/2}$, obtained by the two methods. The potentials obtained by the dc polarography are more negative and dependent on the pH values; $E_{1/2}$=−2.033 V at pH=2.9, $E_{1/2}$=−2.059 V at pH=3.5. A similar dependence is observed by the dc polarographic reduction of Eu(II) to Hg(Eu).[11] On the other hand, the half-wave potentials obtained by the radiopolarography are independent of the pH values; $E_{1/2}$=−2.016 V at pH=2.8, $E_{1/2}$=−2.015 V at pH=3.5. The dependency of the potentials on the pH observed by the dc polarography have been explained by the formation of hydroxo complexes.[11] This explanation is not correctly but we ourselves cannot at present explain these differences in pH dependency.

Figure 4 shows the radio and dc polarograms of Gd(III). In the dc polarogram, except for the hydrogen discharge at about −1.5 V, two waves are observed, as has been mentioned above: One at about −1.80 V and another at about −2.07 V. In the radiopolarogram, the wave is found at about −2.15 V, and the half-wave potentials are independent of the pH; $E_{1/2}$=−2.154 V at pH=2.8, $E_{1/2}$=−2.149 V at pH=3.5. As is shown in Fig. 3, this process is limited by the rate of diffusion, while the reciprocal of the slope of logarithmic analysis for the wave is about 35 mV. Therefore, the radiopolarographic wave must be due to the reduction of Gd(III) to Hg(Gd) being irreversible.

By means of radiopolarography, in an aqueous

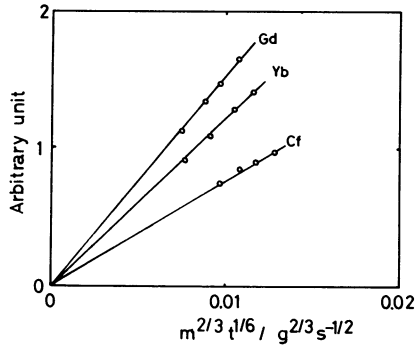

Fig. 3. Dependence of the limiting activity on the mercury column height.
Gd: at −2.202 V in 0.1 M $(CH_3)_4NI$, pH=3.0.
Yb: at −2.082 V in 0.1 M $(CH_3)_4NI$, pH=3.0.
Cf : at −1.845 V in 0.1 M LiCl, pH=2.9.

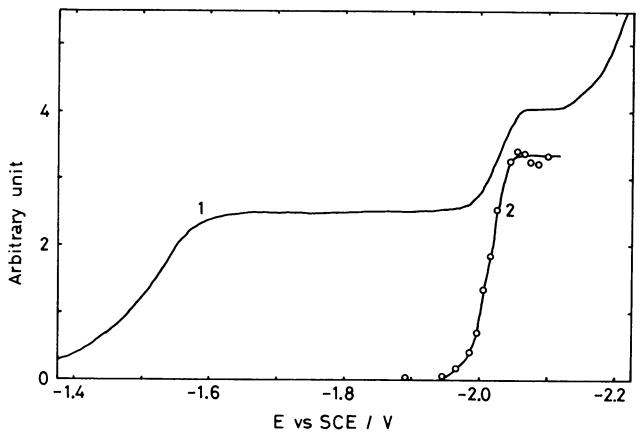

Fig. 2. Polarograms of Yb in 0.1 M $(CH_3)_4NI$, pH=3.0.
1: dc polarogram, [Yb]=1.46×10^{-3} M, 0.02% gelatin.
2: radiopolarogram, [Yb]=6×10^{-7} M.

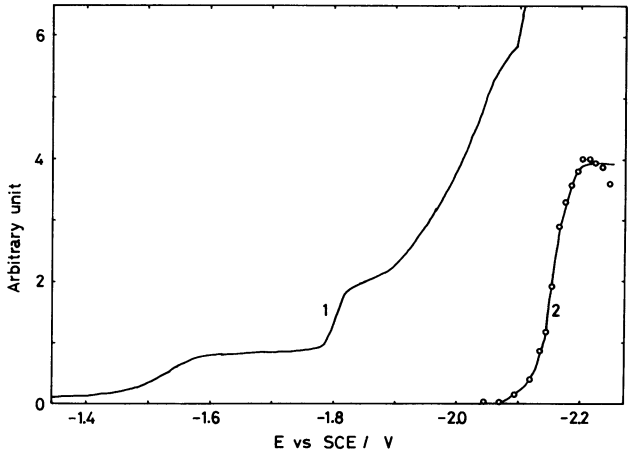

Fig. 4. Polarograms of Gd in 0.1 M $(CH_3)_4NI$, pH=3.0.
1: dc polarogram, [Gd]=1.30×10^{-3} M, 0.01% gelatin.
2: radiopolarogram, [Gd]=5×10^{-7} M.

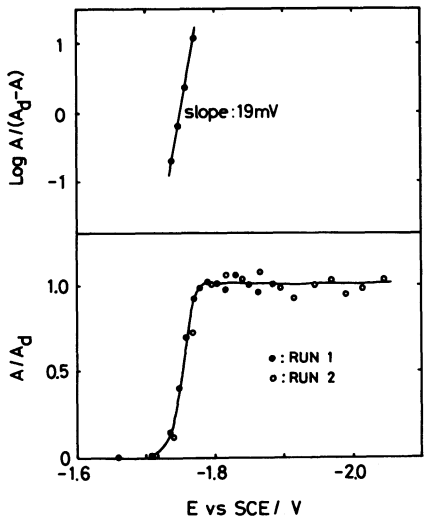

Fig. 5. Radiopolarogram and logarithmic analysis of Cf in 0.1 M $(CH_3)_4NI$, pH=3.0.
A: radioactivity in mercury drops. A_d: limiting activity.

solution the reduction wave of not only lanthanoid(II) but also lanthanoid(III) can be detected, as has been mentioned above. Thus radiopolarography can be expected to elucidate the reduction process of Cf(III) in an aqueous solution.

Figure 5 shows the radiopolarogram and logarithmic analysis of Cf(III). The half-wave potential and the reciprocal of the slope are −1.750 V and 19 mv respectively, and this process is limited by the rate of diffusion, as is shown in Fig. 3. The half-wave potential obtained is almost in agreement with that obtained by David and Shahoun through radiopolarography,[5,6] but not with that obtained by Musikas *et al.* through dc polarography.[4] According to Musikas *et al.*, the half-wave potential is −1.71 V for Cf(III)/Cf(II) and −1.93 V for Cf(II)/Hg(Cf). At this amalgamated potential, as is shown in Run 2 of Fig. 5, no appreciable change in the radiopolarogram is observed. The disagreement is not due to the difference in the concentration of Cf(III), because, as is shown in Fig. 2, the potentials obtained by radio and dc polarography are almost in agreement. The disagreement may be attributed to the difference in the specfic activity of a solution. In this work, the specific activity of $^{250,252}Cf$ was about 0.3 μCi/ml (the concentration of Cf: 4×10^{-9} M), while Musikas *et al.* carried out at about 0.5 mCi/ml (10^{-4}—10^{-3} M). The difference in the potentials, $E_{1/2}$, may be attributed to the influence of the α activity in the electrical double layer at the electrode.

From the logarithmic analysis of the radiopolarographic wave, David and Samhoun have drawn the conclusion that Cf(III) is reduced by a single step to Hg(Cf). Our reciprocal of the slope, as is shown in Fig. 5, supports their conclusion. However, as the reduction wave of Cf(III) to Cf(II), even if the reduction can occur, cannot be detected by radiopolarography, it is desirable to investigate the electrode reaction from a different viewpoint. In the present work, therefore, the shift of half-wave potentials in the presence of

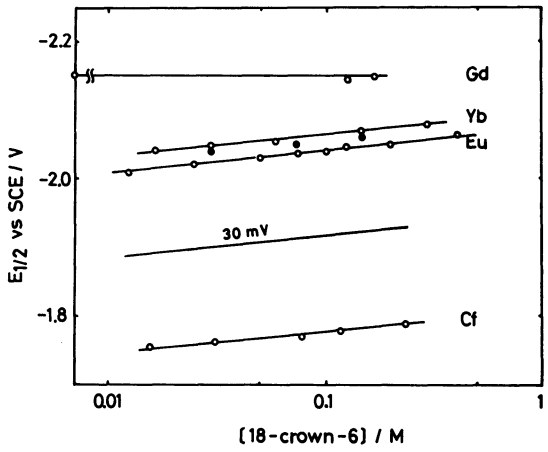

Fig. 6. $E_{1/2}$ of Eu, Gd, Yb, and Cf as a function of 18-crown-6 concentration.

18-crown-6 was investigated.

It is well known that 18-crown-6 forms stable complexes with cations whose ionic diameters are very close to the cavity diameter of 18-crown-6. Izatt *et al.* showed that, in an aqueous solution, 18-crown-6 with a cavity diameter of 280 pm[12] does not form complexes with La(III) with an ionic radius $r_{La^{3+}}$=103 pm[13] upon the calorimetry.[14] Therefore, it cannot form complexes with Cf(III) with a smaller radius $r_{Cf^{3+}}$=95 pm[13] than La(III). On the other hand, 18-crown-6 is expected to form complexes with Cf(II) because of two adavantages, its radius, $r_{Cf^{2+}}$=107 pm[13], is larger than that of Cf(III), and its hydration energy is lower than that of La(III).

Figure 6 shows the dependence of the half-wave potentials of the reduction to the amalgam on the concentration of 18-crown-6. The potentials $E_{1/2}$ of Gd, Cf, and a part of Yb (blackened circles in Fig. 6) were obtained by radiopolarography, and the others, by dc polarography.

For the case of Gd, the potentials $E_{1/2}$ shown in Fig. 6 are due to the reduction of Gd(III) to Hg(Gd); the potential $E_{1/2}$ in the absence of 18-crown-6 is also shown in this figure. No shift of potentials $E_{1/2}$ and no appreciable change in the irreversibility are observed, even in the presence of 18-crown-6.

For Eu and Yb, the potentials $E_{1/2}$ shown are due to the reversible reduction of M(II) to Hg(M). The observed slope of the half-wave potentials *vs.* the logarithmic concentration of 18-crown-6 is 30 mV, as is shown in Fig. 6. As is well known, if the reduction is reversible, such a plot has a slope of $P(RT/nF)$, where P is the coordination number of 18-crown-6. Figure 6 suggests that 18-crown-6 forms 1:1 complexes with Eu(II) and Yb(II). Their stability constants are estimated to be log $K_{Eu^{2+}}$=2.7 and log $K_{Yb^{2+}}$=2.4.

The observed shift of the half-wave potentials of Cf indicates that 18-crown-6 forms complexes with Cf(II), as has been mentioned above, and that Cf(II) reduces to Hg(Cf). However, the mean reciprocal of the slope of logarithmic analysis in the presence of 18-crown-6 is 23 mV, which is nealy equal to that in the absence of 18-crown-6, as is shown in Fig. 5, and corresponds to a Cf(III)→Hg(Cf) process, not a Cf(II)→Hg(Cf) process. We cannot interpret these conflicting results. Miranda *et al.* have pointed out, in their critical survey of radio-

polarography, that the logarithmic analysis of the radiopolarogram cannot always be taken at its face value.[15] Therefore, at the present time the results of the logarithmic analysis of Cf remain as the question to be solved later.

It is of interest that the observed dependence of the half-wave potentials of Cf on the concentration of 18-crown-6 has the same slope as that of Eu(II) to Hg(Eu) and that of Yb(II) to Hg(Yb). Therefore, we may suppose that the reduction of Cf is reversible. Figure 6 shows that 18-crown-6 forms 1:1 complexes with Cf-(II) and its stability constant is estimated to be log $K_{Cf^{2+}}$=2.0. The estimated stability constants of 18-crown-6 with Eu(II), Yb(II), and Cf(II) satisfy the relationship between the stability constants of alkaline-earth elements and their ionic radii.[12]

References

1) J. F. Wild, E. K. Hulet, R. W. Lougheed, W. N. Hayes, J. R. Peterson, R. L. Fellows, and J. P. Young, *J. Inorg. Nucl. Chem.*, **40**, 811 (1978).

2) H. A. Friedman, J. R. Stokeley, and R. D. Baybarz, *Inorg. Nucl. Chem. Lett.*, **8**, 433 (1972).

3) J. C. Mailen and L. M. Ferris, *Inorg. Nucl. Chem. Lett.*, **7**, 431 (1971).

4) C. Musikas, R. G. Haire, and J. R. Peterson, *J. Inorg. Nucl. Chem.*, **43**, 2935 (1981).

5) K. Samhoun and F. David, *J. Inorg. Nucl. Chem.*, **41**, 357 (1979).

6) F. David, K. Samhoun, and G. D. O'Kelley, *J. Inorg. Nucl. Chem.*, **43**, 2941 (1981).

7) E. K. Hulet, R. G. Gutmacher, and M. S. Coops, *J. Inorg. Nucl. Chem.*, **17**, 350 (1961).

8) G. R. Choppin, B. G. Harvey, and S. G. Thompson, *J. Inorg. Nucl. Chem.*, **2**, 66 (1956).

9) R. F. Large and A. Timnick, *Anal. Chem.*, **36**, 1258 (1964).

10) All electrode potentials in this paper are with respect to the saturated calomel electrode(SCE).

11) S. Misumi and Y. Ide, *Bull. Chem. Soc. Jpn.*, **32**, 1159 (1959).

12) J. D. Lamb, R. M. Izatt, J. J. Christensen, and D. J. Eatough, "Coordination Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum Press, New York (1979), Chapter 3.

13) R. D. Shannon, *Acta Cryst., Sect. A*, **32**, 751 (1976); N. B. Mikheev, *Radiochimica Acta.*, **32**, 69 (1983).

14) R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, *J. Amer. Chem. Soc.*, **98**, 7620 (1976).

15) C. F. Miranda, R. Muxart, J. Vernois, and G. Zuppiroli, *Radiochimica. Acta*, **19**, 153 (1973); **20**, 11 (1973).