RADIOPOLAROGRAPHY OF Am, Cm, Bk, Cf, Es AND Fm[¶]

K. Samhoun[*] and F. David[†]

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

INTRODUCTION

The aim of this work is to determine the standard E°III - 0 or E°II - 0 electrode potentials for some transplutonium elements in aqueous solution, and to obtain information on the electrochemical properties of 5f elements. On the other hand, the standard electrode potentials are essential for the determination of some thermodynamic functions such as the enthalpy of formation $\Delta H_f(M^{3+})$. This function, combined with others, is used for correlation between 4f and 5f series, allowing predictions of some unknown data on the heavy actinides elements [F.David, 1].

In this work the radiopolarography technique is applied to study Am, Cm, Bk, Cf, Es and Fm. This technique permits a radiochemical determination of the half-wave E 1/2 potential, by studying the electrochemical behavior of the aquo-ion at the dropping mercury cathode.

Principle

When a radioisotope is reduced to the metallic state at the dropping mercury cathode, the activity A collected in a given number of drops, where a given potential -E is imposed, is proportional to the number of reduced ions. This activity is thus proportional to the corresponding polarographic current. The radiopolarogram obtained by plotting A against -E should parallel the known current-potential curves.

For a controlled diffusion radiopolarographic wave the limiting activity A_d measured in the mercury collected each θ seconds could be calculated from the transformed Ilkovic equation:

$$A_d = 0.627 \times m^{2/3} \times t^{1/6} \times D^{1/2} \times \theta \times A_s$$

where A_s is the activity of 1 ml of the solution; m, t and D have their usual meanings and are expressed in $g \times s^{-1}$, sec and $cm^2 \times s^{-1}$ respectively. This equation shows [J.Heyrovsky, 2] that the limiting activity is proportional to the pressure of mercury, or to the square-root of the height of the mercury head:

$$A_d = k \times \sqrt{h}$$

The observation of this linear variation is essential and convenient to control an experimental diffusion wave. On the other hand, provided that A_d is measured with reasonably accuracy (~ 5%), the diffusion coefficient D could be calculated from the measured limiting activity of the radiopolarogram. The number n of electrons exchanged in the electrode process does not figure any more in the transformed Ilkovic equation. However, this number could be obtained from the slope (0.059/αn) of the logarithmic analysis of the wave:

$$E = E\ 1/2 - \frac{0.059}{\alpha n} \log \frac{A}{A_d - A} .$$

In the case of a reversible electrode process ($\alpha = 1$), this slope should be 60 mV if $n = 1$, 30 mV if $n = 2$, and 20 mV if $n = 3$. It is understood that this slope is less steep if $\alpha < 1$ (quasireversible or irreversible electrode process).

[¶] This work performed under the auspices of the U. S. Energy Research and Development Administration.

EXPERIMENTAL

Automatic Radiopolarograph

The main technical difficulty in radiopolarography is the collection of the amalgamated mercury drops without either contamination when crossing the relatively high level of radioactive solution or an eventual loss of activity by disamalgamation when drops are stored for a few minutes in the insulating phase (carbon tetrachloride in our technique), and then collected.

In order to avoid these phenomena and to assure a good reproducibility of radiopolarograms, a systematic study of the method was engaged by P. Rogelet, G. Thiriet and F. David [3], and an automatic radiopolarograph has been realized. This apparatus was tested [P.Rogelet, 4] with ^{54}Mn. The contamination of the mercury was controlled from the background of the radiopolarogram which was less than 3% the height of the wave. The diffusion law $A_d = k \times \sqrt{h}$ was observed and the limiting activity was quantitatively checked: the diffusion coefficient $D_{Mn^{2+}}$ calculated from the Ilkovic equation was in good agreement with the known data.

Supporting Electrolyte and pH

All radiopolarograms described were obtained from an original solution of 5 M lithium chloride (supporting electrolyte) and 0.2 M HCl. This solution was diluted to have suitable pH while keeping $[LiCl]/[HCl] \simeq 25$. This ratio, whatever the pH is, had to be conserved in order to avoid the migration current of the hydrogen discharge. Under this condition, radiopolarograms were obtained at potentials more negative than -1.50 V/SCE up to -2.10 V.

Radioisotopes

The radioisotopes investigated are listed in Table 1 in column 1. Half-life and α energy of each one is reported in columns 2 and 3. The average of the amounts used in one experiment are expressed in nanograms and by concentration (mM/mℓ) and are listed in columns 4 and 5 respectively.

TABLE 1. Radioisotopic investigation in this work.

M	T 1/2	Energy MeV	Nanogram	mM/mℓ
^{241}Am	433 y	5.49	15	2×10^{-8}
^{244}Cm	18.11 y	5.81	0.4	7×10^{-10}
^{249}Bk	314 d	β^-	0.27	3×10^{-10}
^{249}Cf	360 y	5.81	10	1.2×10^{-8}
^{254}Es	276 d	6.44	0.025	3×10^{-11}
^{255}Fm	20.1 h	7.02	3×10^{-15}	3×10^{-15}

The 20.1 hour ^{255}Fm was available in a mixture of ^{249}Cf - $^{254-255}$Es. ^{255}Fm was ~ 0.01% (by activity) in this mixture. The elution with 0.4 M α-hydroxyisobutyrate at pH 3.5 from Dowex cationic resin was applied to the "milking" of ^{255}Fm [G.Higgins, 5].

In order to insure a determination on these elements with equal precision, a mixture of 2 or 3 actinides is generally used in one experiment. An element for comparison is also added to the mixture; in our conditions the γ emitter ^{54}Mn was added. In the mean time the radiopolarogram of Mn is used to check the normal functioning of the radiopolarogram.

DATA

Radiopolarograms of Am, Cm, Bk, Cf and Fm were obtained with a good reproducibility (see Fig. 1). The standard deviation of the experimental points is less than 3%. The accuracy on the measured half-wave E 1/2 potentials is less than 3 mV. On the other hand the diffusion law was verified for each element by observing the linear variations of A_d with $\sqrt{h}$ (see Fig. 2). The experimental points obtained for Fm in Figs. 1 and 2 are less accurate because of the small amount of ^{255}Fm available. The activities measured were not sufficiently high to neglect the statistical counting fluctuations.

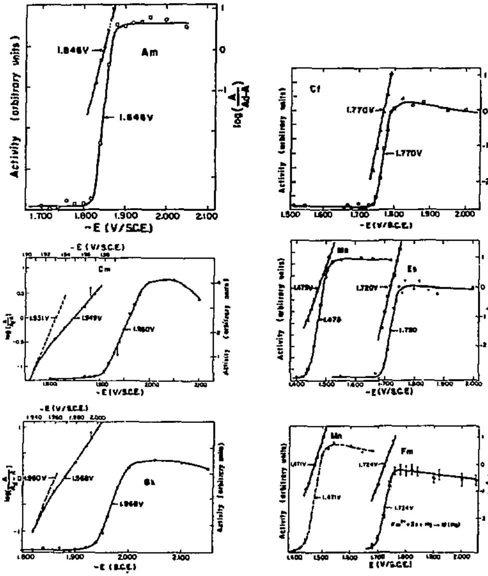

Fig. 1. Radiopolarograms of: Am, pH 2.0, LiCl 0.26M; Cm, pH 2.5, LiCl 0.10M; Bk, pH 2.5, LiCl 0.10M; Cf, pH 2.5, LiCl 0.10M; Es, pH 2.5, LiCl 0.10M; Fm, pH 2.5, LiCl 0.10M.

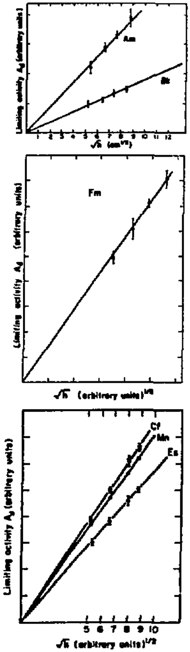

Fig. 2. Linear variation of the limiting activity of Am, Bk, Fm, Cf, and Es with the square-root of the height of the mercury head.

Mechanism of the Electrode Process

Am, Cm, Bk, Cf, Es

The slope of the curve $-E = f(\log A/A_d - A)$ was measured for each investigated element. Most of the measured slopes for Am, Cf and Es lie within 25 ± 5 mV, and this is consistent with the following electrochemical process

$$M^{3+} + 3e + Hg \rightarrow M(Hg) \ .$$

The transfer coefficient α is estimated to vary between 0.7 and 1. This is characteristic of a "quasireversible" electrode process. Supposing the same electrochemical process for Bk and Cm, less reversible waves were obtained ($0.4 < \alpha < .6$). It is known that for quasireversible processes the logarithmic analysis of the radiopolarogram is not linear [J.Heyrovsky, 6]. In fact, the curve starts with a slope of 20 mV corresponding to a reversible process and ends with a less steep slope. Consequently the measured half-wave potential is a few mV more negative than the half-wave $(E\ 1/2)_{rev}$ potential corresponding to the reversible process. However, $(E\ 1/2)_{rev}$ could be determined by extrapolating the straight line starting from the bottom of the wave with a slope of 20 mV (see Fig. 3).

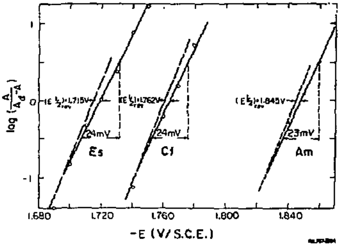

Fig. 3. Examples on Es, Cf, and Am showing the determination of $(E\frac{1}{2})_{MeV}$ by plotting the straight lines that have a slope of 20 mV (dashed lines).

Diffusion Coefficients

When the limiting activity of a radiopolarogram is measured with good accuracy, three conditions are required to undertake a determination of the diffusion coefficient D from the Ilkovic equation:

1) A_d should be the limiting activity of a controlled diffusion wave, and for that the diffusion law $A_d = k \times \sqrt{h}$ should be verified.

2) No contamination should interfere in the activity measured in the collected mercury. This could be checked from the background of the radiopolarogram.

3) No loss in the activity of the collected mercury should affect the A_d measurement. An eventual loss should be quantitatively estimated with a reasonable accuracy.

Conditions 1) and 2) were precisely attained, as shown in Fig. 1 and 2. However, a loss in the activity during the accumulation of the mercury is possible. This loss was simply estimated by varying the accumulation time θ of the mercury in a fixed potential at the plateau. The activity per minute of accumulation A/θ was plotted against θ and the extrapolation of this experimental curve to $\theta = 0$ gives the real A_d that has to be fitted in the Ilkovic equation. The diffusion coefficients determined for Am, Cm, Cf, and Es from preliminary assays were about $6 \times 10^{-6}\ cm^2 \times s^{-1}$, and this is in agreement with the average value of D for trivalent ions of lanthanides elements.

Fm

As with the preceding elements, the slope was found to be 29 ± 4 mV. The number of electrons exchanged in this case, according to α, could be two or three. However, the fact that the standard electrode E°III - II of Fm is less negative than -1.15 V/NHE [N.Mikheev, 7] suggests the Fm ion to be in the divalent state at the dropping mercury cathode since the radiopolarographic wave is detected at -1.47 V/NHE. The following mechanism is therefore suggested:

$$Fm^{2+} + 2e + Hg \rightarrow Fm(Hg)$$

In order to confirm this mechanism, study of the radiopolarogram behavior in the presence of a complex agent (lithium citrate) was undertaken. The calculated shift on the half-wave potential of Fm should be about 60 mV in the presence of 0.005 M lithium citrate, when the electrode process is $Fm^{2+} \rightarrow Fm^0$. This shift in the same conditions should be more than 200 mV if the electrode process is $Fm^{3+} \rightarrow Fm^0$. The measured shift confirmed $Fm^{2+} \rightarrow Fm^0$ mechanism.

Half-Wave Potentials and Standard Electrode Potentials

Frequently in polarography pH may affect the half-wave potential determination. Searching for the minimum value of E 1/2 at suitable pH, radiopolarograms of Am, Cm, Bk, Cf and Es were obtained in several pH media (from pH 1.7 to 2.5). From the analysis of half-wave E 1/2 potentials measured for each of these elements, it appears that minimum values for Am, Cf and Es are obtained in pH between 2 and 2.2. However, all measured E 1/2 beyond this range are more negative by only a few mV. As to Bk and Cm, the measured E 1/2 are less accurate because of the irreversibility of the electrode process ($0.3 < \alpha < 0.8$). On the other hand, the number of experiments on Bk and Cm was too low to confirm the reproducibility of these data and to discuss the pH effect. In Table 2, column 3, the retained measured E 1/2 are listed for all investigated elements. In column 2 the corresponding pH is listed, and in columns 4 and 5 the number n of electrons and the transfer coefficient α, both obtained from the measured slope of $-E = f(\log A/A_{\alpha} - A)$. In column 6 the deduced $(E\ 1/2)_{rev}$ are tabulated and will be used for the standard electrode potential determination.

TABLE 2. All electrode potentials E are with reference to the normal hydrogen electrode (NHE).

M	pH	-(E 1/2) (volts)	n	α	$-(E\ 1/2)_{rev}$ (volts)	δE_3 (volts)	δE_2 (volts)	$-E^{\circ}_{III-II}$ (volts)	$-E^{\circ}_{II-0}$ (volts)
^{241}Am	2.0 - 2.2	1.598	3	0.78	1.594(5)	0.46	--	2.06	--
^{244}Cm	1.7 - 2.0	1.66	3	0.40	1.62 (1)	0.445	--	2.07	--
^{249}Bk	2.0 - 2.2	1.64	3	0.45	1.62 (1)	0.50	--	2.12	--
^{249}Cf	2.0 - 2.2	1.503	3	0.90	1.500(5)	0.51	--	2.01	--
^{254}Es	2.0 - 2.2	1.456	3	0.80	1.452(5)	0.53	--	1.98	--
^{255}Fm	2.5	1.474	2	0.90	1.474(6)	--	0.90	1.95	2.37

Since the mechanisms of the electrode process correspond to the reduction of the *divalent or trivalent* ion to the metallic state, the measured half-wave E 1/2 potentials include the energy of amalgamation. δE_3 for trivalent ion or δE_2 for divalent ion, so that:

$$(E\ 1/2)_3 = \delta E_3 + E^{\circ}_{III-0}$$

and

$$(E\ 1/2)_2 = \delta E_2 + E^{\circ}_{II-0}$$

δE_3 of Bk, Cf and Es are estimated by correlating the intra-series variation in δE_3 known for Gd, Tb, Ho and Lu, and δE_3 deduced for Am and Cm from the standard electrode E°III-0 potentials measured by Fuger et al [8,9], and our experimental half-wave E 1/2 potentials. The estimated δE_3 are listed in column 7 of Table 2. δE_2 of Fm is estimated (column 8) by interpolating the variation in known δE_2 of divalent elements Mg, Ca, Sr, Ba, Ra, Eu and Yb with the corresponding radii of the divalent metals. Finally, E°III-0 and E°II-0 are listed in column 9 and 10.

CONCLUSION

The standard electrode potentials determined in this work are affected by the accuracy of determining δE_2 and δE_3, since these energies of amalgamation were estimated by correlation with those of some 4f elements. The accuracy on the measured half-wave potential itself, as is shown in column 6 of Table 2, is 5 mV for all elements, Bk and Cm excepted.

Finally, we note that these standard potentials are in good agreement with those calculated by correlating the variation in P(M) function for 4f and 5f series |see ref. 1|.

ACKNOWLEDGMENTS

The authors would like to express deep gratitude to Professor G. T. Seaborg for his acceptance of this work being undertaken in his laboratory at the Lawrence Berkeley Laboratory and for his support. We are deeply indebted to Dr. N. Edelstein for his suggestions and encouragement. We appreciate the assistance and advice of T. Parsons during this work.

FOOTNOTES AND REFERENCES

*K. Samhoun, on leave from CNRS of Lebanon. Present address: Institut de Physique Nucleaire, Bat. 100 B.P. No. 1, 91406 Orsay, France.

+F. David, Institut de Physique Nucleaire, Bat. 100, B.P. No. 1, 91406 Orsay, France.

1. F. David, K. Samhoun, R. Guillaumont and L. J. Nugent, "Study of Some Thermodynamic Properties of 5f Elements", 4th International Transplutonium Elements Symposium (1975), Baden-Baden, Germany.

2. J. Heyrovsky, J. Kuta, "Principles of Polarography", Academic Press, New York and London (1966), p. 86.

3. P. Rogelet, G. Thiriet, and F. David, Electroanal. Chem. Interf. Electrochem. 61 (1975) 125.

4. P. Rogelet and F. David, Electroanal. Chem. Interf. Electrochem. 61 (1975) 131.

5. G. H. Higgins, Report UCRL-6134, Lawrence Radiation Laboratory, Livermore (1960).

6. J. Heyrovsky, J. Kuta, "Principles of Polarography", Academic Press, New York and London (1966), p. 209.

7. N. B. Mikheev, A. N. Kamenskaia, I. A. Rumer, V. I. Spitzyn, R. A. Diatchkova, and N. A. Rosenkevich, Radiochem. Radioanal. Lett. 9(4),(1972), 247.

8. J. Fuger, J. C. Spirlet and W. Müller, Inorg. Nucl. Chem. 8 (1972) 709.

9. J. Fuger, J. Reul and W. Müller, Inorg. Nucl. Chem. Lett. 11 (1975) 265.