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Polarography of Iron(III)- and Europium(III)-Acetylacetonate Complexes in *N,N*-Dimethylformamide

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The reduction potentials of $Fe(acac)_3$ and $Eu(acac)_3$ in DMF are shifted to more positive potentials by the addition of cations (Li^+ and Mg^{2+}) to the supporting electrolyte of tetraethylammonium perchlorate. Studies of the complexes show that the effect is caused by coordinative relaxation reaction of the $Fe(acac)_3^-$ reduction product in which acetylacetonate ligand becomes transferred to the cation. However, in the case of $Eu(acac)_3^-$, acetylacetonate ligands seemed to be completely stripped off. Cyclic voltammetric data indicate reduction and reoxidation processes of the complexes.

Polarography in non-aqueous solvent is more advantageous for the study of a metal complex than that in aqueous solution, and investigations in non-aqueous solvents have been reported recently. However, the interaction of the supporting electrolyte with either the electrode reactant or product which remains innocuous in aqueous medium, should be taken into consideration in lower dielectric solvents such as in acetonitrile ($\varepsilon=37.5$) and dimethylformamide, DMF ($\varepsilon=36.7$). Schaap[1] developed polarographic theory for ion pairing of metal ion reactant with electrolyte anions. Murray and Hiller[2] studied the interaction of $Fe(acac)_3^-$ reduction product with Li^+ ion in acetonitrile. We are interested in the interaction of the supporting electrolyte with electron transfer products of a neutral complex in non-aqueous solvents and wish to describe cation (Li^+ and Mg^{2+}) effects on the iron(III)- and europium(III)-acetylacetonate complexes, ($Fe(acac)_3$ and $Eu(acac)_3$) in DMF.

Experimental

Solvent and Materials. *N,N*-Dimethylformamide by Wako Junyaku Co. of extra pure reagent grade was used. DMF was shaken with potassium carbonate anhydride and sodium sulfate, left standing for several days and then upper layer of the solution was distilled three times under reduced pressure in a nitrogen atomosphere. Moisture in the distillate was determined by Karl-Fischer titration to be only 0.03%. There were no impurities, which caused a detectable current at negative potentials less than -2.8 V in the polarogram. $Fe(acac)_3$ and $Eu(acac)_3$ were prepared by the ordinary method.[3]

Found: C, 50.90; H, 5.89%. Calcd for $Fe(acac)_3$: C, 51.01; H, 5.99%.

Found: C, 38.07; H, 4.88%. Calcd for $Eu(acac)_3$ H_2O: C, 38.55; H, 4.96%.

Tetraethylammonium perchlorate (abbreviated as TEAP) was prepared through the reaction of tetraethylammonium bromide with perchloric acid, recrystallized in water and dried at 60°C over $Mg(ClO_4)_2$.

Found: C, 41.89; H, 8.71; N, 5.96%. Calcd for $(C_2H_5)_4NClO_4$: C, 41.83; H, 8.77; N, 6.09%.

All other reagents were of extra pure grade.

Apparatus. The electrolysis cell has two diaphragms of sintered glass and consists of three electrodes as shown in Fig. 1. The reference electrode was SCE with a salt bridge devised by Takaoka.[4] DME was used as the working electrode (m=0.833 mg/sec, t=4.50 sec in 0.1M TEAP-DMF medium at -1.7 V *vs.* SCE).

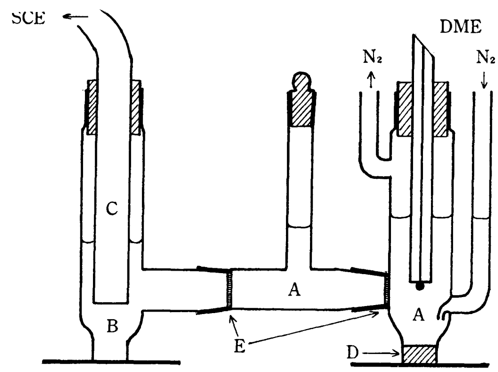

Fig. 1. Electrolysis cell.
A: Sample solution
B: 0.1M TEAP in DMF
C: Agar salt bridge connected with SCE
D: Counter electrode
E: Sintered glass

A Yanagimoto PA 102-type polarograph connected with a liquid resistance compensator P8-PT, was used

1) W. B. Schaap, *J. Amer. Chem. Soc.*, **82**, 1837 (1960).
2) R. W. Murray and L. K. Hiller, Jr., *Anal. Chem.*, **39**, 1221 (1967).
3) J. G. Stites, C. N. McCarthy and L. L. Quill, *J. Amer. Chem. Soc.*, **83**, 4533 (1961); T. Moeller and W. F. Ulrich, *J. Inorg. Nucl. Chem.*, **2**, 164 (1956).
4) K. Takaoka, *Rev. Polarog.* (Kyoto), **14**, 63 (1966).

for recording polarograms. Cyclic voltammograms were recorded by Iwasaki Synchroscope SS-5302 with preamplifier SP-O1H-A.

Triangular potential signals were obtained from a Yokogawa-Hewlett-Packard 3300A Function Generator. A compensator P8-PT was used as a potentiostat. A Pt wire electrode was used for a counter electrode. Current-measuring resistance was 10—30Ω.

Procedure. A sample of 0.1 M TEAP-DMF, containing $Fe(acac)_3$ or $Eu(acac)_3$ (10^{-3} M), was taken into a cell. After dried nitrogen gas was passed through it for 20 min, DME and the agar bridge connected with SCE were inserted in the cell. A polarogram was then recorded. The junction potential was measured by using SCE with a slowly flowing-type aqueous saturated KCl salt bridge. All experiments were carried out at 25.0±0.1°C. Cyclic voltammogram was photographed during the growth of a mercury drop and the value of its maximum current was analysed.

Results

$Fe(acac)_3$ in 0.1M TEAP. The polarogram of 1 mM $Fe(acac)_3$ in 0.1 M TEAP in DMF developed a well-defined wave (Fig. 2). The half-wave potential was −0.58 V *vs.* SCE. The electrode reaction was found to be a reversible (reciprocal slope: 52 mV) one-electron reduction and diffusion-controlled.

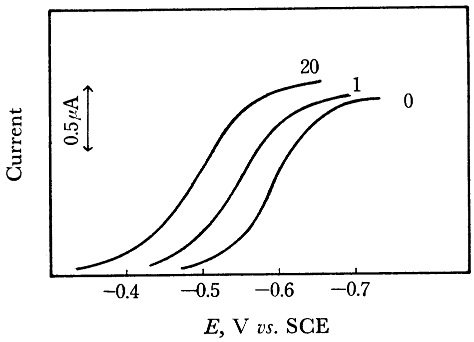

Fig. 2. Polarograms for 1.00 mM $Fe(acac)_3$ in 0.1 M TEAP in DMF. Numbers above curves are mM of $LiClO_4$ added.

$Fe(acac)_3$ in TEAP-$LiClO_4$ Electrolyte Mixtures. As shown in Fig. 2 the reduction wave of 1 mM $Fe(acac)_3$ was shifted to less negative potentials by increasing concentrations of $LiClO_4$ in 0.1 M TEAP medium. In this case, the electrode reaction was diffusion-controlled. As is seen in Table 1, the half-wave potential is shifted to more negative potential by increasing concentrations of $Fe(acac)_3$ with constant concentration of 30 mM $LiClO_4$.

$Fe(acac)_3$ in TEAP-$Mg(ClO_4)_2$ Electrolyte Mixtures. The same results as those for TEAP-$LiClO_4$ electrolyte mixtures were obtained (Table 2).

TABLE 1. POLAROGRAPHIC DATA FOR $Fe(acac)_3$ IN 0.1 M TEAP IN DMF (Effect of $LiClO_4$)

$[Fe(acac)_3]$ mM	$[LiClO_4]$ mM	$-E_{1/2}$ V *vs.* SCE	i_d μA	Slope E *vs.* $\log((i_d-i)/i^2)$
0.5	30	0.46_7	0.93	a
1.0	0	0.58_5	1.17	0.052
	1	0.54_7	1.26	0.056
	2	0.54_4	1.28	0.056
	5	0.52_4	1.15	0.053
	10	0.51_7	1.25	0.054
	20	0.49_2	1.22	0.057
	30	0.48_2	1.41	0.054
3.0	30	0.51_4	4.64	a

a: plot curved

TABLE 2. POLAROGRAPHIC DATA FOR $Fe(acac)_3$ IN 0.1 M TEAP IN DMF (Effect of $Mg(ClO_4)_2$)

$[Fe(acac)_3]$ mM	$[Mg(ClO_4)_2]$ mM	$-E_{1/2}$ V *vs.* SCE	i_d μA	Slope
0.5	20	0.49_4	0.78	
1.0	0	0.58_5	1.27	0.052
	3	0.54_3	1.31	0.044
	10	0.52_7	1.30	0.044
	20	0.51_2	1.21	0.053
	30	0.50_7	1.29	0.046
2.0	20	0.65_7	3.24	

$Eu(acac)_3$ in 0.1M TEAP. A single wave with the half-wave potential of −1.55 V *vs.* SCE, was obtained for 1 mM $Eu(acac)_3$ in 0.1 M TEAP in DMF (Fig. 3). The electrode reaction was diffusion-controlled. Addition of water up to 0.5% has no effect on the half-wave potential and the diffusion current remained. However, addition of water more than 0.5% caused the decrease of the diffusion current.

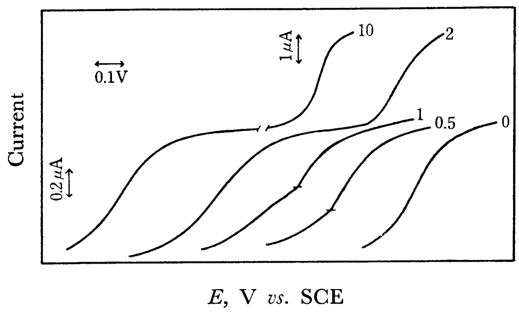

Fig. 3. Polarograms for 1.00 mM $Eu(acac)_3$ in 0.1 M TEAP in DMF. Numbers above curves are mM of $LiClO_4$ added.

$Eu(acac)_3$ in 0.1M TEAP-$LiClO_4$ Electrolyte Mixtures. Differing from the case of $Fe(acac)_3$, the original single wave of the complex split into two waves by addition of $LiClO_4$ and a new wave appeared at less negative potentials than the original. The height of this wave increased with increasing $LiClO_4$ concentrations and the original wave disappeared, whereas the new wave remained and was shifted again to less negative potentials at $[LiClO_4]/[Eu(acac)_3] \geqq 2$ (Fig. 3). The electrode reaction was diffusion-controlled. As shown in Table 3-1, the half-wave potential was shifted to more negative potentials by increasing concentrations of $Eu(acac)_3$ with constant concentration of $LiClO_4$. By addition of $LiClO_4$ at $[LiClO_4]/[Eu(acac)_3] \geqq 2$, a second wave appeared close to the potential of -2.0 V *vs.* SCE. The diffusion current became almost constant at $[LiClO_4]/[Eu(acac)_3] \geqq 10$(Fig. 3 and Table 3-2).

TABLE 3-1. POLAROGRAPHIC DATA FOR $Eu(acac)_3$ IN 0.1 M TEAP IN DMF (Effect of $LiClO_4$)

$[Eu(acac)_3]$ mM	$[LiClO_4]$ mM	$-(E_{1/2})_1$ V *vs.* SCE	i_d μA
0.5	30	1.30_7	0.61
1.0	0.5	——[a), ——[a)	0.25, 1.08
	1	——[a), ——[a)	0.54, 0.78
	2	1.49_5	1.40
	5	1.44_9	1.36
	10	1.41_3	1.26
	20	1.36_8	1.28
	30	1.33_9	1.20
2.0	30	1.35_2	2.80

a) ill defined

TABLE 3-2. POLAROGRAPHIC DATA FOR $Eu(acac)_3$ IN 0.1 M TEAP IN DMF (Effect of $LiClO_4$)

$[Eu(acac)_3]$ mM	$[LiClO_4]$ mM	$-(E_{1/2})_2$ V *vs.* SCE	i_d μA	Slope
1	2	2.08_7	0.85	68
	3	2.08_0	1.70	38
	5	2.06_5	2.27	36
	10	2.05_0	2.61	35
	20	2.04_7	2.65	31
	30	2.03_3	2.70	32

$Eu(acac)_3$ in 0.1 M TEAP-$Mg(ClO_4)_2$ Electrolyte Mixtures. Differing from the case of $LiClO_4$, by addition of $Mg(ClO_4)_2$ to 1 mM $Eu(acac)_3$ in 0.1 M TEAP medium the wave split into three steps and became considerably complicated.

Positive shifts in the half-wave potentials of the reduction waves of $Fe(acac)_3$ and $Eu(acac)_3$ were observed by addition of the cations (Li^+ and Mg^{2+}). Negative shifts in the half-wave potentials of those waves resulted from the increase of both complex concentrations at a constant concentration of the cation.

Assuming that metal complex ML_p is reduced reversibly with n-electron transfer, the electrode reaction is given by

$$ML_p + ne \rightleftharpoons ML_p^{n-} \tag{1}$$

If metal-ligand bond in ML_p^{n-} reduction product is more labile than that in ML_p complex, then ligand dissociation may occur from ML_p^{n-}. The extent of such dissociation is limited by the nature of the cation C^+. According to Murray and Hiller,[2] this particular interaction is a "theft" of ligand(s) from ML_p^{n-} by C^+ (coordinative relaxation), which produces a positive shift of the reduction potential of the reaction (1). In this case it seems that a sequence of the following coordinative relaxation reaction may occur.

$$\left.\begin{array}{l} ML_p^{n-} + C^+ \rightleftharpoons ML_{p-1}^{(n-1)-} + CL \\ \qquad\vdots \\ ML_{p-q+1}^{(n-q+1)-} + C^+ \rightleftharpoons ML_{p-q}^{(n-q)-} + CL \end{array}\right\} \tag{2}$$

Denoting the overall equilibrium constants of the above relaxations as K_1, K_2, $\cdots$, K_q, and solving for $[ML_p^{n-}]$, we obtain from the Nernst equation

$$E = E^0 + \frac{0.059}{n}\log\frac{[ML_p][1+\sum K_j[C^+]^j/[CL]^j]}{[ML_p^{n-}]_{total}} \tag{3}$$

where $[ML_p^{n-}]_{total}$ is the total concentration of all forms of the product complex.

If $n=q=1$ and essentially complete relaxation to ML_{p-1} is assumed, Eq. (3) is reduced to

$$E = E^0 + 0.059\log\frac{K_r K_{CL} K_1}{K_0} + 0.059\log[C^+] + 0.059\log\frac{i_d - i}{i^2} \tag{4}$$

where K_r, K_0 and K_{CL} are the current-concentration proportionality constants for ML_{p-1}, ML_p and CL, respectively. Eq. (4) shows that the half-wave potential $E_{1/2}$ is shifted positively with increase in $[C^+]$ and is shifted negatively with increase in the concentration of the complex (at $i=i_d/2$, the last term of Eq. (4) is reduced to $0.059\log(2/i_d)$). Plots of $E_{1/2}$ for $Fe(acac)_3$ and $Eu(acac)_3$ complexes against log $[Li^+]$ are shown in Fig. 4, where the following dissociation constants were used to calculate the concentration of dissociated lithium ions, $[Li^+]$.

$(K_a)_{LiClO_4} = 65.5$ (calculated by using the data of electric conductivity of Prue and Sherrington)[5]

$(K_a)_{TEAP} = 4.0$ (obtained by Peover and Davies)[6]

In the case of $Fe(acac)_3$ complex, $\Delta(E_{1/2})/\Delta\log[Li^+] = 0.062$. This value coincides with the theoretical value 0.059 for $q=1$. Consequently, the overall electrochemical process should be

$$Fe(acac)_3 + e \rightleftharpoons Fe(acac)_3^- \tag{5}$$

$$Fe(acac)_3^- + Li^+ \rightleftharpoons Fe(acac)_2 + Li(acac) \tag{6}$$

5) J. E. Prue and D. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1967).

6) M. E. Peover, J. D. Davies, *J. Electroanal. Chem.*, **6**, 46, (1963).

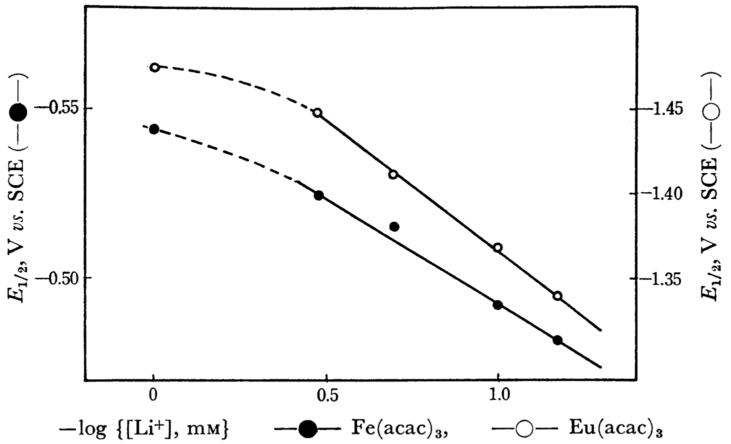

Fig. 4. Plot of $E_{1/2}$ values against log{[Li$^+$]}.

However, in the case of Eu(acac)$_3$ complex we have $\Delta(E_{1/2})/\Delta\log[Li^+]=0.16$. This value is almost equal to the theoretical value of coordinative relaxation reaction of three ligands by Li^+ ions (Eq. (8)). As the half-wave potential of the second wave corresponds to that for the reduction of Eu(II) →Eu(0) in DMF ($(E_{1/2})_2$: −2.0 V *vs.* SCE), it seems that all ligands of the reduction product of Eu(acac)$_3^-$ are completely stripped off by the addition of $LiClO_4$. The electrode reaction is presumed to be quasi-reversible and one-electron transfer, but the wave denotes apparently the value of the slope of an irreversible wave, caused by the succeeding controlled reaction in coordinative relaxation reaction. Thus, the overall electrochemical reaction would be

$$\mathrm{Eu(acac)_3} + \mathrm{e} \rightleftharpoons \mathrm{Eu(acac)_3^-} \quad (7)$$

$$\mathrm{Eu(acac)_3^-} + 3\mathrm{Li^+} \rightleftharpoons \mathrm{Eu^{2+}} + 3\mathrm{Li(acac)} \quad (8)$$

$$\mathrm{Eu^{2+}} + 2\mathrm{e} \rightleftharpoons \mathrm{Eu^0} \quad (9)$$

In a low concentration of $LiClO_4$, a stepwise relaxation reaction of ligand sould occur by the deficiency of Li^+ ions. Though the effect of Mg^{2+} ion on the electrode process of Fe(acac)$_3$ complex is similar to that of Li^+ ion, a quantitative treatment was omitted because of the lack of data for ion association constants.

The cyclic voltammetry for Fe(acac)$_3$ complex was carried out. As shown in Fig. 5, both peaks of reduction and reoxidation were obtained only for Fe(acac)$_3$ complex, the results being ΔE_{peak} equals 60 mV.

An increase in [$LiClO_4$] shifted the cathodic wave

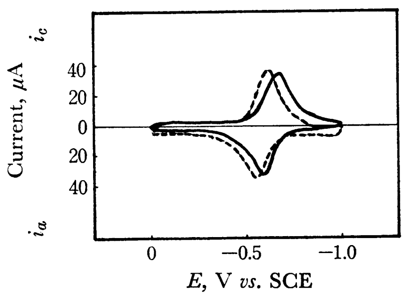

Fig. 5. Cyclic voltammograms for 1.00 mM Fe(acac)$_3$ in 0.1 M TEPA in DME.
Scan rate : 1.01 V/sec
——— 0 mM $LiClO_4$, ------ 5 mM $LiClO_4$

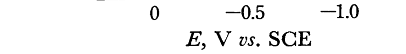

Fig. 6. Cyclic voltammograms for 1.00 mM Fe(acac)$_3$ in 0.1 M TEAP in DMF with 20 mM $LiClO_4$.
Scan rate:
——— 1.01 V/sec, ------ 10.1 V/sec

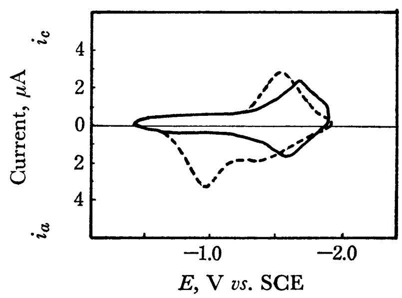

Fig. 7. Cyclic voltammograms for 1.00 mM Eu(acac)$_3$ in 0.1 M TEAP in DMF.
Scan rate : 0.151 V/sec
——— 0 mM $LiClO_4$, ------ 20 mM $LiClO_4$

7) G. Gritzner, V. Gutmann and G. Schöber, *Monatsh. Chem.*, **96**, 1056 (1965).

positively and its reoxidation process appeared. These data indicate Eq. (6) to be reversible under this condition. However, as given in Fig. 6, under fast scan of the applied voltage and high lithium concentration, the coordinative relaxation reaction by Li^+ becomes rate-controlled and prevents complete generation of $Fe(acac)_3^-$ species which will give the anodic wave. It was observed that the anodic wave decreased in this case.

In the cyclic voltammetry for $Eu(acac)_3$ complex, as shown in Fig. 7, ΔE_{peak} was found to be approximately 80 mV.

An increase in $[LiClO_4]$ also shifted the cathodic wave positively as the wave in the D.C. polarography. However, the value of ΔE_{peak} became very large and seemed to be an irreversible electrode process controlled by the following coordinative relaxation reaction. This fact supports the results obtained by D.C. polarography of the complex.

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