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The Polarographic Behavior of Bis(acetylacetonato)nickel(II) and Bis(hexafluoroacetylacetonato)nickel(II) in Dimethyl Sulfoxide

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The d.c. polarographic reduction of $Ni(acac)_2$ and $Ni(hfac)_2$ was studied in detail in dimethyl sulfoxide. Two kinds of tetraalkylammonium perchlorates and sodium perchlorate were used as supporting electrolytes. $Ni(acac)_2$ gave three waves in all the supporting electrolytes, while $Ni(hfac)_2$ gave two waves in the presence of tetraalkylammonium perchlorate. These waves were explained on the basis of the polarographic properties, molecular weights, and conductivities. The electrode reaction mechanism of $Ni(acac)_2$ can be expressed by:

$$\begin{tikzcd}
\mathrm{Ni(acac)^+} \arrow[r, shift left] \arrow[d, "2e"] & \mathrm{Ni(acac)_2} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "2e"] & \mathrm{[Ni(acac)_2]_2} \arrow[l, shift left] \arrow[r, shift left] \arrow[d, "4e"] & \cdots\cdots \arrow[l, shift left] \arrow[r, shift left] & \mathrm{[Ni(acac)_2]_p} \arrow[l, shift left] \arrow[d, "(2p)e"] \\
\text{1st wave} & \text{2nd wave} & \underbrace{\hspace{3cm}}_{\text{3rd wave}} & &
\end{tikzcd}$$

where the second wave includes a kinetic current. The first wave of $Ni(hfac)_2$ is due to the reduction of $Ni(hfac)^+$ and $Ni(hfac)_2$ themselves; the second wave corresponds to that of free hexafluoroacetylacetonate.

The nonaqueous electrochemistry of bis(β-diketonato)nickel(II) complexes has been reported by several investigators. Murray and Hiller[1] gave preliminary data on bis(acetylacetonato)nickel(II) in acetonitrile from the standpoint of the supporting-electrolyte effect. The number of electrons participating in the electrode processes, *n*, is particularly interesting, for certain complexes may partly polymerize even in coordinating solvents. According to the results of Dessy *et al.*,[2] the *n* value of bis(acetylacetonato)nickel(II) was equal to unity in 1,2-dimethoxyethane. Bond *et al.*[3] presumed a one-electron transfer step for the reduction wave observed in the d.c. polarography of bis(dipivaloylmethanato)nickel(II) in acetone. Recently, Gritzner *et al.*[4] reported on the polarographic and voltammetric behavior of various acetylacetonato and hexafluoroacetylacetonato complexes in acetonitrile. They determined the *n* value of two for bis(acetylacetonato)nickel(II) coulometrically.

The present paper will report the results of a detailed investigation of the d.c. polarographic reduction of bis(acetylacetonato)nickel(II), $Ni(acac)_2$, and bis(hexafluoroacetylacetonato)nickel(II), $Ni(hfac)_2$, in dimethyl sulfoxide (DMSO).

Experimental

Reagents. Merck analytical reagent-grade DMSO was used without further purification. The content of water was determined with a gas chromatograph. The DMSO contained 0.02—0.06% water.

Sodium perchlorate was dried *in vacuo* for 24 h prior to use. The Nakarai Chemicals tetramethylammonium perchlorate (TMAP) and tetrabutylammonium perchlorate (TBAP) purified for polarography were dried *in vacuo* for 12 h. The Kishida Chemicals nickel(II) perchlorate hexahydrate was brought to a constant weight in a desiccator over magnesium perchlorate.[5] Hexafluoroacetylacetone (Hhfac) from Nakarai Chemicals, Ltd., was used without further purification.

Two extra-pure-reagents, $Ni(acac)_2$ and $Ni(hfac)_2$, were obtained from Nakarai Chemicals, Ltd. These compounds were identified as $Ni(acac)_2 \cdot 2H_2O$ and $Ni(hfac)_2 \cdot H_2O$ by elemental analysis.

Potassium acetylacetonate was prepared by the following procedure. Into a solution of 6 cm^3 of acetylacetone (Hacac) in 30 cm^3 of methanol–water (1:1), 2 mol dm^{-3} potassium hydroxide in methanol–water (1:1) was dropwise added until a pH value of 9.0 was reached. The precipitated salt was filtered off and dried *in vacuo*. The analysis of potassium acetylacetonate gave the following results. Found: C, 38.20; H, 5.76%. Calcd for $C_5H_9O_3K$: C, 38.44; H, 5.81%.

Reagent-grade chemicals were used unless otherwise stated.

Apparatus and Procedures. The current-potential curves were obtained with a Yanagimoto Polarograph PA-101 and a Yanagimoto Potentiostat PT-P8.

The polarographic measurements were made at 25.0 ± 0.2 °C except for the experiments of the temperature effect. An H-type electrolysis cell was used for the measurements. An aqueous SCE-KCl was isolated from the test solution by the use of a compartment with a glass filter (G-4). All the solutions were deaerated with nitrogen gas. Two dropping-mercury electrodes were used. The A electrode had an m value of 1.06_2 mg s^{-1} and a drop time, t_d, of 6.18 s in a deaerated 0.05 mol dm^{-3} TMAP–DMSO solution at -1.0 V and at a height of the mercury reservoir, h, of 47 cm. The B electrode had an m value of 1.24_8 mg s^{-1} and a t_d value of 4.95 s in a deaerated 0.1 mol dm^{-3} TBAP–DMSO solution at -1.0 V and h=45 cm.

In the following sections, i and $\bar{i}$ denote the maximum current and the average current respectively.

The *n* values were determined on a Yanagimoto Controlled Potential Electrolyzer and a Nikko Keisoku Digital Coulometer NDCM-2.

The conductivities were measured with a Yanagimoto Conductivity Outfit MY-8. The absorption spectra in the visible and ultraviolet regions were obtained with a Spectronic 88-UV Shimadzu-Bausch & Lomb Spectrophotometer at room temperature. The molecular weights were measured in DMSO at 18 °C by cryoscopy, with tris(acetylacetonato)cobalt(III) as the standard material.

Results

Dissolved State of the Complexes in DMSO. Con-

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TABLE 1. MOLECULAR WEIGHTS OF $Ni(acac)_2$ IN DMSO AT 18 °C

m/mmol kg^{-1}	Molecular formula	Calcd	Found	Found/Calcd
2.0	$Ni(acac)_2 \cdot DMSO$	335.05	430±50	1.3
3.3	$[Ni(acac)_2 \cdot DMSO]_2$	670.10	650±50	1.0
6.6	$[Ni(acac)_2 \cdot DMSO]_3$	1005.2	1200±200	1.2

TABLE 2. POLAROGRAPHIC DATA OF THE REDUCTION OF $Ni(acac)_2$ AND $Ni(hfac)_2$ IN DMSO

Complex	Supporting electrolyte	$E_{1/2}$/V *vs.* SCE$^{a)}$	Slope/mV$^{b)}$	$\bar{i}_j/\bar{i}_t$$^{c)}$
$Ni(acac)_2$	0.05 mol dm^{-3} $NaClO_4$	−1.12	63	0.15
		−1.33	48	0.15
		−1.64	115	0.70
	0.05 mol dm^{-3} TMAP	−1.22	48	0.21
		−1.44	80	0.41
		−1.83	124	0.38
	0.05 mol dm^{-3} TBAP	−1.25	77	0.49
		−1.46	62	
		−2.00	217	0.51
$Ni(hfac)_2$	0.05 mol dm^{-3} $NaClO_4$	*ca.* −1.0 (Max.)		
	0.05 mol dm^{-3} TMAP	*ca.* −1.0 (Max.)		
		— (Max.)		
	0.05 mol dm^{-3} TBAP	*ca.* −1.0 (Max.)		
		−2.58		
	0.1 mol dm^{-3} TBAP	−1.04	52	
		−2.52	96	

a) The half-wave potentials for $Ni(acac)_2$ were obtained at the concentration of 2 mmol dm^{-3}. b) The slopes of the log-plot analyses for $Ni(acac)_2$ were obtained at the concentration of 5 mmol dm^{-3}. c) The $\bar{i}_j/\bar{i}_t$ ratios for $Ni(acac)_2$ were obtained at the concentration of 1 mmol dm^{-3}. The meanings of $\bar{i}_j$ and $\bar{i}_t$ are shown in Fig. 1.

ductivity measurements at 25 °C indicate that $Ni(acac)_2$ is little dissociated into ionically-conducting species, while $Ni(hfac)_2$ is dissociated into the 1:1 electrolyte.

The apparent molecular weights of $Ni(acac)_2$ in DMSO are given in Table 1. This complex was polymeric in the concentration range studied here. On the other hand, the cryoscopic results of $Ni(hfac)_2$ were in conflict with the conductance data, showing the molecular weight of undissociated $Ni(hfac)_2 \cdot 2DMSO$. The cryoscopy of $Ni(hfac)_2$ appears to afford no true information; however, the reason for this is not known.

The spectoscopic data indicate that the complexes are of a hexa-coordinate octahedral structure,[6,7] though the cryoscopic data of $Ni(acac)_2$ seem to suggest a penta-coordinate structure.

Reduction of the Complexes in DMSO. Some typical polarograms and polarographic data of the complexes in DMSO are shown in Fig. 1 and Table 2. Sodium perchlorate, tetramethylammonium perchlorate, and tetrabutylammonium perchlorate were used as supporting electrolytes. $Ni(acac)_2$ gave three reduction waves, of which the one at the most negative potential was very irreversible, regardless of the kind of supporting electrolyte used. When TBAP was used as a supporting electrolyte, the first two waves at less negative potentials overlapped; hence, the polarogram of 1 mmol dm^{-3} $Ni(acac)_2$ appeared just like two steps.

$Ni(hfac)_2$ gave two reduction waves in the presence of tetraalkylammonium perchlorate as the supporting electrolyte. When sodium perchlorate was used as the supporting electrolyte, the second wave, at a far negative potential, overlapped with the sodium-ion reduction. Interestingly, the first wave of $Ni(hfac)_2$ resembled the wave of nickel(II) perchlorate in its polarographic properties. When 0.1 mol dm^{-3} TBAP was chosen as the supporting electrolyte, the maximum at the first wave disappeared and the second wave was a well-defined one (see Fig. 2 and Table 2). The ratio of their heights was equal to 1:4 for the first and the second wave under the controlled drop time. The polarogram of $Ni(hfac)_2$ is compared with that of hexafluoroacetylacetone in Fig. 2. Hexafluoroacetylacetone gave two waves: the first wave is considered to be a hydrogen reduction of the enol form, and the second wave, to be an enolate reduction.[8] The second

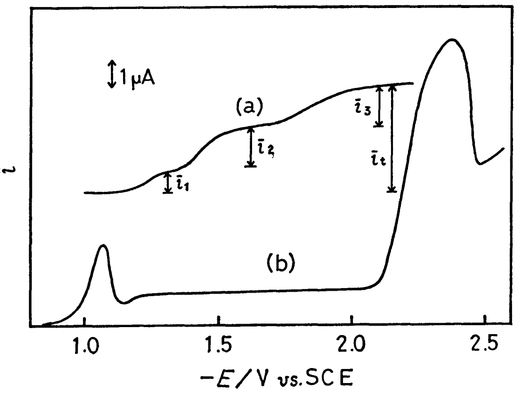


Fig. 1. Polarograms of (a) 3.0 mmol dm^{-3} $Ni(acac)_2$ and (b) 0.5 mmol dm^{-3} $Ni(hfac)_2$ in 0.05 mol dm^{-3} TMAP-DMSO. With the DME (A).

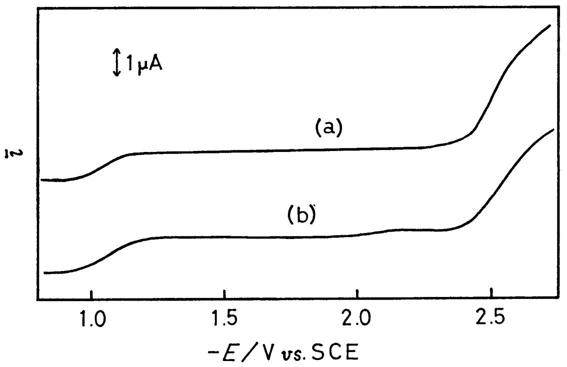


Fig. 2. Polarograms of (a) 0.5 mmol dm^{-3} Ni(hfac)$_2$ and (b) *ca.* 0.9 mmol dm^{-3} Hhfac in 0.1 mol dm^{-3} TBAP-DMSO. With the DME (B).

wave of Ni(hfac)$_2$ appeared at the same potential as that of hexafluoroacetylacetone.

The first limiting currents (i) of Ni(acac)$_2$ and Ni(hfac)$_2$ were proportional to $h^{1/2}$ in all the supporting electrolytes used. The measurements of the current-time (i-t) curve were made in the potential region giving each limiting current of three waves of Ni(acac)$_2$ in 0.05 mol dm^{-3} solution of each supporting electrolyte during the life of a mercury drop. In a TMAP or TBAP solution, the slopes of the plots for log i *vs.* log t were larger than those in a sodium-perchlorate solution. This finding is related to the supporting-electrolyte effect on the total limiting current, i_t, of Ni(acac)$_2$ to be described later.

All the waves of Ni(acac)$_2$ were not due to the reduction of the ligand, because acetylacetonate itself gave no wave in the potential range observed. The polarographic waves of 1 mmol dm^{-3} Ni(acac)$_2$ were affected by the addition of a small amount of acetylacetonate. The first wave disappeared after the addition of 0.5 mmol dm^{-3} acetylacetonate. The i_t decreased as the concentration of acetylacetonate increased. The dependence of the i_t on the acetylacetonate concentration suggested the formation of electroinactive Ni(acac)$_3^-$. When 1 mmol dm^{-3} nickel(II) perchlorate was made to react with 1 mmol dm^{-3} potassium acetylacetonate, the polarogram had two waves in the presence of each supporting electrolyte of 0.05 mol dm^{-3}: one was the wave of the nickel ion, and the other was that of Ni(acac)$^+$, which appeared at *ca.* -1.2 V in the TMAP solution. Accordingly, the first wave of Ni(acac)$_2$ corresponds to the reduction of Ni(acac)$^+$.

In Fig. 3 the limiting currents of Ni(acac)$_2$ and Ni(hfac)$_2$ are plotted against their concentrations. In contrast to the linearity of plots for the first wave of Ni(hfac)$_2$, that for the i_t of Ni(acac)$_2$ gave curves. The supporting-electrolyte effect on the i_t was observed after the correction for the drop time; that is, the i_t was low in the presence of tetraalkylammonium perchlorate. This may be explained by the double-layer effect on the reduction rate,[9] judging from the i-t curve data mentioned above.

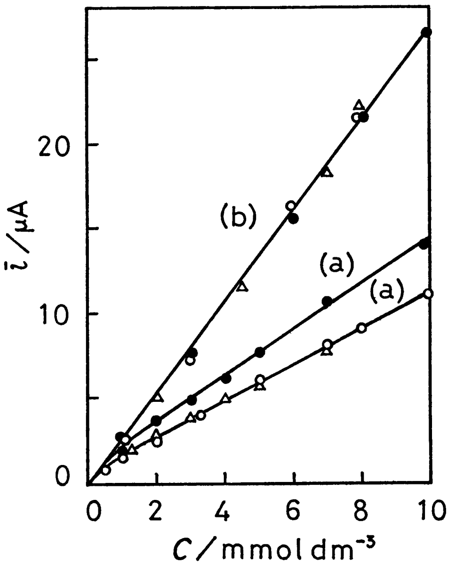


Fig. 3. Dependence of (a) the total limiting current of Ni(acac)$_2$ and (b) the first limiting current of Ni(hfac)$_2$ on the concentration of each complex in DMSO. Supporting electrolyte: (○) TMAP, (△) TBAP and (●) sodium perchlorate. Each in 0.05 mol dm^{-3}. With the DME (A).

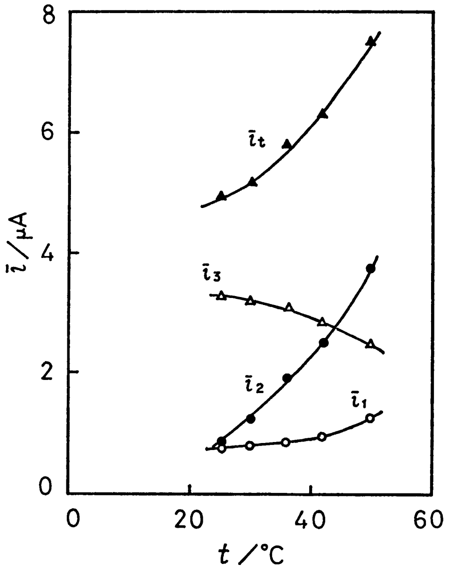


Fig. 4. Effect of temperature on the limiting currents of 3.0 mmol dm^{-3} Ni(acac)$_2$ in 0.05 mol dm^{-3} sodium perchlorate-DMSO. For i_j (j=1—3), see Fig. 1. With the DME (A).

The plots of the i_j and i_t values of Ni(acac)$_2$ *vs.* the temperature gave the curves shown in Fig. 4. With an increase in the temperature, the $(i_1+i_2)/i_t$ ratio increased and the i_3/i_t ratio decreased: in a 3 mmol dm^{-3} Ni(acac)$_2$–0.05 mol dm^{-3} sodium perchlorate solution, these ratios were 0.34 and 0.66 respectively at 25 °C, while they were 0.67 and 0.33 respectively at 50 °C.

The controlled potential coulometric experiments were carried out at -1.70 V for 0.5 mmol dm^{-3} Ni(hfac)$_2$ and at -2.30 V for 0.5 mmol dm^{-3} Ni(acac)$_2$

in the presence of 0.05 mol dm^{-3} TMAP. These coulomertic data gave 2.0 and 1.9 respectively as the apparent numbers of electrons per nickel atom.

The effect of water on the polarographic waves was examined below 10%. When 0.05 mol dm^{-3} TMAP was used as the supporting electrolyte, there was no variation in $Ni(acac)_2$ after the addition of 10% water. When 0.05 mol dm^{-3} sodium perchlorate was used as the supporting electrolyte, though, the i_2/i_t ratio increased and the i_3/i_t ratio decreased as the content of water increased in the range of 2—10%. The effect on $Ni(hfac)_2$ was checked in the presence of 0.1 mol dm^{-3} TBAP, for these conditions gave two well-defined waves. The addition of 5% water led to more irreversible waves. Further, the first and second waves shifted a little to more negative and less negative potentials respectively.

Discussion

Many chemists have been interested in the structures of β-diketone chelate compounds in various nonaqueous solvents. They have mainly investigated them by means of NMR, ESR, electronic-spectra, molecular-weight measurements, *etc.* It is well known that the anhydrous $Ni(acac)_2$ exists as a trimer with an octahedral coordination about the nickel(II) in crystals and also in noncoordinating solvents.$^{7)}$ Yoshida *et al.*$^{10)}$ have proposed a dimer, $(NiL_2 \cdot H_2O)_2$, for each prevalent form of bis(1,5-dialkyl-2,4-pentanedionato)-nickel(II) monohydrate complexes in noncoordinating solvents, where L represents a β-diketonato anion. Using the rotating-disk-electrode method, Ritzler and Gross$^{11)}$ have proposed a dimer for the prevalent form of about 1 mmol dm^{-3} $Co(acac)_2$ in propylene carbonate. The present work affords useful information on the molecular association of $Ni(acac)_2$ in DMSO with a great donor-number.

$Ni(acac)_2$ and $Ni(hfac)_2$ in DMSO are involved in the following chemical equilibria:

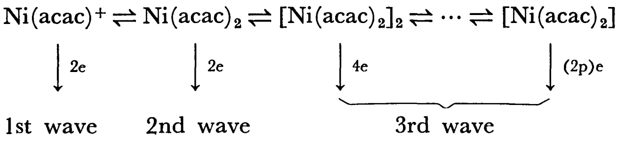
$$[Ni(acac)_2]_p \rightleftharpoons \cdots \rightleftharpoons [Ni(acac)_2]_2 \rightleftharpoons Ni(acac)_2 \rightleftharpoons Ni(acac)^+ + acac^- \quad (1)$$

$$Ni(hfac)_2 \rightleftharpoons Ni(hfac)^+ + hfac^-, \quad (2)$$

on the basis of the conductance and the molecular-weight data. The degree of the dissociation of $Ni(acac)_2$ to the ions is negligibly small in the absence of a supporting electrolyte, as has been mentioned in the preceeding section.

The polarographic behavior of $Ni(hfac)_2$ is very similar to that of the only species which is diffusion-controlled, judging from the linearity of the limiting current on $h^{1/2}$ and the complex concentration. Further, the apparent diffusion-current constant of the first wave was approximately equal to that of the wave of the nickel(II) ion, which follows a two-electron reduction process to the metal.$^{12)}$ The n value, determined coulometrically, is consistent with this finding. Both $Ni(hfac)^+$ and $Ni(hfac)_2$ participate, presumably as electroactive species, in the first wave. A comparison between the polarograms of (a) and (b) in Fig. 2 indicates that the second wave of $Ni(hfac)_2$ comes from free hexafluoroacetylacetonate. The complex gave a nickel anodic stripping peak (spike pattern) at −0.1 V in cyclic voltammetry at a platinum electrode; such a peak was also found in nickel perchlorate. This suggests that the ligand is liberated after the reduction of the complex itself at the first wave. Thus, the second wave does not mean the reduction of the only free ligand from the dissociation reaction in the bulk of the solution.

The first wave of $Ni(acac)_2$ does not include the kinetic current due to the preceding chemical reaction, judging from the dependence of the limiting current on $h^{1/2}$. The first wave is due to the reduction of $Ni(acac)^+$, judging from the disappearance of the wave after the addition of acetylacetonate and from the agreement between the half-wave potential of $Ni(acac)^+$ and that of the first wave of $Ni(acac)_2$. However, the i_1/i_t ratio is too large to explain the conductance data. It is, therefore, reasonable to consider the dissociation of $Ni(acac)_2$ to $Ni(acac)^+$ in the bulk of the solution in the presence of a supporting electrolyte. The second and third waves come from the reduction of the monomeric $Ni(acac)_2$ and the polymeric species respectively, judging from the dependence of the i_2 and i_3 on the temperature and from that of the i_t on the complex concentration. Consequently, the electrode reaction mechanism can be expressed by:



(3)

where the $Ni(acac)_2 \rightleftharpoons Ni(acac)^+ + acac^-$ reaction is so slow that it practically does not proceed in the vicinity of the electrode surface during electrolysis. The i_2/i_3 ratio was dependent on the drop time; the temperature effect on the i_2 can not be interpreted merely by the chemical equilibria shift in the bulk of the solution, so that the second wave includes the kinetic current due to the preceding reaction, the polymeric species $\rightleftharpoons$ $Ni(acac)_2$, in Eq. 3.

The dissolved state is apparently dependent on the nature of the ligands of the complexes. Such behavior of other bis(β-diketonato)nickel(II) complexes will be discussed in the following paper.

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