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The Electrolyte Effect on the Chemical Equilibria of Bis(β-diketonato)nickel(II) Complexes in Dimethyl Sulfoxide

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The electrolyte effect on the homogeneous chemical equilibria of Ni(bfac)$_2$, Ni(ftac)$_2$, and Ni(ttac)$_2$ in dimethyl sulfoxide has been studied by means of polarographic and ultraviolet spectral measurements, where bfac$^-$, ftac$^-$, and ttac$^-$ represent the enolate anions of benzoyltrifluoroacetone, 2-furoyltrifluoroacetone, and 2-thenoyltrifluoroacetone respectively. The chemical equilibria of these complexes in 0.05 mol dm^{-3} TBAP solutions found previously:

$$\mathrm{Ni(bi\text{-}L)_2} \rightleftharpoons \mathrm{Ni(bi\text{-}L)(uni\text{-}L)} \rightleftharpoons \mathrm{Ni(bi\text{-}L)^+ + L^-} \rightleftharpoons \mathrm{Ni(uni\text{-}L)^+ + L^-}$$

shifted more to the right in the presence of one of the electrolytes (NaClO$_4$, KClO$_4$, RbClO$_4$, CsClO$_4$, TMAP, or TEAP) at the same concentrations as TBAP; bi- and uni- mean that the ligands coordinate to the metal as bidentate and unidentate respectively. Under the conditions of [NiL$_2$]=1 mmol dm^{-3} and [MClO$_4$]= 0.05 mol dm^{-3}, the molar fractions of the species of the Ni(bi-L)$_2$ type decreased with an increase in the inverse of the cationic radii. Such a tendency was explained mainly in terms of the interaction between the π-electron system of Ni(bi-L)$_2$ and those cations. For the same metal perchlorates, except NaClO$_4$, the stability of Ni(bi-L)$_2$ decreased in the order of: bfac$^-$>ftac$^-$>ttac$^-$.

The homogeneous chemical equilibria and the electrode reactions of ten bis(β-diketonato)nickel(II) complexes in dimethyl sulfoxide (DMSO) were investigated by means of conductivity and electronic spectral measurements, cryoscopy, polarography, and cyclic voltammetry.[1–5] It was found polarographically that five complexes, viz., Ni(bzac)$_2$,[1,6] Ni(dbm)$_2$,[2,6] Ni(bfac)$_2$,[2] Ni(ftac)$_2$,[2] and Ni(ttac)$_2$,[2] were involved in the following homogeneous chemical equilibria:

$$\mathrm{Ni(bi\text{-}L)_2} \rightleftharpoons \mathrm{Ni(bi\text{-}L)(uni\text{-}L)} \rightleftharpoons \mathrm{Ni(bi\text{-}L)^+ + L^-} \rightleftharpoons \mathrm{Ni(uni\text{-}L)^+ + L^-} \quad (1)$$

where bi- and uni- mean that the ligands coordinate to the metal as bidentate and unidentate respectively.

The present paper deals with the electrolyte effect on the above chemical equilibria of Ni(bfac)$_2$, Ni(ftac)$_2$, and Ni(ttac)$_2$ in DMSO polarographically and spectrophotometrically, where bfac$^-$, ftac$^-$, and ttac$^-$ indicate the enolate anions of benzoyltrifluoroacetone, 2-furoyltrifluoroacetone, and 2-thenoyltrifluoroacetone respectively.

Experimental

Reagents. The alkali metal perchlorates,[1] tetrabutylammoium β-diketonates (n-Bu$_4$NL),[2] and DMSO[7] were the same as those described previously. Tetramethylammonium perchlorate (TMAP) and tetraethylammonium perchlorate (TEAP), purified for polarographic measurements, were obtained from Nakarai Chemicals, Ltd. These salts were recrystallized once from ethanol, followed by drying in vacuo at 60 to 70 °C for a minimum of 10 h. Tetrabutylammonium perchlorate (TBAP) was prepared in the usual way.[8]

Apparatus, etc. The apparatus was the same as that described in a previous paper.[7] The scan rate of polarographic measurements was 2 mV s^{-1}. Two dropping-mercury electrodes were used. The A electrode had an m value of 0.890 mg s^{-1} and a drop time, t_d, of 6.60 s at −1.0 V vs. SCE when measured in an air-free 0.05 mol dm^{-3} TBAP–DMSO solution at a height of 50 cm in the mercury reservoir. The B electrode had an m value of 1.055 mg s^{-1} and a t_d value of 5.48 s at −1.0 V when measured under the above conditions.

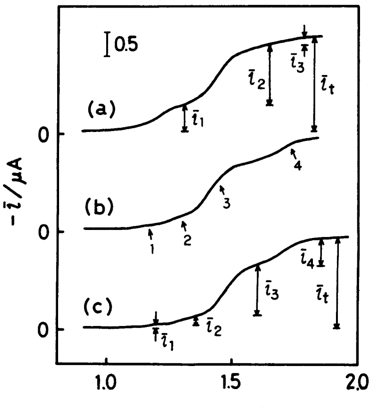

Fig. 1. d.c. Polarograms of 1 mmol dm^{-3} Ni(bfac)$_2$ in DMSO.
Supporting electrolyte; (a): NaClO$_4$, (b): RbClO$_4$, (c): TMAP. Each in 0.05 mol dm^{-3}. t_d=1.5 s. With the DME (A).

The current-potential curves and ultraviolet spectra were obtained at 25.0±0.2 and 25.0±0.5 °C respectively, except in the temperature-effect experiments.

Results

Polarography. The polarographic behavior of Ni(bfac)$_2$, Ni(ftac)$_2$, and Ni(ttac)$_2$ was studied in DMSO containing 0.05 mol dm^{-3} TBAP as a supporting electrolyte.[2] In Fig. 1, three typical polarograms of Ni(bfac)$_2$ in other supporting-electrolyte solutions are shown in the potential range less negative than

Table 1. d.c. Polarographic Data of the Reduction of $Ni(bfac)_2$, $Ni(ftac)_2$, and $Ni(ttac)_2$ in DMSO

Complex	Supporting electrolyte[1]	($E_{1/2}$ vs. SCE)/V	Slope/mV	$\bar{i}_j/\bar{i}_t$[2]
$Ni(bfac)_2$	$NaClO_4$	−1.20[3]	39	0.26
		−1.40	70	0.68
		−1.66		0.06
	$KClO_4$	−1.08		0.03
		−1.20		0.11
		ca. −1.4 (Max.)		0.70
		ca. −1.6		0.16
$Ni(ftac)_2$	$NaClO_4$	−1.16[3]	45	0.32
		−1.36	75	0.63
		ca. −1.6		0.05
	$KClO_4$	ca. −1.1		0.86
		ca. −1.2		
		ca. −1.3 (Max.)		
		ca. −1.6		0.14
$Ni(ttac)_2$	$NaClO_4$	−1.12[3]		0.33
		−1.38	74	0.62
		−1.64		0.05
	$KClO_4$	ca. −1.1		0.15
		−1.19		
		ca. −1.35 (Max.)		0.74
		ca. −1.65		0.11

1) Each in 0.05 mol dm^{-3}. 2) The $\bar{i}_j/\bar{i}_t$ ratios were obtained at a concentration of 1 mmol dm^{-3} under a controlled drop time, where j=1—4. The meanings of $\bar{i}_j$ and $\bar{i}_t$ are shown in Fig. 1. 3) The first wave split into two peaks in differential-pulse polarography.

−2.0 V.[9] In this potential range, $Ni(bfac)_2$, $Ni(ftac)_2$, and $Ni(ttac)_2$ each gave four reduction waves in DMSO containing an electrolyte—$KClO_4$, $RbClO_4$, $CsClO_4$, TMAP, TEAP, or TBAP—at a concentration of 0.05—0.1 mol dm^{-3}. When $NaClO_4$ was used as the supporting electrolyte, these complexes each gave three d.c. polarographic waves, of which the first wave at less negative potential split into two peaks differential-pulse (DP) polarographically.[10] The d.c. polarographic data assembled in Table 1 are those for the complexes obtained in the presence of either $NaClO_4$ or $KClO_4$ at a concentration of 0.05 mol dm^{-3}.

Because of partial overlapping, the polarographic properties of the following waves could not be examined in detail: (a) the second and the third waves of $Ni(bfac)_2$ in a TEAP solution and of $Ni(ftac)_2$ in $KClO_4$, $RbClO_4$, $CsClO_4$, and TEAP solutions; (b) the first and the second waves of $Ni(ttac)_2$ in $KClO_4$, $RbClO_4$, and TEAP solutions. The temperature effect on these DP polarograms, however, was closely similar to that observed previously.[2]

In other cases except in $NaClO_4$ solutions, most of the polarographic and cyclic voltammetric properties were the same as those in 0.05 mol dm^{-3} TBAP solutions;[2] the $\bar{i}_j/\bar{i}_t$ values only were dependent on the cations of the supporting electrolytes used (the meanings of $\bar{i}_j$ and $\bar{i}_t$ are shown in Fig. 1). The half-wave potentials ($E_{1/2}$) of the four waves shifted to more negative potentials with a decrease in t_d. When either $KClO_4$, $RbClO_4$, $CsClO_4$, TMAP, or TEAP is chosen as the supporting electrolyte, therefore, it is reasonable to presume the same electrode reaction as that proposed previously.[2] That is to say, the four waves for the complexes are due to the irreversible two-electron reduction of different species with the Ni(II) involved in the homogeneous chemical equilibria (1) but for which the rate of the reestablishment of the equilibria is slow:[11,12] the first, the second, the third, and the fourth waves come from the reduction of Ni(uni-L)$^+$, Ni(bi-L)$^+$, Ni(bi-L)(uni-L), and Ni(bi-L)$_2$ respectively.

In $NaClO_4$ solutions, the first limiting currents ($\bar{i}_1$) were diffusion-controlled for all the complexes. The plots of $\bar{i}_1$ against the mole ratio (L/Ni) indicated that the respective first waves were due to the reduction of the corresponding mono-complexes. Furthermore, the polarographic properties of the second and the third waves in $NaClO_4$ solutions were similar to those of the third and the fourth waves respectively in the other supporting-electrolyte solutions. Thus, the polarographic behavior of the complexes in $NaClO_4$ solutions can be explained by the following electrode reaction:

$$\begin{tikzcd}
\mathrm{NiL}^+ \arrow[r, rightleftharpoons, "\text{slow}"] \arrow[d, "2e"] & \mathrm{Ni(bi\text{-}L)(uni\text{-}L)} \arrow[r, rightleftharpoons, "\text{slow}"] \arrow[d, "2e"] & \mathrm{Ni(bi\text{-}L)_2} \arrow[d, "2e"] \\
\text{1st wave} & \text{2nd wave} & \text{3rd wave}
\end{tikzcd}$$

On the basis of the splitting of the d.c. polarographic first waves into DP polarographic peaks mentioned above, it seems likely that the respective first waves result from the reduction of the two mono-complexes.

Assuming that the diffusion coefficients for the different species in the solution are equal, the polarographic current ratios, the $\bar{i}_j/\bar{i}_t$ values, represent their molar fractions for the total complex concentration

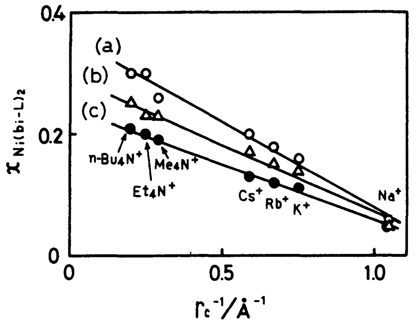

Fig. 2. Plots of the molar fraction of Ni(bi-L)$_2$ vs. the inverse of the cationic radii of supporting electrolytes.
Concn of supporting electrolyte: 0.05 mol dm^{-3}. Complex; (a): Ni(bfac)$_2$, (b): Ni(ftac)$_2$, and (c): Ni(ttac)$_2$ of 1 mmol dm^{-3}, respectively.

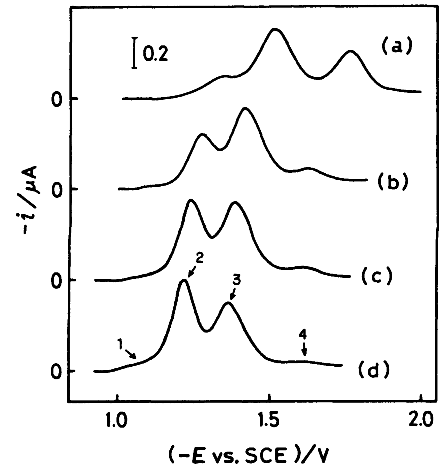

Fig. 3. Effect of sodium ion on DP polarogram of 0.5 mmol dm^{-3} Ni(ftac)$_2$ in DMSO.
Supporting electrolyte; (a): 0.1 mol dm^{-3} TBAP, (b): 0.02 mol dm^{-3} NaClO$_4$+0.08 mol dm^{-3} TBAP, (c): 0.05 mol dm^{-3} NaClO$_4$+0.05 mol dm^{-3} TBAP, (d): 0.1 mol dm^{-3} NaClO$_4$. Modulation amplitude: 50 mV, pulse interval: 1.0 s. With the DME (B).

(see Table 1). The degree of the dissociation of Ni(bi-L)$_2$ increased with a decrease in the crystallographic (unsolvated) radii of the cations of the supporting electrolytes; linear relationships were obtained between the molar fractions of species of the Ni(bi-L)$_2$ type, the $\bar{i}_4/\bar{i}_t$ values, and the inverse of the cationic radii ($1/r_c$), as is depicted in Fig. 2. For the same metal perchlorates, except NaClO$_4$, the stability of Ni(bi-L)$_2$ decreased in the order of: bfac$^-$>ftac$^-$>ttac$^-$. On the other hand, no difference in their stabilities could be detected in NaClO$_4$ solutions. As can be seen from the DP polarograms in Fig. 3, the sodium ion significantly influenced the chemical equilibria (1) (see also the $\bar{i}_j/\bar{i}_t$ values in Table 1). The first peak at the least negative potential in Curve (a) was detected only at a high sensitivity, because the complex concentration measured was low. It appears that the shift of the peak potentials (E_p) to less negative potentials with an increase in the sodium-ion concentration is attributed to the interaction between the reduction products and the sodium ion, e.g., the formation of ion pairs.[13] In addition, the slope of the regression line is considered as the measure of the sensitivity of the stability of Ni(bi-L)$_2$ to the effect of electrolyte cations for a given complex. From this point of view, the stability of Ni(bi-L)$_2$ was subject to the cationic effect in the order of: bfac$^-$>ftac$^-$>ttac$^-$.

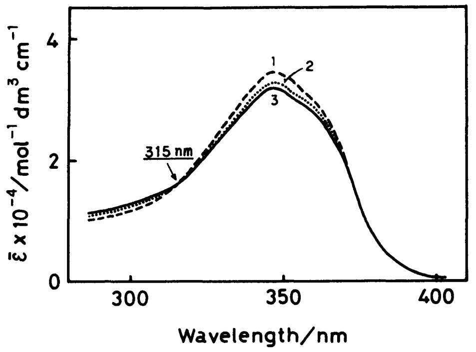

Fig. 4. UV spectra of Ni(ttac)$_2$ at different concentrations in DMSO.
Concn (mol dm^{-3}); (1): 4.0×10^{-6}—1.0×10^{-5}, (2): 1.0×10^{-4}, (3): 7.0×10^{-4}.

Ultraviolet Spectra. In Fig. 4, the electronic spectra of Ni(ttac)$_2$ in the near-ultraviolet region are shown at different concentrations. In this region, similar spectra were obtained for all the complexes. There were isosbestic points at 298, 308, and 315 nm respectively for Ni(bfac)$_2$, Ni(ftac)$_2$, and Ni(ttac)$_2$, though their spectra did not change with time. In the vicinity of the absorption maxima, the apparent molar absorption coefficients ($\bar{\varepsilon}$)[14] increased with a decrease in the concentration of the complexes. Such a tendency corresponds to the dissociation of the complexes, compared with that of some bis(β-diketonato)nickel(II)[4] and -cobalt(II)[7,15] complexes in the same solvent.

The electronic spectra of the complexes varied slightly in the presence of any one of the electrolytes except NaClO$_4$, while they varied considerably upon the addition of NaClO$_4$. The effects of the sodium ion on the electronic spectra of Ni(bfac)$_2$ and Ni(ttac)$_2$ are illustrated in Figs. 5 and 6 respectively, where the total concentration of the electrolyte is adjusted to 0.1 mol dm^{-3} with TBAP. The addition of the sodium ion at different concentrations to a certain complex solution gave two isosbestic points, of which the one at the shorter wavelength was in agreement with that described above. The isosbestic points for Ni(bfac)$_2$, Ni(ftac)$_2$, and Ni(ttac)$_2$ at longer wavelengths were 347, 352, and 358 nm respectively. They were values near to the isosbestic points observed in the corresponding n-Bu$_4$NL/NaClO$_4$ media—that is, 342, 353, and 358 nm for L$^-$=bfac$^-$, ftac$^-$, and ttac$^-$ respectively.

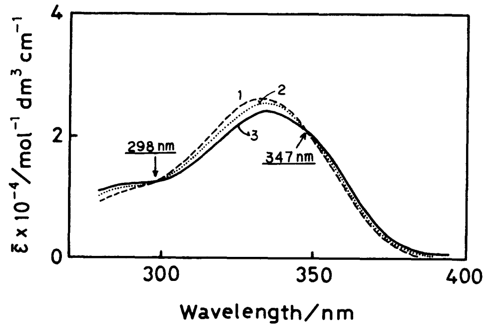

Fig. 5. Effect of sodium ion on the UV spectrum of 0.5 mmol dm^{-3} Ni(bfac)$_2$ in DMSO.
Coexisting electrolyte; (1): 0.1 mol dm^{-3} NaClO$_4$, (2): 0.02 mol dm^{-3} NaClO$_4$+0.08 mol dm^{-3} TBAP, (3): 0.1 mol dm^{-3} TBAP.

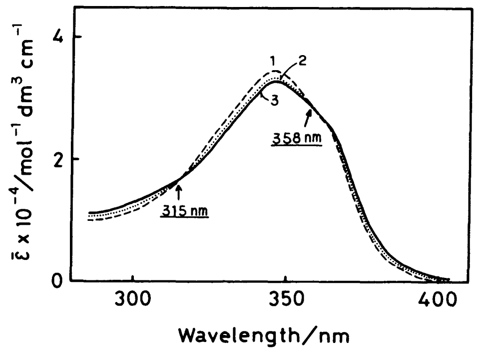

Fig. 6. Effect of sodium ion on the UV spectrum of 0.5 mmol dm^{-3} Ni(ttac)$_2$ in DMSO.
Coexisting electrolyte; (1): 0.1 mol dm^{-3} NaClO$_4$, (2): 0.02 mol dm^{-3} NaClO$_4$+0.08 mol dm^{-3} TBAP, (3): 0.1 mol dm^{-3} TBAP.

Discussion

It was described in a previous paper$^{2)}$ that the dissociation of Ni(bfac)$_2$, Ni(ftac)$_2$, and Ni(ttac)$_2$ in DMSO was enhanced by the presence of TBAP as the supporting electrolyte for polarographic measurements. From the linear relationships given in Fig. 2, it may be concluded that the chemical equilibria (1) in 0.05 mol dm^{-3} TBAP solutions found previously$^{2)}$ shift more to the right in the presence of one of the electrolytes (NaClO$_4$, KClO$_4$, RbClO$_4$, CsClO$_4$, TMAP, or TEAP) at the same concentrations as TBAP and that the sodium ion is the most effective among the cations used here.

The cationic effect on the chemical equilibria (1) is first considered from the standpoint of the lowering of the activity of the DMSO as a result of the solvation of the electrolyte cations. This effect can be estimated conveniently on the basis of the chemical equilibria (2):

$$\begin{aligned}&\text{Ni(bi-L)}_2\cdot(\text{DMSO})_m\\&\rightleftharpoons \text{Ni(bi-L)(uni-L)}\cdot(\text{DMSO})_{m+1}\\&\rightleftharpoons \text{Ni(bi-L)}^+\cdot(\text{DMSO})_{m+2} + \text{L}^-\cdot(\text{DMSO})_n\\&\rightleftharpoons \text{Ni(uni-L)}^+\cdot(\text{DMSO})_{m+3} + \text{L}^-\cdot(\text{DMSO})_n \qquad (2)\end{aligned}$$

Since the solvation of the Ni(II) species on the right hand requires more DMSO molecules, the above equilibria will shift to the left when the addition of a large amount of smaller cations lowers the activity of DMSO; this is contrary to the observed trend.

The isosbestic points at shorter wavelengths (shown in Figs. 4—6) are interpreted as being caused by one of the chemical equilibria (1), and those at longer wavelengths (shown in Figs. 5 and 6), by the interaction of the sodium ion with L$^-$ or a free carbonyl oxygen of the unidentate ligand of Ni(bi-L)(uni-L). Such ion-pair or complex formation should shift the chemical equilibria (1) to the right; however, it seems unlikely to be responsible for the promotion of the dissociation of the Ni(II) complexes in the case of the other cations, especially tetraalkylammonium ions.

Kalinowski and Galazka$^{16)}$ found that bis(acetylacetonato)copper(II) was involved in complicated equilibria in the presence of the lithium ion in various organic solvents. It was suggested spectrophotometrically that the lithium ion might interact in the unsolvated form. Furthermore, it was stated that the interaction of the lithium ion with the π-electron system of acetylacetonato groups in cyclic form was the more probable of the two possibilities. It is plausible that the linear relationships shown in Fig. 2 are also caused by such an interaction, that is, the interaction between the π-electron system of Ni(bi-L)$_2$ and the cations, though no definite statement can be made at the moment concerning the degree of solvation for the interacting cations. A smaller ion generates in its vicinity a more powerful electrostatic field than a large ion of the same charge. The above interaction seems to be the reason for the complication of the quantitative treatment of the chemical equilibria (1). The stability of Ni(bi-L)$_2$ observed, i.e., bfac$^-$> ftac$^-$>ttac$^-$, did not coincide in order with that to be expected from the aromaticity of the substituents,$^{17)}$ the pK_a values of the ligands,$^{18)}$ and the carbonyl ^{13}C NMR chemical shifts of the ligands in DMSO,$^{19)}$ i.e., bfac$^-$>ttac$^-$>ftac$^-$. As has been suggested from the order of susceptibility of the stability of Ni(bi-L)$_2$ to the cationic effect, i.e., bfac$^-$>ftac$^-$>ttac$^-$, it is necessary to take into account the competitive interaction of the cations and the DMSO molecules with Ni(bi-L)$_2$.

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