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# A Polarographic Study of Bis(benzoylacetonato)nickel(II) in Dimethyl Sulfoxide

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(Received April 10, 1981)

The chemical equilibria of bis(benzoylacetonato)nickel(II) in dimethyl sulfoxide solutions were investigated, mainly by means of d.c. polarography. In 0.05—0.1 mol dm$^{-3}$ $NaClO_4$, TMAP, and TBAP solutions, the following chemical equilibria were found: $Ni(bi\text{-}bzac)_2 \rightleftarrows Ni(bi\text{-}bzac)(uni\text{-}bzac) \rightleftarrows Ni(bi\text{-}bzac)^+ \rightleftarrows Ni(uni\text{-}bzac)^+$ where bi- and uni- are the abbreviations of bidentate and unidentate respectively. The species of $Ni(bi\text{-}bzac)_2$ and Ni(bi-bzac)(uni-bzac) comprised 35% and 57% respectively of the total complex of 1 mmol dm$^{-3}$ in a TMAP or TBAP solution, while they accounted for 15% and 77% respectively in a $NaClO_4$ solution. Such a difference in the equilibrium distribution was explained on the basis of the interaction between $\pi$ electrons of the ligand and cations of the supporting electrolytes. The tris-complex was formed by the addition of excess benzoylacetonate to the complex solution.

In a previous paper,[1] the d.c. polarographic reduction of bis(acetylacetonato)nickel(II) and bis(hexafluoroacetylacetonato)nickel(II) was studied in dimethyl sulfoxide as a solvent. The study led to the conclusion that the dissolved state of bis($\beta$-diketonato)nickel(II) complexes is dependent on the nature of their ligands; therefore, a systematic study of the complexes with various ligands was required.

In the present paper, a d.c. polarographic study of bis(benzoylacetonato)nickel(II) will provide useful information about the chemical equilibria of the complex in the same solvent. To judge from the conductance and the cryoscopic data, the complex existed predominantly in the monomeric $Ni(bzac)_2 \cdot 2DMSO$ form. However, three or four kinds of species were polarographically observed in the presence of such supporting electrolytes as alkali-metal perchlorates and tetraalkylammonium perchlorates. The coexisting sodium ion significantly influenced the chemical equilibria of bis(benzoylacetonato)nickel(II). The dissolved state of bis($\beta$-diketonato)nickel(II) complexes in nonaqueous solvents thus far reported, except in a few papers,[1,4,26] was confined to that in noncoordinating solvents.[3,18–20] Choplin-Gast and Hugel[20] determined the equilibrium constant of $Ni_3(bzac)_6 \rightleftarrows 3Ni(bzac)_2$ in dichloromethane by the spectroscopic method: $\log K = -4.7$ at 25 °C.

## Experimental

*Reagents.* The dimethyl sulfoxide (DMSO), nickel(II) perchlorate hexahydrate, tetramethylammonium perchlorate (TMAP), and tetrabutylammonium perchlorate (TBAP) were the same as described in the previous paper.[1] The TBAP was recrystallized from ethanol when necessary. The sodium perchlorate and potassium perchlorate were dried *in vacuo* at 60 to 70 °C for a minimum of 24 h prior to use. The rubidium perchlorate and caesium perchlorate of a 99.9% purity were used.

Bis(benzoylacetonato)nickel(II) monohydrate was prepared by the following procedure. Into 20 cm$^3$ of an aqueous solution of 2 mmol of nickel(II) acetate ($Ni(CH_3COO)_2 \cdot (H_2O)_4$), a solution of 4 mmol of benzoylacetone (Hbzac) in *ca.* 20 cm$^3$ of ethanol was added, followed by the addition of *ca.* 10 cm$^3$ of an aqueous solution containing 7 mmol of sodium acetate ($CH_3COONa \cdot (H_2O)_3$). The mixed solution was then kept for *ca.* 30 min at 50 °C. The product thus precipitated was recrystallized twice from methanol and then dried *in vacuo* at room temperature. Found: C, 59.87; H, 5.05%. Calcd for $C_{20}H_{20}O_5Ni$: C, 60.19; H, 5.05%.

Tetrabutylammonium benzoylacetonate ($Bu_4N(bzac)$) was prepared according to Buchta and Evans.[2] The salt was stored in the dark under nitrogen. Found: C, 76.73; H, 11.19; N, 3.52%. Calcd for $C_{26}H_{45}O_2N$: C, 77.36; H, 11.23; N, 3.47%.

Reagent-grade chemicals were used unless otherwise stated.

*Apparatus.* The current-potential curves were obtained with a Yanagimoto Voltammetric Analyzer P-1000 and a Watanabe X-Y Recorder WX-4404. The electrolysis cell and other apparatus have been reported previously.[1] Two dropping-mercury electrodes were used. The A electrode had an $m$ value of $0.89_0$ mg s$^{-1}$ and a drop time, $t_d$, of 6.60 s in a deaerated 0.05 mol dm$^{-3}$ TBAP–DMSO solution at $-1.0$ V *vs.* SCE at a height of the mercury reservoir, h, of 50 cm. The B electrode had an $m$ value of $1.06_2$ mg s$^{-1}$ and a $t_d$ value of 6.18 s in a deaerated 0.05 mol dm$^{-3}$ TMAP–DMSO solution at $-1.0$ V and $h = 47$ cm.

In the following sections, the word "current" denotes the mean current.

*Procedures.* Nickel(II) perchlorate was made to react with tetrabutylammonium benzoylacetonate in deaerated solutions containing 0.05 mol dm$^{-3}$ of the supporting electrolyte at room temperature in the dark overnight (Fig. 3). The reaction of the complex with tetrabutylammonium benzoylacetonate was also carried out under the same conditions (Fig. 2). Unless otherwise stated, the polarographic measurements were made at 25.0±0.2 °C. All the test solutions were deaerated for 30 min with nitrogen gas in a thermostat before measurements.

## Results and Discussion

*Conductance, Molecular Weight,* etc. The molar conductivity of 2 mmol dm$^{-3}$ of bis(benzoylacetonato)nickel(II) was 0.4 $\Omega^{-1}$ cm$^2$ mol$^{-1}$ at 25 °C. According to the conductance results of DePalma and Arnett,[10] the molar conductivity at an infinite dilution ($\Lambda_0$) and the dissociation constant of tetrabutylammonium dibenzoylmethanate were $30.8 \pm 1.6$ $\Omega^{-1}$ cm$^2$ mol$^{-1}$ and $(62 \pm 24) \times 10^{-4}$ mol dm$^{-3}$ respectively in dimethyl sul-

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Table 1. Polarographic data for the reduction of $Ni(bzac)_2$, Hbzac, and $Bu_4N(bzac)$ in DMSO

| Compound | Supporting electrolyte | ($E_{1/2}$ *vs.* SCE)/V | Slope/mV | $\bar{i}_j/(\bar{i}_t)_B$[a] |
|---|---|---|---|---|
| $Ni(bzac)_2$ | 0.05 mol $dm^{-3}$ $NaClO_4$ | −1.12<br>−1.30 | | 0.08 |
| | | −1.63 | 115 | 0.77 |
| | 0.05 mol $dm^{-3}$ TMAP | −1.21 | 45 | 0.03 |
| | | −1.38 | | 0.05 |
| | | −1.63 | 110 | 0.57 |
| | | −2.16 | 63 | 0.35 |
| | 0.05 mol $dm^{-3}$ TBAP | −1.24<br>−1.36 | | 0.08 |
| | | *ca.* −1.7 (Max.) | | 0.57 |
| | | −2.24 | 86 | 0.35 |
| | | −2.68 | | |
| Hbzac | 0.05 mol $dm^{-3}$ TBAP | −1.54 | 70 | |
| | | −2.44 | 63 | |
| | | −2.70 | | |
| $Bu_4N(bzac)$ | 0.05 mol $dm^{-3}$ TBAP | −2.65 | | |

a) The $\bar{i}_j/(\bar{i}_t)_B$ ratios for $Ni(bzac)_2$ were obtained at the concentration of 1 mmol $dm^{-3}$ under the controlled drop time of 2.0 s, where the $(\bar{i}_t)_B$ represents the $\bar{i}_t$ in a TMAP or TBAP solution. The meanings of $\bar{i}_j$ and $\bar{i}_t$ are shown in Fig. 1.

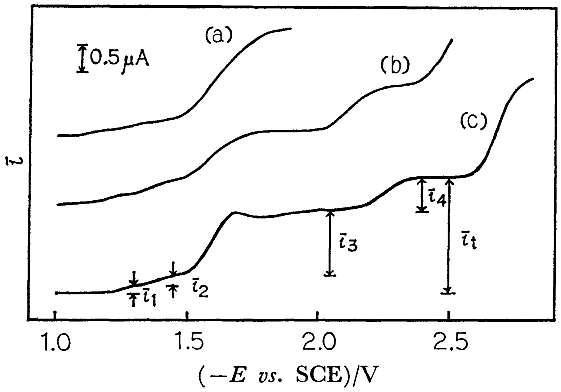


Fig. 1. Polarograms of 1 mmol $dm^{-3}$ $Ni(bzac)_2$ in DMSO solutions. Supporting electrolyte: (a) $NaClO_4$, (b) TMAP, (c) TBAP. Each in 0.05 mol $dm^{-3}$. With the DME (A).

foxide at 25 °C. The investigators of the conductance of quaternary ammonium halides in dimethyl sulfoxide have reported that these salts are almost entirely dissociated[15,16] and that the $\Lambda_0$ values are 32—43 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ at 25 °C.[15] In our preliminary experiments, the $\Lambda_0$ value of bis(hexafluoroacetylacetonato)nickel(II) was 38 $\Omega^{-1}$ $cm^2$ $mol^{-1}$ at 25 °C: This complex was considerably dossociated into the 1:1 electrolyte, but the $\Lambda$ *vs.* $C^{1/2}$ plot did not follow quantitatively the Onsager relation,[17] where $\Lambda$ and $C$ denote the molar conductivity and the concentration respectively. It therefore seems likely that the degree of dissociation of 2 mmol $dm^{-3}$ of bis(benzoylacetonato)nickel(II) is less than 2%. The cryoscopic data of the complex agreed with the molecular weight of $Ni(bzac)_2 \cdot 2DMSO$. Thus, the complex probably exists in the predominant form of the monomeric bis-complex in the absence of electrolytes. The spectroscopic data indicate that the complex has a hexacoordinate octahedral structure.[3,4]

*Polarographic Behavior.* Some typical polarograms of the complex are shown in Fig. 1. The polarographic data of the complex, benzoylacetone, and tetrabutylammonium benzoylacetonate are summarized in Table 1. The complex gave three waves in the presence of sodium perchlorate as the supporting electrolyte. On the other hand, it gave four waves in a solution of tetramethylammonium perchlorate and five waves in one of tetrabutylammonium perchlorate. These polarograms were not appreciably affected by the change in the concentration of each supporting electrolyte in the range of 0.05—0.1 mol $dm^{-3}$.

The fifth wave at the most negative potential in a TBAP solution corresponds to the reduction of benzoylacetonate, judging from a comparison of the two half-wave potentials (Table 1).

For the complex of 1 mmol $dm^{-3}$, the total limiting current in a $NaClO_4$ solution was 85% of that at −2.30 V in a TMAP solution and of that at −2.45 V in a TBAP solution, under a controlled drop time. The latter currents were approximately equal to that of 1 mmol $dm^{-3}$ of nickel(II) perchlorate. The diffusion coefficient for the solvated nickel(II) ion obtained from the Ilkovič equation was $2.3_3 \times 10^{-6}$ $cm^2$ $s^{-1}$ in all the supporting-electrolyte solutions of 0.05 mol $dm^{-3}$. It is known that the coordinated water of nickel(II) perchlorate hexahydrate is replaced by dimethyl sulfoxide in this solvent.[5] The controlled-potential coulometry at −2.30 V in a TMAP solution gave the number of electrons participating in the electrode processes, $n$, of 2. All the waves, except for the wave at the most negative potential in a TBAP solution, are considered to be due to the reduction of nickel(II).

The first limiting current ($\bar{i}_1$) at the least negative potential was diffusion-controlled: it was proportional to $h^{1/2}$. The $\bar{i}_2/\bar{i}_3$ ratio was dependent on the drop time, indicating that the second wave included a kinetic current; however, all the $\bar{i}_j/\bar{i}_t$ ratios were constant at $t_d \leqslant 2.0$ s, where $j = 1$—4. These results were con-

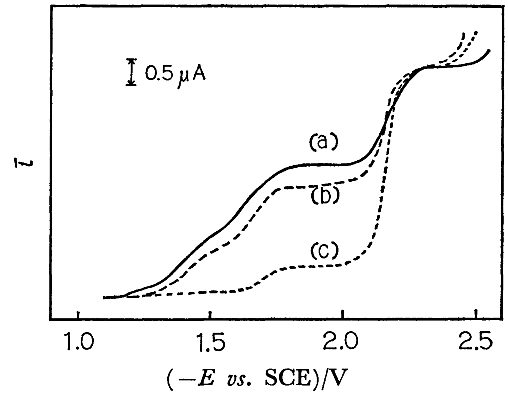


Fig. 2. Effect of addition of free ligand to 2 mmol $dm^{-3}$ $Ni(bzac)_2$ in 0.05 mol $dm^{-3}$ TMAP–DMSO solutions. Concn (mmol $dm^{-3}$) of $Bu_4N(bzac)$ added: (a) 0, (b) 0.5, (c) 3.0. With the DME (A).

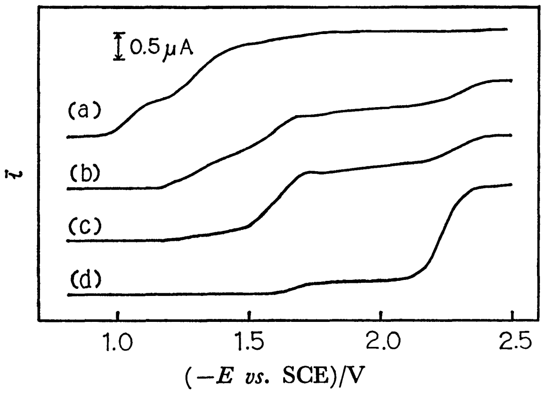


Fig. 3. Polarograms of bzac-complexes of nickel(II) in DMSO solutions containing the ligand in different concentrations. 1 mmol $dm^{-3}$ $Ni(ClO_4)_2$, 0.05 mol $dm^{-3}$ TBAP. Concn (mmol $dm^{-3}$) of $Bu_4N(bzac)$: (a) 0.7, (b) 1.5, (c) 2.0, (d) 5.0. $t_d=2.0$ s. With the DME (A).

firmed in all the supporting-electrolyte solutions. The $i_t$ was proportional to the concentration of the complex in solutions containing TMAP or TBAP. None of the $i_j/i_t$ ratios were affected by the addition of 0.14 mol $dm^{-3}$ of water.

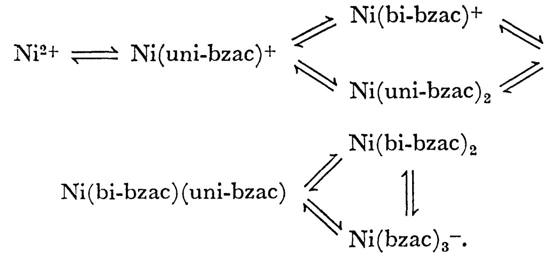
The effect of the addition of free benzoylacetonate to the complex is shown in Fig. 2. The two waves at less negative potentials disappeared successively as the concentration of benzoylacetonate increased, and the low wave at *ca.* −1.7 V and the high wave at −2.16 V finally remained. Evidently, the chemical equilibria exist between the species giving each reduction wave in Fig. 2, judging from the above findings. The limiting current at the least negative potential in Figs. 2(a) and (c) was diffusion-controlled, while that in Fig. 2(b) was partially kinetic-controlled. The constant diffusion-controlled $i_t$ values for the three curves suggest that the diffusion coefficients of all the species are almost equal; the $i_j/i_t$ ratio obtained under the controlled drop time of $t_d \leqslant 2.0$ s in a TMAP or TBAP solution in Fig. 1 represents the molar fraction for each species.

No wave in the least negative potential in Fig. 1 is due to the reduction of the free nickel ion, because it is reduced at *ca.* −1.0 V.[5,6] Figure 3 shows the polarograms measured after the reaction of 1 mmol $dm^{-3}$ of nickel(II) perchlorate with tetrabutylammonium benzoylacetonate in various concentrations. In Fig. 3 (a), the two waves at less negative potentials correspond to the reduction of the main species, which are the nickel ion and the mono-complex. The first two waves in Figs. 1 (a)—(c) appear, judging from a comparison of the half-wave potentials of Curves (a) and (c) in Fig. 3, to be due to the mono-complex reduction. This was confirmed by the plot of $(i_1+i_2)$ *vs.* bzac/Ni mole-ratio, where each $(i_1+i_2)$ value was the diffusion-current obtained under the controlled drop time of 1.0 s. Provided that the first and the second waves, the third wave, and the fourth wave of Curve (c) in Fig. 3 come from the reduction of $Ni(bzac)^+$, $Ni(bzac)_2$, and $Ni(bzac)_3^-$ respectively, the total concentration of the ligand bonded to the nickel ion comes to be higher than that actually contained in the solution; thus, this assumption can not be accepted. Further, the $i_3/i_4$ ratio was constant in Figs. 3(a)—(c). It is, therefore, reasonable to consider that the complex behaves as a mixture of $Ni(bzac)^+$ and $Ni(bzac)_2$ in the supporting-electrolyte solution. Octahedral complexes involving unsymmetrical *β*-diketonates and unidentate ligands of the $M(AB)_2X_2$ type possess five possible geometrical isomers, three with the two X ligands *cis* to one another, and two with the two X ligands *trans* to each other.[7] In view of the known structure of $Ni(acac)_2 \cdot 2H_2O$,[3] the latter isomers may be present for $Ni(bzac)_2 \cdot 2DMSO$. Even if these isomers exist in the solution, however, they are not responsible for the third and the fourth waves in Fig. 1, because bis(dibenzoylmethanato)nickel(II) involving symmetrical *β*-diketonates also gave four polarographic waves due to the reduction of nickel(II). Consequently, the possible assignments for the four waves in a TMAP or TBAP solution are as follows:

$$\begin{tikzcd}
\mathrm{Ni(uni\text{-}bzac)^+} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "2e"] & \mathrm{Ni(bi\text{-}bzac)^+} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "2e"] & {} \\
\text{1st wave} & \text{2nd wave} & \\
\mathrm{Ni(bi\text{-}bzac)(uni\text{-}bzac)} \arrow[r, phantom, "\rightleftharpoons"] \arrow[d, "2e"] & \mathrm{Ni(bi\text{-}bzac)_2} \arrow[d, "2e"] & \\
\text{3rd wave} & \text{4th wave} &
\end{tikzcd}$$

where uni- and bi- are the abbreviations of unidentate and bidentate respectively. The second wave includes the kinetic current due to the preceding reaction, $Ni(bi\text{-}bzac)(uni\text{-}bzac) \rightleftharpoons Ni(bi\text{-}bzac)^+$. As will be shown below in Fig. 5, the temperature effect on the $i_j$ and $i_t$ values is consistent with the above conclusion. In a $NaClO_4$ solution, the existence of $Ni(bi\text{-}bzac)_2$ of 15% is presumed for the total complex of 1 mmol $dm^{-3}$ from a comparison of the $i_t$ in this solution with that in a TMAP or TBAP solution, though the wave of its species can not observed because of the overlap with that of the sodium ion. In accord with the general expectations, the kinetic nature of the second wave suggests that the rate of the dissociation of Ni(bi-bzac)(uni-bzac) is faster than that of Ni(bi-bzac)$_2$.

The three waves at less negative potentials were little observed in the solution containing 0.5 mmol dm$^{-3}$ Ni(bzac)$_2$, 25 mmol dm$^{-3}$ Bu$_4$N(bzac), and 0.05 mol dm$^{-3}$ TBAP. Further, the $i_1/i_2$ ratio decreased by the addition of benzoylacetonate to the complex under the controlled drop time of $t_d \leqslant 2.0$ s. These findings and Fig. 3 suggest that there are several paths for the reaction of nickel ions with benzoylacetonate, as is shown in the following scheme:



With an increase in the concentration of tetrabutylammonium benzoylacetonate added to a solution of nickel ions, the above equilibria shifted to the right. In the curves of (b) and (c) in Fig. 2, and in the curve of (d) in Fig. 3, the formation of the tris-complex is apparent as a consequence of the mass-action law; however, it is unknown polarographically whether or not Ni(bzac)$_3^-$ is electroactive at the fourth wave. The several species would likely be formed for Ni(bzac)$_3^-$ in the bulk of the solution. Though the quantitative treatment of the equilibrium distribution in Fig. 3 is a very interesting subject, it is really complicated. At the present stage, the accurate evaluation of the free-ligand concentration is also difficult in the presence of a large excess of electrolytes. Generally, $\beta$-diketones themselves have been used as the ligands for the determination of the formation constants of their metal complexes.[21–23] This method can not be applied in the present work, because the species of Ni(bi-bzac)(uni-bzac) and Ni(bi-bzac)$_2$ are reduced at more negative potentials than the first wave of benzoylacetone, which is considered to come from the hydrogen reduction of the enol form[2,24] (see Table 1). This is the reason for the use of tetrabutylammonium benzoylacetonate. The formation constants of the nickel(II) complex with benzoylacetonate anion have been determined only in 75 vol% dioxane–25 vol% water at 15, 25, and 40 °C: $\log K_1 = 9.13$ and $\log K_2 = 7.76$ at 25 °C.[25] In this paper, the only change in the equilibrium distribution is shown in the complex concentration range of 0.5—5 mmol dm$^{-3}$ in the presence of 0.05 mol dm$^{-3}$ TMAP (Fig. 4). A higher dissociation of Ni(bi-bzac)$_2$ to Ni(bi-bzac)(uni-bzac) attendant upon a decrease in the total complex concentration was found, but the molar fractions for Ni(uni-bzac)$^+$ and Ni(bi-bzac)$^+$ were constant within the range of experimental error. The total molar fraction of Ni(uni-bzac)$^+$ and Ni(bi-bzac)$^+$, 0.08, in the solutions containing the electrolyte is higher than would be expected on the basis of the conductance, indicating the electrolyte effect on the dissociation of the bis-complex to the mono-complex.

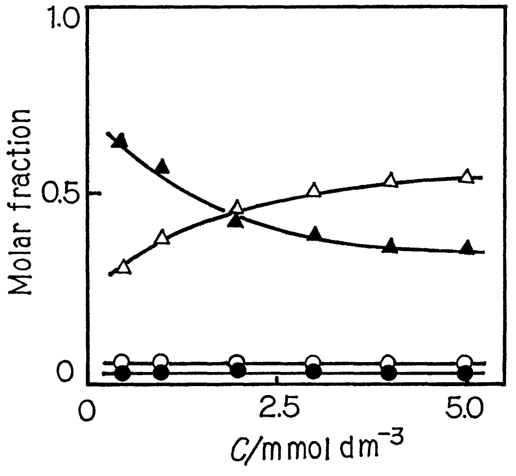


Fig. 4. Equilibrium distribution of four nickel(II) species present in 0.05 mol dm$^{-3}$ TMAP–DMSO solutions containing Ni(bzac)$_2$ in different concentrations. (●) Ni(uni-bzac)$^+$, (○) Ni(bi-bzac)$^+$, (▲) Ni(bi-bzac)(uni-bzac), (△) Ni(bi-bzac)$_2$.

Table 2. Effect of sodium-ion concentration on the $i_j/(i_t)_B$ ratios

| NaClO$_4$ (mol dm$^{-3}$)[a] | $(i_1+i_2)/(i_t)_B$[b] | $i_3/(i_t)_B$[b] |
|---|---|---|
| 0.010 | 0.08 | 0.65 |
| 0.025 | 0.08 | 0.74 |
| 0.050 | 0.08 | 0.77 |

a) The total concentration of the supporting electrolyte was adjusted to 0.050 mol dm$^{-3}$ with TBAP. b) See Table 1.

In the concentration of the supporting electrolyte of 0.05 mol dm$^{-3}$, the species of Ni(bi-bzac)(uni-bzac) comprised 57% of the total complex of 1 mmol dm$^{-3}$ in a TMAP or TBAP solution, while its species formed 77% in a NaClO$_4$ solution (Table 1). It should be noted that the concentration of Ni(bi-bzac)(uni-bzac) is high in a NaClO$_4$ solution. The complex gave three waves in each supporting-electrolyte solution—in 0.05 mol dm$^{-3}$ portions of KClO$_4$, RbClO$_4$, and CsClO$_4$, where each $i_t$ was roughly equal to $(i_1+i_2+i_3)$ at −2.00 V in a TBAP solution. In these solutions, the distribution of the species is similar to that in a TMAP or TBAP solution: the waves for Ni(bi-bzac)$_2$ could not be observed because of overlap with those of potassium, rubidium, and caesium ions. The $i_3/(i_t)_B$ ratio, *i.e.*, the molar fraction of Ni(bi-bzac)(uni-bzac), increased with an increase in the concentration of sodium perchlorate, as is shown in Table 2, where $(i_t)_B$ denotes the $i_t$ in a TMAP or TBAP solution. Apparently, the sodium ion is related to the dissociation of Ni(bi-bzac)$_2$ to Ni(bi-bzac)(uni-bzac). Probably the cations in the solutions cause the decrease in the $\pi$ delocalization in the ligand, thereby labilizing the complex; the sodium ion is considered to be the most effective among the cations used here. This cationic effect will be reported on in detail in the polarographic studies of the nickel(II) complexes with 2-thenoyltrifluoroacetonate, 2-furoyltrifluoroacetonate, and benzoyltrifluoroacetonate anions in the following paper. The sodium ion may contribute to the chelation with free benzoylacetonate anion as well as with several β-diketonate anions:[8–12)]

$$\mathrm{Ni(bi\text{-}bzac)_2} \rightleftharpoons \mathrm{Ni(bi\text{-}bzac)(uni\text{-}bzac)}$$

$$\begin{tikzcd}[column sep=small]
\rightleftharpoons \mathrm{Ni(bi\text{-}bzac)^+} \arrow[d, shift left] & + & \mathrm{bzac^-} \arrow[d, shift left, "\mathrm{Na^+}"] \\
\mathrm{Ni(uni\text{-}bzac)^+} \arrow[u, shift left] & & \mathrm{Na(bzac)} \arrow[u, shift left]
\end{tikzcd}$$

However, as can be seen in Table 1, the $(i_1+i_2)/(i_t)_B$ ratio, *i.e.*, the molar fraction of the mono-complex, in a $NaClO_4$ solution is equal to that in a TMAP or TBAP solution; thus, it seems unlikely that the chelation of the sodium ion by benzoylacetonate anion plays an appreciable role in the equilibrium distribution of Ni(II)-complexes.

Murray *et al.*[27)] found that the reduction potentials of a number of metal acetylacetonates in acetonitrile are shifted to less negative potentials by the addition of lithium perchlorate to tetraethylammonium perchlorate as the supporting electrolyte. Their detailed studies of $Fe(acac)_3$ led to the conclusion that this effect is caused by a coordinative relaxation reaction of the $Fe(acac)_3^-$ reduction product, where an acetylacetonate ligand is transferred to the lithium ion. The interaction between reduction products and the lithium ion has been studied for complexes of the $[ML_n]^\circ$ type in such nonaqueous solvents as acetonitrile[28)] and *N*,*N*-dimethylformamide.[29,30)] According to the results of Gritzner *et al.*,[31)] the reduction product, $Mn(acac)_3^-$, of $Mn(acac)_3$ forms ion-pairs with lithium, sodium, and potassium ions in various solvents. There was no difference between the half-wave potential of the third wave in a $NaClO_4$ solution and that in a TMAP solution in the present work (Table 1). In the case of a completely irreversible electron transfer, however, special experimental approaches will be required to discuss the above interaction.[27)]

The temperature effect on the $i_j$ and $i_t$ of the complex was examined in a TMAP solution (Fig. 5). The species of $Ni(bi\text{-}bzac)_2$ and Ni(bi-bzac)(uni-bzac) were readily dissociated in the bulk of the solution with an increase in the temperature, and there was a marked tendency for the latter. Little dissociation of $Ni(bi\text{-}bzac)^+$ to $Ni(uni\text{-}bzac)^+$ was observed, judging from the temperature coefficient of *ca.* 1.6% $K^{-1}$ for $i_1$.

A study was not made as to whether or not $Ni(bi\text{-}bzac)_2$ is somewhat dissociated to Ni(bi-bzac)(uni-bzac) in the absence of the electrolyte. No useful information from the electronic spectra can be expected concerning such a study. However, the observation of such species involving a unidentate ligand as Ni(bi-bzac)(uni-bzac) and $Ni(uni\text{-}bzac)^+$ in the present work is of interest in connection with the intermediates in the various reaction mechanisms of metal complexes in solution. The high basicity of dimethyl sulfoxide[13,14)] might contribute to the stabilization of those species. Further, the properties of the central metal seem to be very important for the stabilization, but the solution to this problem will require a systematic study of β-diketonate complexes with various metals.

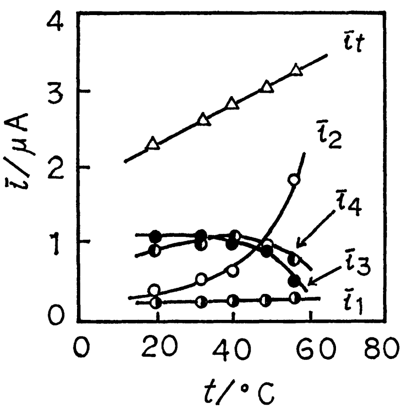


Fig. 5. Effect of temperature on the limiting currents of 1 mmol $dm^{-3}$ $Ni(bzac)_2$ in 0.05 mol $dm^{-3}$ TMAP–DMSO solution. With the DME (B).

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