Polarographic Study of Iron-Benzoylacetonate in Dimethylformamide

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Summary

The electrode process of $\text{Fe}(\text{BA})_3$ in DMF has been investigated by polarography and controlled potential electrolysis. The effects of water and acid on the behavior of $\text{Fe}(\text{BA})_3$ in DMF have been studied. $\text{Fe}(\text{BA})_3$ is reversibly reduced to $\text{Fe}(\text{BA})_3^-$ in DMF at a dropping mercury electrode in the presence of large excess of ligand. Addition of water affects the D.C. and A.C. wave heights and the half-wave potentials, but the electrode process is essentially identical with that in water free DMF. In acidic media, are observed several polarographic waves, which correspond to different species of iron-benzoylacetonates in the solution. From the polarographic data, the concentration of each species of the chelates can be determined and the consecutive formation constants of iron-benzoylacetonate have been calculated as $\log K_1=13.8$, $\log K_2=12.7$ and $\log K_3=10.9$. The acid dissociation constant of benzoylacetonate in DMF determined by pH titration with a glass electrode is 13.2.

Introduction

Polarography has been one of the most advantageous methods for the studies of chemical or electrochemical behaviors of metal chelate compounds in aqueous media.¹⁾ Recently, however, some dipolar aprotic solvents such as acetonitrile, dimethylformamide (DMF) and dimethylsulfoxide have been used extensively as solvents for the polarographic studies of organic and inorganic compounds and many informations have been obtained on the mechanisms of the electrode processes.²⁾ These solvents would also be useful for the polarographic studies of water-insoluble metal chelates, because they have reasonably large solubilities in these solvents.

As far as the metal β -diketone chelates are concerned, previous polarographic investigations have dealt mainly with metal acetylacetonates which are relatively soluble in water. Petek and Branica³⁾ and Cosovic and Branica⁴⁾, for example, have studied the dissociation process of metal acetylacetonates in aqueous solution and have determined their consecutive formation constants polarographically. From analytical viewpoint, Dehn et al.⁵⁾ could determine acetylacetonate of Be in water-chloroform-dimethylsulfoxide medium after extraction with chloroform. Afgahn et al.⁶⁾ also performed the solvent extraction of various metal ions with acetylacetonate and determined In and Pd polarographically in toluene-ethanol system.

During the course of this study, Murray and Hiller⁷⁾ have reported the effect of some cations on the electrode process of tris(acetylacetonato)-iron ($\text{Fe}(\text{AA})_3$) in acetonitrile.

They have found that the reduction wave of $\text{Fe}(\text{AA})_3$ is remarkably affected by the addition of lithium ion, because of the ion pair formation between the reduction product of $\text{Fe}(\text{AA})_3$ and lithium ion followed by ligand relaxation processes.

As the chemical behavior of metal chelate compounds are subject to the acidity of the solution, it seems worth-while to explain the effects of proton donors by taking into account the acidity of the solution. Few investigations in the solvents mentioned above, however, have been undertaken from such standpoint. In the present report, some electrochemical experiments have been conducted on the iron- β -diketone chelates in DMF, by taking into account the acidity of the solution to elucidate the effects of proton donors. pH in dipolar aprotic solvents can be defined as follows;

$$\text{pH}_e = -\log [\text{H}^+]$$

where pH_e is the pH represented by the concentration of the solvated proton. As Ritchie and Megerle⁸⁾ have demonstrated, the pH_e in DMF solution can be obtained by measuring with a pH meter the electromotive force of cell composed of a glass and a reference electrodes. The electromotive force changes by 59 mV with a unit change of pH_e ⁹⁾. In the present report, a solution containing $10^{-2} M$ of perchloric acid, being completely dissociated in DMF, was used as a standard solution of $\text{pH}_e=2$ and the electromotive force was measured using an aqueous SCE as the reference electrode. pH_e is then given as follows;

$$\text{pH}_e = (E - E_0)/59 + 2.0$$

where E and E_0 are the electromotive forces in the sample solution and the standard solution, respectively.

Thus, the electrode process of tris(benzoylacetato)-iron ($\text{Fe}(\text{BA})_3$) at DME in DMF and the effects of proton donors on the electrode process and on the dissociation of $\text{Fe}(\text{BA})_3$ have been elucidated by means of polarography and controlled potential electrolysis. The consecutive stability constants of iron-benzoylacetate in DMF have also been determined polarographically.

Experimental

Apparatus; A Yanagimoto polarograph PA-102 and a Yanagimoto Controlled Potential Electrolyzer were used. The iR drop was corrected for by measuring ohmic resistance of the solution with a conductance bridge. The electrolytic cell for polarographic measurement was an H-type cell with a sintered glass between the two compartments. An aqueous saturated calomel electrode with an agar salt bridge was inserted in one compartment of the cell. pH_e of the solution was measured with a conventional glass electrode, Horiba No. 1326, and an aqueous saturated calomel electrode with a tip of sintered glass disk. A pH meter of Hitachi-Horiba Co. Ltd. was used by connecting a potentiometer in series with the glass electrode system to apply bias voltage. The response of the glass electrode against pH_e of the solution was checked with a picrate buffer solution in DMF. The potential of the glass electrode changed by 59 mV for a unit change of $\log C_{\text{acid}}/C_{\text{salt}}$.

Reagents; Reagent grade DMF was dried over anhydrous sodium carbonate for a few days and purified twice by vacuum distillation. Tetraethylammoniumperchlorate (Et_4NClO_4) was prepared following the method of Given¹⁰⁾. Ten percent tetraethylammoniumhydroxide (Et_4NOH) of Wako Pure Chemicals Co. Ltd. and 70%-perchloric acid were used to control the acidity of the solution. Tris(benzoylacetato)-

iron ($\text{Fe}(\text{BA})_3$) was prepared as follows; Benzoylacetone, which is in small excess to ferric iron was dissolved in warm ammoniacal ethanol and the resulting solution was added to an aqueous solution of ferric chloride. The dark red $\text{Fe}(\text{BA})_3$ began to separate immediately and precipitation was complete within a few minutes. The solution was cooled and added with water and then filtered. After being washed with water, the precipitate was air-dried at 50°C and dissolved in benzene. Pure $\text{Fe}(\text{BA})_3$ was crystallized from benzene solution by adding cyclohexane. Iron content of the chelate determined by phenanthroline method was 10.34% in good agreement with the theoretical value of 10.36%. Benzoylacetone (HBA) was a guaranteed grade reagent of Wako Pure Chemicals Co. Ltd. and was used without further purification.

Results

1. Polarographic behavior and stability of $\text{Fe}(\text{BA})_3$ in DMF.

Polarographic behavior of $\text{Fe}(\text{BA})_3$ was studied in the presence of various concentrations of HBA. DMF solution containing $5 \times 10^{-4} M$ - $\text{Fe}(\text{BA})_3$, $0.1 M$ - Et_4NClO_4 and various concentrations of HBA were allowed to stand overnight and polarograms were recorded under nitrogen atmosphere. Relations between the polarographic properties of $\text{Fe}(\text{BA})_3$ and ligand concentrations are presented in Figs. 1 and 2.

If the concentration of HBA is more than five times larger than that of $\text{Fe}(\text{BA})_3$, $\text{Fe}(\text{BA})_3$ gives a single reduction wave whose half-wave potential is constant at $-0.62 V$ vs. SCE. independently of the concentration of HBA. The slope of the plot of E vs. $\log(i_a - i)/i$ is almost equal to the theoretical value for reversible one electron reduction. The A.C. polarographic reversibility constant K , which is defined by $K = \frac{i_p}{n\sqrt{t}i_d}$, is approximately $95 A^{-1} \cdot \text{V} \cdot \text{sec}^{-1/2}$ (K for the reversible reduction of Tl^+ ion in aqueous $1 M$ - KNO_3 is 140), and the half-width of A.C. wave is 140 mV. In the presence of $3 \times 10^{-2} M$ -HBA, the height of D.C. wave of $\text{Fe}(\text{BA})_3$ increases linearly with its concentration in the range of $5 \times 10^{-5} M$ to $1 \times 10^{-3} M$. The D.C. wave height of $\text{Fe}(\text{BA})_3$ also changes linearly with the square root of mercury column height and with the tempera-

Fig. 1. Relation between the half-wave potential of $\text{Fe}(\text{BA})_3$ and concentration of HBA.

$5 \times 10^{-4} M$ - $\text{Fe}(\text{BA})_3$, $0.1 M$ - Et_4NClO_4 in DMF

Fig. 2. Change of polarographic property with concentration of HBA
 $5 \times 10^{-4} M$ -Fe(BA)₃, $0.1 M$ -Et₄NClO₄ in DMF.

Curve A : slope of $\log \frac{i_d - i}{i}$ vs. E , Curve B : K .

ture of the solution. The temperature coefficient is $1.0\%/^{\circ}C$. From these results, the polarographic wave of Fe(BA)₃ seems to be diffusion controlled. The diffusion current constant of Fe(BA)₃ in DMF is $2.60 \mu A \cdot sec^{1/2} \cdot l \cdot mM^{-1} \cdot mg^{-2/3}$.

If there is no excess ligand in the solution, Fe(BA)₃ gives two irreversible polarographic wave at $-0.60 V$ and $-1.1 V$ vs. SCE, respectively. The wave at more negative potential seems to be due to the reduction of the species partially decomposed from Fe(BA)₃ by solvolysis. Fe(BA)₃ is decomposed gradually in DMF. The red color of the chelate fades with time and finally, after two days, brown precipitate appears. From these results, it can be concluded that Fe(BA)₃ is stable in DMF only in the presence of large excess of HBA and gives almost reversible, diffusion controlled polarographic wave.

In a cell of 100 ml beaker, 50 ml of the solution containing $5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA and $0.1 M$ -Et₄NClO₄ was electrolyzed by controlling the potential of Hg

Fig. 3. Polarograms during controlled potential electrolysis.
 $5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA, $0.1 M$ -Et₄NClO₄ in DMF.
 Electrolysis time 1 ; 0, 2 ; 21, 3 ; 87, min.

Fig. 4. Change of wave heights with electrolysis time.
 $5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA, $0.1 M$ -Et₄NClO₄.

pool (surface area 12.6 cm²) at -0.75 V *vs.* SCE. The color of the solution changed from red ($\lambda_{\max}=450$ mμ) to purple ($\lambda_{\max}=490$ mμ) as electrolysis went on. During the course of controlled potential electrolysis, the DME and the SCE were inserted into the solution under electrolysis and polarograms were recorded. Composite redox waves as in Fig. 3 were obtained. As is shown in Fig. 4, when the electrolysis proceeded, the oxidation current increased at the expense of the reduction current, the total wave height being maintained almost constant. The height of oxidation wave reaches a constant value after long period of electrolysis, indicating that the reduction product of Fe(BA)₃ is reasonably stable in DMF.

From the results of polarography and controlled potential electrolysis, it is found that the electrode reaction of Fe(BA)₃ in DMF proceeds by the following equation producing stable Fe(BA)₃⁻ ions;

2. Effects of water on the polarographic properties of Fe(BA)₃.

The change of the polarographic properties of Fe(BA)₃ with the addition of water is given in Fig. 5. The heights of A.C. and D.C. waves decrease with the increase of water content in the solution, but the value of the product of the D.C. wave height and the square root of the viscosity of the solvent is constant from 0 to 40 vol. % of water. Therefore, the decrease in D.C. wave height seems to be due to the increase of the viscosity of the solution. The rapid decrease of the A.C. wave height with the addition of water is probably due to the decrease of the reversibility of the electrode reaction.

Polarograms recorded with the solution under controlled potential electrolysis at -0.75 V *vs.* SCE. gave a composite redox wave in the presence of various concentrations of water and the half-wave potentials of the redox waves were identical with those of the reduction wave of Fe(BA)₃. From these, the electrode process of Fe(BA)₃ in water-DMF system seems to be essentially identical with that in water-free DMF. The half-wave potentials shift to more positive direction with the increase of water. The change of the properties of the solution, such as the acidity and the dielectric constant might be responsible for this shift, but available data are not sufficient to explain the shift quantitatively. Effects of water on the polarographic properties of Fe(BA)₃ is not large when the water content is less than 1 vol.%, so the effect of small amount

Fig. 5. Effect of water on the wave height of $\text{Fe}(\text{BA})_3$.
 $5 \times 10^{-4} M$ - $\text{Fe}(\text{BA})_3$, $3 \times 10^{-2} M$ -HBA, $0.1 M$ - Et_4NClO_4 .
 ● $i_{A.C.}$ ○ $i_{D.C.}$ ● $i_{D.C.} \cdot \eta^{1/2}$

of water which is introduced when 70% HClO_4 is added to control the acidity of the solution may be negligible.

3. Behavior of $\text{Fe}(\text{BA})_3$ in the presence of acid.

3.1. Dissociation of $\text{Fe}(\text{BA})_3$ in the acidic media.

The behavior of $\text{Fe}(\text{BA})_3$ in the presence of various concentrations of perchloric acid was polarographically investigated. D.C. polarograms of the solution containing $5 \times 10^{-4} M$ - $\text{Fe}(\text{BA})_3$, $3 \times 10^{-2} M$ -HBA and $0.1 M$ - Et_4NClO_4 , varied with the concentration of HClO_4 , as shown in Fig. 6. When the concentration of HClO_4 is smaller than $2 \times 10^{-4} M$, $\text{Fe}(\text{BA})_3$ gives a reversible wave at $-0.63 V$ vs. SCE, which is identical with the wave of $\text{Fe}(\text{BA})_3$ in acid-free DMF solution. In the range of $3 \times 10^{-4} M$ to $5 \times 10^{-2} M$ HClO_4 ,

Fig. 6. Polarograms of $\text{Fe}(\text{BA})_3$ in the presence of HClO_4 . $5 \times 10^{-4} M$ - $\text{Fe}(\text{BA})_3$, $3 \times 10^{-2} M$ -HBA, $0.1 M$ - Et_4NClO_4 . Conc. of HClO_4 1: $2.5 \times 10^{-2} M$, 2: $1 \times 10^{-2} M$, 3: $5 \times 10^{-3} M$, 4: $1 \times 10^{-3} M$, 5: $5 \times 10^{-4} M$, 6: $1 \times 10^{-4} M$.

Fig. 7. Change of wave height with pH of solution.
 $5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA, $0.1 M$ -Et₄NClO₄.
 1; first wave, 2; second wave, 3; third wave.

the polarograms of Fe(BA)₃ split into two waves whose half-wave potentials are about $-0.55 V$ and $-0.1 V$ *vs.* SCE, respectively. The height of the first wave (more negative wave) decreases with the increase of the acid concentration, whereas that of the second wave (more positive wave) increases. In more concentrated acid solution, a new wave appears at more positive potential, approximately $+0.2 V$ *vs.* SCE, and the first wave disappears. The height of the second wave decreases with the increase of the acid concentration, while that of the third (most positive wave) increases. All of these waves are diffusion-controlled. Therefore, each wave height seems to indicate the concentration of each species in the solution. The first wave corresponds to the reduction of Fe(BA)₃ and the second and the third waves seem to be due to the reduction of Fe(BA)₃⁺ and Fe(BA)₂²⁺, respectively. The pH_e of the solution was measured using a glass electrode and the change of each wave with pH_e was obtained. The results are given in Fig. 7. The pH_e of the solution varied linearly at a rate predicted theoretically with the logarithm of the acid concentration between $2 \times 10^{-3} M$ and $10^{-1} M$, but when the concentration of the acid was smaller than $10^{-3} M$, pH_e of the solution increased more abruptly with the decrease of acid concentration. It is probably due to the buffer action of dimethylamine which might be present in DMF. From Fig. 7, Fe(BA)₃ seems to be dissociated as in Table 1 with the change of pH_e of the solution.

Table 1. Scheme of dissociation reaction of Fe(BA)₃,
 $5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA, $0.1 M$ -Et₄NClO₄

pH _e	Dissociation reaction	Predominant species
pH _e > 5		Fe(BA) ₃
5 > pH _e > 2.5	Fe(BA) ₃ + H ⁺ ⇌ Fe(BA) ₂ ⁺ + HBA	Fe(BA) ₃ , Fe(BA) ₂ ⁺
2.5 > pH _e > 1	Fe(BA) ₂ ⁺ + H ⁺ ⇌ Fe(BA) ₂ ²⁺ + HBA	Fe(BA) ₂ ⁺ , Fe(BA) ₂ ²⁺
1 > pH _e	Fe(BA) ₂ ²⁺ + H ⁺ ⇌ Fe ³⁺ + HBA	Fe(BA) ₂ ²⁺ , Fe ³⁺

3.2. Electrode reaction of Fe(BA)₃ in the presence of acid.

Linear relations are obtained between the half-wave potentials of each polarographic wave and the pH_e of the solution, if pH_e is smaller than 5 as in Fig. 8. This

Fig. 8. Relation between half-wave potentials and pH_e of solution.
 $5 \times 10^{-4} M\text{-Fe(BA)}_3$, $3 \times 10^{-2} M\text{-HBA}$, $0.1 M\text{-Et}_4\text{NClO}_4$

shows that proton might take part in the electrode process of iron-benzoylacetonate. The changes of the half-wave potentials for a unit change of pH_e are 90 mV for the first wave and 25 mV for the second and the third waves, respectively. Solutions consisting of $5 \times 10^{-4} M\text{-Fe(BA)}_3$, $3 \times 10^{-2} M\text{-HBA}$, $0.1 M\text{-Et}_4\text{NClO}_4$ and various concentrations of HClO_4 were electrolyzed at controlled potentials using Hg-pool electrode and the reduction products were investigated by measuring the change of polarograms in the solutions under controlled potential electrolysis.

$\text{pH}_e > 5$: In the presence of $1 \times 10^{-4} M\text{-HClO}_4$, the solution was electrolyzed at the cathode potential of -0.75 V vs. SCE and, during the electrolysis, the change of the polarographic behavior of the solution was traced. In any stage of the electrolysis, a composite anodic-cathodic wave was obtained at -0.62 V vs. SCE , though the anodic current increased with time at the expense of the cathodic current. This shows that the reduction product Fe(BA)_3^- is stable and reversibly oxidized and that a proton does not take part in the reaction. This is also supported by the relation between the half-wave potential and the pH_e of the solution in Fig. 8.

$5 > \text{pH}_e > 2.5$: At pH_e 3.5, there are two species in the solution; namely, Fe(BA)_3 and Fe(BA)_2^+ . The half-wave potentials of the reduction waves of these species are -0.53 V and -0.10 V vs. SCE , respectively. Using the mercury pool working electrode, the solution was first electrolyzed at the potential of -0.25 V , so that only Fe(BA)_2^+ would

Fig. 9. Change of polarograms during controlled potential electrolysis in acidic media.

$5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA, $0.1 M$ -Et₄NClO₄.

pH_c = 3.5. Set potential 1~3, -0.25V, 4~5, -0.75V vs. SCE.,

be electrolyzed. After the polarographic reduction wave of Fe(BA)₂⁺ had disappeared, the cathode potential was switched to -0.75 V and the electrolysis was carried on. Polarograms obtained in the solution under controlled potential electrolysis are presented in Fig. 9. By electrolysis at -0.25 V, Fe(BA)₂⁺ was reduced and the reduction products gave oxidation waves at +0.15 V and -0.10 V vs. SCE, respectively. The wave at -0.10 V is a composite redox wave due to the reduction of Fe(BA)₂⁺ and the oxidation of its reduced form. The more positive wave at +0.15 V seems to be the oxidation wave of Fe(BA)⁺ which was produced by the acid dissociation of Fe(BA)₂. Thus, the reaction mechanism can be concluded as follows; Fe(BA)₂ is reduced by eq. (1) to Fe(BA)₂, which is in equilibrium with Fe(BA)⁺ as shown by eq. (2).

The heights of the oxidation waves of Fe(BA)₂ and Fe(BA)⁺ have a tendency to decrease in a long period of electrolysis. This may be due to the partial decomposition of the reduction products. After Fe(BA)₂⁺ had been completely reduced, the cathode potential was settled to -0.75 V vs. SCE. and Fe(BA)₃ was electrolyzed. The anodic oxidation waves at -0.10 V and +0.15 V increased in heights but no oxidation wave was observed at -0.62 V vs. SCE. This indicates that the reduction of Fe(BA)₃ at this pH_c occurs as follows; Fe(BA)₂ is formed by eqs. (3) and (4).

then, Fe(BA)₂ is in equilibrium with Fe(BA)⁺ as shown by eq. (2).

Fig. 10. Change of polarograms during controlled potential electrolysis in acidic media.

$5 \times 10^{-4} M$ -Fe(BA)₃, $3 \times 10^{-2} M$ -HBA, $0.1 M$ -Et₄NClO₄, pH=2. Set potential; 1~3, +0.05V, 4~6, -0.25V vs. SCE.

$2.5 > \text{pH}_c > 1$: At pH_c 2, the reduction waves of Fe(BA)²⁺ and Fe(BA)₂⁺ are found at +0.16 V and -0.06 V vs. SCE, respectively. Controlled potential electrolysis was carried out by setting the cathode potential first at +0.05 V and then at -0.25 V. Polarograms obtained in the course of electrolysis are presented in Fig. 10. As the reduction of Fe(BA)²⁺ at +0.05 V goes on, a composite redox wave appears at +0.16 V, but the wave is ill-shaped and the height of the reduction wave of Fe(BA)₂⁺ increases although only temporarily at the beginning of the electrolysis. This is probably due to a chemical reaction taking place between the reduction product and the solution in the course of the electrolysis. The following mechanism would be proposed as the electrode process and the successive chemical process.

Electrode reaction : $\text{Fe(BA)}^{2+} + e \rightleftharpoons \text{Fe(BA)}^+$ (5)

$\text{Fe(BA)}^+ + \text{H}^+ \rightleftharpoons \text{Fe}^{2+} + \text{HBA}$ (6)

Chemical reaction : $\text{Fe(BA)}^{2+} + \text{Fe(BA)}^+ \rightleftharpoons \text{Fe(BA)}_2^+ + \text{Fe}^{2+}$

Similar reactions have been proposed by Murray and Hiller for tris(acetylacetonato)-iron system in acetonitrile. As the electrolysis proceeds and the concentration of Fe(BA)²⁺ in the solution decreases, the successive chemical reaction becomes difficult and the height of the reduction wave of Fe(BA)₂⁺ does not increase any more. After the electrolysis of Fe(BA)²⁺ had been completed, the cathode potential was set at -0.25 V and Fe(BA)₂⁺ was electrolyzed. A cathodic wave at -0.06 V disappeared and the oxidation wave at +0.16 V increased in height. From these results, the electrode reaction of Fe(BA)₂⁺ seems as follows:

$\text{Fe(BA)}_2^+ + e \rightleftharpoons \text{Fe(BA)}_2$ (8)

$\text{Fe(BA)}_2 + \text{H}^+ \rightleftharpoons \text{Fe(BA)}^+ + \text{HBA}$ (9)

4. Polarographic determination of consecutive formation constants of iron-benzoylacetonate in DMF.

In section 3.1, iron-benzoylacetonate was found to show three diffusion controlled waves which correspond to three kinds of chelate species present in the solution. These phenomena are available to determine the consecutive formation constants of iron-benzoylacetonate in DMF. In this experiment, higher concentration of ligand is used

Fig. 11. Change of wave height of each chelate with pH of solution. $5 \times 10^{-4} M$ -Fe(BA)₃, 0.15*M*-HBA, 0.1*M*-Et₄NClO₄.

Fig. 12. Change of molar fraction of each chelate with pH of solution. $5 \times 10^{-4} M$ -Fe(BA)₃, 0.15*M*-HBA, 0.1*M*-Et₄NClO₄.

so that the dissociation of Fe(BA)₃ takes place in the lower pH region where the buffer action of the solution is larger. A solution containing 0.15*M*-HBA, $5 \times 10^{-4} M$ -Fe(BA)₃, 0.1*M*-Et₄NClO₄ gives four different polarographic waves in the range of $5 > \text{pH}_e > -1$. Change of the height of each wave is shown in Fig. 11. From this figure, it is concluded that four species, that is, Fe(BA)₃, Fe(BA)₂⁺, Fe(BA)²⁺, Fe³⁺ are present in the acidic media. The height of total wave is not constant over the whole pH range, but decreases with the increase of the acidity of the solution probably because the diffusion coefficient decreases with the decrease of the number of BA chelated to Fe²⁺. By assuming that the diffusion coefficient of each species does not change with pH, the concentration of Fe(BA)₃, Fe(BA)₂⁺, Fe(BA)²⁺, Fe³⁺ could be calculated from Fig. 11 as

the function of pH. The results are given in Fig. 12. Consecutive formation constants could be estimated using these values and the acid dissociation constant of benzoylacetone in DMF. The acid dissociation constant of benzoylacetone and the consecutive formation constants of iron-benzoylacetone can be written as;

$$\text{from eq. (10), } [\text{BA}^-] = K_a \frac{[\text{HBA}]}{[\text{H}^+]} \quad (15)$$

$$\text{then, } \log K_i = \log \frac{[\text{Fe}(\text{BA})_i^{(3-i)+}]}{[\text{Fe}(\text{BA})_{(i-1)}^{(3-(i-1))+}]} + pK_a - \log [\text{HBA}] - \text{pH} \quad (16)$$

The acid dissociation constant of benzoylacetone was obtained by pH titration in DMF. A solution containing $2 \times 10^{-3} M$ -HBA and $0.1 M$ - Et_4NClO_4 was titrated with 10% aqueous solution of Et_4NOH under nitrogen atmosphere. Measurement of pH was carried out as mentioned before with a glass electrode. In order to elucidate the effect of water which was introduced with the titrant of aqueous Et_4NOH solution, titrations were carried out in the presence of various concentration of water. When the water content was smaller than 1 vol.%, the change of the electromotive force of half equivalent point is negligible and is 5 mV in the presence of 2 vol.% of water. Hence, the effect of the water upon the pK_a value seems to be small. From these experiment, the pK_a value of benzoylacetone was determined to be 13.2. Using eq. (16), the consecutive formation constants $\log K_1=13.8$, $\log K_2=12.7$ and $\log K=10.9$ were obtained for iron-benzoylacetone. The over-all stability constant of iron-benzoylacetone was, therefore, 37.4. This relatively large stability constant of iron-benzoylacetone in DMF is probably due to the low dielectric constant of this solvent. But there is no available data concerning the stability constant of this compound. Correlation between the pK_a and the dielectric constant of the solution have been found in dioxan-water and alcohol-water system⁽¹¹⁾⁽¹²⁾. pK_a obtained in this experiment is nearly equal to the value in 75% dioxan-water system. Further work is in progress on the stability constant of iron- β -diketone chelates in water-DMF system in order to determine the solvent effect on the stability constant of the metal chelate compounds.

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ジメチルホルムアミド中におけるベンゾイルアセトン-鉄(Ⅲ)錯体の ポーラログラフ的研究

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ジメチルホルムアミド (DMF) 等の非プロトン性極性溶媒は、水に難溶な金属キレート化合物の電気化学的研究に有用な溶媒と考えられる。今回、著者はトリス(ベンゾイルアセトナト)鉄(FeBA_3)の DMF 中における挙動をポーラログラフ法と定電位電解により検討した。DMF 中において、 $\text{Fe}(\text{BA})_3$ は多量の配位子の存在下で安定に存在し、滴水水銀電極により可逆的に還元され FeBA_3^- を生ずる。水の添加によって、直流波および交流波の波高が減少し、半波電位はより正側に移行するが、定電位電解途中のポーラログラムは、連続した酸化還元波を与え、電極反応は DMF 中における電極反応と同じように進むと考えられる。

酸の存在下では、酸濃度の変化に伴って数種の異な

った拡散律速のポーラログラフ波が観察される。これらは鉄ベンゾイルアセトンキレートの異なったキレートイオン種の還元に対応する波であると考えられる。ポーラログラフ波の波高の変化から溶液中に存在する各キレートイオンの濃度を求め、これらの値と、pH 滴定によって求められたベンゾイルアセトンの DMF 中における酸解離定数とから、鉄ベンゾイルアセトンキレートの逐次生成定数を求めることを試みた、DMF 中におけるベンゾイルアセトンの酸解離定数として $\text{pK}_a=13.2$ の値が得られ、また、DMF 中の鉄ベンゾイルアセトンキレートの逐次生成定数として、 $\text{pK}_1=13.8$, $\text{pK}_2=12.7$, $\text{pK}_3=10.9$ の値が得られた。