Distribution Equilibria of Five $\beta$-Diketones and Their Complexes of Copper(II) and Iron(III) in 4-Methyl-2-pentanone–Aqueous Perchlorate Solution Systems

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Chemical equilibria of liquid-liquid distributions of acetylacetone, benzoylacetone, trifluoroacetylacetone, benzoyltrifluoroacetone, and hexafluoroacetylacetone, (HA), and solvent extraction of Cu(II) and Fe(III) with these $\beta$-diketones were determined in 4-methyl-2-pentanone(MIBK)-aqueous perchlorate solution systems. The results are compared with those obtained in systems where carbon tetrachloride is the solvent. The distribution constant of HA in the MIBK systems is higher when the acid is stronger. This dependence is opposite to that found in the carbon tetrachloride systems. The extraction of Cu(II) into MIBK with the $\beta$-diketones having trifluoromethyl group is better than into carbon tetrachloride. However, such a better extraction is usually not found with acetylacetone and benzoylacetone. Although iron(III) is extracted as cationic chelates with perchlorate ions into MIBK, its extraction as the FeA$_3$ chelate with the $\beta$-diketones is in most cases poorer than into the latter solvent. Two types of equilibrium constants for the metal extraction were calculated, they are critically discussed.

Keywords Solvent extraction, 4-methyl-2-pentanone, carbon tetrachloride, diluents, $\beta$-diketones, copper(II), iron(III)

Solvating diluents such as 4-methyl-2-pentanone (MIBK) are sometimes very favorable for certain chelating extractants. For example, Kiba and Mizukami$^1$ reported that strontium(II) could be extracted with 2-thenoyltrifluoroacetone (TTA) in MIBK, though this reagent was not effective for this purpose when the diluent was nonpolar. Solvent extraction of copper(II) and zinc(II) with TTA was studied by Sekine and Dyrssen$^2$ when the diluent was carbon tetrachloride, chloroform or MIBK. They reported that the extraction was much better into MIBK than into the two inert solvents, due to solvation or adduct formation with the diluent molecules on the metal chelates. The present paper describes the distribution equilibria of five $\beta$-diketones as well as the extraction equilibria of copper(II) and iron(III) with them. Copper(II) was chosen because it is much more effectively extracted with acetylacetone and its trifluoromethyl derivatives than other divalent transition metal ions, so the extraction can be studied more accurately. Iron(III) was chosen because its coordination sites in the extractable chelate are saturated by the ligand and thus no adduct formation with MIBK is expected.

Statistical

In the present paper, any species in the organic phase is denoted by a subscript "org", those in the aqueous phase have no subscript. The volume of the two phases is always assumed to be the same.

Two phase distribution equilibria of $\beta$-diketones

The acid dissociation and two phase distribution equilibria of a $\beta$-diketone, HA, may be written as

\[ \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad K_a = [\text{H}^+][\text{A}^-]/[\text{HA}]^{-1} \quad (1) \]

\[ \text{HA} \rightleftharpoons \text{HA}_{\text{org}} \quad K_d = [\text{HA}]_{\text{org}}/\text{HA}^{-1} \quad (2) \]

The initial concentration of the acid in one phase, $C_{HA}$, can be written as

\[ C_{HA} = [\text{HA}]_{\text{org}} + [\text{HA}] + [\text{A}^-] \quad (3) \]

By introducing Eqs. (1) and (2), Eq. (3) can be rewritten as

\[ C_{HA} = [\text{A}^-]((K_d + 1)/K_a) \times [\text{H}^+] + 1. \quad (4) \]

Thus from the values of $K_a$ and $K_d$ previously reported$^3$ and those obtained in the present work, the value of [A$^-$] can be calculated on the basis of Eq. (4).
Extraction equilibria of metal ions as chelate complexes

The stability constant of the "n-th" complex of a metal ion M_{m+} with \(\beta\)-diketonate ions may be written as

\[
\beta_n = [M_{An}^{m-n}][M_{m+}]^{-1}[A^{-}]^{-n}. \quad \text{........... (5)}
\]

The distribution constant of the uncharged complex, M_{An}, may be written as

\[
K_{dm} = \frac{[MA_{n \text{org}}]}{[M_{m+}][A^{-}]^n}. \quad \text{........... (6)}
\]

When only the uncharged species is extracted, the distribution ratio, \(D\), can be written as

\[
D = \frac{[MA_{n \text{org}}]}{[M_{m+}][A^{-}]^n}. \quad \text{........... (7)}
\]

By introducing Eqs. (5) and (6) into Eq. (7), the following equation is obtained:

\[
D = \frac{K_{dm} \times \beta_m[A^{-}]^n}{1 + \beta_1[A^{-}] + \cdots + \beta_m[A^{-}]^m}. \quad \text{........... (8)}
\]

The extraction equilibrium can also be written as

\[
M_{m+} + mHA_{\text{org}} \rightleftharpoons MA_{m \text{org}} + mH^+ \quad \text{........... (9)}
\]

\[
K_{ex} = \frac{[MA_{m \text{org}}][H^+]^m}{[M_{m+}][HA]_\text{org}^m}. \quad \text{........... (10)}
\]

Equation (7) can also be written as

\[
D = \frac{K_{ex} \times K_{dm} \times K_a}{1 + \beta_1[A^{-}] + \cdots + \beta_m[A^{-}]^m}. \quad \text{........... (11)}
\]

\[
K_{ex} = \frac{[MA_{m \text{org}}][HA]_\text{org}^m}{[M_{m+}][A^{-}]^n}. \quad \text{........... (12)}
\]

When ion-pairs of the cationic metal species are also extracted, the extraction equilibria may be written as

\[
M_{m+} + aA^{-} + (m-a)ClO_4^- \rightleftharpoons MA_{a}(ClO_4)_{m-a \text{org}} \quad \text{........... (13)}
\]

\[
K_{ex(a, m-a)} = \frac{[MA_{a}(ClO_4)_{m-a \text{org}}]}{[M_{m+}][A^{-}]^n[ClO_4^-]^{m-a}}. \quad \text{........... (14)}
\]

where "a" is zero to \(m\). Under such conditions, the distribution ratio may be written as

\[
D = \frac{[MA_{a}(ClO_4)_{m-a \text{org}}] + [MA_{(m-a)}(ClO_4)_a \text{org}]}{[M_{m+}][A^{-}]^n + [M_{(m-a)}][A^{-}]^m + \cdots + [MA_{m}][A^{-}]^{m}}. \quad \text{........... (15)}
\]

By introducing Eq. (5) and (14), Eq. (15) can be rewritten as

\[
D = \frac{K_{ex(a, 0)}[ClO_4^-]^m + K_{ex(1, m-1)}[ClO_4^-]^{m-1}[A^{-}] + \cdots + K_{ex(m, 0)}[A^{-}]^m}{1 + \beta_1[A^{-}] + \cdots + \beta_m[A^{-}]^m}. \quad \text{........... (16)}
\]

The last term in the numerator, \(K_{ex(n,0)}[A^{-}]^n\), may be replaced by \(K_{dm} \times \beta_m[A^{-}]^m\) like as in Eq. (8);

\[
K_{ex(m, 0)}[A^{-}]^m = K_{dm} \times \beta_m[A^{-}]^m. \quad \text{........... (17)}
\]

Experimental

Reagents

All the reagents were of a reagent grade. The \(\beta\)-diketones studied were acetylacetone (Hacac, 2,4-pentanedione), trifluoroacetylacetone (Htfa, 1,1,1-trifluoro-2,4-pentanedirole), hexafluoroacetylacetone (Hhfa, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione), benzoylacetonel (Hbza, 1-phenyl-1,3-butanediazone), and benzoyletrifluoroacetone (Hbfa, 1-phenyl-4,4,4-trifluoro-1,3-butanediazone). These reagents and iron(III) acetylacetonate were obtained from Dojindo Laboratories. The MIBK was washed with 0.1 mol dm\(^{-3}\) perchloric acid, 0.1 mol dm\(^{-3}\) sodium hydroxide solution and then several times with water. The sodium perchlorate was recrystallized three times from water. Metallic copper or iron was dissolved in nitric acid. The solution was evaporated and then the residue was dissolved in an aqueous sodium perchlorate solution containing a small amount of perchloric acid.

Procedures

All the procedures were made at 298 K. Stoppered glass tubes (capacity 20 cm\(^3\)) were used for the two-phase agitation. The two phases in the tubes were agitated mechanically and were centrifuged.

The hydrogen-ion concentration in the aqueous phase was determined by titration with a standard solution of sodium hydroxide or barium hydroxide but it was determined by potentiometry in some experiments using a series of solutions containing 1.00, 1.00\times10\(^{-1}\), or 1.00\times10\(^{-2}\) mol dm\(^{-3}\) perchloric acid and the same amount of sodium perchlorate as the sample solution as the standard of \(-\log[H^+]=0.00, 1.00,\) or 2.00. Thus it was in stoichiometric units.

Distribution of \(\beta\)-diketones

A weighed amount of one of the \(\beta\)-diketones was dissolved in the diluent and the concentration of the reagent was checked by titration with a standard sodium hydroxide or barium hydroxide solution. The sample organic solution was left standing at least one day before use. A portion of an aqueous solution adjusted at \(-\log[H^+]=2.0\) and the same volume of the \(\beta\)-diketone solution were equilibrated. The \(\beta\)-diketone was determined by spectrometry at 400 to 600 nm after their iron(III) complex was formed. With acetylacetone, trifluoroacetylacetone and hexafluoroacetylacetone, the concentration in the two equilibrated phases was also measured by titration with a barium hydroxide solution. The two phases in the absence of any \(\beta\)-diketone but otherwise identical was also titrated and the distribution of the perchloric acid was determined.
The titration data of β-diketones were corrected for this extraction of perchloric acid.

Solvent extraction of metal ions

The aqueous sodium perchlorate constant ionic media was 1 mol dm$^{-3}$ for Cu(II) and 4 mol dm$^{-3}$ for iron (III). A 6 cm$^3$ portion of the aqueous solution containing no metal ions was placed in the glass tube. The hydrogen-ion concentration was adjusted with perchloric acid. However, in some experiments with copper(II), acetate buffer whose total concentration was less than 0.01 mol dm$^{-3}$ was also used for this purpose. Then an organic solution containing one of the β-diketones was added and the two phases were agitated for 5 min. After this agitation, the metal ions were added and the agitation was continued for 30 min. The volume of the two phases was same. The two phases were then centrifuged. The copper(II) complex in the organic phase was back-extracted with 1 mol dm$^{-3}$ perchloric acid, but the iron(III) complex was washed with 1 mol dm$^{-3}$ hydrochloric acid. Extraction experiments of copper(II) with benzoylacetone and benzoyltrifluoroacetone into carbon tetrachloride were also made in a similar manner to that into MIBK.

Solubility measurement of iron(III) acetylacetonate

A measured amount of tris(acetylacetonato)iron(III) crystals was placed in a glass tube and carbon tetrachloride or MIBK containing 0.1 mol dm$^{-3}$ of acetylacetone was added. The mixture was left standing and was agitated by hand at intervals. After a certain time, a portion was taken from the solution. The iron(III) was washed with 1 mol dm$^{-3}$ hydrochloric acid; then the content of iron(III) in the solution was measured by an atomic absorption method.

Results

Liquid-liquid distribution of β-diketones

The liquid-liquid distribution constants of the β-diketones obtained are listed in Table 1 (when the aqueous phase is 1 mol dm$^{-3}$ NaClO$_4$) and in Table 2 (when the aqueous phase is 4 mol dm$^{-3}$ NaClO$_4$).

Extraction of copper(II) and iron(III)

Figure 1 gives the distribution ratio of copper(II) and Fig. 2 gives that of iron(III), both as a function of the β-diketonate concentration in the aqueous phase. The figures also give previous and some present results obtained when the diluent was carbon tetrachloride.

The extraction of iron(III) with hexafluoroacetylacetone into MIBK was only slight when $-\log [H^+]$ was lower than 2. Above this $-\log [H^+]$, hydrolysis of the metal ions may occur and thus no data of solvent extraction with this extractant were obtained.

These experimental data were analyzed on the basis of Eqs. (8) and (16) by using a least squares computer program. The equilibrium constants were obtained, as listed in Tables 1 and 2, together with some values when the diluent was carbon tetrachloride. It was concluded that the extraction of the [Fe(acac)$_3$] complex into MIBK was negligible under the experi-
The solubility of iron(III) acetylacetonate
The solubility of the [Fe(acac)₃] crystals in the solvent, which as water-saturated or dried by ordinary distillation and which contained 0.1 mol dm⁻³ of acetylacetone, was as follows.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Iron content found</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCl₄ water-saturated</td>
<td>5.6×10⁻¹ mol dm⁻³</td>
</tr>
<tr>
<td>CCl₄ dry</td>
<td>3.0×10⁻¹ mol dm⁻³</td>
</tr>
<tr>
<td>MIBK water-saturated</td>
<td>9.9×10⁻¹ mol dm⁻³</td>
</tr>
<tr>
<td>MIBK dry</td>
<td>6.3×10⁻¹ mol dm⁻³</td>
</tr>
</tbody>
</table>

From Berthelot’s law and Eq. (6), the ratio of the solubility in the solvents, R, is given by the following relation:

\[ R = \frac{\text{solubility in CCl₄}}{\text{solubility in MIBK}} = \frac{K_{\text{dm}}(\text{CCl₄})}{K_{\text{dm}}(\text{MIBK})} \]

(18)

Since R is about 5.7, the K_{dm} in the carbon tetrachloride-aqueous perchlorate systems should be about
6 times higher than in the MIBK systems.

Discussion

In this discussion, the volumes of the two phases are assumed to be the same. As seen from Tables 1 and 2, the distribution constant, $K_d$, of a $\beta$-diketone is always higher when the diluent is MIBK than when it is carbon tetrachloride. The difference is only slight with acetylacetone but it is large with trifluoroacetylacetone and very large with hexafluoroacetylacetone. In other words, the stronger the acid, the better the extraction into MIBK, although the difference is to some extent smaller with the phenyl derivatives.

In the present study, two types of extraction equilibria are considered. Those given by Eqs. (9) and (10) and those given by Eqs. (13) and (14). The concentration of the extractant considered in analytical work is very often the initial value in the organic solution added to the sample aqueous solution. However, the chemical equilibria are calculated by the concentrations at equilibrium. Thus, when the data are treated by Eq. (12), the concentration in the organic phase at equilibrium should be used. For this kind of studies, $K_{ex(m,o)}$ in Eq. (14) is useful because, as seen from Eq. (17), it is the product of the stability and two-phase distribution constant of the uncharged complex. So it gives the relation between the magnitude of the extraction and the chemical properties of the complex.

The extraction constant in Eq. (9) or (14) indicates that a solvent extraction system is efficient if extraction occurs (i) at lower concentration of the extractant and/or (ii) at lower pH. To use another expression, if a certain extraction is possible at a lower $[HA]_{org}/[H^+]$ or a lower $[A^-]$, the system is more efficient.

For several practical purposes, the concentration of extractant in the organic phase in (i) is regarded as similar to the total amount of the extractant in the system, $[HA]_{org}=[HA]_{org}+[HA]^++[A^-]$. When $K_d$ is high and/or pH is not very high, this is approximately true, but when $K_d$ is low, the extractant concentration in the organic phase at equilibrium is much lower than that at the start. This is seen from the data of trifluoroacetylacetone and hexafluoroacetylacetone, which are not "organophilic"; they are present mainly in the aqueous phase when the diluent is nonpolar. In such cases, an apparently high value of $K_{ex}$ in Eq. (10) is obtained. For example, the value of $K_{ex}$ of copper(II) extraction with hexafluoroacetylacetone is $10^4$ times higher than that with acetylacetone as seen from Table 1.

However, as seen from Fig. 1, the 50% extraction ($\log D=0$) occurs at five order lower $[A^-]$ with acetylacetone, in this sense, it is a much more effective extractant than the latter. This is due to the very low $K_d$ of the latter; its concentration in the organic phase for the calculations in Eqs. (9) to (12) is relatively low. As already reported (Fig. 1 in ref. 5), the extraction curves with these reagents as a function of $-\log[H^+]$ are quite similar to each other when the initial concentration of the extractant is identical, as seen from Fig. 3.

A similar tendency is also found about the extraction of iron(III) with these extractants. As seen from Table 2 (i), the value of $K_{ex}$ for iron(III) is higher in the order of $K_{ex}(Htfa)>K_{ex}(Hhfa)>K_{ex}(Hacac)$, but as seen from Fig. 2, the extraction into carbon tetrachloride is better in the order of Hacac>Htfa>Hhfa (the extraction with Hhfa is quite poor and is not given in Fig. 2).

The chemical properties of the diluent should affect the distribution of the extractant and, consequently, the complex formation in the aqueous phase. They also affect the distribution of the extractable complex.

In the extraction of copper(II), the values of $K_{dm}$ are higher with $[Cu(tfa)_{2}]$ and much higher with $[Cu(hfa)_{2}]$ in the MIBK system than in the carbon tetrachloride system. Such a tendency has been recognized in the studies of synergic effects. However, the adduct formation with the solvent is treated as an enhancement of $K_{dm}$ in Eq. (6) in the present study. From Eq. (10) or (17), the following relations are obtained:

$$
\frac{K_{ex(MIBK)}}{K_{ex(CCl4)}} = \frac{K_{dm(MIBK)}}{K_{dm(CCl4)}}$$

$$
\frac{K_{ex(m,o)(MIBK)}}{K_{ex(m,o)(CCl4)}} = \frac{K_{dm(MIBK)}}{K_{dm(CCl4)}}$$

The extraction of either copper(II) or iron(III) with acetylacetone is unfavorable into MIBK, because $K_{dm}$ is lower and $K_d$ is higher in the MIBK system than in the carbon tetrachloride system.

When adduct formation occurs with MIBK, both $K_{dm}$ and $K_d$ are higher in the MIBK system than in
carbon tetrachloride system, as seen from Eq. (19), one effect reduces the other. As was pointed out (Fig. 4 in ref. 7), when the diluent is "regular", $K_{dm}$ is proportional to $K_{dn}$ and the value of $K_{ex}$ is not affected by the diluent. However, when it is not "regular", no general discussion is possible and the results are often complicated. Figure 3 gives the extraction curves of copper(II) with the $\beta$-diketones as a function of $-\log[H^+]$ when the extractant concentration in the initial organic phase is 0.1 mol dm$^{-3}$. Here the difference in the extraction curves with different extractants is much smaller than that found in Fig. 1. The difference of the extraction curves with a certain extractant in different diluents is also smaller. This can be well explained statistically by using the equations already given.

Extractions of metal perchlorate and those of ion-pairs of a cationic complex and perchlorate ions are not important when the diluent is non-polar or even when the diluent is polar, if the perchlorate concentration in the aqueous phase is low. In the present study, extractions of such perchlorates into MIBK is marked with iron(III) in 4 mol dm$^{-3}$ perchlorate solutions. In these experiments, the FeA$_3$ species is only a minor component in the organic phase. This is also seen by comparing the extraction curves with acetylacetone from 1 mol dm$^{-3}$ perchlorate solutions with that from 4 mol dm$^{-3}$ perchlorate solutions. Since the concentration of perchlorate ions is lower in the former, the distribution ratio is much lower at the same $[A^-]$, as seen from Eq. (16). As already pointed out, the coordination sites of the FeA$_3$ type chelates are saturated by the ligand and no room is left for solvation with the MIBK molecules, but in the lower complexes, solvation could occur easily. In the present study, the concentration of the background salt in the aqueous phase is very high, in order to control the activity of the chemical species. However, in aqueous solutions containing a much lower amount of salt, such as in many analytical samples, the extraction of iron(III) into MIBK with the $\beta$-diketones should be poorer than into nonpolar solvents.

When the distribution constant of a certain extractant, $K_d$, becomes higher by the use of a diluent, it lowers its concentration in the aqueous phase and reduces the complexes. Thus if an increase in the distribution constant of the complex, $K_{dm}$, is not caused by the diluent, the extraction should be impaired.

As seen from the extractions of iron(III) with $\beta$-diketones and also from those of copper(II) with acetylacetone and benzoylacetone, the use of MIBK as the diluent of $\beta$-diketones is not always favorable, if an effective solvation is not expected with the extractable complex.

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References


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