Solid-liquid separation after liquid-liquid extraction

Distribution of oxine (8-hydroxyquinoline) and copper oxinate between naphthalene and aqueous phase at 90°C

Masatada Satake*

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The distribution equilibria of oxine or copper oxinate between naphthalene and aqueous phase were studied by the method of liquid-liquid extraction followed by solid-liquid separation using naphthalene as the solvent, and compared with the result obtained by the conventional method of liquid-liquid extraction using chloroform as the solvent. In a previous paper, Fujinaga, Kuwamoto, Nakayama and the author showed that the copper oxinate was extracted quantitatively into naphthalene at 90°C in the pH range larger than 4. This extraction behavior is quite identical to that into chloroform at room temperature, in spite of the difference in the experimental temperature and of the solvent used. The present investigation was performed to elucidate the reason of this similarity of both method in the extraction of copper oxinate and to determine the equilibrium data of oxine and copper oxinate at 90°C.

1 Introduction

The author et al. have found a new method “analysis by solid-liquid separation after liquid-liquid extraction” and this method was successfully applied for the spectrophotometric determination of micro amounts of metals by using melted organic compound with appropriate degree of melting point (namely, solidified at room temperature and liquefied at higher temperature below 100°C) as extractants, e.g., naphthalene, diphenyl, 2-hydroxydiphenyl, etc.

By this method, they have already reported on the determination of copper, zinc, magnesium using oxine and of nickel, palladium using dimethylglyoxime. Of these, the oxinates of zinc, magnesium, cadmium, etc. are difficult to extract directly and completely into chloroform, benzene, etc., owing to their structures of hydrated form. It is the characteristic of this method that the metal chelates mentioned above are also easily extracted quantitatively into the melted naphthalene, and can be determined spectrophotometrically by dissolving the naphthalene mixture in appropriate organic solvent.

In the present work, the distribution of oxine or copper oxinate between organic and aqueous phase has been discussed, considering that the equilibrium takes place

* Division of Applied Science
as shown in Fig. 1. Analysing this equilibrium distribution, the author has determined the fundamental equilibrium data at high temperature (90°C), such as the distribution coefficient of oxine or copper oxinate, the acid dissociation constants of oxine, and the overall formation constant of copper oxinate. These values obtained from the experiments were compared with the results obtained with the equilibria between chloroform and aqueous phase at room temperature.

2 Experimental method

2.1 Reagents

Standard copper solution (1.0 x 10⁻² M) was prepared by dissolving 1.2485 g of copper sulfate in water containing a few drops of concentrated sulfuric acid and diluting to 500 ml. This solution was standardized titrimetrically against EDTA solution. More dilute copper solutions were prepared as required by diluting this standard solution.

Standard oxine solution (1.0 x 10⁻² M) was prepared by dissolving 1.4516 g of oxine in 3 ml of glacial acetic acid on a water bath and diluting to 1 litre with water.

Chloroform, naphthalene and all other reagents were of analytical reagent grade, and were used without further purification.

The redistilled water was used after deionization.

2.2 Apparatus

Absorbance measurements were performed on a Hitachi 139 spectrophotometer, in matched 10 mm glass or quartz cells.

The pH values of the solutions were measured with Toa-Dempa, HM-6A, high temperature glass electrode pH meter.

The solutions were shaken using an Iwaki KM shaker.
3 Results and discussion

(1) Distribution of oxine between chloroform and aqueous phase at 20°C

The test solutions containing 10 ml of 1.0 x 10⁻² M oxine solution in total volume of 20 ml were prepared in separatory funnels. The ionic strength was maintained at 0.1 with sodium perchlorate and the pH was adjusted to various values with hydrochloric acid, sodium acetate or sodium hydroxide. The test solutions prepared above were extracted with 10 ml of chloroform by shaking for 15 min. After standing for 15 min., the two phases were separated, and the organic phase was dehydrated by adding 1 g of anhydrous sodium sulfate. The absorbance of organic phase was measured at 370 m\(\mu\) and the concentration of oxine in the phase was determined at various pH values. In the pH range of 5-10, the absorbance of oxine in aqueous phase was measured at various pH values and its concentration was determined. During the experimental operation, the temperature was held at 20°C. The acid dissociation constants and distribution coefficient of oxine were calculated under the conditions mentioned above. Fig. 2 shows the experimental results.

From the equilibrium distribution shown in Fig. 1, it is considered that oxine is amphoteric and dissociates in two steps in the aqueous solution, as shown in eqs. (1) and (2).

\[
\begin{align*}
\text{H}_2\text{Ox}^+ &\rightleftharpoons \text{H}^+ + \text{HOx} \\
K_1 &= \frac{[\text{H}^+][\text{HOx}]}{[\text{H}_2\text{Ox}^+]} \quad \cdots \cdots (1) \\
\text{HOx} &\rightleftharpoons \text{H}^+ + \text{Ox}^- \\
K_2 &= \frac{[\text{H}^+][\text{Ox}^-]}{[\text{HOx}]} \quad \cdots \cdots (2)
\end{align*}
\]

where \(K_1\) and \(K_2\) are the primary and secondary dissociation constants of oxine.

The distribution of the neutral oxine molecule, HOx between chloroform and aqueous phase may be written as:

\[
\frac{[\text{HOx}]_o}{[\text{HOx}]_w} = K_{D\cdot ox}
\]

where \(K_{D\cdot ox}\) is the distribution coefficient of oxine.

The distribution ratio of oxine, \(D_{ox}\) may be represented as:

\[
D_{ox} = \frac{[\text{HOx}]_o}{[\text{HOx}]_w + [\text{HOx}]_o + [\text{Ox}^-]_w}
\]

substituting Eqs. (1), (2) and (3) into Eq. (4), the following equation can be obtained:

\[
D_{ox} = \frac{K_{D\cdot ox}}{K_1 + 1 + \frac{K_2}{[\text{H}^+]}}
\]
Assuming that only the neutral oxine molecule is extracted into chloroform from the aqueous solution over the pH range of 5—10, then,

\[ K_1 \gg [H^+] \gg K_t \]

hence, the distribution ratio may be written as follows:

\[ D_{Ox} = \frac{[HOx]_D}{[HOx]_W} = K_{D \cdot Ox} \]

\[ \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots 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add 10 ml of $1.0 \times 10^{-2}$ M oxine solution and hydrochloric acid, sodium acetate or sodium hydroxide to adjust the pH of the solution to 1.60-4.94. The ionic strength was maintained to 0.1 with sodium perchlorate. After diluting the volume to 20 ml with water, mix thoroughly. Extract copper oxinate with 10 ml of chloroform by shaking the solution for 15 min. Allow it to stand at 20°C, and after the equilibrium is attained, the absorbance of the chloroform solution was measured at 400 mJ and then the distribution ratio was calculated. The results obtained are shown in Fig. 4. In the figure, it can be seen that copper ion reacts with oxine to form a 1:2 chelate, or CuOX₂, above pH 3.5, and below pH 3.0 two ionic species of CuOX⁺ and/or Cu²⁺ can exist in the solution depending on the acidity.

![Figure 3](image1)

**Fig. 3** Distribution ratio of oxine between naphthalene and aqueous phase as function of pH

- Oxine: $1.0 \times 10^{-4}$ mol; $C_{10}H_{8}(10\text{ml})/H_{2}O(20\text{ml})$
- Ionic strength: 0.1
- Temperature: 90°C

![Figure 4](image2)

**Fig. 4** Distribution ratio of Copper between Chloroform and aqueous phase as function of [$pH+log(\text{HOx})_0$]

- Copper: $1.0 \times 10^{-4}$ mol; Oxine: $1.0 \times 10^{-4}$ mol; CHCl₃(10ml)/H₂O(20ml);
- Ionic strength: 0.1
- Temperature: 20°C

Now, consider the distribution of copper oxinate between chloroform and aqueous phase. The distribution ratio, $D_w$, of copper between chloroform and aqueous phase is represented by the following equation:

$$D_w = \frac{[\text{CuOX}_2]_w}{[\text{Cu}^{2+}]_w + [\text{CuOX}^+]_w + [\text{CuOX}_2]_w}$$

where $[\text{Cu}^{2+}]_w$, $[\text{CuOX}^+]_w$, and $[\text{CuOX}_2]_w$ are the concentration of Cu²⁺, CuOX⁺ and CuOX₂ in the aqueous phase, respectively and $[\text{CuOX}_2]_o$ is the concentration of CuOX₂ in chloroform phase.

Assuming that only the neutral molecular species of copper oxinate, CuOX₂, is extracted into chloroform, the distribution ratio, $D_w$, is written as follows:

$$D_w = \frac{[\text{CuOX}_2]_o}{[\text{CuOX}_2]_w} = K_{D \cdot w}$$
where $K_{D,M}$ is the distribution coefficient of copper oxinate between two phases.

In the pH range above 3.0,

$$[\text{Cu}^{2+}]_w + [\text{CuOx}^+]_w < [\text{CuOx}_2]_w$$

hence, $D_M$ of Eq. (9) is equal to $K_{D,M}$, and the value is amounted to 81.3.

In the pH range between 2.5 and 2.7,

$$[\text{Cu}^{2+}]_w < [\text{CuOx}^+]_w > [\text{CuOx}_2]_w$$

hence,

$$D_M = \frac{[\text{CuOx}_2]_0}{[\text{CuOx}^+]_w} \cdot \frac{[\text{CuOx}]_w}{[\text{CuOx}_2]_w} \cdot \frac{[\text{CuOx}]_w}{[\text{Cu}^{2+}]_w}$$

$$= K_{D,M} \cdot K_{M''} \cdot [\text{Ox}^-]_w = K_{D,M} \cdot K_{M''} \cdot \frac{K_1 \cdot [\text{HOx}]_0}{K_{D,ox} \cdot [\text{H}^+]_w}$$

Therefore,

$$\log D_M = \log \frac{K_{D,M} \cdot K_{M''} \cdot K_1}{K_{D,ox}} + \{\text{pH} + \log[\text{HOx}]_0\}$$

Here, $K_{M''}$, the secondary formation constant of copper oxinate, is given by $K_{M''} = \frac{[\text{CuOx}_2]_w}{[\text{CuOx}^+]_w \cdot [\text{Ox}^-]_w}$ and $[\text{HOx}]_0$, the oxine concentration in chloroform phase, can be obtained from the experimental data in Fig. 2. From Eq. (12), the plots of distribution ratio, $\log D_M$ vs. $\{\text{pH} + \log[\text{HOx}]_0\}$ give a slope of 1 as shown in Fig. 4. Substitution of the experimental data obtained in the pH range of 2.5–2.7 into Eq. (11) give the value of $1.65 \times 10^{11}$ as the secondary formation constant $K_{M''}$.

In the acidic solution below pH 2.5,

$$[\text{Cu}^{2+}]_w > [\text{CuOx}^+]_w + [\text{CuOx}_2]_w$$

Therefore, $D_M$ of Eq. (9) may be written as :

$$D_M = \frac{[\text{CuOx}_2]_0}{[\text{CuOx}^+]_w} \cdot \frac{[\text{CuOx}]_w}{[\text{CuOx}_2]_w} \cdot \frac{[\text{CuOx}]_w}{[\text{Cu}^{2+}]_w}$$

$$= K_{D,M} \cdot K_{M'} \cdot K_{M''} \cdot [\text{Ox}^-]_w = K_{D,M} \cdot K_{M''} \cdot K_1^2 \cdot \frac{[\text{HOx}]_0}{[\text{H}^+]_w}$$

Hence,

$$\log D_M = \log \frac{K_{D,M} \cdot K_{M'} \cdot K_{M''} \cdot K_1^2}{K_{D,ox}} + 2 \{\text{pH} + \log[\text{HOx}]_0\}$$

where $K_{M'}$ is the primary formation constant of copper oxinate given by $K_{M'} = \frac{[\text{CuOx}^+]_w}{[\text{Cu}^{2+}]_w \cdot [\text{Ox}^-]_w}$.

From Eq. (14), the plots of distribution ratio, $\log D_M$ vs. $\{\text{pH} + \log[\text{HOx}]_0\}$ give a slope of 2 as shown in Fig. 4. Substitution of the distribution data obtained in the pH range below 2.5 into Eq. (13) yields the numerical value $9.05 \times 10^{24}$ for the overall formation constant $K_{M'} \cdot K_{M''}$.

By using the value of $K_{M''}$ obtained from Eq. (11), the value of $K_{M'}$ is estimated to be $5.4 \times 10^{12}$.

(4) Distribution of copper oxinate between naphthalene and aqueous phase at 90°C

Test solution containing $1.0 \times 10^{-6}$ mol of copper and $1.0 \times 10^{-4}$ mol of oxine was prepared according to the recommended procedure shown in (2), and was extracted with 10 ml of naphthalene at 90°C. After the phase separation, the concentration of
copper remained in the aqueous phase was determined with oxine–chloroform extraction method and the distribution ratio of copper was calculated. The results thus obtained are shown in Fig. 5. It can be found from Fig. 5 that above pH 4.0 copper forms chelate of the type CuOx₄−, which is almost completely extracted into the melted naphthalene, and at the pH range between 2 and 4 CuOx⁺ exists as a stable species. The simple copper ion, Cu²⁺ can exist below pH 2.0. The deviation of some plots at the pH range of 3-4 from the theoretical 1:1 line, is not explained fully at the present stage and must be studied further. By substituting the experimental data obtained in the given pH range into Eqs. (10), (11) and (13), the values of the $K_D$, $K'_M$ and $K''_M$ are determined to be 140.9, $4.5 \times 10^{11}$ and $1.2 \times 10^9$, respectively.

Tables I and II summarize the distribution equilibrium constants of oxine and copper oxinate between the organic and aqueous phase in both extraction methods. The following facts can be realized from the Tables:

**Table I** Distribution coefficient and acid dissociation constants of oxine at 20°C and 90°C

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>Temperature</th>
<th>$K_D$</th>
<th>$pK_1$</th>
<th>$pK_2$</th>
<th>$pK_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>20°C</td>
<td>285</td>
<td>4.92</td>
<td>10.04</td>
<td>14.96</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>90°C</td>
<td>2.42</td>
<td>3.30</td>
<td>9.94</td>
<td>13.24</td>
</tr>
</tbody>
</table>


**Table II** Distribution coefficient and overall formation constants of copper oxinate at 20°C and 90°C

<table>
<thead>
<tr>
<th>Organic solvent</th>
<th>Temperature</th>
<th>$K_D$</th>
<th>$K'_M$</th>
<th>$K''_M$</th>
<th>$K_M = K'_M \cdot K''_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>20°C</td>
<td>81.3</td>
<td>$5.4 \times 10^{12}$</td>
<td>$1.7 \times 10^{13}$</td>
<td>$9.1 \times 10^{24}$</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>90°C</td>
<td>141</td>
<td>$4.5 \times 10^{11}$</td>
<td>$1.2 \times 10^9$</td>
<td>$5.4 \times 10^{33}$</td>
</tr>
</tbody>
</table>

(1) The primary and secondary acid dissociation constants of aqueous oxine solution at 90°C are larger than those at 20°C (2) The distribution coefficient of oxine into naphthalene at 90°C is much smaller than that into chloroform at 20°C (ca. 1 : 100). (3) The formation constant of copper oxinate at 90°C is much smaller than that at 20°C (ca. 1 : 10^4). (4) The distribution coefficient of copper oxinate into naphthalene at 90°C is larger than that into chloroform at 20°C. The fact that the copper oxinate can be extracted similarly quantitatively into chloroform at 20°C and into naphthalene at 90°C in the pH range over 4 can be explained as the combined effect of the above mentioned equilibrium behavior.

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References
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