ANODIC EXCHANGE REACTIONS OF EXTRACTED METAL CHELATES WITH 1-PYRROLIDINECARBODITHIOIC ACID IN ISOBUTYL METHYL KETONE

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The metal-1-pyrrolidinecarbodithioate \( M(pcd)_m \), \( M=\text{Mn(III), Fe(III), Co(III), Ni(II), Cu(II), Zn(II), In(III), Sb(III), Tl(I), Pb(II), and Bi(III)} \), extracted from tartrate into isobutyl methyl ketone (IBMK, 4-methyl-2-pentanone), gives reduction and oxidation waves. The oxidation process is the anodic exchange reactions of the type \( (2/m)M(pcd)_m + \text{Hg} \rightleftharpoons \text{Hg}(pcd)_2 + (2/m)M^{m+} + 2e^- \) that can be studied electrochemically with Nernstian treatments. The formation constants of \( M(pcd)_m \) in IBMK were calculated from the half-wave potentials of the anodic exchange reactions at a dropping mercury electrode. The adsorption pre-wave was observed in the oxidation wave for \( \text{Zn}(pcd)_2 \) and the surface excess was calculated.

INTRODUCTION

Dithiocarbamic acids, which contain two coordinating sulfur atoms in a molecule, are used as precipitation and solvent extraction reagents for many metal ions. 1-Pyrrolidinecarbodithioic acid (Hpcd), one of the dithiocarbamic acids, is widely used for the determination of metal ions in extraction-spectrophotometry and extraction-atomic absorption spectrophotometry because it decomposes slowly compared to other dithiocarbamic acids in an acid media. The metal ions can then be extracted into an organic phase with Hpcd from the acidic aqueous solution. Polarographic determination of metal ions after solvent extraction with diethylthiocarbamic acid was also reported. These methods utilized the reduction waves of the extracted chelates after the addition of the suitable supporting electrolyte and the secondary solvent to an extraction solvent such as chloroform in order to facilitate the electrochemical measurements.

In the course of our studies of electrochemistry in a nonaqueous solvent, we found that isobutyl methyl ketone (IBMK) is suitable for electrochemical use as an organic solvent. With the use of this solvent, we reported the polarographic behavior of metal chelates after only tetrabutylammonium perchlorate (TBAP), as the supporting electrolyte, was added to the IBMK extract. In this paper, we

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extend this method to the metal pcd chelates, which exhibit oxidation waves from anodic exchange reactions at a mercury electrode as well as reduction waves, and characterize the anodic exchange reactions.

**EXPERIMENTAL SECTION**

**Apparatus**

Voltammograms were obtained with a Yanagimoto P-8 Polarograph. The characteristics of the dropping mercury electrode (DME) were the rate of mercury flow, \( m = 1.81 \, \text{mg/s} \) and the drop time, \( t_d = 3.60 \, \text{s} \) at the mercury column height, \( h = 72 \, \text{cm} \) in IBMK containing 0.1 M TBAP. A hanging mercury drop electrode (HMDE) was prepared with a Metrohm Model E410. An aqueous SCE and a platinum wire were used as a reference and a counter electrode respectively.

**Reagents**

Unless otherwise noted, all chemicals were of reagent grade. Doubly distilled mercury was used for the DME and HMDE. TBAP was prepared by metathesis from an aqueous solution of sodium perchlorate and tetrabutylammonium bromide which had been synthesized with purified tributylamine and butyl bromide, thoroughly washed with water, recrystallized twice from ethanol, and dried under vacuum at 60 °C. Commercial IBMK was distilled using a column packed with stainless steel helices after the addition of small amounts of an aqueous solution of tetrabutylammonium hydroxide. The distillate, at 116 °C, was further purified by redistillation. No significant electrochemical impurities were detected in the 0.1 M TBAP-IBMK system. The concentration of the stock solution of each metal ion, (ca. 10^{-2} \, \text{M}) prepared by dissolving the appropriate salt in dilute acid, was determined by chelatometry with EDTA^{15}. Ammonium and tetrabutylammonium salts of pcd^- were respectively prepared according to previously described methods^{13}^{16}.

**Procedures**

To a 50 ml glass stoppered centrifuge tube, the required amounts (0.1-10 \, \mu\text{mol}) of metal ions and 5 ml of 0.1 M sodium tartrate were added. After the pH of the solution was adjusted to 7-8 (vide infra), 5 ml of 2x10^{-2} \, \text{M} \, \text{NH}_4\text{pcd} and 10 ml of IBMK were added. The two phases were shaken for 3 min at ambient temperature. At this stage, all metal ions of interest were quantitatively extracted into the organic phase. After centrifugation, the organic phase was transferred to a voltammetric cell to which solid TBAP had been added in advance to be 0.1 M in the concentration of the supporting electrolyte. Oxygen was removed by the passage of nitrogen (99.9995% up) and the nitrogen flow was maintained over the solution during the voltammetric measurements. The polarographic current at the DME was measured as the average current.

**RESULTS AND DISCUSSION**

**Extraction-Polarography of Hpcd**

The extracted Hpcd into IBMK exhibits a diffusion-controlled oxidation wave at
-0.75 V. The limiting diffusion current depends on the pH of the aqueous phase: it is not seen above pH 7.0; increases with decrease in pH in the range of 7.0 to 4.3; and decreases abruptly below pH 4.3 due to the decomposition of Hpcd to pyrrolidine and carbon disulfide\(^6\) in the aqueous phase. The percent extraction of Hpcd was determined by comparing the limiting current for the extracted Hpcd to that for (C\(_2\)H\(_5\))\(_4\)Npcd dissolved in IBMK as a standard and was found to be 24\% at pH 4.30. The pH of the extraction for the metal ions with Hpcd is chosen to be 7-8, because the oxidation wave for the extracted ligand makes it difficult to measure the polarographic waves for the extracted chelate which exhibits an oxidation wave at a more positive potential (vide infra).

The electrode reaction for the ligand is expressed as follows:

\[
2\text{Hpcd} + \text{Hg} \rightleftharpoons \text{Hg(pcd)}_2 + 2\text{H}^+ + 2\text{e}^- \tag{1}
\]

for the extracted Hpcd, and

\[
2\text{pcd}^- + \text{Hg} \rightleftharpoons \text{Hg(pcd)}_2 + 2\text{e}^- \tag{2}
\]

for the pcd\(^-\) anion. The current-potential relationship in dc polarography for Reaction 2 would be described by

\[
E = E_0' - \frac{(RT/2F)\ln K_{\text{Hg}}}{} + \frac{(RT/2F)\ln((kD_{\text{pcd}^-})/2D_{\text{Hg(pcd)}_2})^{1/2}}{} + \frac{(RT/2F)\ln(I/(I_d-I))^2}{\text{(3)}}
\]

where \(E_0'\) is the formal redox potential of Hg\(^{2+}/\text{Hg}\) in IBMK; \(K_{\text{Hg}}\), the concentration formation constant of Hg(pcd)\(_2\); \(D\), the diffusion coefficient of each component, and \(k\), the Ilkovic constant and identical to \(607m^2/3t_d^{1/6}\) when using the following units: \(I\) in mA, \(D\) in \(cm^2/s\), the concentration in \(M\), \(m\) in mg/s, and \(t_d\) in s. In the equations above and below one molar in concentration is taken as the standard state because of the difficulty of estimating the activity. Assuming \(D_{\text{pcd}^-} = D_{\text{Hg(pcd)}_2}\), the half-wave potential, \(E_{1/2}\), results in

\[
E_{1/2} = E_0' - \frac{(RT/2F)\ln K_{\text{Hg}}}{\text{(4)}} - \frac{(RT/2F)\ln[\text{pcd}^-]^*}{\text{(4)}}
\]

where \([\text{pcd}^-]^*\) is the bulk concentration of a pcd\(^-\) anion. A plot of \(E\) vs. \(\log(I/(I_d-I)^2)\) for the oxidation wave of pcd\(^-\) gives a straight line with a slope of 30 mV, indicating that the electrode reaction is a reversible, two-electron oxidation for the ligand to form the mercury(II) chelate Hg(pcd)\(_2\).

**Extraction-Polarography of chelates**

When silver(I) and cadmium(II) ions were extracted into IBMK with Hpcd, the precipitation of the chelates was formed between the two phases. The solubility of these pcd chelates is too small to measure their polarograms. Manganese(II) and cobalt(II) are found to be respectively oxidized by air to the manganese(III) and cobalt(III) chelates during the extraction; the voltammetric behavior on a platinum disk electrode in IBMK for these extracted chelates is in fair agreement with that
for the synthesized chelates which have been well characterized as chelates with tervalent state\(^{17)-19}\).

Reduction. The extracted chelates exhibit at least one reduction wave at the DME. All the reduction waves were found to be diffusion-controlled although the reduction wave for the thallium(I), lead(II), bismuth(III), and antimony(III) chelates and the second wave for the copper(II) chelate are accompanied by the maximum wave. Table 1 summarizes the half-wave potentials and the \(n\) values which were evaluated with the aid of the diffusion-current constant. The chelate filled d-electron shells is reduced to the metal amalgam in one step; whereas, the first reduction step for the transition metal chelates is a one-electron transfer to the anion.

The linear dependence of the diffusion current for the extracted chelates on the concentration of their metal ions in an aqueous phase may be used for determining metal ions directly to the concentration level of \(10^{-5}\) M without back extraction or the addition of a secondary solvent. However, some of the half-wave potentials of the reduction waves are too close to each other to be determined simultaneously.

Anodic Exchange Reaction. All the extracted pcd chelates exhibit an oxidation wave at the DME as well as the reduction wave described above. Figure 1 shows the dc polarograms for some metal pcd chelates. The oxidation process for all the chelates studied, except Mn(pcd)_3, Fe(pcd)_3, and Co(pcd)_3, is diffusion-controlled and the half-wave potential is characteristic of central metal. Figure 2 shows the cyclic voltammograms for the extracted zinc(II) chelate, Zn(pcd)_2, which gives a reversible redox couple at the HMDE; whereas, it produces no faradaic current at a platinum disk electrode in the potential range of interest. These findings indicate that the mercury participates in the oxidation of the chelate. Thus, the electrode reaction is the anodic exchange reaction of zinc(II) and other chelates except manganese(III), iron(III), and cobalt(III) with mercury from the electrode and can be expressed as follows:

\[
(2/m)M(pcd)_m + Hg \leftrightarrow Hg(pcd)_2 + (2/m)M^{m+} + 2e^- \quad (5)
\]

<table>
<thead>
<tr>
<th>Chelate</th>
<th>(E_{1/2}/V) vs. SCE</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(pcd)_3</td>
<td>-0.56</td>
<td>1</td>
</tr>
<tr>
<td>Fe(pcd)_3</td>
<td>-0.60</td>
<td>1</td>
</tr>
<tr>
<td>Co(pcd)_3</td>
<td>-0.96</td>
<td>1</td>
</tr>
<tr>
<td>Ni(pcd)_2</td>
<td>-1.40</td>
<td>1</td>
</tr>
<tr>
<td>Cu(pcd)_2</td>
<td>-0.56</td>
<td>1</td>
</tr>
<tr>
<td>Zn(pcd)_2</td>
<td>-1.81</td>
<td>2</td>
</tr>
<tr>
<td>Sb(pcd)_3</td>
<td>-0.71</td>
<td>3</td>
</tr>
<tr>
<td>Tl(pcd)</td>
<td>-0.63</td>
<td>1</td>
</tr>
<tr>
<td>Pb(pcd)_2</td>
<td>-0.79</td>
<td>2</td>
</tr>
<tr>
<td>Bi(pcd)_3</td>
<td>-0.60</td>
<td>3</td>
</tr>
</tbody>
</table>

Figure 1 Dc polarograms of extracted pcd chelates at a DME in IBMK, \(m^+ = 0.6\) mM, 1)Cu(II), 2)Bi(III), 3)Sb(III), 4)Zn(II), 5)Tl(II), 6)pcd\(^-\).
where \( m \) is the charge of the metal ion or the number of ligands in the chelate \( M(pcd)_m \). The anodic exchange reaction is divided into the two-electron oxidation of mercury and the exchange reaction of the metal chelate with \( Hg^{2+} \) to form \( Hg(pcd)_2 \).

\[
\text{Hg} \leftrightarrow \text{Hg}^{2+} + 2e^- \quad (6)
\]

\[
\text{Hg}^{2+} + (2/m)M(pcd)_m \rightleftharpoons \text{Hg(pcd)}_2 + (2/m)M^{m+} \quad (7)
\]

The equilibrium constant for the exchange reaction expressed by Equation 7 is related to the concentration formation constants, \( K_M \) for \( M(pcd)_m \) and \( K_{Hg} \) for \( Hg(pcd)_2 \), in IBMK, i.e.,

\[
K = \frac{[\text{Hg(pcd)}_2][\text{M}^{m+}]^{2/m}}{[\text{M(pcd)}_m]^{2/m}[\text{Hg}^{2+}]} = \frac{K_{Hg}}{K_M^{2/m}} \quad (8)
\]

Under the condition that both the electron transfer (Equation 6) and the exchange reaction (Equation 7) are sufficiently fast, the thermodynamic or Nernst equation for Reaction 5 is

\[
E = E^{0'} - \frac{(RT/2F)\ln K}{(RT/2F)\ln ([\text{Hg(pcd)}_2]_0[\text{M}^{m+}]_0^{2/m}/[\text{M(pcd)}_m]_0^{2/m})} \quad (9)
\]

where \( E^{0'} \) is the formal redox potential for Reaction 6 and \([ ]_0 \) is the concentration at the electrode surface. Under the reversible dc polarographic condition, the average dc current would be described by Equations 10 and 11 according to the simple diffusion model.
In the equations, \([M(pcd)_m]^{*}\) is the bulk concentration of the metal chelate extracted into IBMK and the other symbols are the same as those in Equation 3. For the special case where \(D = D_{M(pcd)m} = D_{Hg(pcd)2} = D_{M^{m+}}\), one can obtain the current-potential relationship for the anodic exchange reaction by introducing the concentration terms in Equations 10 and 11 to Equation 9.

\[
E = E^{o'} - \frac{(RT/2F)\ln K}{(RT/2F)\ln(1^{(m+2)}/m)} + \frac{(RT/2F)\ln(1^{(m+2)}/m)}{(I_d - I)^2/m} \tag{12}
\]

In this case the half-wave potential, \(E_{1/2}\), should be given by

\[
E_{1/2} = E^{o'} - \frac{(RT/2F)\ln K}{(RT/2F)\ln(I_d/4KD^{1/2})} + \frac{(RT/2F)\ln(m[M(pcd)_m]^{*}/4)} \tag{13}
\]

A plot of the current-potential relationship for the anodic exchange reaction of pcd chelates between Zn(II) and Hg(II) gives a straight line as shown in Figure 3. From Equation 12, it can be seen that the expected reciprocal slope for the plot is 30 mV at 25 °C. The value obtained, 34 mV, is in reasonable agreement. For the oxidation wave of the extracted Tl(pcd), Pb(pcd)_2, Cu(pcd)_2, Bi(pcd)_3, and In(pcd)_3 chelates, logarithmic plots, similar to Zn(pcd)_2 in Figure 3, gave a straight line with the reciprocal slope of 40 mV, 37 mV, 31 mV, 34 mV, and 34 mV, respectively. For the oxidation wave of Ni(pcd)_2 and Sb(pcd)_3, however, the current-potential relationship expressed by Equation 12 was not observed although the oxidation process for these chelates must be the anodic exchange reaction which follows Equation 5.

The half-wave potential for the anodic exchange reaction depends on the concentration of the extracted chelates; Equation 13 predicts a straight line with a slope of 30 mV in a plot of \(E_{1/2}\) vs. the logarithmic concentration of \(M(pcd)_m\). The experimental slope of the straight line obtained for the chelates exhibiting the anodic exchange reaction ranges from 60 mV to 100 mV which is larger than the expected 30 mV. This may be caused by an uncompensated resistance, which is present in IBMK having a low dielectric constant (\(\varepsilon=10\)) and shifts the oxidation wave toward a more positive potential as the concentration increases.

It is seen from Equation 13 that the half-wave potential for the anodic exchange reaction also depends on the formation constant of \(M(pcd)_m\); the larger the formation constant \(K_M\), the more positive the half-wave potential. The formation constants are calculated from the half-wave potentials of the oxidation waves of metal pcd chelates and the pcd^- anion by using Equations 4 and 13 and are presented
in Table 2. All the values of $K_M$ are larger by several orders of magnitude than the literature values which correspond to the two-phase formation constants measured by solvent extraction in metal ion-Hpcd-chloroform$^{21,22}$ and metal ion-diethyldithiocarbamic acid-carbon tetrachloride$^{23}$ systems. The great difference between the formation constants in IBMK and two-phase formation constants may be interpreted in terms of the solvation to metal ions: water molecules possessing a large dipole moment stabilize metal ions better than IBMK and hence the formation constant between the two phase is smaller than IBMK.

The number of electrons transferred for the anodic exchange reaction is expected to be $m$ per one mole of $M(pcd)_m$ from Equation 5 and thus the limiting diffusion current of this process is represented by Equation 11. Results shown in Figure 1 are obviously consistent with the above description: the limiting diffusion current of the oxidation wave for $M(pcd)_m$ at the concentration of $0.6/m$ mM is almost identical respectively. However, for the extracted $Mn(pcd)_3$, $Fe(pcd)_3$, and $Co(pcd)_3$ chelates, which give oxidation waves at the DME with $E_{1/2}$ of $-0.31$ V, $-0.21$ V, and $+0.45$ V respectively at the concentration of 0.2 mM, the limiting diffusion current of the oxidation wave is smaller than that corresponding to a three-electrons transfer which is expected if the oxidation is the anodic exchange reaction represented by Equation 5. This can be attributed to the substitution inertness of these (III) pcd chelates. In an extraction study of metal ions with metal diethyldithiocarbamates, Wyttenbach and Bajo showed the kinetic inertness of the Fe(III) and Co(III) chelates$^{20}$.

Adsorption. Among the extracted pcd chelates, $Zn(pcd)_2$ exhibits most clearly a pre-wave and a main wave in the dc polarograms for the anodic exchange reaction at a concentration of more than $8.7\times10^{-5}$ M. The pre-wave is assigned to the adsorption wave of the product$^{24}$ from the results that: (a) the current-time curves during a single mercury drop life show that the current at the potential where the pre-wave is observed is approximately proportional to $t^{-1/3}$, while the current for main wave is proportional to $t^{1/6}$; and (b) the temperature coefficients of the limiting currents of the pre-wave and the total wave are $-1.1$% and $+1.3$% per degree, respectively, in the temperature range of 15 to 30°C. The surface excess of the electrode reaction product $Hg(pcd)_2$ at saturation is calculated from the average limiting current of adsorption$^{24}$ and found to be $\Gamma_s = 3.06\times10^{-10}$ mol/cm$^2$.

### REFERENCES

5) A. Hulanicki: Talanta, 14, 1371 (1967).

Keyword phrases
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