Studies on the Polarographic Analysis. (XXIV)

Use of Double Complexing Agents as Supporting Electrolyte. (2)

The EDTA–KCN Base Solution

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In the polarographic method of analysis, usually, a single complexing agent has been
used as a supporting electrolyte. However, it is difficult to mask the major component regulat-
ing at the same time the minor component in the proper reduction potentials.

In this paper, the use of double complexing agents is reported. For example, the base
solution consisting of EDTA and KCN has been proved to be effective for the analysis of
bismuth in the presence of much copper.

Besides these ions, the polarographic behaviors of 12 metals other than copper and bismuth
in this medium are also examined and the relations between the complexes formed in this
double complexing agents, the half wave potentials, the dissociation constants, reversibilities
of the electrode reactions and the dissociation rates of the complexes are all discussed.

Since such double complexing agent solution gives a new polarographic spectre series,
other sorts of double complexing agents besides EDTA–KCN are also discussed from the
point of polarographic analysis.

INTRODUCTION

The polarographic determination of trace of metals in the presence of much other
metal which is reduced at a more positive potential is usually difficult without preliminary
separation. For example, Stout et al., determined bismuth in the presence of copper
by using 0.5N ammonium acetate, 0.1N citric acid solution as supporting electrolyte
without separation of copper. But large amount of copper would make the determination
of bismuth impossible because the reduction wave of copper proceeds that of bismuth.
Therefore, the authors11 applied controlled potential electrolysis for the separation of
copper from trace amount of bismuth prior to the polarographic determination of bismuth.

It is well known that copper is masked with potassium cyanide and made polaro-
graphically inactive. Trace of metals such as Pb, Cd, Ni and Zn can be determined in the
presence of much copper in potassium cyanide base solution, but it is not suitable for
the determination of bismuth because it is precipitated as hydroxide in alkaline media.

The authors attempted to find the complexing agent forming a soluble and reducible
complex with bismuth in the presence of copper, and found EDTA (disodium salt of ethylenediamine tetraacetic acid or complexone III) to be very useful for this purpose. EDTA has been investigated polarographically by Schwarzenbach, Pribil, Pecsok, etc., and is known as a good complexing agent for the majority of cations. In this paper, the use of EDTA-KCN base solution is described as an example of the double complexing agents for the polarographic analysis of trace of bismuth in the presence of a large amount of copper by which the interference of copper is eliminated completely without any preliminary chemical separation.

Besides the above, polarographic characteristics of several ions such as Pb, Cd, Sn, As Mn, Ni, Co, Zn, Fe, Ag, Hg and Au are also investigated in the same base solution.

EXPERIMENTAL

Apparatus

Qualitative observations were carried out with the aid of pen-recording polarograph, and for quantitative measurements photo-recording polarograph was used. The saturated calomel electrode of H-type cell was used as the reference electrode and as anode. The pH was adjusted with the aid of a Beckmann glass electrode pH meter.

Reagent

EDTA solution: A 0.2M stock solution, was prepared by dissolving 37.2g. of pure EDTA, made by Kwanto Chemicals Co. Ltd., in 500ml. of water.

Potassium cyanide solution: 4M and 0.4M stock solutions containing 0.0007M potassium hydroxide were prepared.

Bismuth nitrate solution: A 0.01M stock solution containing 0.095M nitric acid was prepared.

Cupric sulfate solution: A 0.01M stock solution was prepared.

Two tenths per cent gelatin solution, 99% ethanol and 2M ammonium hydroxide-ammonium chloride solution were also prepared as stock solution.

The purity of supporting electrolytes was checked by running a residual current curve. The concentration of bismuth nitrate and cupric sulfate solutions was checked by a gravimetric method as the oxide.

Procedure

Bismuth nitrate solution in the presence or absence of cupric sulfate solution was made slightly alkaline by adding dilute sodium hydroxide using methylred as an indicator. Then potassium cyanide and EDTA solution were added in turn. The pH was adjusted with ammonium hydroxide-ammonium chloride solution and dilute hydrochloric acid solution with the aid of pH meter. This solution was diluted to the definite volume in the volumetric flask. Aliquot was transferred to the polarographic cell, and dissolved air was removed from the solution by bubbling purified hydrogen prior to the polaro-
graphic measurements.

Unless stated otherwise, concentrations of cations were 0.001M and those of EDTA and KCN were 0.1N in final solution.

(A) POLAROGRAPHIC CHARACTERISTICS OF BISMUTH

A series of experiment was performed to find a suitable condition for the estimation of bismuth in EDTA-KCN base solution.

(1) Effect of pH and the Concentration of Potassium Cyanide on the Bismuth Wave. The current voltage curves of bismuth solution containing EDTA-KCN base solution at a various pH are shown in Fig. 1. All curves are consisted of two ill-defined waves which are unsuitable for analytical purpose. When the concentration of potassium cyanide is 1N instead of 0.1N, the wave starts from the oxidation potential of cyanide ion and therefore the measurement of its half wave potential is impossible.

(2) Effect of Drop Time on the Bismuth Wave. The above-mentioned two-step waves are peculiar ones, for bismuth should show one reduction wave from trivalent bismuth ion to its metallic state, because its intermediate reduction step is not known. Effect of drop time of the mercury on the shape of bismuth wave was examined to determine whether two-step waves are due to the kinetic current or not. As the ratio of height of prewave to that of total wave was independent of the change of drop time, it is concluded that the two-step waves are not the kinetic ones.

(3) Effect of Gelatin on the Bismuth Wave. The shape of reduction wave of bismuth is little affected by the addition of gelatin and effective improvement of the wave is not expected.

(4) Effect of Ethanol on the Bismuth Wave. Polarographic characteristics of some materials are so often affected by ethanol that the addition of ethanol to the solution was examined. Fig. 2. shows that current-voltage curves of bismuth are strongly affected by ethanol. With increasing concentration of ethanol, prewave disappears gradually and well-defined single wave is obtained. However, addition of too much ethanol is useless because total wave height are decreased and the half wave potential is transferred toward more negative values.
From these experiments, 10% ethanol solution is supposed to be the most suitable for the analytical purpose.

(5) Relation between pH and the Half Wave Potential of Bismuth. From the results of foregoing experiments it is concluded that 0.1N EDTA, 0.1M KCN base solution containing 10% ethanol (pH 9.7) is the most suitable for the determination of bismuth. By using this base solution the dependence of the half wave potential of bismuth upon pH was investigated. Changing the pH from 8 to 9.5, the half wave potential is gradually shifted from -0.8V to -0.85V (vs. S.C.E.). Above the pH of 9.5, the half wave potential is independent of pH keeping a constant value of -0.85V.

(6) Discussion on the Bismuth Complexes. Bismuth in 0.1N EDTA solution (pH 9.7) in the absence of potassium cyanide and ethanol is reduced at the half wave potential of about -0.7V (vs. S.C.E.). The reduction wave coincides with that in the EDTA-KCN solution in the absence of ethanol. Typical polarograms are shown in Fig. 3. Bismuth is also reduced in 0.1N EDTA solution containing 10% ethanol (pH 9.7) and the wave is well defined and half wave potential is -0.85V (vs. S.C.E.), which coincides with that of bismuth in EDTA-KCN solution containing 10% ethanol.
From these experimental evidences following two postulates concerning the bismuth complexes in EDTA and or KCN solution may be possible;

(1) Two-step wave of bismuth in the absence of KCN and ethanol would be due to two species of complex; one is bismuth aquo ion and the other is EDTA complex. In the EDTA-KCN solution a part of bismuth aquo ion is replaced by cyanide ion. Here, the ratio of height of first wave to that of second wave would be equal to the ratio of concentrations of two species of bismuth complex.

(2) On the other hand, well-defined single wave in the presence of EDTA and ethanol is due to the bismuth EDTA complex.

Species of ligands in bismuth complexes may be represented as the following scheme:

<table>
<thead>
<tr>
<th>Base Solution</th>
<th>EDTA Ethanol</th>
<th>EDTA KCN</th>
<th>EDTA KCN Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>First Step</td>
<td>H₂O</td>
<td>—</td>
<td>H₂O CN</td>
</tr>
<tr>
<td>Second Step</td>
<td>EDTA</td>
<td>EDTA</td>
<td>EDTA</td>
</tr>
</tbody>
</table>

However, the explanation mentioned above is only a hypothetical one and further substantiation is needed.

(B) POLAROGRAPHIC CHARACTERISTICS OF COPPER

Cupric ion, when present together with EDTA or KCN, is soluble even in the basic medium, forming complex with them. As Cu-EDTA complex is less stable than Cu-cyanide complex (K_{Cu-EDTA} = 10^{-19}, K_{Cu-cyanide} = 10^{-27})⁹, all copper ion is expected to form cyanide complex Cu(CN)₄⁻⁻ and to produce no reduction wave in the mixed base solution regardless of the order of addition of both complex agents.

The following experiments which were different in preparing sample solution were carried out to ascertain this.

Procedure A: To the neutral cupric sulfate solution, KCN solution at first and then EDTA were added as in the case of bismuth analysis.

Procedure B: Similar to the procedure A, but EDTA solution was added at first to the cupric sulfate solution, then potassium cyanide was added to it.

In the case of procedure A, copper showed no reduction wave, on the other hand, in the case of procedure B, small reduction current which followed the anodic wave of cyanide ion was observed. The wave height did not decrease by further removal of the dissolved oxygen. Solution made by the procedure A was colorless but solution made by the procedure B had pale purple color at the beginning and gradually changed to blue and finally disappeared completely after about an hour.
According to the facts mentioned above, trace of Cu-EDTA complex once formed may exist in solution together with potassium cyanide for a fairly long time. This assumption was also ascertained by the following experiment.

A solution containing cupric ion and EDTA (purple color) and the other solution containing potassium cyanide (colorless) were separately deaerated by bubbling hydrogen. Then they were mixed and polarograms were recorded after 20, 40, 60, 80, and 120 minutes. These results are shown in Fig. 4. It seems to be reasonable to conclude that Cu-EDTA complex gradually changes to the cyanide complex in EDTA-KCN base solution, but the rate of transformation is so slow that a part of cupric ion remains as Cu-EDTA complex for a fairly long time.

It is obvious that procedure A is suitable for the masking of copper. Further, permissible maximum concentration of copper which is masked under given condition is about $10^{-2}$M. With increasing the concentration of copper above $10^{-2}$M, very ill-defined wave appears and it is followed by a gradually increasing current.

(C) DETERMINATION OF BISMUTH IN THE PRESENCE OF MUCH COPPER

From the foregoing experimental evidences described in sections (A) and (B), following procedure is recommended for the polarographic determination of trace of bismuth in the presence of much copper.

Sample solution is neutralized with dilute sodium hydroxide solution using methylred as an indicator. Then potassium cyanide, EDTA and ethanol are added in turn to make the solution containing 0.1N EDTA, 0.1M KCN and 10 % ethanol in the final definite volume. Aliquot of sample solution is transferred in the polarographic cell and after the removal of oxygen by bubbling hydrogen for about 20 minutes. Polarograms are recorded and the diffusion current at $-1.0V$ (vs. S.C.E.) is measured. In the presence or absence of copper the diffusion current is proportional to the concentration of bismuth in the range of $10^{-3}$M and $10^{-5}$M bismuth ion (See Fig. 5). Precise pH
adjustment in the final solution is not necessary because pH of the solution will be above 9.5 provided that the above procedure is followed, and the half wave potential of bismuth is constant in this pH range. Bismuth EDTA complex thus formed is very stable and is not precipitated after long standing.

(D) POLAROGRAPHIC CHARACTERISTICS OF SEVERAL CATIONS

Polarographic characteristics of several cations in EDTA-KCN base solution were also investigated. Concentrations of supporting electrolyte and cations and the procedure in preparing the solution were the same with the case of bismuth. The pH of the solution was always maintained at 9.7, and the results obtained are summarized in Table 1.

Fe, Hg, Au, Ag: Reduction waves of these ions proceed anodic wave of cyanide ion in this base solution.

Cd, Mn, Zn: These ions produce well defined waves in KCN solution but no reduction wave in EDTA solution. In EDTA-KCN solution, no reduction wave is observed, therefore they must form EDTA complexes.

Cu, Ni, Co: From the same reason as above, it is concluded that cyanide complex only is formed in the mixed base solution. This is also reasonable as is seen from their dissociation constant in EDTA and KCN solution (e.g. $K_{Ni\text{-EDTA}}=10^{-18}$, $K_{Ni\text{-cyanide}}=10^{-22}$). Nickel in this mixed base solution shows well defined wave identical with that in KCN solution, however, cobalt shows ill-defined wave followed by a gradually
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Table 1. Half wave potentials of cations (V vs. S.C.E.)

<table>
<thead>
<tr>
<th>Cations</th>
<th>0.1N EDTA</th>
<th>1M KCN</th>
<th>0.25M EDTA (pH 9.5)</th>
<th>0.1N EDTA (pH 9.5)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.1M KCN</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>-0.77*</td>
<td>ppt</td>
<td>-</td>
<td>-0.75*</td>
<td>*Prewave appears</td>
</tr>
<tr>
<td>Ca</td>
<td>NR</td>
<td>NR</td>
<td>-0.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>-1.25</td>
<td>-0.72</td>
<td>NR</td>
<td>-1.38 (-1.6)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>-1.42</td>
<td>-1.40</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co^{2+}</td>
<td>-1.40*</td>
<td>-1.3</td>
<td>NR</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb^{3+}</td>
<td>-0.75*</td>
<td>-1.20</td>
<td>-0.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn^{3+}</td>
<td>-1.0*</td>
<td>N R</td>
<td>N R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As^{3+}</td>
<td>N R</td>
<td>N R</td>
<td>N R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn^{2+}</td>
<td>N R</td>
<td>-1.33</td>
<td>N R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>N R</td>
<td>-1.18</td>
<td>N R</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>N R</td>
<td>-1.4*</td>
<td>N R</td>
<td></td>
<td>*0.1M KCN</td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>+</td>
<td>+</td>
<td>-0.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>+</td>
<td>+</td>
<td>-0.048*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au^{3+}</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td></td>
<td>*See REFERENCES (5)</td>
</tr>
</tbody>
</table>

NR: No reduction  ppt: precipitation.
+: Wave start at 0 applied e.m.f.

increasing current.

Bi, Sb: Bismuth shows two-step wave in EDTA-KCN solution as is reported in the preceding chapter. Sb^{3+} shows fairly well defined wave in EDTA-KCN solution but is gradually precipitated as hydroxide, therefore Sb-EDTA complex may be rather unstable.

Pb, Sn: They show peculiar behavior in EDTA-KCN base solution. Lead may be present as cyanide complex in this mixed base solution but half wave potential is shifted to the more negative potential than that of cyanide complex, therefore lead ion may be coordinated with EDTA to some degree in this medium. Stannic ion shows a poorly defined wave which starts at about -1.0V, but this ion is gradually precipitated in the mixed base solution.

As: Arsenic ion is not reduced at the dropping mercury electrode under above-mentioned conditions.

(E) DISCUSSIONS ON THE DOUBLE COMPLEXING AGENTS IN POLAROGRAPHY

Relation between dissociation constant of complex ions and their reduction poten-
When a complex ion is reduced reversibly at the dropping mercury electrode, its half wave potential is shifted to the more negative potential than that of simple ion and the difference is given by,

\[ (E_{1/2})_c - (E_{1/2})_s = \frac{RT}{nF} \ln K - \frac{RT}{nF} \ln C_x \]

where \( K \) is the dissociation constant of complex ion, \( p \) is the coordination number, and \( C_x \) is the concentration of complexing agent. Therefore, when double complexing agents of equal concentrations are used as supporting electrolyte, the complex ion of smaller \( K \) should be predominantly formed in the solution, and from equation (1) the complex ion thus formed should be the one having negative half wave potential among these two complex ions, as the negatively reducible complex ion should have less dissociation constant and should be predominantly formed in the mixed base solution. Actually, in EDTA-KCN solution, it is realized for the Cu, Cd, Mn and Zn ions. However, in the case of Ni, Co, Sb and Sn, the positively reducible wave remains. Moreover, in the reduction of Pb, the new half wave potential is observed in the double complexing electrolyte.

These opposite phenomena are interpreted as follows. (1) In the reduction of Ni, Co, etc., the complex ion formed in the mixed base solution are positively reduced, because of their better reversibility at the electrode, or (2) the complex ion formed is transferred to the another complex ion at the electrode surface as the reduction proceeds, or (3) the new complex ion of mixed ligands is formed such as in the reduction of Pb.

Besides EDTA-KCN base solution, other couples of double complexing agents may also be useful for the same purpose. But the base solution consisting of two chelating agents is supposed to be of little use because both dissociation constants would be almost parallel with each other as to many metal ions. Therefore, it would be preferable to select the agent in which one is the chelating agent and the other is an unidentate agent. Solutions such as tartrate-KCN and citrate-NaF etc. would be another interesting couples in the use of double complexing agents.

**SUMMARY**

Polarographic determination of trace of bismuth in the presence of a large amount of copper was successfully carried out by using double complex agent consisting of 0.1 N EDTA, 0.1M KCN, and 10 % ethanol (pH=9.7).

Only Sb\(^{3+}\) and relatively large amounts of Fe, Hg, Au and Ag interfere this determination.

To prepare sample solution, it must be noted to add potassium cyanide at first to the neutralized sample solution, and EDTA to the next, otherwise trace of Cu-EDTA
complex shows reduction wave which coalesces bismuth wave.

EDTA-KCN base solution would be also good medium for determining traces of bismuth and antimony in the presence of a large amount of lead, cadmium and zinc.

REFERENCES

(1) M. Ishibashi and T. Fujinaga, Japan Analyst 2, 344 (1953).