Extraction-Polarography of Cobalt(II)-Diethyl-dithiocarbamate Using Acetonitrile as a Solvent

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Cobalt(II)-diethyl-dithiocarbamate in a salted-out acetonitrile gives two waves of the d.c. polarogram with a dropping mercury electrode. The first wave with $\bar{E}_f = -0.45$ V vs. SCE is due to the adsorption of the complex onto the mercury electrode. The second wave with $E_f = -0.98$ V is of diffusion-controlled nature and its wave-height is directly proportional to the concentration of cobalt(II) in the range of 0.5–10 μg/ml (the organic phase). Conversely the first wave becomes gradually high with increased concentration of cobalt(II), but there is no linear relationship between them. The square-wave polarographic determination of cobalt(II) in aqueous solutions is possible at the concentration range 0.05–2.0 μg/ml, after it was salted-out with sodium citrate into the acetonitrile phase. Nickel(II), copper(II) and bismuth(III) at the same amount of cobalt(II) do not interfere with the determination. Iron(III) is masked by addition of sodium fluoride.

INTRODUCTION

Several polarographic methods coupled with the use of solvent extraction have been reported for the determination of metal ions. It is considered preferable that the organic solvent used has a high dielectric constant, a low viscosity and inertness in addition to the property as being a good extractant. In this laboratory acetonitrile has been used as the most suitable solvent for the polarographic determination of metal ions after salting-out extraction of their ion-pair compounds. This method has the

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advantage over the conventional polarography that the sensitivity of determination is improved because the organic solvent is not viscous (0.325 cP) and inert (e.g., DN=14.1), and of course that matrix or interfering ions are eliminated through the salting-out extraction process. This salting-out procedure probably seems useful for other analytical purposes.

As part of a series of studies, we describe the polarographic behavior of metal diethyldithiocarbamates (non-ionic chelates) and its application to the determination of micro amounts of cobalt(II) in aqueous medium.

EXPERIMENTAL

Apparatus.

D.c. and square-wave (s.w.) polarograms were recorded with the Yanagimoto (Kyoto) Model P-8 and PA-202 polarographs respectively. The dropping mercury electrode has the characteristics: m = 0.873 mg/sec, t = 4.63 sec in acetonitrile at open circuit. A capacitor of 100 μF was inserted between a platinum wire counter-electrode and a saturated calomel electrode (SCE). A controlled drop-time of 1 sec was used with the mechanical drop timer unless otherwise stated. A Toa-Dempa HM-5A pH meter was used for pH checks.

Reagents.

All reagents used were of analytical reagent grade. All solutions were prepared with distilled water. Standard solutions of metal ion were from the Wako Pure Chemical Co Ltd. (1000 ppm standard solution). Tetra-n-butylammonium perchlorate (TBAP) and acetonitrile were the same previously mentioned\(^{10}\).

Procedure.

Place a standard solution containing less than 0.5 μg of cobalt(II) in a 50-ml stoppered centrifuge tube. Add 1 ml of 0.1 M sodium diethyldithiocarbamate solution and make up to 10 ml with distilled water. After a few minutes, add 10 ml of 0.1 M TBAP solution in acetonitrile and 5 g of sodium citrate, shake the mixture for 1 min, and allow it to stand for 1 min to separate the two phases. Take a portion of the acetonitrile phase in a polarographic cell and bubble nitrogen through the extract for 3 min. Record the d.c. or the s.w. polarogram against SCE (25±0.1)°C.
RESULTS AND DISCUSSION

D.c. polarograms for metal diethyldithiocarbamates.

It is well-known that such metal ions as copper(II), iron(III), bismuth(III), cobalt(II), nickel(II) and manganese(II) react with the diethyldithiocarbamate ion in a moderately acidic aqueous medium and the metal complexes formed are extracted into chloroform or methylisobutyl ketone\(^{12}\). We have examined to extract the metal diethyldithiocarbamates into an acetonitrile phase from ammonium dihydrogen citrate solutions. Preliminary experiments indicated that the copper(II), manganese(II), iron(III), bismuth(III) and cobalt(II) diethyldithiocarbamates could be extracted into the acetonitrile to a greater extent, while the lead(II), cadmium(II) and zinc(II) complexes showed no extractability even through the present salting-out extraction step. It seems likely that ammonium dihydrogen citrate plays a role as the masking agent for some metal ions as well as the buffering one; the selectivity of determination should be highly enhanced if this masking effect due to the citrate ion is utilized.

Fig.1 shows typical d.c. polarograms obtained for metal diethyldithiocarbamates in a salted-out acetonitrile. The cobalt(II), manganese(II), copper(II), iron(III) and bismuth(III) complexes showed distinct d.c. waves at potentials between -0.4 V and -0.6 V vs. SCE. In cases of copper(II) and manganese(II), higher wave-height was obtained owing to good extractability. On the other hand, lead(II), cadmium(II), zinc(II) and indium(III) showed no d.c. wave as we originally expected. The d.c. wave for the nickel(II) complex was appeared at -0.90 V, being in close contact with the second d.c. wave of the cobalt(II) complex. The cobalt(II) complex gave two reduction waves with \(E_{1/2} = -0.45\) V and -0.98 V vs. SCE. The \(E_{1/2}\) value of the second wave is widely different from those of the other metal complexes except for nickel(II). Accordingly the d.c. polarographic determination of cobalt(II) following the extraction is expected to be more selective than the d.c. polarography run in aqueous medium. The relationship between wave-height and concentration of cobalt(II) was investigated. It can be seen from Fig.2 that the second d.c. wave-height was proportional to the concentration of cobalt(II) taken. The first d.c. wave-height of the cobalt(II) complex became gradually high as the metal ion was increased, and at higher concentrations it
Fig. 1. D.c. polarograms of metal di-thiocarbamates in acetonitrile.

1: Co(II); 2: Mn(II); 3: Cu(II); 4: Fe(III); 5: Bi(III); 6: Ni(II); 7: blank
each metal ion taken: 100 µg

Fig. 2. Relationship between limiting current and concentration of Co(II).
O: first wave; ●: second wave
approached to an approximately constant value.

Nature of the d.c. waves.

In order to know whether the metal diethyldithiocarbamate adsorbs onto the mercury electrode or not, the drop-time of the mercury electrode was examined at potentials ranging from +0.1 V to -1.3 V in a salted-out acetonitrile. Fig.3 shows the electrocapillary curves obtained for the diethyldithiocarbamate complexes of cobalt(II), nickel(II), manganese(II), iron(III) and copper(II). A sharp decrease of drop-time due to adsorption was observed between -0.2 V and -0.6 V in all cases except for the iron(III) complex. From this result, it is clear that the first d.c. waves appearing at nearly -0.4 V, e.g. the cobalt(II), manganese(II) and copper(II) complexes, are produced as a result of their strong adsorption with the mercury electrode followed by reduction. The data obtained for the cobalt(II) complex showed that the degree of adsorption was gradually large as the metal concentration was increased and it had a great influence on the first d.c. wave-height. The d.c. wave of the iron(III) complex is probably a diffusion-controlled one because no adsorption was observed at its concentration of 10 μg/ml. It is interesting that Kitamura et al. 13) have obtained a similar result for iron(III)-pyroridinedithiocarbamate in methylisobutyl ketone.

The second d.c. wave of the cobalt(II) complex showed a diffusion-controlled nature, because the limiting current at -1.1 V depended upon the mercury pressure according to $h^{\frac{1}{2}}$, and upon temperature. A plot between wave-height of the second step and concentration of cobalt(II) was found to be linear in the range from 0.5 to 10.0 μg/ml.

S.w. polarographic determination of Co(II).

It is possible to greatly improve the sensitivity of determination for cobalt(II) by using the s.w. polarography in the place of the d.c. mode. A typical s.w. polarogram is given in Fig.4. A sharp peak at -1.05 V was obtained for the extracted cobalt(II) complex in an acetonitrile, and was based on the electron transfer Co(II)$\rightarrow$Co(I). It is evident from Fig.5 that the maximum peak-current was obtained for extractions at the pH values ranging from 8.0 to 10.5. When sodium citrate was used as the salting-out agent, the peak-current was proportional to the cobalt(II) concentration over the range of 0.05–2.0 μg/ml with respect to the aqueous phase. As a result, the
Fig. 3. Electrocapillary curves of metal dithiocarbamates in acetonitrile.
1: blank; 2: Fe(III); 3: Co(II); 4: Cu(II); 5: Ni(II); 6: Mn(II)
each metal ion taken: 50 µg
Fig. 4. Typical s.w. polarograms of Co(II).

Concentration of Co(II): a 0.5; b 1.0 µg/ml

Fig. 5. Effect of pH on extraction of Co(II).
Concentration of Co(II): 1.0 µg/ml
The present s.w. polarographic method is very sensitive and therefore suited for the determination of traces of cobalt(II) in aqueous solutions.

The effect of foreign ions on the determination of cobalt(II) (10 μg) was investigated. The following metal ions were tolerable as given below in parentheses: K(I), Mn(II), Zn(II), Cr(III) (1000 μg); Fe(III), Pb(II), Cd(II), Mo(VI), Sb(III), Sn(II), Ti(IV) (100 μg); Cu(II), Ni(II), Bi(III) (10 μg). Interference from 1.0 g of iron(III) could be eliminated by adding 0.2 g of sodium fluoride. If large amounts of copper(II), nickel(II), and bismuth(III) are present, cobalt(II) may be determined after it was separated from those metal ions by extraction from 1–2 N hydrochloric acid with 1% sodium diethyl-dithiocarbamate in benzene\textsuperscript{12}.

**REFERENCES**