The Solvent Extraction-Polarographic Determination of Cadmium(II) as the Tris(2,2′-bipyridine)iron(II) Tetraiodocadmate(II) Complex*

Kiyoshi HASEBE, Tsukasa OHTSUKI, and Tomihito KAMBARA

Department of Chemistry, Faculty of Science, Hokkaido University, Kita-ku, Sapporo 060

(Received March 18, 1974)

A new method for the solvent extraction-polarographic determination of cadmium has been proposed. The quaternary complex formed by the tris(2,2′-bipyridine)iron(II) cation and the tetraiodocadmate(II) anion can be readily extracted into benzyl alcohol. The extracted complex shows a well-defined reduction wave in the ternary electrolyte-solvent mixture, composed of benzyl alcohol, an aqueous electrolyte solution, and methyl cellosolve. The available range of the present method covers from 5.7×10^{-6} to 91.4×10^{-6} M of cadmium(II) in the aqueous phase. The optimum pH range for extraction is 3—9, and the extracted species is stable in the ternary solvent mixture for 5 hr. Zinc (II), bromide, and chloride ions do not interfere, but copper (II), mercury(II), and iron(III) do interfere.

Among the several methods devised for the determination of cadmium, especially the spectrophotometric method using dithizone[1] and the polarographic method,[2] are the most useful. 2,2′-Bipyridine (bpy) and related compounds are well known as remarkably useful colorimetric reagents for analytical use.[3] As to the determination of cadmium, for example, a spectrophotometric determination employing the ion-pair formation of the tetraiodocadmate(II) anion with the tris(2,2′-bipyridine)iron(II) cation has been reported.[4] However, this method makes it necessary to pay careful attention to the absorbance of the reagent blank solution. Fujinaga *et al.*[5] and the present authors[6,7] have already reported a polarography in a ternary solvent mixture consisting of chloroform, water, and methyl cellosolve (MCS). Recently, Kitagawa and Ichimura[8] have reported an interesting extraction-polarography of an extracted complex of tris(acetylacetonato)iron(III) and similar complexes in the methyl iso-butyl ketone. These methods are very useful since the concentration and separation can be achieved simultaneously. In the present paper, the solvent extraction-polarographic method is applied to the quaternary complex of tris(2,2′-bipyridine)iron(II) tetraiodocadmate(II) $[Fe(bpy)_3][CdI_4]$.

Experimental

Reagents. *2,2′-Bipyridine solution*: An aqueous 2×10^{-2} M solution was prepared.

Standard Iron(II) Solution: Mohr's salt was dissolved in water containing a small amount of sulfuric acid to give a 2×10^{-2} M solution. This was then standardized by EDTA titration.

Standard Cadmium(II) Solution: Guaranteed cadmium nitrate (Wako Chemicals) was dissolved in water containing sufficient nitric acid to give a 2×10^{-3} M solution. This was then standardized by EDTA titration with Eriochrome Black T as the indicator. This stock solution was used after accurate dilution.

Buffer Solutions: The pH was adjusted with the following solutions: hydrochloric acid (pH 1—3), acetic acid-sodium acetate (pH 3—6), and potassium dihydrogen phosphate-sodium borate (pH 9—10).

All the reagents used were of an analytical reagent grade.

Apparatus. A Yanagimoto polarograph, model PA-102, was used for recording the DC and AC polarograms. The DME had these characteristics: $m=1.88$ mg s^{-1} in pure water and $t=4.96$ s in the electrolysis solution at open circuit at $h=39$ cm. The experiments were carried out by using a cell with a mercury pool or a modified H-type cell with an SCE in a water bath thermostated at (20+0.1) °C. Before each polarographic measurement, all the solutions were deaerated by bubbling through for 15 min nitrogen gas which has been presaturated with the same solution as that used in the measurements.

A Hitachi-Horiba glass electrode pH meter, model F-5, was used. An Iwaki shaker, model KM, was used for the shaking.

Results and Discussion

Established Procedure. Twenty millilitres of a 2×10^{-2} M 2,2′-bipyridine solution was pipetted into a 100-ml separatory funnel. Five millilitres of a 3 M iron(II) solution, 3 ml of a 3 M sodium acetate solution, 1 ml of a 3 M potassium iodide solution and the sample solution containing the cadmium ion were pipetted into the funnel in that sequence. After adjusting the volume to 35 ml with water, the solution was let stand for about 2 min. It was then shaken with 10 ml of benzyl alcohol for 3 min. After the separation of the two phases, a 6-ml portion of the extract was pipetted into a 20-ml volumetric flask, and then 6 ml of aqueous 1 M potassium iodide was added as a supporting electrolyte. The flask was filled up to the mark with MCS. After deaeration with nitrogen gas, a polarogram was recorded.

Choice of Extracting Solvent. Five of the extracting solvents examined—namely, nitrobenzene, methyl *iso*-butyl ketone, 1, 2-dichloroethane, cyclohexanone, and chloroform, all of which have a relatively large dielectric constant,—extracted only a small amount of cadmium (II) in the form of the quaternary complex of $[Fe(bpy)_3$-$CdI_4]$, and some of the above-mentioned solvents also caused a film at the interface between the two phases. Therefore, the above solvents were not suitable. When benzyl alcohol was used, however, tetraiodocadmate (II) was extracted quantitatively as the quaternary complex with the tris(2, 2′-bipyridine)iron(II) complex. Benzyl alcohol was, therefore, used in the present work.

Extractability. In order to confirm that tetraiodocadmate(II) anions were quantitatively extracted into benzyl alcohol as a quaternary complex, hydrogen

* Presented at the 19th Annual Meeting of the Polarographic Society of Japan, Sapporo, October, 1973.

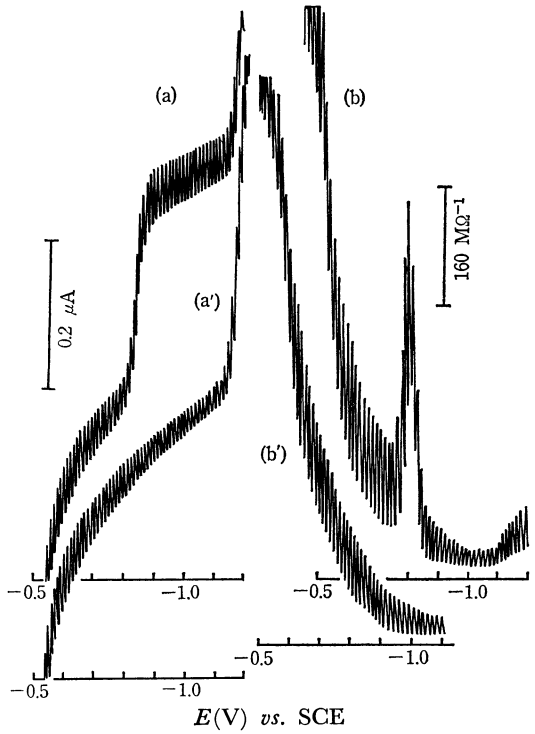

Fig. 1. The polarograms of the quaternary complex composed of tetraiodocadmate(II) anion with tris(2,2'-bipyridine)iron(II) cation into the ternary solvent mixture.
Concentration of iodide ion in aq. phase: $[I^-]_w = 8.58 \times 10^{-2}$ M, Concentration of bpy in aq phase: $[bpy]_w = 1.14 \times 10^{-2}$ M, Concentration of iron(II) in aq. phase: $[Fe(II)]_w = 2.86 \times 10^{-3}$ M, pH 7.5, Volume of aq. phase $V_w = 35$ ml, Volume of org. phase $V_0 = 10$ ml, (a) and (b): 6.86×10^{-5} M of Cadmium(II) in aq. phase, (a') and (b'): Without cadmium(II), (a) and (a'): DC polarogram, (b) and (b'): AC Polarogram.

sulfide was bubbled into the aqueous phase after the extraction. No yellow precipitate was formed. Upon carrying out a second extraction, cadmium could not be found in the aqueous phase; *i.e.*, the cadmium has been removed completely from the aqueous phase by a single extraction.

Polarograms of the Extracted Quaternary Complex in the Ternary Solvent Mixture. The polarograms obtained by the use of the established procedure are shown in Fig. 1. The half-wave potential of the complex was about −0.80 V *vs.* SCE. As may be seen from Fig. 1, no DC polarographic wave and no AC peak appeared in the absence of cadmium.

Effect of pH. The effect of the pH on the extraction of the quaternary complex was studied with several buffer solutions and sodium acetate. An approximately constant DC wave height and AC peak height were obtained between pH 3.72 and 9.39. Thus, the pH of the aqueous solution was adjusted to about 7 by adding sodium acetate solution, according to the Kotsuji method.[4]

Effect of Shaking Time and Standing Time. A constant DC wave height, or the corresponding AC peak height, was obtained by shaking for more than

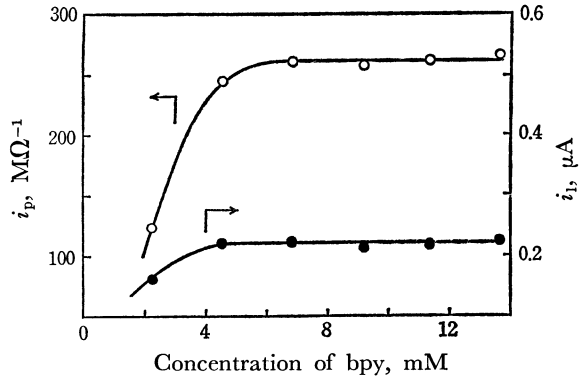

Fig. 2. Effect of 2,2'-bipyridine concentration on the extraction of the quaternary complex, $[Fe(bpy)_3CdI_4]$. ○: AC peak height, ●: DC wave height, $[Cd(II)]_w = 5.72 \times 10^{-5}$ M. Other conditions are the same as in Fig. 1.

1 min; we chose the shaking time of 3 min. The extracted species was very stable, its polarographic DC wave height in the ternary solvent mixture showed no change for 5 hours, and the corresponding AC peak height also remained unchanged.

Effect of the 2,2'-Bipyridine Concentration. With the concentrations of cadmium(II), iodide ion, and iron(II) kept constant, various amounts of 2,2'-bipyridine were added, after which the extraction was carried out according to the above procedure. The DC wave height, or the corresponding AC peak height of the ternary mixture, was found to be constant and at its maximum when the mole ratio of bipyridine to cadmium(II) was in the range from 100 to 250, as is shown in Fig. 2.

Effect of the Iodide and Iron(II) Concentrations. The DC wave height and the corresponding AC peak height in the ternary solvent mixture consisting of the extract, aqueous electrolyte, and MCS were found to be constant when the concentrations of iodide and iron(II) ions in the aqueous phase were higher than 4×10^{-2} M and 3×10^{-3} M respectively. Figure 3 shows the effect of the iron(II) concentration on the DC polarographic wave height, and the corresponding AC peak height. When the concentration of iron(II) was lower than

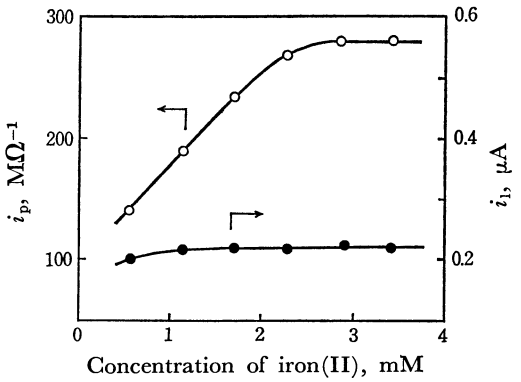

Fig. 3. Effect of iron(II) concentration on the extraction of the quaternary complex.
○: AC peak height, ●: DC wave height, $[Cd(II)]_w = 5.72 \times 10^{-5}$ M. Other conditions are the same as in Fig. 1.

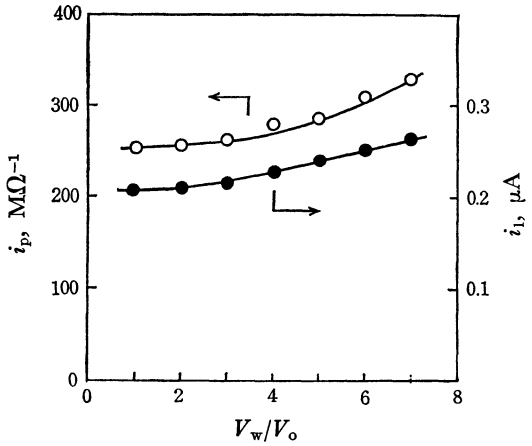

Fig. 4. Effect of aqueous-to-organic volume ratio (V_w/V_o) on DC wave height, or the corresponding AC peak height.
$V_o = 10$ ml, $V_w = 10$—70 ml, $[Cd(II)]_w = 5.72 \times 10^{-5}$ M.
Other conditions are the same as in Fig. 1.

3×10^{-3} M in the aqueous phase, a decrease of the AC peak height was observed. It can be seen that the excess of bpy reacts with cadmium(II) and produces a non-reducible complex, which is more stable than the tetraiodocadmate(II) complex.[9] Therefore, it is desirable that the excess of bpy be changed into the tris(2,2'-bipyridine)iron(II) chelate,[9,10] by the addition of an excess amount of iron(II).

Effect of the Aqueous-to-Organic Volume Ratio on the Polarogram. While keeping other conditions constant, the effect of the aqueous-to-organic volume ratio on the polarogram was studied by the polarographic method. The results are shown in Fig. 4, from which it is found that an increase in the volume ratio produced an increase in the DC wave height and also in the corresponding AC peak height. This is caused by the decrease in the volume of the organic phase by the mutual dissolution. Consequently, the aqueous-to-organic volume ratio should be adjusted to an approximately constant value.

Choice of Supporting Electrolyte. Several supporting electrolytes were investigated; the results are summarized in Table 1. As the supporting electrolyte, potassium iodide was the most suitable for the polarographic measurement.

Miscible Organic Solvent. As possible miscible solvents, methanol, ethanol, dioxane, and MCS were selected and investigated. Methanol and ethanol were found not to be suited for being miscible solvents, however, because these solvents were easily evaporated by bubbling nitrogen gas and did not mix well. The other two solvents were found to be very miscible. However, a better-defined polarogram was obtained by using MCS rather than dioxane.

Effect of Diverse Ions. The interference of diverse ions was examined; the results are given in Table 2. According to the familiar *t*-tests, not even a 100 : 1 mole ratio of zinc and bromide ions, or a 50 : 1 mole ratio of the chloride ions to cadmium(II) ions interfered with the solvent extraction-polarographic measurement. Copper(II), iron(II), and mercury(II) ions interfered seriously, however.

Calibration Curve. According to the established procedure described above, the calibration curve was drawn; the results are given in Fig. 5. It was found that the difference between the two averages of the two days was not found to be significant at the 95% level by the familiar *t*-test, using the data obtained

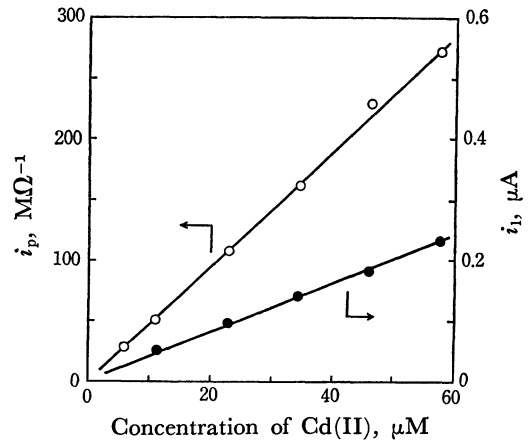

Fig. 5. Calibration curve of cadmium(II) in aqueous phase.
Data obtained under the same conditions as in Fig. 1.

Table 1. List of aqueous supporting electrolyte solutions utilized in preparation of the water-benzyl alcohol-MCS ternary mixture

Supporting electrolyte		Remark	
Name	Final Concn., M	DC Wave	AC Peak
H_2SO_4	0.3	Good Adsorption wave appears	Adsorption wave appears
$HClO_4$	0.3—0.9	Bad Adsorption wave appears	Bad
HCl	0.3—1.2	Bad	Good
HNO_3	0.3	Maximum wave appears	Good
LiCl	0.3	Not well-defined	Good
NaCl	0.3	Not well-defined	Good
KCl	0.3	Not well-defined	Good
KI	0.09—0.9	Very good When the concn. is decreased, adsorption wave appears.	Very good

TABLE 2. EFFECT OF INTERFERENCE OF DIVERSE IONS ON THE EXTRACTION OF 5.72×10^{-5} M Cd(II)

Ion	Molar concn. ratio to cadmium(II)	DC wave height and AC peak observed					
		DC (μA)			AC ($M\Omega^{-1}$)		
None		0.226	0.222	0.224	268	276	266
Cu^{2+}	10	a)			264	270	274
(as $CuSO_4$)	50	a)			194	192	196
	100	a)			160	162	160
Zn^{2+}	10	0.224	0.222	0.226	262	256	262
(as $ZnSO_4$)	50	0.218	0.216	0.214	258	264	260
	100	0.222	0.220	0.222	280	276	280
Fe^{3+}	10	0.230	0.226	0.222	264	272	264
(as iron alum)	50	b)					
	100	b)					
Hg^{2+}	10	c)			164	158	164
(as $HgSO_4$)	50	c)			136	136	136
	100	c)			56	52	54
Br^-	10	0.234	0.234	0.228	266	252	260
(as KBr)	50	0.216	0.210	0.210	264	266	268
	100	0.210	0.212	0.208	266	268	264
Cl^-	10	0.218	0.218	0.218	252	252	252
(as KCl)	50	0.206	0.200	0.208	264	266	258
	100	0.206	0.210	0.206	248	248	254

a) Well-defined DC polarogram is not obtainable. b) An inhomogeneous solution is formed. c) Mercury(II) ion behaves similarly to cadmium(II), therefore, the tris(2,2'-bipyridine)iron(II) complex cation concentration decreases.

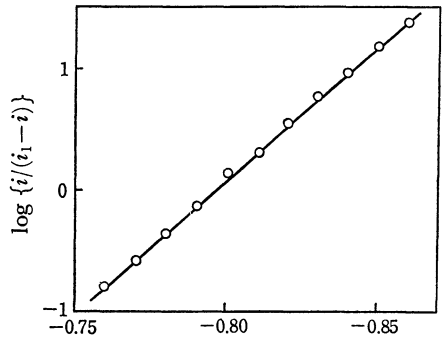

Fig. 6. Relationship between E and $\log\{i/(i_l-i)\}$. $[Cd(II)]_w=6.67\times10^{-5}$ M, $[I^-]_w=0.1$ M, $[bpy]_w=1.33\times10^{-2}$ M, $[Fe(II)]_w=3.33\times10^{-3}$ M, pH 7.5; Slope=45 mV, iR-drop: not corrected.

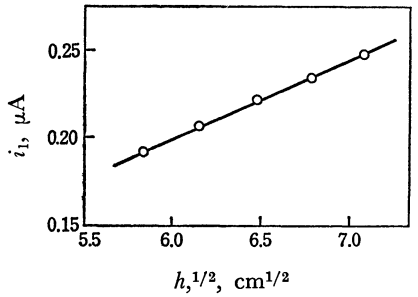

Fig. 7. Variation of i_l with the height of mercury column, h.
$[Fe(II)]_w=2.86\times10^{-3}$ M. Other conditions are the same as in Fig. 3.

with the 4.75×10^{-5} M cadmium(II) ion in the aqueous phase.

Characteristics of Limiting Current. The tetraiodocadmate(II) ion undergoes a two-electron reduction to the cadmium amalgam in a single step. An analysis of the log plot indicated the quasi-reversible nature of the process, the value of the slope being 45 mV at 20 °C, as is shown in Fig. 6. The reduction was diffusion-controlled as is evident from the linear plot of i_l against $h^{1/2}$, shown in Fig. 7. The relative temperature coefficient of the limiting current was 1.83% K^{-1} at 20 °C.

The authors wish to thank the Ministry of Education for the financial support granted for this research.

References

1) The Japan Society for Analytical Chemistry, ed., "Bunseki Kagaku Binran," Maruzen Publishers, Tokyo (1971), p. 142.
2) B. Breyer and H. H. Bauer, "Alternating Current Polarography and Tensammetry," Interscience Publishers, New York, N.Y. (1963), p. 147.
3) A. A. Schilt, "Analytical Applications of 1, 10-Phenanthroline and Related Compounds," Pergamon Press, London (1969).
4) K. Kotsuji, This Bulletin, **38**, 988 (1965).
5) T. Fujinaga, H. Brodowsky, T. Nagai, and K. Yamashita, *Rev. Polarog.* (Japan), **11**, 217 (1963).
6) T. Kambara and K. Hasebe, *Bunseki Kagaku*, **14**, 491 (1965).
7) T. Kambara, T. Ishii, and K. Hasebe, *Nippon Kagaku Kaishi*, **1972**, 920.
8) T. Kitagawa and A. Ichimura, *Bunseki Kagaku*, **22**, 1042 (1973).
9) H. Freiser and Q. Fernando, "Ionic Equilibria in Analytical Chemistry," John Wiley & Sons Inc., New York, N. Y. (1963), p. 310; translated in Japanese by T. Fujinaga and E. Sekido, Kagakudojin, Kyoto (1967), p. 256, 257.
10) L. G. Sillen and A. E. Martell, ed., "Stability Constants of Metal-Ion Complexes," The Chemical Society, London (1964), pp. 616, 617.