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Polarographic Trace Analysis of Cadmium(II) after Solvent Extraction Using the Salting-out Method

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A selective and sensitive method is presented for the determination of cadmium(II), based on polarography after salting-out extraction into acetonitrile. The effect of nonaqueous solvents, salting-out agents, and the concentration of reagents has been studied. Under the conditions established, the cadmium(II) iodide complex extracted into the solvent gives a well-defined d.c. wave and a sharp a.c. peak, with $E_{1/2}$ and $E_p = -0.72$ V *vs.* SCE respectively. Down to 0.50 ppm of cadmium(II) in the original aqueous solution can be determined by the proposed method. Lead(II) and In(III) do not interfere up to a 1000-fold amount relative to Cd(II). Interference from Fe(III) and Tl(III) can be eliminated by the addition of ascorbic acid.

The polarographic behavior of metal complexes in nonaqueous solvents has been reported in various papers.[1,2] As for analytical applications, the polarographic analysis of methods after extraction have been studied using chloroform,[3] 4-methyl-2-pentanone (MIBK),[4] and benzyl alcohol,[5] in which cases the extract has been diluted with other polar solvents, such as water, methyl cellosolve, or methanol, to obtain a higher conductivity of the medium. Recently, Kitagawa and Ichimura[6] have reported the d.c. polarographic determination of metals in the MIBK extract. These methods, however, still seem insufficient with respect to the sensitivity and selectivity of the determination.

The salting-out effect is useful for analytical purposes in order to increase the extractability of species and to facilitate phase separation in the liquid-liquid extraction. Matkovich and Christian[7] have used the salting-out phenomenon in the separation of acetone from an aqueous solution and have determined the cobalt(II) in the extract by means of atomic-absorption spectrophotometry. Kawamoto and Akaiwa[8] have also studied a spectrophotometric determination of iron(III) after extraction into 2-propanol by the salting-out method.

In a previous paper,[9] an attempt has been made to utilize the salting-out technique for the extraction-polarographic method of analysis, in which both extraction and polarography have been carried out with acetonitrile. In the present paper, the phase separation of various organic solvents from an aqueous solution has been investigated and has been used for the polarographic determination of cadmium(II) after the salting-out extraction of the iodide complex. Acetonitrile as the solvent has a relatively low viscosity (0.345 cP) and a high dielectric constant (37.5), and it dissolves many ion-pair compounds, particularly tetraalkylammonium salts as supporting electrolytes; the resulting solution has a high conductivity. Further, the solvent is easily salted-out from an aqueous solution with various inorganic compounds. With ammonium sulfate as the salting-out, cadmium(II) in an aqueous solution can be extracted quantitatively into the acetonitrile phase as the ion-pair of tetrabutylammonium tetraiodocadmate, $NR_4[CdI_4]$; tetrabutylammonium iodide (TBAI) has been added not only as the reagent to form the tetraiodocadmate(II) complex, but also as the supporting electrolyte for the polarographic measurements. The present method constitutes a useful means of solving some problems in polarographic analysis.

Experimental

Reagents. Standard cadmium(II) solution (100 ppm): 0.247 g of cadmium(II) nitrate was dissolved in 20 cm^3 of 0.1 mol dm^{-3} nitric acid, after which the solution was diluted to 1 dm^3 with water. The acetonitrile was purified by distillation once from phosphorus pentaoxide. The ammonium sulfate (Wako Junyaku Co., Ltd.) for atomic-absorption spectrometry, the TBAI (Tokyo Kasei Co., Ltd.), and the Karl Fisher reagent (Mitsubishi Kasei Co., Ltd.) were used without further purification. The other chemicals were of guaranteed grade. Redistilled water was used throughout this study.

Apparatus. Two Yanagimoto polarographs, Model P8-D with a three-electrode system and PA-102, were used for the d.c. and a.c. polarographic measurements. In the a.c. polarographic measurements, a capacitor of 100 μF was inserted between the platinum wire counter electrode and the aqueous saturated calomel reference electrode. The DME had the following characteristics at a mercury head of 60 cm: $m = 0.783$ mg s^{-1}, $t = 3.98$ s in acetonitrile with an open circuit. A Toa Denpa pH meter, Model HM-5A, was used for the pH measurements.

Salting-out Experiment. Aliquots of water and an organic solvent were placed in a 50.0-cm^3 stoppered volumetric cylinder which had been calibrated before use. After a salting-out agent had been added to the mixture, the volume of the two phases was measured and the amount of the water present in the organic phase was determined by the Karl Fisher titration method.

Procedure. An aliquot of the standard cadmium(II) solution was placed in a 50.0-cm^3 stoppered centrifuge tube, and the volume was adjusted to 20.0 cm^3 with water. After 10.0 cm^3 of a 0.1 mol dm^{-3} TBAI solution in acetonitrile had then been added to it, the mixture was shaken with 10.0 g of ammonium sulfate for 1 min and then allowed to stand for 1 min. A portion of the extract was placed in a polarographic cell and deaerated for 3 min. The d.c. and a.c. polarograms were recorded against SCE at (25±0.1) °C.

Results and Discussion

Solvent for Polarographic Use. The phase separation of various organic solvents suitable for the polarography after salting-out extraction was investigated with ammonium sulfate. Table 1 summarizes the salting-out

Table 1. Salting-out data with ammonium sulfate for water-miscible solvents

Solvent	Organic phase-volume recovered/cm^3	Water content of organic phase/(v/v %)	Dielectric constant	Viscosity/cP
Acetonitrile	10.2	9.8	37.5	0.325
Acetone	12.2	29.1	20.7	0.304
Dioxane	10.0	35.6	2.2	1.087
Tetrahydrofuran	10.0	6.2	7.5	0.460
Ethanol	14.5	50.6	24.6	1.078
1-Propanol	12.5	19.5	20.3	2.004
1-Butanol	10.3	7.7	17.5	2.271
2-Methoxyethanol	15.5	44.3	29.6	1.85
2-Buthoxyethanol	10.4	10.6	9.3	3.12
1,2-Dimethoxyethane	13.7	43.4	7.2	0.455
Propylene carbonate	9.9	4.7	64.4	2.53

The initial volumes of the water and the non-aqueous solvent were 10.0 cm^3 each. The phase separations were carried out from a saturated ammonium sulfate solution.

data: the volume and the water content of the organic phase after phase separation, together with the dielectric constant and the viscosity of the pure solvents. In the polarography after extraction, it is considered preferable for the solvent to have such properties as a low mutual solubility with water, a high dissociation constant of extracted species, and a high conductivity. Acetonitrile was found to be the most useful among the solvents examined. Propylene carbonate and 1-butanol seem fairly useful, provided a suitable salting-out agent is present. Methanol, *N,N*-dimethylformamide, dimethyl sulfoxide, and pyridine did not cause any phase separation.

Salting-out Agent. Various inorganic salts were investigated as possible salting-out agents for the phase separation of acetonitrile from aqueous solution. Table 2 summarizes the minimum salt quantities required to cause phase separation, and also the volume and the water content of the acetonitrile phase after saturation with the salt. It may be concluded from Table 2 that the phase separation takes place more easily with the salt of multivalent ions than with that of univalent ions. The water content of the acetonitrile phase decreased in this order: alkali ion>alkaline earth ion>aluminum ion, with respect to their chloride salts. Among the inorganic salts tested, all the sodium and ammonium salts showed a water content of about 10%, except for sodium acetate. Ammonium sulfate as a salting-out agent is useful for the polarographic determination of cadmium(II) because of the high extractability of the complex.

Volume Ratio after Phase Separation. The initial volume of water was varied from 10.0 to 50 cm^3 against 10.0 cm^3 of acetonitrile. The aqueous and acetonitrile phase-volumes were measured after the mixture was saturated with ammonium sulfate. The results are shown in Table 3, from which it may be found that the acetonitrile phase-volume recovered decreased with an increase in the volume of the aqueous solution and that the water content remained almost constant under the conditions studied; this can be presumed from the fact that the amount of acetonitrile dissolved in the aqueous phase increases with the volume of the aqueous solution taken initially. The addition of TBAI to this system

Table 2. Salting-out data for inorganic compounds causing phase separation in the acetonitrile–water system

Compound	Minimum quantity causing phase separation/mmol	Acetonitrile phase-volume recovered from sat. salt solution/cm^3	Water content of acetonitrile phase/(v/v %)
$AlCl_3$	2.48	7.52	0.81
$SrCl_2$	3.23	7.70	1.37
$BaCl_2$	3.36	6.69	1.32
$MgCl_2$	3.93	6.75	1.36
$CaCl_2$	4.08	6.85	1.30
$NaCl$	6.86	8.30	14.2
KCl	8.05	7.43	11.4
NH_4Cl	11.2	7.05	10.4
$LiCl$	11.8	5.95	6.70
Na_2SO_4	2.81	10.5	11.2
$Na_2S_2O_3$	2.82	9.26	—
Na_2CO_3	2.83	10.3	18.3
CH_3COONa	6.80	8.17	4.30
$NaBr$	14.5	5.62	14.7
$NaNO_3$	23.5	6.51	12.1
$(NH_4)_2SO_4$	3.03	10.2	9.87

The initial volumes of the water and the acetonitrile were 10.0 cm^3 each.

TABLE 3. EFFECT OF INITIAL VOLUME RATIO ON PHASE SEPARATION

Initial volume ratio (V_w/V_o)	Acetonitrile phase-volume recovered/cm^3	Aqueous phase-volume recovered/cm^3	Water content of acetonitrile phase/(v/v %)
1	10.2	13.0	9.87
2	9.7	27.2	9.32
3	9.2	40.5	10.0
4	8.5	54.3	10.0
5	7.7	68.3	9.32

The initial volume of the acetonitrile was 10.0 cm^3. The phase separations were carried out from a saturated ammonium sulfate solution.

TABLE 4. EFFECT OF AMOUNT OF AMMONIUM SULFATE ON PHASE SEPARATION

$(NH_4)_2SO_4$/g	Acetonitrile phase-volume recovered/cm^3	Water content of acetonitrile phase/(v/v %)
1.5	9.9	24.2
2.0	10.1	20.5
2.5	10.2	18.0
3.0	10.2	16.6
3.5	10.3	15.0
4.0	10.1	14.6
4.5	10.2	13.8
5.0	10.3	11.5
5.5	10.1	10.6
6.6	10.2	9.8

The initial volumes of the water and the acetonitrile were 10.0 cm^3 each.

caused a slight increase in the final acetonitrile phase-volume because of a salting-in effect.

Varying amounts of ammonium sulfate (1.5—6.0 g) were added to a mixture of acetonitrile (10.0 cm^3) and water (10.0 cm^3), and the phase-volumes were measured after the phase separation. According to the results shown in Table 4, the phase separation was initiated by the addition of 1.2 g of the ammonium salt, while the final acetonitrile phase-volume became almost constant (10.2 cm^3) with a salt amount of more than 1.5 g. The content of water present in the acetonitrile phase decreased with an increase in the salt amount added. In this extraction system, the addition of a large amount of a salting-out agent is desirable to accelerate the phase separation and to increase the extractability of the species, provided no significant contamination with the coexisting impurities results. The volumes of the two phases were measured under varying experimental conditions. On the basis of the results, a ternary-phase diagram composed of acetonitrile, water, and ammonium sulfate was obtained, as is shown in Fig. 1. The solid lines of 1—4 in Fig. 1 represent the volume ratio of the two phases recovered after the separation. A homogeneous solution is produced on the left side of the dotted line.

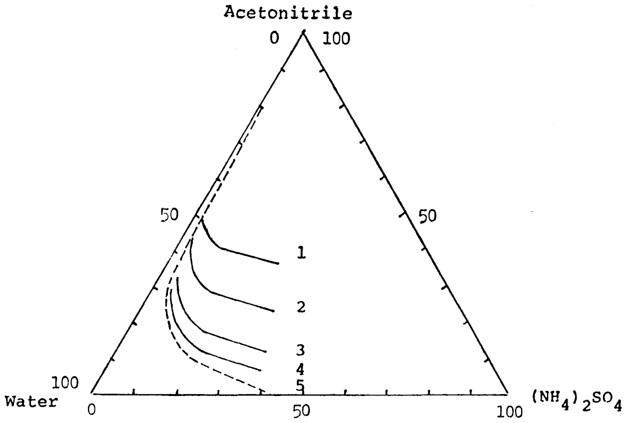

Fig. 1. Phase diagram of acetonitrile/water/ammonium sulfate 1, $V_w/V_o=1$; 2, $V_w/V_o=2$; 3, $V_w/V_o=5$; 4, $V_w/V_o=10$; 5 represents a line producing a homogeneous solution.

Polarography of the Cadmium(II) Iodide Extracted into Organic Solvents. The polarographic constants were determined for the cadmium(II) complex extracted into the four solvents with ammonium sulfate as the salting-out agent. As the results in Table 5 show, the largest

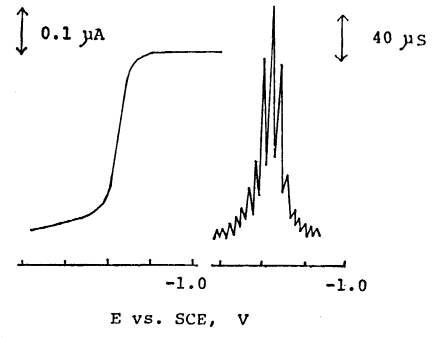

Fig. 2. D.c. and a.c. polarograms of cadmium(II) iodide extracted into acetonitrile. Cd(II) taken: 100 μg.

TABLE 5. POLAROGRAPHIC DATA WITH VARIOUS SOLVENTS

Cd(II): 100 μg

Solvent	D.c. wave height μA	A.c. peak height μS	$E_{1/2}$/V *vs.* SCE	Volume of extract cm^3
Acetonitrile	0.495	239	−0.82	10.0
Acetone	0.214	143	−0.77	12.5
Ethanol	0.108	156	−0.73	13.0
Propylene carbonate	0.145	48	−0.80	10.0

TABLE 6. EFFECT OF TBAI CONCENTRATION
Cd(II): 100 μg

Concn of TBAI mol dm^{-3}	D.c. wave height μA	A.c. peak height μS	$E_{1/2}$/V vs. SCE	Volume of extract cm^3
0.030	0.302	157	−0.77	9.5
0.040	0.395	220	−0.78	9.8
0.050	0.507	247	−0.79	9.9
0.075	0.498	246	−0.81	10.0
0.100	0.495	239	−0.82	10.0
0.125	0.495	226	−0.83	10.0
0.150	0.493	215	−0.85	10.1
0.200	0.463	180	−0.86	10.2

d.c. wave and a.c. peak heights were obtained in the case of the acetonitrile extraction; this suggests that acetonitrile is the best solvent to obtain a good sensitivity. Under the conditions established, the cadmium(II) complex gave a well-defined d.c. wave and a sharp a.c. peak usable for the polarographic determination, as can be seen in Fig. 2. The available potential range was from −0.53 to −1.47 V *vs.* SCE, between which potentials no metal except for cadmium(II) gave polarographic waves. The half-wave potential of the cadmium(II) complex varied with the solvent; this is presumably a result of the difference in the liquid junction potential between SCE and the organic solvent, or to that in the electrode reaction.

Effect of pH. Extractions were carried out at varying pH values, while the other experimental conditions were kept constant. It was found that the d.c. wave and the a.c. peak heights were approximately constant at pH values between 1.7 and 6.8, in which range there was no shift of the half-wave potential. Beyond this pH range, the final acetonitrile phase-volume was decreased somewhat by salting-out with added hydrochloric acid or sodium hydroxide.

Effect of TBAI Concentration. Hitherto, TBAI has often been used as a complexing agent[10] for the formation of metal iodides in acetonitrile, a supporting electrolyte[11] for the polarographic measurement in the solvent, and an extraction reagent[5] after ion-pairing with anions. In the present study, it was examined whether or not TBAI simultaneously played the three roles over the concentration range from 0.03 to 2.00 mol dm^{-3}. The results in Table 6 show that a well-defined d.c. polarogram and a sharp a.c. polarogram of cadmium(II) were observed at all the TBAI concentrations studied. The d.c. wave and the a.c. peak heights decreased gradually with an increase in the TBAI concentration above 0.05 mol dm^{-3}, probably because of the increase in the final volume and in the viscosity of the acetonitrile phase. As the TBAI concentration was increased, the half-wave potential shifted toward negative values and the content of water in the acetonitrile phase increased. The negative shift may be interpreted as resulting from the increase in the concentrations of the complexing agent and the supporting electrolyte. The extractability of TBAI into acetonitrile in the absence of cadmium(II) was determined by the titration method[12] to be 98.9%. The electrolytic conductivity and the viscosity of the acetonitrile extract obtained under the conditions of the procedure were 1.07×10^{-2} S cm^{-1} and 0.439 cP respectively. A 0.1

TABLE 7. EFFECT OF AMOUNT OF AMMONIUM SULFATE
Cd(II): 100 μg

$(NH_4)_2SO_4$ g	D.c. wave height μA	A.c. peak height μS	$E_{1/2}$/V vs. SCE	Volume of extract cm^3
2.0	0.654	291	−0.76	6.3
3.0	0.586	270	−0.75	7.5
4.0	0.540	264	−0.78	8.7
6.0	0.525	253	−0.80	9.3
8.0	0.503	244	−0.81	9.8
10.0	0.495	239	−0.82	10.0
12.0	0.492	236	−0.82	10.1

TABLE 8. EFFECT OF VOLUME OF AQUEOUS SOLUTION TAKEN INITIALLY
Cd(II): 100 μg

Volume of aqueous solution cm^3	D.c. wave height μA	A.c. peak height μS	$E_{1/2}$/V vs. SCE	Volume of extract cm^3
10	0.479	220	−0.83	10.6
15	0.486	223	−0.83	10.4
20	0.495	239	−0.82	10.0
25	0.541	251	−0.82	9.6
30	0.623	277	−0.81	8.4

mol dm^{-3} TBAI solution in acetonitrile was used in the present investigation.

Effect of Amount of Ammonium Sulfate. Preliminary experiments indicated that ammonium sulfate was effective in obtaining a high extractability of the cadmium(II) complex, in addition to being a good salting-out agent for the phase separation. Table 7 shows the polarographic data obtained with varying amounts of ammonium sulfate. The d.c. wave and the a.c. peak heights decreased linearly with an increase in the salt concentration. This is mainly caused by the increase in the final volume of the extract. The half-wave potential shifted toward more negative values with an increase in the salt concentration. The amount of the ammonium sulfate involved in the acetonitrile extract was determined to be below 0.1 mg cm^{-3} after evaporating under reduced pressure and drying at 110 °C. Approximately constant heights of the d.c. wave and the a.c. peak were obtained when ammonium sulfate was added in the range between 8.0 and 12.0 g; 10.0 g of the salt was chosen for the determination of cadmium(II).

Effect of Volume of Aqueous Solution. The initial volume of the aqueous solution was varied from 10.0 to 30.0 cm^3 against 10.0 cm^3 of acetonitrile, while the other conditions were kept constant. As can be seen from Table 8, the d.c. wave and the a.c. peak heights of the cadmium(II) complex increased as the initial volume of the aqueous solution was increased; in the volume range, the degree of extraction is quantitative. The extracted cadmium(II) complex is enriched at a higher concentration as the acetonitrile phase-volume recovered is decreased. A slight shift of the half-wave potential was observed. The initial volume of the aqueous solution was adjusted to a constant volume of 20.0 cm^3.

Calibration Curves. Under the established procedure, the d.c. wave and the a.c. peak heights were determined at varying amounts of cadmium(II). The calibration curves constructed were linear over the concentration range from 0.05 to 10.0 ppm cadmium(II) in the original aqueous solution. The sensitivity of the proposed method was about twice as much as that obtained in a 1.0 mol dm^{-3} KI solution.[13] The relative standard deviation for 100 μg of cadmium(II) were 1.8% and 1.5% in the d.c. and a.c. methods respectively. The extractability of cadmium(II) was $>$99% over the working range. The polarographic parameters were determined to be 30 mV for the slope of the plot of log $[i/(i_d-i)]$ *vs.* E and 5.20 μA·dm^3·mmol^{-1}·mg$^{-2/3}$·s$^{1/2}$ for the diffusion-current constant; this indicates that the cadmium(II) complex extracted into acetonitrile is reduced by two-electron transfer.

Effect of Diverse Ions. The interference from coexisting ions was studied for the a.c. polarographic determination of 100 μg of cadmium(II). The results are summarized in Table 9. Each ten-fold amount of Bi(III), Hg(II), Fe(II), Cu(II), and Tl(III) did not interfere; Fe(III) and Tl(III) were tolerable up to 100 mg in the presence of 1 g of ascorbic acid. Indium(III) and Pb(II), both non-extractable into acetonitrile, had no effect up to 100 mg, but interfered on the addition of 0.5 g of KI. None of the metals such as Mn(II), Co(II), Ni(II), and Zn(II) interfered. Of the anions examined, MoO_4^{2-}, $S_2O_4^{2-}$, and EDTA showed a serious interference, even with the same amount of cadmium(II).

TABLE 9. EFFECT OF DIVERSE IONS ON THE DETERMINATION OF Cd(II)

Element added	Amount of ion added mg	Cd(II) found μg	Error %
Bi(III)*	1.0	103.0	+3.4
Hg(II)*	1.0	97.7	−2.3
Tl(III)	1.0	96.0	−4.0
Tl(III)+1 g ascorbic acid	100.0	100.5	+0.5
Fe(III)*	1.0	100.2	+0.2
Fe(III)+1 g ascorbic acid	100.0	102.8	+2.8
Cu(II)*	1.0	96.7	−3.3
In(III)	100.0	101.8	+1.8
Pb(II)	100.0	98.4	−1.6
Cr(III)	15.0	100.9	+0.9
Sn(IV)	2.0	101.0	+1.1
Zn(II)	10.0	97.2	−2.8
Ni(II)	10.0	101.2	+1.2
Co(II)	10.0	99.5	−0.5
Mn(II)	10.0	100.7	+0.7
Cl^-	100.0	96.9	−3.1
Br^-	100.0	96.3	−3.7
I^-	100.0	100.6	+0.6
PO_4^{3-}	10.0	98.6	−1.4
F^-	10.0	102.8	+2.8
SCN^-	11.4	102.0	+2.0
ClO_4^-	13.0	96.9	−3.1
WO_4^{2-}	10.0	98.7	−1.3
VO_4^-	10.0	103.4	+3.4
Na·Citrate	20.0	99.5	−0.5
Na·Tartrate	20.0	101.1	+1.1

Cd(II) taken: 100 μg;* denotes the maximum amount tolerable, within an error of ±4%.

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