ANALYTICAL POLAROGRAPHIC SEPARATION OF Cu(II)-Cd AND Cu(II)-Ni BY DIFFERENTIAL COMPLEXATION WITH SALICYCLIC ACID AND IMINODIACETIC ACID

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CONTENTS

ABSTRACT

The polarographic waves of mixtures of Cu(II)–Cd and Cu(II)–Ni have been separated by differential complexation. The separation with salicylic acid (SA) and iminodiacetic acid (IDA) is fruitful in the Cu(II)–Cd system, where the waves are 0.15±0.02 V apart. For the Cu(II)–Ni system, SA is effective for separation and the waves are separated by 0.20±0.02 V. The separation of this system with IDA is not reproducible.

INTRODUCTION

The separation of the polarographic waves of two or three metals (having $E_{1/4}$ values close to each other), is a very difficult problem, when the waves of the metal ions are so close together as to be almost superimposed. An inorganic analyst usually deals with the problem of wave separation by differential complexation. A suitable complexing agent may improve the shape of one or more of the waves, or bring them to a more readily accessible region of the applied potential /1/. In a previous communication, the authors have already reported the separation of Zn (II), Ni(II) and Co(II) in potassium chloride by using their complexation with salicylic acid (SA) or iminodiacetic acid (IDA) /2/.

Copper (II), cadmium and nickel separately give well defined polarographic waves in potassium thiocyanate with gelatin, as a supporting electrolyte and maximum suppressor respectively /3/. The waves are also observed in ammonium thiocyanate. When present in a mixture, however, the waves as such are not perfectly separated, but by using a suitable complexing agent, the separation of these waves is possible. The present paper reports the separation of these polarographic waves using differential complexation with SA and IDA.

EXPERIMENTAL

Analar (BDH grade) chemicals were used. Metal solutions (0.1 M) were prepared by dissolving the requisite amount of the corresponding salt (*viz.* $CuSO_4.5H_2O$, $Cd(NO_3)_2.2H_2O$ and $NiSO_4.(NH_4)_2SO_4.6H_2O$) in double distilled water. Ammonium thiocyanate (2.0 M), gelatin 0.1% and ligand solutions were also prepared in double distilled water.

Test solutions containing varying amounts (1–10 mM) of single metal ion or a mixture of two metal ions in 1.0 M ammonium thiocyanate as

supporting electrolyte + 0.01% gelatin were prepared separately. For the purpose of wave separation, salicylic acid and iminodiacetic acid were used as necessary. The ionic strength was kept at μ = 1.0 by ammonium thiocyanate. The pH of the test solutions was fixed at 6.0±0.2 by the addition of hydrochloric acid or sodium hydroxide and was measured on an Elico digital pH meter (Model LI-120).

Polarograms were recorded on a CIC (Baroda, India) automatic pen recording polarograph. The capillary characteristics were m = 2.3733 mg/sec, t = 3.0 sec. in 1.0 M ammonium thiocyanate (open circuit) at 35 cm effective height of the mercury column ($m^{\frac{2}{3}} t^{\frac{1}{6}}$ =2.136 $mg^{\frac{2}{3}} sec.^{-\frac{1}{2}}$). Pure nitrogen gas was passed through the test solutions before recording the polarograms. All the observations were recorded at room temperature 27±1°C.

RESULTS AND DISCUSSION

It was observed that each of the three metal ions separately gave a well defined single reduction wave in 1.0M ammonium thiocyanate + 0.01% gelatin at pH 6.0±0.2. The half wave potential values for these ions are Cu(II) = -0.50 V Vs SCE, Cd = -0.598V Vs SCE and Ni = -0.63 V Vs SCE respectively. When two of the three metal ions are present in admixture (without SA and IDA) the waves are almost superimposed.

(i) *Separation of Cu(II) and Cd System:*

On polarographing a sample containing 2.0 mM Cu(II) and 1.0 mM Cd, the wave of Cu(II) precedes that of Cd. The plateau of the Cu(II) wave is well defined and the measurement of polarographic data is possible. But as the concentration of either of the two ions is increased, the separation becomes poorer and waves are finally superimposed. The separation of the waves is possible by complexation with SA or IDA. Both the complexing agents are equally effective in bringing out the separation (Fig. 1 A,B). The waves are 0.15±0.02 V apart from each other. The $E_{½}$ value for Cu(II) = -0.52 ±0.02 V Vs SCE and that of Cd = -0.67 ± 0.02 V Vs SCE with both the ligands under study. Other polarographic data are summarized in Table 1.

The log plot slope values are in agreement with the irreversible nature of the Cu(II) wave and reversible nature of Cd, even in the presence of each other. The separation is possible even if the concentration of either

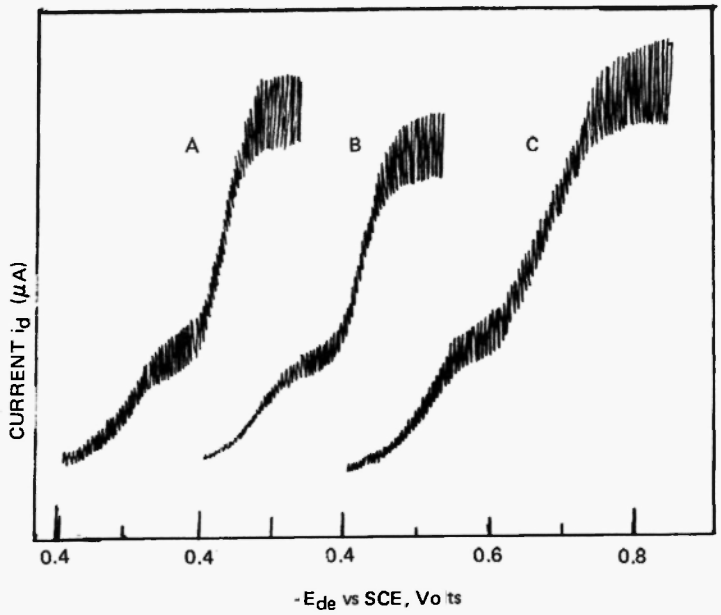

Fig. 1. Polarograms of : (A) 1 mM Cu(II) + 1mM Cd(II) in 1 OM NH_4CNS using IDA
(B) 1 mM Cu(II) + 1mM Cd(II) in 1 OM NH_4CNS using SA.
(C) 1 mM Cu(II) + 2mM Ni(II) in 1.OM NH_4CNS using SA.

TABLE 1. Separation of the polarographic waves of Cu(II) and Cd in 1.0 M ammonium-thiocyanate + 0.01% gelatin at pH 6.00 ±0.2

Concentration Cu(II) in mM	Cd(II)	Ligand	Polarographic data for Cu (II) $-E_{1/2}$ VVs SCE	$i_d(\mu A)$	i_d/C	$i_d C m^{\frac{2}{3}} t^{\frac{1}{6}}$	log plot slope	Polarographic data for Cd $-E_{1/2}$ VVs SCE	$i_d(\mu A)$	i_d/C	$i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$	log plot slope
1	1	S A	0 50	4.0	4.0	1.873	60	0 65	10.8	10.8	5.056	30
2	1		0 503	7.2	3.6	1.685	61	0 652	10.8	10 8	5.056	32
3	1		0 50	12.8	3.2	1.498	60	0 66	12 4	12.4	5 805	34
4	1		0.504	15.2	3 8	1.779	62	0.67	12.6	12 6	5.898	32
1	2		0.51	3 6	3.6	1.685	62	0.683	20.0	10 0	4 681	32
1	3		0.51	5.2	5 2	2.434	65	0.685	28 6	9 5	4.447	30
1	10		0.51	4 6	4 6	2.153	62	0.69	43 6	4 36	2 0112	32
10	1		0.54	48.0	4 8	2.247	62	0.70	9 6	9.6	4.494	32
1	1	IDA	0 508	5 0	5 0	2 340	60	0.65	11.6	11 6	5.430	30
2	1		0 51	7.4	3 7	1 732	60	0.68	12.2	12 2	5.711	34
3	1		0.512	12 8	4 27	1 999	65	0.672	12.0	12.0	5 617	34
4	1		0.516	17.2	4 3	2 013	62	0.665	12.0	12 0	5.617	35
1	2		0 52	3 4	3 4	1 5917	62	0.67	21 2	10.6	4 962	32
1	3		0.52	3 6	3 6	1.685	60	0.68	27.4	9 13	4.274	33
1	4		0.52	3 6	3.6	1.685	60	0.665	38.0	9 5	4 447	38
10	1	Poor – Separation										
1	10		0.46	4.8	4.8	2.247	60	0.67	69 6	6.96	3 258	30

TABLE 2. Separation of the polarographic waves of Cu(II) and Ni in 1.0M ammonium -thiocyanate + 0 01% gelatin at pH 6 0 ± 0.20

Concentration Cu(II)	Ni(II)	Ligand	Polarographic data for Cu (II) $-E_{1/2}$	$i_d(\mu A)$	i_d/C	$i_d/Cm^{\frac{2}{3}}t^{\frac{1}{6}}$	log plot slope	Po arographic data for N $-E_{1/2}$	$i_d(\mu A)$	i_d/C	$i_d\ Cm^{\frac{2}{3}}t^{\frac{1}{6}}$	log p ot slope
in mM												
2	1	Without	0.50	7.2	3.6	1.685	60	0.62	8.0	8.0	3.747	65-
3	1	ligand	0.50	10.8	3.6	1.685	60	0.62	10.2	10.2	4.775	65
4	1		0.518	14.0	3.65	1.713	65	0.62	9.8	9.8	4.588	62
1	2		0.51	4.0	4.0	1.873	65	0.62	14.8	7.4	3.454	65
1	3		0.51	3.8	3.8	1.779	62	0.62	22.0	7.3	3.417	62
1	4		0.50	3.2	3.2	1.498	75	0.622	28.0	7.0	3.277	65
1.	1	S.A.	0.51	5.6	5.6	2.621	85	0 67	6.8	6 8	3.183	80
2	1		0.501	7.8	3.9	1 825	78	0.67	6.5	6 5	3.089	82
3	1		0.50	13 0	6 5	3.043		0 69	8.4	8 4	3.932	90
4	1		0 50	15.6	3.9	1.825	65	0 682	9 8	9 8	4 588	81
1	2		0.51	6 2	6 2	2.90	80	0 685	11.6	5.8	2 715	85
1	3		0.50	4 8	4 8	2.247	80	0 68	19.6	6 6	3 089	80
1	4		0.51	5.0	5.0	2 34	85	0 68	24.4	6 1	2 855	80
1	10	Poor Separation										
10	1		0 505	28.8	2.88	1.348	80	0.71	9.6	9.6	4.494	80

Note: With IDA Separation is possible in only equimolar amount of the metal ions, on further increase of either of the ions causes superimposition of the polarographic waves.

of the ions is ten to thirty fold with SA. With IDA, the separation is possible up to 20 fold concentration of Cu(II) to that of Cd.

(ii) *Separation of Cu(II)-Ni System:*

Korshunov and Kirillova /4/ worked on the polarographic analysis of Cu(II) and Ni in fats in 0.2M ammonium chloride without any added ligand. In the present study, separation of Cu(II) and Ni waves has been observed (the waves are 0.1 ± 0.02 V apart), but on increasing the concentration of either of the ions, the two waves become superimposed. The use of SA or IDA as complexing agent facilitates the separation of these two waves. Though the separation with IDA is not perfect, SA is quite effective, even if the concentration of either of the two ions is ten to twenty-five fold that of the other ion. The waves are 0.20 ± 0.02 V apart from each other with IDA. The half wave potential of Cu(II) = -0.52 ± 0.05 V Vs SCE and that of Ni = -0.69 ± 0.01 V Vs SCE in this system (Fig. 1C).

The other polarographic data are listed in Table 2. Thus the separation of the polarographic waves of Cd(II) and Ni in the presence of both ligands is effective.

The separation of polarographic waves in the cases discussed above may be presumed to be due to the differences in the stability constants of the complexes of the metal ions under study. Severally the greater the stability constant of the complex the more negative is its half wave potential value /5/.

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