Polarographic Determination of In(III) and Cd(II) by pH Adjustment of a Potassium Chloride Medium

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Synopsis. A polarographic determination of In(III) and Cd(II), the reduction potentials of which are very close to each other, was investigated by a pH adjustment of a potassium chloride medium. The reduction wave of In(III) decreased linearly with the pH. At pH 7.0, the reduction wave of In(III) completely disappeared, while that of Cd(II) remained unchanged. This fact enables us to determine In(III) and Cd (II) separately; In(III) can be determined from the merged-wave height of In(III) plus Cd(II) by subtracting that of Cd(II), which can be directly determined.

The polarographic determination of ions, such as In(III) and Cd(II), whose difference in the reduction potentials are very small, is often carried out by using a supporting electrolyte which forms a complex with target ions,[1—4] or at the presence of an ion-selective reagent, such as polyethylene glycol or crown ether.[5—8] Such a reagent, however, often reduces the reversibility of the reduction process. On the other hand, an increase in the pH differentiates the ions by precipitation of coexisting ions in a different pH range, showing a masking effect. In this case, the reversibility of the reduction process remains almost unchanged to give a well-defined reduction wave. In a solution containing In(III) and Cd(II), the former ion begins to precipitate below the neutral pH region. Thus, at pH 7.0 the reduction wave of In(III) completely disappears, while the wave height of Cd(II) remains unchanged. A determination of these two ions is, therefore, possible by using the solubility difference at pH 7.0.

Experimental

Apparatus and Reagents. The polarogrphic limiting current was measured using a Yanagimoto P-1100 polarographic analyzer at 25±0.05°C. The dropping mercury electrode had the following characteristics: m=2.03 mg s^{-1} in water and t=1.50 s (a forced drop time) in 0.1 mol dm^{-3} KCl at a mercury column height of 70 cm. These parameters were obtained with an open circuit at 25±0.05°C. A saturated calomel electrode (SCE) was employed as a reference electrode. The solutions were deaerated with pure nitrogen for 5 min before measurements. Reagent-grade $InCl_3 \cdot 4H_2O$, $2CdSO_4 \cdot 5H_2O$, and $Pb(CH_3COO)_2 \cdot 3H_2O$ were supplied by Kanto Chemical Co., and were used without further purification.

Results and Discussion

Figure 1 shows the pH dependence of the reduction currents for Cd(II), In(III), and Pb(II), whose half-wave potentials are −0.59, −0.55, and −0.38 V vs. SCE, respectively. The reduction current of In(III) decreases linearly with increasing pH, while that of Cd(II) remains unchanged. A linear relationship between the concentration of Cd(II), C (mmol dm^{-3}) and its diffusion current, i_d, (μA) was obtained at pH 7.0:

$$i_d = 3.0436 \cdot C + 0.0018, \quad (1)$$

for r=0.998, root mean square error (RMSE)=0.0546 (n=6), (C: 0.20, 0.40, 0.50, 0.60, 0.80, 1.0 mmol dm^{-3}). The above facts suggest the feasibility of determination for In(III) and Cd(II) separately as follows: Polarographic measurements on a solution containing In(III) and Cd(II) are carried out at pH 7.0 and 4.5. At pH 7.0, only the reduction wave for Cd(II) is observed. The determination of Cd(II) is carried out by using Eq. 1. In(III) is determined by the difference between the merged-wave height of In(III) plus Cd(II) at pH 4.5 and that of Cd(II). The latter was obtained from a measurement on the same solution at pH 7.0. The

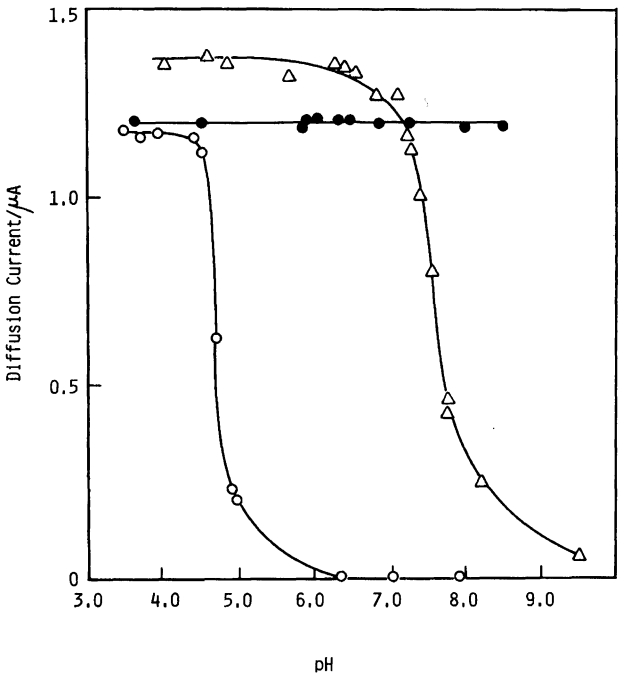

Fig. 1. pH dependence of the reduction currents for Cd(II), In(III), and Pb(II) in potassium chloride.
●: Cd(II), ○: In(III), △: Pb(II)
Supporting electrolyte: 0.1 mol dm^{-3} KCl, Concn of Cd(II): 4.00×10^{-4} mol dm^{-3}, Concn of In(III): 4.00×10^{-4} mol dm^{-3}, Concn of Pb(II): 4.00×10^{-4} mol dm^{-3}, temp: 25±0.05°C.

Table 1. Determination of Synthetic Mixtures of In(III) and Cd(II)

No.	Composition		Total current	Current for each ion	Found
		mol dm^{-3}	μA	μA	mol dm^{-3}
1.	Cd(II):	4.00×10^{-5}	0.752	0.122	3.95×10^{-5} b)
	In(III):	2.00×10^{-4}		(0.630)[a]	2.18×10^{-4} c)
2.	Cd(II):	4.00×10^{-5}	2.572	0.122	3.95×10^{-5} b)
	In(III):	8.00×10^{-4}		(2.450)[a]	8.23×10^{-4} c)
3.	Cd(II):	4.00×10^{-5}	6.965	0.122	3.95×10^{-5} b)
	In(III):	2.00×10^{-3}		(6.843)[a]	2.28×10^{-3} c)
4.	Cd(II):	4.00×10^{-4}	1.320	1.230	4.03×10^{-4} b)
	In(III):	4.00×10^{-5}		(0.090)[a]	3.91×10^{-5} c)
5.	Cd(II):	1.00×10^{-3}	3.095	3.050	1.00×10^{-3} b)
	In(III):	2.00×10^{-5}		(0.045)[a]	2.40×10^{-5} c)

a) Calculated by the difference between the currents for the merged wave of Cd(II) plus In(III) and that of Cd(II) which is directly determined (just above the parenthesis). b) Determined by Eq. 1. c) Determined by Eq. 2.

calibration curve for In(III) at pH 4.5 was found to be

$$i_d = 3.0079 \cdot C - 0.0275, \quad (2)$$

for r=0.991, RMSE=0.0360 (n=6), (C: 0.10, 0.20, 0.40, 0.50, 0.60, 0.80 mmol dm^{-3}). This method is practically efficient when only small amounts of sample are available. An advisable procedure may be as follows. The total wave height of In(III) plus Cd(II) is measured for a sample solution; a subsequent measurement is then carried out after the addition of a base, such as NaOH in order to eliminate the wave of In(III). A determination of Cd(II) in large amounts of In(III) was performed at a molar concentration ratio of 1 to 55. A precipitation of Cd(II) in the presence of large amounts of In(III) was, however, observed at a ratio less than 1/55. A determination of In(III) in large amounts of Cd(II) was indirectly carried out at a molar concentration ratio of 1 to 42—55[9] (Table 1).

As we reported earlier,[5] In(III) interferes with the wave height for Pb(II) in a medium of potassium chloride or sodium perchlorate. The addition of an alkaline solution, however, removes the interference by In(III), since the reduction wave of In(III) completely disappears. The reduction current of Pb(II) shows a small decrease (ref. to Fig. 1). There was no interference between Cd(II) and Pb(II) in this medium. A determination of these three ions is, therefore, possible by taking into account the calibration factor (γ) for Pb(II) (in this case, γ=0.837) at pH 7.0.

In previous papers,[7,8] we also reported on the effects of crown ether on the polarographic behavior of pairs of ions, such as In(III) and Cd(II) or Zn(II) and Ni(II); the reduction potentials of the ions in each pair are very similar. The addition of small amounts of crown compounds, such as Kryptofix-22 ($C_{12}H_{26}N_2O_4$), -23 ($C_{14}H_{30}N_2O_5$) or -222 ($C_{18}H_{36}N_2O_6$) caused a sharp decrease in the reduction current for In(III) and a small decrease in that for Pb(II), keeping the wave height for Cd(II) unchanged. The reduction potentials of these ions were constant in the presence of reagents. This type of polarographic behavior in the presence of reagents is essentially the same as the pH dependence of the reduction currents for the ions given in Fig. 1. This fact suggests that the reagents work as a base to increase the pH of the solution, rather than a ligand for complex formation, in spite of having a crown-ether like ring.

In conclusion, a determination of In(III) and Cd(II) is possible by taking advantage of the difference in their solubilities at pH 7.0. The hydroxyl ion works as a masking reagent in differentiating these ions as well as Kryptofix. This method is, thus, practical without having to use any specific reagent, such as crown ether or polyethylene glycol, which allows one to differentiate the merged-wave of In(III) and Cd(II).

References

1) M. Ishibashi, T. Fujinaga, and A. Saito, *Collect. Czech. Chem. Commun.*, **25**, 3387 (1960).
2) K. Matsumae, *Denki Kagaku*, **27**, 549 (1956).

3) H. Uehara, *Rev. Polarogr.*, **7**, 81 (1959).
4) T. Iga, S. Yamashita, and H. Uehara, *Bunseki Kagaku*, **10**, 227 (1961).
5) T. Kurotu, *Bull. Chem. Soc. Jpn.*, **63**, 592 (1990).
6) T. Kurotu, *Anal. Chim. Acta*, **233**, 325 (1990).
7) T. Kurotu, *Fresenius' J. Anal. Chem.*, **344**, 554 (1992).
8) T. Kurotu, *Fresenius' J. Anal. Chem.*, **345**, 759 (1993).
9) The determination of In(III) in large amounts of Cd(II) depends on a instrumental factor: a reliable minimum wave height for In(III) is about 3—4 mm in full scale of the recording chart (180 mm), therefore, the detection limit of In(III) in large amounts of Cd(II) is about 3—4/170 in molar concentration ratio, since the wave height for both ions are almost the same at the same molar concentration.