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Polarographic Determination of In(III) and Cd(II) in the Presence of Polyethylene Glycol in Hydrochloric Acid†

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The simultaneous determination of In(III) and Cd(II) was investigated by d.c. polarography in the presence of polyethylene glycol (PEG) in 0.1 mol dm^{-3} hydrochloric acid. The PEG shifts the half-wave potential of Cd(II) from −0.67 to −0.82 V vs. SCE and reduces the wave height. A linear relationship between the wave height for Cd(II) and the concentration was obtained in the presence of various molecular weights of PEG. An increase in the molecular weight of PEG also causes a decrease in the wave height. On the other hand, a reduction wave of In(III) was not observed down to the reduction potential for hydrogen at a certain concentration of PEG. It is, therefore, possible to determine In(III) and Cd(II) separately, since Cd(II) can be determined by multiplying by a calibration factor. In(III) can also be determined by the difference between the merged-wave height for In(III) plus Cd(II) and the wave height for the determined Cd(II).

In a previous paper,[1] it was reported that In(III) and Cd(II), whose reduction potentials are very close together,[2-4] can be simultaneously analyzed in a potassium chloride supporting electrolyte in the presence of polyethylene glycol (PEG). PEG works as a reduction potential-shift reagent on these ions in this medium, although it renders those polarographic reduction process irreversible. In a hydrochloric acid supporting electrolyte, PEG also plays an important role in the determination of these ions. In the presence of PEG, the reduction wave height of Cd(II) decreases and then remains constant, while that of In(III) does not appear. This fact makes it possible to determine both ions simultaneously. The results agree quite well with those obtained in a KI medium.[5]

Experimental

Apparatus and Reagents. Polarographic limiting currents were measured using a Yanagimoto Model P-8 Polarograph at 25±0.05 °C. The dropping mercury electrode had the following characteristics: m=0.863 mg s^{-1} in water, t=1.28 s (a forced drop time) in 0.1 mol dm^{-3} HCl at mercury column height of 70 cm. These characteristics were obtained with an open circuit at 25±0.05 °C. A saturated calomel electrode was employed as a reference electrode. The solutions were deaerated with pure nitrogen for 5 min before measurements. Polyethylene glycol (M_w=1000, 2000, 3000, 7500, 20000) was supplied by Tokyo Kasei Co., Ltd. Reagent grade $CdCl_2 \cdot 2 \cdot 1/2H_2O$ and $InCl_3 \cdot 4H_2O$ were from Wako Pure Chemical Ltd. and used without further purification.

Results

Figure 1 shows polarograms of Cd(II), followed by the hydrogen wave, in the presence of various amounts of PEG. As the concentration of PEG increases, the reduction wave height decreases, reaching a certain value. The half-wave potential of the polarogram gradually shifts toward the negative side as the polarogram changes into an irreversible reaction. The wave current of In(III), also followed by a hydrogen wave, decreased sharply and then did not appear in this potential range along with an increase in the concentration of PEG (Fig. 2). Figure 3 shows the dependence of the currents for Cd(II) and In(III) on the concentration of PEG. When the mole ratio, f, of ethylene glycol residue to Cd(II) exceeds 10, the reduction current for Cd(II) remains a definite value, while that for In(III) completely disappears. The ratio of the limiting current to the square root of the mercury

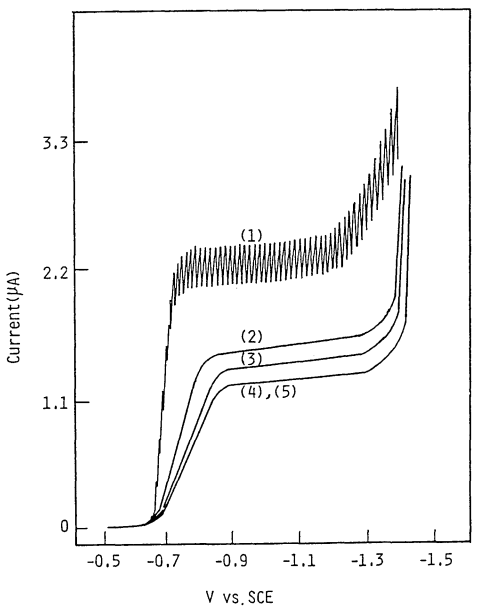

Fig. 1. D.c. polarograms for Cd(II) in the presence of PEG.
Concn of PEG: 1) 0, 2) 1.2×10^{-3} mol dm^{-3}, 3) 3.0×10^{-3} mol dm^{-3}, 4) 6.0×10^{-3} mol dm^{-3}, 5) 1.2×10^{-2} mol dm^{-3}, concn of Cd(II): 6.0×10^{-4} mol dm^{-3}, M_w of PEG: 1000, concn of HCl supporting electrolyte: 0.1 mol dm^{-3}, temperature: 25±0.05 °C.

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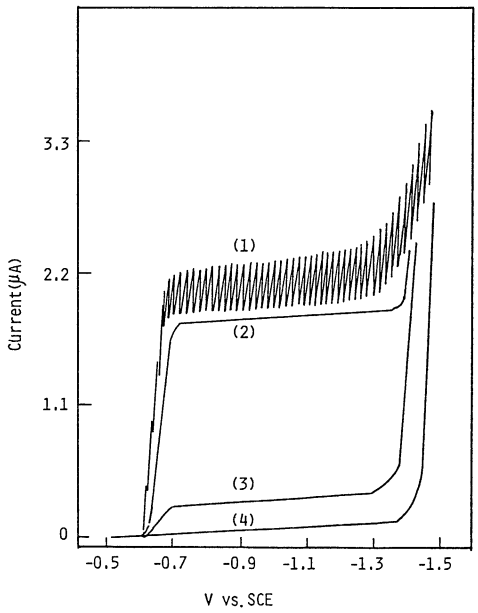

Fig. 2. D.c. polarograms for In(III) in the presence of PEG.
Concn of PEG: 1) 0, 2) 6.0×10^{-4} mol dm^{-3}, 3) 3.0×10^{-3} mol dm^{-3}, 4) 6.0×10^{-3} mol dm^{-3}, M_w of PEG: 1000, concn of In(III): 6.0×10^{-4} mol dm^{-3}, concn of HCl supporting electrolyte: 0.1 mol dm^{-3}, temperture: 25±0.05 °C.

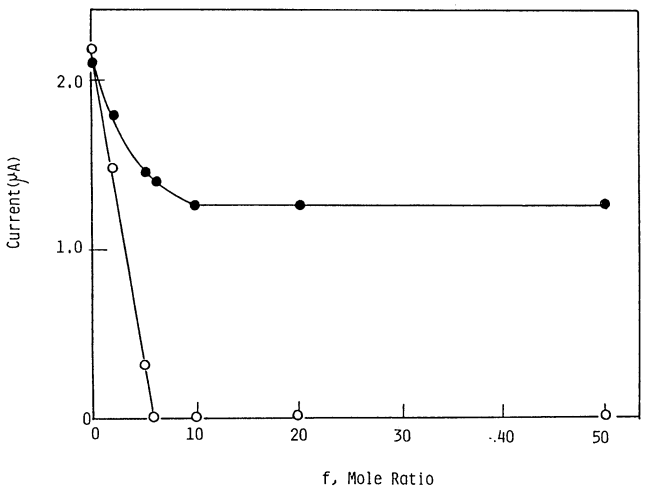

Fig. 3. Dependence of currents for Cd(II) or In(III) on concentration of PEG. ●: Cd(II), ○: In(III), f=[PEG]/[Cd] or [In(III)], concn of In(III): 6.0×10^{-4} mol dm^{-3}, concn of Cd(II): 6.0×10^{-4} mol dm^{-3}, concn of HCl supporting electrolyte: 0.1 mol dm^{-3}, M_w of PEG: 1000, temperature: 25±0.05 °C.

column height for In(III) or Cd(II) was constant, indicating that the reduction process for both ions is diffusion controlled. Figure 4 shows electrocapillary curves for 0.1 mol dm^{-3} hydrochloric acid containing various amounts of PEG. PEG begins to absorb on a mercury drop at −0.20 V vs. SCE. Figure 5 shows the dependence of the diffusion currents for Cd(II) on the molecular weight of PEG. The diffusion current for

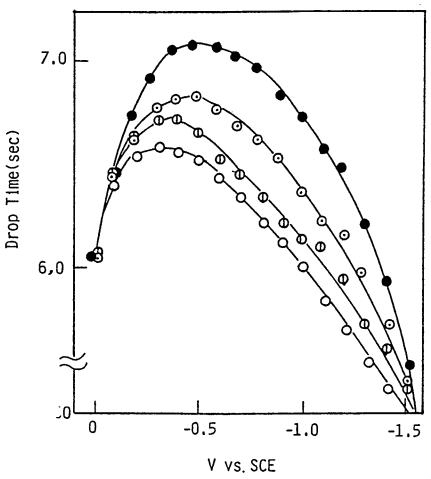

Fig. 4. Electrocapillary curves for 0.1 mol dm^{-3} HCl containing various amounts of PEG.
●: 0, ⊙: 4.8×10^{-4} mol dm^{-3}, ⓓ: 1.2×10^{-4} mol dm^{-3}, ○: 2.4×10^{-4} mol dm^{-3}, M_w of PEG: 1000, temperature: 25±0.05 °C.

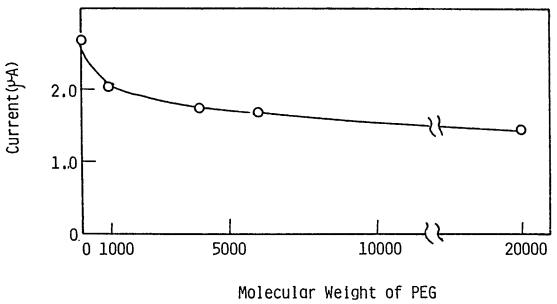

Fig. 5. Dependence of I_d for Cd(II) on molecular weight of PEG.
Concn of Cd(II): 6.0×10^{-4} mol dm^{-3}, concn of PEG: 8.0×10^{-3} mol dm^{-3}, concn of HCl supporting electrolyte: 0.1 mol dm^{-3}, temperature: 25±0.05 °C.

Cd(II) gradually decreases as the molecular weight increases. In a previous paper,[1] the reduction wave of Cd(II) was shown to change into a two-step reduction wave in the presence of PEG in 0.1 mol dm^{-3} KCl. The molecular weight dependence of the wave height for Cd(II) in 0.1 mol dm^{-3} HCl is almost similar to that of the first wave for Cd(II) in 0.1 mol dm^{-3} KCl. However, it is difficult to be certain whether the second wave of Cd(II) will appear at a more negative potential in 0.1 mol dm^{-3} HCl, since the reduction wave of a hydrogen atom appears. On the contrary, the dependence of the wave height for In(III) on the molecular weight is in contrast to that for Cd(II). At a certain concentration of PEG, the wave height for In(III) becomes small; then, it gradually increases as the molecular weight increases (Fig. 6). The cause of the decrease and increase in the diffusion current for In(III) has not yet been clarified. In a potassium chloride medium, the polarographic wave for In(III) in the presence of PEG becomes irreversible, and shifts to the negative side, leaving its wave height

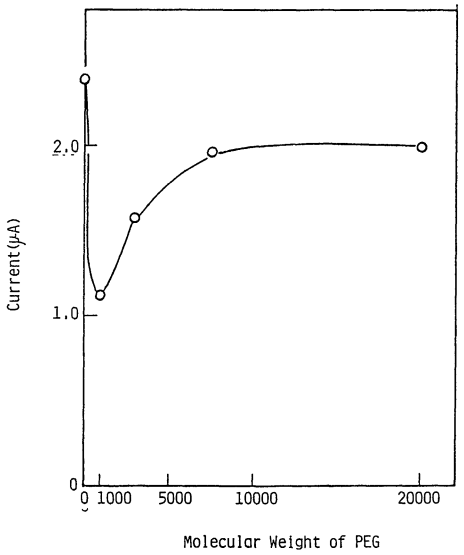

Fig. 6. Dependence of I_d for In(III) on molecular weight of PEG.
Concn of In(III): 6.0×10^{-4} mol dm^{-3}, concn of PEG: 6.0×10^{-4} mol dm^{-3}, concn of HCl supporting electrolyte: 0.1 mol dm^{-3}, temperature: 25±0.05 °C.

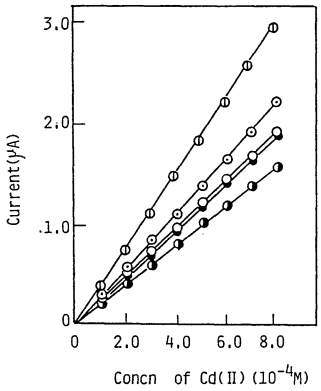

Fig. 7. Relationship between diffusion current for Cd(II) and concentration in the presence of In(III) and different molecular weight of PEG.
⊕: without PEG, ⊙: 1000, ○: 4000, ●: 6000, ◑: 20000. Concn of PEG: 8×10^{-3} mol dm^{-3}, concn of In(III): 6.0×10^{-4} mol dm^{-3}, concn of HCl supporting electrolyte: 0.1 mol dm^{-3}, temperature: 25± 0.05 °C.

unchanged. In a hydrochloric acid supporting electrolyte, the polarographic behavior of In(III) within the potential range of ca. −0.70 through −1.50 V is similar to that in a potassium chloride medium. However, it is almost impossible to assure whether the reduction wave for In(III) will be observed at a much more negative potential in 0.1 mol dm^{-3} HCl or whether no wave for In(III) will appear in this medium, as in $NaNO_3$,[6] due to interference of the hydrogen wave. The polarographic behavior therefore seems to be significantly affected by the nature of supporting electrolyte.

Linear relationships between the diffusion currents

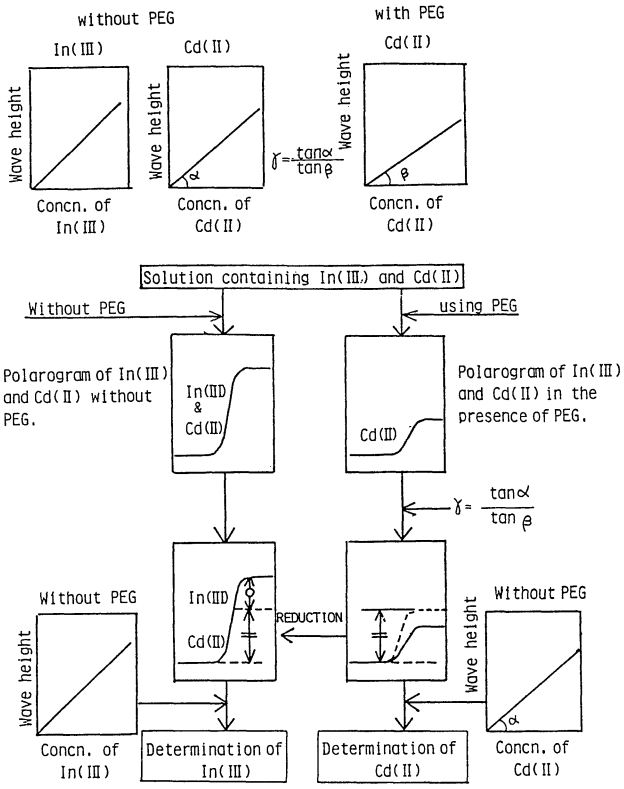

Fig. 8. Procedure for polarographic determination of In(III) and Cd(II) in 0.1 mol dm^{-3} HCl.

for Cd(II) and the concentration were obtained using different molecular weight of PEG (Fig. 7). The same relationships were obtained when 6×10^{-4} mol dm^{-3} In(III) co-existed. The effect of In(III) on the current for Cd(II) was investigated in the presence of PEG. The wave height for Cd(II) was not affected by the presence of In(III) in a 50-fold excess over Cd(II). These facts suggest that it is feasible to determine In(III) and Cd(II) separately by the procedure shown in Fig. 8.

At first, it is recommended that one obtains the relationship between the wave current for In(III) and the concentration without PEG. Similar relationships for Cd(II) both in the presence of PEG and without PEG should also be obtained. Thus, the calibration factor, γ, for the wave height of Cd(II) is given. Then, polarograms for the targeted solutions containing In(III) and Cd(II) are measured both with and without PEG. For the above-mentioned solution with PEG, only the reduced-height wave for Cd(II) will be obtained.

A determination of Cd(II) is, therefore, carried out by using the calibration factor, while referring to the relationship between the current for Cd(II) and its concentration. A determination of In(III) is also possible using the difference between the merged-wave current for In(III) plus Cd(II) and that for the determined Cd(II), while referring to the relationship between the wave height for In(III) and its concentra-

Table 1. Determination of the Concentration for In(III) and Cd(II) in 0.1 mol dm^{-3} HCl or 1 mol dm^{-3} KI

Sample No.	Composition of sample	Results I	Results II
	mol dm^{-3}	In 0.1 mol dm^{-3} HCl with PEG[a] mol dm^{-3}	In 1 mol dm^{-3} KI mol dm^{-3}
1	Cd(II): 2.00×10^{-4}	2.00×10^{-4}	2.05×10^{-4}
	In(III): 2.00×10^{-4}	1.95×10^{-4}	1.95×10^{-4}
2	Cd(II): 4.00×10^{-4}	4.00×10^{-4}	4.00×10^{-4}
	In(III): 2.00×10^{-4}	1.95×10^{-4}	2.00×10^{-4}
3	Cd(II): 8.00×10^{-4}	8.05×10^{-4}	7.95×10^{-4}
	In(III): 2.00×10^{-4}	1.95×10^{-4}	1.95×10^{-4}

a) Concn of PEG: 1.2×10^{-1} mol dm^{-3}, M_w of PEG: 1000, temparature: 25±0.02 °C.

tion.

Polarographic measurements were carried out on sample solutions containing various ratios of In(III) and Cd(II) using 1 mol dm^{-3} KI supporting electrolyte and this medium. The obtained results using this method practically agree with the theoretical values and are also comparable to those in a KI medium (Table 1). The above mentioned method is suitable for practical purposes. When it is difficult to prepare sufficient amounts of solution with and without PEG for the polarographic measurements, for example; as in the case of very small amount of sample. This procedure may be advisable, since a solution containing In(III) and Cd(II) can be prepared and supplied to the polarographic measurement; then, PEG is added to the solution in order to eliminate the wave of In(III) for a subsequent measurement.

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