Polarographic Behavior of Metal Ions in the Presence of Polyethylene Glycol in Potassium Chloride[†]

Takuzo Kurotu
Department of Chemistry, The National Defense Academy, Hashirimizu 1-10-20, Yokosuka 239

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The polarographic behavior of Cu(II), Pb(II), Tl(I), Sn(II), In(III), Cd(II), and Zn(II) was investigated in the presence of polyethylene glycol (PEG) in 0.1 mol dm^{-3} potassium chloride. PEG was adsorbed on mercury drops within the potential range from ca. −0.2 through −1.50 V vs. SCE, and shifted the half-wave potentials of Sn(II), In(III), Cd(II), and Zn(II) toward the negative direction, leaving the wave heights unchanged. On the other hand, the polarograms of Cu(II), Pb(II), and Tl(I) were not affected by the presence of PEG. Linear relationships between the wave heights for Cu(II), Pb(II), In(III), Cd(II), Zn(II), and their concentrations were obtained in the presence of PEG. Among these ions, the polarographic waves of In(III) and Cd(II), whose reduction potentials are very close together, became well separated in the presence of PEG. It is, therefore, possible simultaneously determine In(III) and Cd(II) in this medium. Interference between In(II) and Pb(II) was observed in freshly prepared solutions. It is, however, feasible to precisely determine both ions by using PEG as a reduction potential-shift reagent for In(III) in order to eliminate the interference.

It is well known that some kinds of surfactants suppress the maximum waves of d.c. polarograms or render the polarographic reaction irreversible, resulting in shifts of half-wave potentials of ions toward the negative side.[1-3] Reilley et al.[4] successfully determined Bi(II) and Pb(II) by amperometric titration in the presence of gelation, which exhibits an electrochemical masking effect upon the reduction of Pb(II). Fujinaga et al.[3] also applied this effect for the determination of Cu(II) and Tl(I).

There seems, however, to have been few studies on the polarographic behavior of other metal ions in addition to those mentioned above in the presence of a surfactant. This paper deals with the effect of polyethylene glycol (PEG) on the behavior of polarograms for Cu(II), Pb(II), Tl(I), Sn(II), In(III), Cd(II), and Zn(II). Among these ions, the half-wave potentials for In(III) and Cd(II) are generally very close together; it is therefore not easy to determine them separately using a conventional supporting electrolyte, such as hydrochloric acid or potassium chloride.

Several attempts[5-7] have been made to simultaneously determine the ions by using different supporting electrolytes, such as KI or KBr, where the difference of the reduction potentials becomes somewhat large through selective complexation. In the presence of PEG the reduction potentials of these ions become quite separated, although their polarograms become irreversible. It was, therefore, feasible to determine In(III) and Cd(II) simultaneously.

Furthermore, the reduction potentials for Pb(II) and In(III) are also close together. Although interference between these two ions was observed, it could be eliminated by using PEG as a reduction potential shift-reagent for In(III). PEG, therefore, plays an important role in a simultaneous determination of the ions. The wave height, reduction potential, relationship between the wave height and the concentration were also investigated for the simultaneous determination of these ions in the presence of PEG in this medium.

Experimental

Apparatus and Reagents. The polarographic limiting current was 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} KCl 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, and 20000) was supplied by Tokyo Kasei Co., Ltd. Stock solutions of Cu(II), Pb(II), Tl(I), Sn(II), In(III), Cd(II), and Zn(II) were prepared from reagent-grade $CuSO_4 \cdot 5H_2O$, $Pb(NO_3)_2$, $TlNO_3$, $SnCl_2$, $InCl_3 \cdot 4H_2O$, $CdCl_2 \cdot 2 \cdot 1/2H_2O$, and $ZnSO_4 \cdot 5H_2O$ were supplied by Kanto Chemical Ltd. and used without further purification.

Results

Polarographic Behavior for In(III) and Cd(II) in the Presence of PEG. Figure 1 shows polarograms of In(III) in 0.1 mol dm^{-3} KCl in the presence of various amounts of PEG. The limiting current for In(III), with a half-wave potential of −0.59 V vs. SCE, gradually decreased with an increase in the PEG concentration, whereas another wave was observed at −1.65 V vs. SCE. Above 2.4×10^{-4} mol dm^{-3} in PEG concentration, the reduction wave for In(III) appeared to be negative with a value of ca. −1.65 V vs. SCE. The polarographic behavior of In(III) in the presence of PEG was almost independent on the molecular weight of the polymer (Fig. 2). The limiting current

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of In(III) obtained without PEG was equal to that shifted to ca. −1.65 V vs. SCE. Figure 3 shows polarograms of Cd(II) at different concentration of PEG. As the concentration of PEG increases, the reduction wave of Cd(II) shifts toward the negative side, comprising two waves. The sum of these limiting currents for Cd(II) with half-wave potentials at −0.72 and −1.10 V vs. SCE was equal to that without PEG. The first and second reduction currents remained almost unchanged in the PEG concentration range from 2.4×10^{-4} mol dm^{-3} to 1.2×10^{-1} mol dm^{-3}. As the molecular weight of PEG increased, the current of the first wave decreased; the current of the second one increased so as to compensate each wave height, maintaining the total current constant, equal to that obtained without PEG (Fig. 4). The behaviors of In(III) and Cd(II) induced by the presence of PEG were not observed when ethylene glycol was employed. The ratio of the limiting current to the square root of the mercury column height for In(III) or Cd(II) was constant, indicating that the reduction process for both ions are diffusion controlled. Figure 5 shows electrocapillary curves for solutions containing various amounts of PEG. PEG begins to absorb on the mercury drop from ca. −0.20 through −1.60 V vs. SCE within this potential range, the electro-

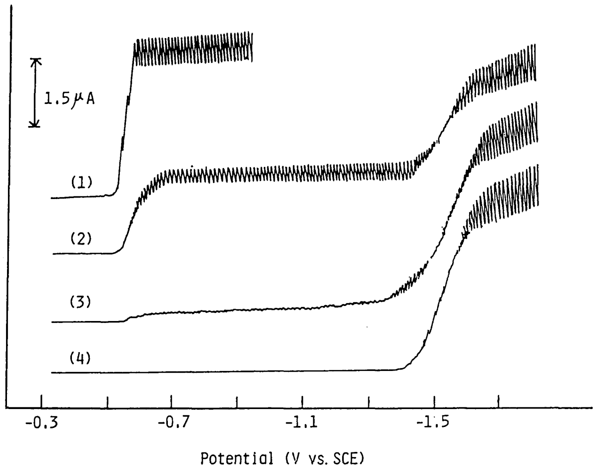

Fig. 1. D.c. polarograms for In(III) in the presence of PEG.
Concn of PEG: 1) 0, 2) 9.6×10^{-4} mol dm^{-3}, 3) 2.4×10^{-3} mol dm^{-3}, 4) 2.4×10^{-2}—1.2×10^{-1} mol dm^{-3}, concn of In(III): 4.0×10^{-4} mol dm^{-3}, concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, molecular weight (M_w) of PEG: 20000, temperature: 25±0.05 °C.

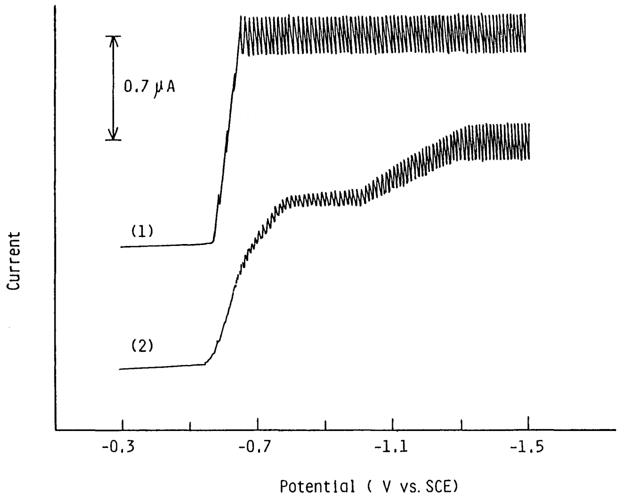

Fig. 3. D.c. polarograms for Cd(II) in the presence of PEG.
Concn of PEG: 1) 0, 2) 2.4×10^{-4}—1.2×10^{-1} mol dm^{-3}, concn of Cd(II): 4.0×10^{-4} mol dm^{-3}, concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, M_w of PEG: 20000, temperature: 25±0.05 °C.

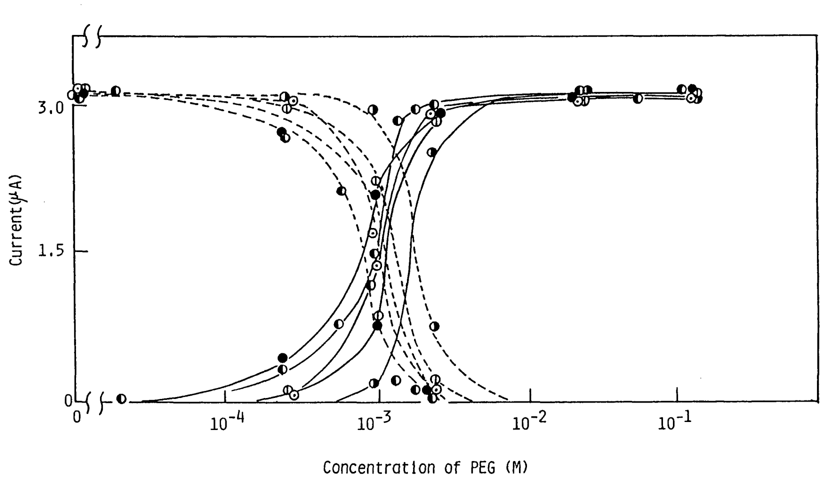

Fig. 2. Dependence of limiting current for In(III) on concentration of PEG.
M_w of PEG: ●: 1000, ⊙: 2000, ◐: 3000, ⦶: 7500, ○: 20000. Concn of In(III): 4.0×10^{-4} mol dm^{-3}, ----: limiting current with $E_{1/2}=-0.67$ V, ——: limiting current with $E_{1/2}=-1.67$ V, concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, temperature: 25± 0.05 °C.

chemical reductions of In(III) and Cd(II) become irreversible.

Nezu et al.[8,9] reported that crown ether absorbs on a mercury drop while rendering the electrochemical reaction of metal ions irreversible, or to shift their reduction potentials toward the negative side, while keeping the reduction current unchanged. PEG also absorbs on a mercury drop while collecting metal ions and forming a complex like crown ether. PEG is supposed to have a sufficient number of oxygen atoms to form a ring that would grasp a cation inside the ring.[10]

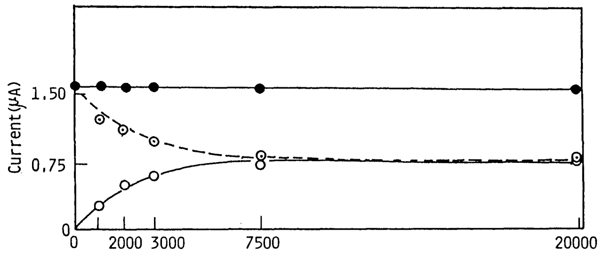

Fig. 4. Dependence of limiting current for Cd(II) on molecular weight of PEG.
⊙: current for 1st wave, ○: current for 2nd wave, ●: current for total wave, concn of Cd(II): 4.0$\times 10^{-4}$ mol dm^{-3}, concn of PEG: 2.4$\times 10^{-2}$ mol dm^{-3}, M_w of PEG: 20000, concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, temperature: 25±0.05 °C.

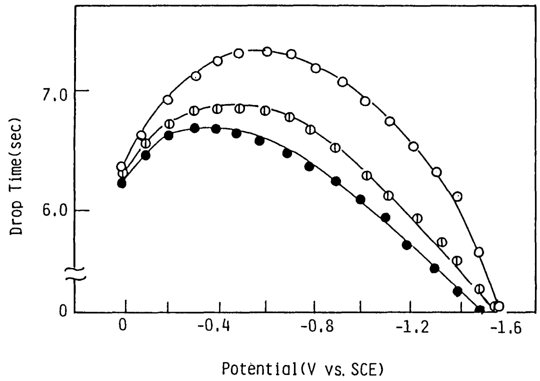

Fig. 5. Electrocapillary curves for 0.1 mol dm^{-3} KCl solution containing various amounts of PEG.
Concn of PEG: ○: 0, ⦶: 1.2$\times 10^{-3}$ mol dm^{-3}, ●: 2.4$\times 10^{-2}$ mol dm^{-3}, M_w of PEG: 20000, temperature: 25±0.05 °C.

Matsuda et al.[11-13] tried to interpret the mechanism of a two-step reduction of Cd(II) using PEG in NaNO$_3$ supporting electrolyte in terms of the formation of a polymer-metal ion complex on an electrode. The reduction of ions in this experiment would also be due to the formation of complexes with the PEG absorbed on the mercury drop. The fact that the diffusion currents for In(III) and Cd(II) remain unchanged in this experiment explains the formation of the complexes mentioned above. The diffusion current drastically decreases when reducible ions form a complex with a polymer in a bulk solution to diffuse to an electrode, since the diffusion coefficient of the polymer-metal ion complex becomes much smaller than that of only the ion.[14] The reduction wave of In(III) did not appear when NaNO$_3$ was used as a supporting electrolyte instead of KCl, while the polarogram of Cd(II) is a two-step reduction wave like that in KCl medium. The polarographic behavior of Cd(II) and In(III) in the presence of PEG, therefore, seems to be so complicated that a precise interpretation of this reduction mechanism should be the subject for future study. At any rate, PEG is a noteworthy example as a reduction potential-shift reagent in polarography.

In the presence of PEG, the reduction potentials of In(III) and Cd(II) become much separated from each other, implying that a simultaneous determination of these ions is feasible in a KCl medium. Linear relationships between the concentration of In(III) and the reduction current were found, passing through the origin in the presence of PEG and/or Cd(II) (Table 1).

Table 1. Relationship between the Diffusion Current for In(III) and the Concentration in 0.1 mol dm^{-3} KCl

Concn of In(III)	No PEG present		PEG[a] present		PEG[a] and Cd(II)[b] present	
mmol dm^{-3}	$i_d/\mu A$	$I=i_d/Cm^{2/3}t^{1/6}$	$i_d/\mu A$	$I=i_d/Cm^{2/3}t^{1/6}$	$i_d/\mu A$	$I=i_d/Cm^{2/3}t^{1/6}$
0.1	0.765	8.099	0.747	7.908	0.750	7.940
0.2	1.536	8.132	1.538	8.142	1.520	8.046
0.3	2.303	8.128	2.304	8.131	2.301	8.120
0.4	3.106	8.222	3.069	8.123	3.111	8.234
0.5	3.840	8.131	3.870	8.195	3.900	8.258
0.6	4.615	8.143	4.626	8.163	4.590	8.099
0.8	6.230	8.245	6.154	8.145	6.100	8.073
		Av.: 8.157		Av.: 8.115		Av.: 8.110
		s: 0.054		s: 0.094		s: 0.109
		c.v.: 0.66%		c.v.: 1.16%		c.v.: 1.35%

a) Concentration of PEG: 1.2$\times 10^{-1}$ mol dm^{-3}, M_w of PEG: 20000. b) Concentration of Cd(II): 4.0$\times 10^{-4}$ mol dm^{-3}, C: concentration of In(III): m=0.863 mg s^{-1}, t=1.28 s, s: standard of deviation, c.v.: coefficient of variation, temperature: 25±0.05 °C.

Table 2. Relationship between the Diffusion Current for Cd(II) and the Concentration in 0.1 mol dm^{-3} KCl

Concn of Cd(II)	No PEG present		PEG$^{a)}$ present		PEG$^{a)}$ and In(III)$^{b)}$ present	
mmol dm^{-3}	$i_d/\mu A$	$I=i_d/Cm^{2/3}t^{1/6}$	$i_d/\mu A$	$I=i_d/Cm^{2/3}t^{1/6}$	$i_d/\mu A$	$I=i_d/Cm^{2/3}t^{1/6}$
0.1	0.358	3.790	0.354	3.748	0.355	3.758
0.2	0.690	3.653	0.699	3.700	0.700	3.706
0.3	1.065	3.759	1.080	3.812	1.079	3.808
0.4	1.455	3.851	1.410	3.732	1.420	3.759
0.5	1.755	3.713	1.713	3.627	1.725	3.653
0.6	2.115	3.732	2.073	3.658	2.070	3.653
0.8	2.882	3.810	2.931	3.879	2.940	3.891
		Av.: 3.758		Av.: 3.736		Av.: 3.747
		s: 0.065		s: 0.087		s: 0.086
		c.v.: 1.74%		c.v.: 2.33%		c.v.: 2.29%

a) Concentration of PEG: 1.2×10^{-1} mol dm^{-3}, M_w of PEG: 20000. b) Concentration of In(III): 4.0×10^{-4} mol dm^{-3}, C: concentration of Cd(II), m=0.863 mg s^{-1}, t=1.28 s, s: standard deviation, c.v.: coefficient of variation, temperature: 25±0.05 °C.

Table 3. Effects of the Co-existence of In(III) and Cd(II) on Their Currents in 0.1 mol dm^{-3} KCl

Concn of In(III)	Concn of Cd(II)	i_d for In(III)	c.v.(%)	i_d for Cd(II)	c.v.(%)
mmol dm^{-3}	mmol dm^{-3}	μA	(n=6)	μA	(n=6)
0.1	0	0.656	1.10	—	—
0.1	0.1	0.651	2.07	—	—
0.1	0.5	0.645	1.89	—	—
0.1	1.0	0.650	0.83	—	—
0.1	5.0	0.654	1.22	—	—
0	0.1	—	—	0.369	0.51
0.1	0.1	—	—	0.369	2.30
0.5	0.1	—	—	0.366	1.95
1.0	0.1	—	—	0.364	1.25
5.0	0.1	—	—	0.369	1.28

c.v.: coefficient of variation, n: number of measurement, concentration of PEG: 2.4×10^{-1} mol dm^{-3}, M_w of PEG: 20000, temperature: 25±0.05 °C.

Similar relationships for Cd(II) were also obtained in the presence of PEG and/or In(III) (Table 2). The effects of the co-existence of In(III) and Cd(II) on their currents were also investigated (Table 3). These facts suggest that a simultaneous determination of both ions is possible without any interference in the presence of a fifty-fold excess of the other ion. Indium and cadmium often exist in sphalerite. From a metallurgical point of view, there are practical needs for determing small amounts of cadmium in large amouts of indium. The reduction potential of Cd(II) is more positive than that of In(III) in this method. Therefore, it is suitable that this kind of determination uses PEG as a reduction potential-shift reagent rather than using KI as a supporting electrolyte, since the reduction potential of Cd(II) is more negative than that of In(III) in a KI medium.

Polarographic Behavior of Pb(II)-In(III) and Pb(II)-Cd(II) in the Presence of PEG. Pb(II)-In(III). Since the polarographic reduction potentials of Pb(II) and In(III) are also close together, interference was observed between both ions in a freshly prepared solution. Although the reduction potential for Pb(II) is not affected by the presence of PEG, the wave height for Pb(II) increases up to ca. 10% of its original height when In(III) co-exists (Fig. 6). This kind of interference was observed when using HCl or $NaClO_4$ as a supporting electrolyte. This is probably because part of the In(III) is subject to reduction with Pb(II). On the other hand, the wave height for In(III) remained unchanged because the amounts of In(III) reduced beforehand at the reduction potential for Pb(II) was negligibly small compared to the total In(III) content in bulk solution. The interference, however, was removed by the presence of PEG, which shifted the reduction potential of In(III) to a much more negative value. A linear relationship between the reduction current for Pb(II) and its concentration was obtained in the presence of PEG and In(III). Similar relationships were also obtained for a solution of In(III) in the presence of PEG and Pb(II). It is, therefore, possible to precisely determine both Pb(II) and In(III) in this medium using PEG.

Pb(II)-Cd(II). Although the difference in the reduction potentials of Pb(II) and Cd(II) is almost the same as that for Pb(II) and In(III), no interference was

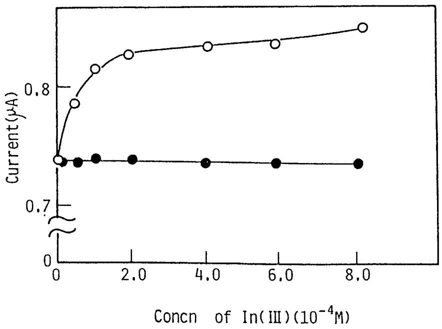

Fig. 6. Effect of In(III) on limiting current for Pb(II).
●: in the presence of PEG, ○: without PEG, concn of Pb(II): 2.0×10^{-4} mol dm^{-3}, concn of PEG: 1.2×10^{-1} mol dm^{-3}, concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, M_w of PEG: 20000, temperature: 25±0.05 °C.

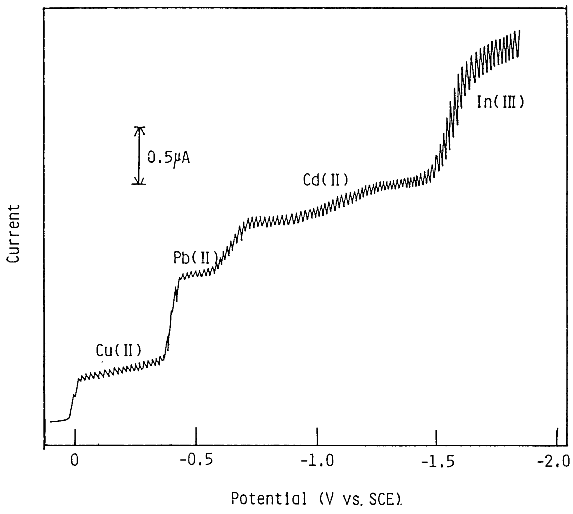

Fig. 7. D.c. polarogram for solution containing Cu(II), Pb(II), In(III), and Cd(II) in the presence of PEG.
Concn of each ions: 2.0×10^{-4} mol dm^{-3}, concn of PEG: 1.2×10^{-1} mol dm^{-3}, concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, M_w of PEG: 20000, temperature: 25±0.05 °C.

observed for the former pair, different from the latter case. A linear relationship between the reduction current and the concentration for Pb(II) or Cd(II) was obtained in the presence of PEG.

As mentioned above, in this medium the interference between In(III) and Pb(II) would give rise to an appreciable error in any determination of the Pb(II) concentration; also, the reduction potentials for In(III) and Cd(II) are so close together that any precise determination of the concentration for these ions is almost impossible. However, these difficulties were overcome by using PEG as a reduction potential-shift reagent in the determination of these ions. Figure 7 shows successful polarograms of Cu(II), Pb(II), Cd(II), and In(III) obtained in the presence of PEG.

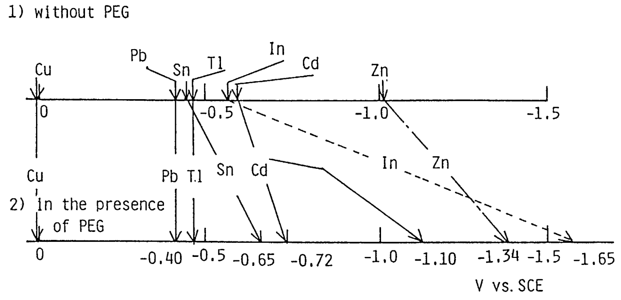

Fig. 8. Half wave potentials for ions in the presence of PEG and without PEG.
Concn of KCl supporting electrolyte: 0.1 mol dm^{-3}, M_w of PEG: 20000.

Other Ions. Polarograms of Cu(II) and Tl(I) were not affected by the presence of PEG, while the reduction potentials of Sn(II)[15] and Zn(II) shifted toward the negative side: from −0.45 to −0.65 V vs. SCE, and from −1.03 to −1.34 V vs. SCE, respectively. The wave heights for all these ions remained unchanged. The change in the half-wave potentials is shown in Fig. 8. When simultaneous determinations of these ions are necessary, PEG would be a useful reagent for separating the ions by selectivity.

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