POLAROGRAPHIC DETERMINATION OF Sb, In, Co, Cu, AND Tl WITH CROTONIC ACID

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The polarographic determination of Sb, In, Co, Cu, and Tl, with Crotonic Acid has been studied. In all the cases well-defined diffusion controlled reduction waves are obtained. The diffusion current is proportional to the concentration of Sb(III), In(III), Co(II), Cu II) and Tl(I) and this method can be used for the quantitative determination of Sb(III), In(III), Co(II), Cu(II) and Tl I).

Many organic reagents have been used for the qualitative and quantitative determinations of the metal ions polarographically due to more specificity and selectivity of the method[1]. Sb(III), In(III), Cu(II) and Tl(I) has already been determined by using acetic acid,[2-4] and dicarboxylic acid,[5-6] but so far no attempt has been made to use crotonic acid as the supporting electrolyte.

EXPERIMENTAL

Polarograms were recorded at 25±0.1°c with a manual Polarograph. A saturated calomel electrode was used as the reference and was connected to the polarographic cell by a potassium chloride-agar bridge. Oxygen was expelled by passing a stream of nitrogen through the solution before recording the polarograms. Double distilled mercury was used and the values of m and t were 2.08 mg/sec. and 3.1 sec. respectively in distilled water and on open circuit. Antimony, Indium, Cobalt, Copper and Thallium solutions were prepared from their salts and the metal contents were determined by classical methods. A freshly prepared solution of recrystallized crotonic acid was used.

Effects of Crotonic acid concentration : The effect of variation in concentration of Crotonic acid from 0.05 M to 0.4 M has been studied. $E_{\frac{1}{2}}$ shifted to more negative in the case of Sb, In, Co and Cu, while the diffusion current decreased with crotonic acid concentration, but in the case of Tl it remains constant.

Effect of pH : In the case of Sb and Cu, $E_{\frac{1}{2}}$ shifted to more negative potential with increase in pH. But in the case of In and Tl, $E_{\frac{1}{2}}$ remains constant in pH range 2.5 — 5.5. In the case of Co, the wave mixes with the hydrogen wave below pH 4. The $E_{\frac{1}{2}}$ remains almost constant in the pH range 4.5 — 6.8. In the case of In and Tl there is no need of pH adjustment as the pH of the solution containing the metal ion and crotonic acid becomes 2.7, and all the polarograms are recorded at this pH. In the case of Co (pH–5), Sb and Cu, the pH is adjusted with sodium hydroxide.

Results and Discussion

The linear plot of I_d vs. $\sqrt{h}$ indicated diffusion controlled nature of the reduction wave of Sb(III) In(III), Co(II), Cu(II) and Tl(I) in crotonic acid. The value of $E_{\frac{3}{4}} - E_{\frac{1}{4}}$ and the slope of log plot indicates that these metals reduced irreversibly. Due to this irreversibility no deduction can be made on the composition and nature of the complex formed. The value of I was calculated from the Ilkovic equation which indicates that Sb(III) reduces to Sb(O), In(III) to In(O), Co(II) to Co(O), Cu(II) to Cu(O) and Tl(I) to Tl(O).

Relation between current and metal concentration : Polarograms in 0.1 M. Crotonic acid [0.2 M in case of In(II) and Tl(I)] for different concentrations of each metal were drawn and diffusion currents were measured by the extrapolation method. A calibration graph for each of the metals was prepared by plotting diffusion current against the concentration of the metal ion, the polarograms of unknown concentration was recorded under identical conditions, and the concentration of the metal in the solution was determined. The determination of metals is possible in the range of 0.400-2.4mM (Sb), 0.100-2.8mM(In), 0.4mM–2mMCo(II), 0.600–2.4mM Cu, 0.4–1.648mM Tl(I), with relative errors not exceeding ± 1%. The polarographic characteristics are given in Table.

Interferences : The metal ions like Th(IV), W(VI) Se(IV), Pt(IV), Ti(IV) and Pd(II) do not undergo reduction in crotonic acid while Ag, Bi and Au get precipitated. Therefore, these metal ions do not interfere. Mo(VI), and Cd interfere only in the determination of In, Ni, Zn and Te(IV) interfere only in the determination of Co(II). Lead interferes in the determination of Sb and Tl. The advantage of this method is that it does not require the addition of any other auxilliary electrolyte, maximum suppressor and rigorous adjustment of pH.

Table. 1 Polarographic Characteristics of metal ions in Crotonic acid. Sensitivity = 1/50, m = 2.08 mg/sec t = 3.1 sec.

Metal	$E_{\frac{1}{2}}$ from log plot	I	n	Slope of $\log(i/i_d-i)$ -mV	Remarks
Sb(III)	— 0.4_0	5.10	3	49	Irreversible
In(III)	— 0.575	4.32	3	28	— do —
Co(II)	— 1.10	2.90	2	125	— do —
Cu(II)	— 0.08	3.08	2	48	— do —
Tl(I)	— 0.475	1.43	1	96	— do —

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