COMPARATIVE STUDIES OF ALTERNATING AND DIRECT CURRENT POLAROGRAPHY: EFFECT OF pH

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Analysis of a mixture of two or more electro-oxidisable or reducible substances with their characteristic half-wave potentials, in a given supporting electrolyte, close to each other, cannot be carried out on the conventional direct current polarography; thus a mixture of Cd++ and In+++ which have their half-wave potentials as $-0.610$ and $-0.565$ volts vs. S.C.E. could not be analysed on dc. polarography.\(^1\) This appeared to be a limitation to the polarographic work using dc. potentials. This difficulty could, however, be overcome by using alternating current polarography in which a known ac. voltage was superimposed over the dc. potentials fed to the dropping mercury electrode (d.m.e.) and the alternating current passing through the system was measured as a function of the applied dc. potential\(^2\); these studies led to the observation of well-defined peaks due to the reversible reduction or oxidation, at d.m.e., of the substances, with their summits occurring at the potentials corresponding to the characteristic half-wave potentials recorded on dc. polarography and with the peak or summit current being proportional to the concentrations of the electro-active substances.\(^1\) \(^2\) A significant feature of these studies was that the alternating polarograms were remarkably sharp in the sense that the potential width of the waves was small, at low superimposed ac. voltages, say 5–10 millivolts (500 cycles/sec.), which led to the possibility of the analysis of the mixture containing Cd++ and In+++\(^1\). Further, comparative studies of the potential-widths of the dc. and ac. polarograms obtained at different concentrations of the electro-active substance also revealed that the alternating current polarography had remarkable advantage over the dc. polarography to the effect that by using low concentrations the former can be suitably employed for analysis of mixtures of two components with their half-wave potentials close to each other.\(^9\) These studies have now been extended to the investigation of the effect of pH on the wave-widths of ac. and dc. polarograms of cadmium, on which no data exist in the literature.
The apparatus and the electric circuit employed have been described in the previous communication.\textsuperscript{3}

The dropping mercury electrode had the following characteristics: at a pressure of 32 cm. of mercury, drop time \((t)\) was 1.6 secs. in 0.1 M KCl solution with open circuit; and the weight of mercury dropping per sec. \((m)\) was 2.5 mg.

In the alternating current polarography, 30 millivolts (50 cycles/sec.) was used, throughout the present series of experiments, as the superimposed ac. voltage.

Cadmium sulphate used was Merck sample and was recrystallised several times in twice distilled water and later dried at 160°C.

The pH of the solution of \(\text{Cd}^{++}\) of a fixed concentration was altered by using citrate buffers. Potassium citrate used for this purpose was of B.D.H. quality; hydrochloric acid and sodium hydroxide employed were Merck

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![Graph](image)

**Fig. 1.** D.C. polarograms of \(\text{Cd}^{++}\) at different pH values. Curves 1 to 8 refer to pH values 4 to 11 respectively.