

SHORT COMMUNICATIONS

A.C. POLAROGRAPHIC-TENSAMMETRIC TRANSITION WAVES*

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It has been shown in previous communications that wave shaped current-voltage curves are obtained when a small sinusoidal alternating potential is superimposed onto the direct potential applied to a dropping mercury electrode in the presence of either dischargeable ions (A.C. polarography; cf. Breyer, Gutmann, and Hacobian 1950*a*, 1950*b*, 1951; Breyer and Hacobian 1951*a*, 1951*b*) or of surface active substances (Tensammetry; Breyer and Hacobian 1952). In the case of A.C. polarography, the waves have their origin in electron transfer across the electrode boundary, whereas tensammetric waves are due to adsorption-desorption equilibria at the electrode-solution interface, without electron transfer.

It is the object of the present communication to discuss briefly A.C. waves obtained when a surface active substance is not added to the electrolyte, but is formed at the electrode in virtue of electron transfer. These waves are thus intermediate between A.C. polarographic and tensammetric waves, that is, the electron transfer results in the formation of a surface active substance which then gives rise to a tensammetric wave. It is proposed to call this type of wave a "transition wave".

For example, when solutions of halogen ions were subjected to A.C. polarography, the resulting waves (Fig. 1) showed characteristics distinctly different from those obtained with cations. These characteristics can be summed up as follows:

- (i) Unlike ordinary A.C. polarographic curves, the waves were narrow and sharp; the summit potential could be determined to better than ± 0.5 mV., properties generally shown by tensammetric waves.
- (ii) The base current on the *positive* side of the summit potential was considerably depressed, indicating the presence of a surface active substance at the electrode (cf. Breyer and Hacobian 1952). The fact that the base current is decreased on the positive side of the summit potential and towards the lower part of the D.C. polarographic step, shows that the surface active substance is mercurous halide, formed at the electrode boundary by the halogen ion discharge.
- (iii) The A.C. waves of chloride and bromide ions strongly interfered with one another in the sense that the chloride wave height was considerably reduced in the presence of Br^- ions. This behaviour can be explained

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by recalling that Br^- ion is reduced at more negative potentials than Cl^- and that mercurous bromide is more strongly adsorbed at the interface than mercurous chloride. Thus bromide lowers the Cl^- wave height by displacing some of the chloride from the interface.

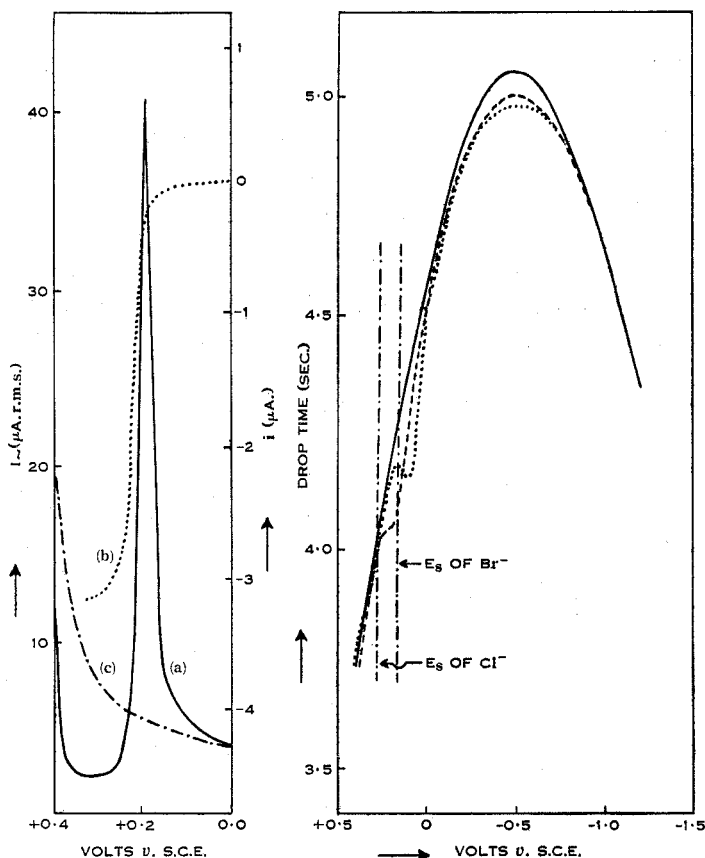


Fig. 1

Fig. 2

Fig. 1.—(a) A.C. polarogram of 10^{-3}N Cl^- in $5 \times 10^{-1}\text{N HClO}_4$.
 (b) D.C. polarogram of the same solution.
 (c) A.C. polarogram of supporting electrolyte ($5 \times 10^{-1}\text{N HClO}_4$).

Fig. 2.—Drop time-potential curves.

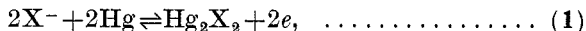
- (a) ——— $5 \times 10^{-1}\text{N NaClO}_4 + 5 \times 10^{-3}\text{N HClO}_4$.
 (b) - - - - - as in (a) + 10^{-2}N Cl^- .
 (c) as in (a) + 10^{-2}N Br^- .

All potentials are referred to the saturated calomel electrode.

Drop time-potential measurements were then carried out in order to prove that adsorption-desorption processes occur at the electrode in the potential region corresponding to the formation of mercurous halide. The results confirmed the conclusions set out above (Fig. 2). A distinct kink appeared in the potential region corresponding to the halide ion discharge showing the formation of a surface active substance at the electrode boundary.

The waves are thus the outcome of two processes occurring simultaneously :

(a) The polarographic process, that is, the formation of mercurous halide in the equilibrium reaction



and

(b) The tensammetric process, given by



It is obvious that process (2) depends on the formation of mercurous halide and consequently the value of the summit potential (E_s) and wave height are determined entirely by those factors which influence equilibrium (1) and which have been discussed in detail in a previous paper (Breyer and Hacobian 1951b).

Work in progress at present in this Laboratory on A.C. polarography of organic compounds has shown that many of the waves obtained are of the transition type. Details of these investigations will be published in due course.

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