A. C. Polarography and Reversibility: Behaviour of Methyl Orange

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(Received November 4, 1963)

The appearance or non-appearance of an a.c. polarographic wave provides information on the mechanism and rate of an electrochemical process. If no wave is observed, the process may be a relatively complex one (reactions preceding or following the electron-transfer step); or a simple one (diffusion and electron transfer only) in which the rate of the electron-transfer is relatively small. If one or other of these factors is involved, it may be that a small a.c. wave is still observed; consequently, preliminary studies by a.c. polarography are usually carried out with comparatively large (~mM) concentrations of depolarizer in order to facilitate the detection of even a small wave. Such a procedure may, however, produce misleading information in the case of processes that are "reversible" at low concentrations but "irreversible" at higher concentrations; the reduction of methyl orange in alkaline solution represents, as far as we are aware, the first system in which such behaviour has actually been observed.

Methyl orange in 1M potassium nitrate and 0.05M sodium hydroxide produces a detectable a.c. polarographic wave at concentrations less than 10^{-6} M; the wave has a maximum height at concentrations of ca. 2×10^{-5} M, and at concentrations above ca. 2×10^{-4} M no a.c. wave is observed (cf. Fig. 1). The d.c. polarographic calibration curve is quite normal in this range of concentrations; but the d.c. step exhibits a maximum at concentrations above ca. 10^{-4} M, and the logarithmic plot changes with concentration (slope=31 mV. at 10^{-5} M, 38 mV. at 2×10^{-5} M, 44 mV. at 5×10^{-5} M).

Solutions of methyl orange show deviations from Beer's law at concentrations above ca. 10^{-5} M, both in acid and in alkaline media; however, the a.c. polarographic calibration curve is anomalous (in the sense indicated above) only in alkaline solution (cf. Fig. 1) and not in acid (cf. Fig. 2).

Elucidation of the mechanism of the reduction requires additional data; our present purpose, however, is merely to report this new type of effect and to point to the implication that, in the testing of reversibility by a.c. polarography, it is essential to bear in mind the possible effect of concentration of the depolarizer.

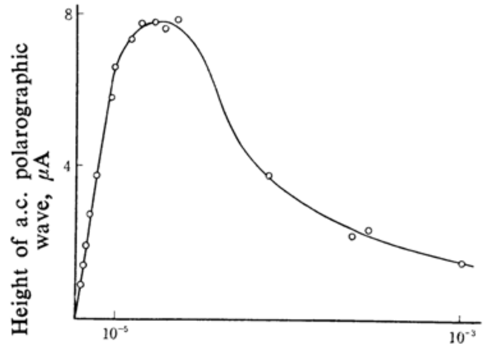

Fig. 1. Calibration curve for solutions of methyl orange in 1M KNO_3 and 0.05M NaOH; 15mV. r.m.s., 50 c.p.s.

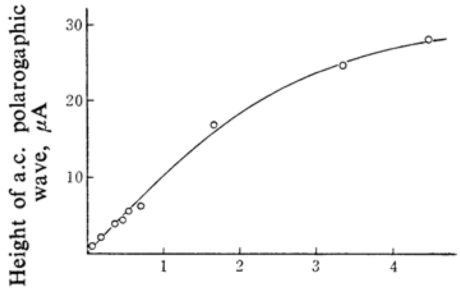

Fig. 2. Calibration curve for solutions of methyl orange in 1M KNO_3 and 0.005M H_2SO_4; 15 mV. r.m.s., 50 c.p.s.

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