The Polarography of Molybdenum(VI) in Organic Media

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The precise nature of the polarographic behaviour of molybdenum(VI) at d. m. e. has been investigated, employing 0.5 M tartaric acid and 0.1 M succinic acid media as supporting electrolytes in the presence of 0.005% thymol. The effect of the variation in the concentration of reducible ions, the height of the Hg column, and the pH on the wave characteristics have been studied. In a tartaric acid medium, molybdenum(VI) produced two well-defined steps, the height of which was found to be diffusion-controlled and concentration-dependent up to about 2.0 mM of molybdenum(VI). In a succinic-acid medium, a single-step polarogram was obtained, the height of which does show a linear relationship with the molybdenum(VI) concentration but which is found to vary linearly with the height of the mercury column.

Several sets of data are found in the literature concerning the polarographic behaviour of molybdenum(VI) in the presence of various inorganic supporting electrolytes, but studies in the presence of different organic acids are rare. Some of the investigators[1-5] have employed few organic acids; besides the grent variance in their conclusions, their results could not be confirmed later. The present investigation has, therefore, been undertaken with a view to studying the polarography of molybdenum(VI) in tartaric acid and succinic acid, and also the possibility of its determination in solutions.

Experimental

Anala R. (BDH) reagents, sodium molybdate, tartaric acid, succinic acid and thymol, were used, and their solutions were prepared in air-free conductivity water.

A manual polarograph was employed for the entire polarographic work. A dropping-mercury electrode with $m^{2/3}t^{1/6}=1.918\ mg^{2/3}sec^{-1/2}$ was used in conjunction with a saturated calomel electrode connected to the cell by a resistance-salt bridge. Redistilled mercury was used for d. m. c. The cell solution was deaerated by passing hydrogen through for 10—15 min and was then kept in an electrically-maintained thermostat at a constant temperature (23±0.1°C). A glass electrode with a pH range of 0—8 and a Cambridge null-deflection-type pH meter was used for the pH measurements.

Results and Discussion

Using 0.5 M tartaric acid (pH 2.15) as a supporting electrolyte, the polarographic behaviour of molybdenum(VI) has been investigated. In this medium molybdenum(VI) is reduced at d. m. e., producing two waves with half-wave potentials of about −0.17 V. and −0.44 V. (*vs.* SCE). Both the waves are well-defined. The height of the first wave is approximately one-half that of the second wave, indicating that molybdenum(VI) is probably reduced first to

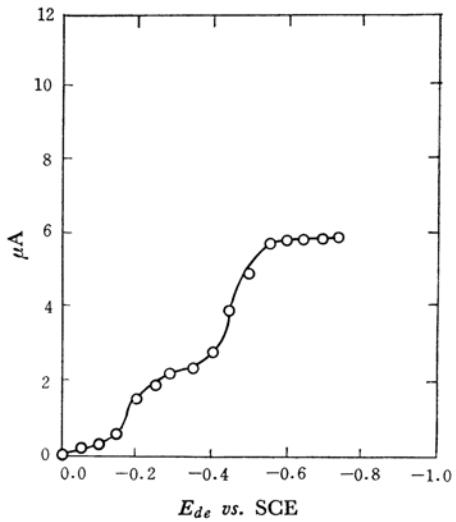

Fig. 1. Polarogram of 1 mM Mo in 0.5 M tartaric acid contains 0.005% thymol.

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2) M. A. DeSesa, D. N. Hume, A. C. Glamm, Jr., and D. D. Deford, *Anal. Chem.*, **25**, 983 (1953).
3) L. Meites, *ibid.*, **25**, 1752 (1953).
4) E. P. Parry and M. G. Yakubik, *ibid.*, **26**, 1294 (1954).
5) J. W. Grenier and L. Meites, *Anal. Chim. Acta*, **14**, 482 (1956).

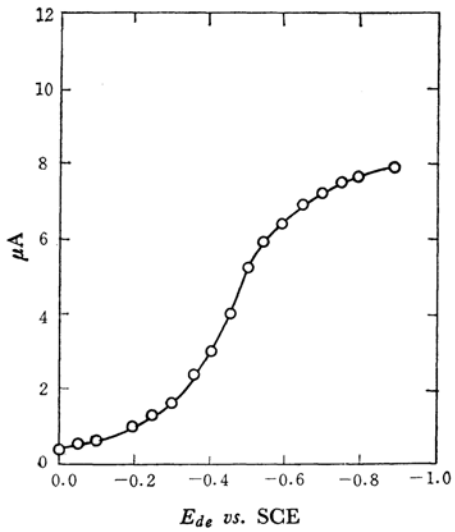

Fig. 2. Polarogram of 1 mM Mo in 0.1 M succinic acid contains 0.005% thymol.

the +5 state and then to the +3 state (Fig. 1). No constant-diffusion-current region is reached for the first wave, but for the second an almost horizontal well-defined limiting current plateau is obtained up to a quite a wide range of potential. At higher pH levels the height of the first wave decreases with the increase in pH, resulting in its disappearance at pH 7; under these conditions, only the second step appears to be present around −0.82 V. The pH value has an appreciable effect on the waves produced due to the reduction of of molybdenum(VI).

A series of polarograms of solutions containing different concentrations of molybdenum(VI) in 0.5 M tartaric acid have been recorded. The diffusion current values at each concentration were determined, and the values of i_d/C and I (the diffusion current constant) were calculated; they were found to be constant up to molybdenum(VI) concentrations of 2 mM. This current is purely diffusion-controlled; when the mercury column height is increased, the current increases linearly with the square root; also, the variation in the polarographic characteristics with the temperature is regular.

In a medium composed of 0.1 M succinic acid and 0.005% thymol, molybdenum(VI) yields a single-step reduction wave with a half wave potential of about −0.51 V; this wave was found to be irreversible. The residual current region does not show any constancy; affer the beginning it rises with the applied potential. A similar phenomenon was observed for the limiting-current plateau, which was found to be almost parallel to the residual current plateau only up to the short range of the potential; after −1.0 V. the current begins to rise sharply as a result of the reduction of hydrogen ions. In this case the height of the wave after correction for i_r does not show a strict proportionality with the molybdenum(VI) concentration. However, a linear relationship was found between i_d and the square root of the effective height of the mercury column, indicating that the wave is diffusion-controlled. At higher pH values, the slope of the limiting-current plateau of the wave increases with pH and, consequently, ill-defined waves were obtained at higher pH values.

It is apparent that molybdenum(VI) produces a well-defined double-wave polarogram in a tartaric acid medium, the total height of which varies linearly with the concentration of molybdenum(VI); the wave can be successfully utilised for the determination of molybdenum(VI) in this medium. In the case of succinic acid, molybdenum(VI) produces a diffusion-controlled wave, but its height in each case does not show a strict proportionality with the molybdenum(VI) concentrations. Further work is in progress.

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