

Polarographic Investigation of Diallyldithiocarbamidohydrazine

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Polarographic studies of diallyldithiocarbamidohydrazine "Dalzin" at the dropping mercury electrode showed that the anodic electrode reaction corresponds to the formation of an insoluble mercury complex. Two electrons are involved in the process and the mercuric-Dalzin complex is sufficiently strongly adsorbed at the electrode to give a pre-wave which has all the characteristics of an adsorption wave. At Dalzin concentrations less than 4×10^{-4} M, the limiting current of the main anodic wave is proportional to the concentration. At higher Dalzin concentrations the limiting current is practically constant, because the thickness of the adsorbed film increases and prevents further interaction between the solution and the mercury.

Diallyldithiocarbamidohydrazine, "Dalzin", has been used as reagent in colorimetric^{1,2} and gravimetric³⁻⁵ determination of various metals. Recently we studied the application of Dalzin as a reagent in amperometric titration of copper and found that Dalzin yields an anodic wave at the dropping mercury electrode⁶. The present work was carried out in order to investigate this anodic behaviour of Dalzin.

EXPERIMENTAL

Materials. The Dalzin was prepared and standardized as described previously⁶. A 0.2 M acetic acid/ammonium acetate buffer with pH 4.60 was used as supporting electrolyte in most experiments. Some polarograms were also recorded from 0.04 M phosphate/borate/acetate buffer. The pH of this electrolyte was adjusted to desired value by addition of 4 M nitric acid or potassium hydroxide and measured with a pH meter. No maximum suppressor was needed in the experiments.

Apparatus. All polarograms were recorded with a Tast-Polarograph, Selector D (Atlas Werken, Bremen, Germany). The conventional type of dropping mercury electrode (D.M.E.) and of electrolysis cell were used. The capillary characteristics measured in open circuit at a corrected mercury height of 50.7 cm were: $m = 2.998$ mg/sec and $t = 3.52$ sec. The "back pressure" was found to be 1.7 cm. Some polarograms were recorded using a rotating platinum electrode as indicator electrode. The electrode (approximately 0.5 mm in diameter and 5 mm in length) was rotated at a speed of 700 r.p.m. by means of a synchronous motor. An external saturated calomel electrode (S.C.E.) served as reference electrode. Dissolved air was removed from the solution, by bubbling oxygen-

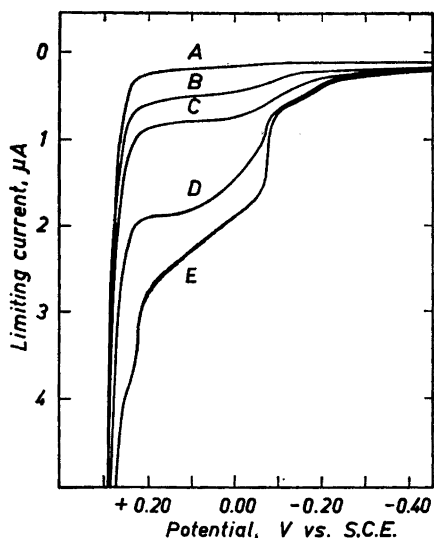


Fig. 1. Current-voltage curves at the D.M.E. of Dalzin in 0.2 M acetic acid/ammonium acetate buffer of pH 4.60. Concentration of Dalzin: A: 0, B: 0.5×10^{-4} M, C: 1.0×10^{-4} M, D: 2.5×10^{-4} M, E: 5.0×10^{-4} M.

free nitrogen through the cell for 10 min and passing it over the solution during the electrolysis. All experiments were performed at $25 \pm 0.1^\circ\text{C}$. The pH of the solutions was measured with a Beckman Zeromatic pH meter.

RESULTS AND DISCUSSION

Preliminary tests. Experiments with the rotating platinum electrode showed that Dalzin is neither reduced nor oxidized in aqueous media. When the dropping mercury electrode was used as indicator electrode, anodic waves appeared on the polarograms. Fig. 1 shows a few current-voltage curves of Dalzin in acetate buffer. All these polarograms exhibit a characteristic pre-wave at the negative side of the main wave and, at Dalzin concentrations above 5×10^{-4} M, a third wave at the positive side of the main wave appeared on the polarograms. Similar observations were made with supporting electrolytes of higher pH values. In order to get more information of this anodic behaviour of Dalzin, the height of each wave was measured at different Dalzin concentrations and different heights of the mercury column above the capillary.

The pre-wave. At Dalzin concentrations less than 10^{-4} M the height of the pre-wave was found to increase proportionally to the concentration but remained practically constant at higher Dalzin concentrations. The height of the pre-wave increased with the height of mercury above the capillary and the value i/h , where h is the height of the column after correction for the "back-pressure", was constant at all Dalzin concentrations. These data indicate that the pre-wave is an adsorption wave⁷.

The main wave. The limiting current of the main anodic waves was found to be proportional to the Dalzin concentration when the latter was less than 3.5×10^{-4} M. In this concentration range the height of the wave was found to increase proportionally to the square root of the mercury height above the

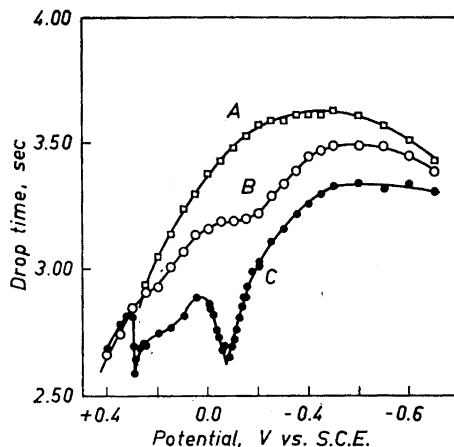


Fig. 2. Electrocapillary curves in 0.2 M acetic acid/ammonium acetate buffer and pH 4.60 Concentration of Dalzin: A: 0, B: 0.75×10^{-4} M, C: 5.0×10^{-4} M.

capillary, indicating a diffusion controlled reaction at the D.M.E. At Dalzin concentrations above 5×10^{-4} M, however, the limiting current became practically independent of the concentration. At these concentrations the limiting current increased linearly with the height of the mercury column, indicating that the current is controlled by the rate of the growth of the mercury surface and not by diffusion when the Dalzin concentration exceeds 5×10^{-4} M.

These experiments indicate that an insoluble film of a mercury-Dalzin complex is adsorbed on the electrode. An increase of the concentration of Dalzin results in an increase of the thickness of the film, and, at a certain thickness (obtained with Dalzin concentrations above 5×10^{-4} M), this film prevents further interaction between the solution and the mercury. The electrode reaction is then no longer diffusion controlled and a further increase in the Dalzin concentration will not result in an increase of the limiting current.

Polarograms recorded from supporting electrolytes of different pH, showed that the main anodic wave is shifted linearly to more negative potentials with increasing pH. In the pH range 2–11 the shift was -0.056 V/pH unit, indicating that two hydrogen ions are involved in the electrode reaction. The diffusion current constant $I = i_d C m^{2/3} t^{1/6}$ was found = 2.64 and indicates that the electrode reaction involves two electrons and that a mercuric Dalzin complex is formed on the electrode according to the equation:



where DH_2 denotes Dalzin and DHg the mercuric complex.

Another indication of the formation of a mercuric complex rather than a mercurous complex is given by the following experiments. A slight excess of Dalzin was added to solutions of mercurous nitrate. In all solutions a black precipitate of mercuric Dalzin complex and metallic mercury were formed. The mercury globuli were easily observed with a low power microscope. It must be concluded that the mercurous Dalzin complex is unstable and that it will disproportionate rapidly according to the equation:



The post wave. The third wave on the positive side of the main wave, which appeared on polarograms of 5×10^{-4} – 10^{-3} M Dalzin, was found to be diffusion controlled and the height of the wave increased proportionally to the Dalzin concentration. This wave seems to indicate that the adsorbed film on the electrode is broken down at about + 0.3 V vs. S.C.E. and thus making a diffusion controlled electrode reaction possible.

Electrocapillary curves. Further confirmation of an insoluble film which is adsorbed on the mercury surface, was obtained by measuring the drop time of the capillary at different potentials in presence and absence of Dalzin. As seen from the electrocapillary curves in Fig. 2, the presence of Dalzin causes a large decrease in the drop time indicating that the product of the anodic reaction is adsorbed on the electrode. Comparison of Figs. 1 and 2, both of which were obtained from acetate buffer of pH 4.60, shows that the potential range where the depression occurs in the electrocapillary curves corresponds to that in which the anodic waves are observed on the polarograms.

At a potential of + 0.3 V vs. S.C.E. (Curve C, Fig. 2) the droptime increases and becomes practically equal to that in the supporting electrolyte. This indicates that the adsorbed film breaks down at this potential as was suggested above.

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