THE POLAROGRAPHIC DETERMINATION OF SOME DERIVATIVES OF 2-ETHYLANTHRAQUINONE

L. M. Shtifman, S. V. Siavtsillo, and L. G. Kuriakova

A number of studies have been devoted to the problem of the polarography of compounds of the anthraquinone series.

The reduction potential of anthraquinone in a water-alcohol solution in the presence of 0.2 N tetramethylammonium hydroxide was first determined by H. Adkins and F. Cox [1]; these authors obtained a value for the half-wave potential of anthraquinone equal to −0.6 v with respect to a saturated calomel electrode. Iu. I. Vainshtein [2] worked out a polarographic method for the quantitative determination of benzanthrone in the presence of anthraquinone in 80% methyl alcohol which contained 0.1 N H_2SO_4. According to his data, the half-wave potential for anthraquinone was −0.36 v. A polarographic study of the hydroxy derivatives of anthraquinone (alizarine, quinalizarine, anthrarufine and others) in an alkaline medium at pH 10-12 in the presence of ammonia, phosphate, and borate buffers was carried out by N. Furman and K. Stone [3]. These authors observed that for these compounds they obtained a normal wave, suitable for quantitative determination of the substances. A. M. Vasil'ev

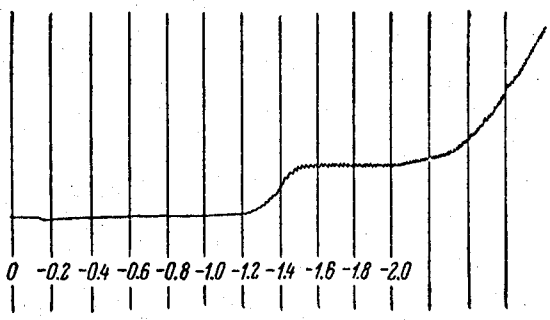

Fig. 1. Polarogram of 2-ethylanthrone.

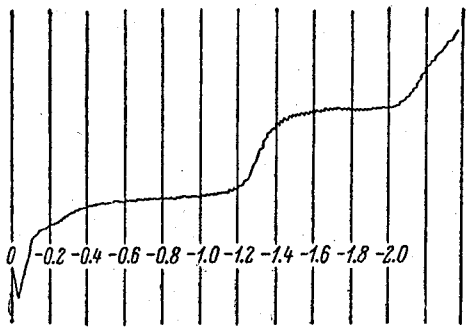

Fig. 2. Polarogram of 2-ethyl-10-hydroxyanthrone.

and A. I. Kostromin [4] determined the half-wave potential of quinalizarine (1,2,5,8-tetrahydroxyanthraquinone) in an ammonia medium (0.25 N) on a base of ammonium nitrate; they observed two waves, and the height of the first wave, whose half-wave potential was −0.78 v (with respect to a saturated calomel electrode), changed linearly with change in quinalizarine concentration. Therefore the authors recommended carrying out a quantitative determination of this substance by the first wave. K. Stone and N. Furman [5] studied the polarography of anthrone and 10-methyl-10-hydroxyanthrone dissolved in dioxane in the presence of acetate, phosphate, and borate buffers. They established that at pH 7.0-8.2 the half-wave potential of anthrone varied from −0.85 to −0.89 v, and for 10-methyl-10-hydroxyanthrone the half-wave potential varied from −1.1 to −1.27 v. They showed that in a medium of 0.1 N KCl at pH 7.1 the half-wave potential of 10-methyl-10-hydroxyanthrone was −1.29 v. R. Day and J. Kirkland [6] studied anthrone polarographically and observed that in aqueous alcohol solution at different pH values one or two anthrone waves were found. At pH 6.9 they found one wave with a half-wave potential of 1.26 v.

In the present work we have studied polarographically the 2-ethylanthraquinone derivatives: 2-ethylanthrone

and 2-ethyl-10-hydroxyanthrone. 2-Ethylanthrone was synthesized by the method described earlier [7]. The substance forms white needles with m.p. 60-62°.

Found %: C 86.39; H 6.40. $C_{15}H_{14}O$. Calculated %: C 86.50; H 6.30.

2-Ethyl-10-hydroxyanthrone was obtained by bromination of ethylanthrone and oxidation of 2-ethyl-10-bromoanthrone [7]; m.p. 92-93°.

Found %: C 80.5; H 6.1. $C_{16}H_{14}O_2$. Calculated %: C 80.7; H 5.9.

We submitted 0.001-0.01 M solutions of 2-ethylanthrone and 2-ethyl-10-hydroxyanthrone to polarography. Because of their poor solubility in aqueous alcohol, the compounds were dissolved in benzene and to 1 ml of the benzene solution was added 5 ml of a 3 M water solution of tetramethylammonium bromide and the resulting mixture was diluted to 25 ml with 80% aqueous methyl alcohol. Thus, the polarogram was taken on a base of 0.6 M$[(C_2H_5)_4N]Br$ in a mixture which contained about 61 volume % of methyl alcohol, 35 volume % of water, and 4 volume % of benzene; the pH of the solution lay between 7.0 and 7.5.

The polarography was carried out in the "Geological Survey" polarographic plant (Leningrad). The measurements were made at a temperature of 25 ± 0.5°. The capillary constant was $m^{2/3} t^{1/6} = 0.94$ $mg^{2/3} sec^{1/6}$ where m is the weight of mercury passing from the capillary per second and t is the period of dropping. The sensitivity of the galvanometer was 10^{-9} a/mm. The electrode for comparison was a saturated calomel half-element. The half-wave potential was determined by the graphical method of Gon. The resulting polarograms are given in Figs. 1 and 2.

TABLE

Relation of Height of Wave (h) to Concentration (c)

c (in mg/ml	h (in mm)
2-Ethylanthrone	
1.010	6
2.024	13
3.036	18
4.048	23
2-Ethyl-10-hydroxyanthrone	
4.3	15.8
8.6	31.8
12.9	47.5
17.2	62.0

The half-wave potential for 2-ethylanthrone determined under these conditions was −1.4 ± 0.03 v. For 2-ethyl-10-hydroxyanthrone the half-wave potential measured under the same conditions was −1.3 ± 0.03 v.

Special experiments were carried out to show that when benzene solutions of 2-ethylanthrone stood for several weeks, the height of its wave did not change. Under the same conditions, for solutions of 2-ethyl-10-hydroxyanthrone we found a decrease in the height of the wave from the half-wave potential of −1.3 v and the appearance of a wave with half-wave potential −0.7 v which corresponded to 2-ethylanthraquinone; this could be explained by tautomeric change of 2-ethyl-10-hydroxyanthrone into 2-ethylanthrahydroquinone with its subsequent oxidation to 2-ethylanthraquinone.

For 2-ethyl-10-hydroxyanthrone and for 2-ethylanthrone we established a straight line relationship between height of wave (h) and concentration of substance (c) in the solution. The data are given in the Table.

The same relationship is preserved in the presence of 2-ethylanthraquinone (m.p. 199°) and 1,2,3,4-tetrahydro-2-ethylanthraquinone (m. p. 169°).

It follows from the Table that the content of 2-ethyl-10-hydroxyanthrone and 2-ethylanthrone in solution can be determined polarographically.

SUMMARY

1. We have determined the half-wave potentials of 2-ethylanthrone and 2-ethyl-10-hydroxyanthrone in a base of 0.6 M of tetramethylammonium bromide in aqueous methyl alcohol solution which contains a small amount of benzene. The half-wave potentials of these compounds are 1.4 and 1.3 v respectively (with respect to a saturated calomel electrode).

2. We established a linear relation between height of wave for 2-ethylanthrone and 2-ethyl-10-hydroxyanthrone and their concentrations within the limits of 0.001-0.01 M solutions.

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