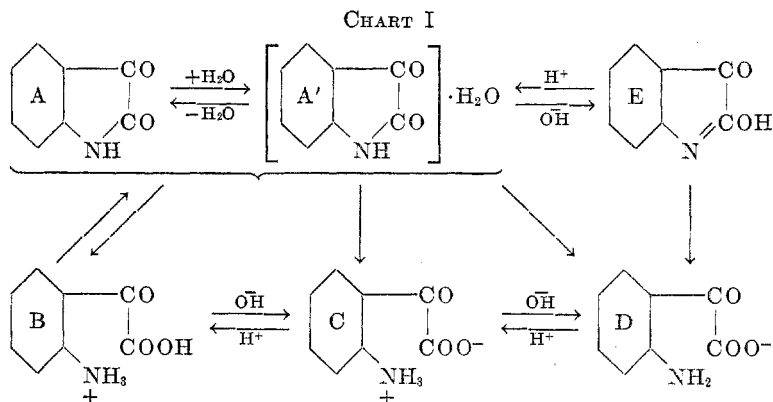


THE POLAROGRAPHIC BEHAVIOR OF ISATIN. II. BEHAVIOR OF ISATIN AND N-ALKYLISATINS IN ETHANOL SOLUTIONS

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Received August 28, 1950

The polarographic behavior of aqueous solutions of isatin has been discussed in a previous communication (1). In that paper evidence was presented indicating the presence in isatin solutions of six molecular (or ionic) species related to one another as shown in Chart I.



Evidence for the one-electron reduction of variety A and the two-electron reductions of varieties B, C, and D was presented. It was stated in the same paper that the polarographic behavior of the purple solutions, for which variety E was assumed to be responsible and which resulted when aqueous solutions of isatin were made strongly alkaline, could not be investigated in aqueous solution because variety E changed to variety D with corresponding disappearance of the purple color before the solution could be degassed and investigated. However in 50% ethanol solutions variety E is sufficiently permanent to permit polarographic studies.

EXPERIMENTAL

The apparatus and techniques were identical with those described in the previous paper. The stock solution of 0.002 M isatin was prepared in ethanol. The capillary employed in these measurements was the same one used in the previous work. The pH values reported are "apparent values" not corrected for non-aqueous solvent errors.

Results. It has been shown (1) that variety A alone is present in the freshly prepared

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50% alcoholic solutions of isatin (see also Curve 1, Fig. 1). The purple color first appears at pH 10.22 with the simultaneous appearance of a second polarographic wave (Curve 1, Fig. 2). It will be noticed that as the height of the second wave (Variety E) increases, the

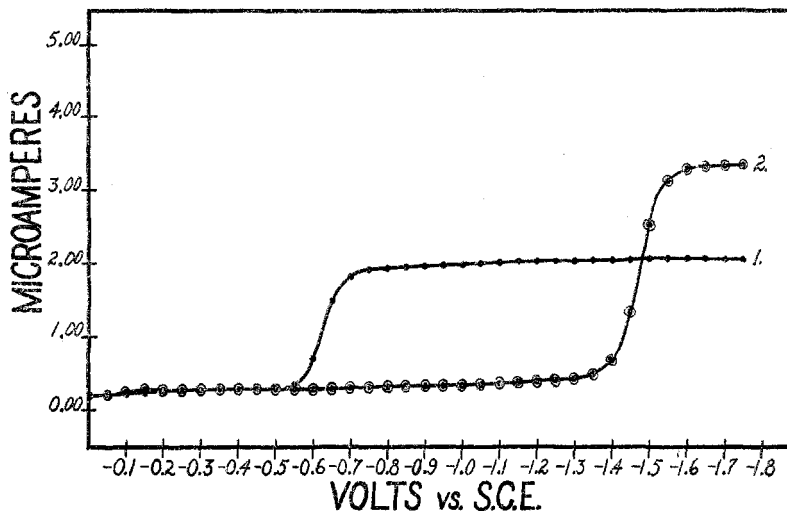


FIG. 1. 0.001 M Solution of isatin in 50% ethanol. Buffered at pH 9.02. Curve 1 is the initial polarogram. Curve 2 is the polarogram at equilibrium.

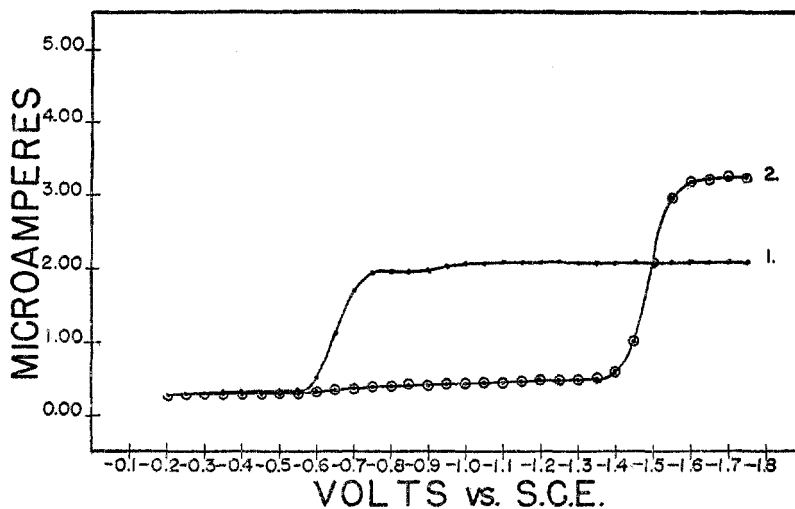


FIG. 2. 0.001 M Solution of isatin in 50% ethanol buffered at pH 10.22. Curve 1 is the initial polarogram. Curve 2 is the equilibrium polarogram.

first wave does not decrease as might be expected, but actually increases slightly (Curve 1, Figs. 2 and 3). As these solutions stand, the initial color of the solutions disappears, and the colorless solutions exhibit only one polarographic wave due in all cases to variety D (Curve 2, Figs. 1 through 5).

As the pH of the solution increases, the stability of variety E decreases and the purple color becomes more transitory. Thus at pH 10.87 and 11.51 (Curve 1, Figs. 4 and 5 respec-

tively) even the freshly mixed solutions contain some of variety D by the time the solutions can be degassed and the curves run. In addition, it will be noted that the half-wave potential of the first wave becomes increasingly negative with increasing pH (Curve 1,

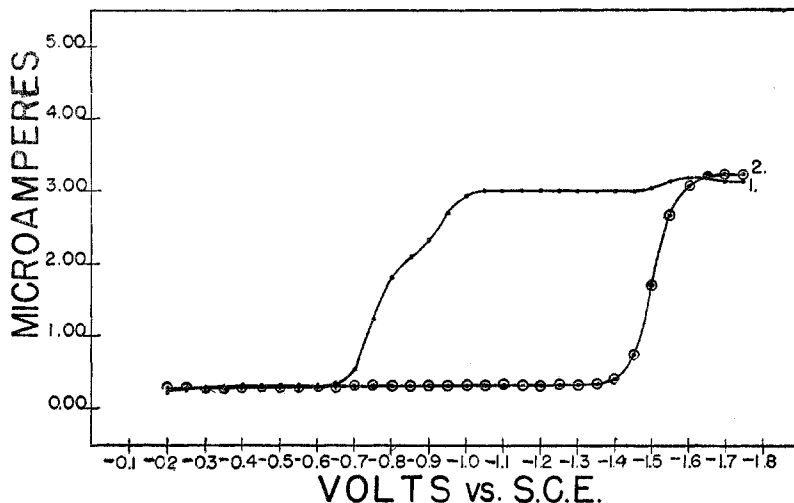


FIG. 3. 0.001 M Solution of isatin in 50% ethanol buffered at pH 11.45. Curve 1 is the initial polarogram. Curve 2 is the equilibrium polarogram.

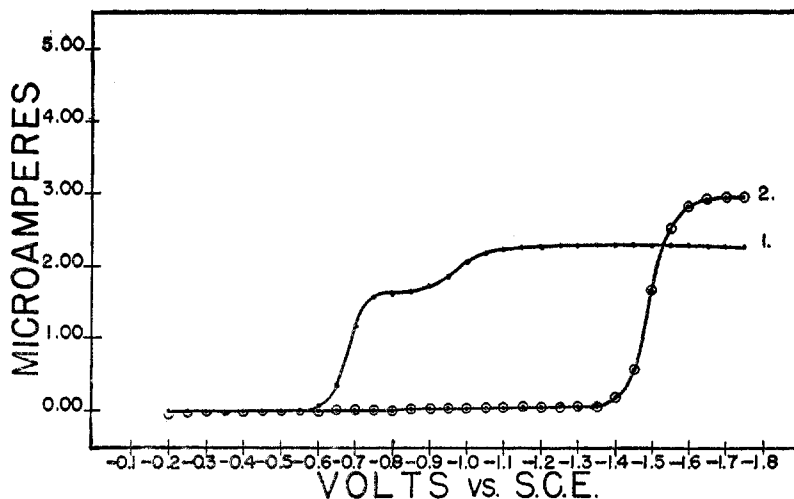


FIG. 4. 0.001 M Solution of isatin in 50% ethanol buffered at pH 10.87. Curve 1 is the initial polarogram. Curve 2 is the equilibrium polarogram.

Figs. 1 through 5) while the second wave due to variety E remains essentially stationary. At very high pH (Fig. 5) the first two waves of the initial curve have fused so that it is impossible to analyze this curve in the manner indicated below.

Studies of aqueous solutions of N -alkyl isatins revealed polarographic behavior paralleling that of aqueous isatin solutions (Chart I). Waves were exhibited indicating the presence of species corresponding to varieties A, A', B, C, and D in solutions of N -methylisatin and of N -ethylisatin (Chart IV). 5-Methylisatin parallels isatin in both color and polarographic behavior.

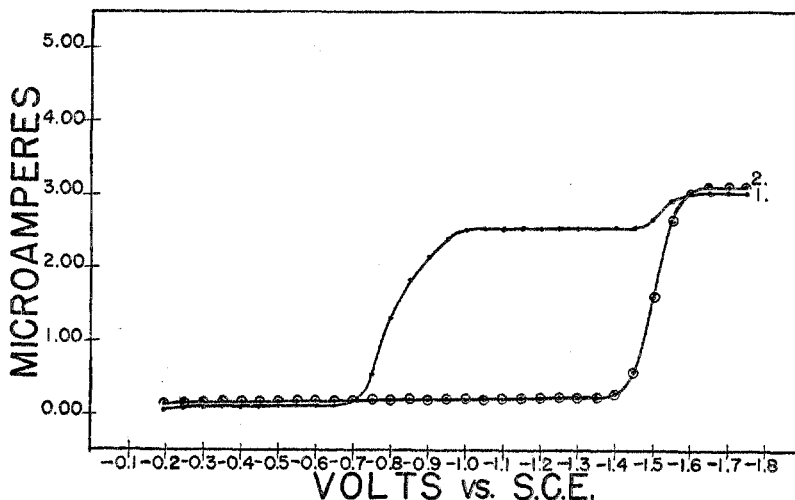


Fig. 5. 0.001 *M* Solution of isatin in 50% ethanol buffered at *pH* 11.51. Curve 1 is the initial polarogram. Curve 2 is the equilibrium polarogram.

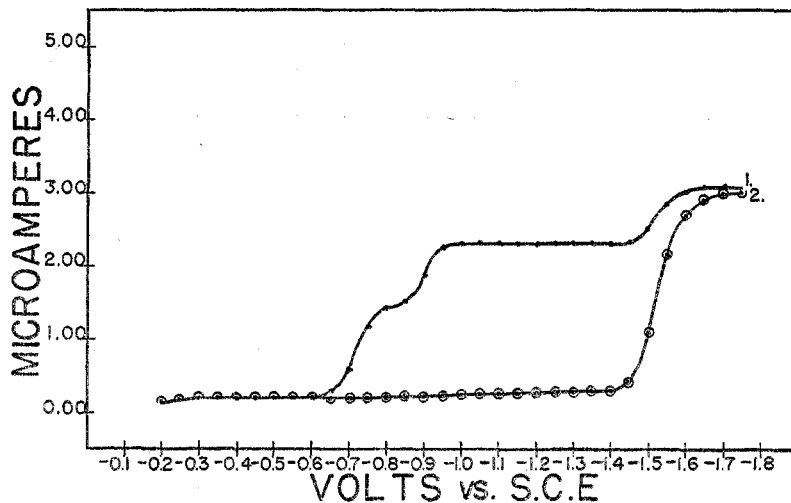
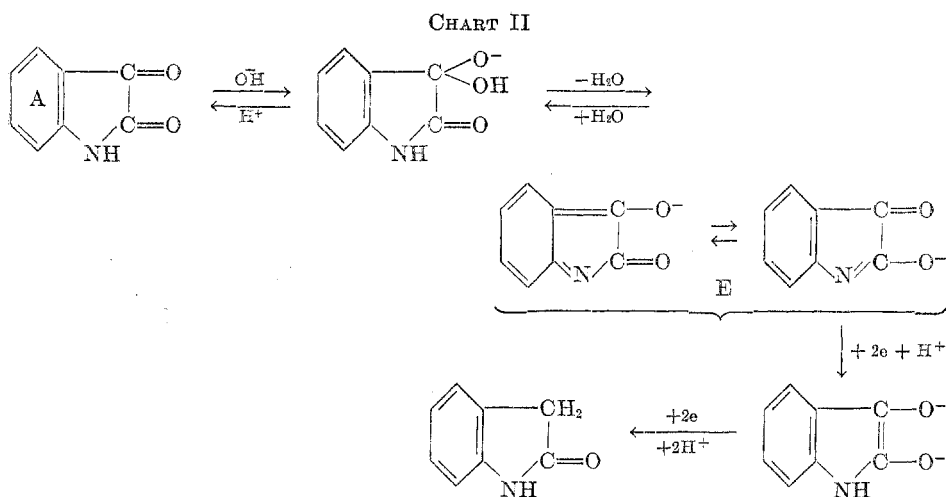


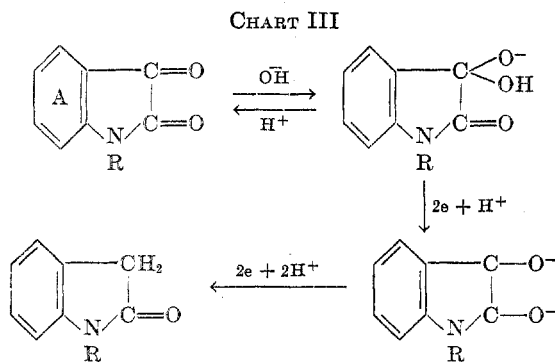
Fig. 6. 0.001 *M* Solution of *N*-methylisatin in 50% ethanol buffered at *pH* 11.58. Fifteen drops of 1% gelatine solution were added to suppress a maximum. Curve 1 is the initial polarogram. Curve 2 is the equilibrium polarogram.

Investigation of the polarographic behavior of solutions of *N*-alkylisatins in 50% ethanol buffered in the alkaline range revealed somewhat surprisingly that while these solutions failed to develop the purple color found in the isatin solutions, they exhibited the same type of polarographic behavior as did isatin itself (Fig. 6). Waves corresponding to the waves of varieties A, E, and D in isatin solutions are also found initially in *N*-methylisatin solutions at *pH* 11.58 (Curve 1, Fig. 6), and the equilibrium wave corresponding to that due to variety D in isatin is again shown after the solutions have stood several days (Curve 2, Fig. 6). The polarographic behavior of *N*-ethylisatin and of *N*-phenylisatin corresponds to that exhibited by *N*-methylisatin.

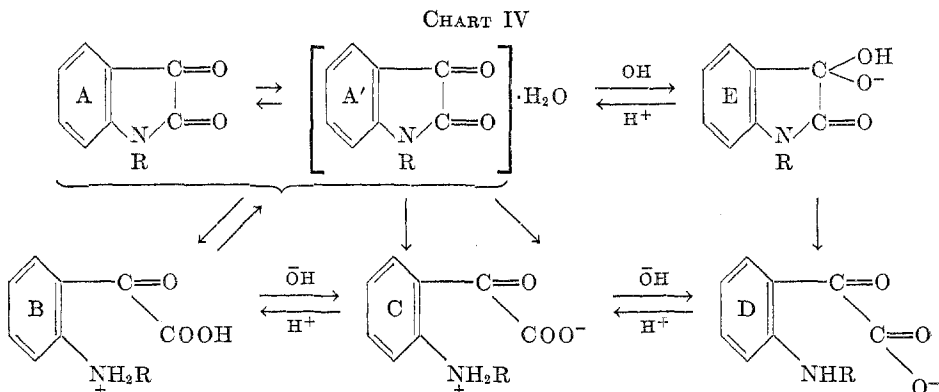
Discussion. In the previous paper the authors postulated (Chart I) that the purple color and the corresponding polarographic wave were due to the lactim form (or the lactim ion) of isatin designated as variety E. However the fact that the polarographic behavior of isatin and of the N-alkylisatins so completely parallel one another although the former is capable of yielding a lactim ion and exhibits the purple color while the latter cannot yield the lactim ion and does not exhibit the purple color, has necessitated slight revisions in our assumptions as to the nature of variety E. The complete analogy of behavior can be explained by assuming that in all cases the first action at high pH values is one of addition of hydroxyl ion to the respective β -carbonyl groups. Subse-



quent splitting out of water in the case of isatin (Chart II) yields a form which is capable of resonance and is responsible for the purple color. The corresponding product of the initial hydroxyl ion addition in the case of the N-alkylisatins is not capable of splitting out water as its isatin analog does, and the resonance responsible for the purple color is likewise impossible. The subsequent two step polarographic reduction is, however, completely analogous (Chart III).



It should be observed that in the case of both isatin (Chart I) and the N-alkylisatins (Chart IV) variety A undergoes a one-electron reduction, and variety D a two-electron reduction, while variety E undergoes the postulated four-electron reduction giving two polarographic steps, each requiring two



electrons. The basis for this assumption of a two-step, four-electron polarographic reduction of variety E lies in a comparison of the relative wave heights of the polarographic curves. The assumption that variety E is reduced first to the endiolate ion (of dioxindole) which is then reduced further to oxindole is in keeping with the well known fact that isatin can be reduced by chemical reducing agents to dioxindole which on more drastic reduction yields oxindole (2).

It will be remembered that at *pH* 10.22 (Curve 1, Fig. 2) in the isatin series the appearance of a new polarographic wave due to variety E was not at the expense of the wave height of the first wave as would have been the case had this first wave been due entirely to variety A. If it is assumed that the reduction of variety E exhibits two equal steps at the dropping mercury electrode, and that the half-wave potentials of variety A and of the first step of the reduction of variety E coincide, the increase in total wave height of these initial curves is easily accounted for. To test the validity of this assumption an analysis of the calculated and experimentally measured values of the wave heights at equilibrium (Curve 2, Figs. 3 and 4) was made.

The curves were analyzed on the basis of the contribution of each variety found in the initial curve (Varieties A, E, and D) to the final wave height of the equilibrium curve, variety D alone being present at equilibrium. Since variety A undergoes a one-electron reduction it should (on changing to variety D) contribute twice its experimentally measured wave height to the final wave height of D which undergoes a two-electron reduction. Similarly each of the two steps in the reduction of variety E should contribute one-half of the experimentally measured wave height to the final wave height of D if it is assumed that each step is a two-electron reduction. Such an analysis follows together with the experimentally measured wave height of D (equilibrium curve).

Curve 1, Fig. 3.

Variety A contributing 0.90 microamps. yields at equilib. D contributing	1.80 microamps.
Variety E contributing 1.80 microamps. yields at equilib. D contributing	0.90 microamps.
Variety D contributing 0.20 microamps. yields at equilib. D contributing	0.20 microamps.
Diffusion current of equilibrium curve calculated from breakdown of initial curve.	2.90 microamps.
Experimental diffusion current (Curve 2, Fig. 3) at equilibrium	2.90 microamps.

A similar analysis of the curves at pH 10.87 (Fig. 4) in the isatin series is in agreement with the assumptions made above. The fusion of the first two waves of the initial curve at pH 11.51 (Curve 1, Fig. 5) made such an analysis im-

TABLE I
E_{1/2} VALUES VOLTS *vs.* S. C. E.)

pH	ISATIN		
	First Wave (Variety A)	Second Wave (Variety E)	Third Wave (Variety D)
9.02	-0.63	—	-1.47
	COMPOSITE (Varieties A and E)		
10.22	-0.66	-0.95	-1.48
10.87	-0.68	-0.95	-1.50
11.45	-0.75	-0.95	-1.50
	N-METHYLISATIN		
11.58	-0.72	-0.90	-1.54

m 0.9824 mg/sec.

at -0.68 v. t = 7.0 sec. $m^{2/3} t^{1/6} = 1.37 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$

at -0.95 v. t = 6.9 sec. $m^{2/3} t^{1/6} = 1.36 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$

at -1.50 v. t = 5.6 sec. $m^{2/3} t^{1/6} = 1.32 \text{ mg.}^{2/3} \text{ sec.}^{-1/2}$

possible since it is impossible to determine what contribution each variety makes to this wave.

Analysis of the polarograms of the N-alkylisatin solutions likewise gave support to the assumption of a two-step four-electron reduction of variety E. Such an analysis for a solution of N-methylisatin at pH 11.58 (Fig. 6) follows:

Curve 1, Fig. 6.

Variety A contributing 0.44 microamps. yields at equil. variety D contributing	0.88 microamps.
Variety E contributing 1.66 microamps. yields at equil. variety D contributing	0.83 microamps.
Variety D contributing 0.80 microamps. yields at equil. variety D contributing	0.80 microamps.
Diffusion current of equilibrium curve calculated from breakdown of initial curve.	2.51 microamps.
Experiment diffusion current (Curve 2, Fig. 6) at equilibrium	2.63 microamps.

It should be stated here that at lower pH values the agreement between the calculated and measured diffusion currents for variety D (at equilibrium) of the N-alkylisatin series is not as satisfactory as in the case in the comparison of the curves shown in Fig. 6. This is due to the fact that maxima occurring in the second waves of the curves at lower pH values are not completely eliminated by the addition of gelatin solution.

The complete parallel of the polarographic behavior of isatin and of the N-alkylisatins together with the above comparisons of calculated and observed wave heights seems to lend valid support to the assumptions made by the authors as to the probable structures of the several molecular and ionic species found to exist in aqueous and alcoholic solutions of these compounds. That the effects discussed are due to changes in pH and not to formation of borate complexes was established by repeating the experiments with solutions brought to the same pH by use of NaOH-KH₂PO₄ mixtures. The polarographic behavior of the solutions paralleled that of the solutions buffered with sodium hydroxide-sodium borate mixtures.

Acknowledgment. The senior author (W. C. S.) is grateful to the Research Corporation for a grant which made this investigation possible.

SUMMARY

Studies of the polarographic behavior of isatin solutions have been extended to cover the behavior of isatin and N-alkylisatins in solution in 50% ethanol. A rationalization of the behavior of these compounds has been suggested.

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