[Contribution from the Frick Chemical Laboratory of Princeton University]

A Polarographic Study of Certain Anthraquinones[1]

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Introduction

The general importance of the anthraquinones in connection with the chemistry of dyestuffs and pharmaceuticals appeared to us to justify a detailed polarographic study of typical anthraquinones. Certain anthraquinones were subjected to a thorough potentiometric study in various buffered media by Conant, Kahn and Fieser.[2] It appeared of interest to determine to what extent polarographic measurements would correlate with the equilibrium measurements of the oxidation–reduction potentials of these compounds. The latter equilibria were in many cases established rather slowly.

No detailed systematic work has been reported on the polarography of the anthraquinones. Adkins and Cox[3] reported reduction potentials of 9,10-anthraquinone and 9,10-phenanthrenequinone in unbuffered tetramethylammonium hydroxide solutions. Wawzonek, *et al.*[4] reported half-wave potentials for anthraquinone in buffered media of undetermined *p*H. The measurements that are to be described were made with well-buffered solutions. In several instances buffers of the same *p*H but of different components were used. Many instances of specific buffer effects were found: for example, the slopes of waves of the same compound were often different at the same *p*H in buffers of different composition. In many instances the slopes of the waves indicated semiquinone formation (slope for $n = 1$), and in a number of cases the semiquinone waves were separate. In other cases the slopes of the single waves were close to the theoretical for a process in which $n = 2$. Evidence of complex formation is marked, as might be expected, in phosphate and borate buffers with various hydroxanthraquinones. If a sulfonic acid group is *alpha* to one or both of the oxygen atoms of the quinone group, the waves in acidic buffers are of peculiar long drawn-out form. It is not known whether the hindered reduction is due to steric effects, inductive effects or possibly to hydrogen bonding.

The quantitative estimation of the majority of the anthraquinones is found to be possible over part of the *p*H range. In aqueous media buffers of high *p*H (9–12) must be used to dissolve many of the compounds. The 2,6- and the 2,7-disulfonates of anthraquinone were able to be estimated over a greater range of *p*H than the hydroxy-substituted compounds. In a few instances neither the half-wave potentials nor the value of i_d per millimole per liter were constant with change in concentration. This behavior was shown, for example, by anthraquinone 1-amino-2-sodium sulfonate.

Experimental

Apparatus and Materials.—The majority of the polarographic measurements were made with a Leeds and Northrup Electrochemograph equipped with the type of cell assembly that was described by Furman, Bricker and Whitesell.[5] The temperature was noted during experiments. It was generally between 23 and 25°. A mercury anode was used and the anode potential was measured relative to a saturated calomel electrode. A students' type potentiometer and a research-model *p*H meter of the Leeds and Northrup Co. were used. Certain critical observations were repeated by D. R. Norton of this Laboratory, using a locally built polarograph of the photographic recording type.[5] Some of these observations were made directly against a saturated calomel electrode as anode. The half-wave potentials checked those measured less directly in the course of experiments with the electrochemograph. An agar salt bridge saturated with potassium nitrate was used.

It was necessary to measure *p*H and the anode potentials in solutions that contained 1% of alcohol by volume and also in 40% dioxane solutions. The aqueous buffers differed by only about 0.1 *p*H unit from aqueous buffers of the same molarity of buffer components. The apparent *p*H of buffers that contained 40% of dioxane differed from the comparable aqueous buffers by amounts varying from 0 to 2 *p*H units, depending on the *p*H range and the buffer components (Table I). The anode potentials in

Table I

Buffers and *p*H

Nature of buffer	Components	*p*H in aq. medium	Apparent *p*H in 40% dioxane
Acetate	Sodium acetate–acetic acid	4	5.6
		5	6.7
Citrate	Citric acid–sodium hydroxide	6	7.0
Phosphate	Potassium dihydrogen- sodium hydroxide phosphate	6	6.8
		7	7.9
		8	8.9
Acetate	Ammonium acetate–ammonia	7	7.4
		8	8.2
Borate	Boric acid–sodium hydroxide	8	10.0
Ammonia	Ammonium chloride–ammonia	9	9.0
		10	9.7
Tartrate	Tartaric acid–sodium hydroxide	11	11.5
Phosphate	Disodium phosphate–sodium hydroxide	11 and 12	. .
Borax	Borax–sodium carbonate	12	11.2

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[1] Abstracted from a thesis submitted by K. G. Stone in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Princeton University, May, 1946.

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[2] J. B. Conant, H. M. Kahn, L. F. Fieser and S. S. Kurtz, Jr., This Journal, **44**, 1382 (1922).

[3] H. Adkins and F. W. Cox, *ibid.*, **60**, 1151 (1938); *cf.* also R. H. Baker and H. Adkins, *ibid.*, **62**, 3305 (1940).

[4] S. Wawzonek, H. A. Laitinen and S. J. Kwiatkowski, *ibid.*, **66**, 827 (1944).

[5] N. H. Furman, C. E. Bricker and E. B. Whitesell, *Ind. Eng. Chem., Anal. Ed.*, **14**, 333 (1942).

TABLE II

COMPOUNDS STUDIED AND COMPOSITION OF STOCK SOLUTIONS

	Compound	Solvent	Conc. mg. per ml.	Remarks
1	Anthraquinone	Buffer–dioxane	Satd.	Buffers in 40% dioxane were saturated with anthraquinone
	Substituted anthraquinones:			
2	Anthraquinone-2-sodium sulfonate	5% Ethanol	0.95	
3	2,6-Disodium sulfonate	5% Ethanol	1.84	
4	2,7-Disodium sulfonate	5% Ethanol	1.85	
5	1-Amino-2-sodium sulfonate	5% Ethanol	2.00	
6	3-Amino-2-sulfonic acid	10% Ethanol	1.00	
7	1-Amino-2-$NaSO_3$-4-Br	5% Ethanol	1.86	Technical sample
8	Anthraquinone-1-sodium sulfonate	5% Ethanol	1.00	
9	1,5-Disodium sulfonate	5% Ethanol	1.94	
10	1-$NaSO_3$-5-NO_2	5% Ethanol	0.92	
11	1-$NaSO_3$-8-NO_2	5% Ethanol	0.86	
12	1,2-Dihydroxy-(Alizarin)	5% Ethnaol	1.00	1.0 g. sodium hydroxide per liter
13	1,4-Dihydroxy-(Quinizarin)	5% Ethanol	1.00	1.0 g. sodium hydroxide per liter
14	1,5-Dihydroxy-(Anthrarufin)	5% Ethanol	1.00	1.0 g. sodium hydroxide per liter
15	1,2,4-Trihydroxy-(Purpurin) (a)	Dioxane	1.00	
	(b)	5% Ethanol	1.00	1.0 g. sodium hydroxide per liter
16	1,2-Dihydroxy-3-$NaSO_3$ (Alizarin red S)	5% Ethanol	1.00	Technical sample
17	1,8-Dihydroxy-3-CH_2OH-(Aloe Emodin)	5% Ethanol	0.50	0.5 g. sodium hydroxide per liter
18	1,5-Dihydroxy-4,8-diamino-2-$NaSO_3$ (Alizarin saphirol E)	5% Ethanol	1.84	Technical sample
19	1,3,4,6-Tetrahydroxy-2-$C_6H_{11}O_5$-8-CH_3-(Carminic acid)	5% Ethanol	2.00	1.0 g. sodium hydroxide per liter

dioxane media differ largely from those in aqueous solutions, and the $E_{1/2}$ values are not comparable with those in aqueous media because of liquid junction effects and changed activities.

Resistance measurements were made with a Solar Conductivity Bridge, Model RC-1B, made by the Industrial Instruments Co. These measurements were used, when necessary, in connection with the plotting and analysis of current–potential curves.

A single capillary of Corning marine barometer tubing was used throughout the measurements that were made with the Electrochemograph. The characteristics were: $m = 0.8173$ mg. per sec. at 46.5 cm. of mercury. Drop times were measured in the half-wave potential region with the current flowing.

Volumetric apparatus was checked as to correctness of calibration.

Materials.—The buffers that were used are indicated in Table I. Each had 0.25 mole of the first-mentioned buffer component per liter and the *p*H was adjusted by a suitable addition of the second component.

The acetate buffers of *p*H 4 and 8, respectively, are near the end of the buffering range for such mixtures. It was desirable to have a *p*H 8 buffer that did not contain phosphate or borate since these substances have specific complexing action on certain substituted anthraquinones in this *p*H region. In general the buffer components were present in concentrations from 70 to 100 times that of the anthraquinone. The buffer mixtures were tested polarographically and showed no interfering waves at the polarographic sensitivities that were used. In general observations were taken at $^1/_{20}$th of the maximum sensitivity of the instrument.

Anthraquinones.—A du Pont sublimed sample of anthraquinone of m. p. 284.5° was used. Because of slight solubility it was necessary to use buffer solutions in 40% dioxane that were saturated with anthraquinone.

Aloe emodin was prepared by oxidizing aloin with ferric chloride as described by Cahn and Simonsen.[6] The product, after recrystallization from toluene, melted at 218°. 3-Aminoanthraquinone 2-sulfonic acid was prepared by sulfonation of 2-aminoanthraquinone.[7] The carminic acid was a product from the National Aniline and Chemical Co.; it was labeled "Carmine, C. P." Alizarin Saphirol E, alizarine-3-sodium sulfonate and 1-amino-4-bromoanthraquinone-2-sodium sulfonate were technical products supplied by the Calco Chemical Co., which also supplied the remaining anthraquinones in purified form.

Dioxane was purified by the procedure of Hess and Frahm.[8] When so freed from the glycol acetal that occurs in the commercial material it is stable, with moderate protection from oxygen, for three weeks or longer as far as peroxide formation is concerned.

The nitrogen was passed through alkaline pyrogallol to remove oxygen.

General Procedure.—The solutions were prepared in such a way that when polarographed they were 0.1 molar in the principal buffer component and approximately 0.001 molar in the compound that was being studied. The concentration of the anthraquinone was calculated from that of the stock solution of the compound in those cases where the compound was sufficiently soluble. The maxima that were encountered were suppressed either by adding methyl red or methyl cellulose. The compounds that were studied and the nature of the stock solutions is shown in Table II.

Diffusion Coefficients.—The diffusion coefficients of aloe emodin and alizarin were measured at 25° by the method of Northrop and Anson.[9] The concentrated solution of aloe emodin within the diffusion cell contained 5 mg. per ml. in 1% sodium hydroxide solution. The amounts of the emodin that diffused were measured by the colorimetric method of Stone and Furman.[10] The

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(6) R. S. Cahn and J. L. Simonsen, *J. Chem. Soc.*, 2573 (1932).

(7) F. Ullmann and R. Medenwald, *Ber.*, **46**, 1728 (1913).

(8) K. Hess and H. Frahm, *ibid.*, **71**, 2627 (1938).

(9) J. H. Northrop and M. L. Anson, *J. Gen. Physiol.*, **12**, 543 (1929).

(10) K. G. Stone and N. H. Furman, *Ind. Eng. Chem.*, *Anal. Ed.*, **19**, 105 (1947).

TABLE III

$E_{1/2}$ *vs.* THE SATURATED CALOMEL ELECTRODE FOR CERTAIN ANTHRAQUINONES IN 1% ETHANOL SOLUTION; THE SUBSTITUENTS ARE INDICATED; ALL $E_{1/2}$ VALUES ARE NEGATIVE

Buffer	pH	2[a] 2-NaSO$_3$	3 2,6-diNaSO$_3$	4 2,7-NaSO$_3$	5 1-NH$_2$-2NaSO$_3$	6 3NH$_2$-2-HSO$_3$	7 1NH$_2$-4-Br-2NaSO$_3$	8 1-NaSO$_3$	9 1,5-di-NaSO$_3$	10 1-NaSO$_3$-5-NO$_2$	11 1-NaSO$_3$-8-NO$_2$
Acetate	4	0.50	0.44	0.44	0.61	0.57	0.60	0.69	0.50 0.58	.. .. ..	0.46
Acetate	5	.51	.43	.42	.63	.55	.59	.69	0.66	0.50 0.67 1.03	.45
Acetate	7	.45	.45	.44	.59	.52	.56	.56	.63	.43 .70 1.02	0.45 0.64
Acetate	8	.50	.47	.46	.60	.56	.58	.55	.56	.44 .72 0.99	.35 .64
Phosphate	6	.61	.54	.56	.73	.66	.72	.76	.81	.56 .77 1.15	.46 .76
Phosphate	7	.54	.48	.50	.67	.60	.67	.65	.71	.47 .71 1.05	.39 .69
Phosphate	8	.61	.50	0.49 0.58	.73	.69	.73	.69	.72	.56 .83 1.07	.45 .74
Phosphate	11	.67	.62	.63	.76	.75	.79	.70	.74	.55 .79 .96	.51 .81
Phosphate	12	.63	.58	.56	.75	.72	.77	.70	.76	.54 .86	.53 .86
Citrate	6	.47	.43	.44	.59	.55	.61	.65	.68	.44 .68 1.04	.. ..
Borate	8	.63	.58	.58	.70	.70	.71	.61	.66	.. .. ..	.46 .76
Borax	11	..	.63	.60	.78	..	.78	.71	.76	.57 .81 0.97	.54 .86
Ammonia-NH$_4$Cl	9	.55	.50	.50	.64	.62	.62	.57	.60	.45 .72 0.95	.37 .65
Ammonia-NH$_4$Cl	10	.60	.58	.57	.68	.68	.69	.61	.62	.52 .81 1.01	.44 .73
Tartrate	11	.61	.54	.54	.71	. .72	.72	.70	.73	.52 .86	.49 .85
0.1 *M* KCl[b]		.60	.55	.55	.70	0.36 1.33	..	.60	.67	.. .. ..	.42 .74

Buffer	pH	12 1,2-Di-OH Alizarin	13 1,4-Di-OH Quinizarin	14 1,5-Di-OH Anthrarufin	15 1,2,4-Tri-OH Purpurin	16 1,2-Di-OH-3-NaSO$_3$ Alizarin Red S	17 1,8-Di-OH-3CH$_2$OH Aloe Emodin	18 1,5-Di-OH, 4,8-Di-NH$_2$-2-NaSO$_3$	19 1,3,4,6-Tetra-OH 2-C$_6$H$_{11}$O$_5$-8-CH$_3$
Acetate	4	..	..	..	.. ..	0.57	..	0.62 1.17	0.64 0.73
Acetate	5	..	..	..	.. ..	.56	..	.61 1.11	0.70
Acetate	7	0.61	..	..	0.42 0.66	.56	..	.65 1.16	.68
Acetate	8	.62	..	..	.42 .67	.58	..	.67 1.19	.71
Phosphate	6	..	..	..	.80	.67	..	.. ..	.81
Phosphate	7	..	..	..	.45 .69	.63	..	.69 1.19	.73
Phosphate	8	.72	0.56	..	.53 .78	.58	..	.75 1.28	.80
Phosphate	11	.84	.71	0.63	.68 .92	.83	0.68	0.74	..
Phosphate	12	.89	.73	.73	.70	.89	.73	.70	..
Citrate	6	.60	..	..	.43 .56	.52	..	..	.69
Borate	8	.73	..	..	..	.75	..	.76	.72 .83
Borax	11	.87	.69	.71	.67	.85	.71	.76	..
Ammonia-NH$_4$Cl	9	.71	..	..	..	.73	..	.69	..
		.78	..	..	..	.73	..	.76	..
Ammonia-NH$_4$Cl	10	..	.78	.77	.68 .94	..	.77	.74	..
Tartrate	11	.69	..	..	.49	.67 .92	..	.79	.79

[a] Numbers correspond to those in Table II. [b] The stock solutions were frequently alkaline; see Table II.

diffusion coefficient of aloe emodin was found to be 2.4 × 10^{-6} cm.^{2} per sec. at 25°. The constant of the diffusion cell was determined by measurements with potassium chloride and the published data of Clack.[11] The diffusion coefficient for a solution containing 1 mg. of alizarin per ml. in 1% sodium hydroxide was 4.0 × 10^{-6} cm.^{2} per sec. at 25°. For anthraquinone β-sodium sulfonate the diffusion coefficient that was calculated from the polarographic data was 7.1 × 10^{-6} cm.^{2} per sec. whereas the experimentally determined coefficient was 4.8 × 10^{-6} cm.^{2} per sec. In the latter case the solution was 25 times as concentrated as the solutions that were polarographed and the medium contained 11 g. of ammonium chloride and 30 ml. of concd. ammonia at the start of the diffusion experiment, with 5 mg. of the compound per ml.

Diffusion coefficients were calculated for the other anthraquinones on the basis of the Ilkovic equation[12] on the assumption that two electrons per molecule were involved in the reductions.

A general summary of observed half-wave potentials in aqueous solutions is given in Table III. In order to show the rather slight variation of $E_{1/2}$ with pH the data for buffers of similar composition are grouped together in the table.

Half-wave data for certain compounds in 40% dioxane solution are shown in Table IV.

General data on the polarographic behavior of the substances that were studied are presented in Table V.

Slopes of Waves.—In the pH region 4–8 the slopes of the waves were frequently close to that for a one electron process. In many instances semiquinone formation is a factor and the merging of the waves for the two processes: Quinone $\rightleftarrows$ semiquinone $\rightleftarrows$ hydroquinone, gives

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[11] B. W. Clack, *Proc. Roy. Soc.* (*London*), **29**, 49 (1917).

[12] D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).

TABLE IV

$E_{1/2}$ *vs.* S. C. E. FOR SOME ANTHRAQUINONES IN MEDIA CONTAINING 40% OF DIOXANE (ALL VALUES FOR $E_{1/2}$ ARE NEGATIVE)

Buffer	Apparent *p*H	1 Anthra-quinone	5 Anthraquinone 1-NH_2-2-$NaSO_3$	15 1,2,4-Tri-OH anthra-quinone
Acetate	5.6	0.51	0.58	0.67
Acetate	6.7	.62	.66	.72
Acetate	7.4	.54	.63	.70
Acetate	8.2	.65	.70	.78
Citrate	7.0	..	.75	.80
Phosphate	6.8	.70	.78	.86
Phosphate	7.9	.71	.78	.86
Phosphate	8.9	.73	.77	.87
Borate	10.0	.74	.77	..
Borax	11.2	.79	.82	.95
Tartrate	11.5	..	.82 0.92	..
Ammonia	9.0	.65	.69	.78
Ammonia	9.7	.70	.72	.84
0.1 *M* KCl	7.1	.69	.77	.88

TABLE V

GENERAL DATA ON THE REDUCTION OF VARIOUS ANTHRAQUINONES

Substituents in anthraquinone^{a}	Concn., millimoles per liter^{b}	Diffusion coeff. × 10^6 calcd.^{c} sq. cm. per sec.	Diffusion current, i_d per millimol. per liter^{c}	$i_d/m^{2/3}t^{1/6}$,^{c,d}
2-$NaSO_3$	0.610	7.1	3.94	3.22
2,6-Di-$NaSO_3$	.890	5.8	3.60	2.92
2,7-Di-$NaSO_3$	.896	5.1	3.40	2.74
1-NH_2-2-$NaSO_3$	1.23	6.2	3.71	3.01
	1.23^{e}	4.1	2.99	2.44
3-NH_2-2-HSO_3	0.641	5.6	3.49	2.78
1-$NaSO_3$^{b}	.645	8.4	4.34^{f}	3.60
1,5-Di-$NaSO_3$	.937	6.3	3.85^{f}	3.11
1-$NaSO_3$-5-NO_2	.556	6.0	14.80^{g}	11.84^{g}
1-$NaSO_3$-8-NO_2	.524	7.4	16.18^{h}	13.16^{h}
1,2-Di-OH Alizarin	.834	6.5	3.84	3.09
1,5-Di-OH Anthrarufin	.834	4.7	3.26	2.61
1,2,4-Tri-OH	.780	3.6	2.87^{h}	2.30^{h}
Purpurin	.780^{e}	3.9	3.08	2.50
1,2-Di-OH-3-$NaSO_3$ Alizarin Red S.	.570	3.5	2.80	2.26
1,8-Di-OH-3-CH_2OH Aloe Emodin	.370	6.8	3.89	3.14
Carminic Acid	.810	1.8	1.98	1.60

[a] Certain compounds listed in Table II are omitted because of unknown concentrations of the solutions. [b] In 1% ethanol and 0.1 *M* buffers, unless otherwise indicated. [c] Based on the most frequent current. In many cases the same diffusion current was found per millimole in a number of different buffers. [d] In the buffer solutions $m^{2/3}t^{1/6}$ fell in the range 1.23–1.25. [e] In 40% dioxane; 0.1 *M* buffers. [f] In alkaline buffers. See the discussion of each compound. [g] Total current for three waves. [h] Total current for two waves.

a composite wave of slope different from that for a two electron per molecule process. In alkaline buffers many of the waves approach the slope of a two electron process more closely. It should be pointed out, however, that in the phosphate buffers the slopes are frequently less than for a 2-electron process, and at times two well-defined waves appear. The wave form in citrate buffers of *p*H 6 is almost invariably poor. In Fig. 1 are shown the various forms of waves that are realized with a single compound, anthraquinone 2,7-disodium sulfonate. Similar families of curves with minor differences are found for anthraquinone-2-sodium sulfonate and with the 2,6-disodium sulfonate except for the double wave in phosphate buffer of *p*H 8. When one or more sulfonate groups are alpha to the oxygen atoms of the quinone group, long drawn-out waves are formed. This type of wave is shown in Fig. 2 (curve 4) together with a number of other types of waves that were realized in various cases. Some details as to the behavior of the individual compounds follow.

Anthraquinone could be studied only in buffer mixtures containing 40% of dioxane. The wave forms were good in acid or in strongly alkaline buffers but poor in neutral or slightly alkaline media.

Anthraquinone-1-sodium Sulfonate.—In buffers of *p*H 8 or less the waves were long drawn-out as is characteristic of all the 1-sulfonates that were examined. In alkaline buffers the waves were of conventional S-form. As can be seen from Table III the difference in $E_{1/2}$ for the 1- and 2-sodium sulfonates is about 0.2 volt which is about the energy of hydrogen bonding. An explanation of the mechanism of this hindered reduction must await further physical and chemical studies. Quantitative results were found for solutions of various concentrations in buffers of *p*H 4, 7 (phosphate), 10 (ammonia) and 11 (borax) as well as in 0.1 *N* potassium chloride.

In the *p*H 4 acetate buffer i_d per millimole per liter was 3.72 whereas in the other four buffers a constant value of 4.34 was found. This is good evidence that the species present in acidic solution is different from that in neutral or alkaline solution. Presumably the new ring formed by the bonding of the hydrogen of the sulfonic acid group to the quinone oxygen accounts for the lower diffusion current in acidic solution.

Anthraquinone-2-sodium Sulfonate.—The waves were reasonably well formed in all buffers. Quantitative variance of i_d *vs.* concentration was observed in buffers of *p*H 4 (acetate), 7 (phosphate) and 10 (ammonia).

Anthraquinone-2,6-disodium Sulfonate.—In phosphate buffers of *p*H 6 and 7 the second half of the wave is steeper than the first. This compound like the 2,7-compound gives waves of regular form in most buffers. Values of i_d were found to be proportional to concentration in buffers of *p*H 4 (acetate), 10 (ammonia) and 11 (tartrate). Presumably others could be used for quantitative work.

Anthraquinone-2,7-disodium Sulfonate.—The formation of two waves for the quinone reduction in *p*H 8 (phosphate) buffer was the unusual feature of the polarography of this compound (Fig. 1). i_d was found to be proportional to concentration at *p*H 4 (acetate), 7 (phosphate) and 12 (phosphate).

Anthraquinone-1,5-disodium Sulfonate.—Since both substituent groups are alpha to the reducible groups in this compound, the waves were again long drawn out in acidic media as in case of the 1-sodium sulfonate. Above *p*H 8 well-formed waves of normal slope were obtained. At *p*H 4 (acetate) two rather poorly formed waves, close together, were formed. Proportionality between i_d and concentration was found in buffers of *p*H 5 (acetate), 8 (phosphate), 10 (ammonia) and 12 (phosphate). i_d per millimole was, respectively, 3.53, 3.85, 3.96 and 3.85. Hence a separate calibration is necessary for each buffer.

Anthraquinone-1-amino-2-sodium Sulfonate.—The behavior in aqueous media was fairly normal, but quantitative work was possible in buffers of *p*H 5 (acetate), 8 (phosphate) and 10 (ammonia) only with empirical calibration. In a tartrate buffer of *p*H 11.5 in 40% dioxane two waves of almost equal height were formed. The total height of these waves was somewhat less than that found for the single waves in other buffers. No split into two waves occurred at *p*H 11.2 in a borax buffer.

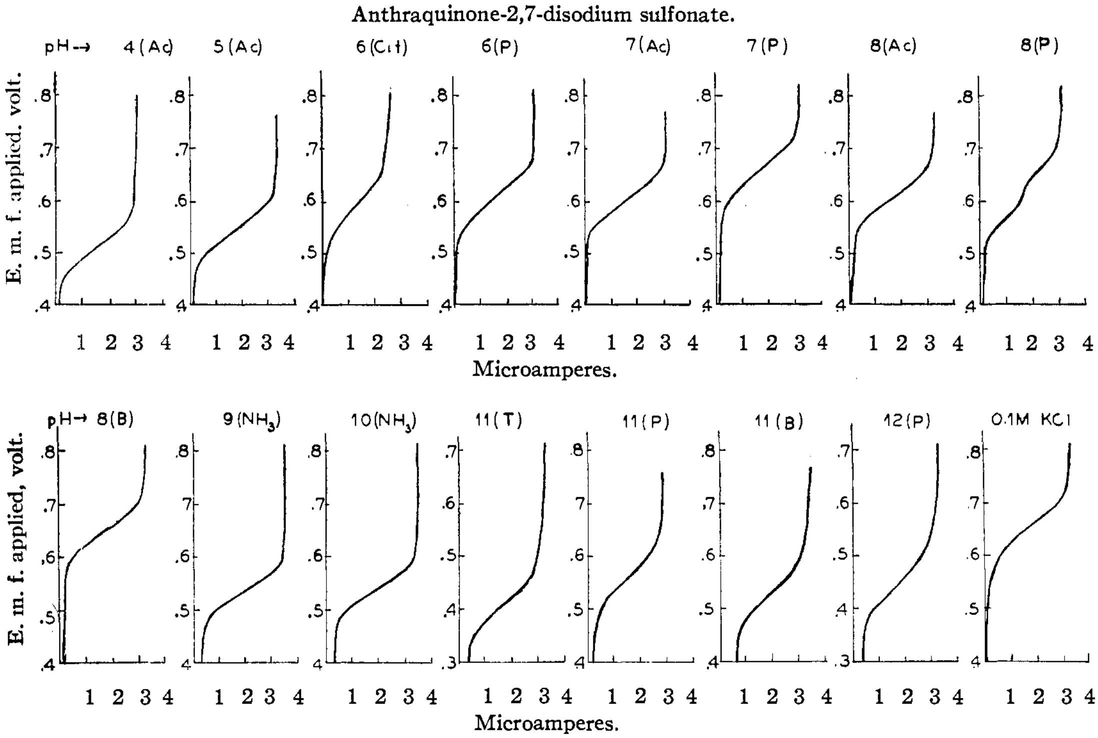

Fig. 1.—The polarography of anthraquinone 2,7-disodium sulfonate as a function of pH. The abbreviations Ac, Cit., P, etc., refer to the buffer components as shown in Table I.

Anthraquinone-3-amino-2-sulfonic Acid.—In 0.1 N potassium chloride there was a hydrogen wave, about 1 volt beyond the quinone wave, due to the sulfonic acid group, i_d per millimole per liter varied for various buffers but with separate calibrations quantitative work was possible at pH 4 (acetate), 7 (phosphate), 10 (ammonia), 12 (phosphate) and 0.1 N potassium chloride at concentrations up to 1.28 millimoles per liter.

Anthraquinone-1-amino-4-bromo-2-sodium Sulfonate.—The quinone waves were well formed in most media, but part of the compound was precipitated in 0.1 N potassium chloride, so that this medium could not be used for quantitative work. A second wave, presumably due to the removal of bromine, was observed to be coalesced with the terminal wave.

Anthraquinone-5-nitro-1-sodium Sulfonate.—Poorly formed waves were obtained in pH 4 (acetate) and 8 (borate) buffers. In most other buffers three waves of relative heights 2:1:1 were found (curve 7, Fig. 2). The first wave is believed to represent the reduction of the nitro group to the hydroxylamino stage, which is presumably stabilized by hydrogen bonding. The second wave is apparently due to reduction of the quinone to hydroquinone and the third group to reduction of the hydroxylamino group to the amino group. The ratios of the wave heights are not strictly constant presumably because of anion effects in the various buffers upon the quinone reduction. In tartrate buffer of pH 11 and in a phosphate buffer of pH 12 only two almost equal waves are found (Fig. 2, curve 8). The sum of the waves is almost equal to the sum of the three waves that are obtained in other buffers. It is therefore believed that the second wave represents the simultaneous reduction of the quinone and the hydroxylamino groups.

Anthraquinone-8-nitro-1-sodium Sulfonate.—The waves were poorly formed in an acetate buffer of pH 4. In alkaline buffers two waves of nearly equal height were formed as with the 5-nitro compound. The second wave is believed to represent the reduction of both the quinone and the hydroxylamino groups.

Alizarin, Quinazarin and Anthrarufin.—These compounds were soluble only in alkaline media. The wave forms were regular and suitable for quantitative work at pH 10–12 in ammonia, phosphate or borax buffers.

Purpurin.—In 40% dioxane solutions the wave forms were regular and well suited for quantitative work except that in a borate buffer of pH 8 two nearly equal waves are formed. A buffer of pH 9 (ammonia) is recommended for quantitative work. In aqueous media two nearly equal waves are formed in acetate, borate and phosphate buffers; the wave heights were irregular and the forms of the waves were poor in buffers of pH 8 (borate) and pH 9 and 10 (ammonia). The 40% dioxane medium should be used for quantitative work.

Aloe Emodin.—Buffers or other solutions of pH 9 or higher must be used. It was found that i_d is proportional to concentration in an alkaline solution containing 0.1 N potassium chloride and in a phosphate buffer of pH 11.[10]

Alizarin Saphirol E.—The material was of technical grade and gave a second wave beyond that characteristic of the reduction of anthraquinones. The latter was in the range that is characteristic of the reduction of a substituted anthrone. Apparently a partial reduction of the compound may have occurred during its preparation. The waves for the quinone reduction were well formed in the acetate buffers and poorly formed in alkaline media.

Alizarin Red S.—Single waves of good form were found in buffers of pH 4, 5, 7, 8 (acetate), 9, 10 (ammonia), 11, 12 (phosphate) and 11 (borax). The waves were unsymmetrical in other buffers. It was found that i_d was proportional to concentration in buffers of pH 4 (acetate), 7 and 12 (phosphate). Presumably others could be used for quantitative work.

Carminic Acid.—This was the most completely substituted anthraquinone that was available to us. The quinone reduction wave behaved much as in simpler compounds. A split into two nearly equal waves occurred in acetate, phosphate and borate buffers of pH 4, 7 and 8, respectively. An interesting point was that the double waves in the buffers of pH 4 and 7 appeared with fresh

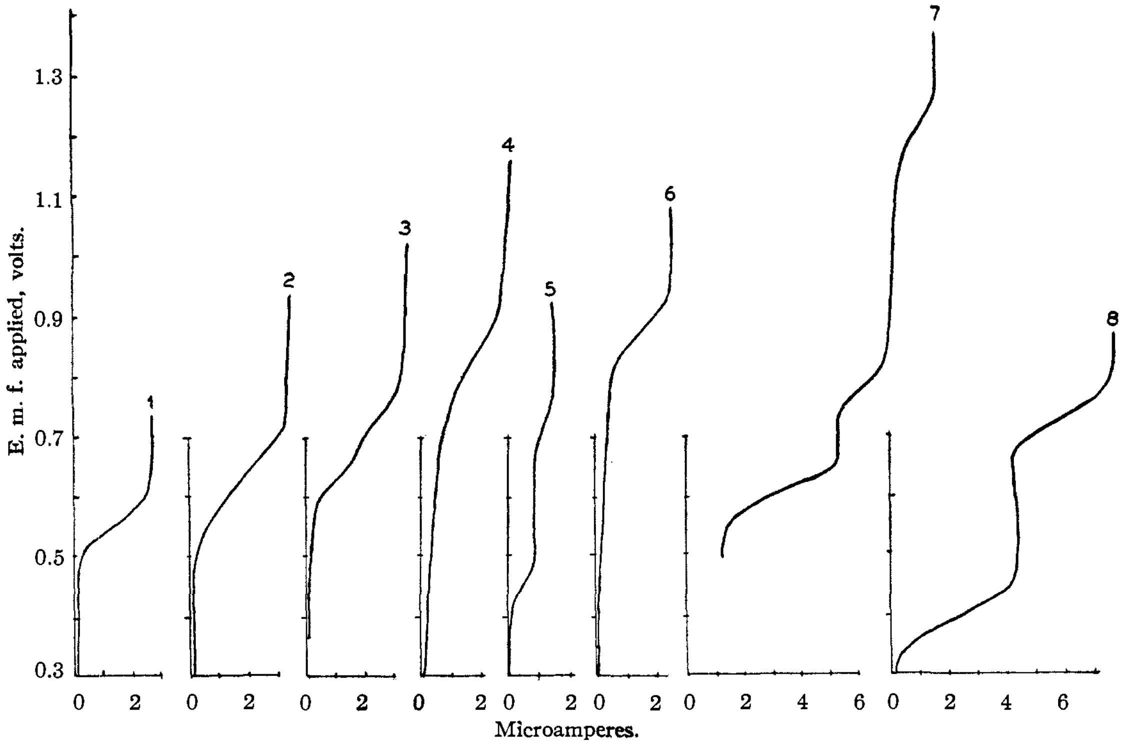

Fig. 2.—Varieties of wave forms in the polarography of anthraquinones: 1, normal curve given by the 2-sodium sulfonate at *p*H 10 (ammonia); 2, composite wave apparently made up of two merged waves; given by the 2,6-disodium sulfonate at *p*H 7 (phosphate); 3, showing two waves due to semiquinone formation, compound 1-NH_2-2-$NaSO_3$ at apparent *p*H 11 (tartrate buffer) in 40% dioxane; 4, long wave characteristic of compounds with α-SO_3H group in acidic buffers, given by the 1-sodium sulfonate at *p*H 5 in an acetate buffer; 5, two waves well separated by semiquinone formation plus complexing action, given by 1,2,4-trihydroxyanthraquinone (purpurin) at *p*H 11 in a tartrate buffer; 6, normal wave for purpurin in a *p*H 6 phosphate buffer; 7, waves given by the 1-$NaSO_3$-5-NO_2 derivative at *p*H 5 in an acetate buffer; 8, showing the merging of the second and third waves of the 1-$NaSO_3$-5-NO_2 compound at *p*H 11 in a tartrate buffer. These waves are almost identical with the two that are given at like concentration by the 1-$NaSO_3$-8-NO_2 at *p*H 12 in a phosphate buffer.

solutions, but after a short time a repetition of the polarogram showed a single wave of the same over-all height as the two waves. In borate of *p*H 8 the two waves persisted when repeated polarograms were taken. In the latter case it is believed that complexing with the borate stabilizes the intermediate structure. i_d per millimole per liter varied with concentration in acetate of *p*H 7. The sum of the two waves was proportional to concentration up to 1.8 millimolar in buffers of *p*H 4 (acetate) and 8 (borate) and a value of i_d per millimole per liter of 1.98 was found.

Half-wave Potentials and *p*H.—In the course of our work it was noted that for buffers that were made up of the same components, *e. g.*, acetates, the half-wave values in the *p*H region 4–6 varied slightly or not at all in the reduction of various anthraquinones (Table III). In more acidic solutions that were not well buffered there was a significant shift in $E_{1/2}$ with *p*H. Conant, *et al.*[2] found a shift of about 0.06 in the apparent E_0 values (midpoints of titration curves upon reduction) per unit change of *p*H of the buffered medium. A comparison of typical data from the potentiometric observations with the polarographic half-wave data is shown in Fig. 3. Data on various compounds are given in Table VI. The values π_0 and π_0' are related as follows: $\pi_0 = \pi_0' - 0.0295 \log K_1K_2$, π_0 being a measure of the free energy of formation of AH_2 from A, and π_0' of the free energy of formation of $A^=$ from A.[2]

Although the $E_{1/2}$ values vary considerably with buffer composition, their values (Table III) are much closer to π_0' than to π_0 which suggests that even in acidic media the polarographic reduction mechanism is chiefly concerned with the primary formation of doubly ionized anthrahydroquinones.

TABLE VI

REDUCTION POTENTIALS *vs.* S. C. E. FOR ANTHRAQUINONES

Anthraquinone: (substituents)	π_0[2]	π_0'[2]	$E_{1/2}$[a]	$K_3 \times 10^{11}$
2-$NaSO_3$	−0.059	−0.63	−0.63	0.45
1-$NaSO_3$	− .007	....	− .70	0.0025
2,6-Di-$NaSO_3$	− .018	− .57	− .58	2.5
2,7-Di-$NaSO_3$	− .017	− .56	− .56	2.0
1,5-Di-$NaSO_3$	− .005	....	− .74	0.005

[a] In phosphate buffer of *p*H 12.

Geake and Lemon[13] have shown for anthraquinone-2-sodium sulfonate that a medium of lower dielectric constant than water is necessary to obtain semiquinone formation. It is believed that semiquinone behavior was frequently found in our work because the anions present were able to form structures that stabilized the semiquinones. All the buffers in which two waves were obtained are known to associate with organic substances of the types in question. The buffer components were present in sufficiently great excess to promote complex formation. It was also noted that most of the compounds that had a hydroxyl group alpha to the oxygen of the quinone group formed a

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(13) A. Geake and J. T. Lemon, *Trans. Faraday Soc.*, **34**, 1395 (1938).

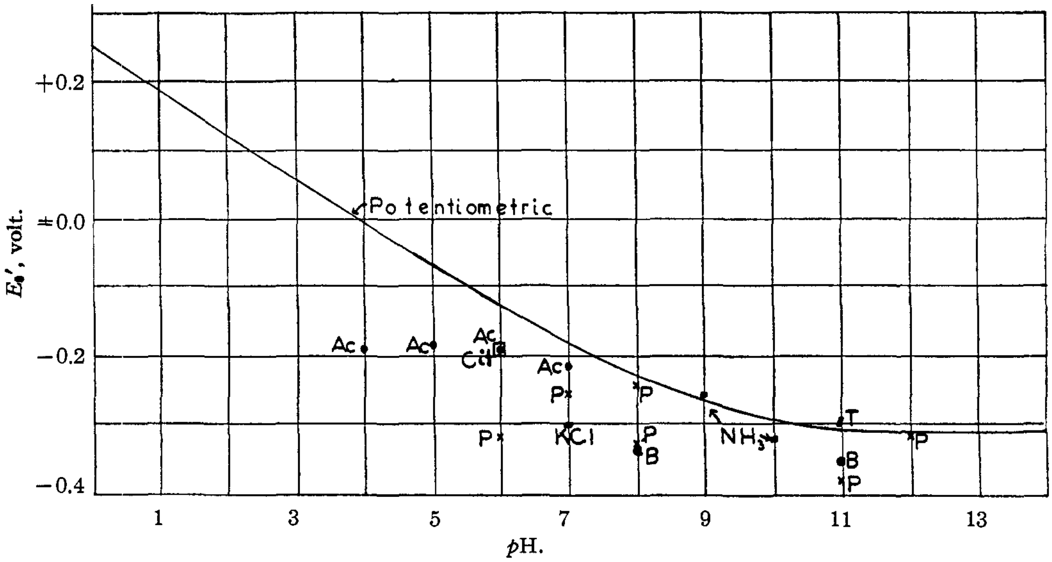

Fig. 3.—A comparison of potentiometric and polarographic data for anthraquinone-2,7-disodium sulfonate: the potentiometric curve is derived from the data of Conant, *et al.*[3] Ac, Cit, P, etc., refer to the components of the supporting solutions as shown in Table I. Specific buffer effects appear to change the polarographic $E^1/_2$ values more than does a change of pH with the same buffer components. A similar lack of change of $E^1/_2$ with pH is found in all cases with the more acidic buffers.

semiquinone in a borate buffer of pH 8. The borate undoubtedly forms the usual ring with the diol.

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Summary

Anthraquinone and its derivatives that possess the quinone structure give an early polarographic reduction wave that is usually in the neighborhood of −0.6 to −0.7 volt relative to the S.C.E. in alkaline buffers. Nineteen anthraquinones were studied.

In acidic buffers of the same qualitative composition the reduction wave is but slightly displaced with change in pH. Comparison of the polarographic $E_{1/2}$ values with the potentiometric data indicates that the quinone nucleus is first reduced to the ionized hydroquinone nucleus at the mercury surface even in acidic buffers.

Semiquinone formation is often made evident by separate waves or by unusual wave form (slope approaching a process in which $n = 1$). Certain buffer components tend to stabilize the semiquinone structure.

Waves of unusual slope are formed in acidic media when there is a sulfonic acid group in the 1- or in both 1- and 5-position. Specific complexing effects appear to occur with buffer components, *e. g.*, borates or phosphates.

The quantitative estimation of anthraquinones by the polarographic method is generally possible. These studies have gone only to concentrations as high as 1–2 millimolar. Buffers of pH 9–12 are in general suitable for quantitative estimations. Buffers containing 40% of dioxane are needed to dissolve the less soluble compounds.

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