340. *A Polarographic Investigation of the Redox Behaviour of Certain Hydroxy- and Sulphonic Acid Derivatives of Anthraquinone.*

By R. Gill and H. I. Stonehill.

The redox potential (E) and semiquinone formation constant (K) have been determined polarographically at 25° for aqueous solutions of the 1- and 2-sulphonic acid, and the 1- and 2-hydroxy- and 1 : 2-, 1 : 4-, 1 : 8-, and 2 : 6-dihydroxy-derivatives of anthraquinone, over the pH range 7—13 approx., at constant ionic strength. The reversibility of the polarographic oxidation–reduction is demonstrated by the agreement with earlier potentiometric results for some of the compounds, as well as by the independence of the results of the state of reduction of the solutions polarographed, except for the 2-hydroxy- and 2 : 6-dihydroxy-compounds, which in the reduced state tautomerise (see following paper).

Semiquinone formation is favoured by the increased ionisation at high pH, but is not completely absent even at the lowest pH used. The influence of the substituent groups on E and K for the fully ionised compounds is explained in terms of inductive, resonance, and *ortho*-effects. Addition of ethanol renders E more negative, increases K, and decreases diffusion current constant, and increase of ionic strength at constant pH in aqueous solutions renders E more negative and decreases K, although superimposed repression of ionisation complicates both the latter sets of observations. There is no evidence for association or polymerisation of any of the compounds in any state of oxidation or ionisation.

As a preliminary to the polarographic examination of some anthraquinonoid dyes, we have thought it desirable to investigate polarographically the redox behaviour of a series of substituted anthraquinones. The only published detailed investigation in this field by the same technique is by Furman and Stone (*J. Amer. Chem. Soc.*, 1948, **70**, 3055), who briefly summarise earlier work. The present investigation was completed before that paper appeared (cf. Gill, Thesis, London, 1948), and the two investigations cover some common ground, although the results are not always in agreement.

Many quinonoid systems have been shown to undergo reversible polarographic reduction, giving half-wave potentials E_m equal to potentiometrically determined virtual standard redox potentials $E^{\circ\prime}$ for a given pH, and in some cases semiquinone formation constants K (where applicable) in fair accord with potentiometric values. Such agreement has been found for *p*-benzoquinone (Müller and Baumberger, *Trans. Electrochem. Soc.*, 1937, **71**, 169, 181; Müller, *J. Amer. Chem. Soc.*, 1940, **62**, 2434; Kolthoff and Orlemann, *ibid.*, 1941, **63**, 664), *o*-xyloquinone, 4 : 7-indanequinone and 1 : 2 : 3 : 4-tetrahydro-5 : 8-naphthaquinone (Arnold and Zaugg, *ibid.*, 1941, **63**, 1317), *p*-benzoquinone, toluquinone, *p*-xyloquinone, duroquinone, and 2 : 3-dimethyl-1 : 4-naphthaquinone (Smith, Kolthoff, Wawzonek, and Ruoff, *ibid.*, 1941, **63**, 1018), α-hydroxyphenazine (Müller, *Cold Spring Harbor Symp. Quant. Biol.*, 1939, **7**, 59), and methylene-blue (Brdička, *Z. Elektrochem.*, 1942, **48**, 278). Even when the polarographic reduction (or oxidation of the corresponding reduced species) is irreversible, apparent K values, calculated on the assumption of reversibility, may sometimes be related significantly to other properties of the system which involve semiquinone formation, as, *e.g.*, for acridine and its amino-derivatives (Kaye and Stonehill, *J.*, 1951, 27, 2638), for crystal-violet, brilliant-green, and auramine, and for riboflavin, cozymase, Nile-blue, Capri-blue, and cresyl-blue (*J.*, in preparation).

We shall therefore regard polarographic current–voltage oxidation (reduction) waves as theoretically equivalent to potentiometric oxidative (reductive) titration curves, the ratio of the polarographic current at any point (reckoned from the bottom of the wave as zero) to the diffusion current or total wave-height being treated as the fractional extent of oxidation, α (reduction, 1 — α), and E_m as if it were $E^{\circ\prime}$ (cf. Kolthoff and Lingane, "Polarography," Intersci. Publ., New York, 1941, p. 185). This equivalence requires, apart from reversibility, the reasonable assumptions that the diffusion coefficients of the reduced, oxidised, and semiquinone forms of the electroactive material are all equal, and that the concentration gradient between the dropping-mercury electrode (d.m.e.) surface and the bulk of the solution is linear.

EXPERIMENTAL

Materials.—Anthraquinone 1- and 2-sulphonic acids (commercial) were recrystallised four times from water. Commercial anthraquinone 1 : 2-dihydroxy-3-sulphonic acid (alizarin-red S) was recrystallised twice from water; some difficulty was encountered, owing to its high solubility. Commerical alizarin paste was dried and extracted (Soxhlet) with glacial acetic acid, and the evaporated extract recrystallised three times from this solvent, and then twice from 95% ethanol. 2-Hydroxy- and 2 : 6-dihydroxy-anthraquinone (commercial) and technical " pure " 1-hydroxy- and 1 : 4- and 1 : 8-dihydroxy-anthraquinone were recrystallised four times from 95% ethanol. In each case the progress of purification was checked by comparing polarographic wave-height at a given concentration before and after the final recrystallisation. Ethanol was the middle cut from the fractional distillation of " absolute " alcohol. It was checked for the absence of any polarographically active impurities by determining the residual current of 0·1N-sodium hydroxide in water containing 50% by volume of the ethanol.

Sodium hydroxide, potassium chloride, and all buffer constituents were of " AnalaR " grade. Commercial sodium dithionite (hydrosulphite, Brotherton's Ltd.), described as 98—99% pure, was used as received. Mercury was redistilled, treated with mercurous nitrate solution, washed with distilled water, then acetone, and finally dried.

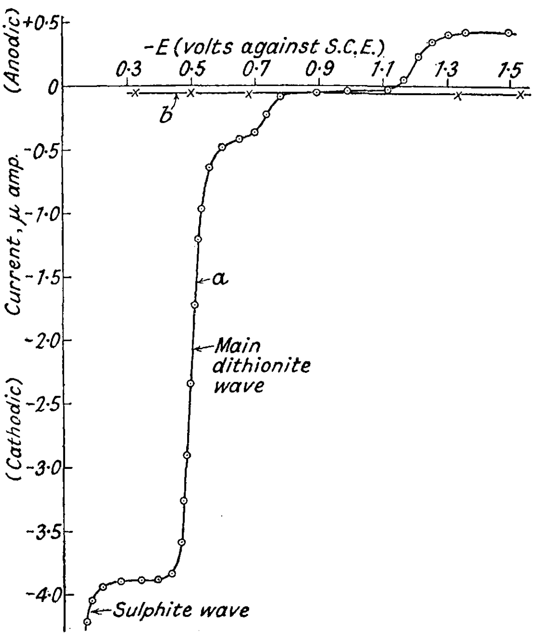
Apparatus.—A manual polarographic circuit was used. The potential was applied to the cell by a potential divider giving steps of 1/1000 of the full range, which was adjustable from ±4 v to ±0·2 v by additional series resistances. The polarographic current was measured by determining the voltage drop across a standard resistance in series with the cell, a Tinsley potentiometer being used and, as null instrument, a sensitive moving-coil galvanometer with lamp and scale; the galvanometer was shunted to damp excessive oscillations caused by variation of current during drop-life. Current accuracy was 0·005 μamp. up to 2 μamp., 0·01 μamp. between 4 and 6 μamp., and 0·03 μamp. between 8 and 10 μamp., the accuracy decreasing with increasing current because of the need for heavier damping by shunting. The polarographic cell was essentially similar to that described by Kaye and Stonehill (*J.*, 1951, 27), but in order to add dithionite to the cell contents when necessary, the cell was provided with a 1-ml. microburette, fitted by means of a ground-glass joint into a tube passing through the stopper at the top of the cell. The immersion-type saturated calomel electrode, against which the potential of the dropping-mercury electrode was measured to within 0·1 mv with the same potentiometric equipment as used for current measurement, employed electrolytic calomel (Lipscomb and Hulett, *J. Amer. Chem. Soc.*, 1916, **38**, 21). The hand-drawn Pyrex capillary had the following characteristics: drop time $t = 4{\cdot}68$ seconds with no applied potential; mercury flow rate $m = 0{\cdot}924$ mg./sec. in aqueous phosphate buffer at pH 11·27, ionic strength 0·1, at 25°. The capillary was connected to the mercury reservoir by a short glass tube in order to avoid any contact of rubber with the mercury. The small pressure due to the short head of mercury was supplemented by connecting the stoppered reservoir with a length of rubber pressure tubing to a 2-litre air-pressure reservoir bottle fitted with a mercury manometer and pressure-release cock, and charged with air *via* a cycle-tyre valve by using a cycle pump. The cell was kept at 25° ± 0·01°, unless otherwise stated, by means of a water thermostat bath.

Procedure.—Known weights of the anthraquinones were dissolved in suitable buffers of known pH and ionic strength as supporting electrolytes, and the solutions added to the cell and deoxygenated by bubbling purified cylinder nitrogen through them for 30 minutes. The nitrogen was purified by passage through two 1-metre columns packed with copper gauze kept moistened with saturated ammonium carbonate–concentrated ammonia mixture by means of lift-pump circulators (Kraus and Parker, *J. Amer. Chem. Soc.*, 1922, **44**, 2429) to remove oxygen, then through wash-bottles containing successively dilute sulphuric acid and concentrated sodium hydroxide solution to remove ammonia, acid spray, and carbon dioxide. The efficiency of deoxygenation of the nitrogen was demonstrated by the polarographic indication that the percentage reduction in a 4×10^{-4}M-solution of anthraquinone-2-sulphonic acid in 0·1N-sodium hydroxide, half-reduced with sodium dithionite, was unchanged after passing the gas stream through it for 30 minutes. In cases where the solubility of the anthraquinone compound was too low in the buffer supporting electrolyte, a solution suitable for polarography was prepared by suspending the solid compound in supporting electrolyte in the cell, deoxygenating it for 20 minutes, adding a known quantity of standard dithionite solution from the microburette, sufficient to cause partial or complete reduction, and bubbling nitrogen for at least a further 10 minutes to ensure complete reaction. Polarograms were generally corrected for residual currents, which were determined on the pure supporting electrolytes.

Results.—(1) *Sodium dithionite.* Although it would have been preferable to reduce the anthraquinones to their leuco-compounds catalytically with hydrogen and platinum or palladium, rather than by adding dithionite and thus affecting the ionic strength and composition of the solution, the highly negative reduction potentials of the anthraquinones render this impracticable (Burstein and Davidson, *Trans. Electrochem. Soc.*, 1941, **80**, 175). It was obviously desirable to examine the polarographic behaviour of the sodium dithionite used. Two independent samples gave identical polarograms, typified by Fig. 1*a*. The half-wave potentials of the various waves were scarcely affected by varying the pH over the range 8—13, but the relative wave-heights were somewhat dependent on pH. This suggests that the small waves may be due to substances (or to oxidation and reduction respectively of a single substance) in equilibrium with dithionite. In support of this view, the solution of dithionite, after oxidation by contact with air overnight, gave a polarogram (Fig. 1*b*) in which all waves had disappeared, including the cathodic wave at about —1·205 v, which would probably have been unaffected by oxidation had it been due to an impurity not in equilibrium with dithionite. No further investigation was made, however, as the suitability of the sodium dithionite for the present purpose is adequately demonstrated by Fig. 1*b*, which shows that, provided no excess unused dithionite be present, no interfering polarographic waves due to oxidation products of the dithionite will appear over the potential range employed in polarographing the anthraquinones. Brearly and Starkie (*J. Soc. Dyers Col.*, 1948, **64**, 278) obtained for zinc dithionite in ammonium phosphate a single anodic wave at —0·4 v against the saturated calomel electrode, obviously distinct from waves for sulphite, thiosulphate, and sulphide in the same medium, which start at —0·1, —0·2, and —0·8 v, respectively.

FIG. 1. *Polarograms for sodium dithionite* (0·170*g./l.*) *in* 0·1N-NaOH, 25° (*uncorrected for residual current*).

a, In oxygen free solution.
b, After atmospheric oxidation.



(2) *Anthraquinone-2-sulphonic acid.* This substance was chosen for preliminary work in establishing the applicability of polarography to semiquinone-constant investigation, because its reversible redox characteristics have been well investigated by potentiometric titration (Conant, Kahn, Fieser, and Kurtz, *J. Amer. Chem. Soc.*, 1922, **44**, 1382; Geake and Lemon, *Shirley Inst. Mem.*, 1937—38, **16**, 111, 125; *Trans. Faraday Soc.*, 1938, **34**, 1409; Burstein and Davidson, *loc. cit.*). Typical polarograms are shown in Figs. 2*a*, *b*, and in Table 1 are listed for

TABLE 1. *Results for aqueous solutions.*

Substituents	c	Supporting electrolyte *	pH	d	$-E_m$ (v)	$-E_1$ (v)	$-E_2$ (v)	$\sqrt{K}$	I
1-SO$_3$H ...	0·4	0·1N-NaOH	12·87	3·00	0·6774	—	—	0·47	0·1
,, ...	1·0	,,	12·87	2·97	0·6748	—	—	0·39	0·1
2-SO$_3$H ...	2·0	Borate	6·14	—	0·413	—	—	—	0·1
,, ...	2·0	,,	6·97	—	0·460	—	—	—	0·1
,, ...	2·0	,,	7·82	—	0·506	—	—	—	0·1
,, ...	0·314	,,	7·82	3·02	0·5064	—	—	0·24	0·1
,, ...	2·0	,,	8·69	—	0·553	0·584	0·522	0·30	0·1
,, ...	2·0	,,	9·48	—	0·576	0·602	0·550	0·36	0·1
,, ...	2·0	,,	10·23	—	0·595	0·602	0·588	0·76	0·1
,, ...	2·0	Phosphate	11·17	—	0·614	0·602	0·626	1·71	0·1
,, ...	2·0	,,	12·00	—	0·617	0·600	0·634	1·94	0·1
,, ...	1·705	,,	12·58	3·00	0·6183	0·6013	0·6353	1·94	0·1
,, ...	2·0	0·1N-NaOH	12·87	—	0·618	0·600	0·636	2·02	0·1
1-OH	1·00	Phosphate	12·00	—	0·6831	—	—	0·24	0·1
,, ...	0·402	0·1N-NaOH	12·87	2·91	0·7118	—	—	0·22	0·1
,, ...	2·29	,,	12·87	2·86	0·7098	—	—	0·35	0·1
,, ...	1·35	0·25N-NaOH	13·25	2·93	0·7178	—	—	0·14	0·25
2-OH	1·00	Borate	8·15	—	0·630	—	—	—	0·1
,, ...	1·00	,,	8·85	3·04	0·6882	0·7167	0·6597	0·33	0·1
,, ...	1·00	,,	9·59	3·09	0·7314	0·7591	0·7037	0·34	0·1
,, ...	1·00	,,	9·95	3·07	0·7462	0·7724	0·7200	0·36	0·1
,, ...	1·00	,,	10·22	3·13	0·7615	0·7820	0·7410	0·45	0·1
,, ...	1·00	Phosphate	10·79	3·16	0·7732	0·7863	0·7601	0·60	0·1
,, ...	1·00	,,	11·27	3·12	0·7910	0·7949	0·7871	0·86	0·1
,, ...	1·00	,,	12·00	3·03	0·8112	0·7966	0·8258	1·77	0·1
,, ...	1·00	0·1N-NaOH	12·87	3·08	0·8258	0·7948	0·8570	3·32	0·1
,, ...	1·00	0·25N-NaOH	13·25	3·02	0·824	0·792	0·856	3·49	0·25
,, ...	1·00	N-NaOH	13·82	3·00	0·827	0·794	0·860	3·56	1·0
,, ...	1·00	0·1N-NaOH + 0·15N-KCl	12·87	3·08	0·8163	—	—	2·96	0·25
,, ...	1·00	0·1N-NaOH + 0·5N-KCl	12·87	3·12	0·8104	—	—	2·54	0·6
,, ...	1·00	0·1N-NaOH + N-KCl	12·87	3·13	0·8072	—	—	2·04	1·1
,, ...	1·00	0·1N-NaOH + 2N-KCl	12·87	3·04	0·8008	—	—	1·59	2·1
1 : 2-(OH)$_2$	2·00	Borate	7·82	2·85	0·5528	—	—	—	0·1
,,	2·00	,,	8·69	2·88	0·6080	—	—	—	0·1
,,	2·00	,,	9·67	2·90	0·6730	0·6884	0·6576	0·55	0·1
,,	2·00	Phosphate	10·79	2·89	0·7680	0·7775	0·7585	0·69	0·1
,,	2·00	,,	11·27	2·89	0·8058	0·8061	0·8055	0·99	0·1
,,	2·00	,,	11·77	2·92	0·8352	0·8222	0·8482	1·66	0·1
,,	2·00	,,	12·00	2·84	0·8370	0·8226	0·8514	1·75	0·1
,,	2·00	0·1N-NaOH	12·87	2·89	0·8775	0·8728	0·8822	1·20	0·1
,,	2·00	0·25N-NaOH	13·25	2·91	0·8795 †	0·8771 †	0·8819 †	1·10 †	0·25
,,	2·00	0·1N-NaOH + 0·5N-KCl	12·87	3·00	0·8660	—	—	1·12	0·6
,,	2·00	0·1N-NaOH + N-KCl	12·87	3·07	0·8643	—	—	0·89	1·1
1 : 4-(OH)$_2$	1·00	Phosphate	11·27	2·85 (av.)	0·6500	—	—	0·36	0·1
,,	1·00	,,	12·00	,,	0·6801	—	—	0·19	0·1
,,	1·00	0·1N-NaOH	12·87	,,	0·7377	—	—	0·16	0·1
,,	1·00	0·25N-NaOH	13·25	,,	0·7500	—	—	0·22	0·25
1 : 8-(OH)$_2$	1·00	Phosphate	11·27	2·85 (av.)	0·6844	—	—	0·21	0·1
,,	1·00	,,	12·00	,,	0·7204	—	—	0·33	0·1
,,	1·00	0·1N-NaOH	12·87	,,	0·7599	—	—	0·28	0·1
,,	1·00	0·25N-NaOH	13·25	,,	0·7797	—	—	0·28	0·25
2 : 6-(OH)$_2$	1·00	Borate	8·25	—	0·694	0·711	0·677	0·55	0·1
,,	1·00	,,	8·85	2·99	0·750	0·769	0·731	0·52	0·1
,,	1·00	,,	9·41	2·99	0·808	0·823	0·793	0·60	0·1
,,	1·00	,,	9·95	2·99	0·844	0·850	0·838	0·80	0·1
,,	1·00	,,	10·22	2·98	0·8544	0·8574	0·8514	0·90	0·1
,,	1·00	Phosphate	10·79	2·99	0·8850	0·8764	0·8936	1·40	0·1
,,	1·00	,,	11·27	3·01	0·9122	0·8992	0·9252	1·60	0·1
,,	1·00	,,	12·00	2·97	0·9340	0·9110	0·9570	2·45	0·1
,,	1·00	0·1N-NaOH	12·87	2·99	0·9630	0·9280	0·9980	3·90	0·1
,,	1·00	0·25N-NaOH	13·25	2·92	0·9665 †	0·9267 †	1·0063 †	4·70 †	0·25

* " Borate " and " Phosphate " represent the respective buffers. † Value corrected to $I = 0·1$.

various pH values the half-wave potential E_m, and the virtual standard redox potentials at a given pH for the first and the second one-electron reduction stage (E_1, E_2); E_m was determined for each polarogram by averaging the potentials E of the dropping-mercury electrode for pairs of points having α values equidistant from 0·5; this minimises error due to any slight departure from the theoretical symmetry of the curve about the midpoint. Then, for a given value of α and of the corresponding value of $(1 - \alpha)$, the values of $|E_m - E|$ were read off the curve and averaged. The semiquinone-formation constant

$$K = [\text{semiquinone form}]^2/[\text{oxidised form}][\text{reduced form}]$$

was then calculated from the equations (Geake, *Trans. Faraday Soc.*, 1938, **34**, 1395)

$$P = e^{2\boldsymbol{F}(E_m - E)/\boldsymbol{R}T}$$

$$\sqrt{K} = 2[P - 1) - (1/\alpha - 2)]/(1/\alpha - 2)\sqrt{P}$$

in which $\boldsymbol{R}$, T, and $\boldsymbol{F}$ have their usual significance. For this purpose, Geake's tables of $2/\sqrt{P}$ and $(P - 1)$ for given values of $(E_m - E)$ were used; K values were obtained for $\alpha = 0{\cdot}1$, 0·2, 0·3, and 0·4, and the averaged value was used to calculate E_1 and E_2 from the equations

$$E_1 - E_m = E_m - E_2 = (\boldsymbol{R}T/2\boldsymbol{F}) \ln K$$

Table 1 also gives values of the diffusion current constant $d = \bar{i}_d/m^{\frac{2}{3}}t^{\frac{1}{6}}c$ ($\bar{i}_d$ = mean wave-height or diffusion current in μamp., and c = concentration of electroactive matter in m.-mol./l.).

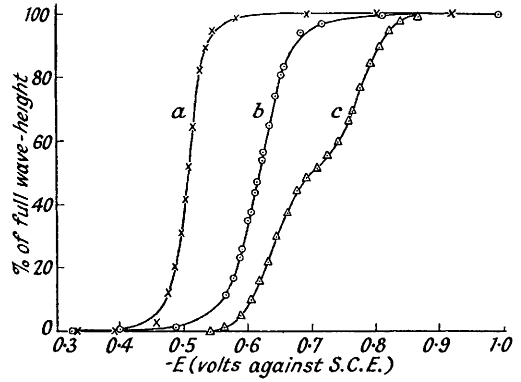


FIG. 2. *Polarograms for anthraquinone-2-sulphonic acid at* 25°; $I = 0{\cdot}1$.

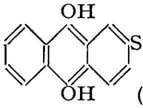
a, $3{\cdot}14 \times 10^{-4}$M, pH 7·82, *in water.*
b, $1{\cdot}705 \times 10^{-3}$M, pH 12·87, *in water.*
c, 0·3—$3{\cdot}0 \times 10^{-3}$M, 0·1N-NaOH, *in* 50% *ethanol.*

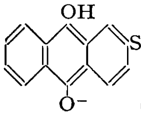
Clearly, d is practically independent of pH, and, as implied by Ilkovič's equation (*Coll. Czech. Chem. Comm.*, 1934, **6**, 498), $d = 605nD^{\frac{1}{2}}$ (n = number of electrons required per molecule reduced or oxidised = 2, and D = diffusion coefficient of electroactive molecule in cm.^{2} sec.$^{-1}$), also independent of concentration. However, the value differs from that (3·22) observed by Furman and Stone (*loc. cit.*), as well as from the value 2·65 calculated from their independent determination of D.

The graphs of E_m, E_1, and E_2 against pH (Fig. 3) contain linear sections with slopes which are multiples of —29·5 mv, in agreement with theory. The results of Burstein and Davidson (*loc. cit.*) for $c = 0{\cdot}5$, temperature 30°, I (ionic strength) = 0·2, as well as those of Geake and Lemon and of Conant *et al.* (*locc. cit.*) for 25°, fit our graphs reasonably well, but not so the polarographic results of Furman and Stone (*loc. cit.*), especially where citrate, phosphate, and borate buffers were used. The cross-over point where $E_1 = E_m = E_2$, $K = 1$, occurs at pH 10·5, in exact agreement with Burstein and Davidson. Our $\sqrt{K}$–pH data (Fig. 3) are in fair accord with values calculated from the results of Burstein and Davidson, after taking into account the increase in T and I which will tend to make their K values smaller than ours. The results of Conant *et al.* lead to $\sqrt{K}$ values of *ca.* 0·5 at pH 8—10, and of 1·93 at pH 12—13, in fair agreement with Fig. 3. Bends in the E_m–pH graph give the acid pK values of the quinol as pK_1^r = 8·65, pK_2^r = 11·05 (cf. 7·65 and 11·05, Burstein and Davidson; 8 and 11·3, Conant *et al.*; 11·35, Furman and Stone). Thus the quinol exists in the forms $R^- = (I)$ ($6 <$ pH $<$ pK_1^r), $R^= = (II)$ (p$K_1^r <$ pH $<$ pK_2^r), and $R^{\equiv} = (III)$ (pH $>$ pK_2^r).

The E_1–pH graph shows distinct evidence of a bend indicating a semiquinone pK value of pK^s = 9·02. Over the entire pH range examined, the semiquinone exists in only two forms.

Since at pH > pK^s the E_1–pH graph is horizontal, formation of semiquinone from quinone [which exists only in the form $T^- = $ (IV)] involves no protons, and is thus represented by


(I)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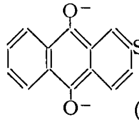
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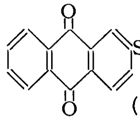
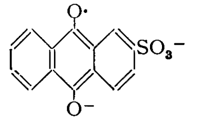
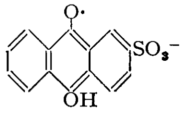

(IV)

$T^- + e \longrightarrow S^=$. Hence semiquinone exists as $S^=$ (= V) at pH > pK^s, and as S^- (= VI) at pH < pK^s. Since S^- lacks the possibility of equivalent resonance present in $S^=$, the value of K falls rapidly as pH falls (cf. Fig. 3).

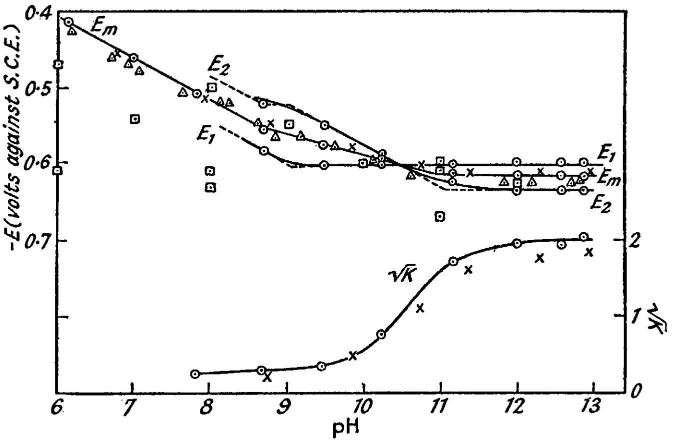
(V)




(VI)

The E_2–pH graph shows the expected bend at pH = pK_2^r. At pH > pK_2^r the second reduction step is clearly $S^= + e \longrightarrow R^{\equiv}$, and at pH's between p$K^s$ and pK_2^r it is $S^= + e + H^+ \longrightarrow R^=$. For pH's between p$K_1^r$ and pK^s it should be $S^- + e \longrightarrow R^=$ corresponding to a zero E_2–pH slope. Again, for pH < pK_1^r the process must be $T^- + e + H^+ \longrightarrow S^-$, corresponding to a 59 mv slope. Thus the E_2–pH graph should have bends at pK_1^r and pK^s, and the sparse data in this pH region are not in disagreement with this, as shown in Fig. 3.

FIG. 3. *Anthraquinone 2-sulphonic acid.*



⊙ *This work :* 2 × 10^{-3}M *in* H_2O, 25°; $I = 0{\cdot}1$.
△ E_m, *Conant* et al., *in water,* 25°.
× E_m *and* $\sqrt{K}$, *Burstein and Davidson,* 5×10^{-4}M, *in water,* 30°; $I = 0{\cdot}2$.
⊡ E_m, *Furman and Stone,* 10^{-3}M *in* 1% EtOH, 24°.

With the above assumptions regarding the various ionic forms present, the equations of the E_m–pH, E_1–pH, and E_2–pH curves may be shown by well-known methods (cf. Kaye and Stonehill, *locc. cit.*) to be as follows :

$$E_m = (E_m{}^\circ - 0{\cdot}0295 \log K_1^rK_2^r) + 0{\cdot}0295 \log (K_1^rK_2^r + K_1[H^+] + [H^+]^2)$$

$$E_1 = (E_1{}^\circ - 0{\cdot}059 \log K^s) + 0{\cdot}059 \log ([H^+] + K^s)$$

$$E_2 = \left(E_2{}^\circ - 0{\cdot}059 \log \frac{K_1^rK_2^r}{K^s}\right) + 0{\cdot}059 \log \frac{K_1^rK_2^r + K_1^r[H^+] + [H^+]^2}{[H^+] + K^s}$$

where $E_m{}^\circ$, $E_1{}^\circ$, and $E_2{}^\circ$ are constants equal to the values of E_m, E_1, and E_2 respectively at pH > pK_2^r, in which region the three graphs are all horizontal and ionisation is complete for all three oxidation levels. We find $E_m{}^\circ = -0{\cdot}618$ v, and therefore $E_m = -0{\cdot}047$ and $-0{\cdot}618$ v at pH = 0 and pH > pK_2^r respectively, in agreement with the values $-0{\cdot}051$ and $-0{\cdot}621$ v obtained from the data of Conant *et al.* (*loc. cit.*), after correction to the saturated calomel electrode standard ($E^{25°}_{\text{S.C.E.}} = 0{\cdot}238$ v).

The effect of including 50% by volume of ethanol in the solvent is shown in Fig. 2*c*, which is a composite polarogram for five different concentrations of the quinone with varying extents of reduction before being polarographed. The wave, which is slightly unsymmetrical about the centre, is two-stepped, indicating a high K value (see Table 2). A similar but smaller increase in K was observed by Burstein and Davidson (*loc. cit.*) when 50% methanol was used as solvent. Another effect of the inclusion of ethanol was the decrease of d (Table 2).

TABLE 2. *Results for aqueous-ethanolic solutions* 0·1N *in* NaOH ($I = 0{\cdot}1$)

Substituents	c	EtOH, vol. %	d	$-E_m$ (v)	$\sqrt{K}$	Substituents	c	EtOH, vol. %	d	$-E_m$ (v)	$\sqrt{K}$
1-SO_3H ...	0·40	0	3·00	0·6774	0·47	2-SO_3H ...	2·00	0	3·00	0·618	2·02
,, ...	1·00	0	2·97	0·6748	0·39	,, ...	0·3—3·0	50	1·94	0·7115	15·0
,, ...	0·55	50	1·78	0·7127	0·44	1-OH	2·29	0	2·86	0·7098	0·35
,, ...	5·30	50	1·82	0·7103	0·33	,, ...	2·33	50	1·81	0·7711	0·72
1 : 2-$(OH)_2$	2·00	0	2·89	0·8775	1·20	2-OH	1·00	0	3·08	0·8258	3·32
,,	2·00	5	2·75	0·8863	1·65	,, ...	1·00	6	2·84	0·8320	4·05
,,	2·00	10	2·26	0·8948	1·81	,, ...	1·00	12·5	2·55	0·8375	4·82
,,	2·00	25	1·76	0·9153	2·50	,, ...	1·00	20	2·35	0·8518	5·15
,,	2·00	50	1·40	0·9521	2·65	,, ...	1·00	30	2·15	0·8752	5·41
2 : 6-$(OH)_2$	1·00	0	2·99	0·9630	3·90	,, ...	1·00	40	1·97	0·8978	5·17
,,	1·00	50	1·71	1·142	6·2	,, ...	1·00	50	1·90	0·9132	4·84
						,, ...	1·00	66	1·93	0·9326	4·41

Visual evidence of semiquinone formation was provided by the colour change sequence, colourless ⟶ amber ⟶ red, observed during reduction of the quinone with dithionite in strongly alkaline solution, confirming previous observations (Burstein and Davidson; Geake and Lemon, *locc. cit.*).

(3) *Anthraquinone*-1-*sulphonic acid.* This was studied only briefly, mainly to investigate the possibility that the large sulphonate group would give rise to an *ortho*-effect in which a carbonyl group is strained out of the coplanar configuration, with consequent decrease in K. The results in aqueous and 50% ethanolic 0·1N-alkali as supporting electrolytes (Tables 1 and 2) exhibit the following points of contrast with the behaviour of the 2-isomer : K is much smaller, and is practically independent of the presence of alcohol; however, d is again decreased by the presence of alcohol. The colour sequence, colourless ⟶ orange ⟶ orange-red, on reduction in alkali confirms the presence of semiquinone.

(4) 1-*Hydroxyanthraquinone.* The low solubility of this compound at pH <12, especially in aqueous solvents, limited the work on it. Results obtained with partly pre-reduced solutions are given in Tables 1 and 2. K is very small in aqueous solutions. The presence of 50% of ethanol causes a large increase, although, since E_m still varies with pH in the region investigated, indicating incomplete ionisation, the effect of the alcohol may be due partly to the pH shift and also to the change in acid dissociation constant caused by its inclusion. The decrease in K in going from 0·1 to 0·25N-aqueous alkali may be due to the effect of the increasing ionic strength opposing and overbalancing the expected increase due to rise of pH. The presence of alcohol again decreases d. Colour changes observed during reduction (red ⟶ orange-red ⟶ orange in water; red ⟶ deep red-brown ⟶ orange in 50% alcohol) indicate little semiquinone formation in water, but appreciable formation of greenish semiquinone in 50% alcohol.

(5) 2-*Hydroxyanthraquinone.* This is sufficiently soluble at pH >8 to permit investigation over a wide pH range. However, the leuco-compound tautomerises in aqueous solutions at pH <12. Therefore, although values of K and E_m are independent of whether the compound is in the oxidised or the reduced form at any pH provided that time is allowed for equilibration of the tautomerism before polarography, the value of d is strongly dependent on pH for the reduced form (Gill and Stonehill, *J.*, 1952, 1857). For the oxidised form, d is independent of pH, and thus the present results were obtained exclusively for this form. In Fig. 4 are plotted the values of E_m, E_1, E_2 and $\sqrt{K}$ against pH. From the bends in the E_m–pH graph the values of three acid pK values for the quinol are determined as $pK_1^r = 8{\cdot}7$, $pK_2^r = 10{\cdot}05$, $pK_3^r = 12{\cdot}60$. The intersection corresponding to pK_1^r is somewhat uncertain, and was determined by drawing through the point at pH 8·22 a straight line with the theoretical slope of -88 mv for a $3H^+$–$2e$ reduction, to meet the neighbouring linear portion of the graph. Apart from the bend at pK_1^r (E_m–pH graph), which constant may, by comparison with the value $pK^t = 7{\cdot}62$ for the

quinone at 18° (Heilbron, " Dictionary of Organic Chemistry," Eyre and Spottiswoode, 1936), be associated with the ionisation of the quinol to the analogue of (I), the graphs of Fig. 4 are similar to the corresponding ones for anthraquinone-2-sulphonic acid, and may be similarly interpreted. By familiar methods we then deduce the equations

$$E_m = \left(E_m{}^\circ - 0{\cdot}0295 \log \frac{K_1{}^rK_2{}^rK_2{}^r}{K^t}\right) + 0{\cdot}0295 \log \frac{K_1{}^rK_2{}^rK_3{}^r + K_1{}^rK_2{}^r[\mathrm{H}^+] + K_1{}^r[\mathrm{H}^+]^2 + [\mathrm{H}^+]^3}{K^t + [\mathrm{H}^+]}$$

$$E_1 = \left(E_1{}^\circ - 0{\cdot}059 \log \frac{K^s}{K^t}\right) + 0{\cdot}059 \log \frac{K^s + [\mathrm{H}^+]}{K^t + [\mathrm{H}^+]}$$

$$E_2 = \left(E_2{}^\circ - 0{\cdot}059 \log \frac{K_1{}^rK_2{}^rK_3{}^r}{K^s}\right) + 0{\cdot}059 \log \frac{K_1{}^rK_2{}^rK_3{}^r + K_1{}^rK_2{}^r[\mathrm{H}^+] + K_1{}^r[\mathrm{H}^+]^2 + [\mathrm{H}^+]^3}{K^s + [\mathrm{H}^+]}$$

where $E_m{}^\circ$, $E_1{}^\circ$, and $E_2{}^\circ$ (values of E_m, E_1, and E_2 at pH $> \mathrm{p}K_3{}^r$) are respectively $-0{\cdot}828$, $-0{\cdot}797$, and $-0{\cdot}858$v, $\mathrm{p}K^t \approx 8$, $\mathrm{p}K^s = 10{\cdot}3$.

The maximum value of $\sqrt{K}$ (*ca.* 3·55), observed at extreme alkalinities, is roughly midway between the corresponding values for anthraquinone (2·6) and for 2 : 6-dihydroxyanthraquinone (5·00). At the lowest pH values studied, $\sqrt{K}$ tends to a non-zero limit of *ca.* 0·3; this is probably not due to experimental error, but is a real lower limit, since it was obtained in several replicate experiments, and is similar to results obtained with other compounds examined.

Fig. 5 shows the effect of progressively increasing the volume percentage of ethanol in the solvent on the redox and polarographic characteristics of 2-hydroxyanthraquinone in 0·1N-sodium hydroxide. $\sqrt{K}$ exhibits a maximum, whereas for anthraquinone-2-sulphonic acid it increases steadily (Burstein and Davidson, *loc. cit.*). The maximum is probably due to decreasing ionisation of the hydroxy-compound with rise in ethanol content, causing diminution in K which eventually overbalances the usual increase due to the effect of alcohol on the purely redox equilibrium. Half-wave potentials E_m, obtained by neglecting alcohol–water junction potentials (see Table 2), steadily become more negative with increasing ethanol content, owing to the effect of solvent change on the purely redox equilibrium, on which is superimposed a smaller opposite shift to more positive values, due to decreasing ionisation of the leuco-compound. The value of d falls initially as alcohol content increases, but then remains practically constant for >45% of alcohol. These effects are due entirely to variation in D; ionisation cannot be concerned, since D is virtually identical for the quinone, semiquinone, and quinol at all ionisation levels, association or polymerisation being assumed to be absent.

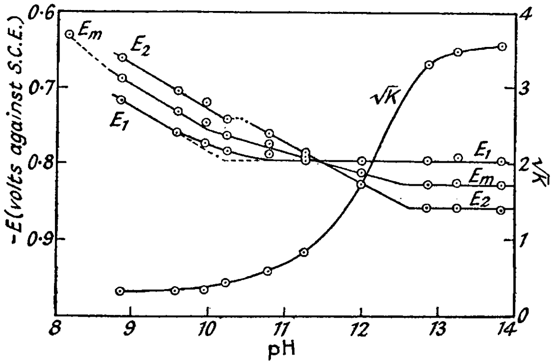


FIG. 4. *2-Hydroxyanthraquinone:* 1 × 10^{-3}M *in* H_2O, 25°; $I = 0{\cdot}1$.

The effect on the redox-polarographic behaviour in 0·1N-aqueous sodium hydroxide of increasing the ionic strength by adding potassium chloride is shown in Fig. 6 and Table 1. While d remains practically constant, $\sqrt{K}$ decreases and E_m becomes progressively more positive. These changes are due mainly to the effect of varying ionic strength on the purely redox equilibrium, but there is also a small contribution from the secondary salt-effect on the acid–base ionisation of the quinol, since in 0·1N-alkali the ionisation is not quite complete.

The colour sequence, red ⟶ dark brown ⟶ green ⟶ yellow, observed during reduction at higher pH values visually confirms semiquinone formation.

(6) 1 : *2-Dihydroxyanthraquinone* (*alizarin*). The variation of E_m, E_1, E_2, $\sqrt{K}$, and d with pH is shown in Table 1 and Fig. 7. The maximum in $\sqrt{K}$ plotted against pH is unique amongst the compounds studied; the small decrease in $\sqrt{K}$ at pH >12 was confirmed by several

replicate experiments. Attempts to investigate solutions in N-alkali were unsuccessful, because of erratic galvanometer deflections, probably caused by salting-out, which also occurred to some extent in experiments with added potassium chloride. Solutions left overnight usually flocculated, and coated the mercury pool with a yellow film (possibly a lake), insoluble in dilute alkali but removed by acid followed by acetone. Because of insufficient data, the slopes and positions of bends in the E_m, E_1, and E_2 graphs are difficult to determine, and only a very speculative assignment of pK values, indicated in Fig. 7, can be made; it is particularly difficult to explain the course of the E_2 graph, and the large change of slope of the E_m graph near pH 11·6.

Increase in ionic strength, by addition of potassium chloride to solutions in 0·1N-aqueous alkali, causes the usual fall in $\sqrt{K}$ and shift of E_m to more positive values (Table 1), and slightly increases d. The inclusion of ethanol in solutions in 0·1N-alkali increases $\sqrt{K}$, makes E_m more negative (liquid-junction potentials neglected), and decreases d considerably (Table 2). However, since for some of the species involved ionisation is not complete in 0·1N-alkali, the effect of both potassium chloride and alcohol on $\sqrt{K}$ and E_m is composite, being due partly to the effect on the purely redox equilibrium, and partly to the effect on acid–base ionisation equilibria.

FIG. 5. 2-*Hydroxyanthraquinone in* 0·1N-NaOH *at* 25°. *Effect of* EtOH *on* $\sqrt{K}$ *and* d.

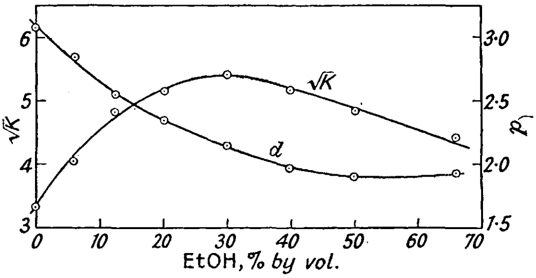


FIG. 6. 2-*Hydroxyanthraquinone in* 0·1N-NaOH at 25°. *Effect of* KCl *on* $\sqrt{K}$ *and* E_m.

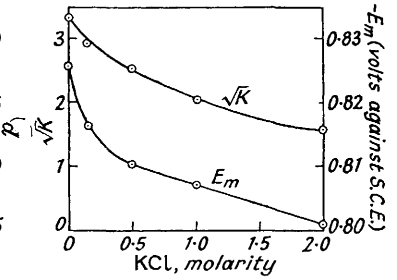


FIG. 7. 1 : 2-*Dihydroxyanthraquinone.* 2 × 10^{-3}M, *in* H_2O *at* 25°; I = 0·1.

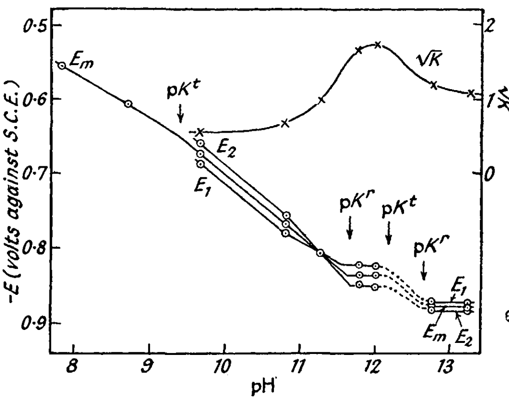
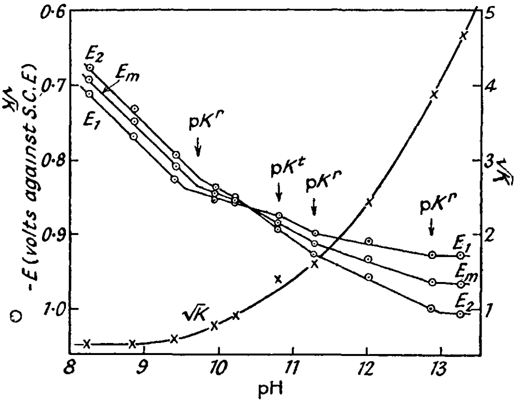


FIG. 8. 2 : 6-*Dihydroxyanthraquinone.* 10^{-3}M, *in* H_2O *at* 25°; I = 0·1.



Confirming the results of Appleton and Geake (*Trans. Faraday Soc.*, 1941, **37**, 45), the colour change, violet, ⟶ olive-green ⟶ orange, observed during reduction at pH ≈12 demonstrates the formation of semiquinone.

(7) 1 : 4- *and* 1 : 8-*Dihydroxyanthraquinones.* These have been titrated potentiometrically by Appleton and Geake (*loc. cit.*), but only in sodium hydroxide solutions in water and 50% aqueous pyridine at 50°. At pH <11·27, the insolubility of these compounds rendered polarography impossible, and even at pH 11·27 results were rather erratic. Results are given in Table 1, and indicate incompleteness of ionisation even at pH 13·25; hence the effects of alcohol in the solvent were not studied, since considerable alteration in acid–base ionisation would interfere. The colour changes observed during reduction (red-violet to orange for the

1 : 4-isomer; red ⟶ orange ⟶ yellow for the 1 : 8-isomer) confirm the virtual absence of semiquinone formation indicated by the low $\sqrt{K}$ values.

(8) 2 : 6-*Dihydroxyanthraquinone.* As with 2-hydroxyanthraquinone, tautomerism of the anthraquinol (Gill and Stonehill, *loc. cit.*) here necessitated working with only the quinone in order to obtain time-independent d values. Results are given in Table 1 and Fig. 8. Again, only a very tentative assignment of pK values corresponding to bends in the E_m, E_1, and E_2 against pH graphs has been made in Fig. 8. Since the anthraquinol is not quite completely ionised even at pH 13·25, $\sqrt{K}$ shows no signs of levelling off to a constant maximum at this pH. For the same reason, only a single determination of the effect of alcohol on E_m and $\sqrt{K}$ was made (Table 2); the decrease in ionisation due to the presence of alcohol makes a considerable contribution to the observed increase in $\sqrt{K}$ and the shift of E_m to a more negative value. The usual decrease in d due to alcohol also occurs.

The colour change during reduction in alkali (red ⟶ dark red-brown ⟶ yellow) confirms the extensive formation of semiquinone indicated by the relatively high $\sqrt{K}$ values at high pH.

DISCUSSION

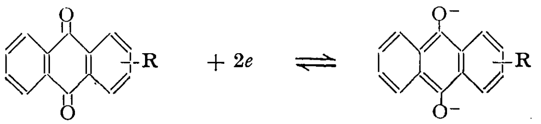
Table 3 gives for aqueous solution the standard redox potentials $E_m°$ and standard semiquinone formation constants $K°$ at 25° and ionic strength $I = 0{\cdot}1$, for all the compounds studied; $E_m°$ and $K°$ are the values of E_m and K for conditions such that the quinone, quinol, and semiquinone species are all fully ionised, and the redox equilibrium is

TABLE 3. $E_m°$ (*on hydrogen-electrode scale*) *and* $\sqrt{K°}$ *for aqueous solutions* ($I = 0{\cdot}1$)

	This work (25°):		Potentiometric data:				$\Delta E_m°$ (mv):	
Substituent	$-E_m°$ (v)	$\sqrt{K°}$	$-E°$ (v)	$\sqrt{K}$	Temp.	Ref.*	Obs.	Calc.
None	—	—	0·444 [a]	—	25°	1	—	—
			0·454 [b]	2·6 [b]	50	1		
1-SO_3H	0·432	0·45	0·444	0·23	25	2	+12	—
2-SO_3H	0·374	1·94	0·381	1·92	25	2	+70	—
			0·374	1·76	25	3		
			0·379	1·83	30	4		
1-OH	0·481	0·22	—	—	—	—	−37	—
2-OH	0·582	3·6	—	—	—	—	−137	—
1 : 2-$(OH)_2$ ...	0·637	1·14	0·624	1·7	20	1	−193	−174
1 : 4-$(OH)_2$ ...	0·506	0·2	0·485	0·05	50	1	−62	−74
1 : 5-$(OH)_2$ ...	—	—	0·478	0·33	50	1	—	—
1 : 8-$(OH)_2$ ...	0·536	0·28	0·578	0·31	50	1	−92	−74
2 : 6-$(OH)_2$ ...	0·724	4·7	—	—	—	—	−280	−274

* (1) Appleton and Geake, *loc. cit.*; (2) Conant *et al.*, *loc. cit.*; (3) Geake and Lemon, *loc. cit.*; (4) Burstein and Davidson, *loc. cit.*

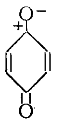
[a] Obtained from the value for the 2-SO_3H compound at 25° by subtracting 70 mv, which difference is stated to be independent of temperature and medium. [b] Approx. value from incomplete titration; not used in evaluating $\Delta E_m°$.

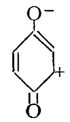


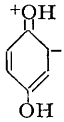
(R = $-O^-$ or $-SO_3^-$)

For several of the compounds, ionisation is complete in 0·1N-sodium hydroxide, and the values of E_m and K in this solvent may be taken as $E_m°$ and $K°$, respectively. Where ionisation is not complete in 0·1N-alkali (indicated by E_m still varying as pH increases), $E_m°$ and $K°$ are estimated by correcting E_m and K values obtained in more concentrated alkali (in which complete ionisation may be assumed) for the variation with I, using for this purpose results obtained with added potassium chloride. For 1 : 4- and 1 : 8-dihydroxyanthraquinones, ionisation was not complete even in N-alkali, and thus the estimated (extrapolated) values of $E_m°$ and $K°$ are less accurate. Some values taken or calculated from earlier potentiometric data in the literature are included in Table 3 for comparison. Agreement with present values is reasonable, except for 1 : 4- and 1 : 8-dihydroxyanthraquinones, for which ionisation is incomplete.

Effect of Substituents on $E_m°$.—The observed shifts $\Delta E_m°$ are listed in Table 3, col. 8. For disubstitution, the observed shifts agree in general with those calculated from simple additivity (Table 3, last column). To explain the results, we assume (cf. Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall Inc., 1941, pp. 305, 315) that for a series of anthraquinones, $\Delta S°$ for the process ox. $+ 2e \longrightarrow$ red. is practically constant, so that variations of $E_m° = -\Delta G°/2F$ measure variations in $-\Delta H° = -H°_{\text{red.}} + H°_{\text{ox.}}$, or in (resonance energy of "red.") — (resonance energy of "ox.") (Evans, *Trans. Faraday Soc.*, 1936, **42**, 113; Evans and De Heer, *Quart. Reviews*, 1950, **4**, 104). The chief ionic resonance in quinones throws a positive charge into the ring, as in (VII) and (VIII), so that


(VII)


(VIII)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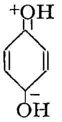
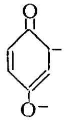
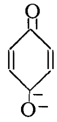
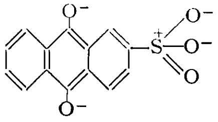

(X)


(XI)


(XII)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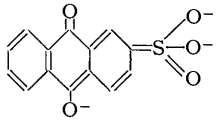
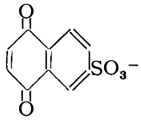
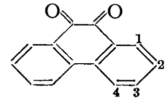

(XIV)

any group such as OH, which by induction or resonance assists the ring to accommodate this positive charge, will stabilise the quinone and thus make $E_m°$ more negative. (In the terminology of Evans and de Heer, "induction" becomes the inductive effects on σ and on π electrons; "resonance" corresponds to the conjugation effect.) Similarly, ionic resonance introduces a negative charge into the ring for un-ionised quinols (IX, X), and with even greater effect for ionised quinols (XI, XII) because of the absence of opposite-charge separation. Thus quinols are stabilised by the electron-attracting SO_3^- substituent, which acts by induction and perhaps also by resonance of the type (XIII) $\longleftrightarrow$ (XIV) (cf. Bryson, *Trans. Faraday Soc.*, 1951, **47**, 528), thereby rendering $E_m°$ more positive.

The smallness of the positive $\Delta E_m°$ for anthraquinone-1-sulphonic acid is probably due to an "*ortho*-effect" caused by steric hindrance, which pushes both the $=$O and the $-SO_3^-$ group out of the ring plane, thereby inhibiting any resonance not only of the carbonyl oxygen atom with the ring (hence the small $\sqrt{K}$ value for the semiquinone), but also of the $-SO_3^-$ group with the ring; thus only the small inductive effect of the latter group remains, and even this is opposed by the effect on $E_m°$ due to the displacement of the carbonyl oxygen from the ring plane. In the 2-sulphonic acid, resonance of the type (XIII) $\longleftrightarrow$ (XIV) reinforces the inductive effect, giving $\Delta E_m° = +70$ mv, almost exactly equal to the $\Delta E°$ value $+75$ mv for the correspondingly substituted 1 : 4-naphthaquinone (XV) in water (Fieser and Fieser, *J. Amer. Chem. Soc.*, 1935, **57**, 491). Introduction of an $-SO_3^-$ group in phenanthraquinone (XVI) leads to a $\Delta E°$ of about $+25$ mv, almost independent of position (*i.e.*, for positions 1, 2, and 3), thus indicating little or no resonance effect (Fieser, *J. Amer. Chem. Soc.*, 1929, **51**, 3101); this result, although found for solutions in 50% alcohol, is probably applicable to aqueous solutions also, as judged by other results of the same author. Accordingly, we may suppose that the total $\Delta E_m°$ of $+70$ mv for anthraquinone-2-sulphonic acid is made up of $+25$ mv for the inductive effect, and $+45$ mv for the resonance effect.

The $\Delta E°$ values of -1 and 0 mv respectively for 2- and 4-hydroxyphenanthraquinones (Fieser, *loc. cit.*), for which resonance stabilisation of the quinone by the substituent is impossible, show that the inductive effect of OH on $E°$ or on $E_m°$ is practically nil. If, however, OH is replaced by $-O^-$, as in the present results, a definite inductive effect is to be expected, which by comparison with that of $-SO_3^-$ is probably about -20 mv, although it may vary with position in the ring. Since $\Delta E_m°$ is -37 mv for ionised 1-hydroxy-anthraquinone, about -17 mv of this must be due mainly to resonance of the form (XVII) $\longleftrightarrow$ (XVIII), but also partly to repulsion of the ionised quinol oxygen by the nearby substituent $-O^-$ group, causing destabilisation of the quinol. For ionised 2-hydroxyanthraquinone, in addition to an inductive $\Delta E_m°$ of -20 mv, there is a large effect due to *para*-resonance (XIX) $\longleftrightarrow$ (XX), which is clearly of greater importance here than in the un-ionised molecule (OH instead of $-O^-$ in the 2-position), for which a separation of opposite charges would be required. For un-ionised 1- and 3-hydroxyphenanthraquinones, ΔE° is -50 and -53 mv, respectively (Fieser, *loc. cit.*), entirely due to resonance, since we have seen that inductive effects are negligible. The rough estimate that *para*-resonance of the ionised hydroxy-group contributes -120 mv of the total $\Delta E_m{}^\circ$ observed (-137 mv) for ionised 2-hydroxyanthraquinone is therefore reasonable.


(XV)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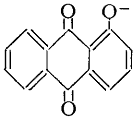
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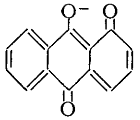
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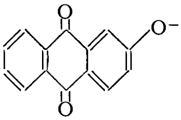
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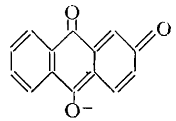
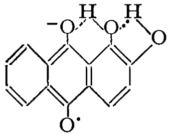
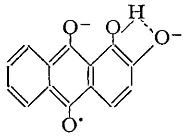

(XX)

Semiquinone Formation.—Semiquinone radicals are stabilised by resonance between a structure in which the odd electron resides on one of the two quinone oxygen atoms, and one in which it resides either (*a*) on the second quinone oxygen atom ("equivalent resonance"), or (*b*) on one or other of the remaining atoms in the molecule. Type (*a*) is far the more important, and where it is possible, *e.g.*, in the fully ionised semiquinones of anthraquinone and its 2-substituted derivatives, high K values result. A substituent in the 1-position interferes with this type of resonance, by steric effects ($-SO_3^-$), hydrogen bonding ($-OH$), or mutual repulsion of negative charges ($-O^-$), resulting in low K values characteristic of the weaker type (*b*) resonance. At lower pH's, where a proton adds to one of the quinone oxygen atoms, type (*a*) resonance is inhibited even for compounds for which it occurs at higher pH's, giving low but non-zero K values corresponding to type (*b*) resonance. The unusual form of the $\sqrt{K}$–pH curve for 1 : 2-dihydroxyanthraquinone (Fig. 7) may be explained as due to the normal initial rise in K with pH increase because of increasing ionisation of the quinol hydroxy-groups, which, at pH's high enough to ionise both substituent hydroxy-groups, is counteracted by mutual repulsion of negative charges ($-O^-$) causing a fall in K. The ionisation sequence for the semiquinone is probably (XXI) $\longrightarrow$ (XXII) $\longrightarrow$ (XXIII).


(XXI)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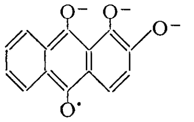
(XXIII)

Effects of Change of Solvent.—Burstein and Davidson (*loc. cit.*) found that, for fully ionised sodium anthraquinone-2-sulphonate in 0·1N-sodium hydroxide at 30°, inclusion in the aqueous solvent of up to 30% of methanol, pyridine, or dioxan caused variation in K according to $\log K = A/\varepsilon$ (ε = dielectric constant), in qualitative agreement with Born's equation (*Z. Physik*, 1920, **1**, 45) for the variation of activity coefficients with ε, but with the constant A much greater than the theoretical value. In the present work, the only compound studied which is completely ionised in 0·1N-alkali, apart from the 2-sulphonic acid, is 2-hydroxyanthraquinone, and even this becomes incompletely ionised on introduction of ethanol; the use of higher alkali concentrations to prevent this would cause complicating effects due to increased ionic strength. For this compound, K rises initially as the alcohol content or $1/\varepsilon$ increases, but eventually the effect of repression of ionisation preponderates, causing a fall in K. The initial rise in K is also found with the 2-sulphonic acid, the 1-hydroxy- and the 1 : 2-dihydroxy-derivative, but not with the 1-sulphonic acid.

The introduction of ethanol renders E_m more negative for all the compounds studied, and also reduces d progressively up to about 50% alcohol. For 2-hydroxyanthraquinone, for which the most complete study of the effect of alcohol was made, d falls until about 45% of alcohol is present, and then remains practically constant up to 70% alcohol content.

Effects of increasing Ionic Strength.—In all cases studied, addition of potassium chloride at constant pH (0·1N-sodium hydroxide in water) makes E_m more positive, does not affect d, and diminishes K. Although salt effects on the incomplete ionisation of weakly acid hydroxyl groups may cause complications, the effects on E_m and K are qualitatively in agreement with deductions from the Debye–Hückel equation for activity coefficients of ions, if it is remembered that E_m and K in this paper refer to equations in which concentrations and not activities of quinone, semiquinone, and quinol species are used.

Diffusion-current Constants.—There is poor agreement between present *d* values and those of Furman and Stone (*loc. cit.*); *e.g.*, for the 1- and 2-sulphonic acid and 1 : 2-dihydroxy-derivative, respectively, the values we obtain (Furman and Stone's values in parentheses) are 2·99 (3·60), 3·02 (3·22), and 2·88 (3·09). In view of the preceding section of this paper, the discrepancy is not due to differences of ionic strength in the two investigations; neither is it because our results relate to aqueous solvent and those of Furman and Stone to 1% ethanol, since any slight effect of including 1% of ethanol would be to decrease *d*, thus increasing the discrepancy.

Furman and Stone suggest that borate and phosphate buffers form complexes with some of the substituted anthraquinones as well as with some of the corresponding semiquinones, thus shifting E_m to more negative values than apply when other buffers are used at the same pH. A similar explanation is suggested by Elving, Komyathy, Van Atta, Tang, and Rosenthal (*Analyt. Chem.*, 1951, **23**, 1218) to account for their observation that both *d* and E_m may be altered for α-bromo-*n*-butyric acid if the concentration, but not the nature, of the buffer components is changed, even if pH and *I* are kept constant; variation of *I* alone scarcely affected *d*.

Since the concentration ratio of buffer to anthraquinone derivative was roughly the same (about 100 : 1) in the present work and in that of Furman and Stone, the discrepancy in *d* values cannot be due to different extents of complexing by the buffer, with consequent increase in molecular size of electroactive species and decrease in *d* to different extents. The large discrepancies in E_m (cf. Fig. 3) are also difficult to explain, and in view of the agreement between our results and earlier potentiometric data, the results of Furman and Stone must be regarded with some doubt.

TECHNICAL COLLEGE, BRADFORD, YORKS.
MEDWAY TECHNICAL COLLEGE, GILLINGHAM, KENT.

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