

and 105 by controlling the time that the first products, either gaseous or liquid, are allowed to stay in the discharge tube—the more secondary action the higher the molecular weight owing to further condensation.

MINNEAPOLIS, MINNESOTA

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THE ABSORPTION SPECTRA OF HYDROQUINOLPHTHALEIN AND HYDROQUINOLSULFONEPHTHALEIN

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The present investigation on the absorption spectra of hydroquinolphthalein and hydroquinolsulfonephthalein was undertaken not only to obtain possible corroborative evidence as to the existence of the meta-quinoid structure in these compounds and their salts, but also to contribute to our knowledge of the effect of hydroxyl substitution in the phthalein and triphenylmethane series generally.²

The preparation of hydroquinolsulfonephthalein has been described in a previous paper³ and from its chemical behavior evidence has been advanced in favor of its possessing the meta-quinoid structure. A study of its absorption spectra, particularly in neutral and acid solution, reveals certain striking characteristics which differentiate it sharply from other sulfonephthaleins now being investigated in this Laboratory. Hence it may be provisionally assumed that to this extent the data support the view that the meta-quinoid configuration has a possible existence in the case of these hydroquinol derivatives. It is felt, however, that primary consideration must be given to the chemical evidence in settling this question, until more extensive data are available concerning the effect of hydroxyl substitution in the phthaleins and until more is known of the intrinsic nature of the several quinoid structures, ortho, meta and para. A comparison of the absorption spectra of hydroquinolphthalein and hydroquinolsulfonephthalein with those of their isomers, fluorescein^{4a} and sulfonefluorescein,^{4b} brings out a marked distinction. To what extent this difference is to be attributed to the different positions of the hydroxyl groups, or to the existence of different quinoid configurations, is still an unsettled question.

¹ This article is based on a portion of a thesis presented to the Faculty of the Graduate School of Cornell University by the author, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Orndorff, Gibbs and co-workers, *THIS JOURNAL*, **47**, 2767 (1925); **48**, 1327, 1994 (1926); **49**, 1541, 1545, 1588 (1927).

³ Orndorff and Shapiro, *THIS JOURNAL*, **50**, 1730 (1928).

⁴ (a) Orndorff, Gibbs and Shapiro, (a) *THIS JOURNAL*, **50**, 819 (1928); (b) Gibbs and Shapiro, *ibid.*, **50**, 1755 (1928).

The absorption spectrum of hydroquinolphthalein has been studied by R. Meyer and his collaborators⁵ in alkaline solution and by Howe⁶ in neutral alcoholic solution. Moir,⁷ working only in the visible region of the spectrum, has reported on its alkaline and sulfuric acid solutions.

Fig. 1 shows the absorption curves for hydroquinolphthalein and hydroquinolsulfonephthalein in absolute ethanol and for hydroquinolsulfonephthalein in distilled water. Curve A for hydroquinolphthalein exhibits four bands, of which the two at frequency numbers 3518 and 3626 are characteristic of the lactoid structure.⁸ The absorption spectra of hydroquinolsulfonephthalein in ethanol and water, Curves B and C, run entirely parallel, with the bands for the alcohol solution displaced toward lower frequency numbers and exhibiting in general a lower intensity. The amount of the displacement is not uniform for the different bands, varying

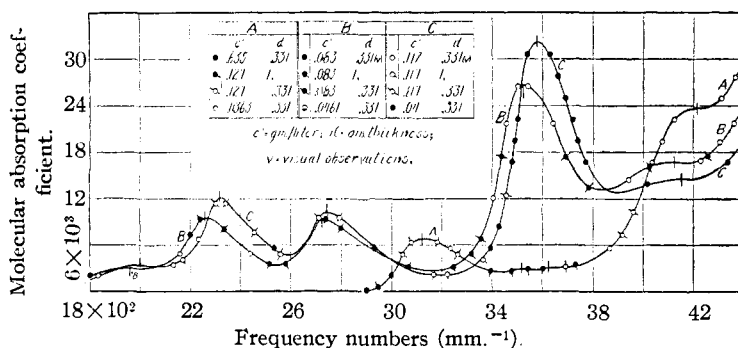


Fig. 1.—Neutral solutions. A, hydroquinolphthalein (alcoholic); B, hydroquinolsulfonephthalein (alcoholic); C, hydroquinolsulfonephthalein (aqueous).

from 20 frequency units in one case up to 59. The significance of this similarity will be considered below in dealing with the acid solutions. Hydroquinolphthalein, admittedly lactoid, yields an absorption spectrum which bears a close relation to those observed for other *lactoid* phthaleins; on the other hand, hydroquinolsulfonephthalein, which is quinoid, does not resemble in absorption spectra either phenolsulfonephthalein or *o*-cresolsulfonephthalein, although both of these latter compounds have like spectra.⁹ It appears reasonable, therefore, to attribute this difference in absorption spectra in part to a difference in internal structure, by denoting the hydroquinol derivative as meta-quinoid and the phenol and *o*-cresol compounds as para-quinoid.

⁵ R. Meyer and Marx, *Ber.*, **40**, 3603 (1907); **41**, 2446 (1908); R. Meyer and Fisher, *Ber.*, **44**, 1944 (1911).

⁶ Howe, *Phys. Rev.*, **8**, 686 (1916).

⁷ Moir, *Trans. Roy. Soc. S. Africa*, **7**, 5 (1918).

⁸ Gibbs and Shapiro, *Proc. Nat. Acad. Sci.*, **14**, 251 (1928).

⁹ Unpublished data.

The absorption spectra of the dibenzoates of hydroquinolphthalein and hydroquinolsulfonephthalein in ethanol solution are given in Fig. 2. The former dissolves to give a colorless solution and its spectrum, Curve A, shows four bands, of which the two at 3549 and 3676 are evidently due to the lactoid structure.⁸ Curve B for the dibenzoate of hydroquinolsulfonephthalein is quite different in character, as it has bands in the visible and near ultraviolet regions, which are responsible for its yellow color, while in the further ultraviolet there are three bands which do not appear to be closely related to those of Curve A. The absence of the characteristic lactoid bands in the region of frequency number 3600 and the bright yellow color of the solution render it probable that this dibenzoate is quinoid in structure, in which case it must be derived directly from the inner salt form of hydroquinolsulfonephthalein.³

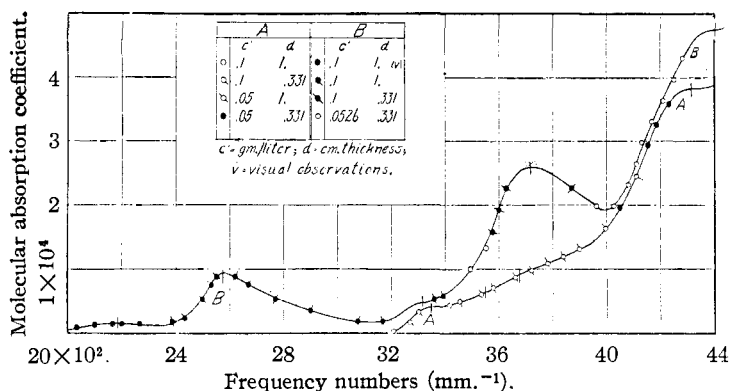


Fig. 2.—Neutral alcoholic solutions. A, hydroquinolphthalein dibenzoate; B, hydroquinolsulfonephthalein dibenzoate.

Hydroquinolphthalein and hydroquinolsulfonephthalein dissolve in concentrated sulfuric acid, yielding orange-yellow colored solutions. The absorption spectra are given in Fig. 3 and it will be noted that the curves are very nearly identical; the bands for hydroquinolphthalein, Curve A, are shifted slightly, though consistently, toward higher frequency numbers. Comparison of the curves of Fig. 3 with those for the neutral solutions of hydroquinolsulfonephthalein reveals a striking similarity, which is again evident in Fig. 4 for solutions of hydroquinolphthalein in alcoholic hydrogen chloride. This type of absorption, which is evidently due to salt formation, is entirely different from that which has been previously found for acid solutions of the other phthaleins and fluoresceins studied thus far. In the latter cases the absorption has been characterized by two prominent bands, one at either end of the spectrum. There have been slight variations: the far ultraviolet band in the fluoresceins³ is double, while fuchson, benzaurin and aurin² have shown a double band

in the visible or near ultraviolet region. Since in all cases salt formation involves the quinoid structure, the exceptional behavior of hydroquinolphthalein and hydroquinolsulfonephthalein may again be attributed to the existence of the meta-quinoid state. That hydroquinolsulfonephthalein exists in the neutral condition as an inner salt is deduced from the general

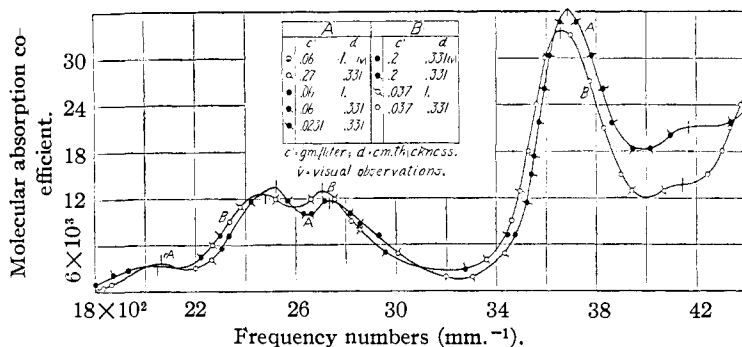


Fig. 3.—Concd. sulfuric acid solutions. *A*, hydroquinolphthalein; *B*, hydroquinolsulfonephthalein.

correspondence of the absorption curves for the neutral and sulfuric acid solutions, as well as for the acid solutions of hydroquinolphthalein. This is further corroborated by the non-formation of a hydrochloride when hydroquinolsulfonephthalein is exposed to dry hydrogen chloride³ and by the fact that the addition of hydrogen chloride in ratios as high as

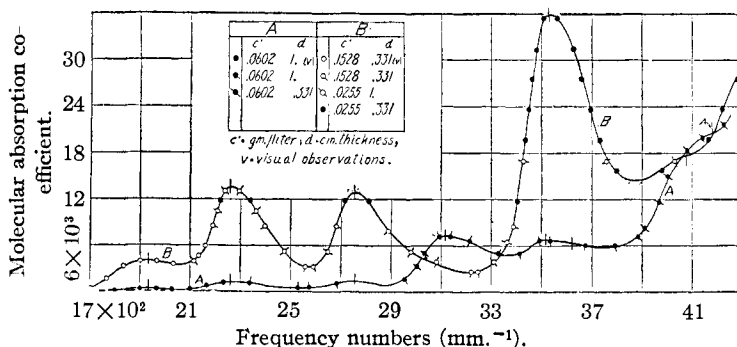


Fig. 4.—Hydroquinolphthalein in alcoholic HCl. *A*, 1 molecule:100 molecules HCl; *B*, 1 molecule:10,000 molecules HCl.

10,000 molecules to one of the sulfonephthalein produces no apparent effect on the absorption spectrum of the neutral solution. Phenol- and *o*-cresolsulfonephthalein in alcoholic solution have likewise been assigned inner salt structures on the basis of the similarity of their absorption spectra in neutral and acid solution.⁹

Fig. 4 shows the effect of adding various amounts of dry hydrogen

chloride gas to an alcoholic solution of hydroquinolphthalein. Curve A for 1000 molecules of hydrogen chloride to one of the phthalein is a transition stage, as bands characteristic of both the neutral and acid condition are present. Thus the bands at 1933, 2259 and 2756 of Curve A occur in Curve B for 10,000 molecules of hydrogen chloride at 1933, 2260 and 2755, while the remaining bands at 3117, 3517, 3621 and 4182 correspond to the four analogous bands in the neutral solution. That the presence of so large an excess of acid as 1000 molecules is ineffective in converting all of the hydroquinolphthalein into the hydrochloride may be taken as a measure of the strength of the lactoid bond. The addition of 10,000 molecules of hydrogen chloride brings out the whole of the acid spectrum as found in the sulfuric acid solution (Curve A, Fig. 3). For purposes of comparison, the frequency numbers of the bands in the various acid solutions of hydroquinolphthalein and hydroquinolsulfonephthalein are listed in Table I.

TABLE I
FREQUENCY NUMBERS OF BANDS IN NEUTRAL AND ACID SOLUTIONS

Substance	Solvent	Frequency Numbers of Bands				
Hydroquinolphthalein	Alcoholic HCl	1933	2260	2755	3528	4075
Hydroquinolphthalein	Concd. H ₂ SO ₄	2065	2523	2735	3685	4170
Hydroquinolsulfonephthalein	Absolute alcohol	1960	2259	2722	3523	4122
Hydroquinolsulfonephthalein	Distilled water	2000	2317	2742	3578	4153
Hydroquinolsulfonephthalein	Concd. H ₂ SO ₄	2050	2481	2706	3656	4145

Hydroquinolphthalein dissolves in aqueous solutions of potassium hydroxide with a blue color which fades out rapidly even in low ratios of alkali. In an alcoholic solution the color is very much fainter but, on the other hand, is much more stable. The low intensity is probably due to the slight dissociation of the dipotassium salt in the alcohol; in this respect hydroquinolphthalein is exceptional, as all of the phthaleins previously studied show the full color development in alcoholic as well as in aqueous alkaline solution. The absorption of an alcoholic solution containing 100 molecules of potassium hydroxide to one of the phthalein is shown in Fig. 5, Curve A, A', and is characterized by three bands. At lower ratios of alkali it was observed that bands due to both the neutral compound and its salt were present, the bands of the former becoming more prominent as the dilution was increased. This reversion effect has previously been noted with dilute, slightly alkaline solutions of phenolphthalein² and fluorescein³ and is to be directly correlated with the weakly acid properties of these compounds. On dissolving hydroquinolphthalein in 33% aqueous potassium hydroxide, a colorless solution is at once obtained due to the formation of the tripotassium salt of the carbinol acid. The absorption spectrum of this solution is given by Curve B; its two bands are shifted toward the further ultraviolet relative to the corre-

sponding bands of Curve A for the alcoholic alkaline solution. It is, therefore, probable that in the alcoholic solution the colored dipotassium salt is in equilibrium with the colorless tripotassium salt.

The effect of adding alkali to an alcoholic solution of hydroquinol-sulfonephthalein leads to somewhat more complex phenomena, owing to the existence of the inner salt bond. The addition of the theoretical amount of potassium hydroxide, two molecules, is not sufficient to rupture this linkage completely and the color of the resulting solution is olive-green, due to the simultaneous presence of the orange-yellow neutral compound and of the blue alkali salt. It is a curious fact that dilution of such a solution does not result in reversion to the neutral color. This may be explained by the strong acid properties of free hydroquinolsulfonephthalein: its salts are not appreciably hydrolyzed in dilute solution.

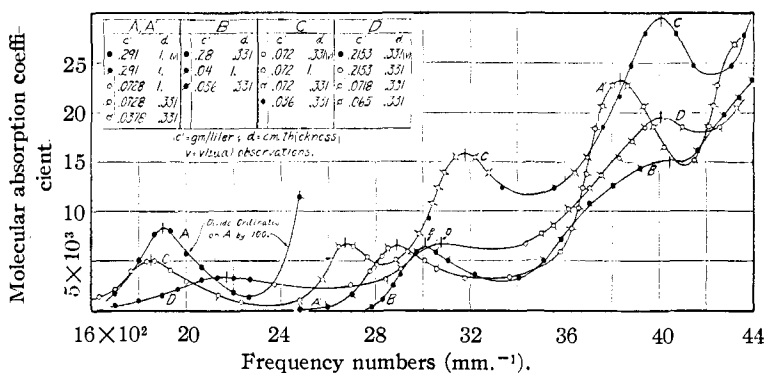


Fig. 5.—Alkaline solutions. Hydroquinolphthalein: A, 1 molecule:100 molecules KOH (alcoholic); B, 33% KOH (aqueous). Hydroquinolsulfonephthalein; C, 1 molecule:100 molecules KOH (alcoholic); D, 33% KOH (aqueous).

It is because of these strong acid properties that hydroquinolsulfonephthalein so readily forms an inner salt. Increasing the ratio of potassium hydroxide to four molecules yields a solution with a more bluish tint, as the concentration of the dipotassium salt is increased at the expense of the inner salt. At 100 molecules of alkali the color has become a pure blue-purple and the absorption spectrum of this solution is represented by Curve C, Fig. 5. There are four bands, as contrasted with the three for an analogous solution of hydroquinolphthalein, but the curves are generally similar in form. Dissolving hydroquinolsulfonephthalein in 33% aqueous potassium hydroxide results in a solution with a pale tan color, the absorption of which is given by Curve D. It is probable that the sulfonephthalein has been converted into the colorless tripotassium salt of the carbinol acid and that the slight color is due to a small amount of an oxidation product, for hydroquinolsulfonephthalein oxidizes with

extreme ease in alkaline solution. That the solution contains primarily the tripotassium salt is confirmed by the close similarity in intensity and form of the ultraviolet portion of Curve D with Curve B for the tripotassium salt of hydroquinolphthalein.

The frequency numbers of the absorption bands for the various solutions studied are presented in Table II, with the exception of the acid solutions, the data for which have been listed in Table I.

TABLE II
FREQUENCY NUMBERS OF BANDS IN NEUTRAL AND ALKALINE SOLUTIONS

Solvent	Hydroquinol- phthalein	Hydroquinol- sulfone- phthalein	Hydroquinol- phthalein dibenzoate	Hydroquinol- sulfone- phthalein dibenzoate
		1960		
		2259		2185
Absolute	3121	2722	3347	2575
Ethanol	3518	3523	3549	3316
	3626	4122	3676	3715
	4213		4316	4410
Alcoholic	1900	1850		
KOH	2888	2670		
(100 m.)		3179		
	3833	4010		
33%		2170		
aqueous	3008	3076		
KOH	4048	4007		

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Summary

1. Evidence is submitted from a study of absorption spectra which provisionally confirms a conclusion previously arrived at from the chemical behavior of the compounds, that hydroquinolphthalein and hydroquinol-sulfonephthalein can exist in the meta-quinoid state. It is also established that hydroquinolsulfonephthalein has an inner salt structure.

2. Data and curves are presented showing the absorption of these two compounds in neutral, acid and alkaline solutions.

3. A comparison of the absorption spectra of the dibenzoates of hydroquinolphthalein and hydroquinolsulfonephthalein shows that the latter is to be considered as a quinoid derivative.