erable to maintain an approximate uniformity in respect to the intensity of the absorption in comparative measurements by means of a suitable variation in indicator concentrations. If such provisions are made as will confine the measurements within the intensity range wherein the eye of the observer is most sensitive, and the employment of the indicator confined within the P_H zone in which dissociation is greater than 10% and less than 90%, the data of the present investigation indicate that the error by the spectrophotometric method should not exceed 0.02 P_H.

Summary

Data are supplied for a relatively convenient and accurate spectrophotometric method for determining the hydrogen-ion concentrations of solutions within the effective dissociation ranges of thymol blue.

The apparent dissociation constants of the indicator in its alkaline and acid ranges are determined to be 8.91 and 1.5, respectively.

The dissociation of the indicator is normal over its useful alkaline range, but is appreciably retarded after the mid-point in its acid range has been passed.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, JOINTLY WITH SOIL FERTILITY INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE, No. 101]

THE SPECTROPHOTOMETRIC DETERMINATION OF HYDROGEN-ION CONCENTRATIONS AND OF THE APPARENT DISSOCIATION CONSTANTS OF INDICATORS. III BROMOCRESOL GREEN

BY WALTER C. HOLMES[1] AND EDWARD F. SNYDER[2]

RECEIVED AUGUST 13, 1924 PUBLISHED JANUARY 8, 1925

The synthesis of bromocresol green (tetrabromo-*m*-cresol-sulfonephthalein) was undertaken by Barnett Cohen in 1922 to supply a sulfonephthalein derivative which would be suitable for substitution in place of methyl red in the Clark and Lubs series of indicators. In the preliminary note on the indicator[3] its apparent dissociation constant was reported as 5.0.

In its alkaline form the indicator is blue, with an absorption band in the red with the maximum at approximately 614 $\mu\mu$.

Through the kindness of Mr. Cohen, the authors were supplied with a sample of his original material and with one of subsequent preparation shown by analysis to be of superior purity. The dissociations of these

---

[1] Associate Chemist, Color Laboratory, Bureau of Chemistry.

[2] Assistant Biochemist, Soil Fertility Investigations, Bureau of Plant Industry.

[3] *U. S. Pub. Health Repts.*, **38,** [5] 199 (1923).

materials in the alkaline range were investigated by the spectrophotometric methods outlined in previous papers of this series.[4]

The apparent dissociation constant of the original preparation was determined as 4.88 and that of the purer material as 4.68. The data obtained with the latter are summarized in Table I. The values recorded in the row R_1 are ratios of the extinction coefficients of the indicator in the various buffer solutions to those of an equal quantity of indicator in 0.1 N alkali. The percentage dissociation of the indicator is obtained by multiplying these values by 100, and the apparent dissociation constant is calculated by the usual formula.

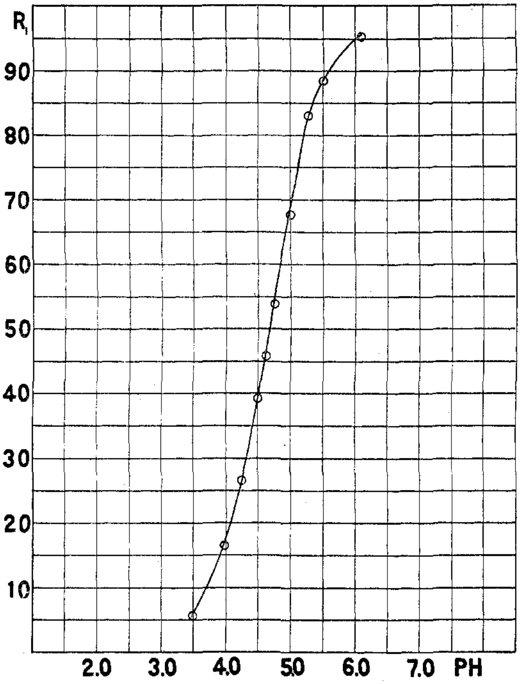

Fig. 1.—Bromocresol green: alkaline range.

The agreement between experimental data and theory is excellent, and it is evident that the dissociation of the indicator is normal over the range between 10% and 90% dissociation in which its practical utility is found.

The high value for K obtained with Cohen's original preparation may doubtless be attributed to incomplete bromination. Analytical evidence of incomplete bromination is supported by a corresponding abnormality in the form of the absorption curve.

TABLE I

BROMOCRESOL GREEN: ALKALINE RANGE

Temperature: 27°

Pure material prepared by Cohen

PH	3.49	3.98	4.23	4.49	4.60	5.75	5.00	5.26	5.52	6.09
R_1	0.057	0.165	0.266	0.393	0.458	0.539	0.678	0.790	0.870	0.953
K	(4.70)	4.68	4.67	4.68	4.67	4.68	4.68	4.68	4.69	(4.78)
									Av.	4.68

Supplies of the indicator have recently been marketed by two commercial firms referred to hereinafter as A and B. Samples of these have been ob-

---

[4] THIS JOURNAL, **46**, 627 (1924); **47**, 221 (1925).

tained and have been examined by the same methods. Values obtained for K are recorded in Table II.

TABLE II

BROMOCRESOL GREEN (COMMERCIAL): ALKALINE RANGE

Temperature: 24°

P_H	5.21	4.97	4.78	4.59	4.39	4.22	
K (Firm A)	4.63	4.66	4.65	4.64	4.65	4.65	Av. 4.65
K (Firm B)	4.70	4.68	4.69	4.69	4.71	4.68	Av. 4.69

Both commercial products resemble Cohen's later material closely in essential respects.

In a previous paper an accuracy of within 0.02 Sörensen (P_H) unit was claimed for spectrophotometric methods in application with the sulfonephthaleins. The probable error in the mean value obtained in an extensive series of careful determinations is very small. The data recorded in Table II, therefore, may unquestionably be accepted as demonstrating an actual, although relatively small, difference in the character of the two products. It is probable that a critical spectrophotometric examination of the market supply of other indicators which offer manufacturing difficulties would reveal similar variations.

In the application of the spectrophotometric method with bromocresol green in the evaluation of solutions of unknown hydrogen-ion concentration, the theoretical dissociation formula may be employed. For ordinary purposes the apparent dissociation constant of the indicator may be assumed to be 4.67, although it is advisable to determine the constant for the sample of indicator which is to be employed if maximum accuracy is desired.

Since the dissociation of the indicator has been shown to be normal over the useful range, the exponential values of various "drop-ratios" may be computed readily from the apparent dissociation constant. The data of Table III are recorded for use in the drop-ratio method[5] for the determination of hydrogen-ion exponents.

TABLE III

DROP-RATIO VALUES FOR BROMOCRESOL GREEN

Drop ratio	1:9	1.5:8.5	2:8	3:7	4:6	5:5	6:4	3:7	2:8	1.5:8.5	1:9
P_H	3.72	3.92	4.07	4.30	4.49	4.67	4.85	4.67	5.27	5.42	5.62

The drop-ratio method was employed in determining the hydrogen-ion exponents of several soil samples as a test of the practical utility of the indicator. (In preparing the 0.02% aqueous solution of the indicator, 2.9 cc. of 0.05 N sodium hydroxide was used for each decigram of dye.) The results obtained were in excellent agreement with the electrometric control.

---

[5] *Soil Science*, **9**, No. 2, Feb. **1920**.

The authors desire to acknowledge their indebtedness to the National Aniline and Chemical Company for the gift of a sample of their product.

Summary

1. The dissociation of bromocresol green conforms to the theoretical formula over the useful portion of its alkaline range.

2. The apparent dissociation constant of a relatively pure sample of the indicator of laboratory origin was determined as 4.68. The values obtained with two commercial products were, respectively, 4.65 and 4.69.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REACTION BETWEEN METALLIC SODIUM AND AROMATIC ALDEHYDES, KETONES AND ESTERS. II. ESTERS

BY F. F. BLICKE

RECEIVED AUGUST 18, 1924 PUBLISHED JANUARY 8, 1925

In a previous paper[1] we have shown that benzaldehyde reacts with one or two atomic equivalents of metallic sodium to form highly colored, very reactive addition products. The study of these addition products is made difficult by the fact that during the formation of the aldehyde-sodium compounds a number of other products are also produced. The benzaldehyde disodium addition compound reacts with bromobenzene to form, among other substances, triphenylcarbinol.

Esters of aromatic acids react, likewise, with sodium to form deeply colored, very reactive addition compounds. Other investigators[2] have already noticed this phenomenon in the case of ethyl benzoate. The study of the reaction between ethyl benzoate and sodium by them, however, has been only of a preliminary nature, since it was not found possible to bring about complete reaction between the ester and the metal.

We have discovered in phenyl benzoate an ester especially suitable for the study of this reaction. When this ester, dissolved in absolute ether, is treated with one atomic equivalent of sodium at ordinary temperature a red-brown crust begins to form at once on the surface of the metal. This crust soon dissolves in the ether and leaves the metal with a bright, reactive surface. A flocculent precipitate also appears and increases in amount as the reaction progresses. It is essential that oxygen, carbon dioxide and moisture be excluded from contact with the reacting materials. After eight days the sodium completely disappears and a red-brown ether solution, which contains a considerable amount of the flocculent precipitate, is obtained.

---

[1] Blicke, THIS JOURNAL, **46**, 2560 (1924).

[2] (a) Wahl, *Compt. rend.*, **147**, 73 (1908). (b) Scheibler and Voss, *Ber.*, **53**, 390, 392, 403 (1920). (c) Scheibler and Emden, *Ann.*, **434**, 268 (1923).