

The spectrophotometer has rendered important service in the investigation of indicators.⁴ The methods outlined in the present paper provide a simple, convenient and relatively accurate means of utilizing the spectrophotometer to advantage in the employment of indicators, and are useful adjuncts to established methods for the determination of hydrogen ions. Data will be supplied in subsequent communications bearing upon the practical application and limitations of the methods in the instances of representative indicators.

The author wishes to take this opportunity to express his appreciation to W. Mansfield Clark of the Hygienic Laboratory, United States Public Health Service, for valuable suggestions and for criticisms of these methods.

Summary

Simple, convenient and relatively accurate methods are outlined for the determination of the hydrogen-ion concentrations of solutions by spectrophotometric means. They are based upon empirical calibration of spectrophotometric ratios with suitable indicators against known hydrogen-electrode values.

The data of such calibrations afford an advantageous means for the calculation of the approximate apparent dissociation curves of indicators and their approximate apparent dissociation constants.

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THE ABSORPTION SPECTRA OF CERTAIN DERIVATIVES OF PARA-CYMENE

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Spectrophotometric data obtained with six mono-azo dyes prepared from *p*-cymene at this Laboratory by M. Phillips are recorded in the following table. For comparison, corresponding absorption measurements on five commercial dyes derived from benzene, of which the former are homologs, are also included. The *p*-cymene derivatives were made from intermediates of good purity and compared favorably with commercial dyes of the best grade in respect to freedom from subsidiary coloring matters.

All values recorded are the averages of ten or more measurements made with a standard spectrometer, provided with a Nutting photometer. Since both the laboratory and the commercial products examined contained various amounts of inorganic salts the absolute value of the measurements is without significance. The data obtained, however, afford a reliable

⁴ See THIS JOURNAL, 41, 1031 (1919).

determination of the form and spectral location of the absorption bands of the dyes investigated.

TABLE I
ABSORPTION (EXTINCTION COEFFICIENT)

Wave length $\mu\mu$	Di(methyl isopropyl) tartrazine conc. = 20	Tartrazine (Nat.) conc. = 20	Methyl isopropyl chromotrope 2R conc. = 40	Chromotrope 2R (M. L. B.) conc. = 40	Methyl isopropyl orange G conc. = 40	Orange G (Bad.) conc. = 40.	Methyl isopropyl resorcin yellow conc. = 20	Resorcin yellow (Bad.) conc. = 20	Methyl isopropyl orange II conc. = 40	Orange II conc. (DHP) conc. = 20	Methyl isopropyl sulfamic acid chromotropic acid conc. = 40
420	0.667	0.745	0.12	0.105	0.418	0.459	0.483	0.598	0.452	0.390	0.17
430	.734	.813	.17	.187	.487	.543	.552	.624	.525	.447	.207
435831
440	.802	.820	.227	.276	.570	.634	.598	.604	.610	.521	.244
445	.813	.774
450	.794	.712	.305	.383	.678	.755	.570	.538	.710	.626	.342
460	.737	.558	.410	.530	.824	.917	.494	.428	.843	.738	.464
470	.650	.403	.561	.726	.99	1.078	.407	.326	1.02	.860	.630
480	.530	.252	.758	.922	1.158	1.233	.312	.240	.119	.952	.827
485	1.23	1.30	1.255	.968
490	.393	.106	.937	1.13	1.272	1.345	.219	.174	1.304	.948	1.025
492	1.281
495	1.271	1.336	1.32	.927
500	.265	.02	1.13	1.336	1.236	1.320	.138	.128	1.29	.885	1.247
505	1.247	1.379	1.189	1.242	1.333
510	.167	1.341	1.394	1.145	1.238	.08	.09	1.195	.790	1.414
515	1.418	1.384	1.440
520	.09	1.433	1.368	1.07	1.092	.045	.06	1.10	.575	1.462
525	1.419	1.35	1.474
530	1.409	1.326	.872	.810911	.312	1.460
540	1.403	1.132	.591	.520619	.09	1.416
550	1.326	.758	.364	.296365	1.210
560974	.380	.194	.134182786
570516	.13	.10	.0508338
58021	.02510
59006

In all instances the solvent was distilled water and the absorbing layer one centimeter. The tabulated concentrations are in terms of parts of dye per million parts of solvent.

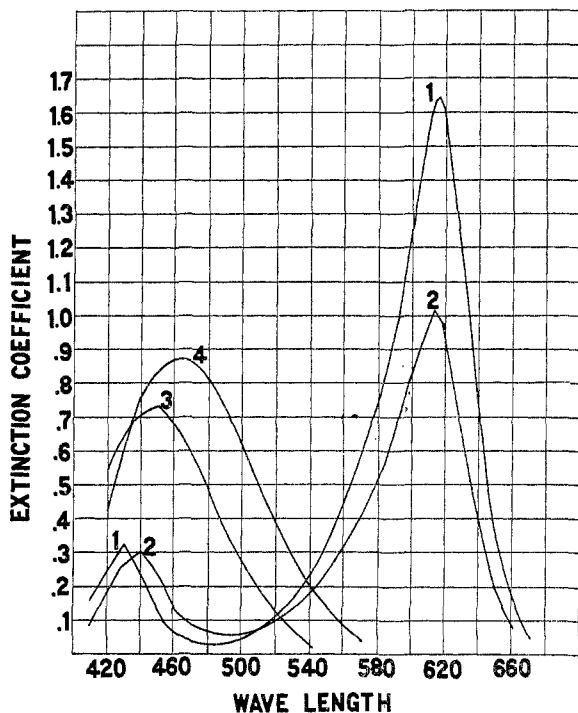
With each pair of homologs the effect of the methyl isopropyl substitution is a shifting of the absorption band toward the region of longer wave length. The displacement of the maxima, in general, is approximately 10 $\mu\mu$.

The accompanying graph records the absorption curves in distilled water and dil. sulfuric acid of Victoria green and of an isopropyl Victoria green in which the isopropyl substitution occurs in the non-aminated nucleus in a *para* position to the methane linking. The latter compound was a crystalline product of excellent purity.

The visible absorption of Victoria green consists of a principal band in the red with a maximum at 616 $\mu\mu$ and a secondary band in the violet with a maximum at approximately 430 $\mu\mu$. In the isopropyl derivative the latter maximum is displaced in the direction of longer wave length by approximately 10 $\mu\mu$, whereas the displacement of the principal band is only approximately 2 $\mu\mu$ and occurs in the opposite direction. Other

differences were noted. With the *isopropyl* derivative the intensity of the secondary band in relation to that of the principal band was greater than with Victoria green. The *isopropyl* derivative also proved more resistant to mineral acids.

With the addition of acid (sulfuric) to the aqueous solutions of the dyes, both bands characteristic of neutral solution gradually disappear and a new band is developed in the same general spectral region as that



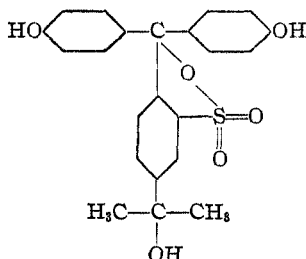
1, Victoria green (Victoria green W B cryst.): 10 parts of dye per million parts of water; 2, *isopropyl* Victoria green: 10 parts of dye per million parts of water; 3, Victoria green: in dil. sulfuric acid; 4, *isopropyl* Victoria green: in dil. sulfuric acid.

of the secondary band of neutral solution. The new band (recorded in the graph for each dye) is that of the diacid salt.

In the phenolsulfonephthalein group of indicators thymolsulfonephthalein and carvacrolsulfonephthalein, in which the substitutions introduced occur in the phenol residues, have received extensive study. The absorption of a homolog of phenolsulfonephthalein, derived from *p*-cymene, in which the substitution occurs in the sulfonated residue, was investigated.

The material examined was prepared by H. A. I.ubs by oxidizing cymene-

2-sulfonic acid to a homolog of *o*-sulfobenzoic acid, transforming to the acid chloride and condensing with phenol. Its constitution may be represented by the following formula.



A comparative study was made of its absorption and of the absorption of phenolsulfonephthalein.

In alkaline solution phenolsulfonephthalein gives an absorption band with a maximum at approximately $559 \mu\mu$. In neutral solution this band disappears, with the formation of a band in the violet which is relatively somewhat poorly defined and was not examined with particular care. In the presence of an excess of acid (sulfuric) this second band disappears with the formation of a third band with a maximum at approximately $507 \mu\mu$.

The absorption of the cymene homolog was practically identical with that of phenolsulfonephthalein. No appreciable displacement of the maximum or modification in the essential form of the absorption could be detected in the band of either alkaline or acid solution. Absorption measurements carried out in buffered solutions with Sørensen (P_H) values of 10.19, 7.52 and 6.29 showed that as the Sørensen value of the solutions was decreased the transition between the absorption forms characteristic of alkaline and neutral solutions occurred somewhat more rapidly in the instance of the cymene derivative. In other words, the color changes which are of service as indicators of hydrogen-ion concentration occur at somewhat higher points in the Sørensen scale with that dye. This change and a decrease in solubility, especially in acid solution, were the only appreciable effects of the substitution noted.

The substantial coincidence of the absorption bands of the two homologs is evidence of the negligible influence upon the color of compounds of the phenolphthalein type of substitution in the particular position involved, previously noted by Moir¹ in an investigation of the effects of halogen substitution.

Summary

The absorptions in the visible spectra of eight dyes derived from *p*-cymene have been investigated and compared with those of seven corresponding homologs derived from benzene.

¹ Moir, *Trans. Roy. Soc. S. Afr.*, 10, 159 (1922).

1. With five mono-azo dyes the effect of the methyl *isopropyl* substitution was that of a deepening of color corresponding to a displacement of the absorption band in the direction of longer wave length amounting to approximately 10 $\mu\mu$.

2. With Victoria green the effect of the *isopropyl* substitution in the non-aminated nucleus in a *para* position to the methane linking was that of a displacement of the two absorption bands in the visible spectrum in opposite directions, the spectral interval between their maxima being decreased.

3. The absorption of a homolog of phenolsulfonephthalein, derived from *p*-cymene, in which the substitution occurred in the sulfonated residue, was practically identical with that of phenolsulfonephthalein. With the *p*-cymene derivative the transition to the alkaline form occurred at somewhat higher points in the Sørensen scale than with phenolsulfonephthalein.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF TORONTO]

THE SOLUBILITY OF HELIUM AND HYDROGEN IN HEATED SILICA GLASS AND THE RELATION OF THIS TO THE PERMEABILITY¹

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According to the law of Graham and Bunsen, the rates of effusion of helium and hydrogen should be inversely proportional to the square root of their densities; that is, the helium rate should be 0.7 times the rate for hydrogen. In the cases of rubber,² rubbered balloon fabrics³ and soap bubbles⁴ the permeabilities observed are in approximate agreement with this law but in the case of silica glass this is not true. For example, at 500° the helium rate is approximately 22 times the hydrogen rate, the ratio increasing slightly at higher and diminishing slightly at lower temperatures. Such a wide discrepancy between theory and experiment seems to indicate that the phenomenon cannot be one of simple effusion.⁵ On the other hand, to call it a case of true solution and diffusion at once raises the question of the relative solubilities of these gases in this medium.

Wüstner⁶ has determined the solubility of hydrogen but no one appears to have made solubility measurements with helium gas. Measurements

¹ Experimental work by G. A. Williams.

² Elworthy and Murray, *Trans. Roy. Soc. Canada*, [III] 13, 37 (1919).

³ Edwards and Pickering, *Bur. Standards Sci. Paper*, 387 (1920).

⁴ McLennan and Shaver, *Phil. Mag.*, 40, 272 (1920).

⁵ Williams and Ferguson, *THIS JOURNAL*, 44, 2160 (1922).

⁶ Wüstner, *Ann. Physik*, 46, 1095 (1915).