[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

A Spectrophotometric Study of Certain Neutralization Indicators[1]

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Various organic compounds have been used extensively as indicators in neutralimetry and for the colorimetric determination of the *p*H value of solutions. While the general nature of the absorption spectra of solutions of such indicators has been known for years, few reliable spectrophotometric data on the transmittancy curves at different *p*H values have been reported until recently.[2] The present availability of objective photoelectric spectrophotometers has led the authors to check some of the earlier data obtained with subjective visual instruments. In addition to the simple systems studied by other workers, the present work includes certain modified and mixed indicators used in titrimetry.

Experimental Work

Apparatus.—All measurements of transmittancies were made on a photoelectric spectrophotometer[3] with cells 1.000 cm. thick and a spectral band 10 mμ wide. The data were secured within fifteen minutes of the time the solutions were prepared, the transmittancy-wave length curves being recorded by the instrument.

Tristimulus values were obtained with a calculator[4] using 10 selected ordinates, a procedure shown to give a precision of 0.2%. The values are based on the I. C. I. illuminant C.

Solutions.—The indicator solutions were prepared by dissolving the purest obtainable commercial reagents in doubly distilled water, or ethanol, if necessary. Dilutions were made from the stock solutions to give the concentrations listed in Table I.

Clark and Lubs' buffer solutions were prepared,[5] with *p*H values ranging from 2.2 to 6.8 at intervals of 0.2 *p*H unit. The salts were recrystallized three times, and the solutions were checked with a glass electrode. An antiseptic was added to prevent the growth of mold.

In preparing a solution for measurement exactly 0.3750 ml. of the indicator solution was transferred to a 25-ml. volumetric flask by means of a micro-buret, buffer solution was added to the mark and the system was mixed. Specifications are given below for the solutions prepared to represent colorless end-points with modified indicators.

TABLE I

SYSTEMS STUDIED

Indicator	Concentration, g./l.	Solvent
Brom cresol green	0.4000	Water
Ethyl orange	.4000	Water
Methyl orange	.4000	Water
Methyl red	.4000	50% ethanol
p-Methyl red	.4000	Water
Propyl red	.4000	50% ethanol
Methyl red	.2000	50% ethanol
Brom cresol green	.2000	
Methyl orange	.0400	Water
Brom cresol green	.2000	
Methyl orange	.4000	50% ethanol
Xylene cyanole FF	.5600	
Methyl red	.2500	95% ethanol
Methylene blue	.1750	

Data and Discussion.—The indicators studied are of three general types, simple, modified and mixed. The various indicators in each group are discussed under the respective group headings.

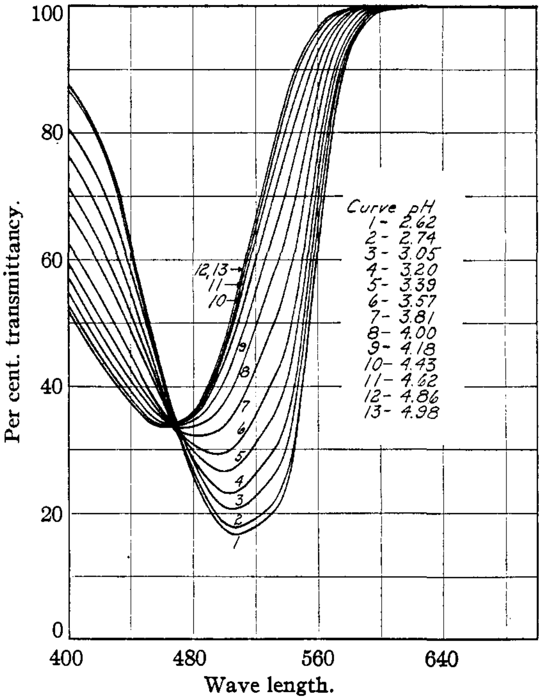

Fig. 1.—Spectral transmission curves for methyl orange solutions at different *p*H values: one cm. cell thickness and 0.375 ml. of a solution containing 0.4 g./l. diluted to 25 ml.

a. Simple Indicators.—The transmittancy curves for methyl orange are shown in Fig. 1. These exhibit a fixed isobestic point at 469 mμ,

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(1) Abstracted from a portion of a dissertation submitted by W. B. Fortune [present address, Eli Lilly and Co., Indianapolis, Ind.] to the Graduate School of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Brode, THIS JOURNAL, **46**, 581 (1924); Uzumasa and Yamawaki, *J. Chem. Soc. Japan*, **58**, 721 (1937); **59**, 24 (1938).

(3) Michaelson and Liebhafsky, *Gen. Elec. Rev.*, **39**, 445 (1936).

(4) Swank and Mellon, *J. Optical Soc. Am.*, **27**, 414 (1937).

(5) Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, Md., 1928, p. 200.

together with a consistent change in intensity of absorption with increase of *p*H. The absorption band of this indicator, an azo compound, shows a definite shift of the wave length of the peak of the band through the transformation range. At *p*H 2.62 the peak is located at 507 mμ; with increase of *p*H the shift of the band is toward the blue, the peak being located at 472 mμ at *p*H 4.0. The shift of the peak follows approximately a hyperbolic spiral.

Ethyl orange, another azo compound, gave curves resembling those for methyl orange but bearing a mirror image relationship to them with respect to the relative heights of the absorption bands for the acidic and the basic forms of the indicator. In the curves for each of the two indicators a weak secondary band shows the same shift as the primary.

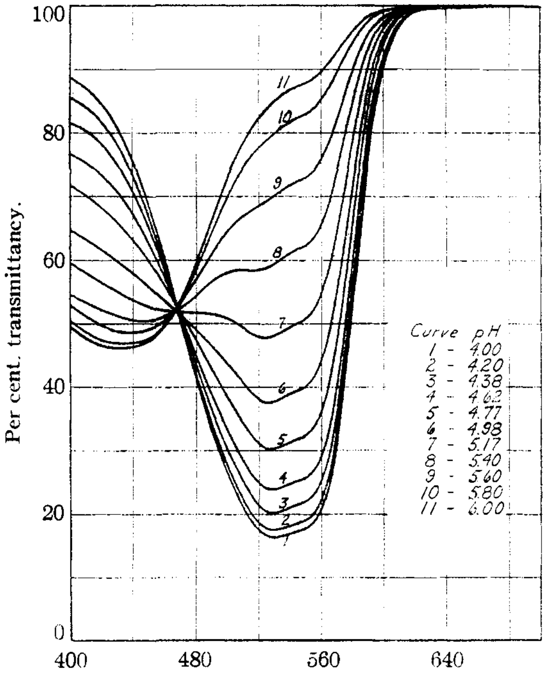

Fig. 2.—Spectral transmission curves for methyl red solutions at different *p*H values: one cm. cell thickness and 0.375 ml. of a solution containing 0.4 g./l. diluted to 25 ml.

The curves for methyl red are shown in Fig. 2. Although some earlier data[2] (p. 588) indicate that the peak of the absorption band apparently does not change in wave length through the transformation range, these curves, like those for methyl orange, show a shift toward the violet with increase in *p*H. The small secondary band shows a similar, but less obvious, shift.

Measurements on tropaeoline 00 gave results very similar to those for other azo indicators, the shift of the peak of the absorption band with change of *p*H being evident.

Unsuccessful attempts were made to secure curves for several other azo compounds. Solutions containing propyl red faded as much as 50% within two minutes after preparation. Paramethyl red precipitated from the buffer solution so rapidly that reliable curves were not obtainable. Dimethylaminoazobenzene gave reproducible curves on the acidic side of the transition point of the indicator; on the basic side fading occurred to the extent of more than 1% per minute. The curves for the acidic side showed a shift of the peak of the absorption band similar to that obtained for the other azo indicators studied.

Figure 3 shows the curves for brom cresol green, a sulfonphthalein type indicator. This is an example wherein the peak of the absorption band, at 615 mμ, does not change in wave length with change of *p*H of the solution. A good isobestic point is shown for this indicator also.

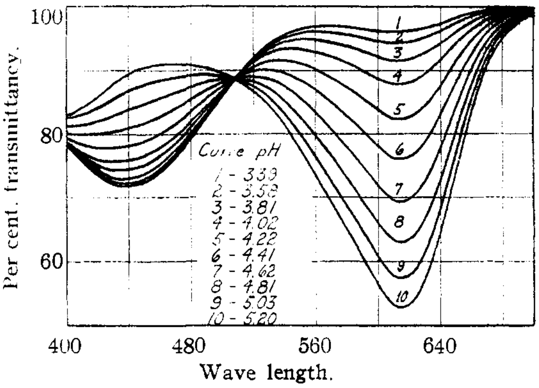

Fig. 3.—Spectral transmission curves for brom cresol green solutions at different *p*H values: one cm. cell thickness and 0.375 ml. of a solution containing 0.4 g./l. diluted to 25 ml.

Reference to Figs. 1 to 3 shows that a shift in the peak of the band is to be expected unless the slope of the top curve is nearly zero at the wave length of the minimum point of absorption for the bottom curve. Intermediate curves represent mixtures of the acidic and basic color forms of the indicator. The direction of the shift depends upon the slope of the top curve, that for methyl orange being toward the violet. In Fig. 3 the top curve for the primary band is nearly flat at 615 mμ while that for the secondary band at 436 mμ has considerable slope.

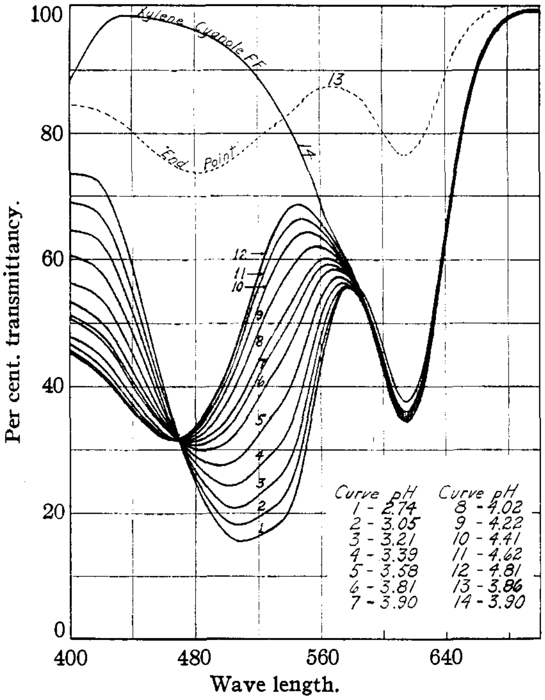

Fig. 4.—Spectral transmission curves for modified methyl orange at different pH values and the modifying agent at one value: one cm. cell thickness and 0.375 ml. of a solution containing 0.4 g./l. of methyl orange + 0.56 g./l. of xylene cyanole FF diluted to 25 ml. For the end-point curve 0.100 ml. of the indicator solution was diluted to 25 ml.

b. Modified Indicators.—A study was made of xylene cyanole FF and of methylene blue, modifying agents for methyl orange and methyl red, respectively. A curve for one concentration of each reagent is shown in Figs. 4 and 5. The curves do not show a shift in wave length of the peak with change of pH above 3.2. These curves represent the same concentration of modifying agent as that in the modified indicator discussed below.

Figure 4 shows the curves for methyl orange modified with xylene cyanole FF. The indicator was prepared according to the directions of Hickman and Linstead.[6] The characteristic shifting of the peak of the methyl orange absorption band is shown here, as with the simple indicator; also a definite isobestic point is exhibited with the modified indicator.

Curves for methyl red, modified with methylene blue, are given in Fig. 5. The solution was prepared according to recommendations of Johnson and Green.[7]

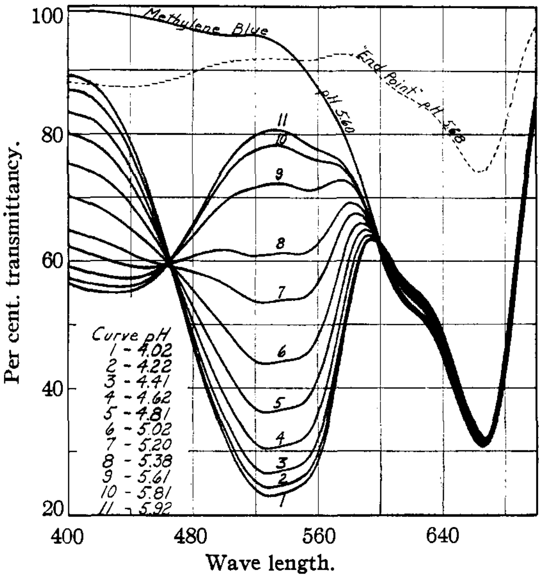

Fig. 5.—Spectral transmission curves for modified methyl red at different pH values and the modifying agent at one value: one cm. cell thickness and 0.375 ml. of a solution containing 0.25 g./l. of methyl red + 0.175 g./l. of methylene blue diluted to 25 ml. For the end-point curve 0.100 ml. of the indicator solution was diluted to 25 ml.

Curves for the colorless end-points obtainable in titrations using modified methyl orange or methyl red also are shown in Figs. 4 and 5. In each case 0.1000 ml. of the indicator solution (Table I) was diluted with a buffer to make 25 ml. of solution. This corresponds to about two drops of the stock solution in 125 ml. of solution to be titrated. Other concentrations gave similar curves.

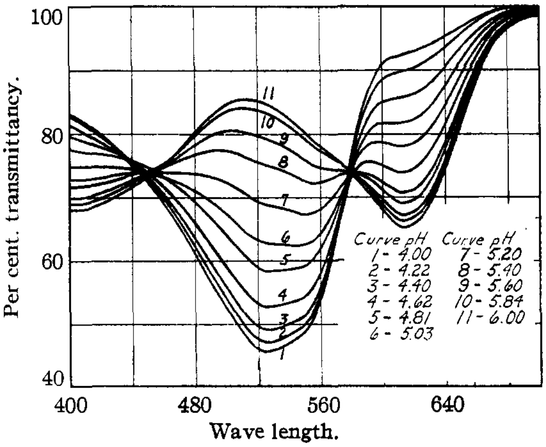

Fig. 6.—Spectral transmission curves for the mixed indicator methyl red + brom cresol green at different pH values: one cm. cell thickness and 0.375 ml. of a solution containing 0.2 g./l. of methyl red + 0.2 g./l. of brom cresol green diluted to 25 ml.

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(6) Hickman and Linstead, *J. Chem. Soc.*, **121**, 2502 (1922).

(7) Johnson and Green, *Ind. Eng. Chem., Anal. Ed.*, **2**, 2 (1930).

TABLE II

COLOR SPECIFICATIONS OF INDICATOR SOLUTIONS

Indicator		Trichromatic			Monochromatic		
		Red, %	Green, %	Violet, %	Dominant wave length mμ	Relative brightness, %	Colorimetric purity, %
Brom cresol green	(3-2)[a]	33.0	34.5	32.5	572.8	90.8	13.0
	(3-10)	27.3	29.8	43.0	484.8	71.1	15.4
Methyl orange	(1-1)	40.8	29.5	29.8	493.6[b]	56.2	27.0
	(1-11)	39.5	39.5	21.0	578.6	83.1	43.8
Methyl red	(2-1)	36.1	22.9	41.0	513.6[b]	42.0	44.6
	(2-11)	36.3	37.8	26.0	575.5	88.1	30.6
B-c. green +	(6-1)	34.4	28.4	37.2	503[b]	63.2	19.4
M. red	(6-11)	30.1	32.6	37.3	505	77.1	3.0
Modified	(4-1)	34.9	25.8	39.4	510.4[b]	35.0	30.6
M. orange	(4-11)	33.7	37.6	28.6	567.4	55.0	23.2
Modified	(5-1)	30.9	22.7	46.5	551.8[b]	38.3	35.8
M. red	(5-11)	29.8	35.8	34.3	532[b]	72.5	8.6
Methylene blue	(5-)	26.6	30.7	42.6	488.4	82.9	17.2
Xylene Cyanole FF	(4-)	25.2	28.0	46.8	483.0	69.0	25.0
Colorless mod. M. orange	(4-)	31.3	31.9	36.8	578	90.2	1.5
Colorless mod. M. red	(5-)	30.8	32.0	37.2	515	95.0	1.9

[a] Figure curve number.

[b] Dominant wave length of the complementary.

c. **Mixed Indicators.**—Since many mixtures of indicators, the individual compounds of which have contrasting hues, have been proposed, representative examples were studied. The results for one of them are included here.

Selected curves for the mixture proposed by Hähnel,[8] consisting of equal parts of methyl red and brom cresol green, are shown in Fig. 6. A definite isobestic point is exhibited at 580 mμ, and a diffuse crossing at 450 mμ.

Color specifications were determined for selected curves for each indicator. Values for one curve on the acidic side and one on the basic side of the indicator are presented in Table II.

Recently De Almeida[9] suggested the use of a graph coördinating dominant wave length with *p*H as a means of determining the *p*H of solutions. In the present work the dominant wave length of representative curves of several indicators was plotted against the *p*H of the solution, but the results have little practical value for indicators whose dominant wave length falls in the purple on one side of the transformation range. Since the dominant wave length of a purple is specified as that of its complementary, the curve consists of two widely separated parts—one for the true dominant wave lengths and one for the complementaries. With sulfonphthalein indicators which show no purple characteristics, the method may be used with some degree of accuracy. Relative brightness also was plotted against the *p*H of the solution, but the resulting curve seemed to have little practical value.

Summary

A spectrophotometric study has been made covering the transformation range of various simple, modified and mixed neutralization indicators. The spectral transmittancy curves show the characteristics of the absorption bands in the visual region at different *p*H values. Colorimetric specifications are included for selected curves for several indicators.

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(8) Hähnel, *Svensk Kem. Tids.*, **47**, 4 (1935).

(9) Dissertation, Lisbon, 1937.