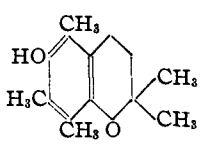
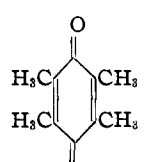
of pyridinium hydroxides to α-hydroxydihydropyridines. According to equation (12) the half wave potential at constant *p*H and temperature should be constant and independent of the concentration. This was actually found. When $\log [i/(i_d - i)]$ is plotted against the potential $\pi$ a straight line should be obtained according to equation (11) with a slope of 0.0296. Such a plot of the analysis of the anodic wave of 2,2,5,7,8-pentamethyl-6-hydroxychroman is given by line II in Fig. 9. A straight line with a slope of 0.0326 was found in good agreement with the theory.

The rate constant $a$ of reaction B to C (equation 2) cannot be derived from the experimental data.

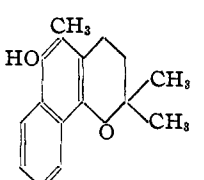
It is of interest to note that the difference in half wave potential of two hydroxychromans was found equal to the difference in oxidation potential of the corresponding quinones, as is shown by the following case



$\pi^1/_2 = +0.232$

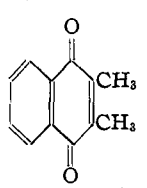


$\pi^1/_2 = -0.093$



$\pi^1/_2 = +0.114$

$\Delta = 0.12$



$\pi^1/_2 = -0.216$

$\Delta = 0.12$

The fact that coumarans were found to be more easily oxidized at the dropping electrode than the corresponding chromans indicates a greater stability of six-membered rings with a double bond than that of five-membered rings with a double bond.[16] Further work on the mechanism of the oxidation and also on the oxidation of Vitamin E is in progress.

## Summary

1. Current–voltage curves at the dropping electrode of 6-hydroxychromans and 5-hydroxycoumarans have been determined in 50% methanol in well buffered solutions. The half wave potentials of the various compounds were found to be unaffected by the concentration. The difference in half wave potentials of chromans and corresponding coumarans was found to be 10 millivolts, the coumarans being more easily oxidized than the chromans. A reaction mechanism of the electrode reactions has been proposed which accounts for the experimental facts.

2. Current–voltage curves and half wave potentials have been determined for a great number of hydroquinones and quinones. The half wave potentials were found to correspond to the standard oxidation potentials of the various systems.

3. Compounds related to Vitamin E can be determined polarographically.

(16) Brockway and Taylor, *Ann. Reports of the Progress of Chemistry*, The Chem. Soc., London, **34**, 219 (1937).

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[CONTRIBUTION FROM THE DOHME LABORATORY OF PHYSICAL CHEMISTRY, THE UNIVERSITY OF MARYLAND]

# A Spectrophotometric Study of the Characteristics of Some Halogen Substituted Sulfonphthalein Indicators

BY MALCOLM M. HARING AND HUGH A. HELLER[1]

The advantages of the sulfonphthaleins as indicators have encouraged numerous efforts to synthesize substituted forms. Among others, Harden and Drake[2] reported the preparation of eleven members of a series having four halogen atoms in the sulfobenzoic acid part of the molecule. They also determined approximately the useful ranges.

Since precision hydrogen ion colorimetry requires a knowledge of the indicator constant, the present study has been undertaken to determine *pK* for each of seven of these indicators which were available. At the same time the useful ranges were redetermined and general suitability studied, but no investigation of salt and protein errors was made. The indicators studied were

(1) Part of a thesis submitted by H. A. Heller to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. For seven additional spectrum photographs, order ADI Document 1494, American Documentation Institute, 2101 Constitution Ave., Washington, D. C., remitting 27¢ for microfilm or $0.90 for photoprint copies.

(2) W. C. Harden and N. L. Drake, THIS JOURNAL, **51**, 562 (1929).

Phenoltetrabromosulfonphthalein (Phenol-4Br)
Phenoltetrachlorosulfonphthalein (Phenol-4Cl)
*o*-Cresoltetrabromosulfonphthalein (*o*-Cresol-4Br)
*o*-Cresoltetrachlorosulfonphthalein (*o*-Cresol-4Cl)
Tetrabromophenoltetrabromosulfonphthalein (4Br-Phenol-4Br)
Tetrabromophenoltetrachlorosulfonpthalein (4Br-Phenol-4Cl)
Dibromo-*o*-cresoltetrachlorosulfonphthalein (2Br-*o*-Cresol-4Cl)

The indicator constant, called by Noyes[3] the "apparent indicator constant," is related to the hydrogen ion activity by the well known equation

$$p\mathrm{H} = pK + \log [x/(1 - x)]$$

where $pK$ is the co-logarithm of the indicator constant and $x$ is the fraction of the indicator transformed into the alkaline form. It is evident that $K$ can be calculated if $x$ can be determined in buffer solutions of known $p$H. Conversely the $p$H of solutions is readily determinable with indicators of known $pK$. Hence $K$ (or $pK$) is the most important quantitative characteristic of an indicator. Various methods and instruments have been devised to measure $x$ and therefore $pK$. Among these may be mentioned the half-transformation method of Salm,[4] the drop ratio method of Gillespie,[5] the colorimeter of Beaver,[6] and the color wedge of Bjerrum.[7] However, none is more accurate or informative than the determination of transmittancy curves with a spectrophotometer. Accordingly it was used for this study.

The procedure and calculation are very simple. The transmittancy ($T$) is determined at a single $p$H value over the entire visible spectrum. $-\log T$ is then plotted against the wave length ($\lambda$). Similar curves are obtained at sufficient $p$H values (increments of about 0.2 $p$H unit) to cover completely the useful range of the indicator. For the whole family of curves, the indicator concentration is the same. At some high $p$H value the curve will be found to coincide with that of the next lower $p$H value; similar behavior is observed at some low $p$H value. These limiting $p$H curves correspond to practically complete transformation of the indicator into its alkaline and acid forms, respectively. If now we divide log $T$ at the lowest minimum on the limiting high $p$H curve into log $T$ for any lower $p$H at the same wave length, the result is the fraction $x$. Similarly $1 - x$ may also be obtained, if desired, by dividing log $T$ at the lowest minimum on the limiting low $p$H curve into log $T$ at any higher $p$H and the same wave length. However, the fact that one of these minima may lie in the invisible spectrum, or be capable of much less precise determination than the other, greatly diminishes its value in checking the first calculation. $pK$ may then be calculated by substitution of $x$ and $1 - x$ in the equation at various $p$H values and averaging the results, or $x$ may be plotted against $p$H. In this case $p\mathrm{H} = pK$ at $x = 0.5$. Both methods were used in this research and showed excellent agreement. The averages of the two values are given in Table II.

(3) A. A. Noyes, THIS JOURNAL, **32**, 815 (1910).
(4) E. Salm, *Z. physik. Chem.*, **63**, 83 (1908).
(5) L. J. Gillespie, THIS JOURNAL, **42**, 742 (1920).
(6) J. J. Beaver, *J. Opt. Soc. and Rev. Sci. Instr.*, **18**, 41 (1929).
(7) N. Bjerrum, "Die Theorie der alkalimetrischen und azidimetrischen Titrierung," Stuttgart, 1914.

## Experimental

The buffer solutions used were those of Clark and Lubs,[8] the range covered being 2.4 to 8.6. The purest salts obtainable were used without further purification. The $p$H of each mixture was actually measured—those below 8 with a quinhydrone electrode and above with a hydrogen electrode. Numerous measurements were made on solutions below $p$H 8 with both electrodes, perfect checks being found in all cases. All $p$H measurements were made at 25 ± 0.03°.

The dry indicator powders prepared by Harden and Drake[2] had been preserved in glass stoppered bottles in the dark. They were used without further purification since each had been recrystallized several times and their analyses were quite satisfactory; 40 mg. of each dye was ground in an agate mortar with sufficient 0.01 $N$ sodium hydroxide to form the sodium salt, and then diluted to 100 ml. This produced 0.04% stock solutions.

The buffer–indicator mixtures were made by adding 40 ml. of the appropriate buffer solution to 1 ml. of the indicator stock solution. However, in the case of tetrabromophenoltetrabromosulfonphthalein the color was not quite so intense. Therefore a 20:1 dilution was used. This procedure was more convenient than varying the spectrophotometer tube length.

The instrument used was a photoelectric spectrophotometer belonging to the National Bureau of Standards. It was equipped with a cesium photocell, galvanometer and Brodhun rotating sector. The light source was a coiled tungsten filament lamp supplied by a large bank of storage batteries. This ensured constant current for long periods, essential to the method of measurement used. The characteristics of the photocell had been studied with care and it was found that the response was very nearly but not exactly linear. However, the use of the rotating sector made exact linearity of response unnecessary. The spectrometer drum was calibrated on the emission spectrum of helium, no filters of any kind being used. This was done by plotting galvanometer readings against the drum readings over the visible spectrum. The true wave lengths were then plotted against drum readings.

(8) W. M. Clark and H. A. Lubs, *J. Biol. Chem.*, **25**, 479 (1916).

The calibration curve thus constructed was used to correct all readings of the drum.

The general procedure was as follows. The tube (4.0 cm. long in all experiments) was filled with the buffer–indicator mixture (hereafter called solution) and placed in the instrument. The sector, which had a scale divided in 100 parts indicating the magnitude of the openings, was set at 100 (full open). The spectrometer drum was then set to the desired wave length and the galvanometer reading noted. An identical cell having been filled with the buffer mixture alone (hereafter called solvent) was then placed in the instrument. Without changing the wave length drum, the sector opening was adjusted until the galvanometer reading was the same as in the first case. The transmittancy was the ratio of the second reading to the first, each reading having been corrected for the galvanometer reading when no light was passing through the instrument. All settings were made several times, the average figures being used. This procedure was repeated throughout the entire visible spectrum, beginning in the red and working up to the violet and then back to the red. Each measurement was thus the average of two sets of figures obtained by moving the drum in opposite directions. Sufficient points (18 or more) of such distribution (about twenty mμ intervals) throughout the spectrum were taken as to ensure smooth curves. No attempt at exact temperature control was made. However, the instrument was located in a room of remarkably constant temperature. As measured frequently each day during the several months required, it remained between 23 and 28°.

The instrument used was very much more sensitive in the red-orange region of the spectrum than in the violet end. This was due to two factors. (1) The cesium cell was much more sensitive to red rays than to violet. (2) The tungsten filament source was much richer in red than in violet. By using a very narrow exit slit width in the red region and opening this as the violet end was approached, inequalities in sensitivity were partially adjusted. Using a wider slit at the violet end did not materially affect the results due to variation in the wave length band. This was so because the dispersion of the prism was so much greater in the violet end than in the red end that selection in the violet end did not need to be very fine. The sensitivity in the violet end was further improved by using filters in this region which removed the red and yellow rays from the source. This prevented stray radiation from falling on the cell. Any absorption effect of the filter cancels out, since the same filter was used for both solvent and solution readings. The exit slit widths used were 0.1 mm. in the red-orange, 0.2 mm. in the yellow-green and 0.5 mm. in the blue-violet.

The useful range for each indicator was determined by making up the buffered solutions to 0.2 *p*H unit beyond the value where no further color change was visible to the eye on both the acid and alkaline sides.

**Data.**—To save space, the spectrophotometric curves for the indicators ($-\log T$ *vs.* λ at numerous *p*H values), are omitted.

The *x vs. p*H and *pK* values for all the indicators are given in Table I and in graphic form in Fig. 1. Table II is a condensed summary of the facts sought.

TABLE I

*o*-Cresol-4Br

| *p*H | *x* | *pK* |
|---|---|---|
| 6.35 | 0.037 | 7.77[a] |
| 6.57 | .074 | 7.67[a] |
| 6.75 | .123 | 7.60 |
| 6.96 | .171 | 7.65 |
| 7.15 | .232 | 7.67 |
| 7.28 | .349 | 7.55 |
| 7.51 | .483 | 7.54 |
| 7.66 | .590 | 7.50 |
| 7.78 | .696 | 7.42 |
| 8.05 | .845 | 7.31 |
| 8.24 | .980 | 6.55[a] |

Average *pK* = 7.53
*p*H (at *x* = 0.5) = 7.53

*o*-Cresol-4Cl

| *p*H | *x* | *pK* |
|---|---|---|
| 6.35 | 0.057 | 7.57[a] |
| 6.57 | .068 | 7.71[a] |
| 6.75 | .105 | 7.68 |
| 6.96 | .167 | 7.66 |
| 7.15 | .246 | 7.64 |
| 7.28 | .360 | 7.53 |
| 7.51 | .456 | 7.59 |
| 7.66 | .602 | 7.48 |
| 7.78 | .687 | 7.44 |
| 8.05 | .864 | 7.25 |
| 8.24 | .983 | 6.48[a] |

Average *pK* = 7.53
*p*H (at *x* = 0.5) = 7.49

Phenol-4Br

| *p*H | *x* | *pK* |
|---|---|---|
| 5.79 | 0.022 | 7.44[a] |
| 5.95 | .051 | 7.22[a] |
| 6.15 | .085 | 7.18[a] |
| 6.35 | .121 | 7.21 |
| 6.57 | .166 | 7.27 |
| 6.75 | .294 | 7.13 |
| 6.96 | .415 | 7.11 |
| 7.15 | .582 | 7.01 |
| 7.28 | .764 | 6.77 |
| 7.51 | .861 | 6.72 |

Average *pK* = 7.03
*p*H (at *x* = 0.5) = 7.03

Phenol-4Cl

| *p*H | *x* | *pK* |
|---|---|---|
| 5.79 | 0.021 | 7.46[a] |
| 5.95 | .058 | 7.16[a] |
| 6.15 | .087 | 7.17[a] |
| 6.35 | .132 | 7.17 |
| 6.57 | .199 | 7.17 |
| 6.75 | .289 | 7.14 |
| 6.96 | .419 | 7.10 |
| 7.15 | .559 | 7.05 |
| 7.28 | .769 | 6.76 |
| 7.51 | .890 | 6.60 |

Average *pK* = 7.00
*p*H (at *x* = 0.5) = 7.08

2Br-*o*-Cresol-4Cl

| *p*H | *x* | *pK* |
|---|---|---|
| 4.76 | 0.086 | 5.79[a] |
| 4.96 | .132 | 5.78 |
| 5.16 | .207 | 5.74 |
| 5.36 | .297 | 5.73 |
| 5.55 | .445 | 5.65 |
| 5.79 | .581 | 5.65 |
| 5.95 | .669 | 5.64 |
| 6.15 | .801 | 5.55 |
| 6.35 | .898 | 5.41 |
| 6.57 | .980 | 4.88[a] |

Average *pK* = 5.64
*p*H (at *x* = 0.5) = 5.64

4Br-Phenol-4Br

| *p*H | *x* | *pK* |
|---|---|---|
| 2.60 | 0.104 | 3.54 |
| 2.82 | .139 | 3.61 |
| 3.00 | .201 | 3.60 |
| 3.20 | .294 | 3.58 |
| 3.40 | .409 | 3.56 |
| 3.60 | .562 | 3.49 |
| 3.80 | .686 | 3.46 |
| 3.99 | .815 | 3.35 |
| 4.18 | .915 | 3.15[a] |
| 4.35 | .947 | 3.10[a] |

Average *pK* = 3.52
*p*H (at *x* = 0.5) = 3.59

4Br-Phenol-4Cl

| *p*H | *x* | *pK* |
|---|---|---|
| 2.60 | 0.104 | 3.54 |
| 2.82 | .148 | 3.58 |
| 3.00 | .216 | 3.56 |
| 3.20 | .302 | 3.56 |
| 3.40 | .421 | 3.54 |
| 3.60 | .526 | 3.55 |
| 3.80 | .705 | 3.42 |
| 3.99 | .829 | 3.30 |
| 4.18 | .912 | 3.16[a] |
| 4.35 | .979 | 2.68[a] |

Average *pK* = 3.51
*p*H (at *x* = 0.5) = 3.60

[a] These values were not used in averaging the *pK*'s. Even with a spectrophotometer, the probable error in *x* values below 0.1 and above 0.9 increases so rapidly that their inclusion is scarcely warranted.

TABLE II

| Indicator | Concn. (%) | Color range and absorption maxima: Acid | Base | *p*H Range | *pK* |
|---|---|---|---|---|---|
| Tetrabromophenol-tetrachloro-sulfonphthalein | 0.001 | Yellow-green-blue 440mμ | 610mμ | 2.6–4.4 | 3.56 |
| Tetrabromophenol-tetrabromo-sulfonphthalein | .002 | Yellow-green-blue 440 | 610 | 2.6–4.4 | 3.56 |
| Dibromo-*o*-cresol-tetrachloro-sulfonphthalein | .001 | Yellow-green-blue 435 | 605 | 4.8–6.6 | 5.64 |
| Phenoltetrabromo-sulfonphthalein | .001 | Yellow-violet 435 | 575 | 5.8–7.7 | 7.03 |
| Phenoltetrachloro-sulfonphthalein | .001 | Yellow-violet 435 | 575 | 5.8–7.7 | 7.04 |
| *o*-Cresoltetrachloro-sulfonphthalein | .001 | Yellow-purple 430 | 590 | 6.6–8.3 | 7.51 |
| *o*-Cresoltetrabromo-sulfonphthalein | .001 | Yellow-purple 430 | 590 | 6.6–8.3 | 7.53 |

## Discussion

All the indicators, except perhaps *o*-cresoltetrabromosulfonphthalein, exhibit a sharp iso-

bestic point. The presumption is, therefore, very strong that two and only two colored forms participate in the tautomeric equilibrium and that the preparations are pure.[9]

The results emphasize what Harden and Drake[2] had observed previously, that the nature of the halogen atoms attached to the sulfobenzoic acid part of the molecule makes no observable difference in indicator behavior. This is well shown in Fig. 1, where one curve serves for a pair of indicators in each of the three cases where corresponding molecules were studied.

Harden and Drake claimed that, for a given pair of indicators, those containing chlorine in the sulfobenzoic acid nucleus had slightly less tinctorial strength than the corresponding bromine compounds. Our results show the reverse in two out of the three cases. It should be noted, however, that the difference in tinctorial strength is small, to the eye much smaller than to the spectrophotometer.

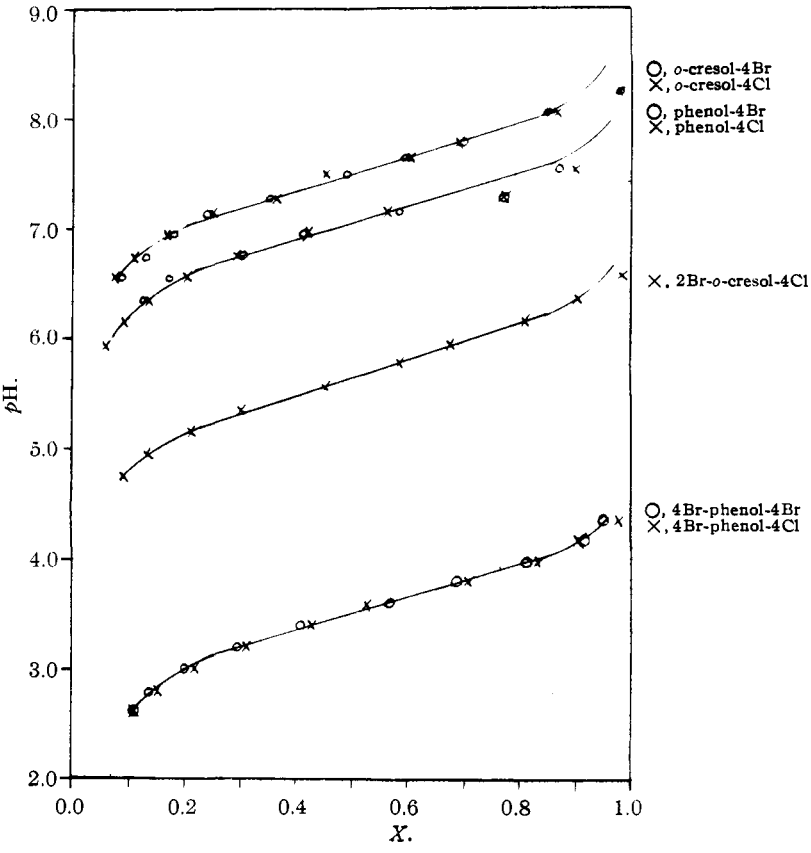


Fig. 1.

A comparison of the indicator constants of these substituted sulfonphthaleins with those of the corresponding compounds without halogen in the sulfobenzoic acid nucleus shows that the former are slightly more acid, the differences in indicator constants ranging from 0.5 to 0.9 *p*H unit.

**Acknowledgments.**—The authors wish to express their appreciation to Dr. Lyman J. Briggs, Director of the National Bureau of Standards, for permission to use one of the Bureau's spectrophotometers. We are especially indebted to Dr. K. S. Gibson of the Colorimetry and Spectrophotometry Section for his practical suggestions and coöperation in the use of the instrument.

(9) W. M. Clark, "The Determination of Hydrogen Ions," 1928, p. 154.

## Summary

Spectrophotometric studies on seven sulfonphthaleins with four halogen atoms in the sulfobenzoic acid nucleus have yielded data from which the indicator constants have been calculated. The useful ranges have also been ascertained. The indicators have been shown to possess but two colored forms whose concentrations are affected by *p*H changes alone.

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