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BASIC IONIZATION CONSTANT OF METACRESOLSULFONPHTHALEIN; pH VALUES AND SALT EFFECTS

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ABSTRACT

Spectral transmittancy values at room temperatures approximating 25° C were obtained for 1.25×10^{-5} *M* metacresolsulfonphthalein in water and in 0.001- to 8-*M* hydrochloric acid. In water the indicator exists in the yellow form (Y), and hydrogen ions (H) from acids convert it into the red form (R). The molar concentrations of each form of the indicator in various concentrations of hydrochloric acid were computed from the spectrophotometric data. The dissociation constant (K_b) for the reaction of the indicator with hydrochloric acid is given by the equation

$$K_b = M_H f_H M_Y f_Y / M_R f_R,$$

in which *M* and *f*, with appropriate subscripts, represent the molarities and activity coefficients, respectively. The value of K_b is 1.98×10^{-2} and that of $-\log K_b$ or pK_2 is 1.703 ± 0.005. The indicator is useful over the pH range 0 to 3.

CONTENTS

I. INTRODUCTION

Metacresolsulfonphthalein, commonly known as metacresolpurple, is a useful indicator for colorimetric pH determinations. It undergoes color changes from yellow (Y) to red (R) in acid solution and from yellow to purple (P) in alkaline solution, as indicated by the structural formulas in figure 1. The indicator is stable in both of its pH ranges. The application of spectrophotometric methods for the precise determination of pH values with an indicator[1] requires a knowledge of the absorptive properties of its different chemical forms, the nature of the transformation from one form to another, the states of equilibrium between the different chemical forms, the thermodynamic ionization constants, and the effects of electrolytes on the equilibrium and ionization constants and spectral properties. In this paper these properties are reported for the acid range of metacresolpurple; work is in progress on the alkaline range.

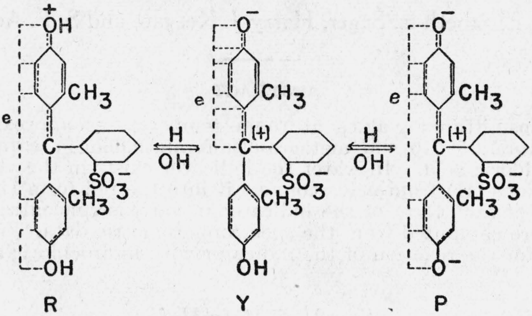

FIGURE 1.—*Metacresolsulfonphthalein in acid, neutral, and alkaline solutions.*

The dotted lines indicate resonance in the respective chromophores. The various colored forms, R, Y, and P, are, for convenience, considered in terms of the two most probable extreme resonant structures, one a pure quinone form and the other a dipolar benzenoid structure with a relatively large negative charge [−] on the oxygen of the quinone group and a corresponding positive charge [+] on the central carbon atom. The symbols representing these various forms are:

R^{+-} =dipolar resonant red form.
Y^{-} =yellow form with typical quinone resonance and without [+] [−] charges.
Y^{--+} =dipolar resonant yellow form with [+] [−] charges.
P^{--} =purple form with quinone phenolate resonance and without [+] [−] charges.
P^{---+}=dipolar resonant purple form with [+] [−] charges.

II. MATERIALS, EQUIPMENT, AND METHOD

1. MATERIALS

Metacresolsulfonphthalein, especially purified for this investigation, was obtained from W. A. Taylor & Co., Baltimore, Md. Before being weighed, the crystals were dried in an oven at 105° to 110° C for 2 hours. Hydrocholric acid that conformed to specifications of the American Chemical Society was used for making 2-*M* solutions from which the lower concentrations were prepared by volumetric procedures. The acidity was determined by titration with standard sodium hydroxide with phenolphthalein as indicator. Potassium chloride, barium chloride, and strontium chloride were each recrystallized twice and dried in an oven for several hours at 110° to 120° C.

2. PREPARATION OF THE SOLUTIONS

All the solutions were prepared by volumetric methods and are expressed as molar concentrations. A stock solution of metacresolsulfonphthalein, 2.5×10^{-4} *M* was made by dissolving 0.0956 g of the dried crystals in conductivity water and diluting to 1 liter. A day or more was required for the crystals to dissolve. From this

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[1] See references [1 to 10] for literature on the theories of indicators, salt effects, and mass-law relations applicable in colorimtetric pH measurements.

stock solution, 5 or 10 ml, as desired, was transferred by pipet to each of the 100-ml volumetric flasks in which the mixtures to be studied were prepared. These amounts resulted in indicator solutions 1.25×10^{-5} *M* or 2.5×10^{-5} *M*, which concentrations were found convenient for the spectrophotometric measurements in the 1-cm absorption cells.

The stock solutions of hydrochloric acid and of salts were first filtered through a sintered-glass filtering crucible to remove any trace of dust or lint that might affect the absorption measurements. The required amounts of the acid solutions or of the salt solutions were added to the 100-ml volumetric flasks either by pipet or buret and diluted to the mark with conductivity water.

Two solutions were necessary for each spectrophotometric curve. The first contained the indicator in the desired medium—either water, acid, or acid and salt—and the other contained the same components of the solution without the indicator. For the amount of stock indicator used in the first solution, an equal volume of water was substituted in the solution without the indicator. All the solutions were freshly prepared, usually the day before the spectrophotometric determinations were made, but the indicator was added on the morning the measurements were made. Special tests showed that the indicator solutions were stable for several days.

3. SPECTROPHOTOMETRIC EQUIPMENT

The spectrophotometric measurements for the visible portion of the spectrum were made in the Photometry and Colorimetry Section of this Bureau, with a recording spectrophotometer of the Hardy type. The calibration and operation of this instrument have been described by Gibson and Keegan [11][2]. All the measurements were made with slits giving a spectral band approximately 4 mμ wide. Absorption cells for the solutions consisted of Pyrex cylindrical tubes with polished parallel ends fitted with removable round plates of polished quartz or Pyrex glass. A pair of blackened brass holders were fitted with sleeves to hold either 1-, 2-, or 5-cm absorption cells. In these experiments the beam of light passed through a layer of solution of 1 ±0.001 cm. All the spectrophotometric measurements were made at room temperatures, varying from 23° to 28° C. The measurements for the ultraviolet portion of the spectrum were made by Geraldine W. Haupt, of the Photometry and Colorimetry Section of this Bureau, with a Hilger sectorphotometer and a Fuess quartz spectrograph, and by P. A. Cole and M. Eicher, of the National Institute of Health, Bethesda, Md., with a Spekker spectrophotometer.

4. SPECTROPHOTOMETRIC MEASUREMENTS IN THE VISIBLE SPECTRUM

The transmittancy data recorded for a typical series of spectrophotometric measurements are shown in figure 2. Each graph sheet is calibrated for wavelength by recording the transmission curve of a standardized didymium glass (Jena BG 11), the wavelengths of the transmission minima being accurately known. The wavelength cor-

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[2] **Figures in brackets indicate the literature references at the end of this paper.**

rections are made as described by Gibson and Keegan. The curves at the 100-percent transmission line are obtained with identical absorption cells filled with water, or with acid-salt mixtures without indicator, and placed one in each of the two light beams of the instrument. The zero transmission curves are obtained by blocking out the light beam normally passing through the indicator solution. Such

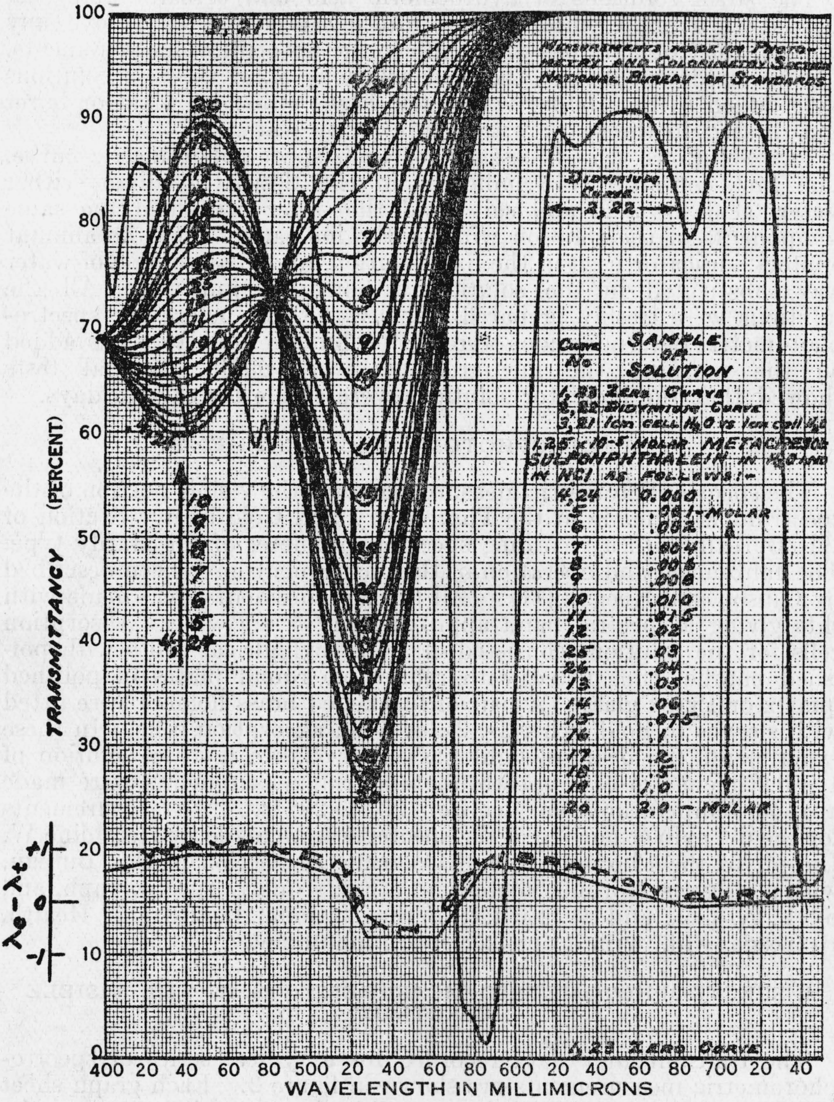

FIGURE 2.—*Recorded spectrophotometric curves showing the transformation of metacresolsulfonphthalein from yellow to red in hydrochloric acid.*

calibration curves are usually made at the beginning and end of each series of curves on one graph sheet. For each spectrophotometric curve of the indicator, one absorption cell is filled with the indicator solution and the other cell with its respective comparison solution.

In this manner the absorption of light by the solvent system and the reflections at the end plates of the cells are compensated, and only the percentage transmittancy of light by the indicator itself in the particular solvent system is recorded. The result is the transmittancy curve of the indicator over the spectral range 400 to 750 mμ.

The transmittancy curves shown in figure 2 represent the transformation [4, 5, 9] of metacresolsulfonphthalein from the yellow to the red form by increased amounts of hydrochloric acid from 0.001 to 2 M. The data in this figure were obtained with an indicator concentration of 1.25×10^{-5} M, and a cell depth of 1 cm. Additional spectrophotometric determinations were made with indicator concentrations of 0.625×10^{-5} and 2.5×10^{-5} M in the same cells to check the validity of Beer's law.

The transmittancy values, in percent, were read from the curves at wavelength intervals of 2, 4, or 10 mμ and were reduced to corresponding molar absorption indices, k, by the relation:

$$k = \frac{-\log_{10} t}{d \times M}, \tag{1}$$

in which t is transmittancy, d is the cell depth, in centimeters, and M is the molar concentration.

5. ELECTROMOTIVE FORCE MEASUREMENTS

Readings of pH at 25° C were made for each indicator solution and its comparison solution without the indicator, using a hydrogen-electrode assembly with saturated potassium chloride calomel half-cell and liquid junction. The hydrogen-electrode assembly was calibrated with 0.05 m potassium acid phthalate, pH 4.008, as described in the Bureau certificate for Standard Sample 84a issued by the National Bureau of Standards. The glass-electrode assembly for the pH meter was also calibrated with this buffer. Potentiometric readings were made first with the hydrogen-electrode assembly, then with the glass electrode. Corrections for the error caused by the liquid-junction potential were not applied. Measurements on some of the most concentrated salt solutions were not made because the salt solutions diffused through the saturated potassium chloride and equilibrium for the potentiometric measurement could not be reached. Since this work was done, it has been shown that these difficulties can be avoided and very precise pH data obtained by use of hydrogen and silver-silver–chloride electrodes in cells without liquid junctions to hold the solutions of indicators and buffers [13].

III. EXPERIMENTAL DATA

1. SPECTRAL ABSORPTIVE PROPERTIES OF METACRESOLSULFONPHTHALEIN IN THE VISIBLE AND ULTRAVIOLET

The molar absorption index curves for the visible and ultraviolet regions of the spectrum are given in figure 3 for the three colored forms of metacresolsulfonphthalein that are in neutral, acid, and alkaline solutions, respectively. The indices are plotted as a function of reciprocal wavelength, or wave number, and corresponding wavelengths are shown at the top of the figure. For measurements in the visible region, 1.25×10^{-5} *M* solutions of metacresolsulfonphthalein were made in water, in 2-*M* hydrochloric acid, and in 1.25×10^{-3} *M* sodium hydroxide. The strong bands in the visible spectrum show maximum absorption for the neutral yellow form in water, curve Y, at a wave number of 22,940 cm^{-1} (wavelength 436 mμ); for the acid red form, curve R, at a wave number of 18,960 cm^{-1} (wavelength 527.$_5$ mμ); and for the alkaline purple form, curve P, at a wave number of 17,360 cm^{-1} (wavelength 576 mμ).

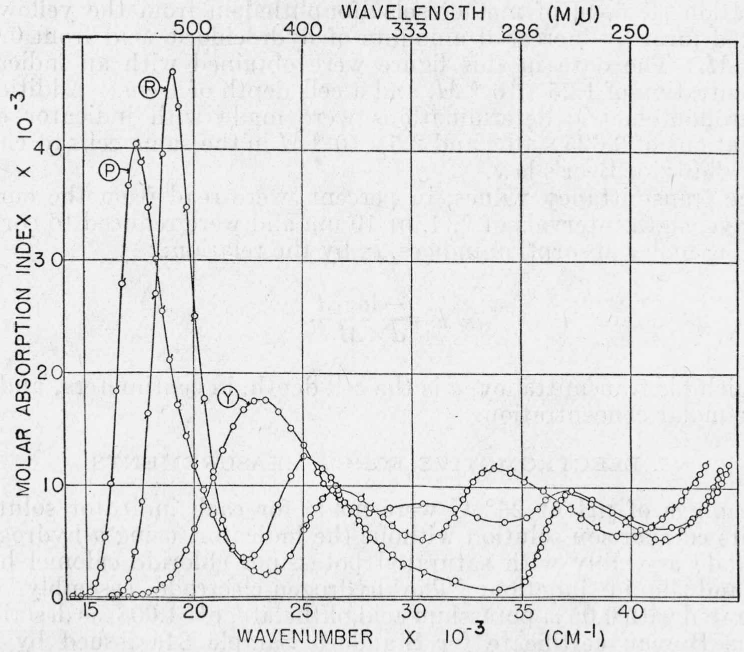

FIGURE 3.—*Molar absorption indices of the three forms of metacresolsulfonphthalein in the visible and ultraviolet portions of the spectrum.*

R, red form; Y, yellow form; P, purple form.

For the ultraviolet [3] measurements, 1.25×10^{-4} *M* solutions of the indicator were used in water, in 2-*M* hydrochloric acid, and 1.25×10^{-2} *M* sodium hydroxide. The spectrophotometric data given in this paper are concerned mainly with the progressive shift of curves Y to R in the visible spectrum for acid solutions.

2. TRANSFORMATION OF METACRESOLSULFONPHTHALEIN FROM THE YELLOW TO THE RED FORM BY HYDROCHLORIC ACID

The transformation of metacresolsulfonphthalein from the yellow to the red form is shown by the 19 curves in figure 4 and appears to be approximately complete in 2-*M* hydrochloric acid. The effect of 1.5-, 2-, 4-, and 8-*M* acid has been studied separately and is shown

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[3] The sulfonphthaleins and many other indicators contain, in addition to the chromophore, other groups (auxochromes) such as carboxylate and sulfonate radicals, which do not absorb visible light, and thus do not affect the calculations presented in this article. Recent measurements on sulfonates, benzoates, and other compounds of polar character show strong bands in the ultraviolet. Any computations on the Y, R, and P bands (fig. 3) to correlate the absorption indices of the chromophore for both the ultraviolet and visible regions must involve recognition of the resonance of the $-SO_3^-$ group and corrections for its own absorption indices in the ultraviolet.

by the additional absorption curves in figure 5. As the quantitative relations between the acidity of the solutions and the optical properties of the indicator, as expressed by the curves in figures 4 and 5, are the basis of the determination of pH values and salt effects with metacresolsulfonphthalein, these spectrophotometric curves will be considered in detail. Below 0.1-*M* acid, the increase in absorption index at any wave number with rise in hydrogen-ion activity is close to the values calculated by use of the mass-law equations discussed below. Between 0.1- and 2-*M* hydrochloric acid, the percentage change in index is slightly larger for the lower wave numbers of the absorption band for the red form (from the peak toward the red) than for the higher wave numbers of the band. The acid in concentrations from 0.5 to above 2 *M* begins noticeably to cause two compensating effects. The first is the completion of the normal reaction of hydrogen ions with the yellow form, which should slightly increase the index at wave number 18,960 (527.$_5$ mμ), and the second is the "abnormal" or specific, effect [1, 8, 21, 22] of the increased electrolyte and surrounding electrical field in decreasing the absorptive properties and index of the indicator, together with the shift of the absorption bands for the red and yellow forms toward the lower wave numbers. The net result is that the acid in concentrations above 2 *M* causes little additional change in the position and height of the main absorption band, except a slight shift, until a concentration of over 4 *M* is reached. With higher acid concentrations, as shown in curve 5, figure 5, there is a decrease in the index at the maximum and an increase at the mini-

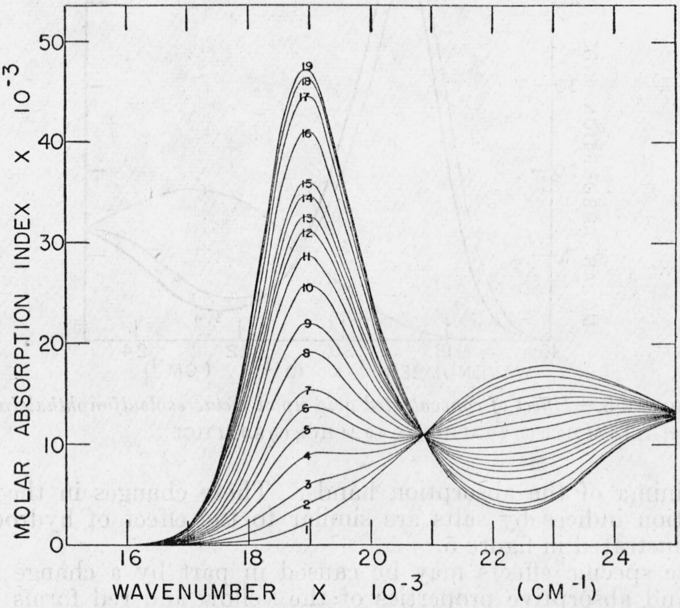

FIGURE 4.—*Transformation of metacresolsulfonphthalein from the yellow to the red form in hydrochloric acid.*

(1) No acid (yellow form); (2) 0.001 *M*; (3) 0.002 *M*; (4) 0.004 *M*; (5) 0.006 *M*; (6) 0.008 *M*; (7) 0.010 *M*; (8) 0.015 *M*; (9) 0.020 *M*; (10) 0.030 *M*; (11) 0.040 *M*; (12) 0.050 *M*; (13) 0.060 *M*; (14) 0.075 *M*; (15) 0.100 *M*; (16) 0.200 *M*; (17) 0.500 *M*; (18) 1.000 *M*; (19) 2.000 *M*.

mum, accompanied by a definite displacement of the isosbestic point.[4]

In order to determine whether these specific effects are due to acids alone or is a general property of all concentrated solutions of electrolytes, the effect of increasing amounts of salts on the absorptive properties of both the yellow and the red forms of the indicator is under investigation and details will be reported later. Neutral salts of low concentration have no important effect upon the absorptive properties of either form other than normal changes in transmittancy arising from variations in ionic strengths, activity coefficients, and ionization. Salts 2 *M* or higher in concentration, however, cause a slight shift in the isosbestic point and in the positions of the maxima and minima of the absorption bands. These changes in the molar absorption indices by salts are similar to the effect of hydrochloric acid, illustrated in figure 5.

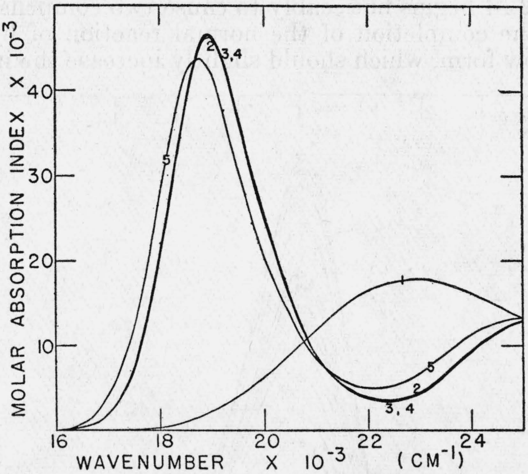

FIGURE 5.—*Effect of concentrated acid upon metacresolsulfonphthalein.*

(1) Water; (2) 1.5 *M* HCl; (3) 2.0 *M* HCl; (4) 4.0 *M* HCl; (5) 8.0 *M* HCl.

These specific effects may be caused in part by a change in the polar and absorptive properties of the yellow and red forms of the indicator in the altered electrical field, or it may denote the beginning of a new type of ionization, hydration, or intramolecular transformation into a lactone. In considering the sources of a new type of ion, a colored impurity is first suspected. In this case it is most likely to be a colored iosmer with one or both phenols attached in the orthoposition instead of in the paraposition characteristic of the sulfonphthaleins (fig. 1). Small quantities of such orthoisomers might have absorption bands and low pH ranges which could account for the observed shifts. This explanation does not seem valid in view of the lack of such abnormalities in the spectrophotometric

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[4] An isosbestic point is found at that wavelength or wave number at which the transmittancies or indices of the yellow and red forms are equal. The word "isobestic," which has appeared in various publications, should be spelled "isosbestic." The word originates from the Greek prefix ἴσος (isos, meaning equal) and the Greek root σβεστός (sbestos, meaning quenched or put out). The word "asbestos" is derived from the same root. Thus, "isosbestic point" means the point of equal extinction by the two colored forms of the indicator. The authors in a previous publication used the term "isobestic."

curves obtained recently in another study on metacresolsulfonphthalein in its high pH range, and particularly when a 500 to 1-*M* ratio of alkali to indicator is used to neutralize any orthoisomer present and probably having a pK value somewhat higher than that for metacresolsulfonphthalein. Formation of a colorless carbinol or lactone or of a dioxonium salt of the indicator would probably reduce the absorption index without a shift. The discussion below seems to eliminate the possibility that repression of the ionization of the sulfonate group accounts for these phenomena. As metacresolsulfonphthalein at pH 7.2 to 9 also shows such shifts of the absorption bands in concentrated salt solutions, we can conclude that the specific salt effect of the concentrated hydrochloric acid is due to the alteration of the spectral properties of the indicator chiefly by the change in the surrounding electrical field of the solutions [8].

TABLE 1.—*Molar absorption indices for the yellow and red forms of metacresolsulfonphthalein*

Wave-length [a]	Wave number	Molar absorption indices	
		Yellow form	Red form
$m\mu$	$cm^{-1}\times 10^{-3}$	k_Y	k_R
399.$_4$	25.04	13390	12580
409.$_3$	24.43	15110	11190
419.$_3$	23.85	16550	8660
429.$_2$	23.30	17570	5660
[a]436.$_2$	22.93	17940	4270
439.$_1$	22.77	17880	3920
449.$_1$	22.27	17080	3570
459.$_1$	21.78	15660	4470
469.$_1$	21.32	13670	6650
[a]479.$_5$	20.86	10930	10930
489.$_3$	20.44	8700	16860
499.$_4$	20.02	6490	24330
509.$_5$	19.63	4600	34540
520.$_1$	19.23	3010	44230
[a]527.$_5$	18.96	2190	47080
530.$_7$	18.84	1890	46870
540.$_7$	18.49	1130	39810
550.$_7$	18.16	630	27210
560.$_7$	17.83	380	15780
570.$_2$	17.54	210	8320
579.$_6$	17.25	140	3740
589.$_3$	16.97	70	1440
599.$_4$	16.68	30	600
609.$_4$	16.41	00	140
619.$_5$	16.14	00	000

[a] The transmittancy values were read at even wavelength intervals from the graph sheet and then corrected to their true wavelengths. In addition, the values for the isobestic point and the maximum absorbancy for the red and yellow forms are given.

The specific salt effects are small and are neglected in the present practical applications of the spectrophotometric data for metacresolsulfonphthalein in hydrochloric acid solutions. Since the absorption index curve is nearly constant for acid contents between 2 and 4 *M*, the 2-*M* curve is taken here as the practical limit for the transformation of the yellow to the red form.[5] The molar absorption indices for various wavelengths and corresponding wave numbers representing the characteristic absorptive properties of the yellow and red forms of this indicator are given in table 1.

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[5] A more precise evaluation of the magnitude of the index for partial and complete transformation and the quantitative formulation of the specific salt effects are under way.

3. COMPUTATION OF THE PERCENTAGES OF THE RED AND YELLOW FORMS OF THE INDICATOR FROM THE MOLAR ABSORPTION INDICES

If it be assumed that the corresponding curves for the partial transformation of the indicator (see figs. 2 and 4) represent linear combinations at each wavelength or wave number of different proportions of only two limiting absorption indices (curves 1 and 19, fig. 4), then the fraction (α) of the indicator changed from yellow to red at a given acid concentration is given by

$$k_\alpha = \alpha k_R + (1-\alpha)k_Y \text{ or } \alpha = (k_\alpha - k_Y)/(k_R - k_Y), \tag{2}$$

where k_Y, k_R, and k_α are, respectively, the molar absorption indices at a given wave number for the yellow, red, and mixed forms of the indicator [1, 4, 5, 6]. The values of k_Y, k_R, and k_α for all the wavelengths and concentrations of indicator, hydrochloric acid, and salts studied were computed from records like figure 2.

Calculations of α for different wavelengths near the maxima of the absorption bands are given in table 2. If the linear variation of k_α with respect to α expressed by eq 2 is strictly correct at all wavelengths, the α values for each curve should all be the same, regardless of wavelength. In general, however, there is a decrease in α with increase in wavelength in each of the bands (420 to 460 mμ and 518 to 540 mμ). The variation from constancy appears to be slightly greater than the estimated accidental variation arising from the experimental uncertainties in the recording and reading of the original transmittancy curves. Since this consistent variation of α occurs in the regions of the spectrum where the specific effects of high acid concentrations clearly affect the calculated values of α (see figs. 4 and 5), it may be ascribed to the same cause. The variation of α with respect to wavelength may be neglected in this paper. The average values of α are close to those found at 527.$_5$ mμ. Since the experimental absorption indices are most accurately determined at wavelength 527.$_5$ mμ (wave number 18,960) at the maximum of the absorption band for the red form, these indices alone, and the corresponding values of α, are given in table 3 and used in the calculations to be described.

From the approximate constancy of α across the spectrum, it is assumed that as the indicator is changed from yellow to red the characteristic absorption bands of the two chemical forms of the indicator are not appreciably shifted, broadened, or otherwise distorted as a result of changing the chemical and physical nature of the solvent medium, or as a result of the presence of more than two chemical forms or of association of the indicator.[6] These assumptions are further borne out by the existence of a sharply defined isosbestic point at wave number 20,860 (wavelength 479.$_5$ mμ) and molar absorption index 10,930. Since the absorption bands overlap, it follows that at least one wave number will be found at which the molar absorption indices of the yellow and red forms of the pure indicator, k_Y and k_R, will be equal for all values of α. Hence, as expressed linearly in eq 2, if a mixture of these two forms alone determines the observed absorp-

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[6] If polar states (electronic tautomers or electromers) of each ion, indicated by [+] and [−] signs in figure 1, are present in instantaneous equilibrium with the nonpolar forms, the absorption bands may still be used at any given temperature to calculate the over-all values of α and $(1-\alpha)$ for the red and yellow ions, including their natural polar states or those "induced" by other ions [1, 4, 7, 8]. This point needs further study for development of exact equations.

tion curve in their overlapping regions of spectral absorption, the isosbestic point must remain unchanged with respect to both index and wave number for all stages of the color transformation. This may not be true when specific salt effects, association, or colored impurities affect this part of the spectrum, as shown in figure 5.

TABLE 2.—*Variations in the values of α as derived from the series of absorption indices at different acid concentrations and given wavelengths*

Wave-length	Molar concentration of hydrochloric acid										
mμ	0.002	0.006	0.01	0.02	0.03	0.04	0.05	0.075	0.20	0.50	1.00
420	0.084	0.195	0.290	0.442	0.550	0.613	0.644	0.723	0.878	0.966	0.989
424	.087	.205	.287	.443	.545	.605	.649	.722	.882	.955	.995
428	.076	.200	.285	.443	.534	.606	.640	.717	.875	952	.989
432	.081	.206	.292	.442	.538	.605	.645	.720	.875	.958	.990
436	.082	.202	.292	.442	.534	.597	.644	.723	.868	.956	.988
440	.082	.203	.294	.439	.533	.596	.641	.720	.865	.952	.983
444	.081	.198	.288	.437	.530	.593	.638	.715	.865	.950	.983
448	.077	.200	.286	.438	.527	.590	.639	.712	.864	.946	.982
452	.083	.202	.288	.438	.531	.590	.638	.713	.864	.946	.982
456	.073	.194	.288	.432	.523	.586	.631	.711	.858	.940	.975
460	.082	.203	.288	.440	.532	.589	.633	.712	.863	.943	.975
518	.085	.207	.295	.444	.532	.598	.647	.730	.871	.947	.988
520	.086	.206	.293	.442	.529	.595	.646	.721	.869	.942	.982
522	.085	.206	.294	.442	.526	.591	.645	.725	.866	.945	.984
524	.083	.206	.293	.442	.527	.593	.644	.723	.865	.945	.985
526	.084	.205	.292	.440	.525	.590	.644	.722	.864	.942	.982
527	.084	.206	.293	.440	.525	.589	.645	.723	.862	.942	.984
528	.084	.204	.292	.440	.525	.589	.645	.723	.862	.942	.984
530	.082	.204	.292	.441	.522	.587	.641	.720	.858	.938	.978
532	.083	.204	.291	.441	.516	.584	.640	.714	.859	.936	.977
534	.082	.203	.289	.439	.519	.582	.640	.714	.856	.934	.977
536	.082	.203	.289	.436	.516	.580	.636	.710	.851	.926	.974
538	.082	.203	.305	.440	.517	.582	.640	.714	.858	.932	.972
540	.081	.204	.292	.438	.518	.579	.637	.712	.857	.935	.989

IV. EQUATIONS FOR CALCULATION OF THE IONIZATION CONSTANT K_b AND pK_b

On the basis of the preceding discussion, a simple reaction may be assumed, in which the yellow (basic) form of the indicator combines, or bonds, with a single hydrogen ion with accompanying change in color from yellow to red (fig. 1). By the law of mass action the apparent ionization constant, K_b, for this reaction [1, 4] is given by

$$K_b = (M_H M_Y / M_R)(f_H f_Y / f_R) = K_c f_H f_Y / f_R, \tag{3}$$

in which M_H, M_Y, and M_R represent, respectively, the molar concentrations of the hydrogen ion, the yellow form, and the red form of the indicator, and K_c is equal to $M_H M_Y / M_R$. The corresponding activity coefficients are represented by f with appropriate subscripts. Substituting $(1-\alpha)/\alpha$ for M_Y/M_R, and writing eq 3 in the usual logarithmic form, we have

$$\mathrm{p}K_b = -\log[M_H(1-\alpha)/\alpha] - \log[f_H f_Y / f_R] = \mathrm{p}K_c - \log[f_H f_Y / f_R] \tag{4}$$

In the above equation, α is determined from the spectrophotometric data by eq 2 and M_H is identical with the molarity of the acid (assuming complete dissociation of hydrochloric acid and neglecting

TABLE 3.—*Calculation of the* pK_c, *activity coefficients and* pH *of metacresolsulfonphthalein in aqueous hydrochloric acid solutions*

Molar concentration of HCl,	Transmittancy at 527.5 mμ,	Molar absorption index,	Fractional ionization of indicator,	Ratio Y/R,	K_c,	pK_c,	Activity coefficients		Calculated pH	
							Spectrophotometric,	Potentiometric,	Spectrophotometric,	Potentiometric,
[H]	t	k	α	$(1-\alpha)/\alpha$	$[H]\times(1-\alpha)/\alpha$	$-\log_{10}K_c$	$\sqrt{f_R f_{Y-}/f_{R+-}}$	$\sqrt{f_H f_{Cl}}$	pH	pH[1]
0.000	0.939	2.186	0.000	---	---	1.703	---	---	---	---
.001	.888	4,146	.044	21.907	0.02191	---	---	---	3.02	3.02
.002	.842	5,954	.084	10.916	.02183	1.661	0.953	0.955	2.71	2.72
.004	.774	8,906	.150	5.682	.02273	1.643	.934	.939	2.42	2.43
.006	.720	11,414	.206	3.866	.02319	1.634	.924	.926	2.26	2.26
.008	.676	13,578	.254	2.941	.02352	1.628	.918	.916	2.13	2.14
.010	.643	15,343	.293	2.412	.02412	1.618	.906	.906	2.04	2.04
.015	.577	19,106	.377	1.654	.02480	1.605	.894	.891	1.87	1.88
.020	.532	21,960	.440	1.271	.02541	1.595	.883	.878	1.75	1.76
.030	.477	25,740	.525	0.906	.02718	1.566	.854	.858	1.59	1.59
.040	.438	28,666	.590	.696	.02782	1.556	.844	.844	1.47	1.47
.050	.408	31,156	.645	.550	.02749	1.561	.849	.832	1.37	1.38
.060	.392	32,581	.677	.477	.02862	1.543	.832	.823	1.30	1.31
.075	.370	34,544	.721	.387	.02906	1.537	.826	.812	1.21	1.22
.100	.347	36,757	.770	.300	.03000	1.523	.813	.798	1.11	1.10
.200	.307	40,984	.864	.157	.03144	1.502	.794	.770	0.80	0.81
.500	.278	44,489	.942	.061	.03067	1.513	.804	.776	.40	.41
1.000	.263	46,350	.984	.027	.02677	1.572	---	---	---	---
2.000	.258	47,084	1.000	---	---	---	---	---	---	---

[1] Measured pH values obtained by using the hydrogen-electrode and glass-electrode assemblies agreed usually within 0.01 with the calculated pH value.

the low concentration of hydrogen ions from the indicator); hence, pK_c is known from the experimental data. The values of K_c and pK_c are given in table 3, and are shown in figure 6 as a function of the ionic strength, μ, computed on the molar basis. The activity coefficients approach unity by definition as the ionic strength decreases to zero on dilution of the solution. Hence, by extrapolation [1, 5, 6, 8] of the pK_c curve of figure 6 to zero ionic strength the value of pK_b will be obtained. As the slope of pK_c near $\mu=0$ is large and its extrapolation uncertain, this procedure may be greatly facilitated by finding exact or even approximate values for the activity coefficients, such that the function $pK_c-\log(f_H f_Y/f_R)$ is approximately independent of μ and its slope so small that the extrapolation can be made with accuracy (see the other curves in fig. 6). This may be done by use of the Debye-Hückel formula or simplifications thereof for the negatives of the logarithms of the ionic activity coefficients,

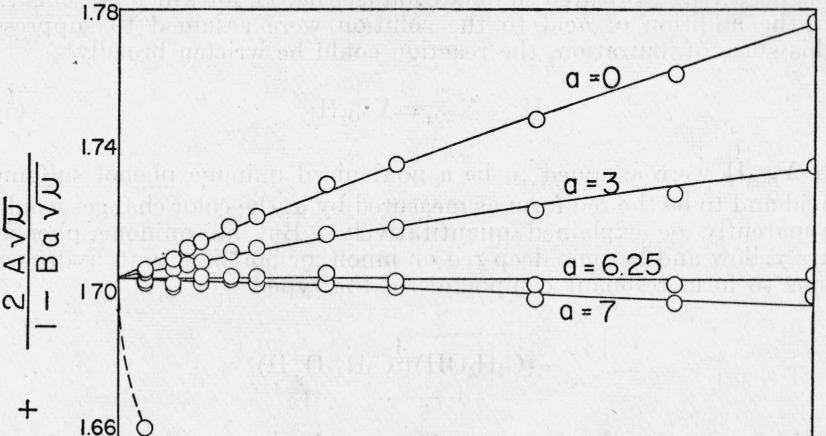


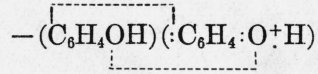
FIGURE 6.—pK_c *values obtained from the spectrophotometric values for metacresolsulfonphthalein in hydrochloric acid at low ionic strengths.*

when the dimensions of the yellow and red forms of the indicator and proper values z for their electric charges are determined as follows.

There is considerable evidence for the assumption that the sulfonic acids may be regarded as almost completely dissociated in water solution [23] and that the yellow form of metacresolsulfonphthalein is a negative substituted sulfonate ion (see fig. 1), for which z equals 1.[7] If the addition of acid to the solution were assumed to suppress this state of ionization, the reaction could be written broadly

$$H^+ + Y_{SO_3^-} \leftrightarrows Y_{SO_3}H. \tag{5}$$

If $Y_{SO_3}H$ were assumed to be a nonionized quinone phenol sulfonic acid and to be the red form as measured by α, the color changes would apparently be explained quantitatively. But all quinone phenols are yellow and become deep red on union, or bonding, with hydrogen ions to form resonant compounds of the type



$$-(C_6H_4OH)(:C_6H_4:\overset{+}{\underset{\cdot}{O}}H)$$

R in figure 1 [1, 4]. It is therefore very likely that the red color is not controlled by eq 5 for the ionization of the sulfonic acid group of metacresolsulfonphthalein in dilute acid solutions (or even up to 2 *M*), but that the addition, or bonding, of hydrogen ions [2, 7] takes place principally at the basic oxygen of the quinone group, giving a resonant ampholytic ion (R, fig. 1) for the red form of the indicator as in eq 6.

$$H^+ + Y^- = R^{+-}, \tag{6}$$

The spectrophotometric data suggest that two separate reactions do not both take place simultaneously to any appreciable extent. Assuming then that the yellow form is a univalent negative ion, represented now as Y^-, and, for the present, that the activity coefficient of the resonant ampholytic ion, represented now by R^{+-}, is approximately unity at low concentrations, the Debye-Hückel theory yields the relation

$$-\log(f_H f_{Y^-}) = \frac{2Az^2\sqrt{\mu}}{1+Ba_1\sqrt{\mu}} + \beta\mu, \tag{7}$$

in which z is unity; A and B have the values 0.5098 and 0.3298 [12], respectively, at 25° C; a_1 is an adjustable parameter used to represent in angstroms the average distance of closest approach of ions; μ is defined as $\sum z_i^2 m_i/2$ as usual; and β is an empirical correction factor. By arbitrarily assigning different reasonable values to a_1, a set of curves is obtained for $\mathrm{p}K_c - \log(f_H f_{Y^-}/f_{R^{+-}})$ with small slopes which can be extrapolated accurately, as shown in figure 6. These curves converge at just one $\mathrm{p}K_b$ value, 1.703, because at zero concentration and ionic strength of the electrolytes all of the activity coefficients

---

[7] This is the ionic charge; the contribution of the resonant polar charges ([+] and [−], fig. 1) is disregarded

become unity, and the activity coefficient term of eq 4 becomes zero, regardless of the value of a_i used. K_b is therefore 1.98×10^{-2}.

It should be emphasized at this point that even though a limiting dissociation constant, K_b in this case, is known very precisely, it is not possible to predict from a given α exactly (i. e., to 0.001) what the pH value will be in any mixture of electrolytes. Knowledge of the concentrations of the electrolytes and their valence types, the average values of a_i and β, the dielectric constant, and preferably an independent measure of the activities, are needed to calculate the pH value with precision, and then only by a long series of approximations. This applies particularly to unknown solutions. For a precision of 0.01 pH, however, the computations can be simplified. If $f_{R^{+-}}=1$ holds approximately in dilute solutions and the relation $f_H=f_{Y^-}$ is assumed as usual, eq 4 and 7 give $(pK_b-pK_c)/2=-\log f_H=-\log f_{Y^-}$. The correct average a_i gives a straight pK_c plot through pK_b, and if it is not horizontal its slope is β. With a_i, β, μ, α, and pK_b substituted in eq 4 and 7, the value of pH or $-\log M_H f_H$ can be calculated. An approximately straight horizontal line results, and β may be neglected (see fig. 6) when a_i equals 6.25 A. Extrapolation to $\mu=0$ also gives a pK_b value of 1.703 with an estimated uncertainty of 0.005. With K_b and a_i thus determined, it is possible to calculate the pH values of the solutions from either spectrophotometric or electrometric data, as shown below.

V. COMPARISON OF THE ACTIVITY COEFFICIENTS OF METACRESOLSULFONPHTHALEIN AND HYDROCHLORIC ACID

By rearrangement of terms in eq 3 and substitution of f_{Y^-} for f_Y and $f_{R^{+-}}$ for f_R,

$$f_H f_{Y^-}/f_{R^{+-}}=K_b\alpha/(1-\alpha)M_H. \qquad (8)$$

The hydrogen-ion concentration (M_H) is that of the hydrochloric acid and the rest of the right-hand side of the equation is determined entirely from the spectrophotometric measurements, which give the values of K_b and α. From eq 4 is obtained

$$pK_b-pK_c=-\log[f_H f_{Y^-}/f_{R^{+-}}]=-2\log\sqrt{f_H f_{Y^-}/f_{R^{+-}}}. \qquad (9)$$

If $f_{R^{+-}}$ is taken as approximately unity because R^{+-} is considered a resonant dipolar form of a nondissociated molecule and f_H is assumed as usual to be equal to f_{Y^-} in the application of the Debye-Hückel equation,

$$(pK_b-pK_c)/2=-\log\sqrt{f_H f_{Y^-}/f_{R^{+-}}}\Bumpeq-\log f_H\Bumpeq-\log f_{Y^-}, \qquad (10)$$

gives an approximate value of f_H or f_{Y^-} listed in column 8, table 3. As the known concentrations of hydrochloric acid are assumed to be equal to M_H, the values of $-\log M_H f_H$ or pH, of all of the solutions of hydrochloric acid and the indicator can be calculated from the spectrophotometric data alone and compared with electrometric measurements of the pH values. The spectrophotometric pH values are listed in column 10, table 3.

It is important to compare these approximate spectrophotometric activity coefficients and pH values with corresponding ones calculated from the emf data obtained with silver-silver–chloride and hydrogen electrodes in hydrochloric acid solutions by Harned and Ehlers [16]. Their data were computed from eq 11.

$$\frac{(E-E_0)F}{2.3026RT}+\log m_{\mathrm{H}}+\log m_{\mathrm{Cl}}=-2\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}. \tag{11}$$

After reducing their published emf values to activity coefficients on a molarity basis, a curve was drawn for $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ as a function of $\sqrt{\mu}$, from which values of $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ were read which corresponded to the concentrations of hydrochloric acid used in the spectrophotometric work, as shown in column 9, table 3. The right side of eq 11 is obtained from the electrometric methods and is analogous to the right side of eq 9 for the spectrophotometric work. Since f_{H} is the same in both cases, it follows that f_{Cl} is to be compared with $f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}$. If $f_{\mathrm{H}}=f_{\mathrm{Cl}}=\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ as usually assumed, then the products of the $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ and the corresponding M_{H} (columns 1 and 9) are the hydrogen-ion activities ($M_{\mathrm{H}}f_{\mathrm{H}}$) whose negatives of their common logarithms are the electrometric pH values (column 11). The spectrophotometric activity coefficients ($f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}$) and electrometric activity coefficients (f_{Cl}) agree well up to 0.05 *M* hydrocholoric acid and even better if the listed experimental values of $\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$ are plotted to obtain a smooth curve from which values may be read for comparison with the smooth curve data listed for $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$. Above 0.05 *M* hydrochloric acid, however, the $\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$ data gradually rise above those for $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$, and probably for the same reasons that cause a similar rise in mixtures of indicator, hydrochloric acid, and salts discussed below; namely, a decrease of $f_{\mathrm{R}^{+-}}$ below unity.

VI. ACTIVITY COEFFICIENTS OF METACRESOLSULFONPHTHALEIN AND 0.01-*M* HYDROCHLORIC ACID IN THE PRESENCE OF SALTS

It has long been known that addition of pure neutral salts to solutions of indicators in dilute acid or alkali causes a normal change in activity coefficients and hence in pH and color. There may be also a specific or abnormal [1, 8] salt effect characterized by a definite change in hue arising from a shift in the absorption band with respect to wave number and accompanied by changes in absorption index. Spectral transmittancy curves were therefore obtained for 1.25×10^{-5} *M* metacresolsulfonphthalein mixed with 0.01 *M* hydrochloric acid and the molar concentrations of potassium chloride, strontium chloride, and barium chloride shown in column 1 of table 4. The transmittancy of each mixture at $527._5\mu$ is given in column 2. The calculation of the spectrophotometric and electrometric activity coefficients and pH values are made by use of eq 4, 9, and 11; 1.703 for pK_{b}; and values of α obtained from the transmittancy data in column 2, table 4. The spectrophotometric activity coefficients are given in column 3, table 4.

TABLE 4.—*Effects of salts upon the transformation of metacresolsulfonphthalein* (1.25×10^{-5} *M*) *in 0.01 M hydrochloric acid*

Concentration of salt in 0.01 *M* HCl	Transmittancy of solution at $527._5$ mμ, *t*	Activity coefficient [a]		Calculated pH		Measured pH	
		Spectrophotometric, $\sqrt{f_{H}f_{Y^-}/f_{R^{+-}}}$	Potentiometric, $\sqrt{f_{H}f_{Cl}}$	Spectrophotometric data	Potentiometric data	Hydrogen electrode	Glass electrode
POTASSIUM CHLORIDE							
0.01	0.659	0.870	0.873	2.06	2.06	2.06	2.05
.02	.666	.852	.851	2.07	2.07	2.06	2.05
.05	.674	.832	.816	2.08	2.09	2.07	2.06
.10	.686	.802	.787	2.10	2.10	2.07	2.08
.50	.695	.780	.715	2.10	2.15	2.07	2.07
.72	.685	.805	.720	2.10	2.14	2.05	2.05
1.27	.663	.861	.762	2.06	2.12	2.00	1.99
1.71	.647	.902	.802	2.04	2.10	1.95	1.96
2.01	.621	.974	.835	2.01	2.08	1.93	1.92
3.42	.530	1.268	1.035	1.90	1.99	1.70	1.69
BARIUM CHLORIDE							
0.01	0.668	0.848	0.840	2.07	2.08	2.05	2.07
.04	.687	.795	.772	2.10	2.11	2.05	2.06
.06	.697	.775	.752	2.11	2.12	2.06	2.06
.10	.701	.763	.730	2.11	2.14	2.05	2.04
.20	.706	.754	.706	2.12	2.15	2.03	2.01
.25	.701	.760	.703	2.11	2.15	2.01	2.00
.36	.696	.781	.710	2.11	2.15	1.97	1.96
.50	.679	.820	.729	2.09	2.14	1.92	1.90
.80	.648	.901	.795	2.05	2.10	1.80	1.78
1.00	.631	.975	.853	2.04	2.07	1.74	1.72
1.12	.602	1.027	.902	1.99	2.05	(b)	1.66
STRONTIUM CHLORIDE							
0.01	0.665	0.854	0.835	2.07	2.08	2.08	2.06
.05	.686	.802	.761	2.10	2.12	2.08	1.96
.10	.696	.778	.729	2.11	2.14	2.08	1.82
.30	.696	.779	.713	2.11	2.15	1.99	1.88
.50	.678	.815	.738	2.09	2.13	1.90	1.87
.70	.656	.877	.799	2.06	2.09	1.82	1.79
.80	.644	.910	.838	2.04	2.08	1.78	1.73
2.00	.468	1.538	1.633	1.81	1.79	(b)	1.00
2.36	.413	1.885	[c] 2.016	1.72	1.70	(b)	.88

[a] These activity coefficients were obtained from the data of Harned and Hamer [14] for KCl, Harned and Geary [15] for $BaCl_2$ and Vance [16] for $SrCl_2$. Their data were corrected from a molal to a molar basis. See footnote 8.

[b] Measurements could not be made with the hydrogen-electrode assembly owing to diffusion of the salt and acid solutions through the saturated KCl solution.

[c] Estimated.

At 0.2 to 0.5 *M* salt concentrations these transmittancies go through maxima, and the corresponding absorption indices and activity coefficients therefore go through minima. Harned, Hamer, Geary, Vance, and Ehlers [14, 15, 16, 17] showed by the use of emf methods that the mean electrometric activity coefficients, $\sqrt{f_{H}f_{Cl}}$, of 0.01 *M* hydrochloric acid go through minima when mixed with approximately the same concentrations of the three salts used in this work. After expressing the molality of each salt in terms of its corresponding molarity,[8] the emf data were used to calculate the activity coefficients

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[8] To obtain the molarities (*M*) from the molalities (*m*), the following equations were used (Hamer, unpublished):

KCl: $M=0.99707m-0.028100m^2+0.0001412m^3$; $BaCl_2$: $M=0.99707m-0.026042m^2-0.003452m^3$; $SrCl_2$: $M=0.99707m-0.019773m^2-0.0027680m^3$; then $f_M=0.99707mf_m/M$.

on the molar basis. The mean activity coefficients (molar basis) were then plotted as a function of the molar concentrations of the salts. The values of $\sqrt{f_H f_{Cl}}$ which corresponded to the molar concentrations of the salts used in the spectrophotometric work were then read from the curves and are given in column 4, table 4.

A comparison of columns 3 and 4 of table 4 shows that the mean spectrophotometric activity coefficients, $\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$, are in general larger than the coefficients calculated from the electrometric data for $\sqrt{f_H f_{Cl}}$. Since f_H is the same in both methods for the given concentration of salt, it follows that $f_{Y^-}/f_{R^{+-}}$ must be larger than f_{Cl}. The difficulty in ascribing definite values to f_{Y^-} and $f_{R^{+-}}$ arises from the unknown contribution of their resonant dipolar states ([+] and [−] in fig. 1) to the values of z and the activity coefficients. The yellow form will be assigned tentatively $z=1$ for the following reasons: (1) The work on the dipole moments of benzeins [7], whose quinone-phenol chromophores are identical with those of Y^-, shows that the concentration of the resonant dipolar form is only a few percent of that of the ionic form (e. g., Y^- without [+] and [−] charges). (2) The resonant dipole structure of R^{+-} does not make $f_{R^{+-}}$ fall much below unity (see columns 4, 8, 12, 16 in table 5). Hence a few percent of the dipolar form of Y^- (e. g., Y^{-+-}, fig. 1) would produce only a minor effect on the over-all $-\log f(Y^- + Y^{-+-})$. In any event, the effects of the dipole contributions are somewhat compensated in the ratio $f_{Y^-}/f_{R^{+-}}$.

If use is now made provisionally of the hypothesis of Lewis and Randall [18] that the activity coefficient of any univalent ion in dilute aqueous solution depends only upon the ionic strength of the solution, a hypothesis that is also inherent in the Debye-Hückel theory of dilute mixed electrolytes, the activity coefficients of the chloride and single-charged indicator ions would be approximately the same. Hence if we place f_{Cl} equal to f_{Y^-}, we must get $f_{R^{+-}}$ and $\sqrt{f_{R^{+-}}}$ values appreciably less than unity, as shown in columns 4, 8, 12, 16, table 5. An expression developed by Kirkwood [19] for the activity coefficient of a fixed dipole (ampholyte) also gives values less than unity, which is in harmony with the present experimental evidence that the resonant dipolar red salt should not be treated as an uncharged molecule in hydrochloric acid or its mixtures with salts. Furthermore, the specific salt effects characterized by the shifts of the absorption bands (fig. 5), discussed above, are also being taken into account in the final corrections of α required for correct application of eq 4 to determine the pK_b and pH values for these acid-salt-indicator mixtures.

A definite departure from unity of the activity coefficients for the red form of the indicator may be taken as further evidence, supported by organic structural relations discussed on page 324, for the assumption that the reaction is expressed by eq 6 for a resonant ampholyte, rather than by eq 5, in which the red form would be an uncharged molecule and have an activity coefficient probably more nearly unity.

As this article is limited to comparisons of the approximate pH values obtained by the spectrophotometric and electrometric methods, the data of table 4 may be treated as follows: The very small effect of $-\log f_{\mathrm{R}^{+-}}$ will be disregarded and the approximate pH values, $-\log (M_{\mathrm{H}}f_{\mathrm{H}})$, of 0.01 *M* hydrochloric acid in the presence of salts obtained by adding to 2 (i.e.,$-\log 0.01$) the values of $-\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$ (computed from column 3, table 4) and those of $-\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ (computed from column 4, table 4) to get the "spectrophotometric" and "potentiometric" pH data, respectively. These pH values are given in columns 5 and 6, table 4. The agreement is within approximately 0.05 pH unit in all cases, even including the most concentrated solutions. For the 30 solutions listed, however, the average spectrophotometric pH values are about 0.03 less than the electrometric pH values of the acid-salt solutions.

Since the pH determined by spectrophotometric measurements is lower than that obtained by electrometric measurements, and $f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}$ values are larger than f_{Cl} for all the solutions studied, the next step is to attempt adjustments of $f_{\mathrm{Cl}}, f_{\mathrm{Y}^-}$, and $f_{\mathrm{R}^{+-}}$ to give the same spectrophotometric and electrometric pH values. If $f_{\mathrm{Cl}}=f_{\mathrm{Y}^-}$ and $\mathrm{pH}=-\log(m_{\mathrm{H}}\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}})=-\log(m_{\mathrm{H}}\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}})$ then the practical use of $\mathrm{pH}=-\log(m_{\mathrm{H}}\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}})=-\log(m_{\mathrm{H}}\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}})+\log\sqrt{f_{\mathrm{R}^{+-}}}$ will give spectrophotometric pH values too low by $\log\sqrt{f_{\mathrm{R}^{+-}}}$. The values for $\sqrt{f_{\mathrm{R}^{+-}}}$ are obtained by dividing $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ by $\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$ at the same ionic strength and are given in columns 4, 8, 12, and 16 of table 5. The first result is that the deviation of $\sqrt{f_{\mathrm{R}^{+-}}}$ from unity is small in comparison with the corresponding differences between unity and $\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$ and $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$, and that the contributions of the $-\log\sqrt{f_{\mathrm{R}^{+-}}}$ values (columns 5, 9, 13, 17 of table 5) to the pH for the four solutions, even though differing somewhat among themselves, are small in comparison with $-\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$ (and hence $-\log\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}}$). For the 30 solutions listed in table 4, the average spectrophotometric pH values are about 0.03 less than the electrometric pH values. The average correction for the $-\log\sqrt{f_{\mathrm{R}^{+-}}}$ for the same solutions is +0.03 pH, which therefore makes the average spectrophotometric pH values practically the same as the electrometric pH values. Similar corrections for the $-\log\sqrt{f_{\mathrm{R}^{+-}}}$ for the hydrochloric acid solutions in table 3 make the average pH values of column 10 practically the same as those of column 11. The second result is therefore that there is still some doubt whether f_{Cl} and f_{Y^-} are absolutely equal, in view of the polar nature of the latter, and whether either or both may have slightly different values in the solutions of different electrolytes of equal ionic strength. This question also applies to buffers. The uncertainties from the above cause, in the pH values are less than 0.05 pH in solutions up to unit ionic strength.

The pH values of these solutions were also measured with saturated calomel half-cells and hydrogen and glass electrodes, in a room controlled at 25° C, to determine the pH errors which may be encountered with routine apparatus. The value 0.24503 volt was assigned to the saturated calomel electrode with the liquid-junction potential by calibration with potassuim acid phthalate. For the 27 values listed in column 7, table 4, the average results obtained with the glass electrode are 0.027 pH lower than those with the hydrogen electrode.

TABLE 5.—*Comparison of the activity coefficients of metacresolsulfonphthalein in in 0.01 M hydrochloric acid*

Ionic strength (molar)	Hydrochloric acid				Potassium chloride in 0.01 *M* hydrochloric acid			
	Activity coefficients				Activity coefficients			
	Spectrophotometric	Potentiometric			Spectrophotometric	Potentiometric		
	$\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$	$\sqrt{f_H f_{Cl}}$	$\frac{\sqrt{f_H f_{Cl}}}{\sqrt{f_H f_{Y^-}/f_{R^{+-}}}}$	$-\log \sqrt{f_{R^{+-}}}$	$\sqrt{f_H f_{Y^-}/f_{R^{+-}}}$	$\sqrt{f_H f_{Cl}}$	$\frac{\sqrt{f_H f_{Cl}}}{\sqrt{f_H f_{Y^-}/f_{R^{+-}}}}$	$-\log \sqrt{f_{R^{+-}}}$
0.01	0.906	0.906	1.000	0.000	0.906	0.906	1.000	0.000
.02	.878	.878	1.000	.000	.873	.873	1.000	.000
.03	.863	.857	.993	.003	.856	.851	.994	.003
.04	.852	.844	.991	.004	.845	.836	.989	.005
.05	.842	.832	.988	.005	.835	.825	.988	.005
.06	.835	.824	.987	.006	.828	.816	.986	.006
.08	.823	.809	.983	.007	.816	.802	.983	.007
.10	.815	.799	.980	.009	.807	.791	.980	.008
.20	.796	.770	.967	.015	.787	.754	.958	.019
.50	.806	.776	.963	.016	.781	.715	.915	.038
1.00	.860	.825	.959	.018	.820	.730	.890	.050
2.00	----------	----------	----------	----------	.946	.837	.885	.053
3.00	----------	----------	----------	----------	1.140	.970	.851	.070

A comparison of the measured pH values (columns 7 and 8, table 4) with the calculated pH values (columns 5 and 6, table 4) throws some light on the errors likely to be encountered in routine pH measurements of fairly concentrated solutions of salts and acids with cells involving a liquid-junction potential of unknown value, for which no correction is attempted. The values in column 6 do not involve a liquid-junction potential, whereas those in columns 7 and 8 were obtained with cells having a liquid-junction between the saturated calomel half-cell and the salt-acid solution. For solutions of 0.01 *M* hydrochloric acid and not over 0.05 *M* salt, the agreement is generally of the order of 0.05 pH, but for the concentrated solutions, discrepancies of 0.3 to 0.4 unit are observed, the results being somewhat erratic because of the difficulty in establishing sharp liquid junctions. In an article recently published [20] caution was recommended against undue optimism in assigning pH values to within 0.05 pH in cases such as the above when liquid junctions are formed between electrolytes of widely different valance types, concentrations, and ionic mobilities. When the pH values of acid or acid-salt solutions of the types reported here are obtained by spectrophotometric and by electrometric measurements without liquid junctions, the average agreement is within about ±0.05 pH unit in even fairly concentrated solutions.

hydrochloric acid, and in potassium chloride, barium chloride and strontium chloride at the same ionic strengths

Barium chloride in 0.01 *M* hydrochloric acid				Strontium chloride in 0.01 *M* hydrochloric acid			
Activity coefficients				Activity coefficients			
Spectrophotometric $\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$	Potentiometric $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$	$\frac{\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}}{\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}}$	$-\log\sqrt{f_{\mathrm{R}^{+-}}}$	Spectrophotometric $\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}$	Potentiometric $\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}$	$\frac{\sqrt{f_{\mathrm{H}}f_{\mathrm{Cl}}}}{\sqrt{f_{\mathrm{H}}f_{\mathrm{Y}^-}/f_{\mathrm{R}^{+-}}}}$	$-\log\sqrt{f_{\mathrm{R}^{+-}}}$
0.906	0.906	1.000	0.000	0.906	0.906	1.000	0.000
.878	.876	.998	.001	.883	.881	.998	.001
.861	.855	.993	.003	.866	.861	.994	.003
.848	.839	.989	.005	.854	.847	.992	.003
.837	.827	.988	.005	.846	.834	.986	.006
.829	.817	.986	.006	.839	.825	.983	.007
.815	.800	.982	.008	.828	.807	.975	.011
.804	.788	.980	.009	.820	.794	.968	.014
.776	.749	.965	.015	.793	.754	.951	.022
.755	.709	.939	.027	.769	.714	.928	.032
.770	.706	.917	.038	.783	.719	.918	.037
.860	.761	.885	.053	.864	.788	.912	.040
.970	.858	.884	.053	.980	.912	.931	.031

VII. REFERENCES

[1] S. F. Acree, et al, Am. Chem. J. **38,** 1 (1907); **39,** 528 (1908); **41,** 483 (1909); **42,** 130 (1909); **48,** 372 (1912); **49,** 347, 379, 485 (1913); J. Am. Chem. Soc. **40,** 1940 (1918).
[2] E. C. White and S. F. Acree, J. Am. Chem. Soc. **39,** 650 (1917); **40,** 1094, 1097 (1918); **41,** 1191, 1207 (1919).
[3] H. A. Lubs and S. F. Acree, J. Am. Chem. Soc. **38,** 2772 (1916).
[4] R. T. Birge and S. F. Acree, J. Am. Chem. Soc. **41,** 1031 (1919).
[5] C. H. Brightman, M. R. Meacham, and S. F. Acree, J. Bact. **5,** 169 (1920).
[6] W. A. Gruse and S. F. Acree, J. Am. Chem. Soc. **39,** 386 (1917).
[7] M. A. Elliott and S. F. Acree, J. Research NBS **23,** 675 (1939) RP1263.
[8] B. Wingfield and S. F. Acree, J. Research NBS **27,** 361 (1941) RP1424.
[9] W. R. Brode, J. Am. Chem. Soc. **46,** 581 (1924); Chemical Spectroscopy (John Wiley & Sons, New York, N. Y., 1939).
[10] W. Ostwald, Lehrbuch der allegemeinen Chemie, p. 799 (1903); Grundriss der allegemeinen Chemie, 6th ed., p. 462 (Theodor Steinkopff, Dresden and Leipzig, 1920).
[11] K. S. Gibson and H. J. Keegan, J. Opt. Soc. Am. **28,** 372 (1938).
[12] W. J. Hamer, J. O. Burton, and S. F. Acree, J. Research NBS **24,** 269 (1940) RP1284.
[13] W. J. Hamer and S. F. Acree, J. Research NBS **23,** 647 (1939) RP1261.
[14] H. S. Harned and W. J. Hamer, J. Am. Chem. Soc. **55,** 2194 (1933).
[15] H. S. Harned and C. G. Geary, J. Am. Chem. Soc. **59,** 2032 (1937).
[16] J. E. Vance, J. Am. Chem. Soc. **55,** 2729 (1931).
[17] H. S. Harned and R. W. Ehlers, J. Am. Chem. Soc. **55,** 2179 (1933).
[18] G. N. Lewis and M. Randall, J. Am. Chem. Soc. **43,** 1112 (1921).
[19] J. G. Kirkwood, J. Chem. Phys. **2,** 351 (1934); Chem. Rev. **24,** 233 (1939).
[20] R. G. Bates, W. J. Hamer, G. G. Manov, and S. F. Acree, J. Research NBS **29,** 183 (1942) RP1495.
[21] H. von Halban and L. Ebert, Z. physik. Chem. **112,** 321 (1924).
[22] H. von Halban and J. Eisenbrand, Z. physik. Chem. **132,** 401 (1928).
[23] W. J. Hamer, G. D. Pinching, and S. F. Acree, J. Research NBS **31,** 291 (1943) RP1567.

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