An equation corresponding to equation (2) can be derived from the equation

$$\phi_A = z_A\epsilon/[Da(1 + \kappa a)] \qquad (14')$$

where a is the average distance of closest approach of the centers of the ions. The resulting equation corresponding to equation (12) is

$$P = e^{1/2}\, e^{-z_A z_B \epsilon^2 L/Dka} \times e^{(z_A z_B \epsilon^2/2DkT)[(3LT - 1)\kappa + 2a\kappa^2 LT]/(1 + a\kappa)^2} \qquad (15)$$

The difference from (12) lies in the exponential term involving κ. Calculations show that P changes twelvefold between zero and 0.200 ionic strength. This equation also involves the assumption that E_A does not change with ionic strength.

Corresponding to equation (13) the use of (14′) yields a theoretical equation for the change of E_A with ionic concentration.

$$(E_A)_{\kappa_1} - (E_A)_{\kappa_2} = \frac{N_0 z_A z_B \epsilon^2}{2D}(LT - 1) \times \left\{\frac{\kappa_1(3 + 2a\kappa_1)}{(1 + a\kappa_1)^2} - \frac{\kappa_2(3 + 2a\kappa_2)}{(1 + a\kappa_2)^2}\right. \qquad (16)$$

This equation predicts that E_A should increase by 0.45 kcal. from $\mu = 0.001$ to 0.200. The experiments reported in this paper are not in agreement with (13) or (16).

Summary

A kinetic study of the fading of chlor phenol blue, brom phenol blue and iodo phenol blue shows that the rate-determining step involves a reaction between the divalent anion of the sulfonphthalein and the hydroxyl ion.

The effects of ionic strength and temperature have been compared with the theory.

PHILADELPHIA, PENNA. RECEIVED JUNE 21, 1937

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Dissociation Constants of Chlor Phenol Blue and Iodo Phenol Blue[1]

BY FRANK W. PANEPINTO AND MARTIN KILPATRICK

In connection with the study of these indicators[1a] the dissociation constants were determined. The experimental method was that used by Kilpatrick[2] in determining the dissociation constant of brom phenol blue. The ratios of the dissociation constant of the indicators and suitable weak acids were determined colorimetrically at low ionic concentrations. Extrapolation to zero ion concentration was made in accordance with the equations

$$\log Kc(\text{Ind})/Kc(\text{acid}) = \log Ka(\text{Ind})/Ka(\text{acid}) + 1.0\sqrt{\mu} \qquad (1)$$

and

$$\log Kc(\text{Ind})/Kc(\text{acid}) = \log Ka(\text{Ind})/Ka(\text{acid}) + 1.0\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \qquad (2)$$

Tables I and II summarize the results with benzoate–benzoic acid buffers.

The extrapolation in accordance with equations (1) and (2) yields the ratios of the dissociation constants of the indicators.

The ratios of the thermodynamic dissociation constants of chlor phenol blue and iodo phenol blue to that of benzoic acid are 0.60 and 1.06,

TABLE I

THE DISSOCIATION CONSTANTS WITH BENZOATE BUFFERS

Indicator Concentration 2×10^{-5} *M*. Temp. 25 ± 1°

μ	0.02008	0.01008	0.00507	0.00257
$\frac{C(\text{Benzoic acid})}{C(\text{Benzoate})}$	0.991	0.985	0.978	0.945
Chlor phenol blue				
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	.821	.757	.722	.719
Iodo phenol blue				
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	1.35 1.33	1.32 1.31	1.27 1.27	1.26 1.24
$\frac{Kc(\text{CPB})}{Kc(\text{HB})}$	0.814	0.746	0.706	0.679
$\frac{Kc(\text{IPB})}{Kc(\text{HB})}$	1.34 1.32	1.30 1.29	1.23 1.23	1.19 1.17
$Kc(\text{HB}) \times 10^5$	8.41	7.71	7.41	7.04
$Kc(\text{CPB}) \times 10^5$	6.84	5.81	5.23	4.83
$Kc(\text{IPB}) \times 10^5$	11.3 11.1	10.0 9.9	9.1 9.1	8.4 8.2

TABLE II

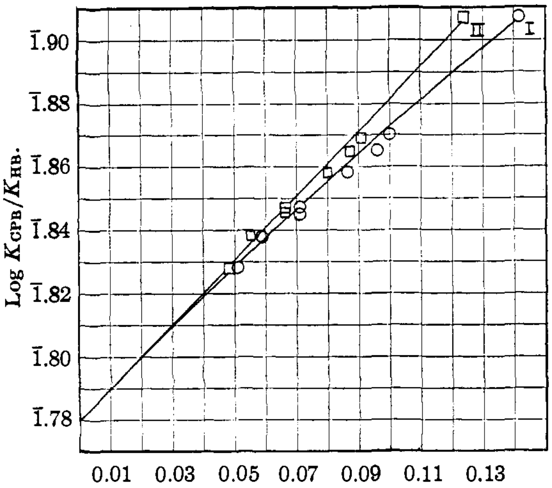
THE DISSOCIATION CONSTANT OF CHLOR PHENOL BLUE WITH BENZOATE–BENZOIC ACID BUFFER

μ	0.00917	0.00757	0.00507	0.00339	0.00257
$\frac{C(\text{Benzoic acid})}{C(\text{Benzoate})}$	0.983	0.980	0.971	0.961	0.946
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	.738	.734	.721	.717	.709
$\frac{Kc(\text{CPB})}{Kc(\text{HB})}$	.731	.719	.700	.688	.671
$Kc(\text{HB}) \times 10^5$	7.68	7.60	7.41	7.10	7.04
$Kc(\text{CPB}) \times 10^5$	5.66	5.46	5.19	4.88	4.72

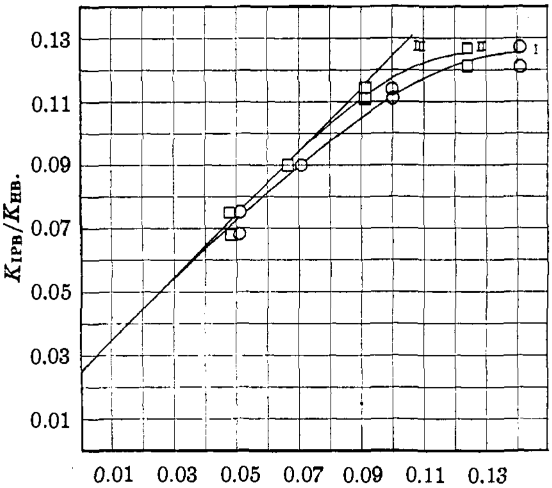
[1] Abstracted from the dissertation of Frank W. Panepinto presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1937.

[1a] Panepinto and Kilpatrick, THIS JOURNAL, **59**, 1871 (1937).

[2] Kilpatrick, *ibid.*, **56**, 2048 (1934).



I, ○ vs. $\sqrt{\mu}$. II, □ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$. III, Slope = 1.00.
Fig. 1.—The dissociation constant of chlor phenol blue.



I, ○ vs. $\sqrt{\mu}$. II, □ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$. III, Slope = 1.00.
Fig. 2.—The dissociation constant of iodo phenol blue.

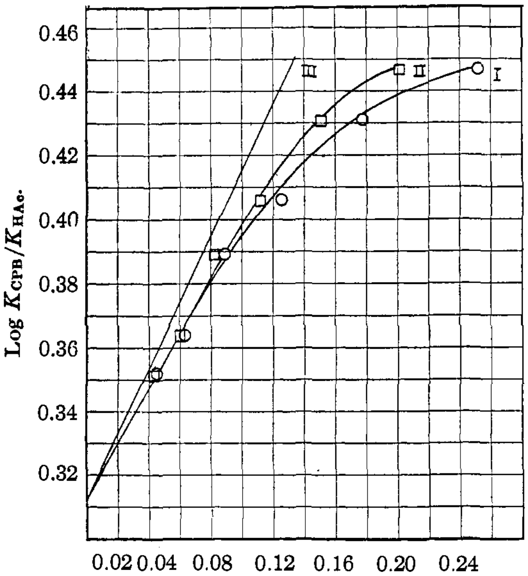
TABLE III

THE DISSOCIATION CONSTANTS OF CHLOR PHENOL BLUE AND IODO PHENOL BLUE IN ACETATE-ACETIC ACID BUFFERS

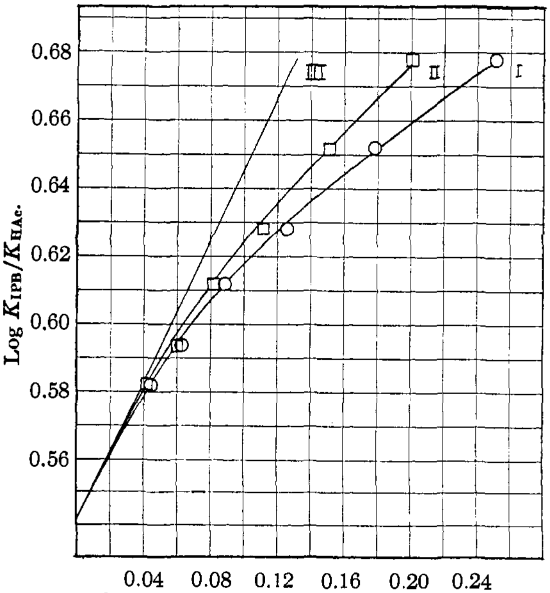
Indicator Concentration 2 × 10^{-5} *M*. Temp. 25 ± 1°

μ	0.0631	0.0316	0.0158	0.0079	0.0040	0.0020
$\frac{C(\text{HAc})}{C(\text{Ac}^-)}$	3.00	2.99	2.98	2.97	2.94	2.91
Chlor phenol blue						
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	0.945	0.901	0.855	0.826	0.787	0.775
Iodo phenol blue						
$\frac{C(\text{Blue})}{C(\text{Yellow})}$	1.58	1.48	1.43	1.36	1.33	1.32
$\frac{Kc(\text{CPB})}{Kc(\text{HAc})}$	2.80	2.70	2.55	2.45	2.31	2.25
$\frac{Kc(\text{IPB})}{Kc(\text{HAc})}$	4.77	4.49	4.25	4.09	3.93	3.82

respectively. From the value of the thermodynamic dissociation constant[3] of benzoic acid at 25°, 6.31 × 10^{-5}, that for chlor phenol blue is 3.8 × 10^{-5} and for iodo phenol blue 6.7 × 10^{-5}. Since the classical dissociation constants of benzoic acid are known at these low ionic strengths the classical dissociation constants of the indicators are computed and given in Tables I and II. The method of extrapolation is independent of the values for benzoic acid.



I, ○ vs. $\sqrt{\mu}$. II, □ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$. III, Slope = 1.00.
Fig. 3.—The dissociation constant of chlor phenol blue.



I, ○ vs. $\sqrt{\mu}$. II, □ vs. $\sqrt{\mu}/(1 + \sqrt{\mu})$. III, Slope = 1.00.
Fig. 4.—The dissociation constant of iodo phenol blue.

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[3] Brockman and Kilpatrick, THIS JOURNAL, **56**, 1483 (1934).

Both indicators were also studied in acetate–acetic acid buffers. The results are summarized in Table III and Figs. 3 and 4.

From Figs. 3 and 4 the ratios of the thermodynamic dissociation constants of chlor phenol blue and iodo phenol blue to that of acetic acid are 2.05 and 3.5, respectively. The thermodynamic dissociation constant of acetic acid is 1.75×10^{-5},[4] which yields 3.6×10^{-5} for chlor phenol blue and 6.1×10^{-5} for iodo phenol blue. These values are to be compared with 3.8×10^{-5} and 6.7×10^{-5} from the benzoate buffers. The average values of the thermodynamic dissociation constants increase in the order chlor phenol blue 3.7×10^{-5}, brom phenol blue 6.0×10^{-5} and iodo phenol blue 6.4×10^{-5}.

Summary

The thermodynamic dissociation constants of chlor phenol blue and iodo phenol blue have been determined.

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(4) Harned and Owen, THIS JOURNAL, **52**, 5079 (1930); MacInnes and Shedlovsky, *ibid.*, **54**, 1429 (1932).

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Conductance of Mixtures of Strong Electrolytes[1]

BY K. A. KRIEGER AND MARTIN KILPATRICK

Of the two effects which tend to diminish the velocity of an ion in solution, only one, the field effect or relaxation effect, will have a different value in a mixture of salts than it would have in a pure salt. According to Onsager and Fuoss[2] the decrease $\Delta\overline{X}_j$ in the external electric field $\overline{X}$ acting upon a j ion in a mixture of ions is

$$\frac{\Delta\overline{X}_j}{\overline{X}} = -\frac{\epsilon^3}{3}\sqrt{\frac{N\pi}{250k^3}}\Big/\frac{\Gamma^{1/2}}{(DT)^{3/2}}z'_j\,(I - H^{1/2})_{j\sigma}\,r_\sigma \qquad (1)$$

where[3] $\Gamma = n_\sigma e_\sigma^2$

ϵ is the unit of electrostatic charge

N is Avogadro's number

z'_j is the valence of the jth ion and z_j is its absolute magnitude

I is the unit or identical matrix

H is a matrix with elements

$$h_{ji} = \mu_\sigma \omega_{\sigma j}\delta_{ji} + \mu_i \omega_{ij}$$

r is a vector with elements

$$r_i = z'_i - \frac{z_\tau \mu_\tau}{\mu_\pi z_\pi}\cdot\frac{\Lambda^\circ{}_\pi z_i}{\Lambda^\circ{}_i}$$

μ_i is the ratio of the concentration of i ions to the total ion concentration

ω_i is the mobility of the ith ion and

$$\omega_{ij} = \omega_i/\omega_i + \omega_j$$

δ_{ji} is the Kronecker symbol:

$$\delta_{ji} = 0 \quad \text{if } j \neq i$$
$$\delta_{ji} = 1 \quad \text{if } j = i$$

Inspection of equation (1) shows that the decrease in velocity due to the field effect is not a function of the properties of the j ion alone, but is a function of the properties of all the ions in the solution.

Bray and Hunt[4] have measured the conductance of mixtures of sodium chloride and hydrochloric acid and Onsager has compared their results with those computed from equation (1). The agreement between observed and calculated values is good at low concentrations, but at higher concentrations the observed mixture effect appears to be about half that calculated.

Due to the high mobility of the hydrogen ion, the mixture effect in an acid–salt mixture is much larger than in a salt–salt mixture and in this respect an acid–salt mixture is more suitable for such measurements. The advantage that might be gained in this way is, however, offset by the fact that measurements of conductance of acids in dilute solution are relatively inaccurate for two reasons. First, it is impossible to make correction for the conductance of the solvent, and, second, small amounts of impurities will often produce changes in conductance large enough to mask entirely an effect as small as the mixture effect. For these reasons it was thought advisable to measure the conductance of a mixture of salts, rather than that of a salt–acid mixture.

A detailed description of the method of computation of the mixture effect will be reserved for a later section.

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(1) Abstracted from the dissertation of K. A. Krieger submitted in April, 1937, to the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Onsager and Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

(3) Throughout this paper Greek letters used as subscripts will indicate summation.

(4) Bray and Hunt, THIS JOURNAL, **33**, 781 (1911).