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

The Classical Dissociation Constant of Brom Phenol Blue in Aqueous Salt Solutions[1]

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In connection with the standardization of benzoic acid–benzoate buffer systems the classical dissociation constants of a number of indicators have been determined.[2]

The present study concerns the indicator brom phenol blue. The base–acid ratio $(c_{I^-})/(c_{HI^-})$ was determined for a series of benzoic acid–benzoate buffers of known acid–base ratio $(c_{HB})/(c_{B^-})$. The product $(c_{HB})(c_{I^-})/(c_{B^-})(c_{HI^-})$ is the ratio of the classical dissociation constant of the indicator to that of benzoic acid. By multiplying this ratio by the dissociation constant of benzoic acid the classical dissociation constant of the indicator was obtained. The values for the dissociation constant of benzoic acid in potassium chloride solution were taken from the paper of Chase and Kilpatrick,[2a] while those in the other salt solutions were determined catalytically.[3] Table I gives the ratios of the dissociation constants and Table II the dissociation constant of brom phenol blue in the various salt solutions.

TABLE I

THE RATIO $K_{c\text{BPB}}/K_{c\text{HB}}$ IN VARIOUS SALT SOLUTIONS

Temperature, 25 ± 3°. Concentration of brom phenol blue, 2×10^{-5} M

μ^a	KCl	NaCl	LiCl	$NaClO_4$	p-$C_6H_4CH_3SO_3Na$
0.1	1.47	1.48	1.47	1.54	1.51
.2	1.67	1.55	1.55	1.56	1.52
.3	1.65				
.4	1.75	1.56	1.59	1.52	1.55
.5	1.70				
.6	1.73	1.56	1.58	1.51	1.62
.7	1.74				
.8	1.75	1.60	1.54	1.55	1.67
.9	1.77				
1.0	1.73	1.65	1.53	1.51	1.75
1.5	1.72	1.65	1.38	1.50	
2.0	1.86	1.60	1.25	1.50	
2.5	1.87		1.14		
3.0	1.72	1.69	0.98	1.43	

[a] $\mu = \Sigma c_i z_i^2$ where c_i is the concentration of the ith ion in moles per liter, and z_i its valence.

The results are presented graphically in Fig. 1. From Table II and Fig. 1 it is evident that at 0.1 M concentration the values of the dissociation constant are the same within the experimental error of 5% in all the salt solutions, while at higher concentrations there are considerable differences between them.

TABLE II

THE DISSOCIATION CONSTANT OF BROM PHENOL BLUE $\times 10^5$

μ	KCl	NaCl	LiCl	$NaClO_4$	p-$C_6H_4CH_3SO_3Na$
0.1	14.9	15.7	15.9	15.0	15.0
.2	17.4	17.8	18.5	16.0	15.5
.3	17.9				
.4	19.6	18.2	20.0	15.9	14.8
.5	19.2				
.6	19.5	18.6	20.4	15.5	13.3
.7	19.7				
.8	19.4	19.0	19.8	14.9	11.0
.9	19.3				
1.0	18.7	18.8	19.6	13.5	9.6
1.5	17.1	16.3	16.8	11.3	
2.0	15.8	13.8	13.5	9.2	
2.5	14.1		11.0		
3.0	11.3	8.4	7.4	5.3	

The following procedure was employed in an attempt to determine the thermodynamic dissociation constant of the indicator. The classical dissociation constant of benzoic acid was measured kinetically in a series of dilute benzoic acid–benzoate buffers, and the ratio $(c_{I^-})/(c_{HI^-})$ was determined colorimetrically in similar buffer solutions to which indicator was added. Table III summarizes the results. The solutions of $\mu >$ 0.0125 contained potassium chloride.

TABLE III

THE DISSOCIATION CONSTANT OF BROM PHENOL BLUE IN DILUTE SOLUTION

μ	$K_{c\text{BPB}}/K_{c\text{HB}}$	$K_{c\text{HB}} \times 10^5$	$K_{c\text{BPB}} \times 10^5$
0.0016	1.01	6.92	6.98
.0031	1.03	7.08	7.30
.0062	1.08	7.59	8.19
.0100	1.10	7.71	8.47
.0125	1.13	7.94	8.97
.0250	1.16	8.51	9.89
.0500	1.30	9.04	11.7
.1000	1.47	10.12	14.9
.1500	1.51	10.47	15.8
.2000	1.67	10.43	17.4

The dissociation constant of benzoic acid is given by the equation

$$K_{c\text{HB}} = K_{a\text{HB}}\, f_{\text{HB}}/f_{H_3O^+}f_{B^-} \qquad (1)$$

where K_a is the thermodynamic dissociation constant and the f's are activity coefficients. If

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(1) Presented at the Florida meeting of the American Chemical Society. March, 1934.

(2) (a) Chase and Kilpatrick, THIS JOURNAL, **53**, 2589 (1931); (b) **54**, 2284 (1932).

(3) Riesch and Kilpatrick, unpublished work. For the catalytic method and its assumptions, see Kilpatrick and Chase, THIS JOURNAL, **53**, 1732 (1931). It is to be noted that there is agreement between the electrometric and catalytic methods up to a concentration of 2 M potassium chloride.

the color change from yellow to purple involves the second dissociation constant of brom phenol blue, as is indicated by the trend in the ratio $K_{c_{BPB}}/K_{c_{HB}}$ shown in the second column of Table III,[4] we have

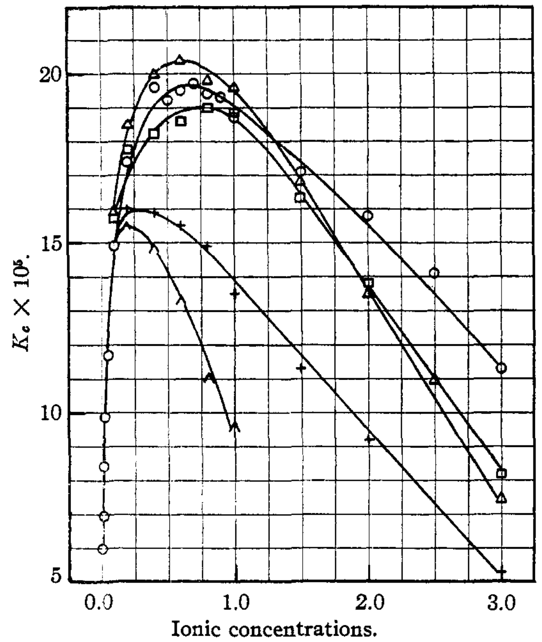

Fig. 1.—The dissociation constant of brom phenol blue: ○, KCl; □, NaCl; △, LiCl; +, $NaClO_4$; ∧, p-$C_6H_4CH_3SO_3Na$.

$$K_{c_{BPB}} = K_{a_{BPB}} f_{HI^-}/f_{H_3O^+} f_{I^-} \quad (2)$$

From (1) and (2) it follows that

$$\log K_{c_{BPB}}/K_{c_{HB}} = \log K_{a_{BPB}}/K_{a_{HB}} + \log f_{HI^-} f_{B^-}/f_{I^-} f_{HB} \quad (3)$$

Assuming that in sufficiently dilute solution

$$-\log f = 0.5 z^2 \sqrt{\mu} \quad (4)$$

we have

$$\log K_{c_{BPB}}/K_{c_{HB}} = \log K_{a_{BPB}}/K_{a_{HB}} + 1.0 \sqrt{\mu} \quad (5)$$

Hence upon plotting the logarithm of the ratio of the classical dissociation constants against $\sqrt{\mu}$, there should be obtained, in sufficiently dilute solution, a line of unit slope and with an intercept equal to the ratio of the thermodynamic dissociation constants. The curve marked I in Fig. 2 is such a curve. Curve III in Fig. 2 is drawn with unit slope; it is evident that the limiting slope is not reached at the concentrations measured. At lower concentrations the buffer system of the indicator has an appreciable influence upon the hydrogen-ion concentration of the solution. If one employs for the activity coefficient the equation

$$-\log f = 0.5 z^2 \sqrt{\mu}/(1 + \sqrt{\mu}) \quad (6)$$

as suggested by Guggenheim and Schindler,[4] (5) becomes

$$\log K_{c_{BPB}}/K_{c_{HB}} = \log K_{a_{BPB}}/K_{a_{HB}} + 1.0 \sqrt{\mu}/(1 + \sqrt{\mu}) \quad (5a)$$

In curve II of Fig. 2 log $K_{c_{BPB}}/K_{c_{HB}}$ is plotted against $\sqrt{\mu}/(1 + \sqrt{\mu})$; the experimental points approach somewhat more closely to the limiting line than in the previous case. Extrapolation gives $K_{a_{BPB}}/K_{a_{HB}} = 0.95$. From the value of the thermodynamic dissociation constant of benzoic acid at 25°, 6.31×10^{-5},[5] that for brom phenol blue is found to be 6.0×10^{-5}. This value is considerably lower than those reported in the literature.[6]

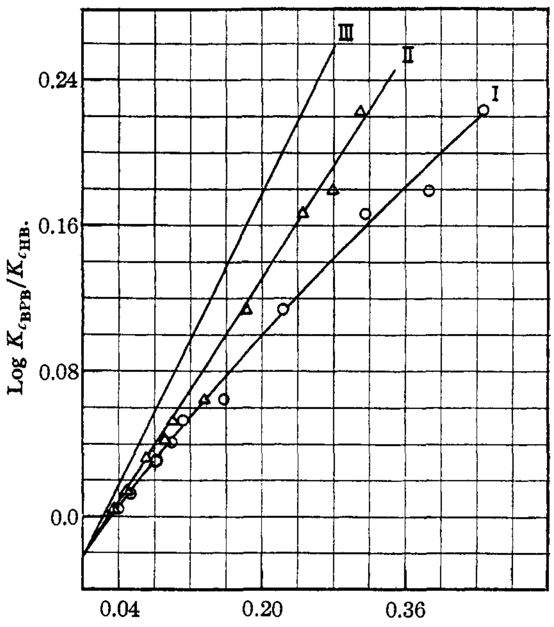

Fig. 2.—Ratio of dissociation constants: I ○, *vs.* $\sqrt{\mu}$; II □, *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$; III slope = 1.0.

From the earlier measurements it seemed probable that the activity coefficients involved in the indicator equilibrium behaved like those of a monobasic acid,[6,7] and one might expect that ions with widely separated charges would not have activity coefficients in agreement with equation (4) or (6). Then too it should be remembered that the limiting slope is not reached except at very low concentrations. For example, in the determination of the dissociation constant of benzoic acid by conductance measurements, equation (4) holds, within the experimental error, up to an ionic strength of 0.0003. To illustrate

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[4] Guggenheim and Schindler, *J. Phys. Chem.*, **37**, 543 (1934).

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

[6] See Güntelberg and Schiödt, *Z. physik. Chem.*, **135**, 393 (1928).

[7] Kolthoff, *J. Phys. Chem.*, **34**, 1466 (1930); Kilpatrick and Kilpatrick, *ibid.*, **34**, 2111 (1930).

this, and to show to what concentration equation (6) might be expected to hold, a few conductimetric and catalytic determinations of the dissociation constant of benzoic acid are shown in Fig. 3.

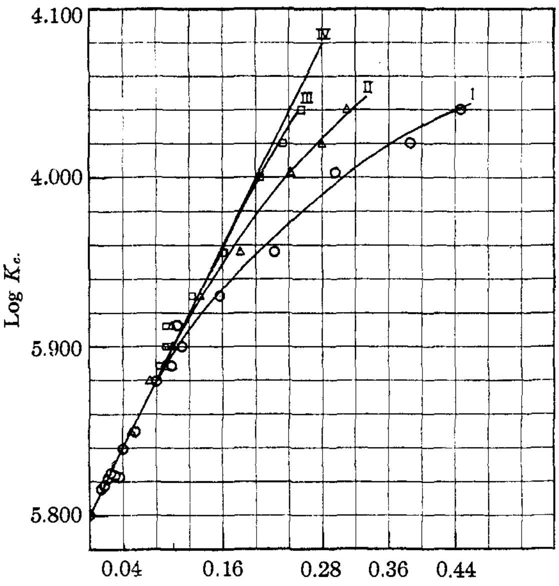

Fig. 3.—The dissociation constant of benzoic acid: I ○, *vs.* $\sqrt{\mu}$; II △, *vs.* $\sqrt{\mu}/(1 + \sqrt{\mu})$; III □, *vs.* $\sqrt{\mu}/(1 + 1.7\sqrt{\mu})$; IV slope 1.01.

Log K_c is plotted against $\sqrt{\mu}$ for curve I; against $\sqrt{\mu}/(1 + \sqrt{\mu})$ for II; against $\sqrt{\mu}/(1 + 1.7\sqrt{\mu})$ for III; and IV, with slope 1.01, represents the limiting law in each case. Curve III represents the first two terms in the empirical equation given by Chase and Kilpatrick for the classical dissociation constant of benzoic acid in potassium chloride solution.[2a]

It is evident that neither equation (4) nor (6) can be expected to hold even within the accuracy of the measurements on brom phenol blue (5%) to ionic strengths above a few hundredths. Although Guggenheim and Schindler[4] claim a greater accuracy for their colorimetric measurements, a plot similar to Fig. 2 shows the same divergence. In studying weak electrolyte equilibria involving neutral molecules it is necessary to consider also the activity coefficients of the non-electrolytes, even in fairly dilute solutions. The effect of sodium benzoate is to decrease the activity coefficient of molecular benzoic acid, while that of potassium chloride is to increase the coefficient. The presence of benzoate will tend to bring the values closer to the theoretical in Fig. 3, and the presence of potassium chloride will increase the divergence from the theoretical. The magnitude of these effects for various solvent salts has been given by Chase and Kilpatrick,[2a] and Osol and Kilpatrick.[8] In another paper it will be shown that upon resolving the ratio of activity coefficients $f_{\mathrm{H_3O^+}}f_{\mathrm{B^-}}/f_{\mathrm{HB}}$ into the two parts, the mean activity coefficient of the ions of benzoic acid at $\mu = 0.1$ has a value of 0.78–0.80 in nine solvent salts. Equation (6) gives a value of 0.76.

Summary

The classical dissociation constant of brom phenol blue for the yellow–purple color change has been determined in solutions of five solvent salts, up to a concentration of three molar. The applicability of the various equations for the activity coefficient has been discussed.

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[8] Osol and Kilpatrick, THIS JOURNAL, **55**, 4430 (1933).