TABLE VI

COMPARISON OF CALCULATED AND OBSERVED VALUES OF $K_{A_xB_0}$

Substituent in para position	Solvent water, De 9.4		Solvent CH$_3$OH, 7.7	
	Calcd.	Obsd.	Calcd.	Obsd.
NO$_2$	4.1	6.0	5.5	12
I	1.6	...	1.7	2.4
Br	1.7	1.7	1.9	2.5
Cl	1.7	1.7	1.9	2.45
F	1.65	1.15	1.85	1.5
CH$_3$	0.87	0.68	0.85	0.62

Westheimer theory predicts that the relative acid strengths are less sensitive to the macro-dielectric constant of the solvent than experiment indicates. In the calculation of $K_{A_xB_0}$ the value of the partial molal volume was taken as approximately 180 Å^3. It is realized that the partial molal volume may be larger in methyl alcohol than in water,[17] and that slightly better agreement between experiment and theory can be obtained by the arbitrary choice of a larger value. A calculation of V (the partial molal volume) for a fixed value of r shows that V would have to be changed very considerably from its value in water to approximate the results in methyl alcohol. A calculation of V from equation (5), using the observed values of log $K_{A_xB_0}$, shows that V is far from constant in a given solvent.

Summary

1. The effect of ionic strength on the equilibrium constants for the reaction between sulfonpthalein indicators and monosubstituted benzoic acids has been investigated.

2. Two methods of extrapolation to infinite dilution have been compared.

3. The acid strength constants relative to benzoic acid have been calculated from the data.

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[17] Traube, *Saml. chem. chem.-tech. Vortr.*, **4**, 255 (1899).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF PENNSYLVANIA]

Acid-Base Equilibria in Ethyl Alcohol*

BY MARTIN KILPATRICK AND WHITNEY H. MEARS

In the preceding paper[1] the equilibrium constants between the yellow-blue forms of brom cresol green and brom phenol blue, and the monosubstituted benzoic acid-benzoate buffers, were reported for the solvent methyl alcohol. This paper summarizes the results in ethyl alcohol and considers the significance of the results in both solvents.

Experimental Part

Ethyl alcohol was purified by the method of Lund and Bjerrum[2] and refluxed with anhydrous copper sulfate. The water content was determined by density measurements and found to be less than 0.04% by weight. The carboxylic acids and indicators were the same as those used in the solvent methyl alcohol. The experimental method was identical with that described in the previous paper.[1]

The extrapolation to infinite dilution is more difficult in ethyl alcohol than in methyl, since the dielectric constant is lower. For ethyl alcohol the dielectric constant[3] is given by the equation

$$\log D = 1,3979 - 0,00264(t - 20) \qquad (1)$$

Figure 1 shows an extrapolation by equation (2) of the previous paper

$$\log K_{A_iB} = \log\,[K_{A_iB}]^0 + A(Z_{A_i} - Z_A)\,\sqrt{\mu} \qquad (2)$$

and Fig. 2 gives the corresponding graph for equation (3)

$$\log K_{A_iB} - A(Z_{A_i} - Z_A)\,\sqrt{\mu} = \log[K_{A_iB}]^0 + B\mu \qquad (3)$$

The value for A at 25° is 5.94.

Table I summarizes the data for the equilibrium constants between brom cresol green and benzoic acid and the substituted benzoic acids. The reproducibility of the extrapolated values is indicated by the values in column three of Tables I and II, for the equilibrium between the indicator and benzoic acid. In general the results are reproducible to 0.02 log unit. The value of the constant B is uncertain to ±3 units and must be considered applicable only at low ionic strengths. If B were the same for all the acids studied we

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* Aided by a grant from the Penrose Fund of the American Philosophical Society.

[1] Kilpatrick and Mears, THIS JOURNAL, **62**, 3047 (1940).

[2] Lund and Bjerrum, *Ber.*, **64B**, 210 (1931).

[3] Åkerlöf, THIS JOURNAL, **54**, 4125 (1932).

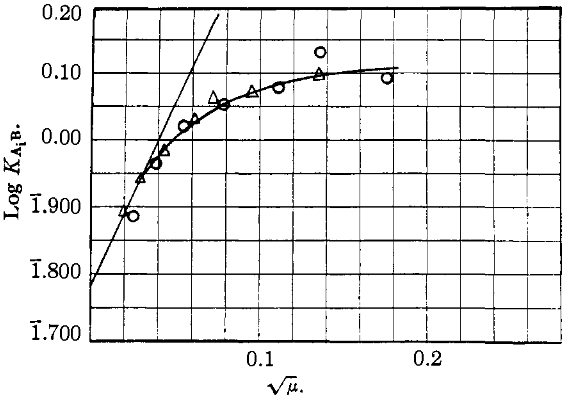

Fig. 1.—Extrapolation by equation (2): O, expt. 2; Δ, expt. 4.

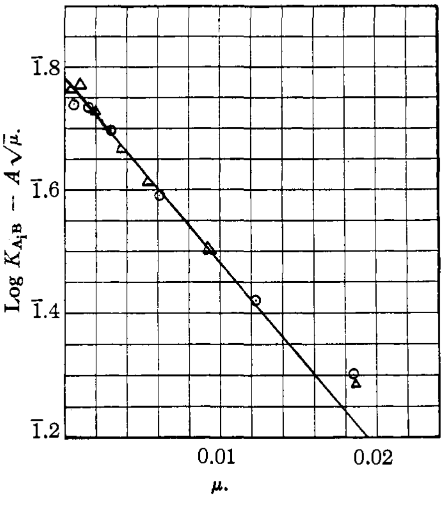

Fig. 2.—Extrapolation by equation (3): O, expt. 2; Δ, expt. 4.

could conclude that there were no detectable specific salt effects up to an ionic strength of 0.02. Kolthoff and Guss[4] find there is no such change in methyl alcohol up to $\mu = 0.05$, but at the higher ionic strengths the electrolyte consists of an added salt as well as the salt of the buffer acid. This would tend to mask any specific effects. Table II summarizes the data for brom phenol blue and Table III gives the acid strength constants relative to benzoic acid for the solvent ethyl alcohol. For comparison, the values calculated from the Kirkwood–Westheimer theory are given. It is again evident that the calculated effect of the dielectric constant of the medium is smaller than that found experimentally.

TABLE I

EQUILIBRIUM CONSTANTS OF SUBSTITUTED BENZOIC ACIDS WITH BROM CRESOL GREEN

Benzoic acid	Temp., °C.	log $[K_{A_iB}]^0$	A	$-B$	log $[K_{A_iB}]^0$ literature
	23.3	$\bar{1}$.770	5.894	23.0	
	23.5	$\bar{1}$.740	5.900	22.5	
	23.2	$\bar{1}$.775	5.892	27.0	
	24.8	$\bar{1}$.780	5.932	30.0	
	23.6	$\bar{1}$.805	5.902	30.5	$\bar{1}$.6[a]
Av.	23.7	$\bar{1}$.766	5.904	26.6	$\bar{1}$.675[b]
Substituent					
o-CH_3	23.5	$\bar{1}$.710	5.900	24.0	
m-Cl	23.2	$\bar{1}$.160	5.892	26.0	
m-CH_3	24.2	$\bar{1}$.840	5.917	31.5	
m-OH	23.8	$\bar{1}$.950	5.907	28.5	
p-Br	23.8	$\bar{1}$.295	5.907	23.0	
p-Cl	23.2	$\bar{1}$.257	5.892	25.4	$\bar{1}$.236[b]
p-F	22.0	$\bar{1}$.535	5.862	25.5	
p-CH_3	25.2	$\bar{1}$.960	5.942	29.3	
p-OCH_3	28.0	0.160	6.013	27.0	
p-OH	24.4	0.150	5.922	36.0	

[a] Guss and Kolthoff, THIS JOURNAL, **62**, 249 (1940).
[b] Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939).

TABLE II

EQUILIBRIUM CONSTANTS OF BENZOIC ACIDS WITH BROM PHENOL BLUE

Benzoic acid	Temp., °C.	log $[K_{A_iB}]^0$	A	$-B$	log $[K_{A_iB}]^0$ literature
	22.9	0.830	5.884	25.0	
	23.2	.785	5.892	26.0	
	23.8	.820	5.906	28.5	
	23.6	.807	5.892	27.0	
Av.	23.4	.811	5.893	26.6	0.85[a]
Substituent					
o-NO_2	21.6	$\bar{2}$.980	5.987	23.5	$\bar{1}$.0[a]
o-I	22.2	$\bar{1}$.670	5.867	24.5	
o-Cl	21.8	$\bar{1}$.645	5.857	22.8	
o-Br	21.0	$\bar{1}$.590	5.836	22.5	
o-F	22.4	$\bar{1}$.740	5.872	24.0	
o-OH	27.0	$\bar{1}$.055	5.987	22.0	
m-NO_2	22.0	$\bar{1}$.565	5.863	23.0	$\bar{1}$.6[a]
m-I	23.2	0.155	5.892	22.5	
m-Br	21.4	0.150	5.847	20.0	
m-F	28.0	0.215	6.013	23.5	
p-NO_2	21.2	$\bar{1}$.535	5.837	20.0	$\bar{1}$.5[a]
p-I	22.0	0.305	5.860	21.5	
p-Br	24.2	0.325	5.917	22.0	
p-Br	23.6	0.305	5.902	23.5	

[a] Guss and Kolthoff, THIS JOURNAL, **62**, 249 (1940). The value reported in an earlier paper (Minnick and Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939)) for the equilibrium constant between brom phenol blue and benzoate is apparently in error, necessitating a correction in the values reported in Table VII of that paper.

In Figs. 3, 4 and 5, the logarithm of the relative acid strength $K_{A_xB_0}$ is plotted against the reciprocal of the dielectric constant for the solvents water, methyl alcohol and ethyl alcohol. For

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(4) Kolthoff and Guss, THIS JOURNAL, **60**, 2517 (1938); **61**, 330 (1939).

TABLE III

RELATIVE ACID STRENGTHS

Substituent	$K_{A_xB_0}$ ortho	meta	para	para, calcd.
NO_2	67.8	17.6	18.9	6.5
I	13.8	4.53	3.20	1.8
Br	16.6	4.58	3.07	2.0
Cl	14.7	4.04	3.23	2.0
F	11.8	3.95	1.70	1.9
CH_3	1.14	0.84	0.64	0.83
OCH_3	..	....	0.40	..
OH	57.0	0.655	0.41	

the ortho substituted acids the relative strengths decrease with decreasing dielectric constant in the case of the nitro, iodo, bromo and chloro and methyl substituents but increase for the fluoro, methoxy and hydroxy substituents. For meta and para substitution there is an increase with decreasing dielectric constant except in the case of methoxy and methyl substitution, where the effect is small. The values of log $K_{A_xB_0}$ for the hydroxy acids do not show the linear relationship. This may be due to the fact that the second dissociation constant is close enough to the first dissociation constant to cause interference. This difficulty has been noted in aqueous solution in the case of *p*-hydroxybenzoic acid, and should be more important in non-aqueous solution as the dissociation constants would probably be nearer together.

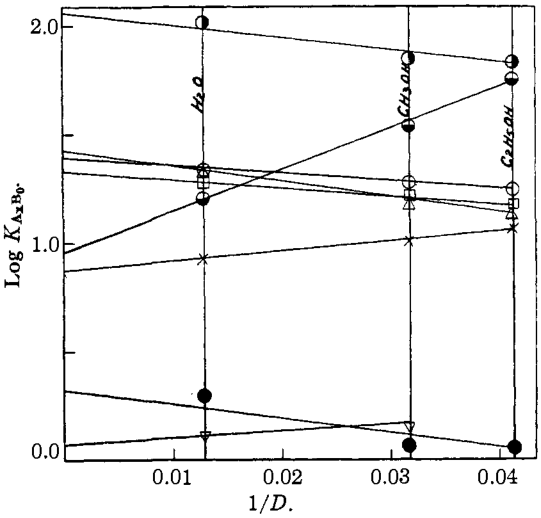

Fig. 3.—Relation between $K_{A_xB_0}$ and dielectric constant of ortho substituted acids: ○, Br; ◑, NO_2; ●, CH_3; ⊖, OH; □, Cl; △, I; ×, F; ▽, OCH_3.

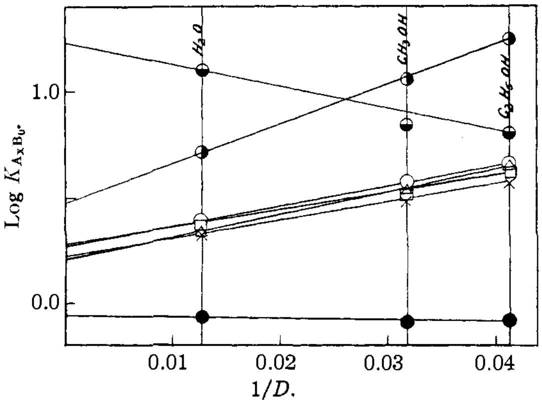

Fig. 4.—Relation between $K_{A_xB_0}$ and dielectric constant for meta substituted acids: ○, Br; ●, CH_3; ◑, NO_2; ⊖, OH, up 1.0; □, Cl; △, I; ×, F.

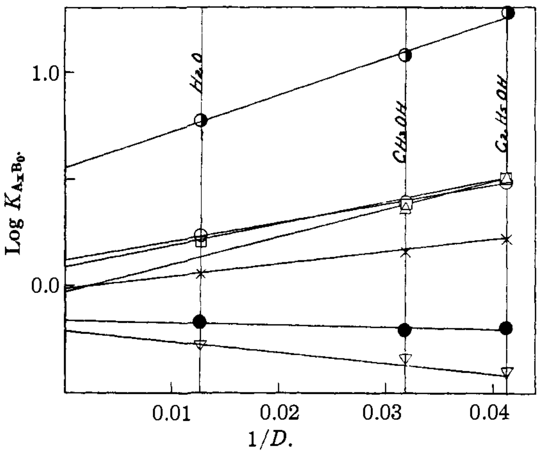

Fig. 5.—Relation between $K_{A_xB_0}$ and dielectric constant for para substituted acids: ○, Br; ◑, NO_2; ●, CH_3; □, Cl; △, I; ×, F; ▽, OCH_3.

On the basis of the electrostatic effect of a substituent it is to be expected that the slopes will increase with decreasing dielectric constant since D_E, the effective dielectric constant, decreases with decreasing dielectric constant (see equation (5) of the previous paper). The exceptions are found in the cases where the dipole moment is small and the electrostatic effect no longer predominates. The dipole moment of toluene (μ = 0.40 Debye unit) compared to chlorobenzene (μ = 1.5 Debye units) indicates that the meta and para toluic acids will not differ greatly from benzoic acid in strength nor will a change in dielectric constant cause any great change in the relative acid strength as far as electrostatic effects are concerned.

The negative slopes in the case of the *o*-halogen and *o*-nitro acids may be explained on the basis of a chelation of the carboxyl hydrogen with the substituent group and an increase of this effect with decreasing dielectric constant of the medium. In the case of the fluoro acid this chelation is unlikely[5] and a predominance of electrostatic effects is in agreement with a positive slope. No explanation is offered for the negative slope of *o*-toluic acid. Branch and Yabroff[6] offer an explanation for the positive slope of salicylic acid. The general qualitative treatment of the effect of substituents based upon the electronic theory of valency has been reviewed recently by Dippy.[7]

The values of the intercept, log $K_{A_xB_0}$, the acid strengths relative to benzoic acid in a medium of infinite dielectric constant, are given in Table IV together with the slopes of the lines in Figs. 3, 4 and 5.

TABLE IV

VALUES OF LOG $K_{A_xB_0}$ AND L

Substituent	Log $K_{A_xB_0}$	L	ΔS_{el} H_2O	ΔS H_2O literature	ΔS_{el} CH_3OH	ΔS_{el} C_2H_5OH
			Ortho acids			
NO_2	2.05	−5.2	−0.4	−2.4	−1.2	−1.8
I	1.43	−7.1	−0.6	−5.1	−1.7	−2.4
Br	1.40	−4.5	−0.4		−1.1	−1.6
Cl	1.33	−3.8	−0.3	−2.6	−0.9	−1.3
F	0.87	+4.6	0.4		1.1	1.6
CH_3	0.33	−6.5	−0.5	−3.5	−1.5	−2.2
OCH_3	0.08	2.7	0.12		0.6	
OH	0.95	19	1.56	8.7	4.4	6.5
			Meta acids			
NO_2	0.48	18.5	1.5	4.2	4.3	6.3
I	0.22	10	0.9	1.9	2.5	3.6
Br	0.27	9.5	0.8		2.2	3.2
Cl	0.28	8.2	0.7		1.9	2.8
F	0.22	8.8	0.7		2.0	3.0
CH_3	−0.06	−0.55	−0.05	−0.3	−0.1	−0.2
OH	0.23	−10	−0.9	−0.8	−2.4	−3.4
			Para acids			
NO_2	0.55	17	1.4		4.0	5.8
I	−0.03	13	1.1		3.0	4.5
Br	0.12	8.9	0.7		2.1	3.0
Cl	0.09	9.9	0.8		2.3	3.4
F	−0.02	5.9	0.5		1.4	2.0
CH_3	−0.16	−1.0	−0.1	0.0	−0.2	−0.3
OCH_3	−0.21	−5.0	−0.4	1.1	−1.2	−1.7

ΔS in cal./degree

The relationships

$$V_{el} = -\frac{2.303\ LRT}{D} \tag{4}$$

and

$$\Delta S_{el} = \frac{d \ln D}{dT} V_{el} \tag{5}$$

have been discussed elsewhere.[8,9] V_{el} is equal to the electrostatic work of transfer of the products of the reaction from a medium of dielectric constant D to one of infinite dielectric constant, minu- the work of transfer of reactants; ΔS_{el} is the ens tropy change for the same process; L is the slope of the line, and D the dielectric constant. Since $d \ln D/dT$ is known for each solvent, ΔS_{el} can be calculated, and compared with ΔS values calculated from ΔF and ΔH by Everett and Wynne-Jones,[10] for the solvent water. A comparison of columns 4 and 5 of Table IV shows that ΔS_{el} calculated from the dielectric change is of the correct sign but smaller than ΔS calculated from temperature coefficient measurements. This confirms the conclusions of Everett and Wynne-Jones[10] and Baughan[11] and indicates that another factor, the entropy of solvation of the ions, must be considered.

Summary

1. The effect of ionic strength on the constants for the equilibrium between certain indicator acids and the anions of monosubstituted benzoic acids has been determined at ionic strengths < 0.02.

2. The acid strengths relative to benzoic acid have been computed and compared with the results in the solvents water and methyl alcohol.

3. Intrinsic acid strengths have been determined by extrapolation.

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[5] Sidgwick, "Electronic Theory of Valence," Oxford University Press, Oxford, 1932, p. 291.

[6] Branch and Yabroff, THIS JOURNAL, **56**, 2568 (1934).

[7] Dippy, *Chem. Rev.*, **25**, 151 (1939).

[8] Kilpatrick, *J. Phys. Chem.*, **43**, 294 (1939).

[9] Kirkwood, *ibid.*, **43**, 294 (1939).

[10] Everett and Wynne-Jones, *Trans. Faraday Soc.*, **35**, 1380 (1939).

[11] Baughan, *J. Chem. Phys.*, **7**, 951 (1939).