Unfortunately, there appears to exist no method by which the degree of what might be termed the "quasi-crystalline structure" of these concentrated electrolyte solutions can be evaluated. Observations of their Raman spectra and temperatures of maximum density indicate an increasing degree of derangement of the tetrahedral structure of water with increasing salt concentration, and show that both the cation and anion exert marked effects on its extent, but they are unable to give any information about the orderliness of the arrangement of the ions even in the bulk of the solution, let alone the considerably more complicated arrangement which must prevail in the neighborhood of the drop.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY]

Effect of Substituents on the Protolytic Constants of Anilinium Type Protolytes[1a,b]

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The protolytic reaction constant of *o*-, *m*- and *p*-nitroanilinium ions, *o*-, *m*- and *p*-chloroanilinium ions, *o*-, *m*- and *p*-methylanilinium ions, *m*- and *p*-fluoroanilinium ions, *p*-dimethylaminoazobenzene and *m*-nitro-*p*-methylanilinium ions have been determined by a colorimetric method in the solvents water, anhydrous methanol and anhydrous ethanol. The effect of small amounts of water on the protolytic constants in anhydrous methanol has been determined. The relative order of the protolytic constants in the various solvents is discussed on a structural basis and comparisons made with the phenol and benzoic acid series. The Hammett relationship is expanded to include the ortho position. Comparisons between calculations of the protolytic constant by means of electrostatic considerations are made with the observed data, and the validity of the Sarmousakis theory with respect to both substituents and solvent is evaluated.

Many data concerning the equilibrium constants of reactions between the anilinium ions and the various hydroxylic solvents have accumulated in the literature. Since a fairly complete series of these protolytic reactions has not been studied by a single investigator using a single method (especially in anhydrous solvents), this investigation was begun to provide an internally consistent set of equilibrium constants for such reactions. This set of internally consistent data leads to some correlation between the structural features of the molecules and the relative magnitudes of the equilibrium constants of the reactions involving these molecules.

The structurally related protolytes investigated were the anilinium ion and various substituted anilinium ions: the *o*-, *m*- and *p*-chloro-; the *o*-, *m*- and *p*-nitro-; the *o*-, *m*- and *p*-methyl-; the *m*- and *p*-fluoro-; the *m*-nitro-*p*-methyl-; and *p*-dimethylaminoazobenzene (butter yellow, hereinafter abbreviated BY).

The equilibria studied may be represented by

$$A_1 + B_2 \rightleftarrows A_2 + B_1 \qquad (1)$$

where the essential structural difference between A and B is a proton.

When B_2 is the solvent S, eq. 1 becomes

$$A^+ + S \rightleftarrows SH^+ + B \qquad (2)$$

where A^+ represents an anilinium ion and SH^+ represents the solvated proton. Therefore

$$K_S = (C_{SH^+}/C_S)\cdot(C_B/C_{A^+}) \qquad (3)$$

where K_S is the concentration protolysis constant. Limiting values obtained at infinite dilution are designated by superscript zero, *e.g.*, K^0_S.

The conventional protolysis constant is

$$K_C = K_S C_S \qquad (4)$$

When, in eq. 1, A_1 is the indicator A_i, then

$$K_{A_iB} = (C_{B_i}/C_{A_i})\cdot(C_A/C_B) \qquad (5)$$

The evaluation of this equilibrium constant is, experimentally, a matter of determining the concentrations at equilibrium of the various species involved. Here the ratio C_{B_i}/C_{A_i} was determined from colorimetric measurements.

For the protolytic reaction between the substituted anilinium ions and aniline eq. 1 becomes

$$A_x + B_o \rightleftarrows A_o + B_x \qquad (6)$$

where the subscript o refers to aniline and the subscript x refers to the substituted aniline. Therefore, the protolytic constant is

$$K_{A_xB_o} = (B_x/A_x)\cdot(A_o/B_o) \qquad (7)$$

in which the solvent is implicit in species solvation.

The advantages of using the ratio of the protolysis constants, $K_{A_xB_o}$, rather than the conventional protolysis constants, are: (1) the elimination of the need to know autoprotolysis constants when comparing with the data of different investigators; (2) its lower sensitivity (of $K_{A_xB_o}$) to small changes in the medium and (3) its emphasis on substituent effects.

Experimental

Procedure.—The indicator used at the start of the investigation was butter yellow (BY), whose acid–base forms are the same charge type as anilinium–aniline. This proved satisfactory in water and methanol but not in ethanol. The indicator *m*-nitro-*p*-methylaniline was used in ethanol.

The determination of the protolytic constant, K_{A_iB}, involved (1) the fixing of the buffer ratio A/B and (2) the measurement, spectrophotometrically, of the ratio B_i/A_i. When Beer's law obtained, the ratio B_i/A_i was determined by the relationship

$$\text{Fraction } A_i = -\frac{\log(I_r/I_x) - \log(I_r/I_{B_i})}{\log(I_r/I_{B_i}) - \log(I_r/I_{A_i})} \qquad (8)$$

where I denotes the light intensity transmitted through the

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(1) (a) In order to avoid the semantic difficulties inherent in the terms *acid* and *base*, Brönsted terminology will be used throughout. (b) This paper was extracted from the dissertation presented by C. Arne Arenberg to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1952.

cell; the subscript r refers to the reference cell, and A_i, B_i and x to solutions containing the indicator completely in the A_i form, completely in the B_i form and a mixture of both forms, respectively.

Equation 9 shows Beer's law explicitly

$$\text{Fraction } A_i = -\frac{\log(I_r/I_x)_{\text{cor.}} - \text{intercept}}{\text{slope} - \log(I^0/I_{B_i})} \qquad (9)$$

where slope and intercept refer to the Beer's law curve, subscript cor. is optical density corrected for the optical density of the B_i form of the indicator and I^0 is the light intensity through the working cell containing only the solvent.

Equation 9 for a one-color indicator reduces to

$$\text{Fraction } A_i = -\frac{\log(I_r/I_x) - \text{intercept}}{\text{slope}} \qquad (10)$$

Thus

$$\frac{C_{B_i}}{C_{A_i}} = \frac{\text{Fraction } B_i}{\text{Fraction } A_i} \qquad (11)$$

When Beer's law does not obtain, a calibration curve must be used. In either instance, knowledge of the absolute concentration of the indicator is unnecessary.

Three experimental quantities, I_r/I_x, I_r/I_{B_i} and I_r/I_{A_i}, were used for the evaluation of the ratio B_i/A_i. The first two were determined readily; but the third, for the indicator BY, with difficulty because BY is a diprotic protolyte. The hydrogen ion concentration range in which one could obtain the indicator as essentially BYH^+ with negligible amounts of BYH_2^{++} and BY present was determined by a spectrophotometric titration of the indicator with hydrochloric acid. In water and methanol the two equilibria did not overlap appreciably and therefore the indicator was satisfactory in these solvents.

With the ratio B_i/A_i determined, K_{A_iB} is calculable, since the buffer ratio A/B is determinable from the stoichiometric composition of the particular solution by the application of the usual buffer corrections.

When A/B was SH^+/S, the indicator buffer ratio was adjusted by using hydrochloric acid. The assumption was used that HCl in solution was completely dissociated into SH^+ and Cl^- ions. This assumption worked well in water and methanol, but not as well in ethanol, where ion association becomes appreciable. Data in the literature[2] indicate that HCl is still a fairly strong electrolyte in ethanol (α = 0.93 at 10^{-3} *M*) and that the same is true for NH_4Cl. Ion pair formation as a physical interaction can be treated by extrapolation. In these solutions the concentration of HCl was corrected for its contribution to the BH^+ form of the indicator. $K^0_{A_iB}$ could then be obtained by extrapolation or, if the electrolyte concentration were low enough ($\sim 10^{-3}$ *M*), by setting $K^0_{A_iB} = K_{A_iB}$. The protolytic constant, $K^0_{A_xB_o}$, can now be calculated from values of $K^0_{A_iB}$ for aniline and the corresponding substituted aniline.

Apparatus.—A spectrophotometer was constructed which could detect very small changes in absorption, *i.e.*, changes in the I/I_r ratio of as little as 0.02%. A stable light source consisted of two automobile-type 6–8 volt bulbs. One was rated at 6 c.p. (G-E 82) and was used with the indicator BY in the 5000 Å. region. The other was rated 15 c.p. (G-E 88) and was used with the nitro compounds in the 4000 Å. region. The power supply consisted of high capacity storage batteries (Willard DH-5). The light bulb was mounted in a ventilated can with a collimating lens as a window. No measurable drift was observed over a five-minute period after sufficient warm-up.

An air thermostat was constructed to contain the absorption cells during a set of measurements. The insulation consisted of inch-thick Celotex. The desired temperature was maintained by a thermoregulator which operated a water pump. This pump circulated water of controlled temperature through copper tubing lining the wall of the air thermostat. This temperature was controllable to within 0.1° between any two points in the air thermostat and to within 0.05° at any given point. A slow stream of dry clean air was circulated through the system to improve heat transfer and to prevent condensation of moisture on the cell windows on hot, humid days.

The absorption cells (Aminco) were a matched pair, with optical paths 24.794 and 24.795 mm. long, fitted with ground glass-stoppered necks and having a volume of approximately 6 ml. They were mounted with removable clamps on a sliding brass block in the air thermostat. The successive juxtaposition of the cells in the light beam was controllable by a rod attached to the brass mounting block and extending out of the air thermostat.

A Hilger spectrometer was converted from visual use by substituting a controllable-width exit slit for the eyepiece. to provide the desired monochromation. The wave length drum was calibrated by means of a mercury arc spectrum, and slit widths determined by means of closely spaced lines in the mercury spectrum. The slit widths used subtended *ca.* 30 Å. in the 5000 Å. and *ca.* 20 Å. in the 4000 Å. region.

The photocell used was one with an S4 surface (RCA 1P39). This cell, chosen instead of the RCA 929 which is identical in response because it had a special non-hygroscopic base, was mounted in an air-tight box that had a plane glass window. The air in this box was kept at very low humidity by use of Drierite.

The photocurrents were amplified by an RCA 954 vacuum tube in a circuit similar to that used by Klotz.[3] This tube was also mounted in the photocell box in order to keep the grid resistor (10^{12} ohms) dry. Null point measurements were obtained with a Leeds and Northrup student potentiometer and a General Electric GR-2 galvanometer.

Materials.—The liquid anilines were fractionally distilled into concentrated hydrochloric acid (C.P., Baker and Adamson) to give their hydrochlorides as white crystals. These hydrochlorides were recrystallized from ethanol, collected on a fritted glass funnel, washed several times with freshly distilled acetone and dried in a vacuum desiccator.

Each of the nitroanilines and *m*-nitro-*p*-methylaniline (Antara Products) was dissolved in hot water, each hot solution treated with Norite decolorizing charcoal, filtered hot, and chilled to precipitate the nitroanilines. Each precipitate was recrystallized from ethanol and dried in a vacuum desiccator. *p*-Methylaniline was purified in this manner and its hydrochloride prepared and purified as with the liquid anilines.

The indicator BY (Matheson) was recrystallized and further purified by chromatography on a silicic acid column.

Lithium chloride (J. T. Baker Analyzed) was recrystallized from concentrated HCl, fused in an atmosphere of dry HCl gas and cooled in an atmosphere of dry nitrogen. The mass was pulverized in a dry box and stored in a vacuum desiccator. The moisture content was determined by the Karl Fischer reagent[4] and found to be 0.05% by weight. The LiCl was tested for excess acidity and basicity in dilute aqueous solution.

The solvents methanol and ethanol were prepared by the method of Bjerrum and Lund[4a] and were stored in two-liter ground glass-stoppered Pyrex bottles in the dry box where they were used. The water content of the alcohols[4] did not exceed 0.02%.

All solid materials were finally dried under vacuum in an Abderhalden pistol. The purity of the hydrochlorides was determined by both melting point and titration; the purity of the nitroanilines, *p*-methylaniline and the indicators, by melting point alone. All of the compounds were stored in a desiccator over Drierite.

All solutions were made up in a set of calibrated volumetric flasks which were selected to differ by not more than 0.1% from their inscribed values.

Through the use of calibrated pipets, similar to those of Minnick and Kilpatrick,[5] the alcohol solutions were made up in the dry box and transferred to the absorption cells by means of a pipet guarded against moisture. The amount of moisture absorbed by the solutions, as handled, was within the experimental error of the Karl Fischer titration, 0.005%.

Solutions of lithium methoxide and lithium ethoxide were made in the dry box by dissolving metallic lithium (Eimer and Amend) in the appropriate alcohol. These solutions were standardized by titration of an aliquot in a large volume of water with standard hydrochloric acid.

Discussion

The Indicators.—The absorption curve of the indicator BY is shown in Fig. 1; (the concentra-

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[2] B. Bezman and F. H. Verhoek, THIS JOURNAL, 67, 1330 (1945).

[3] I. Klotz, Ph.D. Dissertation, University of Chicago (1940).

[4] J. Mitchell, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948.

[4a] J. Bjerrum and H. Lund, *Ber.*, **64B**, 210 (1931).

[5] L. Minnick and M. Kilpatrick, *J. Phys. Chem.*, **43**, 259 (1939).

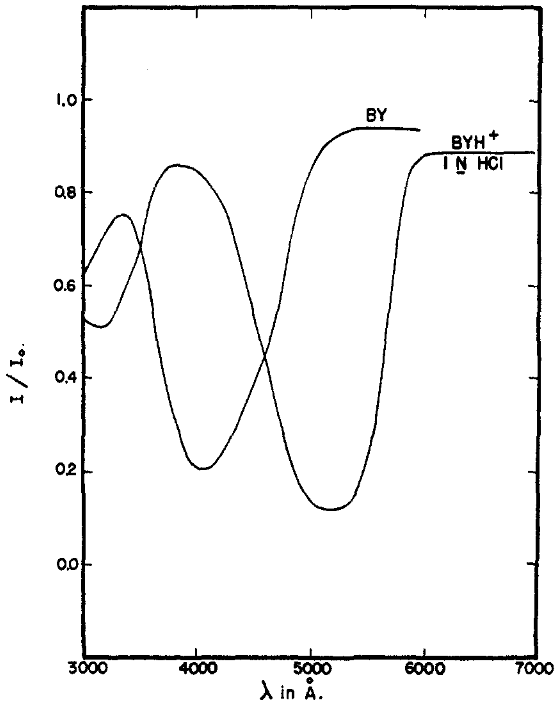

Fig. 1.—Absorption curve of BY in water.

tions of BY and BYH$^+$ are different) the absorption maximum of BYH$^+$ is near 5000 Å. while that of BY is near 4000 Å. and has a much smaller extinction coefficient. The maximum difference in absorption between BYH$^+$ and BY occurring at about 5200 Å. led to the measurements of absorption by BYH$^+$ at 5200 Å. The absorption curves of the nitroanilines are shown in Fig. 2.

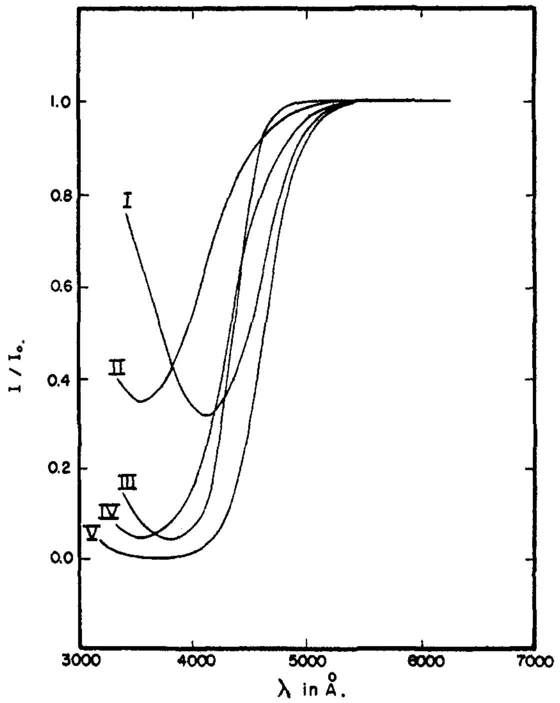

Fig. 2.—Absorption curves of the nitroanilines: I, *o*-nitroaniline in water; II, *m*-nitroaniline in water; III, *p*-nitroaniline in water; IV, *m*-nitro-*p*-methylaniline in water; V, *m*-nitro-*p*-methylaniline in ethanol.

Since BYH$^+$ was capable of accepting a second proton to form BYH$_2^{++}$, absorption by the indicator as a function of hydrochloric acid concentration was studied. Approximate protolysis constants were calculated for $BYH_2^{++} \rightleftarrows BYH^+ + H^+$ from these spectrophotometric titration curves, and also for *m*-nitro-*p*-methylanilinium ion and for BYH$^+$ (Table I). $K_{A^{++}}$ (0.6 *M* HCl in water) = 20 as compared to the values of Rogers and coworkers[6] of 10^4 in concentrated sulfuric acid; $K_{A^{++}}$ (0.19 *M* HCl in methanol) = 6; $K_{A^{++}}$ (0.046 *M* HCl in ethanol) = 0.3. An approximate K_c^0 for BYH$^+$ in ethanol is 1×10^{-3}, compared to 2.8×10^{-4} obtained by Kolthoff and Guss.[7]

TABLE I

PROTOLYSIS CONSTANTS OF THE INDICATORS AT 25.0°

Solvent	K_A^{0+} Butter yellow	K_A^{0+} *m*-NO$_2$-*p*-CH$_3$-aniline	K_A^{++a} Butter yellow
Water	5.94×10^{-4}	1.1×10^{-3}	20 (0.6 *M* HCl)
Methanol	4.47×10^{-4}		6 (.19 *M* HCl)
Ethanol	1×10^{-3}	3.63×10^{-4}	0.3 (.047 *M* HCl)

[a] $K_{A^{++}} = (C_{BYH^+}/C_{BYH_2^{++}})(C_{SH^+})$.

K_c for BY in water was determined at temperatures ranging from 18 to 35°. These results are shown in Table II. The effect of small amounts of ethanol in water on the value of K_c^0 for BYH$^+$ is shown in Table III.

TABLE II

K_c FOR BY AS A FUNCTION OF TEMPERATURE

t, °C.	$1/T°A \times 10^3$	$K_c^0 \times 10^4$	$-\log K$
18.0	3.434	5.01	3.300
18.0	3.434	5.04	3.298
24.0	3.365	5.82	3.235
25.0	3.354	5.94^a	3.226
32.0	3.277	6.99	3.155
33.0	3.266	7.12	3.144
35.0	3.245	7.54	3.123
35.0	3.245	7.58	3.120

[a] Average of several determinations: $\log K_c^0 = -932.1/T - 0.0981$; $\Delta H = -4.30$ kcal.

TABLE III

EFFECT OF ETHANOL IN WATER AT 26.0°

Wt. % ethanol in water	0.0	0.158	0.315	0.631
$K_c^0 \times 10^4$ (BYH$^+$)	6.11^a	6.22	6.32	6.50

[a] Calculated from Table II.

This average value of K_c of 5.02×10^{-4} at 18° is in close agreement with 5.1×10^{-4} obtained by Güntelberg and Schiödt.[8] These workers dissolved BY in ethanol before making up their aqueous stock indicator solution. Their ethanol concentration was approximately 0.1% by weight. If a correction is made for ethanol concentration, the value of Güntelberg and Schiödt becomes 5.0×10^{-4}.

Since a solution of BY changes from yellow to red to colorless with increasing hydrogen ion concentration, and since the nitroanilinium ions are

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(6) M. Rogers, T. Campbell and R. Maatman, THIS JOURNAL, **73**, 5122 (1951).

(7) I. Kolthoff and L. Guss, *ibid.*, **62**, 249 (1940).

(8) E. Güntelberg and E. Schiödt, *Z. physik. Chem.*, **A135**, 393 (1928).

TABLE IV

MEASURED VALUES OF K^0_{AiB}

	Protolyte pair Indicator	Other	Water		Methanol	
1	o-NO$_2$AnH$^+$	Solvent	3.28×10^{-3}	±2.0%	2.03×10^{-2}	±2.0%
2	p-NO$_2$AnH$^+$	Solvent	1.84×10^{-3}	±1.2	1.63×10^{-3}	±1.0
3	m-NO$_2$AnH$^+$	Solvent	6.2×10^{-5}	±1.2	4.0×10^{-5}	±2.3
4a	m-NO$_2$AnH$^+$	o-ClAn	1.53	±1.3	3.27	±1.2
4b	m-NO$_2$AnH$^+$	o-ClAn	1.49[a]		3.23[a]	
5	BYH$^+$	o-ClAn	0.257	±1.7	1.13	±1.2
6	BYH$^+$	Solvent	1.07×10^{-5}	±2.0	1.40×10^{-5}	±2.0
7	BYH$^+$	m-ClAn	1.29	±1.2	8.39	±1.2
8	BYH$^+$	m-FAn	1.45	±1.1	10.0	±1.3
9	BYH$^+$	p-ClAn	3.94	±1.2	28.3	±1.7
10	BYH$^+$	o-CH$_3$An	14.7	±1.7	2.34×10^2[b]	±1.5
11	BYH$^+$	p-FAn	20.2	±2.0	1.36×10^2[b]	±1.0
12	BYH$^+$	An	23.3	±1.7	2.85×10^2[b]	±1.9
13	BYH$^+$	m-CH$_3$An	28.6	±2.0	4.40×10^2[b]	±1.9
14	BYH$^+$	p-CH$_3$An	73.3	±2.4	9.72×10^2[b]	±2.0
15	BYH$^+$	Benzoate	9.58			
16	BYH$^+$	o-NO$_2$-benzoate			1.55×10^4[b]	
17	m-NO$_2$ p-CH$_3$ AnH$^+$	Solvent	1.98×10^{-5}	±1.2		

[a] Calculated from protolyte pairs 3, 5 and 6. [b] No lithium methoxide added for buffering.

colorless, the addition of the first proton is probably not at the amino group. Consideration of various resonance forms of BY reveals that the electron density in the region of the azo-nitrogen is probably higher than that in the region of the amino nitrogen. This should lead to the protonation of the former first. The second protonation should occur at the amino group in concordance with the solution of BY becoming colorless in concentrated HCl. These conclusions are in accordance with those of Rogers and co-workers[6] who measured the protolysis constants of BYH$_2^{++}$ and BYH$^+$.

TABLE V

MEASURED VALUES OF K^0_{AiB} IN ETHANOL

	Protolyte pair Indicator	Other	K^0_{AiB}	
1	o-NO$_2$AnH$^+$	Ethanol	7.2×10^{-2}	±10%
2	p-NO$_2$AnH$^+$	Ethanol	4.5×10^{-3}	± 5.0
3	m-NO$_2$AnH$^+$	Ethanol	4.9×10^{-5}	± 2.2
4	m-NO$_2$-p-CH$_3$AnH$^+$	Ethanol	7.9×10^{-6}	± 2.0
5	m-NO$_2$-p-CH$_3$AnH$^+$	o-ClAn	1.06	± 2.2
6	m-NO$_2$-p-CH$_3$AnH$^+$	m-ClAn	7.94	± 2.4
7	m-NO$_2$-p-CH$_3$AnH$^+$	m-FAn	9.55	± 2.5
8	m-NO$_2$-p-CH$_3$AnH$^+$	p-ClAn	24.2	± 2.5
9	m-NO$_2$-p-CH$_3$AnH$^+$	p-FAn	1.27×10^2[a]	± 2.3
10	m-NO$_2$-p-CH$_3$AnH$^+$	o-CH$_3$An	2.25×10^2[a]	± 2.6
11	m-NO$_2$-p-CH$_3$AnH$^+$	An	2.84×10^2[a]	± 2.5
12	m-NO$_2$-p-CH$_3$AnH$^+$	m-CH$_3$An	5.56×10^2[a]	± 2.7

[a] No lithium ethoxide added for buffering.

TABLE VI

K_{AxBo} FOR SUBSTITUTED ANILINIUM IONS IN WATER. REFERENCE BASE ANILINE

Substituent	This investigation colorimetric 25°	Hammett[a] colorimetric 25°	Goldschmidt[b] conductimetric 20°	Brönsted[c] e.m.f. 19°	Kinetic 15°
o-NO$_2$	7.16×10^4	5.5×10^4			
p-NO$_2$	4.02×10^3	2.9×10^3			
m-NO$_2$	1.36×10^2	0.87×10^2			
o-Cl	90.7			129	89
m-Cl	18.1		12.5	14.6	15.3
m-F	16.0				
p-Cl	5.92		5.0	4.75	4.42
o-CH$_3$	1.59		1.6	1.36	1.58
p-F	1.16				
m-CH$_3$	0.81		0.87		
p-CH$_3$	0.32		0.29		

[a] L. P. Hammett, THIS JOURNAL, **52**, 5115 (1930); *ibid.*, **54**, 3469 (1932); *ibid.*, **56**, 827 (1934); *ibid.*, **59**, 96 (1937). [b] H. Goldschmidt, *Z. physik. Chem.*, **A99**, 116 (1921); *ibid.*, **A112**, 423 (1924); *ibid.*, **A119**, 439 (1925). [c] J. N. Brönsted and H. C. Duus, *ibid.*, **A117**, 299 (1925).

Precision.—The precision of the protolytic constants of Tables IV through VII depends upon: (1) The linear response of the spectrophotometer. This was reproducible within 0.05%.

TABLE VII

K^0_{AxBo} FOR SUBSTITUTED ANILINIUM IONS IN METHANOL AND ETHANOL, REFERENCE BASE ANILINE

	Methanol		Ethanol	
Substituent	This investigation colorimetric 25°	Goldschmidt[a] conductimetric 20°	This investigation colorimetric 25°	Goldschmidt[a] conductimetric 20°
o-NO$_2$	4.1×10^5		2.6×10^6	
p-NO$_2$	3.3×10^4		1.61×10^5	
m-NO$_2$	8.1×10^2		1.75×10^3	
o-Cl	252.1	270	268.6	275
m-Cl	34.0	36.0	35.8	31
m-F	28.5		29.4	
p-Cl	10.1	12	11.7	11
p-F	2.09		2.23	
o-CH$_3$	1.27	1.2	1.26	1.25
m-CH$_3$	0.65	0.61	0.51	0.65
p-CH$_3$	0.29	0.28		0.27

[a] See reference *b*, Table VI.

(2) The exact repositioning of the cell for each measurement to assure constancy in the optical path. The reproducibility of a given measurement of optical density was within 0.05% of the mean of a series of measurements of optical density on a given solution.

(3) Accurate thermostating. K_c for BYH$^+$ changes about 2.3% per degree. This corresponds

to a change of about 0.1% for 0.05° and would have the same effect on the calculation of various protolytic constants as if the hydrogen ion concentration had changed by 0.1%. Actually, any one spot in the air thermostat was usually constant to better than ±0.05° and the temperature of the solutions would change more slowly than that of the air.

(4) The precision of making up solutions. The reproducibility of the stoichiometric concentrations of all of the solutes was better than 0.5% even when aliquots of stock solutions of 1 ml. were used in making up the operating solutions. At worst, this would produce an error of 1% in the value of the protolytic constants.

(5) Possibility of side reactions. Hydrochloric acid may react with methanol or ethanol. Measurements of the optical density of a given indicator solution containing HCl were constant within the reproducibility of the spectrophotometer over a period of 24 hours.

(6) The effect of small amounts of water (of the order of 0.02%) on K_c in methanol. This was less than 1.0%. In the handling of the solutions, no more than 0.005% water was picked up and the original solvent contained no more than 0.02% water.

(7) Errors in extrapolation of the various protolytic constants in water and methanol. These were within the precision of any given K and were slightly larger in ethanol due to the steeper slope. The extrapolation error in ethanol was at worst 2.0%.

(8) Proximity of the ratio B_i/A_i to unity. When, in the determination of K_{A_iB}, the ratio of B_i/A_i was greater than 5/1, the use of the particular aniline hydrochloride was preferred without the addition of NaOH (in methanol and ethanol, LiOMe and LiOEt, respectively) since the primary determination using BY was the fraction A_i. The smaller the fraction A_i, the larger the error in measuring the fraction A_i and, consequently, the larger the error in the ratio B_i/A_i. When *m*-nitro-*p*-methylaniline was used as an indicator, the fraction B_i, when $B_i >> A_i$, produces a large error in A_i and, consequently, a large error in the ratio B_i/A_i. Alkali was not added since another indicator of the same charge type as the anilinium ion, with a smaller K_c value, was not available, and since the errors of extrapolation inherent in the use of a different charge type indicator (especially in ethanol) would probably be as great as the errors obtained by not using a well buffered solution.

From the reproducibility of duplicate determinations, and from the internal consistency of the data in any given set, the precision of the protolytic constants in water and methanol is at least ±2.0%, and in ethanol, at least ±3.0%. The one exception to this is the value of the $K^0_{A_iB}$ for *o*-nitroaniline in ethanol presented in Table V. Here the extrapolation is doubtful since the protolysis constants could not be obtained with any great precision in dilute solution. This general precision is confirmed in Table IV, where are displayed the measured and calculated protolytic constants for the protolyte pair 4.

In order to correlate the data obtained in this investigation with the corresponding equilibrium constants for the benzoic acid series, K_{A_iB} for benzoic acid (protolyte pair 15, Table IV) was determined in water and K_{A_iB} for *o*-nitrobenzoic acid (protolyte pair 16, Table IV) was determined in methanol. However, no data could be obtained in ethanol since K_{A_iB} would be about 10^6 even for *o*-nitrobenzoic acid. K^0_c for benzoic acid in water, as found, is 6.2×10^{-5} as compared with 6.3×10^{-5}, the value of Saxton and Meier.[9] Thus, the precision in water is within 2.0%. K^0_c for benzoic acid in methanol was 4.15×10^{-10} as compared with 4.20×10^{-10}, the value of Morse.[10]

Effect of Electrolyte Concentration.—When the protolyte pairs were both substituted anilines, there was no detectable variation in K_{A_iB} up to 0.02 molar electrolyte concentration in water and methanol. When one of the protolyte pair was the solvent, the protolysis constant K_c showed the electrolyte effects (HCl) presented in Fig. 3. In ethanol, pronounced electrolyte (mainly LiCl) effects were observed for the protolytic constants of the protolyte pairs of substituted anilines (Fig. 4) as well as for protolysis constants for protolyte pairs including the solvent (Fig. 5).

Comparison with Literature.—From the K_{A_iB} values given in Tables IV and V, the protolytic constants, $K_{A_xB_0}$, for eq. 7 where B_0 represents aniline, have been calculated and are presented in Tables VI and VII. Other values were calculated from the data of those investigators whose work included the anilinium ion.

Since log $K^0_{A_xB_0}$ for *o*-chloroanilinium ion changes less than 0.002 log unit per degree,[11] reasonable comparisons with data not too far from 25° of other investigators can be made. The best check for the protolysis constant of *o*-chloroanilinium ion ($K^0_c = 2.31 \times 10^{-3}$) and anilinium ion ($K^0_c = 2.54 \times 10^{-5}$) in water is Pedersen's (K^0_c, *o*-Cl $= 2.32 \times 10^{-3}$ and K^0_c, anilinium ion $= 2.54 \times 10^{-5}$).

For the fluoroanilinium ions in water, only the K_c's of Bennett[12] are available. Their values are 3.9×10^{-4} (*m*-F) and 2.3×10^{-5} (*p*-F) which would give a $K^0_{A_xB_0}$ for *p*-fluoroanilinium ion of less than unity, using the K^0_c of anilinium ion obtained here. Our K_c values are 4.10×10^{-4} (*m*-F) and 2.94×10^{-5} (*p*-F). The best value for K^0_c in water of the anilinium ion is 2.54×10^{-5} and for *o*-chloroanilinium ion, 2.32×10^{-3} at 25°.

Positional Order.—The protolytic constants, $K_{A_xB_0}$, of the chloroanilinium and fluoroanilinium ions in any given solvent, are in the order ortho > meta > para. $K_{A_xB_0}$ gets smaller as either the chloro or fluoro group gets farther from the amino group. This suggests that here the prime effect is inductive.

The order of the protolytic constants, $K_{A_xB_0}$, of the nitroanilinium ions in any of the given sol-

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[9] B. Saxton and H. Meier, This Journal, **56**, 1918 (1934).

[10] J. Morse, Ph.D. Dissertation, Illinois Institute of Technology (1952).

[11] (a) K. J. Pedersen, *Kgl. Danske Videnskab. Selskab. Math.-fys.*, Medd. 14, No. 9 (1937); (b) *ibid.*, Medd. 15, No. 3 (1937).

[12] G. M. Bennett, G. L. Brooks and S. Glasstone, *J. Chem. Soc.*, 1821 (1935).

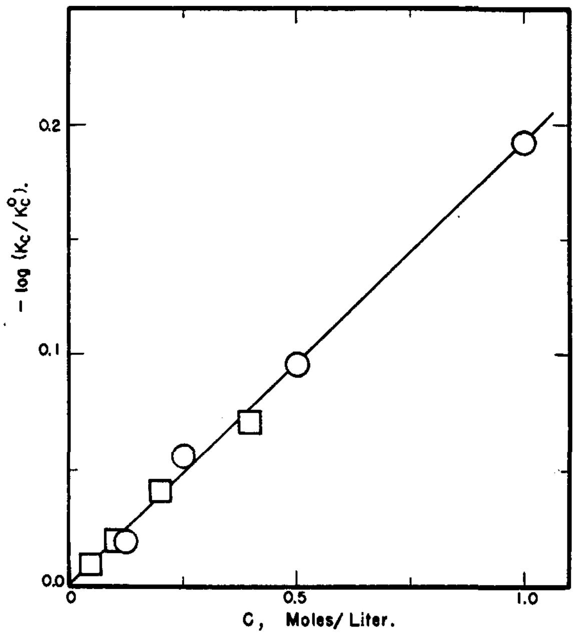

Fig. 3.—Log (K_c/K_c^0) *vs.* electrolyte (HCl) concentration in water: ○, *o*-nitroanilinium ion; □, *p*-nitroanilinium ion.

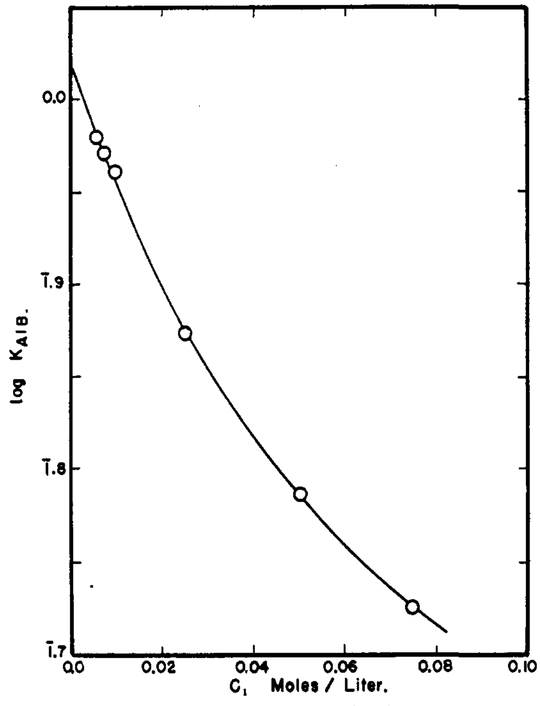

Fig. 4.—Log K_{AiB} *vs.* electrolyte (mainly LiCl) concentration in ethanol at 25.0° (protolyte pair *m*-nitro-*p*-methylanilinium ion, *o*-chloroaniline).

vents is ortho > para > meta. This is also the order of the absorption peaks, λ ortho > λ para > λ meta (see Fig. 2). This can be explained on the basis of the resonance effect being greater than the inductive effect. The greater wave length of the absorption peak for *o*-nitroaniline indicates that here the resonance energy contribution in the ortho position is greater than in the para position. This is demonstrable with one of the resonance forms of *o*-nitroaniline. Since coplanarity is one of the requirements for maximum resonance, chelation of the nitro with the amino group would tend to increase the coplanarity of the molecule.

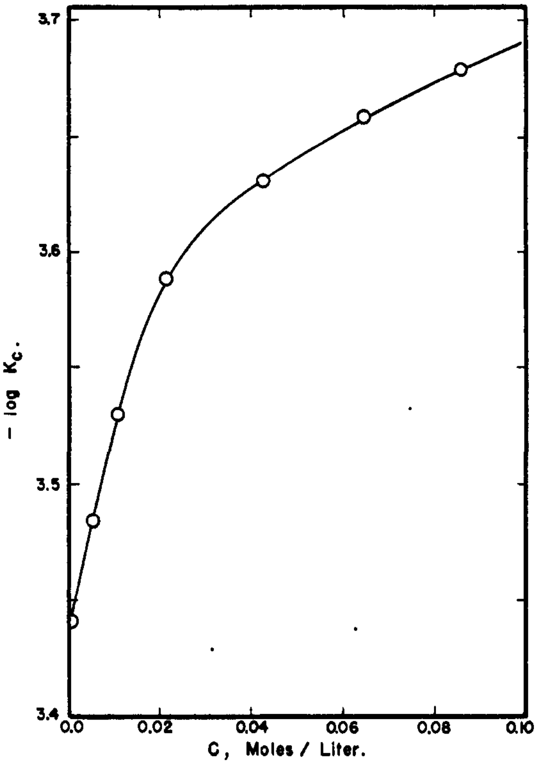

Fig. 5.—Log K_c *vs.* electrolyte (mainly LiCl) concentration for *m*-nitro-*p*-methylanilinium ion in ethanol at 25.0°.

The Fluorine Anomaly.—An article by Evans and co-workers[13] on the dissociation energy of fluorine (based on data for ClF rather than on the extrapolation of the dissociation energies of the other halogens) shows that the electron affinity of fluorine is less than that of chlorine. Therefore, the protolytic constant, $K_{A_xB_0}$, for the *m*-chloroanilinium ion is larger than that for the *m*-fluoroanilinium ion. Since the difference in electron affinities of chlorine and fluorine is slight, the substituent effects on the protolytic constants should be of the same magnitude. In the para position the difference in substituent effect is large. Fluorine does not have d-orbitals readily available whereas chlorine does. Therefore, *p*-chloroaniline should be more stable with a high electron density in the para position than *p*-fluoroaniline.

The Effect of Water on the Protolytic Constants in Methanol.—As shown in Table VIII, the effect of small amounts of water in methanol on the vari-

TABLE VIII

EFFECT OF WATER ON THE VARIOUS PROTOLYTIC CONSTANTS IN METHANOL

Water. wt. %	$10^4 K_0$ BYH$^+$ solvent	K_{AiB} BYH$^+$ An	BYH$^+$ o-CH$_3$An	$K_{A_xB_0}$ o-CH$_3$AnH$^+$ An
0.02	4.47	285	224	1.27
.25	5.78	283	224	1.26
.5	7.47	282	227	1.25
1.0	12.1	278	225	1.24
2.0	23.3	242	183	1.32

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[13] M. Evans. E. Warhurst and E. Whittle, *J. Chem. Soc.*, 1524 (1950).

ous protolytic constants is greatest for K_c, where the reactants have the greatest structural dissimilarity. Braude[14] determined K_c for *m*-nitroanilinium ion in the binary solvent system water–ethanol from pure water to pure ethanol and found a similar effect in the high ethanol range.

$K^0_{A_xB_0}$ and Dielectric Constant.—The variation of log $K^0_{A_xB_0}$ with the dielectric constant of the substituted anilinium ions seems to fall into three groups dependent on the kind of substituent. These substituents are (1) nitro, with a large and continual increase in log $K^0_{A_xB_0}$ with $1/D$; (2) halogen, with a marked increase of log $K^0_{A_xB_0}$ from water to methanol and a small change (not much greater than the experimental error) from methanol to ethanol; and (3) methyl, with a slight decrease of log $K^0_{A_xB_0}$ for the *m*-methylanilinium ion from water to ethanol, a decrease in log $K^0_{A_xB_0}$ for the *o*-methylanilinium ion from water to methanol and no change from methanol to ethanol, and a slight decrease in log $K^0_{A_xB_0}$ for the *p*-methylanilinium ion from water to methanol. Figure 6, for the *m*-substituents, shows the separation into these three classes.

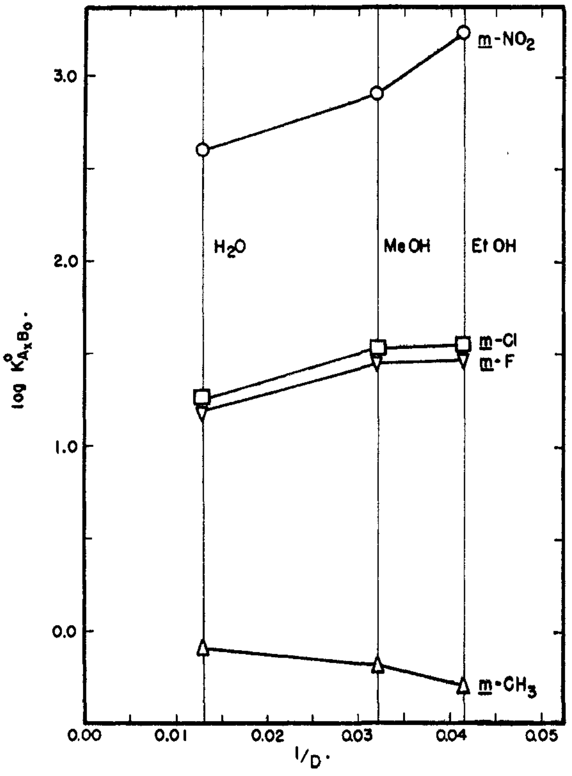

Fig. 6.—Relation between $K_{A_xB_0}$ and dielectric constant of the *meta*-substituted anilinium ions.

Substituent Effect and Protolyte Type.—Perhaps the outstanding feature of the anilinium type protolytes is the large effect of substituents, notably the nitro group, on $K_{A_xB_0}$. The protolytic constants (in water) of the benzoic acid series may be compared with those of the corresponding substituted anilinium ion in Table IX. The protolytic constants of the substituted phenol series are also included.

TABLE IX

SUBSTITUENT EFFECTS AND PROTOLYTE TYPE

Substituent	$K^0_{A_xB_0}$ (in water) Anilinium series	Phenol[a] series	Benzoic acid[b] series
o-NO₂	7.2×10^4	521	107
p-NO₂	4.0×10^3	647	6.00
m-NO₂	136	40.3	5.19
o-Cl	90.7	29.8	19.0
m-Cl	18.1	8.47	2.39
m-F	16.1		2.18
p-Cl	5.9	3.74	1.66
o-CH₃	1.59		1.97
p-F	1.16	1.38	1.15
m-CH₃	0.81		0.87
p-CH₃	0.32		0.68

[a] C. M. Judson and M. Kilpatrick, THIS JOURNAL, 71, 3115 (1949). [b] M. Kilpatrick and W. H. Mears, *ibid.*, 62, 3047 (1940).

The nitro group in the ortho position, besides having inductive and steric effects, contributes to the total stabilization of one of the protolyte forms by increasing the resonance energy and by chelation with the neighboring group. Both the increase in resonance energy and chelation will increase the stability of the acceptor form of *o*-nitroaniline. The increase in resonance energy will stabilize the acceptor form of *o*-nitrophenol, and chelation, the donor form. These opposing effects may account for the reversal in order of the protolytic constants in the *o*- and *p*-nitrophenols as against the anilinium compounds.

Bryson,[15] in studying the mono-nitronaphthylamines, found that when the nitro group was on the same nucleus as an amino group, its effect was similar to that in the nitroanilines, *i.e.*, largest when quinoid contributions are possible.

p-Fluoro and *p*-chloro protolytes may be compared. The ratios of the $K_{A_xB_0}$ for *p*-chloroanilinium ion and *p*-chlorophenol to the $K_{A_xB_0}$ of *p*-chlorobenzoic acid are 3.6 and 2.5, respectively. The corresponding ratios for the *p*-fluoro compounds are approximately unity. The difference is explained as in the section Fluorine Anomaly.

The ratio $K_{A_xB_0}$ (*m*-x-anilinium ion)/$K_{A_xB_0}$ (*m*-x-benzoic acid), where x is nitro, chloro or fluoro, is 26 for nitro, 7.6 for chloro and 7.4 for fluoro. Here the structural differences between aniline and benzoate ion can be used to explain these ratios. Within the substituted benzoate and phenolate ion, the negative charge partially opposes the inductive effect of any electronegative group, the field effect of the carboxylate group being greater than that of the phenolate group. Within the substituted aniline the amino group acts as a source of electrons, and does not oppose the inductive effect of an electronegative group. That the inductive effect of a given substituent is greater on an amino group than on a carboxyl group is shown by the work of Bennett and Niemann[16] on the two protolytic constants of the fluorophenylalanines. $K_{A_xB_0}$ (carboxylic) for the *m*-fluorophenylalanine is 1.15 while $K_{A_xB_0}$ (amino) for *m*-fluorophenylalanine is 1.38.

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[14] E. Braude and E. Stern, *J. Chem. Soc.*, 1976 (1948).

[15] A. Bryson, *Trans. Faraday Soc.*, **45**, 257 (1949).

[16] E. Bennett and C. Niemann, THIS JOURNAL, **72**, 1804 (1950).

The distinction between anilinium type and carboxylic type protolytes has been emphasized by Brönsted and co-workers[17] using *m*-cresol as a solvent. These investigators measured the protolysis constants of a number of substituted anilines and carboxylic protolytes (aliphatic as well as aromatic). They plotted log $K_{\mathrm{A}\cdot\mathrm{M}\ominus}$(*m*-cresol) *vs.* log K_c (water) for all the protolytes investigated and found that the data fell into the two distinct groups, anilines and carboxyl, the slope of both lines being approximately unity.

m-Cresol and water are radically different hydroxylic solvents. The former has a lower dielectric constant ($D = 13$) and is a stronger proton donor (K_c in water $= 10^{-10}$). Thus it emphasized the difference between the anilinium type and the carboxylic type protolytes. The results shown in Table X indicate that $K^0_{\mathrm{A_xB_0}}$ in *m*-cresol and in water are approximately the same, and this is interpreted to mean that when one is dealing with a good proton donor like *m*-cresol, the dielectric constant of the solvent is not as important as the specific solute–solvent interactions.

TABLE X

PROTOLYTIC CONSTANTS FOR SUBSTITUTED ANILINIUM IONS AND ANILINE IN *m*-CRESOL AND IN WATER

	log $K^0_{\mathrm{A_xB_0}}$	
Substituent	*m*-Cresol	Water
o-Cl	1.98	1.96
m-Cl	1.26	1.26
p-Cl	0.73	0.77
p-CH$_3$	−0.50	−0.50

This effect is also evident in the work of Hall[18] in glacial acetic acid. Since K_c of the anilinium ion was not determined, $K_{\mathrm{A_xB_0}}$ had to be referred to the K_c of the *p*-methylanilinium ion. The results are shown in Table XI.

TABLE XI

PROTOLYTIC CONSTANTS FOR SUBSTITUTED ANILINIUM IONS AND *p*-METHYLANILINE IN ACETIC ACID AND IN WATER

	log $K^0_{\mathrm{A_xB_0}}$			log $K^0_{\mathrm{A_xB_0}}$	
Substituent	Acetic acid	Water	Substituent	Acetic acid	Water
m-CH$_3$	0.10	0.42	*o*-Cl	1.67	2.48
p-Cl	.48	1.27	*p*-NO$_2$	3.04	4.10
m-Cl	.74	1.75	*o*-NO$_2$	4.70	5.36

The effect of electronegative groups on the protolytic constants in glacial acetic acid is much smaller than in water. The field effects of the carboxylate and carboxyl groups of the medium surrounding the solute species are large enough to neutralize part of the inductive effect of the substituent, *i.e.*, the medium modifies the structure of the solute species appreciably.

The Hammett Relationship.—The Hammett relationship, log $K^0_{\mathrm{A_xB_0}} = \sigma\rho$ for a particular protolytic reaction, resolves log $K^0_{\mathrm{A_xB_0}}$ into σ and ρ, the former characteristic of the substituent, the latter characteristic of the medium and type of reaction. The assignment of a value to the parameter ρ was made by choosing the protolysis of the benzoic acid series in water as a standard and arbitrarily setting ρ equal to unity. Sigma, then, has inherent in it the medium effects of water on the protolytic reaction constant. Therefore ρ in other solvents can only indicate changes in medium effect from water and not total medium effects. The Hammett relationship assumes that ρ is a characteristic constant for a given type of reaction in a given solvent. In spite of its simplicity, this relationship correlates many protolytic and kinetic reactions with simple structural features of the reacting species, and therefore has proved useful. In the following discussion, the Hammett relationship will be used to emphasize substituent types rather than the constancy of ρ in a given solvent.

Table XII lists Hammett's σ-values and his σ-deviations. All of the σ-values except those for *m*-nitro, *m*-chloro and *p*-chloro, obtained from the data of Table VI, are within the deviations of Hammett's values. The largest discrepancy is that of *m*-nitroaniline which, in this investigation, was used to confirm internal consistency. Hammett's σ-values are the mean of the values obtained from widely diverse sources and, except for the *p*-nitro value, were based primarily on data for the benzoic acid series.

TABLE XII

THE HAMMETT RELATIONSHIP, LOG $K^0_{\mathrm{A_xB_0}} = \sigma\rho$. FOR ANILINIUM PROTOLYTES IN WATER

	$\sigma\rho$		σ	
Substituent	From Table VI	Hammett[a]	From Table VI	Hammett[a]
p-NO$_2$	3.604	3.467	1.320	1.27 ± 0.05
m-NO$_2$	2.604	1.938	0.954	0.71 ± .07
m-Cl	1.257	1.018	.460	.373 ± .05
m-F	1.204	0.920	.441	.337 ± .085
p-Cl	0.772	.619	.283	.227 ± .05
p-F	.061	.169	.022	.062 ± .065
m-CH$_3$	− .091	− .188	− .033	− .069 ± .045
p-CH$_3$	− .495	− .464	− .181	− .180 ± .08

[a] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., New York, N. Y., 1940, pp. 186–191.

Figures 7 and 8, which show the Hammett relationship in methanol and ethanol, respectively, substantiate the observations of the section $K_{\mathrm{A_xB_0}}$ and Dielectric Constant, above, that the substituent effects may be classified into those of the nitro, halogen and methyl groups. The nitro derivatives and the halogen derivatives differ in ρ for a given solvent, and in the change of ρ for the nitro derivative with change in solvent. The solvent is implicit in the solvation of the various species involved in the protolytic reaction, though it is not revealed explicitly in $K_{\mathrm{A_xB_0}}$. The ortho protolytes have been included in Figs. 7 and 8 in order to emphasize the difference in effects of the nitro, methyl and halogen groups. The *o*-nitro value lies below the curve of the other nitro substituents while the *o*-chloro and *o*-methyl values lie above their respective curves. Figures 7 and 8 reveal that the deviations of the points for the ortho substituents from their meta–para curve increase from methanol to ethanol. This is also the order of increase in size of the R group in these solvents. This sug-

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(17) J. N. Brönsted, A. Delbanco and A. Tovorbg-Jensen, *Z. physik. Chem.*, **A169**, 361 (1934).

(18) N. F. Hall, THIS JOURNAL, **52**, 5115 (1930).

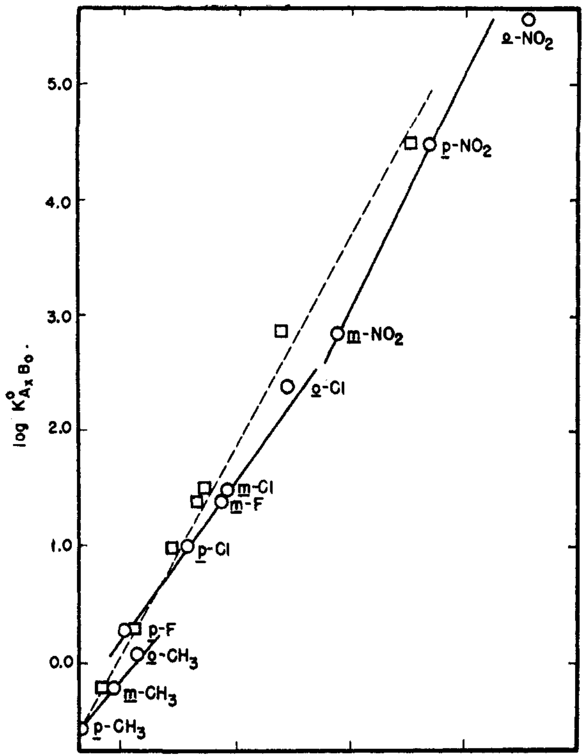

Fig. 7.—Hammett relationship in methanol: □, Hammett's σ values; ○, this investigation.

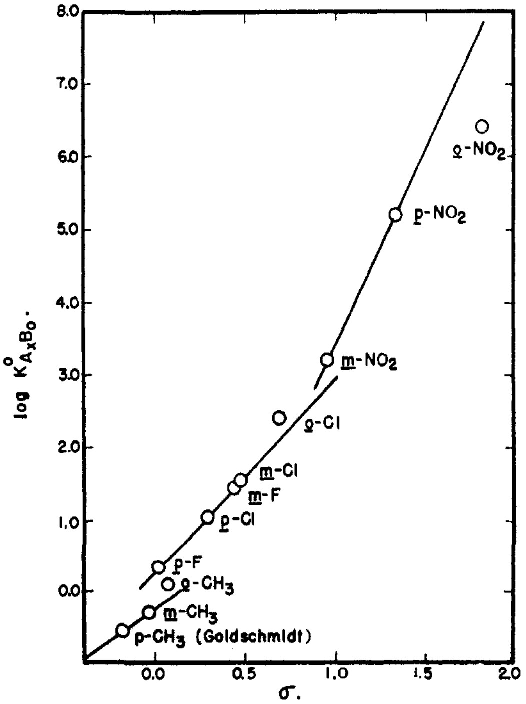

Fig. 8.—Hammett relationship in ethanol.

gests the solute–solvent interaction should be considered in attempting to elucidate ortho effects.

Similar conclusions respecting the classification of the substituents into types are presented by Gutowsky and co-workers[19] on the effect of substituents in benzene derivatives on F^{19} nuclear magnetic shielding. Here the substituent parameter is given the symbol δ. Their various δ plots also showed a separation of the meta and para substituents into the nitro, halogen and methyl. For the ortho position, the methyl group falls into the same class as the halogens.

Calculations from Electrostatic Theory.—Sarmousakis'[20] equation for $K_{A_xB_0}$ is applied to the substituted anilinium ions in various hydroxylic solvents. This equation was set up with the model of the protolyte as a spheroid, oblate rather than prolate.[21] The model, in which the proton and the center of the dipole are located on the focal circle of the oblate spheroid, for the meta-substituted protolyte, leads to

$$\log K_{A_xB_0} = \frac{1}{2.303kT}\left[\frac{-e\,|\mu_\xi|\cos(\mu_\xi\,\mathrm{i}_1.r)}{r^2D_\xi} - \frac{\mathrm{e}\,|\mu_\phi|\cos(\mu_\phi\mathrm{i}_2.r)}{r^2D_\phi}\right] \quad (12)$$

where the point dipole of the substituent has been resolved into two components μ_ξ lying along the focal radius, c, and μ_ϕ perpendicular to μ_ξ; D_ξ and D_ϕ are the effective dielectric constants for the corresponding vector components of the dipole and r is the distance between the point dipole and the proton. For the *p*-substituted protolytes the carbon-substituent bond coincides with the focal radius c and eq. 14 is reduced to one term on the right. D_ξ and D_ϕ were expressed by Sarmousakis in terms of D_i, the internal dielectric constant of the protolyte, D, the dielectric constant of the medium, and a parameter, ξ_0, defining the shape of the molecule. The quantity ξ_0 can be calculated from the molecular volume τ and the focal radius c which defines the spheroidal cavity.

Graphical models, drawn to scale, were used to determine r, c, cos $(|\mu_\xi|\mathrm{i}_1,r)$ and cos $(|\mu_\phi|\mathrm{i}_2,r)$ and to calculate τ, the volume of the spheroidal cavity. The placing of the point dipoles, the value of the dipole moments, and of D_i, the so-called internal dielectric constant, are those of Judson and Kilpatrick.[22]

The results of these calculations are compared with the data of this investigation in Table XIII. The agreement for the meta position in water is well within 0.01 log unit and just about within the experimental error for the halogens. The placement of the point dipole in polynuclear groups like nitro and methyl is uncertain and no adjustment was made here to bring better agreement between the measured and calculated results since it was desired to maintain consistency with Judson's treatment of the phenol and benzoic acid series. The calculated values for the para position in water are consistently higher for the halogens and the methyl group and lower for the nitro group. These results are in agreement with the earlier discussion. The resonance contributions to the para position have been calculated as for the phenol and benzoic acid series[22] and are given in Table XIV along with the values for the phenols and ben-

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[19] H. S. Gutowsky, D. W. McCall, B. R. McGarvey and L. H. Meyer, THIS JOURNAL, **74**, 4809 (1952).

[20] J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944).

[21] J. Kirkwood and F. Westheimer, *ibid.*, **6**, 513 (1938).

[22] C. M. Judson and M. Kilpatrick, THIS JOURNAL, **71**, 3115 (1949).

zoic acid series. Here, again, the results indicate that the largest resonance effects are found for the anilinium ions.

TABLE XIII

LOG $K_{A_xB_0}$ FOR SUBSTITUTED ANILINIUM IONS AND ANILINE

	Water		Methanol		Ethanol	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
m-NO_2	2.604	2.550	2.909	2.639	3.243	2.686
m-Cl	1.257	1.256	1.532	1.288	1.554	1.302
m-F	1.204	1.216	1.455	1.247	1.468	1.261
m-CH_3	−0.091	−0.174	−0.187	−0.180	−0.292	−0.184
p-NO_2	3.604	1.181	4.519	1.273	5.207	1.323
p-Cl	0.772	0.826	1.004	0.867	1.068	0.888
p-F	.061	.823	0.320	0.863	0.348	.883
p-CH_3	− .495	− .123	−0.538	−0.132		− .136

TABLE XIV

RESONANCE CONTRIBUTIONS TO THE PARA POSITION

		Δ log $K_{A_xB_0}$	
Substituent	Anilinium ions	Phenols[22]	Benzoic acids[22]
F	−0.75	−0.40	−0.18
Cl	− .05	− .07	− .05
CH_3	− .29	− .20	− .13
NO_2	2.37	1.81	.29

Table XV presents a Δ' log $K_{A_xB_0}$ which is the change in log $K_{A_xB_0}$ with change in solvent. This emphasizes the structural change in the solvent as against change in dielectric constant. From water to methanol, Δ' log $K_{A_xB_0}$ observed is about an order of magnitude greater than the calculated. There is close agreement between the observed and calculated change for the halogens from methanol to ethanol. This correlates with the fact that the greatest structural change takes place where a methyl group is substituted for a hydrogen in water. These data also indicate the nitro group interacts with the solvent to a greater extent than do the halogens. The dielectric constant, therefore, is insufficient to account for medium effects except where solvents are closely related in structure and interactions between solute and solvent are small. The Sarmousakis or any analogous electrostatic treatment can give consistent results in any given solvent but it contains no structural parameters for the solute–solvent interaction and, therefore, it does not successfully bridge solvents.

TABLE XV

CHANGE IN LOG $K_{A_xB_0}$ WITH SOLVENT

	Δ' log $K_{A_xB_0}$			
	Methanol–water		Ethanol–methanol	
	Obsd.	Calcd.	Obsd.	Calcd.
m-NO_2	+0.305	+0.029	+0.334	+0.047
m-Cl	+ .275	+ .032	+ .022	+ .014
m-F	+ .251	+ .031	+ .013	+ .014
m-CH_3	− .089	− .006	− .105	− .004
p-NO_2	+ .915	+ .092	+ .688	+ .050
p-Cl	+ .232	+ .041	+ .064	+ .021
p-F	+ .259	+ .040	+ .024	+ .020
p-CH_3	− .043	− .009		

CHICAGO 16, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

Heats of Solution of the Cobaltous Chloride Hydrates in Water and Certain Organic Solvents

BY LEONARD I. KATZIN AND JOHN R. FERRARO

RECEIVED MARCH 6, 1953

The heats of solution of cobaltous chloride and its hydrates in water and a number of oxygenated organic solvents are presented. Some relations to heats of solution of other salts are pointed out.

In previous papers we have reported on measurements of the heats of solution of the hydrates of uranyl nitrate[1] and cobaltous nitrate[2] in a series of organic solvents. From these data it has been possible to estimate energies of binding of solvent groups by the metal atom.[2] This report covers the extension of heat of solution measurements to cobaltous chloride and its hydrates and provides data for refining some of the binding energy values, and extension of some of the relations previously noted.

Experimental

The heat measurements and analytical procedures have been described previously.[1,2] The cobaltous chloride hydrates were prepared from commercial chemically pure salt by recrystallization of the hexahydrate, and dehydration of the hexahydrate to the lower hydrates. The crystals of hexahydrate were analyzed, ground in a ball mill and reanalyzed. The lower hydrates were prepared by desiccation of the hexahydrate over sulfuric acid. The anhydrous salt was prepared by heating the monohydrate in a stream of hydrogen chloride gas. Composition of the final product was always checked by analysis at the time of the heat measurements.

Heats of Solution.—The heats of solution of the hydrates and anhydrous salt in the solvents water, dimethylformamide, monoethyl ether of ethylene glycol, tetrahydrofuran, tetrahydrofurfuryl alcohol, tributyl phosphate, acetone and isobutyl alcohol are given in Table I. Measurements were also attempted with methyl isobutyl alcohol, methyl ethyl ketone, diethyl ether of ethylene glycol, diethyl ether and ethyl propionate, but the solubilities in the pure solvents were too limited for satisfactory measurements. In the cases of ethylene glycol diethyl ether and methyl ethyl ketone, heats of solution could be calculated, when solution of the salt was sufficiently complete, from the analysis of the liquid phase. This procedure gave values of −2.58 kcal./mole for the dihydrate in ethylene glycol diethyl ether, and 0.97 kcal./mole in methyl ethyl ketone. Since there is no assurance that the solid phase in contact with the solution was of the same composition as that originally added, these values must be regarded with caution.

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[1] L. I. Katzin, D. M. Simon and J. R. Ferraro, THIS JOURNAL, **74**, 1191 (1952).

[2] L. I. Katzin and J. R. Ferraro, *ibid.*, **74**, 6040 (1952).