$$A = A_d + a$$
$$B = B_d + a \qquad (3)$$
$$C = C_d + a$$

The isotropic coupling constant a is

$$a = \frac{g|\beta|g_N\beta_N}{h}\frac{8\pi}{3}\rho(\vec{r}_N) \qquad (4)$$

where $\vec{r}_N$ is the vector position of the magnetic nucleus. The anisotropic coupling constants may be written[12]

$$A_d = \frac{-g|\beta|g_N\beta_N}{h}\rho(\vec{r})\frac{(1 - 3\cos^2\theta)}{|\vec{r} - \vec{r}_N|^3}\,dV$$

$$B_d = \frac{-g|\beta|g_N\beta_N}{h}\rho(\vec{r})\frac{(1 - 3\sin^2\theta\cos^2\varphi)}{|\vec{r} - \vec{r}_N|^3}\,dV \qquad (5)$$

$$C_d{}^2 = \frac{-g|\beta|g_N\beta_N}{h}\rho(\vec{r})\frac{(1 - 3\sin^2\theta\sin^2\varphi)}{|\vec{r} - \vec{r}_N|^3}\,dV$$

A Critical Re-evaluation of the Hammett Acidity Function at Moderate and High Acid Concentrations of Sulfuric Acid. New H_0 Values Based Solely on a Set of Primary Aniline Indicators

BY MARGARET JEFRAIM JORGENSON[1] AND DONALD R. HARTTER

A uniform, overlapping set of Hammett indicators, consisting solely of primary anilines, was established by the addition of eight new indicators, procured in this work. The pK values of two former indicators were re-evaluated. Employing the new pK values of indicators the Hammett acidity function was redetermined for sulfuric acid above 60%. The newly established H_0 values were found to be progressively more negative than those of the Paul and Long scale. The maximum deviation at the highest acidity was found to be 1.1 units.

Introduction

The demonstrated utility of the H_0 acidity function in aqueous solution and the potential applicability to mixed solvent systems has stimulated a great deal of interest in the correlation of reaction rates with H_0 and in drawing conclusions about mechanisms of acid-catalyzed reactions.[2] The success of such a treatment, however, is intrinsically dependent on the validity of the H_0 scale as well as upon the correctness of the reported H_0 values. The quantitative formulation of the H_0 function[3] (eq. 1) imposes the following conditions on the indicators which are employed for the

$$H_0 = \log a_{H^+}f_B/f_{BH^+} = pK_{BH^+} - \log [BH^+]/[B] \quad (1)$$

$$pK_{CH^+} - pK_{BH^+} = \log\frac{[CH^+]}{[C]} - \log\frac{[BH^+]}{[B]} - \log\frac{f_Cf_{BH^+}}{f_{CH^+}f_B} \quad (2)$$

$$pK_{CH^+} - pK_{BH^+} = \log\frac{[CH^+]}{[C]} - \log\frac{[BH^+]}{[B]} \quad (3)$$

determination of the H_0 scale for any particular acid system: (i) that the pK values of the indicators be accurately and firmly established and (ii) that the indicators employed be valid H_0 indicators such that the relationship between the pK values of two consecutive indicators, described by eq. 2, can be reduced to that of eq. 3; *i.e.*, that the activity coefficient ratio of the free base to the protonated base be equal for both indicators, and hence that the H_0 scale determined be independent of the indicators employed for measurement. Any H_0 scale determined with a particular set of indicators will necessarily incorporate all the inadequacies of such a set.

The present set of indicators, which for the most part consists of the original indicators determined by Hammett and Deyrup,[4] does not comply with either requirement. The colorimetric method employed by Hammett and Deyrup was very inadequate for the measurement of accurate ionization ratios and for the detection of major medium shifts, most important for the determination of accurate pK values.[5] Exami-

nation of the original data reveals these shortcomings in the lack of parallelism and in non-linearity of the plotted ionization curves. The pK values of indicators employed at lower acidity regions have been, in part, re-examined by modern spectrophotometric techniques,[6,7] disclosing a number of failings in Hammett's original data. The indicators used at higher acidities have not been restudied.

The requirement that the indicators employed constitute a valid set has not been seriously examined. The present set of Hammett indicators includes compounds of widely differing chemical constitution. The activity coefficient behavior of these has not been studied, and in the past it has been assumed that eq. 3 adequately describes the protonation behavior of these compounds. This is not true in the light of recent studies on activity coefficient behavior of molecules, especially in more concentrated acid solutions, where the nature of the medium is changing more rapidly. Deno and Perizzolo[8] have shown that for neutral molecules examined, the activity coefficients remained reasonably constant with acid concentration, regardless of structure; the same does not obtain for charged species. The latter show a strong dependence of their activity coefficient behavior on acidity, differing with charge type. Other data[9-11] are available which demonstrate that even for uncharged molecules the activity coefficients may vary over a wide range with acidity.

Other factors also contribute to a potential breakdown of the equivalency of eq. 2 and 3. Taft[12] has shown that the H_0 scale can be demonstrated to be dependent on chemical structure of the indicators, even for chemically closely related compounds. The protonation behavior was found to be different for secondary and tertiary anilines from that for primary

(1) To whom inquiries should be addressed. Grateful acknowledgment is made for a postdoctoral fellowship from the Division of General Medical Sciences, United States Public Health Service, for the years 1959–1961.

(2) See, for example, F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 935 (1957).

(3) For an excellent review of the H_0 acidity function see M. A. Paul and F. A. Long, *ibid.*, **57**, 1 (1957).

(4) L. P. Hammett and A. J. Deyrup, *J. Am. Chem. Soc.*, **54**, 2721 (1932).

(5) We have shown [D. S. Noyce and M. J. Jorgenson, *ibid.*, **84**, 4312 (1962)], for example, that when medium shifts are treated appropriately, the indicator benzylideneacetophenone gives ionization ratios which parallel those of primary anilines, when plotted against sulfuric acid concentration. Hammett's original data result in bad curvature; the previously assigned pK value was shown to be in error by 0.7 unit.

(6) E. Högfeldt and J. Bigeleisen, *ibid.*, **82**, 15 (1960).

(7) K. N. Bascombe and R. P. Bell, *J. Chem. Soc.*, 1096 (1959).

(8) N. C. Deno and C. Perizzolo, *ibid.*, **79**, 1345 (1957).

(9) L. P. Hammett and R. Chapman, *ibid.*, **56**, 1282 (1934).

(10) R. J. Gillespie and J. A. Leisten, *Quart. Rev.*, **8**, 40 (1954).

(11) F. A. Long and R. Bakula, private communication.

(12) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960).

anilines; the differences were ascribed to particular solvation requirements characteristic of the type of anilinium ion present in solution. This serves further to emphasize the need for a cautious selection of indicators.[13]

Our concern with the authenticity of the present H_0 scale in sulfuric acid, and hence with the validity of the pK values of the Hammett indicators, derives in part from interest in employing correlation with H_0 of reactions conducted in partly non-aqueous solutions; this entails a determination of the H_0 scale for these media. Any deviations from ideality found in indicators in aqueous solution are expected to be enhanced in non-aqueous solutions, where activity coefficient behavior or solvation requirements will be more dependent on the medium. For this reason, it is imperative that the indicators employed should be reliable.

It has been amply demonstrated that the present set of indicators, before or after exclusion of those found to be unreliable, is very inadequate both in number and in quality. A thorough re-examination and revision of the H_0 indicator set was urgently warranted. It is the purpose of the present work to: (a) establish a uniform set of H_0 indicators, (b) determine the basicities of these indicators, and (c) utilize the newly established set for the redetermination of the H_0 scale in sulfuric acid.

Experimental[14]

Preparation of Indicators Used for Measurement.—The following indicators were obtained from Aldrich Chemical Co. and were recrystallized and sublimed to constant melting point: 2,5-dichloro-4-nitroaniline, recrystallized from ethanol and sublimed, m.p. 157–158° (lit.[15] m.p. 157°); 2,6-dichloro-4-nitroaniline, recrystallized from benzene–ethanol, m.p. 193–193.5° (lit.[16,17] 189–190°, 195°); 2,6-dinitroaniline, recrystallized from ethanol, m.p. 139–140° (lit.[18,19] 137–138°, 139–140°); the indicators, 2-bromo-4,6-dinitroaniline and 2,4,6-trinitroaniline, part of the Hammett indicator set commercially available, were further purified by recrystallizations and sublimations; m.p.'s 151–151.5° (lit.[4] 150.5–152°) and 190–190.5° (lit.[20] 188–189°), respectively.

2-Chloro-6-nitroaniline was prepared[21] by nitrating o-chloroacetanilide in acetic anhydride at 10°, similar to the general procedure given by Paul[22] for $ortho$ nitration, to give a mixture of 2-chloro-6-nitroacetanilide and 2-chloro-4-nitroacetanilide in a ratio of approximately 2:3. Separation of the isomeric anilines, after hydrolysis, was effected by chromatography on alumina.[23] The compound was further purified by three recrystallizations from benzene–ethanol; m.p. 76.5–77° (lit.[24] 76°).

4-Chloro-2,6-dinitroaniline was prepared by nitration of 4-chloro-2-nitroaniline by the procedure of Elderfield, Gensler and Birstein[25]; it was recrystallized from ethanol and sublimed, m.p. 145.5–146° (lit.[25,26] 147–148°, 144–145°).

(13) The conclusions drawn by Taft were made on the basis of the analysis on two pairs of indicators, and are based on the old ionization data of Hammett and Deyrup. The slopes of ionization curves can be shown to be very strongly dependent on small errors in the assignment of reference coefficients, and hence the Taft analysis amounts to a large part to being a very sensitive measure of the experimental data. It would be highly desirable to confirm the ascribed differences with newly determined ionization data, on a larger sample. No particular significance should be attached to the fact that a Taft analysis results in straight lines only in a restricted acid region. A plot of H_R minus H_0 (the latter as determined with primary anilines) for the full sulfuric acid region shows that this function is non-linear throughout. Linearity can be closely approximated within some acidity regions, such as is the case in 15–35% and 45–65% acid, or when data over a limited range of acid concentration are employed.

(14) Melting points were obtained on a Kofler block and are uncorrected.

(15) A. F. Holleman, A. I. den Hollander and F. E. van Haeften, *Rec. trav. chim.*, **40**, 323 (1921).

(16) R. L. Datta and H. K. Mitter, *J. Am. Chem. Soc.*, **41**, 2028 (1919).

(17) G. Körner and A. Contardi, *Atti accad. Lincei*, **22**, I, 826 (1913).

(18) H. Salkowski, *Ann.*, **174**, 257 (1874).

(19) F. D. Grunstone and S. H. Tucker, *J. Appl. Chem.*, **2**, 204 (1952).

(20) E. Y. Spencer and G. F. Wright, *Can. J. Research*, **24B**, 204 (1946).

(21) We thank Mrs. Jean Howard for the preparation of this compound.

(22) M. A. Paul, *J. Am. Chem. Soc.*, **80**, 5332 (1958).

(23) J. E. Larson and S. H. Harvey, *Chem. Ind.* (London), 45 (1954).

(24) A. F. H. L. de Bruyn, *Rec. trav. chim.*, **36**, 138 (1916).

3-Bromo-2,4,6-trinitroaniline and 3-chloro-2,4,6-trinitroaniline were prepared by the method of de Monchy,[27] *via* nitration of their respective N-ethylcarbamates and subsequent hydrolysis. The crude products were purified by a series of recrystallizations and sublimations; m.p.'s 212–212.3° (lit.[27] 212°) and 186–188° (lit.[27] 188°), respectively.

3-Methyl-2,4,6-trinitroaniline was prepared *via* the N-(3-methylphenyl)-ethylcarbamate, by nitration, followed by hydrolysis, according to the following procedure.

To a stirred mixture of m-toluidine (70 g., 0.65 mole) and anhydrous sodium carbonate (30 g.) in dry benzene (400 ml.) was added dropwise ethyl chlorocarbonate (72 g., 0.66 mole) in benzene (100 ml.). The suspension was refluxed for 1 hour, the insoluble salts filtered, the benzene removed *in vacuo* and the residue distilled to give the N-(3-methylphenyl)-ethylcarbamate (48 g., 40%) as a colorless liquid, b.p. 103° (0.16 mm.). The carbamate (48 g., 0.26 mole) was added dropwise to ice-cooled fuming nitric acid. After 0.5 hour of stirring 120 ml. of concentrated sulfuric acid was added to the reaction mixture, and after an additional period of 1 hour the reaction mixture was poured onto ice. The light yellow precipitate was collected, filtered and dried. The crude product, N-(3-methyl-2,4,6-trinitrophenyl)-carbamate, obtained in a yield over 80%, after four recrystallizations from ethanol gave needles, m.p. 153–154°. The crude carbamate was hydrolyzed by dissolving in a large excess of concentrated sulfuric acid and by the dropwise addition of water, until the acidity was such that the free aniline precipitated out. The mixture was poured onto ice and the bright yellow precipitate collected, washed with water, recrystallized three times from ethanol and sublimed. An additional recrystallization gave yellow needles, m.p. 138–138.5° (lit.[28,29] 136°, 138°).

Measurement of Ionization Ratios.—Stock solutions of each indicator were prepared by dissolving an analytically weighed sample of indicator in chloroform and diluting to volume in a volumetric flask. Aliquots of this solution, of the size required for a particular measurement, were withdrawn into a volumetric flask, the solvent was evaporated and the sample dissolved in water of the requisite strength of sulfuric acid. Short periods of heating were necessary to effect complete dissolution of some indicators at acid concentrations corresponding to a small extent of protonation. It could be shown that the indicator was unaffected after such a treatment. In the case of 3-methyl-2,4,6-trinitroaniline, the prolonged heating which was necessary to dissolve the indicator caused a slow reaction as evidenced by changes in the ultraviolet spectrum. For this reason, the solutions were prepared at room temperature at very high dilution, and measurements were made with 10-cm. cells. Necessary control was taken to ensure complete dissolution of the indicator at the time the measurement was made. Two other indicators, 2-chloro-6-nitroaniline and 3-chloro-2,4,6-trinitroaniline, also exhibited low solubility, and longer path length cells were employed in these cases. All other measurements were made at ambient temperatures with matched 1-cm. cells on a Cary Model 14 M recording spectrophotometer. The same sulfuric acid as used for the preparation of the optical solution was employed as reference solvent.

The ionization ratios $[BH^+]/[B]$ were obtained from the expression $(\epsilon^B - \epsilon)/(\epsilon - \epsilon^{BH^+})$ where ϵ^B and ϵ^{BH^+} are the extinction coefficients of the unprotonated and the fully protonated base, respectively. The ϵ^B values were measured in duplicate or triplicate, to ensure an accurate value, at a concentration of about two H_0 units below the pK of the indicator; the ϵ^{BH^+} values were obtained at an acidity corresponding to greater than 99% protonation. The ionization ratios were generally obtained in duplicate with good reproducibility; the average of the measured values was used.

Results and Discussion

Preparation of New Aniline Indicators and Determination of Ionization Ratios.—Guided by the observed reliability of the various primary anilines currently employed as Hammett indicators, we have sought to augment this set by the inclusion of additional primary anilines, judiciously selected so as to furnish the desired pK value. The selection of these primary anilines was based on prior estimation of the expected effect on the basicity caused by the introduction of halogen, nitro and methyl groups in various positions of the benzene ring.

(25) R. C. Elderfield, W. J. Gensler and O. Birstein, *J. Org. Chem.*, **11**, 812 (1946).

(26) E. Bamberger and F. Stringelin, *Ber.*, **30**, 1248 (1897).

(27) M. M. de Monchy, *Rec. trav. chim.*, **53**, 141 (1934).

(28) F. Reverdin, A. Dresel and E. Delétra, *Ber.*, **37**, 2093 (1939).

(29) J. J. Blanksma, *Rec. trav. chim.*, **21**, 321 (1902).

TABLE I

Ultraviolet Spectral Data of Newly Determined Indicators

Indicator, nitroaniline	λ_{max}, mμ(ϵ) of aniline, B H$_2$O	H$_2$SO$_4$[a]	ϵ of anilinium ion, BH^{+b}	Medium shift, mμ^c	Measured $pK_{BH}+^d$
2,5-Dichloro-4-[e]	370 (9620)	370 (9450)	480–530	5	-1.78 ± 0.02
2-Chloro-6-[e,f]	405 (4440)	408 (4370)	—	4	$-2.43 \pm$ .03
2,6-Dichloro-4-[e]	365 (11,300)	366 (10,480)	—	2	$-3.27 \pm$ .03
2,6-Di-[e]	433 (9670)	440 (9840)	—	4	$-5.54 \pm$ .03
					(5.41^g)
4-Chloro-2,6-di-[e]	440 (9220)	458 (9100)	—	5	$-6.14 \pm$ .02
					(5.92^g)
2-Bromo-4,6-di-	348 (12,150)	350 (12,150)	415–475	2	$-6.68 \pm$ .01
					(6.38^g)
					(6.71^h)
3-Methyl-2,4,6-tri-[e,f,i]	370 (7645)	370 (8790)	573	—	$-8.22 \pm$ .01
					(7.73^g)
3-Bromo-2,4,6-tri-[e,i]	380 (7030)	380 (6420)	615	—	$-9.46 \pm$ .03
					(8.62^g)
3-Chloro-2,4,6-tri-[e,i,j]	375 (6800)	375 (6420)	300	—	$-9.71 \pm$ .01
					(8.80^g)
2,4,6-Tri-	415 (8420)	418 (8500)	170–200	2	$-10.10 \pm$ .02
					(9.03^g)
					9.41^h)

[a] Measured in an acid concentration of about two H_0 units below the pK. [b] Range of values as found at wave lengths corresponding to the maxima of the free base over measured protonation range, at an acid concentration of about two H_0 units above the pK. [c] Over measured protonation range (ca. 10–90% protonation). [d] Values determined in this study by stepwise comparison. [e] New indicator added in this study. [f] Ten-cm. cells employed because of solubility difficulty. [g] Values determined in this work based on the H_0 values of Paul and Long. [h] "Best value" of Paul and Long.[3] [i] The wave lengths used for measurement are values in the vicinity of a broad shoulder. [j] Five-cm. cells employed because of solubility difficulty.

Three indicators, useful in the moderate acid region, were added; these are 2,5-dichloro-4-nitroaniline, 2-chloro-6-nitroaniline and 2,6-dichloro-4-nitroaniline. They either replace unreliable indicators, previously employed, or expand the present set for more accurate measurement. Five new indicators were designed for use in the acid region above 60% sulfuric acid: 2,6-dinitroaniline, 4-chloro-2,6-dinitroaniline, 3-methyl-2,4,6-trinitroaniline, 3-chloro-2,4,6-trinitroaniline and 3-bromo-2,4,6-trinitroaniline. In addition, to provide an internally consistent set of data for all primary anilines, the ionization ratios of both 2-bromo-4,6-dinitroaniline and 2,4,6-trinitroaniline were redetermined.

Determination of ionization ratios for all indicators was accomplished by the spectrophotometric technique. All indicators employed showed strong maxima in the 350–440 mμ region (cf. Table I, columns 2 and 3); in the sterically crowded 3-substituted 2,4,6-trinitroanilines, this long wave length transition appeared as a pronounced shoulder of weaker intensity in the 370–400 mμ region. When the maximum occurred below 400 mμ, the absorption of the protonated base at this wave length was not always negligible (cf. Table I, column 4) and had to be taken into account in the calculation of ionization ratios. The reference extinction coefficient of the free base was measured at an acid concentration of about two units below the pK value. As Table I shows, the medium effects on both the position and the intensity of the medium were only slight in going from aqueous solution to the acid concentration at which the reference extinction coefficient was measured. The observed medium shift in the position of the maximum over the measured protonation range (Table I, column 5) was also minimal and was dealt with by measuring the maximum at the wave length where it was found, regardless of the changes in its position which occurred with increased acidity. It has been shown previously[30] that this treatment reduces to the isobestic point method for the correction of medium effects. Since the medium shifts were only minor in the present case, and since the maxi-

mum of the absorption band was broad, only minor errors would have resulted from a measurement of extinction coefficients at a constant wave length.

In the case of the 3-substituted 2,4,6-trinitroanilines, wave lengths along the shoulder in the 370 mμ region were employed for analysis.[31] Three different wave lengths were chosen for calculation of ionization ratios; they gave exceedingly similar results, but because of the highest precision observed at the wave lengths in the 370–380 mμ region, where the shoulder is relatively broad, a wave length in this region was employed for the final analysis. The indicator 2-bromo-4,6-dinitroaniline also exhibited a weak shoulder in the 400 mμ region, but the absorption curve was steep in this region and measurements at a wave length along this shoulder led to ionization ratios which were less reliable than those measured at the maximum in the 355 mμ region. The pK values obtained from either measurement were in good agreement.

Table II lists ionization ratios for the newly determined anilines; these ionization data are plotted in Fig. 1, together with the ionization ratios for selected primary anilines taken from the data of Hammett and Deyrup.[4] The values obtained in this work give excellent straight lines, with good parallelism. As expected, a progressive steepening in slope with increasing acid concentration is found.[32]

The two indicators, 2-bromo-4,6-dinitroaniline and 2,4,6-trinitroaniline, whose ionization ratios were redetermined, gave ionization curves which were considerably different from those obtained with the data of Hammett and Deyrup. Both ionization curves were displaced to lower acid concentrations; that for 2-bromo-4,6-dinitroaniline was less steep and lacked the curvature apparent in Hammett's data; the sharp upturn observed in the ionization curve for 2,4,6-

(30) D. S. Noyce and M. J. Jorgenson, *J. Am. Chem. Soc.*, **83**, 2525 (1961).

(31) The maximum in the 330 mμ region could also be employed for analysis. However, background absorption from maxima occurring below 300 mμ was substantial, both in the free base and in the protonated base, making a reliable analysis of the data difficult.

(32) The degree of parallelism among ionization curves appears to be, in part, a function of the concentration units employed. The sharp change in slopes observed with ionization curves in the 40–60% region is less pronounced when the log I values are plotted against molarity of sulfuric acid.

TABLE II

IONIZATION RATIOS OF NEWLY DETERMINED ANILINE
INDICATORS

H₂SO₄, %	log I	H₂SO₄, %	log I	H₂SO₄, %	log I
2,5-Dichloro-4-nitroaniline[a]		2-Chloro-6-nitroaniline[a]		3-Methyl-2,4,6-trinitroaniline[b]	
19.38	−0.80	26.57	−0.97	80.10	−0.79
21.98	− .64	29.35	− .74	82.70	− .39
23.65	− .51	32.05	− .63	83.72	− .23
26.57	− .32	34.53	− .40	85.03	− .08
29.35	− .13	37.19	− .17	86.42	+ .16
32.65	+ .065	39.23	− .05	88.08	.44
34.53	.26	41.63	+ .11	88.80	.50
37.19	.44	43.95	.31	90.47	.75
41.63	.77	45.72	.47	91.73	.94
43.95	.94	48.15	.69		
		52.21	.98		
2,6-Dichloro-4-nitroaniline[a]		2,6-Dinitroaniline[a]		3-Bromo-2,4,6-trinitroaniline[b]	
37.19	−1.10	59.77	−1.21	88.08	−0.84
41.63	−0.72	61.94	−0.88	88.80	− .68
43.95	− .49	63.50	− .61	90.85	− .34
45.72	− .36	65.12	− .42	91.93	− .27
48.15	− .08	66.64	− .21	92.70	+ .04
49.60	+ .04	68.65	+ .05	94.21	.26
52.21	.33	70.15	.30	95.48	.52
55.19	.70	72.50	.67	97.26	.86
57.38	.84	74.82	1.04	98.82	.99
4-Chloro-2,6-dinitroaniline[a]		2-Bromo-4,6-dinitroaniline[a]		2,4,6-Trinitroaniline[a]	
63.50	−1.21	79.15	−0.82	90.26	−1.13
65.12	−1.01	70.63	− .78	91.93	−0.78
66.64	−0.84	71.74	− .67	92.70	− .64
68.65	− .58	72.20	− .54	94.21	− .44
70.15	− .33	74.82	− .09	95.48	− .20
71.47	− .13	76.39	+ .18	95.75	− .06
72.50	+ .08	77.65	.27	96.91	+ .16
74.82	.49	78.24	.46	97.26	.17
77.50	.89	79.04	.54	97.91	.34
		80.55	.82	98.25	.36
3-Chloro-2,4,6-trinitroaniline[b]		82.07	.95	98.82	.54
				99.27	.82
90.85	−0.64			99.44	1.02
91.93	− .38				
94.21	− .05				
95.48	+ .28				
97.26	.59				

[a] Measured at λ_{max} at each acidity. [b] Measured at wave length along shoulder (cf. Table I).
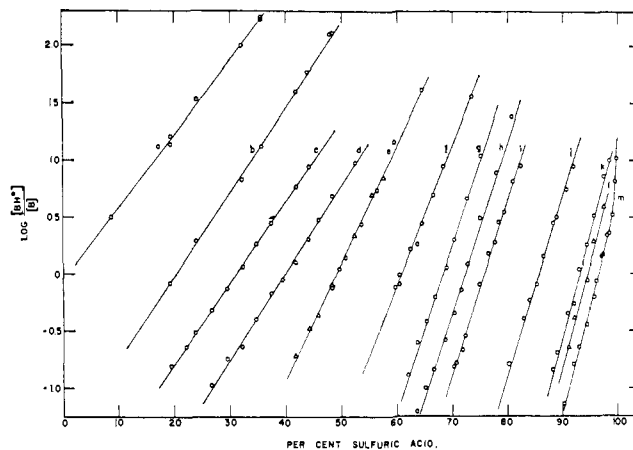

Fig. 1.—Logarithm of ionization ratios of primary aniline indicators plotted against % sulfuric acid. Data of Hammett and Deyrup (ref. 4): a, 2-nitroaniline; b, 4-chloro-2-nitroaniline: e, 2,4-dichloro-6-nitroaniline (circles); f, 2,4-dinitroaniline. Data from present work: c, 2,5-dichloro-4-nitroaniline; d, 2-chloro-6-nitroaniline; e, 2,6-dichloro-4-nitroaniline (triangles); g, 2,6-dinitroaniline; h, 4-chloro-2,6-dinitroaniline; i, 2-bromo-4,6-dinitroaniline; j, 3-methyl-2,4,6-trinitroaniline; k, 3-bromo-2,4,6-trinitroaniline; l, 3-chloro-2,4,6-trinitroaniline: m, 2,4,6-trinitroaniline.

small degrees of protonation, and hence will determine the slope of the ionization curve.

Measurement of pK values of Indicators.—The pK values of the ten indicators measured in this work were obtained by stepwise comparison, employing eq. 3. Since parallelism of the ionization curves was not exact, the pK values obtained by this method, as measured over the major protonation acid range, extended over a small range of values. We have averaged the values obtained by overlapping ionization ratios, taken from the best line drawn through the experimental points, in the region corresponding to $\log I = \pm 0.8$ (15–85% protonation). It is this particular feature, in addition to the care which was taken in obtaining the best spectrophotometric data, which makes the new set of pK values a very reliable one; in the colorimetric procedure, overlapping was often achieved at ionization ratios corresponding to a very high degree of protonation or even at extrapolated values.[33]

The pK values obtained by the above procedure are listed in Table I, column 6, along with the range of error. The two indicators 2-bromo-4,6-dinitroaniline and 2,4,6-trinitroaniline which were re-evaluated were found to have pK values different from the reported values by 0.23 and 0.38 unit, respectively, on the Paul and Long scale. These differences are a direct reflection on the shortcomings of the colorimetric technique. The erroneous assignment of pK values to indicators employed in the previous stepwise comparison procedure for the establishment of pK values of less basic indicators is responsible for the observed cumulative error of about one unit (difference between the value on the Paul and Long scale and the present value) in the pK of the least basic indicator, 2,4,6-trinitroaniline.

The ten indicators newly determined in this work, when supplemented with the Hammett indicators which we have found to be reliable,[34] now constitute an ample

trinitroaniline was observed to occur at an appreciably higher concentration than found in the Hammett and Deyrup data. We believe that these differences are due to the limitations of the colorimetric method employed in the Hammett and Deyrup experiments. An increase in the absorption intensity of the reference coefficients over that measured in purely aqueous solution was found at an acidity corresponding to less than 1% protonation, amounting to 35% and 65% for 2-bromo-4,6-dinitroaniline and for 2,4,6-trinitroaniline, respectively. No such medium effects were observed in this work. Further, failure to take into account the contribution to the absorption intensity by the protonated base explains the curvature and the deviations in slope. The calculated effect on the ionization values resulting from this neglect is, in fact, of the proper magnitude and is in the right direction. It cannot be stressed too strongly that small errors in the reference data will have pronounced effects on the ionization ratios corresponding to very large and very

(33) For example, overlap between the indicators 2,6-dinitro-4-methylaniline and 2-bromo-4,6-dinitroaniline was achieved at 99% protonation, and in the case of anthraquinone and 2,4,6-trinitroaniline an extrapolated ionization value was employed, although the ionization curve of anthraquinone shows alarming curvature in this region.

(34) These are 3-nitroaniline, 4-nitroaniline, 3-nitroaniline, 4-chloro-2-nitroaniline, 2,4-dichloro-6-nitroaniline, 2,6-dichloro-4-methylaniline and 2,4-dinitroaniline.

TABLE III
REVISED H_0 VALUES FOR THE UPPER SULFURIC ACID REGION

H_2SO_4, %	H_0	$\Delta H_0{}^a$	H_2SO_4, %	H_0	$\Delta H_0{}^a$
60	-4.46^b	0.00	85	-8.14^f	-0.48
62	-4.70^b	.00	86	-8.29^f	$-.49$
64	$-4.95^b \pm 0.04$	$-.02$	88	-8.61^f	$-.57$
66	$-5.20^{b,c} \pm .01$	$-.05$	90	$-8.92^{f,g,h} \pm 0.01$	$-.66$
68	$-5.50^{c,d} \pm .01$	$-.11$	92	$-9.29^{g,h} \pm .005$	$-.77$
70	$-5.80^{c,d,e} \pm .01$	$-.15$	94	$-9.68^{g,h,i} \pm .01$	$-.93$
72	$-6.10^{c,d,e} \pm .01$	$-.20$	95	$-9.85^{g,h,i} \pm .01$	$-.99$
74	$-6.41^{c,d,e} \pm .005$	$-.25$	96	$-10.03^{g,h,i} \pm .01$	-1.05
76	$-6.71^{d,e} \pm .01$	$-.28$	97	$-10.21^{h,i}$	-1.08
78	$-7.03^{d,e} \pm .01$	$-.33$	98	-10.41^i	-1.05
80	$-7.34^{e,f} \pm .005$	$-.37$	98.82	-10.62^i	-1.04
82	$-7.66^{e,f} \pm .005$	$-.42$	99.27	-10.92^i	-1.12
84	-7.97^f	$-.47$	99.44	-11.12^i	-1.16

^{a} $\Delta H_0 = H_0$ (present work) $- H_0$ (Paul and Long). H_0 determined from the following indicators: ^{b} 2,4-dinitroaniline. pK_{BH^+} -4.53; ^{c} 2,6-dinitroaniline, pK_{BH^+} -5.54; ^{d} 4-chloro-2,6-dinitroaniline, pK_{BH^+} -6.14; ^{e} 2-bromo-4,6-dinitroaniline, pK_{BH^+} -6.68; ^{f} 3-methyl-2,4,6-trinitroaniline, pK_{BH^+} -8.22; ^{g} 3-bromo-2,4,6-trinitroaniline, pK_{BH^+} -9.46; ^{h} 3-chloro-2,4,6-trinitroaniline, pK_{BH^+} -9.71; ^{i} 2,4,6-trinitroaniline, pK_{BH^+} $- 10.10$.

and uniform set of Hammett indicators, a total of seventeen, for use in the accurate determination of acidity scales. We have correspondingly employed this new set of indicators for the re-evaluation of the H_0 acidity scale of sulfuric acid.
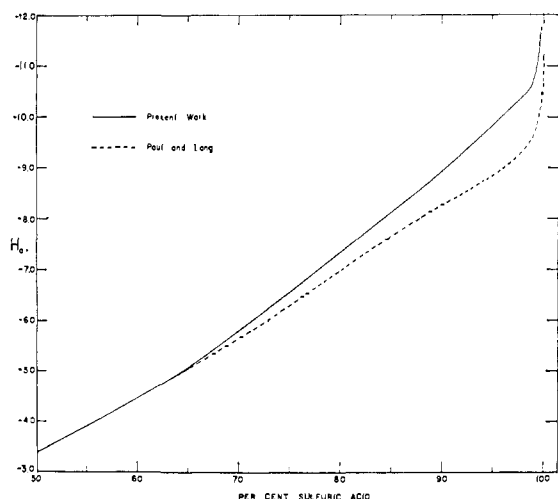

Fig. 2.—Plot of previous H_0 values and revised H_0 values against % sulfuric acid for the upper sulfuric acid region.

Redetermination of the H_0 Scale in Sulfuric Acid.— The observed deviations in the pK values of indicators at the higher acidities, from those reported, clearly established that the present H_0 scale was grossly in error. This fact had been suspected for some time, and a re-examination of the H_0 scale at the higher acidities had been urged by Paul and Long.[3] The majority of indicators used for the establishment of the H_0 scale in this region can be considered to be unreliable. The indicators N,N-dimethyl-2,4,6-trinitroaniline[3] and benzylideneacetophenone[5] have been shown to be poor indicators; the other ketonic indicators 4-benzoylbiphenyl, β-benzoylnaphthalene and anthraquinone are expected to have different activity coefficient behavior and are, in addition, difficult to handle experimentally, as the reference coefficients are subject to large medium effects. Anthraquinone shows a very complex protonation behavior[55] difficult to interpret.

A plot of indicator ionization ratios against the H_0 values of Paul and Long gives ionization curves with slopes of unity for the first three indicators. This establishes the validity of the H_0 scale up to about 60%

(35) L. A. Flexser, L. P. Hammett and A. Dingwall, *J. Am. Chem. Soc.*, **57**, 2103 (1935).

sulfuric acid, and confirms the correctness of the pK values of the more basic aniline indicators, up to 2,4-dinitroaniline. We have employed the pK value of the latter indicator as the ultimate reference for the stepwise comparison in the establishment of pK values of all the less basic indicators in this study.

The H_0 values were obtained with the aid of all the indicators which protonated at a particular acidity, restricting this procedure to include only ionization ratios which were within the range of log $I \pm 1.0$. Table III lists the H_0 values at close intervals obtained by this method, along with the range of error. The agreement of the H_0 values as obtained from various indicators can be seen to be excellent. The difference between the newly determined values and those presently in use is a steadily increasing number, amounting to 1.10 units at the highest acidity. The graphical representation of H_0 as a function of % sulfuric acid is made in Fig. 2. The shape of the H_0 profile is considerably changed; between 60% and 90% the graph approximates linearity much more closely than the previous plot, and the sudden steepening in the 100% region occurs at a much higher acidity, beyond 98% sulfuric acid.

The available H_0 data at the highest acidity afford a bridge to the H_0 data as determined by Brand[36] for oleum. His data were obtained with the use of aromatic nitro compounds as indicators.[37] Employing his data on the ionization of p-nitrotoluene, which was measured down to 95.30%, the substitution of our new H_0 values for those of Paul and Long up to 99% sulfuric acid gives a pK value for p-nitrotoluene of -11.38 ± 0.03, compared to -10.28 on the old scale. The difference of 1.10 units is that observed between the present and the newly established H_0 scale in the highest acid region (Table III) and can be used to adjust all the H_0 values above 100% sulfuric acid, as measured by Brand. The total measured negative H_0 scale of sulfuric acid is thus expanded from 12.8 units to 13.9 units.
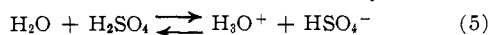
Attempted Theoretical Justification of H_0 Values in Concentrated Sulfuric Acid.—One of the most interesting aspects of the study of H_0 behavior of sulfuric acid in the concentrated acid region is the possible application of the protonation behavior of sulfuric acid to the

(36) J. C. D. Brand, *J. Chem. Soc.*, 997 (1950).

(37) It would be desirable to extend the determination of H_0 into this region with aniline indicators, to preserve continuity in indicator type. From our work on 3-halogen substituted 2,4,6-trinitroanilines, we predict that the indicators 3-fluoro-2,4,6-trinitroaniline and 3,5-difluoro-2,4,6-trinitroaniline will have pK values of approximately -11 and -12, respectively, and hence be suitable in this region.

elucidation of the composition and constitution of sulfuric acid as a solution. Brand[36] and Deno and Taft[38] have proposed that the H_0 values of sulfuric acid between 83% and 99.8% can be derived from the "semi-theoretical" eq. 4 (X = mole fraction) if an equilibrium constant of 50 obtains for eq. 5. Below 83% there is a sharp breakdown of eq. 4, rationalized in terms of a changing equilibrium constant or in terms of anomality of activity coefficient behavior.

$$H_0 \text{ (calcd.)} = -8.47 + \log X_{\text{HSO}_4}^-/X_{\text{H}_2\text{SO}_4} \qquad (4)$$

$$H_2O + H_2SO_4 \rightleftharpoons H_3O^+ + HSO_4^- \qquad (5)$$

The constancy of the equilibrium constant above 83% is surprising, since it implies ideality of sulfuric acid as a solution. That the latter should actually be true has been doubted[36] and severely criticized.[11,39] It is an unrealistic supposition to assume that the activity coefficients of all the species in solution in this acid region are invariant, since existing evidence supports the fact that the activity coefficients of charged species vary with concentration[8] and that neutral molecules also may show acidity dependent activity behavior.[9-11] Although the free water concentration calculated from eq. 5 closely parallels the measured activity of water,[40] this can be taken to mean that the activity coefficient of water is reasonably constant over this region, but can be shown not to be invariant. No such support exists for the constancy of activity coefficients of the species bisulfate ion, hydronium ion and sulfuric acid.
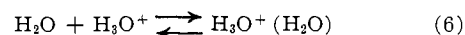
Wyatt[39] has chosen to rationalize the observed deviation of the activity of water from the actual concentration of free water present in solution at any sulfuric acid

(38) N. C. Deno and R. W. Taft. Jr., *J. Am. Chem. Soc.*, **76**, 244 (1954).

(39) P. A. H. Wyatt. *Discussions Faraday Soc.*, **24**, 162 (1957).

(40) W. F. Giauque. E. W. Hornung. J. E. Kunzler and T. R. Rubin. *J. Am. Chem. Soc.*, **82**, 62 (1960).

concentration as the result of the presence of various equilibria of type 6 involving the hydration of hydronium ions. By assigning equilibrium constants for (6) of appropriate magnitude in various acid regions, and by assuming a much larger equilibrium constant for (5), he manages to derive H_0 values in close agreement with experimental values.

$$H_2O + H_3O^+ \rightleftharpoons H_3O^+ \, (H_2O) \qquad (6)$$

We have attempted to derive correlations similar to those above for our new H_0 values. It can be shown that the empirical eq. 4 holds above 95% sulfuric acid with a changed constant of -9.47. Below this concentration, the calculated values from this equation are too negative and the deviations from the experimental values are of changing magnitude. This implies that no adjustment can be made in eq. 4 by assuming a different constant or by invoking a particular equilibrium constant for eq. 5, in the manner of Deno and Taft. A more complex treatment in the fashion of Wyatt may account for the observed H_0 values, but no simple calculations suffice.

It can be concluded that the success of the treatment by Deno and Taft is the fortuitous result of the errors present in the reported H_0 values. The breakdown of eq. 4 with our new H_0 values is not disturbing and is entirely reasonable, since activity coefficients should not be expected to be constant in the concentrated sulfuric acid region.

A Chain Model for Polyelectrolytes. VIII. Further Studies of Counterion Activity in Solutions of Polyethyleneimine Hydrochloride

BY SAVO LAPANJE,[1a] PETER F. JONES[1b] AND STUART A. RICE

Measurements are reported of the activity coefficient of the chloride counterion in solutions of polyethyleneimine hydrochloride with various added 1:1 and 1:2 salts. The results are interpreted to demonstrate that the charge configuration of the added small anion is pertinent in determining the distribution of counterions about a polyion.

I. Introduction

Despite the experimental and theoretical advances of the past decade, our ability to predict quantitatively the behavior of polyelectrolyte solutions is severely limited.[2] The reasons for this are easy to ascertain: polyelectrolyte solutions are complex systems containing several components each interacting with all others with a long range coulomb potential; the available mathematical descriptions of the state of the system are incomplete and approximate; and experiment has not yet turned up a convenient expansion parameter about which a theory can be constructed. Given these circumstances it is important to devise experiments which test the physical interpretations as well as the numerical predictions of approximate theories.

(1) (a) Permanent address: Institute for Physical Chemistry. University of Ljubljana. Ljubljana. Yugoslavia. (b) Department of Chemistry. University of California at Los Angeles.

(2) For a convenient review see S. A. Rice and M. Nagasawa. "Polyelectrolyte Solutions." Academic Press. Inc.. New York. N. Y.. 1961.

One feature common to all polyelectrolyte theories is the intimate association between counterions and polyion. It is now believed that surrounding a polyion skeleton is a region of very high counterion concentration. In some theories the sheath is likened to a one-dimensional fluid and a cell model is used to calculate the properties of the polyion–counterion distribution.[2] The distribution is usually considered to result from non-specific coulomb interactions, and to be a consequence of only the polyion charge density and the magnitude of the counterion charge. The question of the possible role of specific counterion–polyion interactions has not been settled. Should specific interactions exist, the basic premise that only the linear charge density of the polyion and the magnitude of the counterion charge are of importance in determining the counterion distribution would have to be modified.

In this paper we report some experiments designed to test the specificity of the counterion–polyion interaction. The basic question asked is: does the density of coun-