

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A SERIES OF SIMPLE BASIC INDICATORS. II. SOME APPLICATIONS TO SOLUTIONS IN FORMIC ACID¹

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A major incentive for the setting up of the series of indicators described in the previous article³ was the expectation that such a series would be widely applicable to solutions in various solvents. We have therefore applied these indicators, previously standardized in mixtures of strong acids with water, to solutions in the anhydrous solvent formic acid. In this solvent two tests of the indicator system are possible. The results of one, the comparison of the relative basicities of indicators in the anhydrous solvent with the former standardization, have been included in the previous article; the detailed experimental data are given here. The other is the comparison of the results obtained with indicators with the electrometric⁴ and conductivity⁵ data already existing for the solvent. We have further tested the usefulness of the indicator system by extending our knowledge of ionization relations in this solvent and of the general properties of some very weak uncolored bases.

An acid-base system independent of the water system may be referred to formic acid in the same way as was first done by Franklin⁶ with ammonia. We may therefore consider solutions as acid, neutral, or alkaline with respect to it as a solvent, we may speak of a concentration of solvated hydrogen ion, and we may determine that concentration if we possess a strong acid in whose solutions the hydrogen-ion concentration may be taken equal to the stoichiometric acid concentration. Likewise we may determine with reference to some strong base the concentration of formate ion, which in this solvent plays the part of hydroxyl ion in water. We may determine ionization constants of weak acids and bases, which will be different from the constants for the same substances in water or in other solvents. All such quantities partake very deeply of the nature of the particular solvent; we shall call them formic acid functions. They must be sharply distinguished from the H_0 and the pK' of the previous article, which are independent of the solvent system, and which we shall call general acid-base functions.

¹ This article is based mainly upon part of a dissertation submitted by Alden J. Deyrup to the Faculty of Pure Science of Columbia University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, March, 1932.

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³ Hammett and Deyrup, *THIS JOURNAL*, **54**, 2721 (1932).

⁴ Hammett and Dietz, *ibid.*, **52**, 4795 (1930).

⁵ Schlesinger and co-workers, *ibid.*, **33**, 1924 (1911); **36**, 1589 (1914); **38**, 271 (1916); **41**, 72, 1921, 1934 (1919).

⁶ See for instance *ibid.*, **46**, 2137 (1924).

We shall use the following symbols

$$pH(\text{HCOOH}) \equiv -\log C_{\text{H}^+(\text{HCOOH})} \quad (1)$$

where $C_{\text{H}^+(\text{HCOOH})}$ is the concentration of the solvated hydrogen ion in formic acid.

$$pK_s(\text{HCOOH}) \equiv -\log \frac{C_{\text{H}^+(\text{HCOOH})} C_{\text{COOH}'}}{C_{\text{HCOOH}}} \quad (2)$$

$$pK'_B(\text{HCOOH}) \equiv -\log \frac{C_{\text{H}^+(\text{HCOOH})} C_B}{C_{\text{BH}^+}} = pH(\text{HCOOH}) - \log \frac{C_B}{C_{\text{BH}^+}} \quad (3)$$

$$pK_B(\text{HCOOH}) \equiv -\log \frac{C_{\text{BH}^+} C_{\text{COOH}'}}{C_B} = pK_s(\text{HCOOH}) - pK'_B(\text{HCOOH}) \quad (4)$$

$pK'_B(\text{HCOOH})$ is the analog for formic acid solution of the logarithmic hydrolysis constant of the salt of an anhydro base in water, which may also⁷ be considered the ionization constant of the cation of the base. $pK_B(\text{HCOOH})$ is the analog of the ionization constant of the base in water. By combination of equation 3 with equation 4 of the previous article we obtain

$$pK'_B(\text{HCOOH}) - pK'_B = pH(\text{HCOOH}) - H_0 \quad (5)$$

which relates the formic acid functions to the general acid-base functions pK' and H_0 .⁸

Materials and Procedure

The indicators and the sulfuric acid were the materials described in the first article of this series.³ Formic acid, benzene sulfonic acid and sodium formate were obtained or purified as described by Hammett and Dietz.⁴ For comparison, formic acid was also purified by the method of Schlesinger,⁵ distillation from pure phosphorus pentoxide under reduced pressure at room temperature. The product obtained by the Coolidge method (that used by Hammett and Dietz) froze within 0.01° of that purified by the Schlesinger method. This corresponds to a difference in water content of less than 0.005 mole per liter. The bulbs containing the benzene sulfonic acid were filled with dried air before sealing off to eliminate the uncertainty of a buoyancy correction. The product analyzed 100.3% $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ by titration.

Aniline was freshly redistilled, the middle portion (b. p. 183°) only being retained. Acetanilide was recrystallized twice from alcohol, and dried at 90–100°, m. p. 114°. Propionitrile was distilled twice from phosphorus pentoxide (b. p. 98°). Sodium sulfate and sodium bisulfate were dried to constant weight at 120°.

Procedure.—Solutions of weighed quantities of the various solutes in the purified formic acid were made up in volumetric flasks. In the case of benzene sulfonic acid the bulbs were broken and the solutions prepared as described by Hammett and Dietz.⁴ Ten-cc. portions of the various solutions were transferred with a pipet to 12-cc. weighing bottles, which were then kept in a desiccator until used. In a blank experiment all of the manipulations involved in the preparation of the benzene sulfonic acid solutions were carried out on pure formic acid and a subsequent freezing point determination showed that absorption of water from the air under these conditions was negligible. Although the strongly acid solutions evolve bubbles of gas after several hours, the decomposition thus indicated was found to be insufficient to make any measurable difference in the indicator acidity at the beginning and at the end of a series of measurements.

⁷ Brönsted, *Rec. trav. chim.*, **42**, 719 (1923).

⁸ The definitions and equations for weak acids analogous to these for weak bases are obvious.

The indicators were added in the form of a measured number of drops of a solution in anhydrous formic acid exactly as described in the previous article. The colorimetric comparisons were carried out as there described, using the closed cell pictured in Fig. 1 of that article, and with solutions of the indicator in water or in 95% sulfuric acid as reference standards. The concentration of the indicator varied from 2×10^{-5} to 3×10^{-3} , and was in every case kept so low as to produce no significant change in the acidity of the solution under investigation.

Discussion of Results

The Indicator Constants.—From the values of I_w and I_h^3 given in Table II for solutions of sodium formate and of benzene sulfonic acid we have determined on a large scale chart the limiting values corresponding to complete conversion to the colored form. These quantities, S_w and S_h^3 , were found to have in formic acid the values given in Table I. A series of experiments failed to detect any change in the color intensity of the completely converted indicator due to the addition of 0.5 molar sodium benzene sulfonate with indicators 4, 5, 8, 13, 15. It consequently seems safe to assume that S is constant throughout the range of 0 to 0.1 molar concentration and that the error due to the medium effect upon the specific color intensity of the colored form is negligible in the experiments here described.

Having the values of S and I the values of $\log [BH^+]/[B]$ were calculated by equations 10 and 11 of the previous article and from these the relative basicities of the indicators by equation 3 of that article. *o*-Nitraniline was used as a reference base with which the others were compared, its pK' being taken as +0.13, the average of the values obtained in the previous work. The results are given in Table I. The significance of the concordance within experimental error of these values with those obtained in the aqueous mixtures was discussed in the previous article.⁹

TABLE I
PROPERTIES OF INDICATORS

No.	Name	S_w or S_h	$pK_B(\text{HCOOH})$	pK'
2	<i>o</i> -Nitraniline	1.00 ± 0.07	1.22	(+0.13)
3	<i>p</i> -Chloro- <i>o</i> -nitraniline	$1.00 \pm .03$	1.99	-0.64
4	<i>p</i> -Nitrodiphenylamine	$1.00 \pm .03$	3.56	-2.21
5	2,4-Dichloro-6-nitroaniline	$1.00 \pm .05$	4.36	-3.01
8	2,4-Dinitroaniline	$0.63 \pm .02$
7	2,6-Dinitro-4-methylaniline	$.88 \pm .02$
13	6-Bromo-2,4-dinitroaniline	$.68 \pm .02$
15	2,4,6-Trinitroaniline	$.61 \pm .03$
6	<i>p</i> -Nitroazobenzene (extrapolated)	$.50 \pm .03$	4.34	-2.99

⁹ In agreement with predictions based on Table I of the previous article, *p*-nitraniline was found to be very largely ionized even in 0.1 *m* NaHCO₂ solution, and the following indicators were found to be only partially ionized in 0.1 *m* C₆H₆SO₃H solution: 2,6-dinitro-4-methylaniline, 2,4-dinitroaniline, N,N-dimethyl-2,4,6-trinitroaniline; benzalacetophenone, β -benzoylnaphthalene, *p*-benzoyldiphenyl, 6-bromo-2,4-dinitroaniline, anthraquinone, 2,4,6-trinitroaniline.

Strong Acids and Bases.—Values of H_0 are by definition immediately deducible from indicator measurements, and the results for solutions of sulfuric acid, benzene sulfonic acid, sodium formate and aniline are given in Table II, and are plotted against the logarithm of the concentration

TABLE II
STRONG ACIDS AND BASES
Sodium Formate Solutions

Concn.	I_w	$\text{Log} \frac{[\text{BH}^+]}{[\text{B}]}$	H_0	I_w	$\text{Log} \frac{[\text{BH}^+]}{[\text{B}]}$	H_0
		<i>o</i> -Nitraniline		<i>p</i> -Chloro- <i>o</i> -nitraniline		
0.1011	0.54	-0.07	+0.20	0.85		
.0482	.333	+ .30	- .17	.67		
.0263	.243	.51	- .38	.65	-0.28	-0.36
.0245	.234	.52	- .39	.66	- .28	- .36
	.246	.49	- .36			
.0115	.156	.73	- .60	.57	- .12	- .52
	.159	.72	- .59			
.0063	.100	.96	- .83	.44	+ .11	- .75
	.099	.97	- .84			
		Benzene Sulfonic Acid Solutions				
		<i>o</i> -Nitraniline		<i>p</i> -Chloro- <i>o</i> -nitraniline		
0.00555	0.0021	+2.84	-2.71	0.0124	+2.00	-2.64
.0110	.0016	2.98	-2.85	.0073	2.20	-2.84
.0257				.0049	2.40	-3.04
.0378				.0026	2.61	-3.25
				.0031	2.53	-3.17
		<i>p</i> -Nitrodiphenylamine		2,4-Dichloro-6-nitroaniline		
0.00555	0.27	+0.43	-2.64	0.68	-0.33	-2.68
.0110	.222	.55	-2.76	.62	- .21	-2.80
.0257	.111	.90	-3.11	.49	+ .02	-3.03
.0378	.085	1.03	-3.24	.36	.25	-3.26
.144	.0294	1.52	-3.73	.167	.70	-3.71
		<i>p</i> -Nitroazobenzene				
	I_h					
0.00555	0.166	-0.31	-2.68			
.0110	.206	- .15	-2.84			
.0257	.284	+ .12	-3.11			
.0378	.273	.08	-3.07			
		Sulfuric Acid Solutions				
		<i>p</i> -Nitrodiphenylamine		2,4-Dichloro-6-nitroaniline		
0.1064	0.020	+1.69	-3.90			
	.019	1.71	-3.92			
.0903	.022	1.65	-3.74			
	.023	1.63	-3.72			
.0531	.038	1.40	-3.61	0.27	+0.43	-3.44
.0451	.052	1.26	-3.35			
	.054	1.25	-3.34			
.0266	.096	0.97	-3.18	.42	.14	-3.15

TABLE II (Concluded)
 Aniline Solutions

Concn.	I_h	$\text{Log} \frac{[\text{BH}^+]}{[\text{B}]}$	H_0
0.1023	0.53	-0.05	+0.18
	.55	- .09	+ .22
.0511	.39	+ .19	- .06
	.40	+ .18	- .05
.0256	.278	+ .42	- .29

in Fig. 1. In order to calculate any of the formic acid functions it is necessary to refer to solutions of strong acids and bases in that solvent. Hammett and Dietz⁴ found that the behavior in electrometric titrations of benzene sulfonic acid and sodium formate was indistinguishable from that of strong electrolytes. The indicator data confirm this conclusion for sodium formate by showing a close agreement in the acidity of equimolar solutions of sodium formate and aniline and a small deviation of both from the 45° straight line which would be followed by completely ionized bases in the absence of salt effects. Indeed it may be calculated from these data that the ratio of the activity coefficients of a univalent ion in 0.01 and 0.1 molar solution is 1.20, not very different from the value obtained in aqueous solution.

With respect to benzene sulfonic acid the results do indicate a small but probably significant incompleteness of ionization. The reaction of a strong monobasic acid with a basic indicator



should be displaced by a change in ion concentration only as a result of specific variations in activity coefficients.¹⁰ Except for the result of such

¹⁰ Brønsted, *J. Chem. Soc.*, 119, 574 (1921).

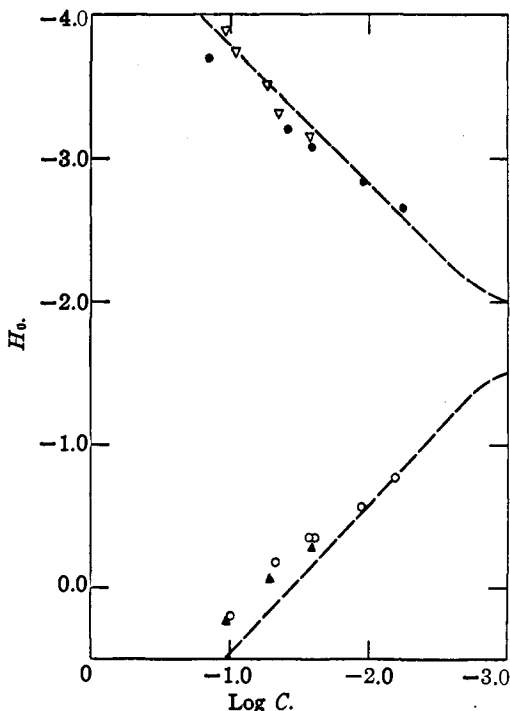
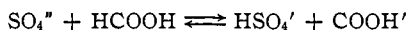


Fig. 1.— ∇ , H_2SO_4 ; \bullet , $\text{C}_6\text{H}_5\text{SO}_3\text{H}$; \circ , NaCHO_2 ; \blacktriangle , $\text{C}_6\text{H}_5\text{NH}_2$.

specific effects the H_0 -log C plots for sulfuric acid and benzene sulfonic acid should coincide with each other and with the 45° straight line if both are strong monobasic acids. The close agreement obtained with sodium formate and aniline makes it improbable that such specific effects are large enough to account for the deviations observed. The difference in the results for the two acids cannot be attributed to the secondary ionization of the sulfuric acid. Using indicator 4 we have found the H_0 value for a 0.14 molar solution of sodium bisulfate in formic acid to be -2.20 , only 0.4 unit more acid than the pure solvent; using indicator 2 we have found the H_0 for a 0.101 molar solution of sodium sulfate to be -0.25 , which is 0.45 unit less "alkaline" than an equimolar sodium formate solution. From the latter figure the extent of the solvolysis



is 35% and the ionization constant $[\text{H}^+(\text{HCO}_2\text{H})][\text{SO}_4'']/[\text{HSO}_4']$ is 2×10^{-5} . The secondary ionization of sulfuric acid must therefore be negligible in the acid solutions under consideration.

Further evidence that benzene sulfonic acid is not quite a strong acid is offered by an experiment in which the acidity, H_0 , of a solution containing 0.0121 molar sulfuric acid and 0.0945 molar sodium benzene sulfonate was determined with indicator 4 and found to be -2.59 , which is 0.25 unit less acid than is benzene sulfonic acid in 0.0121 molar concentration.

We conclude therefore that sulfuric acid is a strong monobasic acid in formic acid, and that benzene sulfonic acid is nearly but not quite a strong electrolyte. The ionization of the latter is estimated at 60% in 0.1 molar solution and very nearly 100% in 0.01 molar solution.

The Ion Product Constant of the Solvent.—We may set the concentration of solvated hydrogen ion in a solution of a strong acid equal to the stoichiometric concentration of the acid and compare the $pH(\text{HCOOH})$ thus obtained with the H_0 value. From Fig. 1 we obtain as a best value

$$pH(\text{HCOOH}) - H_0 = 4.85 \quad (6)$$

Substituting in equation 2

$$pK_S(\text{HCOOH}) = -\log C_{\text{COOH}'} + H_0 + 4.85 \quad (7)$$

Since sodium formate and aniline are strong bases we may set $C_{\text{COOH}'}$ equal to the stoichiometric concentration of base. Substituting the best values of H_0 from Fig. 1 we have for the logarithmic ion product constant $pK_S(\text{HCOOH})$ at 0.1 molar ionic strength, 6.03; at 0.01 molar ionic strength, 6.17. Substituting in equation 7 we have

$$\log C_{\text{COOH}'} = H_0 - 1.32 \quad (8)$$

which we shall use in calculating the ionization constants of weak bases.

From $pK_S(\text{HCOOH}) = 6.17$, the $pH(\text{HCOOH})$ of pure formic acid is 3.09 and from equation 6 the acidity H_0 of the pure solvent is -1.76 . A direct determination of this quantity by measurements on the pure solvent

is possible with a solvent as highly ionized as formic acid, and furnishes a valuable check on the ion product constant. The experiments were carried out with indicator concentrations (given under the heading c_i in Table III) too small to displace significantly the acidity of the pure solvent. The formic acid used, purified by the Schlesinger method, is estimated from its freezing point to contain less than 0.005 mole per liter of water. From the results given in Table III the mean observed value of H_0 is -1.8 in excellent agreement with the above calculated value.

TABLE III
ACIDITY OF PURE FORMIC ACID

c_i	I_w	$\text{Log} \frac{[\text{BH}^+]}{[\text{B}]}$	H_0	c_i	I_w	$\text{Log} \frac{[\text{BH}^+]}{[\text{B}]}$	H_0
		o-Nitraniline				p-Nitroazobenzene	
0.00005	0.081	+1.05	-1.69	0.00005	0.037	-1.10	-1.89
.00004	.084	+1.04	-1.68	.00002	.042	-1.04	-1.95

Comparison with Conductivity and Electrometric Data.—Hammett and Dietz calculated from Schlesinger's conductivity data a value for $pK_S(\text{HCOOH})$ of 6.3. The agreement of indicator and conductivity results is therefore excellent.

It is to be expected that the indicator acidity H_0 will only agree with the electrometrically measured values in the special case of unchanging medium. Barring large specific effects upon activity coefficients or difficulties due to liquid junction potentials there should, however, be agreement between electrometric and indicator values of the formic acid functions. An approximate agreement does indeed exist between the indicator value of $pK_S(\text{HCOOH})$ and the electrometric value of Hammett and Dietz, the difference being about 0.3 unit at 0.1 molar ionic strength, and smaller at lower concentrations. This difference is due chiefly to the assumption made in calculating the electrometric value that benzene sulfonic acid is completely ionized; in fact values of $pK_S(\text{HCOOH})$ calculated from the indicator data on the same assumption agree excellently with the electrometric results. It should be emphasized that the differences between electrometric and indicator results and the previous failure to recognize the incompleteness of ionization of benzene sulfonic acid derive from the inherent uncertainty of any electrometric determination of ion concentrations,¹¹ and that the general picture of the electrolytic properties of the solvent formic acid obtained by Hammett and Dietz is in every way supported by the indicator results.

Some Weak Bases.—By the equation¹²

$$pK' = H_0 - \log \frac{C_B}{C_{\text{BH}^+}}$$

¹¹ Taylor, *J. Phys. Chem.*, **31**, 1478 (1927); Guggenheim, *ibid.*, **33**, 842 (1929); **34**, 1540, 1758 (1930).

¹² Equation 4 of the previous article.

the pK' of a base may be determined by measurement of the acidity, H_0 , of a solution of known concentration of the base and its corresponding ion. We now possess sufficient information about the solvent formic acid to enable us to calculate the requisite concentrations from the H_0 measurement itself. Thus for a moderately strong base we may measure the H_0 of a solution of the base in formic acid, read from the curve in Fig. 1 the concentration of formate ion corresponding to that acidity, set this equal to the concentration of the ion BH^+ , and obtain the concentration of the base B as the difference between the concentration of BH^+ and the stoichiometric concentration of base. For a weaker base we may determine the acidity of a solution containing known concentrations of the base and of a strong acid, read from Fig. 1 the concentration of solvated hydrogen ion, and set the concentration of BH^+ equal to the difference between this and the stoichiometric concentration of acid. In Table IV such data and results are given for three very weak bases. In this C is the stoichiometric

TABLE IV
STRENGTHS OF SOME WEAK BASES

C	C_a	H_0	C_{BH^+}	C_B	$pK_B(HCOOH)$	pK'
Base acetanilide, indicators 2 and 3						
0.0768	0	-0.72	0.0089	0.0679	2.93	-1.60
.1526	0	-0.51	.0158	.1378	2.74	-1.45
Base propionitrile, indicators 4, 5 and 6						
0.1231	0.0134	-2.69	0.0071	0.116	5.25	-3.90
Base water, indicators 4, 5, and 6						
0.167	0.0390	-2.77	0.0301	0.137	4.78	-3.43

concentration of base, C_a is the stoichiometric concentration of acid (for which benzene sulfonic acid was used), C_B is the true concentration of the base, C_{BH^+} the true concentration of the ion of the base, $pK_B(HCOOH)$, calculated by equations 4 and 8, is the logarithmic ionization constant of the base in the formic acid system, H_0 and pK' have their usual meaning in this work.

The results lead to a smaller basicity for the nitrogen compounds than is indicated by previous work in other solvents. From Hall's survey¹³ we may derive a value for the pK' of these substances by comparison of his $pK'_{(HAc)}$ with the value for *p*-nitraniline, the value of +1.40 for the pK' of the latter being the basis of our whole system. The result is -1.9 for propionitrile and -0.83 for acetanilide. The values derived from direct measurements on aqueous solutions differ even more from our values, being -0.8 for propionitrile and +0.4 for acetanilide. These discrepancies are no greater than is to be expected from the attempt to measure the strength of bases as weak as are these in water and even in acetic acid.

¹³ Hall, THIS JOURNAL, 52, 5124 (1930).

Our value (-3.43) for the pK' of water is much smaller than the value (-1.8) calculated by Brönsted and Wynne-Jones¹⁴ and used by them and others in the interpretation of kinetic data in aqueous solution. Their value is based upon the identification of the true concentration of water with the total concentration of water in a dilute aqueous solution, and upon the identification of the concentration of oxonium ion with the total concentration of solvated hydrogen ion in the same solution. The first assumption neglects the association of the water; the second, the possible further hydration of oxonium ion. The sign of the difference indicates that such further hydration decreases the true concentration of OH_3^+ to a greater extent than does association the water concentration.

Our value of the ionization constant of water in formic acid agrees in order of magnitude with the rough estimate which Hammett and Dietz based upon electrometric measurements ($pK_B(\text{HCOOH}) = 5.5$), but much greater confidence may be placed in the new figure. This results not only from the greater speed with which colorimetric measurements may be made and the greater certainty with which the solutions may be protected from atmospheric or other contamination, but from the actually greater precision of colorimetric measurements. It is very easy to be blinded by the precision of a potentiometric measurement to the fact that no measurement of ion concentration or activity based upon a cell with liquid junctions has any significance to a precision greater than that equivalent to a few millivolts.¹¹

Summary

The ease, reliability and precision of properly carried out indicator measurements have been verified on a non-aqueous solvent.

The relative values of basicity of a series of simple basic indicators determined in solutions in formic acid agree very closely with those obtained in mixtures of strong acids and water.

The investigation of the properties of formic acid as an ionizing solvent by the indicator method leads to results in essential agreement with those obtained by electrometric and conductivity methods.

In this solvent sulfuric acid is a strong monobasic acid, benzene sulfonic acid is nearly but not quite a strong acid, sodium formate and aniline are strong bases.

The ionization constants in this solvent of bisulfate ion, propionitrile, acetanilide and water have been determined and also the general acid-base functions (pK') of the bases.

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¹⁴ Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).