Table I. 3-Methylamino-4(3*H*)-quinazolinones[a]

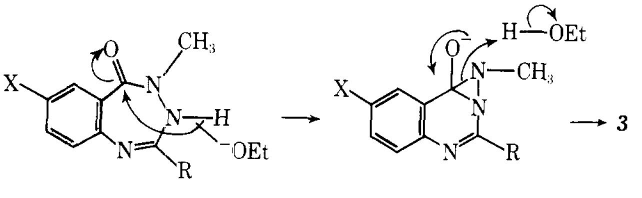
Registry no.	Compd	X	R	Yield, %	Mp, °C	Formula
60512-86-9	**3a**	H	H	50	108–109	$C_9H_9N_3O$
59169-44-7	**3b**	H	CH_3	95	111.5–112.0	$C_{10}H_{11}N_3O$
60512-87-0	**3c**	Cl	H	72	151–152	$C_9H_8ClN_3O$
60512-88-1	**3d**	NO_2	H	59	193–195	$C_9H_8N_4O_3$
60512-89-2	**3e**	Cl	CH_3	93	132–133	$C_{10}H_{10}ClN_3O$
60512-90-5	**3f**	Cl	C_6H_5	86	100.5–101.0	$C_{15}H_{12}ClN_3O$
60512-91-6	**3g**	Cl	C_2H_5	94	154–155	$C_{11}H_{12}ClN_3O$

[a] Analytical data were within ±0.3% for C, H, N. Ed.

oxymethyleneiminobenzoate[6] (4) upon condensation with methylhydrazine yielded **3a**, identical in all respects with the material obtained from the rearrangement of **2a**. In addition, treatment of 4 with 1-acetyl-1-methylhydrazine gave **5**, which was also obtained by acetylation of **3a**.

One plausible mechanism for this ring contraction is depicted in Scheme III. Base extraction of the N_3H proton would lead to a resonance stabilized anion whose transannular attack on the carbonyl could give a diaziridine intermediate. Ring opening of the latter would produce the 3-methylaminoquinazolinones.

Scheme III



Experimental Section

Infrared spectra of solids were obtained in KBr disks and of liquids as thin films between NaCl plates on a Beckman IR-33 spectrophotometer. The ^1H NMR spectra were obtained on a Hitachi Perkin-Elmer R20A nuclear magnetic resonance spectrometer. Combustion analyses were provided by Dr. George I. Robertson, Florham Park, N.J.

A General Procedure for Rearrangement of 3,4-Dihydro-5*H*-1,3,4-benzotriazepin-5-ones (2a–g) to 3-Methylamino-4(3*H*)-quinazolinones (3a–g). A solution of 50 mmol of the requisite benzotriazepine (**2a–g**) in 50 ml of anhydrous ethanol was treated with a freshly prepared solution of 5.0 mmol of NaOEt in 25 ml of absolute ethanol (obtained by dissolution of 0.12 g of sodium in the 25 ml of alcohol). The deep red solution which resulted was heated with stirring at reflux for 20 h, chilled, and filtered in vacuo. The resulting 3-methylamino-4(3*H*)-quinazolinones were recrystallized from ethanol to analytical purity. The nitro isomer (**3d**) was recrystallized from 3:1 acetic acid–ethanol. Yields and properties are reported in Table I.

3-Methylamino-4(3*H*)-quinazolinone (3a) from Methyl 2-Ethoxymethyleneiminobenzoate (4). Methyl 2-ethoxymethyleneiminobenzoate[6] (4, 10.36 g, 50.0 mmol) was treated with 3.00 g (6.0 mmol) of methylhydrazine. Two minutes after the addition, evolution of considerable heat was noted and the product **3a** began to precipitate. The reaction mixture was chilled in an ice bath and the solid collected on a filter and washed with ether. Analytically pure, white crystals of the quinazolinone (8.00 g, 92%) were collected: mp 109–110.5 °C; ir (KBr) 3230 (N–H), 1675 (C═O), and 1650 cm^{-1} (C═N); NMR ($CDCl_3$) δ 2.89 (s, 3, CH_3), 5.97 (s, 1, NH), 7.20–8.30 (m, 5, ArH and C_2 H). The compound was spectrally identical (^1H NMR and ir), of identical melting point, and of undepressed mixture melting point with the material obtained by rearrangement of **2a**.

3-(*N*-Acetyl-*N*-methylamino)-4(3*H*)-quinazolinone (5) from Methyl 2-Ethoxymethyleneiminobenzoate (4). A solution was prepared from 50.0 mmol of 4 and 1-acetyl-1-methylhydrazine.[7] Immediately it developed a deep red color and precipitated the product quinazolinone (5). The mixture was chilled in ice, and the solid was filtered, washed with ether, and recrystallized twice from ethanol to yield 6.40 g (59%) of **5**: mp 119–120 °C; ir (KBr) 1690 (C═O), 1675 (C═O), and 1650 cm^{-1} (C═N); NMR ($CDCl_3$) δ 1.97 and 2.36 (s, 3, $COCH_3$), 3.40 and 3.59 (s, 3, NCH_3),[8] and 7.30–8.50 (m, 5, ArH and C_2 H).

Anal. Calcd for $C_{11}H_{11}N_3O_2$: C, 60.82; H, 5.10; N, 19.34. Found: C, 61.01; H, 5.08; N, 19.17.

Acetylation of 3-Methylamino-4(3*H*)-quinazoline. Preparation of 5. A mixture of 0.10 mol of acetic anhydride and 0.048 mol of **3a** was stirred and heated at reflux for 2 h and cooled to room temperature, and the excess acetic anhydride was removed on a rotary evaporator. The viscous, amber oil which resulted was induced to crystallize by trituration with a small quantity of ether. The crude product was recrystallized from ethanol to give 8.05 g (78%) of analytically pure **5**, mp 120–121 °C, identical in all respects with the material obtained by condensation of 4 and 1-acetyl-1-methylhydrazine.

Acknowledgments. This work was supported by a contract from Stuart Pharmaceuticals, Division of ICI United States Inc., to N.D.H., and was abstracted in part from the Ph.D. Thesis of R.W.L. (Lehigh University, 1975).

Registry No.—**2a**, 59169-76-5; **2b**, 59169-80-1; **2c**, 59169-77-6; **2d**, 59169-79-8; **2e**, 59169-81-2; **2f**, 59169-88-9; **2g**, 59169-84-5; **4**, 59204-51-2; **5**, 60512-92-7; methylhydrazine, 60-34-4; 1-acetyl-1-methylhydrazine, 3530-13-0.

References and Notes

(1) Presented at the 172d National Meeting of the American Chemical Society, Organic Chemistry Division, San Francisco, Calif., Aug. 30, 1976.
(2) H. C. Van Der Plas, "Ring Transformations of Heterocycles", Vol. 2, Academic Press, New York, N.Y., 1973, pp 282–321.
(3) W. Metlesics, G. Silverman, and L. H. Sternbach, *Monatsh. Chem.*, **98**, 633 (1967).
(4) S. Rissi, O. Pirola, and F. Selva, *Tetrahedron*, **24**, 6395 (1968).
(5) R. W. Leiby and N. D. Heindel, *Synth. Commun.*, **6**, 295 (1976).
(6) R. W. Leiby and N. D. Heindel, *J. Org. Chem.*, **41**, 2736 (1976).
(7) R. L. Hinman and D. Fulton, *J. Am. Chem. Soc.*, **80**, 1895 (1958).
(8) As another example of the slow rotation of bulky groups around the N_3 quinazolinone nitrogen [see J. B. Taylor, D. R. Harrison, and F. Fried, *J. Heterocycl. Chem.*, **9**, 1227 (1972)], the *N*-methyl and the acetyl methyl resonances were evidenced as two temperature-dependent double peaks in the ratio of 2:1 at room temperature.

Acidity Functions of Hydrochloric Acid, Perchloric Acid, and Sulfuric Acid and p*K*$_a$ Values of Some Primary Aromatic Amines in 50% Volume/Volume Aqueous Ethanol[1]

William N. White,* Thomas Vogelmann, Michael Morse,
and Hilda S. White

Department of Chemistry, University of Vermont,
Burlington, Vermont 05401

Received January 29, 1976

The general applicability of the Hammett acidity function has been strongly questioned.[2] In spite of this, this parameter still remains the principal measure of the ability of a medium to transfer a proton to a base. In fact many treatments of deviations from Hammett acidity function behavior are expressed in terms of the acidity function.[3] The original deter-

Table I. Physical Properties of Indicators

Aniline	Recrystn solvent[a]	Mp, °C Obsd	Mp, °C Lit.	Absorption max nm[b]	ϵ_B[c]	ϵ_{BH}[d]	$\Delta\lambda$[e]	pK_a[f]	Registry no.
3-NO_2, 4-CH_3	1:5	77.0–78.0	78[g]	361	1460	187		1.91	119-32-4
3-NO_2	1:3	112.0–112.8	112.6[h]	366	1300	62		1.35	99-09-2
3-NO_2, 4-Cl	1:3	102.5–103.5	102.7[i]	363	1180	152	+2	0.63	635-22-3
4-NO_2	1:2	146.0–147.0	147.2[j]	383	15 100	58	+3	−0.19	100-01-6
2-Cl, 5-NO_2	1:3	118.5–119.5	118.5[i]	368	2070	91	+2	−0.88	6283-25-6
2-NO_2	1:9	71.8–72.5	71.6–72.4[k]	415	4900	10	+2	−1.63	88-74-4
2-NO_2, 4-Cl	1:1	115.0–115.5	116.1–116.4[k]	423	4810	19	+3	−2.46	89-63-4
2,5-Cl_2, 4-NO_2	EtOH	153.5–154.0	153–154[l]	367	10 400	159	+4	−3.21	6627-34-5

[a] Ratio designates volume proportions of benzene and cyclohexane in solvent, EtOH = ethanol. [b] Absorption maximum in 50% v/v aqueous ethanol and at lowest percent protonation in acid solution. [c] Extinction coefficient of free base in 50% v/v aqueous ethanol. [d] Extinction coefficient of substituted anilinium ion at absorption maximum of free base measured in solution of $H_0 < \mathrm{p}K_a - 2$. [e] Change in absorption maximum of free base over protonation range of 10% to 90%. [f] Average of pK_a values in HCl, $HClO_4$, and H_2SO_4 obtained by stepwise comparison and extrapolation (see Table II). [g] R. A. Morton and A. McGookin, *J. Chem. Soc.*, 901 (1934). [h] P. Putzeys and J. Brosteaux, *Ann. Soc. Sci. Bruxelles*, **53B**, 118 (1933). [i] M. A. F. Lobry de Bruyn, *Recl. Trav. Chim. Pays-Bas*, **36**, 126 (1917). [j] F. P. Zschiele and J. W. White, *Ind. Eng. Chem., Anal. Ed.*, **12**, 436 (1940). [k] L. C. Smith and L. P. Hammett, *J. Am. Chem. Soc.*, **67**, 23 (1945). [l] N. S. F. Berckmans and A. F. Holleman, *Recl. Trav. Chim. Pays-Bas*, **44**, 851 (1925).

minations of H_0 applied to aqueous acid solutions. This limited the usefulness of H_0 to some degree because of the problem of solubility of organic compounds in water. However, during the past 15 years an increasing number of acidity functions have been defined for nonaqueous or mixed organic–aqueous systems. Unfortunately, many of these have utilized solvents of low polarity in which ion association may become important or solvents with compounds of very different dielectric constant so that solvent segregation might occur. In addition, these H_0 values have been referred to an ideal solution in water as standard state, rather than to an ideal solution in the solvent used.

In the course of an investigation of an acid-catalyzed reaction, solubility problems were encountered. An equal-volume mixture of ethanol and water was chosen as the solvent because (1) it had the needed solvent properties, (2) the two components have about the same volatilities, (3) ethanol and water are "similar" protic solvents with respectable dielectric constants, (4) the two substances are readily available in pure form and are relatively inexpensive, and (5) the mixture is simply and easily prepared. Since acidity function scales for 50% v/v aqueous ethanol referred to the ideal solution in the same medium and employing primary amines[4] throughout as indicators to ensure similar activity coefficient behavior had not been previously determined, it was necessary to do this.

Experimental Section

Purification of Indicators. The various primary amines used in this study were available from the Aldrich Chemical Co. They were purified by initial crystallization from the solvent indicated in Table I followed by chromatography on alumina using ether as eluent and then two further recrystallizations. Physical properties are summarized in Table I.

Preparation of Acid Solutions. Concentrated sulfuric acid, concentrated hydrochloric acid, and 70% perchloric acid were titrated to determine their acid content. Their densities (at 30 °C) were estimated by pycnometer. From these measurements, the amount of water present in each acid was calculated. Then, enough 100% alcohol and water were added to make stock solutions containing 50% v/v water–ethanol. Aliquots of these stock solutions were diluted with 50% v/v water–ethanol to provide series of acid solutions differing in H_0 by 0.2 units or less. The concentrations of these diluted solutions were determined by titration and differed from the concentrations expected from the dilution procedure by less than 0.5%.

Measurement of Ionization Ratios. Stock solutions of each indicator were prepared by dissolving a carefully weighed sample of the substituted aniline in 50% v/v water–ethanol in a volumetric flask (the weight of sample was chosen so that a 31-fold dilution of the stock solution with 50% v/v water–ethanol resulted in a solution with an absorbance of about 0.8 at the absorption maximum of the free base). Mixtures of 0.100 ml of indicator stock solution and 3.00 ml of the various diluted acid solutions in spectrophotometer cells were thermostated at 30 °C and the absorbances of these mixtures at their maxima were determined.

The ionization ratios, $(BH^+)/(B)$, were obtained from the expression $(A_B - A)/(A - A_{BH})$ where A, A_B, and A_{BH} are the absorbances of the solution being measured, the absorbance of the unprotonated base, and the absorbance of the fully protonated base, all determined at the wavelength of maximum absorption for the solution being measured. A_B was obtained from a solution of 0.100 ml of indicator solution in 3.00 ml of 50% v/v water– ethanol and A_{BH} from a solution of 0.100 ml of indicator solution in 3.00 ml of acid solution with an H_0 value at least two units greater than the pK_a of the indicator. Each solution whose absorbance was determined was prepared in duplicate or triplicate with the measured optical densities varying by less than 1%.

In calculations involving the indicator ratios and acid concentrations, the latter were corrected for the amount consumed by reaction with the indicator base.

Results and Discussion

pK_a Values of Indicators. The pK_a values of the indicators employed in this investigation were determined by both the stepwise and extrapolation to infinite dilution procedures with the results shown in Table II. The first of these methods depends upon knowledge of the pK_a of at least one indicator (obtained by the second method), parallelism of plots of log $(BH^+)/(B)$ vs. acid concentration for the various indicators, and the relation

$$\mathrm{p}K_{CH^+} - \mathrm{p}K_{BH^+} = \log\frac{(CH^+)}{(C)} - \log\frac{(BH^+)}{(B)}$$

The maximum deviation from parallelism experimentally is ±0.06 log units (for 2,5-dichloro-4-nitroaniline in the sulfuric acid solutions) and the average deviation is ±0.02 log units for all of the indicators in the various acid solutions. Thus, the stepwise procedure for pK_a estimation has considerable validity in the systems used in this study. The pK_a of 3-nitro-4-methylaniline obtained by the extrapolation method was used as the basis of the stepwise comparison for the hydrochloric and perchloric acid solutions. Since the extrapolation is somewhat ambiguous for the sulfuric acid solutions (vide infra), the average of the pK_a values of 3-nitro-4-methylaniline in hydrochloric and perchloric acid served as the reference point for the sulfuric acid solutions.

pK_a values can also be obtained by extrapolating log $(BH^+)/(B)(H^+)$ vs. (H^+) to infinite dilution [i.e., $(H^+) = 0$]. Usually such plots are linear at low acid concentrations and

Table II. pK_a Values of Indicators in 50% v/v Aqueous Ethanol at 30.0 °C

	HCl solutions[a]		$HClO_4$ solutions[a]		H_2SO_4 solutions[a]			Lit. values	
Aniline	Step[b]	Extn[c]	Step[b]	Extn[c]	Step[b]	Extn[c]	Av[d]	Aq et[e]	H_2O[f]
3-NO_2, 4-CH_3	1.89[g]	1.89	1.92[g]	1.92	1.90[i]	(2.06)[j]	1.91 ± 0.02		2.90[l]
3-NO_2	1.38 ± 0.02	1.37	1.33 ± 0.03	1.34	1.35 ± 0.04	(1.44)[j]	1.35 ± 0.02	1.81[k]	2.50[m]
3-NO_2, 4-Cl	0.69 ± 0.03	0.71	0.59 ± 0.01	0.62	0.56 ± 0.03	(0.66)[j]	0.63 ± 0.05		
4-NO_2	−0.15 ± 0.01	−0.15	−0.22 ± 0.01	−0.19	−0.26 ± 0.01	(−0.09)[j]	−0.19 ± 0.04		0.99[m]
2-Cl, 5-NO_2	−0.81 ± 0.01	(−0.80)[h]			−0.95 ± 0.02	(−0.82)[h]	−0.88 ± 0.07		
2-NO_2	−1.57 ± 0.03	(−1.73)[h]			−1.68 ± 0.03	(−1.67)[h]	−1.63 ± 0.06		−0.29[m]
12-NO_2, 4-Cl	−2.42 ± 0.01	(−2.75)[h]			−2.50 ± 0.02	(−2.86)[h]	−2.46 ± 0.04		−1.03[m]
2,5-Cl_2, 4-NO_2	−3.12 ± 0.04	(−3.36)[h]			−3.29 ± 0.06	(−3.75)[h]	−3.21 ± 0.08		−1.82[m]

[a] Solutions of HCl, $HClO_4$, or H_2SO_4 in 50% v/v aqueous ethanol. [b] pK_a values obtained by stepwise comparison (see text). [c] pK_a values obtained by extrapolation to infinite dilution (see text). [d] Average of pK_a values not in parentheses. [e] 50% v/v aqueous ethanol. [f] Water. [g] Extrapolated value used as basis of stepwise comparison. [h] High acid concentrations cause these extrapolated values to be of questionable validity. [i] Average of pK_a values obtained by extrapolation in HCl and $HClO_4$ solutions. [j] Unknown extent of HSO_4^- dissociation in 50% aqueous ethanol at low (H_2SO_4) makes (H^+) uncertain so the resultant pK_a values are possibly in error. [k] At 20 °C, P. Vetesnik, K. Rothschein, J. Socha, and M. Vecera, *Collect. Czech. Chem. Commun.*, **24,** 1087 (1969). [l] At 25 °C, D. P. N. Satchell and J. L. Wardell, *J. Chem. Soc.*, 4134 (1964). [m] At 25 °C, C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970, p 67.

the extension of the experimental line to zero concentration is a simple matter. In this investigation, the extrapolation was performed by linear regression analysis (average correlation coefficient 0.932). The pK_a values of 2-chloro-5-nitroaniline, 2-nitroaniline, 2-nitro-4-chloroaniline, and 2,6-dichloro-4-nitroaniline derived in this way are of questionable validity since the concentrations of acid are large and the extrapolation to zero is over a wide range. In addition, the treatment of the experimental data in sulfuric acid solutions by the extrapolation procedure is uncertain. (H^+) was set equal to the molar concentration of sulfuric acid, but this is an underestimate, especially in dilute solution, because of the dissociation of HSO_4^-.

The pK_a values obtained by the stepwise comparison technique agree quite closely with those from the extrapolation to infinite dilution procedure. Surprisingly, this is true at all but the highest concentrations of acid (above 1.0 M HCl and H_2SO_4). Furthermore, the pK_a values obtained in different acids are also fairly similar, the maximum average deviation being only ±0.08 pK_a units.

These pK_a values for 50% v/v aqueous ethanol at 30 °C are compared with those for pure water at 25 °C in Table II. The difference between these pK_a values (ΔpK_a) varies from 1.0 to 1.4 units and seems to increase almost linearly with decrease in pK_a. Interpolation of the data of Gutbezahl and Grunwald[5] provides a ΔpK_a of about 0.7 for simple primary aromatic amines in water and 50% v/v aqueous ethanol, both at 25 °C (although other classes of amines have larger ΔpK_a's for this same medium change[6]). The temperature effect on pK_a for a change from 25 to 30 °C (about 0.08 pK_a units[7] for aniline) would increase the expected ΔpK_a when comparing a primary aromatic amine at 25 °C in water with the same compound in 50% v/v aqueous ethanol at 30 °C to about 0.8 units. The larger ΔpK_a's for the nitroanilines that served as indicators may be due to the peculiar activity coefficient behavior of nitro substituted compounds.[8] Substitution in the ortho position also seems to increase ΔpK_a[6] and this may be the cause of the larger ΔpK_a's for the less basic amines, all of which are ortho substituted.

The pK_a of 3-nitroaniline in 50% v/v aqueous ethanol at 20 °C was found to be 1.81 by a "method using buffers".[9] Since the procedure is not described in any more detail, it is impossible to speculate on the reason for the discrepancy between this value and that obtained in this study (1.35). The temperature difference alone would account for only about 0.16 pK_a units[7] of the disagreement.

Acidity Functions. Acidity functions in aqueous organic systems have usually been related to an ideal solution in water (the infinitely dilute solution) as the standard state. However, it is preferable[10] to refer the acidity function scale in an aqueous alcohol solvent to the ideal solution in the same solvent as the standard state. Correlation of reaction rates with H_0 then relate those rates to the standard state in that solvent system. In this study, the acidity functions were referred to infinitely dilute solutions in 50% v/v aqueous ethanol by use of the pK_a values defined for this medium.

Values of the acidity function were obtained from the experimentally determined ionization ratios of the indicators, their pK_a's estimated by the stepwise procedure, and the relation

$$H_0 = pK_{BH} - \log (BH^+)/(B)$$

Values in the overlap regions were averaged to obtain the final H_0 for a particular acid concentration. Interpolation of these results provided the data in Table III. The actual acid concentrations utilized covered the ranges of 0.000969–5.26 M H_2SO_4, 0.00115–2.30 M $HClO_4$, and 0.00108–6.77 M HCl. The concentration increments were chosen so that the measured differences in H_0 between consecutive concentrations were usually less than 0.2 units and never more than 0.3 units.

Inspection of the results for the various acids in Table III yields some interesting comparisons. H_0 values for HCl and $HClO_4$ are almost identical in the region from 0.001 M to 0.10 M as might be anticipated for strong acids behaving independently of the nature of their anions at low concentrations. In this same range, the H_0 values for the H_2SO_4 solutions are less than those for $HClO_4$ and HCl solutions at equivalent molar concentrations. This is undoubtedly due to the second dissociation of H_2SO_4 (i.e., ionization of HSO_4^-) which increases the acidity of the medium. At concentrations above 0.10 M, the H_0 values of $HClO_4$ and H_2SO_4 solutions are similar while those for HCl solutions at the same concentrations are higher. Apparently, the dissociation of HSO_4^- in this region becomes unimportant so that the two strong oxygen acids behave nearly the same. The measurements for $HClO_4$ have probably not been carried to sufficiently high concentrations so that specific ion effects of ClO_4^- vis-à-vis HSO_4^- become obvious, although the small change in the difference between H_0 values of $HClO_4$ and H_2SO_4 over the range from 0.2 to 2.4 M may be a harbinger of a more pronounced effect of this type at higher molarities. The lower acidity of HCl solutions as compared to $HClO_4$ and H_2SO_4 solutions of the

Table III. H_0 Values[a] in 50% v/v Aqueous Ethanol at 30.0 °C

	H_0				H_0		
M	HCl	$HClO_4$	H_2SO_4	M	HCl	$HClO_4$	H_2SO_4
0.001	3.11	3.01	2.78	1.4	−0.59	−0.90	−0.91
0.002	2.77	2.71	2.53	1.6	−0.71	−1.06	−1.07
0.003	2.57	2.53	2.39	1.8	−0.82	−1.22	−1.20
0.004	2.43	2.40	2.27	2.0	−0.94	−1.37	−1.33
0.005	2.32	2.31	2.18	2.2	−1.04	−1.52	−1.46
0.006	2.23	2.22	2.11	2.4	−1.15	−1.66	−1.59
0.007	2.16	2.15	2.05	2.6	−1.25		−1.74
0.008	2.10	2.09	1.99	2.8	−1.36		−1.88
0.009	2.04	2.04	1.94	3.0	−1.46		−2.04
0.01	1.99	1.99	1.90	3.2	−1.57		−2.19
0.02	1.67	1.67	1.60	3.4	−1.67		−2.35
0.03	1.49	1.49	1.43	3.6	−1.79		−2.51
0.04	1.36	1.35	1.31	3.8	−1.90		−2.66
0.05	1.26	1.25	1.20	4.0	−2.01		−2.83
0.06	1.18	1.17	1.11	4.2	−2.12		−3.00
0.07	1.11	1.09	1.03	4.4	−2.24		−3.18
0.08	1.05	1.03	0.96	4.6	−2.35		−3.35
0.09	1.00	0.97	0.90	4.8	−2.45		−3.52
0.10	0.95	0.92	0.84	5.0	−2.56		−3.70
0.2	0.62	0.56	0.46	5.2	−2.67		−3.86
0.3	0.42	0.34	0.23	5.4	−2.78		−4.03
0.4	0.26	0.17	0.05	5.6	−2.88		−4.20
0.5	0.13	0.02	−0.09	5.8	−2.99		−4.36
0.6	0.02	−0.11	−0.21	6.0	−3.20		−4.69
0.7	−0.09	−0.23	−0.32	6.4	−3.30		−4.86
0.8	−0.18	−0.34	−0.42	6.6	−3.40		−5.02
0.9	−0.25	−0.44	−0.51	6.8	−3.49		−5.19
1.0	−0.33	−0.54	−0.60				
1.2	−0.46	−0.73	−0.76				

[a] Interpolated from experimental results.

same molarity at medium and high concentrations observed in this study is also apparent in aqueous solutions.[11] This may result from incomplete ionization of HCl at higher concentrations.[12]

These trends in relative acidity function values for 50% v/v aqueous ethanol are also obvious, although at different concentrations, for these same acids in aqueous solutions.[11] At low acid concentrations (less than 0.10 M), the H_0 values for the various acids in 50% v/v aqueous ethanol and in water are almost identical. However, at higher acid concentrations, the acidity functions in the mixed solvent become more negative than those in water—at equal acid concentrations the aqueous ethanol solutions have a greater acidity than the aqueous solutions. This is undoubtedly due to the poorer solvating ability of the partially organic solvent.

It is also useful to compare the results of this investigation with those obtained in studies of similar mixed solvents. Satchell[13] determined the acidity function of HCl (0.05–6.2 M) in 24.4 mol % ethanol–water (52% v/v ethanol in water) using the ideal solution in pure water as the standard state. His H_0 values should therefore differ from the ones in the present paper by about 1.14 units [the difference between the pK_a of p-nitroaniline in water (0.99) and in 50% v/v aqueous ethanol (−0.15)]. In fact, they do differ by 1.14 ± 0.02. Vecera and his collaborators[9,14] measured H_0 for $HClO_4$ in 50% v/v aqueous ethanol at concentrations from 0.1 to 7.5 M. Using buffer solutions in the mixed solvent, they assigned a pK_a of 1.81 to m-nitroaniline as opposed to 1.33 found in this study. Thus, their H_0 values at low acid concentrations where m- and p-nitroanilines were used as indicators should differ from those found here by 0.48 units. The correlation between the two scales is actually rather poor since the actual difference in the short range between 0.10 and 1.0 M is 0.39 ± 0.04 units. It is unlikely that this discrepancy is due to the temperature difference of the two studies (10 °C). Above 1.0 M $HClO_4$, substituted o-hydroxyazobenzenes were used to establish the acidity functions. Thus, it is not surprising that the results of the two studies differ even more radically at the higher acidities.

This investigation has therefore led to pK_a values of a series of weakly basic primary aromatic amines in 50% v/v aqueous ethanol and the establishment of acidity functions in this medium for hydrochloric, perchloric, and sulfuric acids.

Registry No.—Sulfuric acid, 7664-93-9; hydrochloric acid, 7647-01-0; perchloric acid, 7601-90-3.

References and Notes

(1) This work was supported in part by the National Science Foundation (Grants GP-8996 and GP-1970).

(2) See, for example, R. Curci, F. DiFuria, A. Levi, V. Lucchini, and G. Scorrano, *J. Chem. Soc., Perkin Trans. 2,* 341 (1975); A. Levi, G. Modena, and G. Scorrano, *J. Am. Chem. Soc.,* **96,** 6586 (1974); and references cited therein.

(3) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.,* **44,** 1899, 1917 (1966).

(4) M. J. Jorgenson and D. R. Hartter, *J. Am. Chem. Soc.,* **85,** 878 (1963).

(5) B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.,* **75,** 559 (1953).

(6) W. J. Gelsema, C. L. DeLigny, and G. F. Visseran, *Recl. Trav. Chim. Pays-Bas,* **84,** 1129 (1965).

(7) A. I. Biggs, *J. Chem. Soc.,* 2572 (1961).

(8) K. Yates and R. A. McClelland, *Can. J. Chem.,* **52,** 1098 (1974); R. H. Boyd, *J. Am. Chem. Soc.,* **85,** 1555 (1963).

(9) P. Vetesnik, K. Rothschein, J. Socha, and M. Vecera, *Collect. Czech. Chem. Commun.,* **34,** 1087 (1969).

(10) C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970, p 219.

(11) M. A. Paul and F. A. Long, *Chem. Rev.,* **57,** 1 (1957).

(12) HCl is predicted to have a pK_a of −7 in aqueous solution (F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, p 169) while $HClO_4$ has an estimated pK_a of about −10 (J. E. Huheey, "Inorganic Chemistry, Principles of Structure and Reactivity", Harper and Row, New York, N.Y., 1972, p 213) and H_2SO_4 is probably of intermediate acid strength.

(13) D. P. N. Satchell, *J. Chem. Soc.,* 3524 (1957).

(14) K. Rothschein, J. Socha, P. Vetesnik, and M. Vecera, *Collect. Czech. Chem. Commun.,* **35,** 3128 (1970).