

69. *The Ionisation Constants of Some Substituted Anilines and Phenols: A Test of the Hammett Relation.*

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The ionisation constants of aniline and 21 substituted anilines, and of phenol and 13 substituted phenols, in aqueous solution at 25° have been measured by the spectrophotometric method. The Hammett ρ parameter is found to be 2.889 for the aniline series and 2.229 for the phenol series, these parameters predicting the ionisation constants of 26 *meta*- and *para*-substituted compounds with a mean deviation of 0.04 in pK .

THE ionisation constants of phenol, the cresols, nitrophenols, and methoxyphenols in aqueous solution at 25° have already been determined spectrophotometrically.¹ Measurements are now reported on the twelve halogenophenols and on the corresponding halogeno- and nitro-anilines, the toluidines, and the anisidines. The ionisation constant of *m*-nitrophenol has been redetermined in borax buffers which we believe to be more reliable than the barbitone buffer used previously. Data are now available for 28 *meta*- and *para*-substituted anilines and phenols and they can be used to test Hammett's relation:² $pK = \sigma\rho$, by using a set of σ values obtained by putting $\rho = 1$ for the substituted benzoic acids; with one exception, all the σ values needed can be got from the conductance measurements of Dippy *et al.*;³ the remaining acid, *p*-iodobenzoic acid, has been studied

¹ Biggs, *Trans. Faraday Soc.*, 1954, **50**, 800; 1956, **52**, 35; Robinson and Biggs, *ibid.*, 1955, **51**, 901.

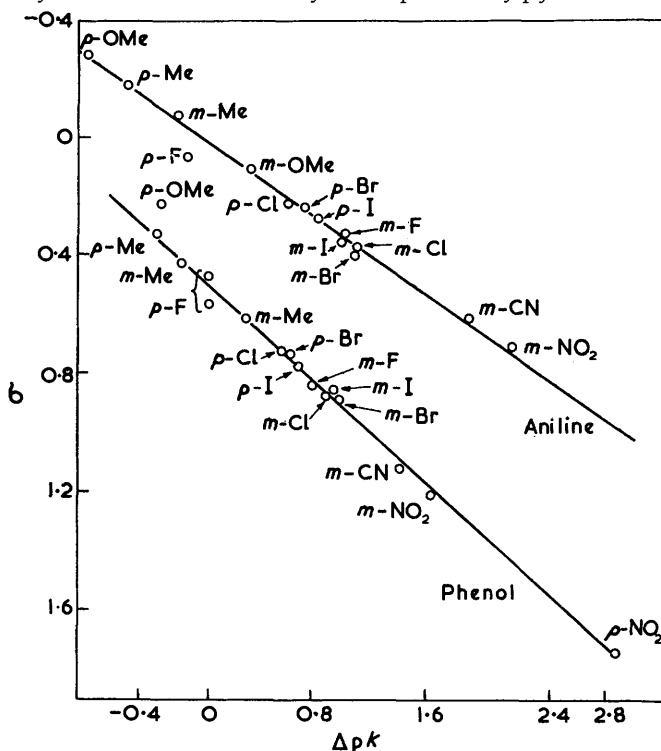
² Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940.

³ Dippy and Williams, *J.*, 1934, 1888; Dippy, Williams, and Lewis, *J.*, 1935, 343; Dippy and Lewis, *J.*, 1936, 644; 1937, 1426.

recently.⁴ It is hoped that the present work, in which all the ionisation constants are measured by the same method, will provide a useful supplement to Jaffe's recent survey⁵ of Hammett's relation.

Table I contains the results of the measurements on the substituted anilines and phenols, together with those obtained previously for phenol, the cresols, methoxyphenols,

pK of substituted anilinium ions and phenols versus σ . The σ -scale is displaced 0.5 to the right in plotting points for the substituted phenols. The σ -values are derived from *pK* data for substituted benzoic acids except for *p*-nitrophenol and *p*-nitroaniline for which $\sigma = 1.239$ is used and for *p*-fluorophenol where two points are plotted, one on the right with $\sigma = 0.062$ derived from the *pK* value of *p*-fluorobenzoic acid, and one on the left with $\sigma = -0.026$ derived from the *pK* value of *p*-fluoroaniline.



and *o*- and *p*-nitrophenol. For the anilines, it is the acid ionisation constant which is given, *i.e.*, that of the acid conjugate to the substituted aniline. It is hoped that the results are accurate to the second decimal place but it is difficult to know if this has been achieved; we have found in the literature fifty *pK* values recorded which agree within 0.06 with those given in Table I, the mean difference being 0.02, but it is not always possible to decide if it is the thermodynamic ionisation constant which has been reported and to what extent liquid-junction potentials have affected *pK* values derived from glass-electrode measurements.

A graph of ΔpK of the substituted anilinium ions, *i.e.*, *pK* (anilinium ion) — *pK* (substituted anilinium ion), against ΔpK of the substituted benzoic acids is given in the Figure. Twelve of the points lie close to a straight line, the exceptions being *p*-nitroaniline (not shown on the graph) and *p*-fluoroaniline. The equation of the best straight line through the points is $pK = 0.023 + 2.889\sigma$, so that the best value of the ρ parameter for the anilinium series is 2.889 and the *pK* values of substituted anilines can be represented by

⁴ Robinson and Ang, *J.*, 1959, 2314.

⁵ Jaffé, *Chem. Rev.*, 1953, 53, 191.

$pK = 4.580 - 2.889\sigma$, with a mean difference of 0.04 between observed and calculated values.

In the phenol series, as the Figure shows, twelve points lie close to a straight line, the value of $\sigma(p\text{-NO}_2)$ being taken from the aniline series. The equation of the best straight line through the points is $pK = 0.079 + 2.229\sigma$, so that the best value of the ρ parameter for the phenol series is 2.229 and the pK values of substituted phenols can be represented by $pK = 9.919 - 2.229\sigma$, with a mean difference of 0.04 between observed and calculated values. *m*-Cyanoaniline and *m*-cyanophenol have been reported⁶ to have pK 2.746 and 8.608 respectively; the above equations predict 2.783 and 8.550, $\sigma(m\text{-CN}) = 0.614$ being used from the measurements of Briegleb and Bieber.⁷

There are, however, some anomalies which can be demonstrated by using the experimental data to calculate σ with $\rho = 1, 2.889$, and 2.229 in the benzoic acid, aniline, and phenol series respectively; the following σ values are calculated for four *para*-substituents:

	Benzoic acid	Aniline	Phenol
<i>p</i> -NO ₂	0.778	1.239	1.243
<i>p</i> -OMe	-0.268	-0.264	-0.130
<i>p</i> -F	0.062	-0.026	0.005
<i>p</i> -CN	0.671	0.983	0.874

TABLE 1. pK Values of substituted aniline and phenols at 25°.

	<i>o</i>	<i>m</i>	<i>p</i>		<i>o</i>	<i>m</i>	<i>p</i>
Aniline		(4.60)		Phenol		(10.00)	
Fluoroaniline ...	3.20	3.59 (+1)	4.65	Fluorophenol ...	8.70 ₅	9.21 (-4)	9.91
Chloroaniline ...	2.65	3.52 (-2)	3.98 (-5)	Chlorophenol ...	8.53	9.13 (-4)	9.42 (0)
Bromoaniline ...	2.53	3.58 (-8)	3.86 (+5)	Bromophenol ...	8.44	9.03 (+2)	9.36 (+4)
Iodoaniline	2.60	3.61 (-4)	3.78 (+1)	Iodophenol	8.51	9.06 (+7)	9.30 ₅ (0)
Toluidine	4.45	4.73 (+5)	5.08 (0)	Cresol	10.29	10.09 (-2)	10.26 (+4)
Anisidine	4.52	4.23 (+1)	5.34 (+1)	Methoxyphenol	9.98	9.65 (+1)	10.21
Nitroaniline ...	-0.26	2.46 (+7)	1.00	Nitrophenol ...	7.21	8.38 ₅ (-5)	7.15 (+1)

The figures in parentheses give the difference in pK ($\times 10^3$) between the observed value and that calculated by: $pK = 4.580 - 2.889\sigma$ for substituted anilinium ions, and $pK = 9.919 - 2.229\sigma$ for substituted phenols, the difference being recorded as positive if the calculated value is greater than the observed.

TABLE 2. Buffer solutions.

Solution	pH	$-\log \gamma_1$	Solution	pH	$-\log \gamma_1$		
<i>Formate buffer</i> : $xM\text{-H}\cdot\text{CO}_2\text{H} + 1.247xM\text{-H}\cdot\text{CO}_2\text{K} + 1.079xM\text{-KCl}$ (see ref. a)			<i>Borax buffer</i> : 50 ml. 0.025M-borax + x ml. 0.1M-NaOH diluted to 100 ml. (see ref. c)				
Formate A	$x = 0.025$	3.77	0.087	Borax G	$x = 15.0$	9.80	0.077
Formate B	$x = 0.010$	3.80	0.063	Borax H	$x = 16.7$	9.90	0.078
<i>Acetate buffer</i> : $xM\text{-C}_2\text{H}_3\text{O}_2 + xM\text{-C}_2\text{H}_3\text{O}_2\text{Na}$ (see ref. 9)			Borax I	$x = 18.3$	10.00	0.079	
Acetate A	$x = 0.1$	4.66	0.102	<i>Borax buffer</i> (see ref. b)			
Acetate B	$x = 0.05$	4.68	0.083	0.025M-Borax	9.17	0.083	
Acetate C	$x = 0.01$	4.72	0.044	0.05M-Borax	9.20	0.102	
<i>Succinate buffer</i> : $xM\text{-C}_4\text{H}_5\text{O}_4\text{Na} + xM\text{-C}_4\text{H}_4\text{O}_4\text{Na}_2$ (see ref. b)			<i>Carbonate buffer</i> (see ref. b)				
Succinate A	$x = 0.05$	5.34	0.117	0.025M-NaHCO ₃ + 0.025M-Na ₂ CO ₃	10.02	0.102	
Succinate B	$x = 0.025$	5.40	0.102				
Succinate C	$x = 0.01$	5.47	0.077				
<i>Borax buffer</i> : 50 ml. 0.025M-borax + x ml. 0.1M-HCl diluted to 100 ml. (see ref. c)							
Borax A	$x = 16.6$	8.40	0.065				
Borax B	$x = 15.2$	8.50	0.065				
Borax C	$x = 13.5$	8.60	0.065				
Borax D	$x = 11.6$	8.70	0.065				
Borax E	$x = 9.4$	8.80	0.065				
Borax F	$x = 7.1$	8.90	0.065				

^a Calc. from data of Harned and Embree (*J. Amer. Chem. Soc.*, 1934, **56**, 1042). ^b Manov, DeLollis, Lindvall, and Acree, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 543; Bates, Pinching, and Smith, *ibid.*, 1950, **45**, 418. ^c Bates and Bower, *ibid.*, 1955, **55**, 197; *Analyt. Chem.*, 1956, **28**, 1322.

⁶ Fickling, Fischer, Mann, Packer, and Vaughan, *J. Amer. Chem. Soc.*, 1959, **81**, 4226.

⁷ Briegleb and Bieber, *Z. Elektrochem.*, 1951, **55**, 250.

TABLE 3. Ionization constants at 25°.

Aniline: $5.3 \times 10^{-4}N$; 281 μ M; $D_1 = 0$; $D_2 = 0.716$				<i>o</i> -Iodoaniline: $2.3 \times 10^{-4}N$; 290 μ M; $D_1 = 0.017$; $D_2 = 0.548$.			
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	Solution	<i>D</i>	$\log \alpha/(1 - \alpha)$	$-\log m_{H^+}$ <i>pK</i>
Acetate A	0.338	-0.049	4.606	0.00262M-HCl	0.295	0.041	2.600 2.559
Acetate B	0.356	-0.005	4.606	0.00210M-HCl	0.325	0.140	2.698 2.558
Acetate C	0.400	0.102	4.598	0.00158M-HCl	0.361	0.265	2.824 2.559
<i>o</i> -Fluoroaniline: $3.4 \times 10^{-4}N$; 277 μ M; $D_1 = 0$; $D_2 = 0.550$				<i>m</i> -Iodoaniline: $2.3 \times 10^{-4}N$; 290 μ M; $D_1 = 0.014$; $D_2 = 0.477$.			
Solution	<i>D</i>	$\log \alpha/(1 - \alpha)$	$-\log m_{H^+}$ <i>pK</i>	Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>
0.0025M-HCl	0.122	-0.545	2.651 3.196	Formate A	0.265	0.073	3.618
0.0020M-HCl	0.147	-0.438	2.757 3.195	Formate B	0.285	0.150	3.598
0.0015M-HCl	0.180	-0.313	2.896 3.209	<i>p</i> -Iodoaniline: $4.6 \times 10^{-4}N$; 290 μ M; $D_1 = 0.030$; $D_2 = 0.658$.			
0.0010M-HCl	0.238	-0.118	3.066 3.211	Formate A	0.309	-0.097	3.791
<i>m</i> -Fluoroaniline: $4.5 \times 10^{-4}N$; 278 μ M; $D_1 = 0.013$; $D_2 = 0.662$				Formate B	0.336	-0.022	3.777
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	(0.00106M-HCl)	0.154	-0.609	3.769
Formate A	0.375	0.101	3.594	<i>o</i> -Toluidine: $4.7 \times 10^{-4}N$; 281 μ M; $D_1 = 0.005$; $D_2 = 0.794$			
Formate B	0.402	0.175	3.582	Acetate A	0.448	0.107	4.450
<i>p</i> -Fluoroaniline: $4.5 \times 10^{-4}N$; 287 μ M; $D_1 = 0.001$; $D_2 = 0.809$				Acetate B	0.467	0.150	4.451
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	Acetate C	0.512	0.255	4.445
Acetate A	0.354	-0.104	4.660	<i>m</i> -Toluidine: $4.7 \times 10^{-4}N$; 281 μ M; $D_1 = 0.002$; $D_2 = 0.644$			
Acetate B	0.377	-0.047	4.647	Acetate A	0.258	-0.178	4.734
<i>o</i> -Chloroaniline: $3.9 \times 10^{-4}N$; 285 μ M; $D_1 = 0.002$; $D_2 = 0.767$				Acetate B	0.274	-0.134	4.734
Solution	<i>D</i>	$\log \alpha/(1 - \alpha)$	$-\log m_{H^+}$ <i>pK</i>	Acetate C	0.311	-0.032	4.715
0.005M-HCl	0.248	-0.324	2.325 2.649	<i>p</i> -Toluidine: $4.7 \times 10^{-4}N$; 287 μ M; $D_1 = 0.000$; $D_2 = 0.674$			
0.004M-HCl	0.288	-0.224	2.425 2.649	Acetate A	0.154	-0.529	5.084
0.003M-HCl	0.347	-0.085	2.555 2.640	Acetate B	0.168	-0.479	5.077
0.002M-HCl	0.426	0.095	2.739 2.644	Acetate C	0.197	-0.384	5.068
<i>m</i> -Chloroaniline: $3.9 \times 10^{-4}N$; 287 μ M; $D_1 = 0.004$; $D_2 = 0.646$				<i>o</i> -Anisidine: $2 \times 10^{-4}N$; 282 μ M; $D_1 = 0.054$; $D_2 = 0.547$			
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	Acetate A	0.309	0.030	4.526
Formate A	0.388	0.173	3.522	Acetate B	0.322	0.076	4.522
Formate B	0.412	0.242	3.515	<i>m</i> -Anisidine: $2 \times 10^{-4}N$; 283 μ M; $D_1 = 0.050$; $D_2 = 0.393$			
<i>p</i> -Chloroaniline: $3.9 \times 10^{-4}N$; 292 μ M; $D_1 = 0.001$; $D_2 = 1.100$; 2 cm. cells				Acetate A	0.281	0.314	4.242
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	Acetate B	0.291	0.373	4.226
Formate A	0.375	-0.287	3.980	<i>p</i> -Anisidine: $2.9 \times 10^{-4}N$; 295 μ M; $D_1 = 0.002$; $D_2 = 0.601$			
Formate B	0.413	-0.222	3.971	Succinate A	0.264	-0.019	5.338
<i>o</i> -Bromoaniline: $2.9 \times 10^{-4}N$; 287 μ M; $D_1 = 0.003$; $D_2 = 0.624$.				Succinate B	0.287	-0.042	5.349
Solution	<i>D</i>	$\log \alpha/(1 - \alpha)$	$-\log m_{H^+}$ <i>pK</i>	Succinate C	0.323	0.063	5.345
0.00318M-HCl	0.308	-0.015	2.518 2.533	<i>o</i> -Nitroaniline: $1.8 \times 10^{-4}N$; 418 μ M; $D_1 = 0.000$; $D_2 = 0.802$			
0.00265M-HCl	0.337	0.066	2.599 2.533	Solution	<i>D</i>	$\log \alpha/(1 - \alpha)$	$-\log m_{H^+}$ <i>pK</i>
0.00212M-HCl	0.372	0.166	2.699 2.533	1.0M-HCl	0.446	0.098	0.098
<i>m</i> -Bromoaniline: $2.9 \times 10^{-4}N$; 286 μ M; $D_1 = 0.004$; $D_2 = 0.524$.				0.9M-HCl	0.474	0.160	0.114
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	0.8M-HCl	0.504	0.228	0.131
Formate A	0.313	0.166	3.527	0.7M-HCl	0.535	0.302	0.147
Formate B	0.330	0.225	3.527	0.6M-HCl	0.567	0.383	0.161
<i>p</i> -Bromoaniline: $2.9 \times 10^{-4}N$; 291 μ M; $D_1 = 0.000$; $D_2 = 0.768$.				0.5M-HCl	0.600	0.473	0.172
Buffer	<i>D</i>	$\log \alpha/(1 - \alpha)$	<i>pK</i>	0.4M-HCl	0.638	0.590	0.192
Formate A	0.306	-0.179	3.870	0.3M-HCl	0.677	0.734	0.211
Formate B	0.336	-0.109	3.857	0.2M-HCl	0.717	0.926	0.227
<i>pK</i> (apparent) extrapolated to zero ionic strength = -0.263.							

TABLE 3. (Continued.)

<i>m</i> -Nitroaniline: $3.6 \times 10^{-4}N$; 360 $\mu\mu$; $D_1 = 0.038$; $D_2 = 0.513$					<i>m</i> -Chlorophenol: $1.9 \times 10^{-4}N$; 300 $\mu\mu$; $D_1 = 0.087$; $D_2 = 0.480$				
Solution	<i>D</i>	$\log \alpha / (1 - \alpha)$	$-\log m_{H^+}$	<i>pK</i>	Buffer	<i>D</i>	$\log \alpha / (1 - \alpha)$	<i>pK</i>	
0.0040M-HCl	0.266	-0.035	2.419	2.454	0.025M-Borax	0.312	0.127	9.126	
0.00262M-HCl	0.313	0.141	2.608	2.467	0.050M-Borax	0.320	0.163	9.134	
0.0025M-HCl	0.320	0.165	2.628	2.463	<i>p</i> -Chlorophenol: $1.9 \times 10^{-4}N$; 300 $\mu\mu$; $D_1 = 0.010$; $D_2 = 0.453$				
0.0021M-HCl	0.340	0.242	2.706	2.464	0.025M-Borax	0.191	-0.161	9.415	
0.0020M-HCl	0.347	0.270	2.727	2.457	0.050M-Borax	0.200	-0.124	9.421	
<i>p</i> -Nitroaniline: $7.2 \times 10^{-5}N$; 382 $\mu\mu$; $D_1 = 0.002$; $D_2 = 0.925$					<i>o</i> -Bromophenol: $2.9 \times 10^{-4}N$; 296 $\mu\mu$; $D_1 = 0.002$; $D_2 = 1.153$				
Solution	<i>D</i>	$\log \alpha / (1 - \alpha)$	<i>pK</i> (apparent)		Borax A	0.586	0.013	8.442	
0.1156M-HCl	0.421	-0.080	1.017		Borax B	0.653	0.115	8.440	
0.0779M-HCl	0.515	0.097	1.012		Borax C	0.713	0.208	8.448	
0.0516M-HCl	0.606	0.277	1.010		<i>m</i> -Bromophenol: $2.9 \times 10^{-4}N$; 294 $\mu\mu$; $D_1 = 0.018$; $D_2 = 0.462$				
Phenol: a repetition of earlier work ¹ using carbonate buffer at 280, 290, and 300 $\mu\mu$ confirms the value of <i>pK</i> 9.998.					0.025M-Borax	0.297	0.228	9.024	
<i>o</i> -Fluorophenol: $4.5 \times 10^{-4}N$; 284 $\mu\mu$; $D_1 = 0.023$; $D_2 = 1.005$					0.050M-Borax	0.305	0.262	9.035	
Buffer	<i>D</i>	$\log \alpha / (1 - \alpha)$	<i>pK</i>		<i>p</i> -Bromophenol: $2.9 \times 10^{-4}N$; 299 $\mu\mu$; $D_1 = 0.027$; $D_2 = 0.663$				
Borax D	0.545	0.055	8.700		0.025M-Borax	0.308	-0.102	9.355	
Borax E	0.596	0.147	8.710		0.050M-Borax	0.320	-0.068	9.365	
<i>m</i> -Fluorophenol: $4.5 \times 10^{-4}N$; 283 $\mu\mu$; $D_1 = 0.038$; $D_2 = 1.107$					<i>o</i> -Iodophenol: $1.2 \times 10^{-4}N$; 298 $\mu\mu$; $D_1 = 0.018$; $D_2 = 0.489$				
0.025M-Borax	0.603	0.050	9.202		Borax B	0.268	0.054	8.506	
0.050M-Borax	0.626	0.087	9.209		Borax C	0.294	0.151	8.509	
<i>p</i> -Fluorophenol: $2 \times 10^{-4}N$; 298 $\mu\mu$; $D_1 = 0.018$; $D_2 = 0.598$					<i>m</i> -Iodophenol: $2.3 \times 10^{-4}N$; 295 $\mu\mu$; $D_1 = 0.043$; $D_2 = 0.756$				
Borax G	0.295	-0.039	9.910		0.025M-Borax	0.480	0.200	9.053	
Borax H	0.328	0.060	9.911		0.050M-Borax	0.493	0.233	9.064	
Borax I	0.362	0.164	9.906		<i>p</i> -Iodophenol: $2.3 \times 10^{-4}N$; 295 $\mu\mu$; $D_1 = 0.125$; $D_2 = 0.504$				
Carbonate	0.377	0.201	9.918		0.025M-Borax	0.304	-0.048	9.301	
Similar measurements at 277 and 240 $\mu\mu$ give <i>pK</i> = 9.907 and 9.905 respectively.					0.050M-Borax	0.312	-0.011	9.308	
<i>o</i> -Chlorophenol: $1.9 \times 10^{-4}N$; 300 $\mu\mu$; $D_1 = 0.002$; $D_2 = 0.593$					<i>m</i> -Nitrophenol: $3.6 \times 10^{-4}N$; 420 $\mu\mu$; $D_1 = 0.008$; $D_2 = 0.452$				
Borax B	0.310	0.037	8.522		Borax A	0.248	0.071	8.831	
Borax C	0.339	0.123	8.536		Borax B	0.272	0.166	8.389	
Borax D	0.372	0.224	8.535						
Borax E	0.403	0.324	8.535						
Borax F	0.429	0.416	8.543						

Thus for *p*-NO₂ substitution the σ -value which holds for both the aniline and the phenol series does not hold in the benzoic acid series, whereas for *p*-OMe substitution the σ -value which is valid in both the benzoic acid and the aniline series does not hold in the phenol series. Again, three different σ -values are needed for *p*-CN substitution, whilst for *p*-F substitution, although the σ -values in the aniline and phenol series are not very far apart, they differ considerably from that in the benzoic acid series.

EXPERIMENTAL

Measurements were made with a "Uvispek" instrument in an air-conditioned room at $25^\circ \pm 0.05^\circ$; a few experiments were made to show that a change of 0.05° corresponds to a change of about 0.007 in *pK*. Unless otherwise mentioned in Table 1, measurements were made with 1 cm. cells. The anilines and phenols were the purest specimens obtainable; these were recrystallised from water wherever possible; otherwise, they were distilled in a stream of nitrogen at low pressure and the middle fractions taken. Table 2 lists the buffers used for the phenols and for those anilines with *pK* > 3.5; for the four *o*-halogenoanilines and the three nitrophenols, *i.e.*, the anilines with *pK* < 3.5, hydrochloric acid was added to the aniline solutions. The ionisation constants calculated from the experimental data proved independent

of the concentration of the buffer solution or of the concentration of hydrochloric acid added, except for *o*- and *p*-nitroaniline. *o*-Nitroaniline showed considerable variation in "apparent" pK with hydrochloric acid concentration, which is not surprising as the implicit assumption that $\log \gamma_{\text{H}^+}/\gamma_{\text{RNH}^+} = 0$ is unlikely to be valid at the high concentrations of hydrochloric acid that had to be used; the "apparent" pK , however, varied linearly with acid concentration and could be extrapolated easily. The "apparent" pK of *p*-nitroaniline showed less variation with acid concentration.

Table 3 gives the experimental details, the symbols having the meaning given in previous papers.^{4,8}

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⁸ Biggs, *J.*, 1956, 2485.
