A Discussion of the Hammett Acidity Function. Study of Some Weak Bases

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Important variations in the pK_a values of several weak bases have been obtained by using different acidity functions H_0 valid for $HClO_4$ and with the application of the Hammett equation; these discrepancies may be reduced by using a corrected form of the Hammett equation in which the ratio intercept slope is constant and coincides with the pK_a irrespective of the H_0 function utilized; the smallest standard deviations are observed within the range log I 1 to −1. The H_+ and H_R functions are not well behaved, even for cationic bases such as *o*-phenylenediamine, adenine, and guanine. All these results may be interpreted by a linear relationship among the activity coefficients.

Study of the protonation of weak organic bases in strong aqueous acidic media led to the definition of some acidity function scales valid for each acidic medium;[1] these functions are based on Hammett's hypothesis[2] according to which the acidity function H_x depends on the activity of hydrogen ions[2] [equation (1) where f_A and f_{AH^+} are the activity coefficients of

$$H_x = -\log(a_{H^+}f_A/f_{AH^+}) \qquad (1)$$

the non-protonated and protonated forms of a given indicator taken as reference].

One of the principal uses of acidity functions is to provide a means of extrapolating measurements made in concentrated acid to dilute solution; such extrapolations have usually been performed with the assumption that log I (ionization ratio) is proportional to an appropriate acidity function H_x [equation (2)].

$$\log I = -H_x + \mathrm{p}K_a \qquad (2)$$

When the correct acidity function is not available, the further assumption that different acidity functions are linearly related to one another[3] and therefore to H_0 (*i.e.* $H_x = mH_0$) is sometimes made, and the extrapolation is then performed with mH_0 [equation (3)].

$$\log I = mH_0 + \mathrm{p}K_a \qquad (3)$$

However, the basis for Hammett's hypothesis, $m = 1$, is not valid when the acidity scales are measured by using structurally different bases and the deviations which arise are explained in terms of specific solvation effects involving the neutral bases and their conjugate acids.[4] At present there is available a very large number of acidity functions,[1,4,5] but unfortunately it is not always possible to find one well-suited to the base under study, and it can be a serious mistake to compare the pK_a values obtained for acidity functions valid for different bases, since the scales are empirical and may be affected by experimental error.

For bases which fulfil Hammett's hypothesis, and which are protonated at overlapping acidity ranges, pK^{i+1} can be calculated if pK^i is previously known [equation (4)]. This

$$\mathrm{p}K_a^i - \mathrm{p}K_a^{i+1} = \log I^i - \log I^{i+1} \qquad (4)$$

equation requires a linear relationship between log I and log C_A (mineral acid concentration); the accuracy of results depends on the parallelism obtained between the straight lines.

Another way of determining pK_a values of indicators by direct stepwise comparison is that proposed by Pytela *et al.*;[6] the pK differences between successive indicators can be written as equation (5) where C_1^{i+1} and C_2^{i+1} are the acid concentrations limiting the concentration range used simultaneously for two indicators.

$$\mathrm{p}K_a^i - \mathrm{p}K_a^{i+1} = \frac{\int_{C_1^{i+1}}^{C_2^{i+1}} \log I^i - \int_{C_1^{i+1}}^{C_2^{i+1}} \log I^{i+1}}{C_2^{i+1} - C_1^{i+1}} \qquad (5)$$

Any interpretation of indicator behaviour as a function of medium acidity must be based on the relationship between its activity coefficients and those of another reference indicator; thus, Bunnett–Olsen,[7] Cox *et al.*[8] and Marziano *et al.*[9] put forward the approximation expressed by equations (6) and (7)

$$\log f_A f_{H^+}/f_{AH^+} = (1 - \varphi)\log f_{A^*} f_{H^+}/f_{A^*H^+} \qquad (6)$$

$$\log f_A f_{H^+}/f_{AH^+} = m^* \log f_{A^*} f_{H^+}/f_{A^*H^+} \qquad (7)$$

where A* refers to the reference indicator; the values of φ may be interpreted in terms of Scorrano's solvation hypothesis.[10]

In the present work a proposal is made for correcting equation (3), one which permits a greater convergence between the pK_a values than that obtained with the various functions already published; similarly, a new H_0^* function is calculated for 0.10—20% w/w $HClO_4$ taking *o*- and *p*-nitroaniline as reference indicators and H_0^{**} for 0.15—40% w/w $HClO_4$ taking various chloronitroanilines as reference indicators. These values have been averaged out whenever more than one indicator is protonated in the same acidity range; relationship (8) arises between

$$H_0^* = (1.105 \pm 0.009)H_0^{**} - (0.017 \pm 0.001) \qquad (8)$$

the two functions with R = 0.9999, $S(y)$ 0.004, and N 26.

Experimental

Reactants.—*p*-Nitroaniline (PNA), *o*-nitroaniline (ONA), *o*-aminobenzonitrile (OABN), *o*-phenylenediamine (OPDA), 2-chloro-4-nitroaniline (2C4NA), 4-chloro-2-nitroaniline (4C2NA), 2-chloro-5-nitroaniline (2C5NA), 4-chloro-3-nitroaniline (4C3NA), adenine, guanine, and thymine were commercially available and further purified; twice distilled and deionized water was used throughout as solvent, over which nitrogen was made to bubble before being used; in every case the solutions used were freshly prepared and kept out of the light.

Equipment.—A Bodenseewerk–Perkin-Elmer 554 spectrophotometer with double beam and thermostatable cells permits expansion in absorbances (±0.001) and wavelengths; the

Table 1. Variation of absorptivities with the medium acidity for different bases within the respective protonation intervals

PNA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2
0.000	226	6 126	378	12 763
0.010	226	5 888	378	12 144
0.050	232	4 764	378	8 402
0.060	234	5 305	378	8 302
0.084	249	5 224	378	6 707
0.100	252	5 475	378	6 038
0.240	255	6 895	378	3 187
0.500	256	7 418	378	1 625
1.000	256	8 120	378	557
1.500	256	8 132	378	221
2.000	256	8 138	378	108

ONA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
0.001	223	15 553	281	4 631	410	4 242
0.010	223	14 924	282	4 845	410	4 140
0.050	223	14 237	282	5 113	410	3 984
0.500	222	12 302	278	5 837	410	3 201
1.000	220	9 421	270	6 010	410	2 501
2.000	214	7 531	262	6 230	410	1 052
3.000	213	6 462	262	6 627	410	390
4.000	212	5 928	262	7 128	410	96

OABN

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	λ_4	ε_4
0.004	210	31 932	237	7 034			314	3 643
0.010	210	30 647	236	6 800			314	3 453
0.040	210	25 788	232	6 637			314	2 772
0.100	211	20 899			278	662	314	2 148
0.200	211	16 505	271	611	278	681	314	1 484
0.500	215	11 441	270	878	278	837	314	761
1.000	223	11 374	270	898	277	841	314	521
1.500	224	10 980	270	920	277	850	314	432
2.000	230	11 128	270	950	277	862	314	302

OPDA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2
0.010	228	7 870	280	2 659
0.040	228	6 720	280	2 597
0.100	228	5 642	280	1 387
0.500	228	3 184	280	620
1.000	228	1 078	280	290
2.000	288	325	280	122

2C4NA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	λ_4	ε_4
0.100	199	18 372	216	8 355	256	4 012	370	12 329
1.001	199	17 989	216	9 232	256	3 130	370	10 526
3.001	204	15 617	216	10 181	256	6 169	370	4 098
3.999	206	15 918	216	10 481	256	6 720	370	1 811
5.998	207	16 868	216	10 699	256	7 506	370	

4C2NA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	λ_4	ε_4
0.100	204	6 094	230	20 436	275	4 539	420	4 483
1.001	203	7 364	230	18 051	275	4 314	420	3 758
1.999	201	8 582	230	14 872	275	4 478	420	2 798
5.001	208	15 519	237	3 796	260	6 077		
5.998	208	16 288	237	3 113	260	6 226		

2C5NA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
0.030	246	10 329	272	5 456	350	2 002
0.100	248	9 378	272	6 240	350	1 719
1.001	232	3 804	272	9 678		
1.999	230	2 837	270	9 544		
3.999	230	2 169	270	9 494		

Table 1. (*continued*)

4C3NA

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
0.001 25	193	21 775	235	14 483	350	1 216
0.0037	193	23 295	235	15 405	350	1 280
0.0120	191	19 802	235	10 070	350	756
0.0200	210	11 824	235	8 261	300	636
3.001	210	14 809	235	3 352	300	1 412

Guanine

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	λ_4	ε_4
3.98×10^{-8}	223	3 133	243	6 100	259	3 800	276	3 866
6.31×10^{-10}	243	5 066	259	3 733	276	4 733	280	4 933
9.77×10^{-11}	230	4 933	244	4 586	260	3 700	272	4 446
7.94×10^{-13}	220		240	3 166	270	6 133	280	8 660

Adenine

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	λ_4	ε_4	λ_5	ε_5
2.5	200	19 450	220	2 250	240	5 970	261	11 469	280	2 263
1.5	200	19 270	220	2 362	240	6 150	261	11 934	280	2 645
0.5	200	19 125	220	2 630	240	6 525	261	12 148	280	2 937
0.1	200	18 540	220	3 294	240	7 080	261	12 720	280	3 460
1.74×10^{-3}	206	17 700	226	3 156	240	6 075	260	13 162	280	2 587
3.16×10^{-6}	206	22 100	224	2 600	240	6 427	258	13 048	270	6 975
1.74×10^{-6}	206	22 275	224	2 584	240	5 987	260	13 005	270	7 048
1.48×10^{-7}	206	22 348	224	2 520	240	5 548	258	12 795	270	6 875
3.98×10^{-8}	206	21 750	224	2 500	240	6 000	259	13 050	267	13 050
6.31×10^{-10}	206	22 000	228	3 250	240	5 748	259	12 675	267	10 350
9.77×10^{-11}			220	14 875	240	4 250	264	11 550	276	8 100

Thymine

$[HClO_4]$/M	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	λ_4	ε_4	λ_5	ε_5
10	200	10 350	220	2 250	240	5 970	261	11 469	280	2 263
9	200	9 700	220	2 362	240	6 150	261	11 934	280	2 645
8	200	9 400	220	2 630	240	6 525	261	12 148	280	2 937
7	200	8 800	220	3 294	240	7 080	261	12 720	280	3 460
6.31×10^{-10}	204	9 300	233	2 300	264	2 300	280	3 660	288	800
9.77×10^{-11}			240	2 660	260	6 380	280	4 860	300	2 300
7.94×10^{-13}	220	45 000	240	3 220	263	4 780	288	5 980	300	3 600

Concentrations are given in mol dm^{-3} and wavelengths in nm.

reference cell contained the same solvent as the sample under measurement. The temperature was kept constant at 25 ± 0.01 °C with a P-Selecta thermostat.

All indicators studied were well behaved in the sense that they showed fixed isosbestic points and no apparent medium effects. The ionization ratios were calculated as $I = (\varepsilon - \varepsilon_A)/(\varepsilon_{AH^+} - \varepsilon)_\lambda$, where ε_{AH^+}, ε_A, and ε are the absorptivities of the protonated and non-protonated forms and at an intermediary level of acidity; if the Lambert law is obeyed at different mineral acid concentrations within the acidity limits between which protonation occurs, then the previous equation can be replaced by $I = (A - A_A)/(A_{AH^+} - A)$. Table 1 contains the results of absorptivities at different acidities. The absorbances A_A and A_{AH^+} have been selected according to the following criteria. An examination was made of the spectral curves obtained upon varying the acidity of the medium; during the first stages of protonation the variation of absorbance with acidity is very small, and later grows noticeably for the same variations in acidity; the inverse process is observed as they get closer to the closing stages of the protonation. In this way, the limits of acidity and the absorbances between which the equilibrium occurs, are obtained with great accuracy at any wavelength. For example, Figure 1 shows this type of behaviour for ONA, although it applies equally to all the bases studied. The wavelength selected will be that which fulfils Lambert's law and yields a flatter sigmoid curve A *versus* H_0; it frequently corresponds to a wavelength at which A_A is maximum and A_{AH^+} is minimum. This is a laborious way of operating but it enables medium effects to be eliminated, which is important when taking values of A_A and A_{AH^+} distant from the protonation limits of the base; this criterion differs from others already published[11–13] and yields similar log I results if the indicator has a single protonation equilibrium, given that outside the protonation limits the variation of absorptivity with acidity is negligible; however, if more than one protonation equilibrium occurs, the behaviour of the absorption bands is modified and errors resulting from the fixation of an acidity interval for A_A and A_{AH^+} may be serious. The criterion described here permitted the calculation of log I and pK of ferrocyanide ion[14] and *m*-aminobenzoic acid,[15] which undergo overlapping equilibria, and of bases with more than one equilibrium,[16,17] although in most cases protonation occurred at low acidity levels.

The acid solutions were made up to constant total volume always using the same pipette and volumetric flask. In the high acidity region, perchloric acid molarities were calculated directly from molar concentrations of perchloric acid, since this species is fully ionized at least up to 60% w/w.[8] The data of percentage acid values at 25 °C were taken from Boyd[18] and Lange;[19] the equation obtained by least squares to convert molarities into % w/w is as follows: % w/w = $-0.0130 + 10.1855C_{H^+} - 0.5592C_{H^+}^2 + 0.0122C_{H^+}^3 + 0.0028C_{H^+}^4 - 0.000\,36C_{H^+}^5 + 0.000\,01C_{H^+}^6$ with $R = 0.9999$ and $S(y) = 0.000\,29$.

Table 2. Results of ionization constants according to different methods

	Equation (5)	Equation (12)[a] $pK'_a \pm$ s.d.	Literature
PNA	1.000	1.003 ± 0.020	1.003 ± 0.002[12] 0.99 and 0.97[2] 1.02,[26] 1.00[22] 1.00,[27] 1.04[2]
ONA	-0.260	-0.282 ± 0.018	-0.240 ± 0.006[12] -0.29,[26] -0.31[21] -0.29,[22] -0.28[23] -0.25,[27] 0.10[2]
OABN	0.757	0.747 ± 0.033	
OPDA	0.634	0.631 ± 0.025	0.78 (HCl)[27] 0.67 (H_2SO_4)[28] 0.643 and 0.769[6] -1.67[29]
2C4NA	-0.966	-0.967 ± 0.032	
4C2NA	-1.038	-1.030 ± 0.042	-1.097,[9a] -1.02[26] -1.03,[27] -1.07[22] -0.62[2]
2C5NA	0.444	0.446 ± 0.027	
4C3NA[b]		1.738 ± 0.274	
Adenine[c]	-0.410	-0.405 ± 0.025	-0.33 to -0.38 (H_2SO_4)[30] -0.43 (H_2SO_4)[31]
Guanine[c]	-1.165	-1.206 ± 0.065	-1.04 to -1.06 (H_2SO_4)[30]
Thymine[b]		-5.162 ± 0.491	

[a] Averaged results of $pK'_a \pm$ s.d. (standard deviation) obtained in the range log I +1 to -1 using the H_0^*, H_0^{**}, H_0^{21}, H_0^{22}, H_0^{23}, H_0^{12}, and H_0^{20} scales. [b] No overlapping with the rest of the bases is observed. [c] The pK'_a values correspond to diprotonated bases; the values pK_1 (adenine) = 4.19 and pK_1 (guanine) = 3.3[32] were characterized by n.m.r.[31,34] and X-ray[33] techniques.

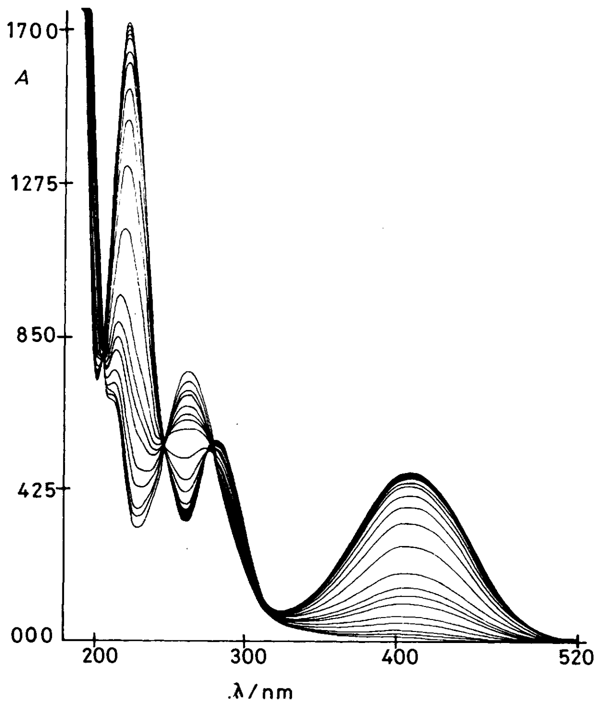

Figure 1. Absorption spectra of ONA (1.034×10^{-4} mol dm^{-3}) in aqueous perchloric acid solutions in the range 0.064—4.470 mol dm^{-3}

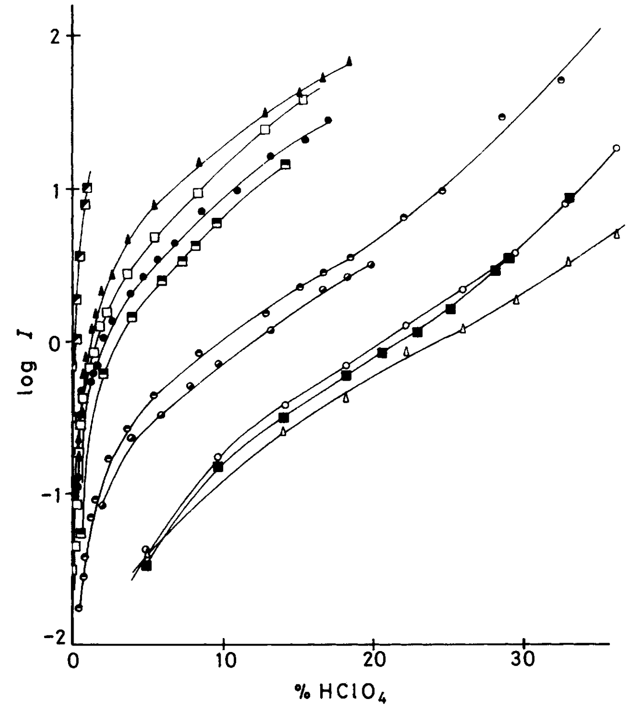

Figure 2. Plot log I *versus* % w/w $HClO_4$ for: ◩ 4C3NA; ▲ PNA; ☐ OABN; ● OPDA; ⊟ 2C5NA; ⊖ ONA; ◑ adenine; ○ 2C4NA; ■ 4C2NA; △ guanine

Results and Discussion

The value pK_a 1.00 for p-nitroanilinium ion was deduced by the method of extrapolation of (log I − log C_A) at zero $HClO_4$ concentration.[1] For the rest of the bases the stepwise comparison method could not be used since the plots of log I *versus* % $HClO_4$ are not parallel in overlapping acidity regions (Figure 2). A certain parallelism is observed, however, in plots of log I *versus* log C_A within the range log $I \pm 1$, as shown in Figure 3. The best parallelism is observed between strong bases, in accord with the already known linear relationship of log I *versus* pH in

Table 3. Values of *n*, *m*, and statistical parameters obtained by least squares with equation (9); results of pK'_a calculated according to equations (10) and (11)

	N	$S(y)$	r_{xy}	n	m	pK'_a
PNA						
H_0^*	12^a	0.005	0.9999	0.996 ± 0.003	−0.996 ± 0.003	1.000 ± 0.004 (1.000)
	15^b	0.005	0.9999	0.999 ± 0.002	−0.999 ± 0.002	1.000 ± 0.003 (0.999)
	18^c	0.005	0.9999	0.998 ± 0.001	−0.999 ± 0.002	0.999 ± 0.001 (0.999)
H_0^{**}	8^a	0.044	0.9984	1.060 ± 0.030	−1.062 ± 0.026	1.000 ± 0.041 (1.002)
	12^b	0.055	0.9981	1.021 ± 0.024	−1.013 ± 0.022	1.008 ± 0.033 (0.999)
	17^c	0.073	0.9973	0.970 ± 0.021	−0.980 ± 0.020	0.990 ± 0.029 (0.994)
H^{20}	12^a	0.014	0.9997	1.003 ± 0.009	−1.000 ± 0.008	1.003 ± 0.012 (0.998)
	15^b	0.019	0.9997	0.997 ± 0.008	−1.006 ± 0.007	0.991 ± 0.010 (0.989)
	18^c	0.018	0.9998	0.993 ± 0.005	−0.998 ± 0.005	0.995 ± 0.007 (0.980)
H_0^{12}	10^a	0.046	0.9950	0.989 ± 0.034	−0.980 ± 0.037	1.009 ± 0.049 (1.003)
	12^b	0.050	0.9953	1.007 ± 0.012	−1.004 ± 0.020	1.003 ± 0.023 (1.005)
	15^c	0.059	0.9975	0.999 ± 0.017	−1.005 ± 0.019	0.994 ± 0.025 (1.026)
H_+^{24}	12^a	0.035	0.9983	0.550 ± 0.015	−0.858 ± 0.016	0.641 ± 0.019 (0.638)
	15^b	0.043	0.9986	0.572 ± 0.013	−0.890 ± 0.013	0.643 ± 0.016 (0.651)
	18^c	0.048	0.9987	0.593 ± 0.012	−0.913 ± 0.011	0.649 ± 0.014 (0.649)
H_R^{12}	12^a	0.158	0.9658	0.742 ± 0.088	−0.986 ± 0.084	0.752 ± 0.108 (1.120)
	15^b	0.204	0.9671	0.706 ± 0.071	−0.900 ± 0.066	0.784 ± 0.089 (0.836)
	18^c	0.216	0.9752	0.597 ± 0.053	−0.790 ± 0.045	0.756 ± 0.070 (0.962)
ONA						
H_0^*	10^a	0.022	0.9994	−0.250 ± 0.008	−0.970 ± 0.010	−0.260 ± 0.009 (−0.276)
	14^b	0.031	0.9994	−0.263 ± 0.009	−0.997 ± 0.010	−0.264 ± 0.009 (−0.262)
	18^c	0.046	0.9992	−0.283 ± 0.011	−1.022 ± 0.010	−0.277 ± 0.011 (−0.250)
H_0^{**}	10^a	0.043	0.9977	−0.275 ± 0.017	−0.988 ± 0.023	−0.278 ± 0.018 (−0.267)
	13^b	0.099	0.9930	−0.273 ± 0.030	−1.015 ± 0.039	−0.269 ± 0.031 (−0.259)
	18^c	0.102	0.9965	−0.315 ± 0.024	−1.166 ± 0.024	−0.270 ± 0.022 (−0.209)
H_0^2	7^a	0.037	0.9983	0.173 ± 0.011	−1.140 ± 0.021	+0.152 ± 0.011 (0.155)
	8^b	0.086	0.9870	0.137 ± 0.043	−1.221 ± 0.081	+0.112 ± 0.037 (0.122)
	9^c	0.080	0.9919	0.133 ± 0.039	−1.241 ± 0.060	+0.107 ± 0.033 (0.141)
H_0^{21}	6^a	0.014	0.9991	−0.335 ± 0.020	−1.144 ± 0.024	−0.293 ± 0.019 (−0.303)
	7^b	0.078	0.9923	−0.354 ± 0.056	−1.223 ± 0.057	−0.290 ± 0.052 (−0.240)
	9^c	0.060	0.9948	−0.383 ± 0.056	−1.300 ± 0.054	−0.295 ± 0.051 (−0.251)
H_0^{22}	6^a	0.015	0.9989	−0.339 ± 0.022	−1.110 ± 0.026	−0.305 ± 0.022 (−0.312)
	7^b	0.051	0.9944	−0.383 ± 0.056	−1.242 ± 0.059	−0.308 ± 0.053 (−0.315)
	8^c	0.048	0.9966	−0.413 ± 0.045	−1.316 ± 0.041	−0.313 ± 0.041 (−0.330)
H_0^{23}	8^a	0.036	0.9979	−0.342 ± 0.026	−1.149 ± 0.035	−0.297 ± 0.026 (−0.315)
	9^b	0.054	0.9959	−0.365 ± 0.036	−1.216 ± 0.042	−0.300 ± 0.035 (−0.310)
	10^c	0.051	0.9973	−0.400 ± 0.031	−1.311 ± 0.031	−0.305 ± 0.029 (−0.338)
H_0^{27}	10^a	0.034	0.9985	−0.259 ± 0.013	−1.023 ± 0.019	−0.253 ± 0.013 (−0.284)
	14^b	0.083	0.9958	−0.269 ± 0.023	−1.073 ± 0.028	−0.251 ± 0.022 (−0.291)
	19^c	0.091	0.9972	−0.293 ± 0.021	−1.125 ± 0.020	−0.260 ± 0.020 (−0.274)
H_0^{12}	8^a	0.040	0.9972	−0.284 ± 0.016	−0.979 ± 0.030	−0.290 ± 0.018 (−0.295)
	11^b	0.046	0.9984	−0.259 ± 0.017	−0.971 ± 0.022	−0.270 ± 0.018 (−0.301)
	13^c	0.053	0.9972	−0.270 ± 0.019	−1.010 ± 0.035	−0.267 ± 0.021 (−0.312)
H_+^{24}	10^a	0.054	0.9923	−0.724 ± 0.032	−1.012 ± 0.031	−0.716 ± 0.039 (−0.769)
	14^b	0.104	0.9935	−0.714 ± 0.035	−1.028 ± 0.034	−0.694 ± 0.042 (−0.780)
	17^c	0.111	0.9949	−0.689 ± 0.031	−0.950 ± 0.027	−0.725 ± 0.037 (−0.759)
H_R^{12}	9^a	0.026	0.9990	−0.501 ± 0.013	−0.598 ± 0.010	−0.838 ± 0.022 (−0.810)
	12^b	0.064	0.9965	−0.557 ± 0.020	−0.642 ± 0.017	−0.868 ± 0.032 (−0.807)
	15^c	0.153	0.9868	−0.639 ± 0.039	−0.714 ± 0.032	−0.895 ± 0.056 (−0.807)
OABN						
H_0^+	10^a	0.013	0.9997	0.749 ± 0.007	−1.035 ± 0.008	0.767 ± 0.009 (0.775)
	14^b	0.068	0.9970	0.841 ± 0.029	−1.137 ± 0.025	0.740 ± 0.035 (0.772)
	15^c	0.066	0.9977	0.845 ± 0.024	−1.140 ± 0.021	0.741 ± 0.029 (0.770)
H_0^{**}	8^a	0.059	0.9959	0.893 ± 0.036	−1.210 ± 0.048	0.740 ± 0.060 (0.751)
	14^b	0.063	0.9970	0.938 ± 0.025	−1.291 ± 0.035	0.726 ± 0.046 (0.735)
	15^c	0.067	0.9976	0.926 ± 0.024	−1.280 ± 0.024	0.723 ± 0.034 (0.721)
H_0^{20}	10^a	0.036	0.9981	0.714 ± 0.018	−0.991 ± 0.022	0.720 ± 0.024 (0.748)
	14^b	0.101	0.9934	0.772 ± 0.041	−1.084 ± 0.038	0.712 ± 0.049 (0.742)
	16^c	0.305	0.9632	0.933 ± 0.097	−1.263 ± 0.094	0.739 ± 0.135 (0.751)
H_0^{12}	10^a	0.054	0.9956	0.795 ± 0.030	−1.041 ± 0.035	0.763 ± 0.041 (0.807)
	11^b	0.056	0.9930	0.836 ± 0.035	−1.120 ± 0.040	0.746 ± 0.049 (0.841)
	13^c	0.120	0.9926	0.833 ± 0.037	−1.117 ± 0.041	0.746 ± 0.050 (0.857)
H_+^{24}	10^a	0.015	0.9996	0.337 ± 0.005	−0.925 ± 0.008	0.364 ± 0.006 (0.359)
	14^b	0.066	0.9972	0.354 ± 0.021	−1.018 ± 0.022	0.348 ± 0.022 (0.368)
	15^c	0.068	0.9975	0.366 ± 0.019	−1.032 ± 0.020	0.355 ± 0.020 (0.367)

Table 3 (*continued*)

	N	$S(y)$	r_{xy}	n	m	pK'_a
OABN						
H_R^{12}	10^a	0.081	0.9900	0.534 ± 0.035	−0.817 ± 0.041	0.654 ± 0.046 (0.759)
	12^b	0.145	0.9812	0.510 ± 0.050	−0.851 ± 0.053	0.600 ± 0.063 (0.769)
	14^c	0.202	0.9800	0.550 ± 0.055	−0.904 ± 0.053	0.608 ± 0.066 (0.791)
OPDA						
H_0^*	17^a	0.034	0.9990	0.631 ± 0.013	−0.992 ± 0.013	0.635 ± 0.015 (0.663)
	20^b	0.037	0.9989	0.651 ± 0.010	−1.012 ± 0.011	0.643 ± 0.012 (0.621)
H_0^{**}	13^a	0.049	0.9978	0.696 ± 0.020	−1.107 ± 0.023	0.629 ± 0.025 (0.626)
	20^b	0.091	0.9934	0.737 ± 0.024	−1.152 ± 0.031	0.640 ± 0.033 (0.666)
H_0^{21}	5^b	0.034	0.9949	0.692 ± 0.038	−1.087 ± 0.055	0.637 ± 0.046 (0.635)
	6^c	0.034	0.9949	0.666 ± 0.025	−1.087 ± 0.055	0.613 ± 0.046 (0.630)
H_0^{20}	17^a	0.031	0.9990	0.640 ± 0.011	−1.017 ± 0.012	0.629 ± 0.013 (0.621)
	20^b	0.035	0.9990	0.660 ± 0.009	−1.038 ± 0.011	0.636 ± 0.011 (0.635)
H_0^{12}	17^a	0.053	0.9967	0.642 ± 0.020	−1.029 ± 0.022	0.624 ± 0.024 (0.653)
	20^b	0.049	0.9980	0.647 ± 0.013	−1.034 ± 0.015	0.626 ± 0.016 (0.655)
H_+^{24}	17^a	0.049	0.9971	0.222 ± 0.013	−0.963 ± 0.017	0.230 ± 0.015 (0.188)
	20^b	0.069	0.9963	0.247 ± 0.015	−0.979 ± 0.018	0.252 ± 0.017 (0.178)
H_R^{12}	17^a	0.084	0.9916	0.355 ± 0.025	−0.806 ± 0.027	0.440 ± 0.32 (0.567)
	20^b	0.095	0.9929	0.315 ± 0.022	−0.756 ± 0.021	0.417 ± 0.029 (0.574)
2C4NA						
H_0^*	4^a	0.022	0.9988	−1.006 ± 0.027	−1.032 ± 0.036	−0.975 ± 0.046
	5^b	0.070	0.9943	−1.122 ± 0.049	−1.178 ± 0.073	−0.952 ± 0.105 (−0.979)
H_0^{**}	7^a	0.032	0.9987	−0.936 ± 0.026	−0.998 ± 0.023	−0.940 ± 0.034 (−0.939)
	9^b	0.070	0.9968	−1.027 ± 0.040	−1.066 ± 0.032	−0.963 ± 0.051 (−0.951)
	10^c	0.066	0.9980	−1.031 ± 0.035	−1.072 ± 0.024	−0.962 ± 0.042 (−0.958)
H_0^2	7^a	0.014	0.9997	−0.572 ± 0.008	−1.127 ± 0.011	−0.507 ± 0.010 (−0.515)
	8^b	0.032	0.9990	−0.584 ± 0.018	−1.160 ± 0.021	−0.503 ± 0.021 (−0.516)
	9^c	0.133	0.9894	−0.639 ± 0.074	−1.287 ± 0.071	−0.496 ± 0.082 (−0.509)
H_0^{21}	7^a	0.011	0.9998	−1.000 ± 0.001	−1.024 ± 0.009	−0.976 ± 0.009 (−1.000)
	8^b	0.036	0.9988	−1.088 ± 0.024	−1.132 ± 0.023	−0.961 ± 0.035 (−0.969)
	9^c	0.149	0.9867	−1.140 ± 0.109	−1.266 ± 0.078	−0.900 ± 0.142 (−0.909)
H_0^{22}	7^a	0.044	0.9975	−1.059 ± 0.040	−1.087 ± 0.034	−0.974 ± 0.054 (−0.934)
	8^b	0.050	0.9976	−1.086 ± 0.041	−1.120 ± 0.032	−0.970 ± 0.053 (−0.935)
	9^c	0.151	0.9860	−1.204 ± 0.114	−1.252 ± 0.079	−0.962 ± 0.150 (−0.923)
H_0^{23}	7^a	0.029	0.9990	−1.043 ± 0.026	−1.067 ± 0.022	−0.977 ± 0.034 (−0.961)
	9^b	0.115	0.9916	−1.218 ± 0.074	−1.264 ± 0.059	−0.964 ± 0.108 (−0.934)
	10^c	0.163	0.9878	−1.286 ± 0.100	−1.298 ± 0.072	−0.991 ± 0.143 (−0.937)
H_0^{20}	7^a	0.012	0.9998	−1.109 ± 0.011	−1.152 ± 0.010	−0.963 ± 0.016 (−0.939)
	9^b	0.038	0.9991	−1.134 ± 0.023	−1.213 ± 0.020	−0.935 ± 0.033 (−0.929)
	10^c	0.128	0.9925	−1.194 ± 0.075	−1.237 ± 0.057	−0.965 ± 0.104 (−0.943)
H_+^{24}	7^a	0.021	0.9995	−1.732 ± 0.027	−1.236 ± 0.018	−1.401 ± 0.044 (−1.393)
	9^b	0.035	0.9992	−1.769 ± 0.029	−1.268 ± 0.019	−1.395 ± 0.048 (−1.385)
	10^c	0.143	0.9908	−1.887 ± 0.113	−1.375 ± 0.066	−1.372 ± 0.190 (−1.428)
H_R^{12}	5^a	0.011	0.9997	−1.183 ± 0.016	−0.584 ± 0.010	−2.025 ± 0.028 (−2.222)
	5^b	0.094	0.9897	−1.375 ± 0.083	−0.696 ± 0.058	−1.975 ± 0.131 (−2.041)
4C2NA						
H_0^*	6^a	0.023	0.9986	−1.080 ± 0.025	−1.025 ± 0.027	−1.054 ± 0.038 (−1.053)
	7^b	0.072	0.9938	−1.209 ± 0.049	−1.161 ± 0.058	−1.041 ± 0.092 (−1.063)
H_0^{**}	9^a	0.019	0.9995	−1.050 ± 0.015	−1.050 ± 0.013	−1.000 ± 0.020 (−0.997)
	10^b	0.061	0.9967	−1.137 ± 0.036	−1.124 ± 0.032	−1.012 ± 0.052 (−0.992)
H_0^2	9^a	0.037	0.9980	−0.669 ± 0.022	−1.191 ± 0.029	−0.562 ± 0.029 (−0.589)
H_0^{21}	9^a	0.026	0.9987	−1.102 ± 0.024	−1.128 ± 0.023	−0.977 ± 0.036 (−0.966)
H_0^{22}	9^a	0.031	0.9986	−1.179 ± 0.027	−1.146 ± 0.023	−1.029 ± 0.039 (−1.025)
H_0^{23}	9^a	0.032	0.9985	−1.164 ± 0.027	−1.124 ± 0.023	−1.035 ± 0.038 (−1.050)
	10^b	0.109	0.9896	−1.327 ± 0.072	−1.249 ± 0.064	−1.062 ± 0.121 (−1.033)
H_0^{20}	9^a	0.028	0.9988	−1.224 ± 0.025	−1.217 ± 0.023	−1.006 ± 0.039 (−1.008)
	10^b	0.037	0.9988	−1.240 ± 0.023	−1.255 ± 0.022	−0.988 ± 0.039 (−0.977)
H_0^{12}	4^a	0.062	0.9879	−1.036 ± 0.076	−0.933 ± 0.104	−1.110 ± 0.129
	5^b	0.092	0.9834	−1.218 ± 0.082	−1.166 ± 0.090	−1.044 ± 0.145 (−1.139)
H_+^{24}	9^a	0.032	0.9985	−1.867 ± 0.041	−1.290 ± 0.026	−1.447 ± 0.070 (−1.467)
	10^b	0.030	0.9992	−1.874 ± 0.027	−1.294 ± 0.018	−1.448 ± 0.048 (−1.467)
H_R^{12}	5^a	0.009	0.9998	−1.248 ± 0.012	−0.573 ± 0.007	−2.178 ± 0.021 (−2.174)
	6^b	0.099	0.9879	−1.464 ± 0.085	−0.690 ± 0.054	−2.122 ± 0.135 (−2.191)
2C5NA						
H_0^*	6^a	0.035	0.9960	0.472 ± 0.015	−1.049 ± 0.047	0.450 ± 0.027 (0.481)
	8^b	0.099	0.9920	0.566 ± 0.036	−1.283 ± 0.065	0.441 ± 0.055 (0.468)
	9^c	0.149	0.9874	0.583 ± 0.049	−1.387 ± 0.084	0.420 ± 0.076 (0.454)

Table 3 (*continued*)

	N	$S(y)$	r_{xy}	n	m	$\mathrm{p}K'_\mathrm{a}$
2C5NA						
H_0^{**}	6^a	0.032	0.9967	0.505 ± 0.014	−1.077 ± 0.044	0.468 ± 0.027 (0.489)
	8^b	0.173	0.9760	0.488 ± 0.064	−1.042 ± 0.130	0.468 ± 0.090 (0.506)
	9^c	0.180	0.9814	0.523 ± 0.060	−1.133 ± 0.113	0.462 ± 0.089 (0.508)
H_0^{20}	6^a	0.026	0.9978	0.454 ± 0.011	−1.060 ± 0.035	0.428 ± 0.020 (0.477)
	8^b	0.101	0.9920	0.446 ± 0.037	−1.012 ± 0.068	0.441 ± 0.048 (0.446)
	9^c	0.152	0.9868	0.493 ± 0.051	−1.420 ± 0.088	0.347 ± 0.071 (0.459)
H_0^{12}	6^a	0.043	0.9940	0.482 ± 0.019	−1.101 ± 0.061	0.438 ± 0.037 (0.451)
	8^b	0.054	0.9935	0.566 ± 0.024	−1.279 ± 0.086	0.442 ± 0.065 (0.475)
	9^c	0.154	0.9865	0.518 ± 0.051	−1.391 ± 0.087	0.372 ± 0.073 (0.395)
H_+^{24}	6^a	0.022	0.9984	−0.005 ± 0.014	−0.981 ± 0.027	−0.005 ± 0.014 (−0.007)
	8^b	0.085	0.9943	−0.102 ± 0.034	−1.196 ± 0.052	−0.085 ± 0.029 (−0.009)
	9^c	0.165	0.9844	−0.098 ± 0.066	−1.310 ± 0.088	−0.075 ± 0.052 (−0.024)
H_R^{12}	6^a	0.031	0.9969	0.109 ± 0.015	−0.741 ± 0.029	0.147 ± 0.020 (0.310)
	8^b	0.148	0.9829	0.096 ± 0.054	−0.921 ± 0.070	0.104 ± 0.059 (0.305)
	9^c	0.142	0.9884	0.100 ± 0.052	−0.951 ± 0.055	0.106 ± 0.055 (0.271)
4C3NA						
H_0^*	6^a	0.037	0.9974	2.097 ± 0.062	−1.129 ± 0.041	1.857 ± 0.111 (1.840)
H_0^{**}	9^a	0.006	0.9999	1.695 ± 0.006	−0.996 ± 0.003	1.702 ± 0.008 (1.702)
	11^b	0.006	0.9999	1.699 ± 0.004	−0.998 ± 0.002	1.702 ± 0.005 (1.702)
H_0^{20}	9^a	0.033	0.9990	2.152 ± 0.038	−1.210 ± 0.021	1.778 ± 0.063 (1.769)
	10^b	0.042	0.9985	2.189 ± 0.045	−1.235 ± 0.024	1.772 ± 0.074 (1.776)
H_0^{12}	5^a	0.051	0.9910	2.947 ± 0.240	−1.822 ± 0.169	1.617 ± 0.915 (1.817)
H_+^{24}	9^a	0.089	0.9917	1.540 ± 0.077	−0.966 ± 0.047	1.544 ± 0.106 (1.626)
	10^b	0.101	0.9911	1.584 ± 0.083	−1.005 ± 0.048	1.576 ± 0.112 (1.629)
H_R^{12}	4^a	0.055	0.9902	2.847 ± 0.217	−1.788 ± 0.178	1.593 ± 0.914
Adenine						
H_0^*	8^a	0.025	0.9995	−0.400 ± 0.012	−0.995 ± 0.022	−0.402 ± 0.015 (−0.411)
	9^b	0.025	0.9990	−0.405 ± 0.009	−1.004 ± 0.016	−0.403 ± 0.011 (−0.414)
H_0^{**}	8^a	0.020	0.9990	−0.372 ± 0.009	−0.922 ± 0.016	−0.403 ± 0.011 (−0.419)
	9^b	0.066	0.9934	−0.394 ± 0.024	−1.000 ± 0.044	−0.394 ± 0.030 (−0.402)
H_0^2	7^a	0.019	0.9990	0.026 ± 0.007	−1.002 ± 0.021	0.026 ± 0.007 (0.198)
H_0^{21}	6^a	0.019	0.9987	−0.375 ± 0.015	−1.006 ± 0.026	−0.373 ± 0.018 (−0.382)
H_0^{22}	5^a	0.032	0.9948	−0.506 ± 0.048	−1.191 ± 0.070	−0.425 ± 0.058 (−0.420)
H_0^{23}	7^a	0.041	0.9951	−0.503 ± 0.031	−1.180 ± 0.052	−0.426 ± 0.040 (−0.421)
H_0^{20}	8^a	0.031	0.9978	−0.410 ± 0.015	−1.017 ± 0.028	−0.403 ± 0.019 (−0.421)
	9^b	0.030	0.9986	−0.417 ± 0.011	−1.032 ± 0.206	−0.404 ± 0.014 (−0.427)
H_0^{12}	8^a	0.038	0.9980	−0.402 ± 0.012	−0.998 ± 0.033	−0.403 ± 0.018 (−0.405)
	9^b	0.046	0.9967	−0.409 ± 0.013	−1.010 ± 0.024	−0.405 ± 0.016 (−0.406)
H_+^{24}	8^a	0.042	0.9958	−0.880 ± 0.035	−1.002 ± 0.038	−0.878 ± 0.048 (−0.912)
	9^b	0.039	0.9976	−0.877 ± 0.023	−0.999 ± 0.026	−0.878 ± 0.032 (−0.919)
H_R^{12}	8^a	0.024	0.9986	−0.617 ± 0.015	−0.583 ± 0.013	−1.058 ± 0.026 (1.024)
Guanine						
H_0^*	4^a	0.070	0.9801	−0.985 ± 0.084	−0.783 ± 0.112	−1.258 ± 0.138
	5^b	0.114	0.9797	−1.113 ± 0.079	−0.993 ± 0.117	−1.161 ± 0.156 (−1.134)
	6^c	0.122	0.9916	−1.213 ± 0.053	−1.116 ± 0.073	−1.103 ± 0.111 (−1.267)
H_0^{**}	8^a	0.072	0.9917	−0.942 ± 0.050	−0.771 ± 0.041	−1.222 ± 0.071 (−1.193)
	10^b	0.133	0.9847	−0.993 ± 0.071	−0.770 ± 0.048	−1.290 ± 0.099 (−1.168)
H_0^2	8^a	0.039	0.9976	−0.698 ± 0.028	−0.916 ± 0.026	−0.762 ± 0.035 (−0.759)
	10^b	0.061	0.9959	−0.639 ± 0.032	−0.850 ± 0.027	−0.752 ± 0.040 (−0.736)
	11^c	0.068	0.9962	−0.655 ± 0.035	−0.876 ± 0.025	−0.748 ± 0.042 (−0.753)
H_0^{21}	9^a	0.047	0.9972	−1.002 ± 0.034	−0.870 ± 0.025	−1.152 ± 0.045 (−1.171)
	10^b	0.052	0.9970	−0.981 ± 0.036	−0.847 ± 0.023	−1.158 ± 0.047 (−1.176)
	11^c	0.066	0.9964	−1.013 ± 0.042	−0.878 ± 0.025	−1.154 ± 0.053 (−1.166)
H_0^{22}	9^a	0.031	0.9988	−1.049 ± 0.024	−0.863 ± 0.016	−1.215 ± 0.031 (−1.214)
	10^b	0.038	0.9984	−1.030 ± 0.027	−0.843 ± 0.017	−1.222 ± 0.035 (−1.212)
	11^c	0.064	0.9966	−1.069 ± 0.042	−0.879 ± 0.024	−1.216 ± 0.053 (−1.829)
H_0^{23}	9^a	0.036	0.9983	−1.046 ± 0.027	−0.858 ± 0.019	−1.219 ± 0.036 (−1.236)
	12^b	0.119	0.9920	−1.186 ± 0.066	−0.938 ± 0.039	−1.264 ± 0.083 (−1.177)
H_0^{20}	9^a	0.045	0.9943	−1.048 ± 0.034	−0.904 ± 0.024	−1.159 ± 0.044 (−1.172)
	11^b	0.084	0.9947	−1.104 ± 0.047	−0.924 ± 0.032	−1.195 ± 0.060 (−1.135)
	13^c	0.119	0.9945	−1.216 ± 0.050	−0.998 ± 0.032	−1.218 ± 0.063 (−1.159)
H_0^{12}	4^a	0.061	0.9946	−0.851 ± 0.059	−0.698 ± 0.063	−1.219 ± 0.092
	5^b	0.196	0.9386	−0.979 ± 0.127	−0.814 ± 0.151	−1.203 ± 0.197 (−1.348)
H_+^{24}	9^a	0.043	0.9977	−1.565 ± 0.045	−0.972 ± 0.025	−1.610 ± 0.059 (−1.627)
	11^b	0.061	0.9972	−1.606 ± 0.045	−0.984 ± 0.025	−1.632 ± 0.060 (−1.598)
	12^c	0.073	0.9967	−1.641 ± 0.051	−1.012 ± 0.026	−1.621 ± 0.066 (−1.613)

Table 3 (*continued*)

	N	$S(y)$	r_{xy}	n	m	pK'_a
Guanine						
H_R^{12}	4^a	0.085	0.9702	-1.114 ± 0.124	-0.440 ± 0.078	-2.532 ± 0.284
	5^b	0.141	0.9688	-1.361 ± 0.123	-0.583 ± 0.086	-2.334 ± 0.222 (-2.254)
	6^c	0.178	0.9819	-1.545 ± 0.093	-0.708 ± 0.068	-2.182 ± 0.151 (-2.466)
Thymine						
H_0^2	10^a	0.067	0.9920	-3.810 ± 0.161	-0.790 ± 0.035	-4.823 ± 0.229 (-4.845)
	11^b	0.070	0.9932	-3.916 ± 0.145	-0.811 ± 0.032	-4.829 ± 0.206 (-4.792)
H_0^{21}	10^a	0.056	0.9948	-4.774 ± 0.168	-0.932 ± 0.034	-5.122 ± 0.235 (-5.097)
	11^b	0.053	0.9960	-4.820 ± 0.137	-0.941 ± 0.028	-5.122 ± 0.193 (-5.085)
H_0^{22}	8^a	0.060	0.9906	-3.931 ± 0.204	-0.749 ± 0.042	-5.248 ± 0.299 (-5.213)
	9^b	0.063	0.9918	-4.081 ± 0.179	-0.779 ± 0.038	-5.238 ± 0.260 (-5.188)
H_0^{23}	9^a	0.052	0.9942	-4.297 ± 0.167	-0.828 ± 0.339	-5.190 ± 1.223 (-5.172)
	10^b	0.051	0.9955	-4.368 ± 0.136	-0.842 ± 0.028	-5.188 ± 0.191 (-5.185)
H_0^{20}	11^a	0.065	0.9945	-4.401 ± 0.153	-0.865 ± 0.030	-5.088 ± 0.210 (-5.123)
	12^b	0.063	0.9956	-4.441 ± 0.128	-0.842 ± 0.026	-5.093 ± 0.178 (-5.131)
	13^c	0.218	0.9683	-5.058 ± 0.399	-1.007 ± 0.078	-5.022 ± 0.561 (-5.207)
H_+^{24}	11^a	0.063	0.9950	-4.778 ± 0.159	-0.981 ± 0.033	-4.870 ± 0.224 (-4.887)
	12^b	0.064	0.9955	-4.868 ± 0.143	-0.998 ± 0.030	-4.878 ± 0.204 (-4.889)
	13^c	0.205	0.9718	-5.529 ± 0.409	-1.147 ± 0.139	-4.820 ± 0.951 (-4.947)

N = number of points; $S(y)$ = standard deviation; r_{xy} = linear correlation coefficient; H_0^*, this paper calculated from PNA and ONA; H_0^{**}, calculated from chloronitro derivatives.

[a] log I 1 to -1. [b] log I 1.5 to -1.5; [c] the entire range of log I.

Results in parentheses correspond to the real root of polynomial according to equation (12).

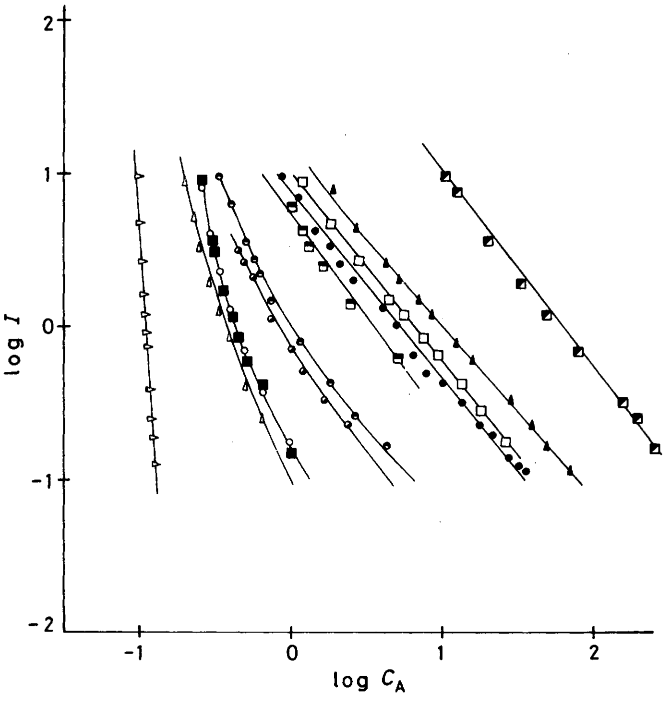

Figure 3. Plot log I *versus* log C_A for: ▷ thymine; △ guanine; ■ 4C2NA; ○ 2C4NA; ◒ adenine; ⊖ ONA; ⊟ 2C5NA; ● OPDA; □ OABN; ▲ PNA; ◩ 4C3NA

aniline derivatives;[17] this relation, however, does not permit extrapolation at zero acid concentration, and the stepwise comparison method is not applicable.

Values of pK_a deduced from equation (5), using Simpson's method of mathematical integration, have proved to be satisfactory; using PNA as reference indicator pK_a has been calculated for the rest of the bases, which in turn has enabled us to obtain all the possible ΔpK_a values between overlapping indicators; Table 2 contains the averaged out values obtained by this method. This behaviour reveals that Hammett's hypothesis is not valid, even for bases of similar structure.

In a previous investigation[17] carried out on strong aniline derivatives, equation (9) has been found

$$\log I = -m\,\mathrm{pH} + n \qquad (9)$$

where $n = m\,pK_a$; given log I 0, then pH = pK. Therefore, equation (10) holds.

$$pK = n/|m| \qquad (10)$$

The value of m is always close to unity and deviation from this value is taken as being non-ideal behaviour. Equation (9) is valid within log $I = \pm 1$; outside this interval the empirical equation (11) enables values to be calculated for pK which coincide with the real root of the grade three polynomial; the other two roots are imaginary.

$$\log I = C_0 + C_1(\mathrm{pH}) + C_2(\mathrm{pH})^2 + C_3(\mathrm{pH})^3 \qquad (11)$$

The similarity between equations (3) and (9) becomes evident; if $m = 1$, Hammett's hypothesis is valid and both equations coincide with equation (2), since H_0 and pH play similar roles; however, it has been amply demonstrated that m can differ widely from unity, even for structurally similar bases, in which case equation (3) can be corrected and pK_a calculated by equation (12).

$$\log I = -m\,\mathrm{H}_0 + m\,pK'_a \qquad (12)$$

For $m = 1$ only the pK_a values deduced from equations (3) and (12) are coincident; by combining equations (1), (2), and (12) we obtain (13) where A* represents the indicator taken

$$\log f_A f_{H^+}/f_{AH^+} = m \log f_{A^*} f_{H^+}/f_{A^*H} + (m - 1)\,pK'_a \qquad (13)$$

as reference in the definition of H_0. The last term of equation (13) is constant for each indicator; this constant becomes zero in the case of ideal behaviour and will be smaller the closer together

Table 4. Statistical parameters and coefficients[a] of the function H_0 *versus* X (% w/w $HClO_4$)

	X	a_0	a_1	a_2	a_3	a_4	a_5	$S(y)$	R	F
H_0^*	0.1 to 0.8	2.659	-7.429	18.69	22.04	9.954	—	0.013	0.9997	1 216
H_0^*	0.8 to 24	1.375	-0.4445	5.655×10^{-2}	-4.106×10^{-3}	1.439×10^{-4}	-1.941×10^{-6}	0.022	0.9998	3 085
H_0^{**}	0.012 to 0.11	3.159	-34.21	3.731×10^{2}	-1.545×10^{3}	—	—	0.008	0.9999	2 247
H_0^{**}	0.10 to 1	2.352	-5.586	1.122	-12.52	5.244	—	0.005	0.9999	10 208
H_0^{**}	1 to 40	89.82	-0.1614	5.544×10^{-3}	-9.656×10^{-5}	—	—	0.046	0.9992	2 481
H_0^{2}	5.96 to 63.9	1.218	-0.1457	4.786×10^{-3}	-9.793×10^{-5}	5.166×10^{-7}	—	0.032	0.9998	19 653
H_0^{21}	7.32 to 63.83	0.833	-0.1519	5.245×10^{-3}	-1.106×10^{-4}	6.302×10^{-7}	—	0.022	0.9999	31 949
H_0^{22}	9 to 48.83	-0.1509	0.0101	-3.896×10^{-3}	9.342×10^{-5}	-9.262×10^{-7}	—	0.013	0.9998	19 936
H_0^{22}	48.83 to 62.37	-24.17	0.9753	-8.839×10^{-3}	-1.083×10^{-4}	1.207×10^{-6}	—	0.018	0.9998	6 653
H_0^{23}	4.78 to 48.83	0.1312	-0.0293	-2.114×10^{-3}	6.059×10^{-5}	-7.096×10^{-7}	—	0.013	0.9999	26 012
H_0^{12}	0.25 to 20	1.637	-0.7086	1.343×10^{-1}	-1.342×10^{-2}	6.271×10^{-4}	-1.096×10^{-5}	0.058	0.9988	9 053

[a] Coefficients of the function $H_0 = a_0 + a_1X + a_2X^2 + a_3X^3 + a_4X^4 + a_5X^5$; H_0^{20} used is that of the authors; R = multilinear correlation coefficient; $S(y)$ = standard deviation; F = value for comparison of variances.

the behaviours of A and A*; this will also occur if $pK_a \longrightarrow 0$. In these cases the linearity between activity coefficients, formulated in equations (6) and (7), is now expressed as (14).

$$\log f_A f_{H^+}/f_{AH^+} = m \log f_{A^*} f_{H^+}/f_{A^*H^+} \qquad (14)$$

This formulation, however, is not as general as (6) and (7), since it requires similar behaviour by A and A*; these results are shown in Table 3. Equation (12) was used applying different H_0 acidity functions reported in the literature[2,12,20–23] and the H_0^* and H_0^{**} functions obtained in this work, as well as the H_R functions[12] defined with 4,4′,4″-trimethoxy-, 4,4′-dimethoxy-4″-methyl-, and 4,4′-dimethoxy-triphenylmethanol and the H^+ functions[24] established by using primary amine cationic bases as indicators. The H_0 functions show noticeable differences between each other; Taft[35] suggests the existence of hydrogen bonds between NH_3^+ and solvent molecules, and assigns an important role to the influence of these interactions on H_0 behaviour; the variation of the activity coefficients with H_2SO_4 concentration has been investigated by Boyd[36] for nitroaniline derivatives with reference to a common standard ion, the tetraethylammonium ion, and each indicator was found to have different behaviour with the medium acidity. The variation of these coefficients with % $HClO_4$ is shown in Table 4; these equations have been used in the interpolation of data from this work.

With respect to the log I results, Kresge and Chen[25] found that the lowest error corresponds to log I 0, the error is low in the log $I \pm 1$ interval and increases in the range ± 1 to ± 2; these authors used the interval log $I \pm 1.5$ to define H_0,[12] whereas most authors restrict themselves to the interval ± 1. In this work the validity of equation (12) is analysed at three different intervals: (a) log $I \pm 1$; (b) log $I \pm 1.5$, and (c) for any value of log I (usually never outside ± 2). Table 3 shows the results obtained with an equation similar to equation (11), substituting pH for H_0; of the three polynomial roots two are imaginary and the third, real one, comes close to pK_a. This empirical equation, however, does not have physical meaning and should only be used as an approximate method for obtaining pK_a values.

Conclusions.—From the intercept of log I *versus* H_0, equation (3), noticeably different pK results are obtained, depending on the acidity scale used and on the log I interval chosen.

Equation (12) provides similar pK values, within experimental error, on applying different acidity functions; the standard deviation is lower in the interval log $I \pm 1$ and increases as the interval gets larger.

Equation (12) is not well behaved when different H_0 functions founded in the literature are used; also, the function H_0^2 does not provide good results, since the colorimetric method employed by Hammett and Deyrup was very inadequate for the measurements of accurate ionization ratios and for the detection of major medium shifts, most important for the determination of accurate values. However, the results supplied by this method (Table 2) agree satisfactorily with those reported in the literature and those obtained from equation (5); this is an indication that the H_0 functions behave well with cationic bases such as *o*-phenylenediamine, adenine, and guanine.

The H_+^{24} function supplies pK values of a wider range by 0.4 units than those provided with H_0; in particular, the results obtained with H_+^{24} for cationic bases do not coincide with those founded in the literature.

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