Thermodynamics of Ionization of Hammett Bases in Concentrated Aqueous Solutions of Perchloric Acid

By **Salem A. Attiga** and **Colin H. Rochester,*** Chemistry Department, The University, Nottingham NG7 2RD

The Hammett acidity function H_0 for aqueous perchloric acid has been measured as a function of temperature. The data are analysed in terms of the enthalpies of protonation of primary amines in aqueous perchloric acid solutions. The enthalpy changes which occur when the species involved in the protonation equilibria of primary anilines are transferred from water to aqueous perchloric acid are in accord with solvation theories of acidity function behaviour. Thus, by analogy to equations relating H_0 to water activity, correlations between the enthalpy data and relative partial molal enthalpies of water in the acid solutions are consistent with proposals that the high acidity of concentrated solutions of strong acids may be largely explained in terms of the release of water molecules of hydration when a weak base B reacts with a solvated proton to give BH^+.

STUDIES of the protonation of weak organic bases in concentrated aqueous solutions of strong acids have led to the definition of several acidity function scales for each acid.[1] The deviations between the scales measured using bases of differing structural type have been explained in terms of specific solvation effects involving the neutral bases and their conjugate acids. Such explanations are consistent with theories in which acidity function behaviour is correlated with activities or concentrations of solvent water in acid solutions [1-3] and which are entirely based on free energy data. It is often found that free energy data are less sensitive to solvation effects than either enthalpy or entropy data.[4,5] It would therefore be expected that measurements of the enthalpies or entropies of ionization of bases in strongly acidic solutions may give more information about the influence on acid–base equilibria of the hydration requirements of the solute species involved. Although several studies of the variation of acidity functions with temperature have been reported,[6-9] enthalpies or entropies of ionization of the indicators have not, with one exception,[10] been evaluated as a function of acid concentration. The present paper reports enthalpy data calculated from the results of measurements of the extent of ionization, over a range of temperature, of six amine (Hammett) bases in aqueous perchloric acid.

EXPERIMENTAL

4-Nitro-, 2-nitro-, 2,4-dinitro-, 2,6-dinitro-, 2,5-dichloro-4-nitro-, and 2,4-dichloro-6-nitro-aniline were recrystallized to constant m.p. from water. Stock solutions of the amines in water were prepared by weight. Solutions of perchloric acid were made by dilution of AnalaR, aqueous 71—73 w/w % perchloric acid with water and were estimated volumetrically.

Solutions of the amine bases in aqueous perchloric acid were prepared by volume and their electronic spectra were measured with respect to blank solutions containing aqueous perchloric acid using a Unicam SP 8000 spectrophotometer and matched silica cells of path length 1 cm. A temperature cycle procedure was adopted. The optical cells were housed within the spectrophotometer compartment in a block which was thermostatically controlled by water circulation. The temperature was varied through a series of small steps in the approximate overall range from 288 to 320 and back to 288 K and spectra were measured after each step. During the heating and cooling cycle *ca.* 30 min were allowed for the solutions to equilibrate at each temperature. Temperatures (±0·13 K) were measured by means of a chromel–alumel thermocouple inserted directly into the stoppered sample cell in such a way as not to interfere with the optical beam. Plots of absorbance at a fixed wavelength against temperature for each indicator at each acid concentration were linear. Hence absorbance values at 288, 298, 308, and 318 K were read off the lines and enabled ionization ratios $I = (C_{BH^+}/C_B)$, where C_B and C_{BH^+} are the equilibrium concentrations of neutral amine B and its conjugate acid BH^+, at these four temperatures to be evaluated by the standard method.[1] Wavelengths chosen for study were 377 for 4-nitro-, 411 for 2-nitro-, 347 for 2,4-dinitro-, 445 for 2,6-dinitro-, 368 for 2,5-dichloro-4-nitro, and 411 nm for 2,4-dichloro-6-nitro-aniline. The results for the heating and cooling stages of temperature cycles always agreed within experimental error. There was never any evidence for the occurrence of irreversible decomposition reactions during the time for which measurements on a particular solution were being made. The thermostatted block held four samples and four reference cells and therefore solutions of a given indicator in aqueous perchloric acid at four concentrations could be studied simultaneously. Spectra were recorded on the same chart paper and for four of the amine bases were well behaved in the sense that they showed fixed isosbestic points and no apparent medium effects. However for the two chloro-substituted amines there were slight medium effects which were corrected for by the isosbestic method.[11]

RESULTS

Ionization ratios for six amine bases at four temperatures and as a function of perchloric acid concentration are given in Table 1. Values of pK_{BH^+} (Table 2), where K_{BH^+} is the acid dissociation constant, for the 4-nitroanilinium ion at the four temperatures were deduced by the standard method [1] involving extrapolation of $\log_{10} (C_{BH^+}/C_B) - \log_{10} C_{HClO_4}$ to zero concentration of perchloric acid. Values of pK_{BH^+}

---

[1] C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

[2] H. Takaya, N. Todo, and T. Hosoya, *Bull. Chem. Soc. Japan*, 1969, **42**, 2748.

[3] T. T. Teng and F. Lenzi, *Canad. J. Chem.*, 1972, **50**, 3283.

[4] D. J. G. Ives and P. D. Mardsden, *J. Chem. Soc.*, 1965, 649.

[5] L. G. Hepler and E. M. Woolley, ' Water, a Comprehensive Treatise, vol. 3, Aqueous Solutions of Simple Electrolytes,' ed. F. Franks, Plenum, New York, 1973, ch. 3.

[6] A. N. Gel'bshtein, G. G. Shcheglova, and M. I. Temkin, *Russ. J. Inorg. Chem.*, 1956, **1**, 96, 167.

[7] P. Tickle, A. G. Briggs, and J. M. Wilson, *J. Chem. Soc. (B)*, 1970, 65.

[8] C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, 1969, **91**, 6654.

[9] E. M. Arnett and R. D. Bushick, *J. Amer. Chem. Soc.*, 1964, **86**, 1564.

[10] R. H. Boyd and C.-H. Wang, *J. Amer. Chem. Soc.*, 1965, **87**, 430.

[11] D. S. Noyce and M. J. Jorgenson, *J. Amer. Chem. Soc.*, 1961, **83**, 2525.

(Table 2) for the other five bases at the same temperatures were hence deduced by the stepwise comparison of ionization ratios in overlapping ranges of perchloric acid concentration.[1] Plots of $\log_{10} I$ against perchloric acid concentration were parallel within experimental error in regions of overlap. Equation (1) and therefore [1] also equation (2), in which y_i is

$$\mathrm{d}\log_{10}(C_{\mathrm{B_1H^+}}/C_{\mathrm{B_1}})/\mathrm{d}C_{\mathrm{HClO_4}} = \mathrm{d}\log_{10}(C_{\mathrm{B_2H^+}}/C_{\mathrm{B_2}})/\mathrm{d}C_{\mathrm{HClO_4}} \qquad (1)$$

$$(y_{\mathrm{B_1H^+}}/y_{\mathrm{B_1}}) \sim (y_{\mathrm{B_2H^+}}/y_{\mathrm{B_2}}) \qquad (2)$$

the activity coefficient of species i, were apparently obeyed for any two bases B_1 and B_2 in the same perchloric acid solution at a particular temperature.

The Hammett acidity function H_0 at a particular temperature was deduced from the dissociation constants of the anilinium ions and the spectrophotometrically determined ionization ratios *via* equation (3). The results for all six

$$H_0 = \mathrm{p}K_{\mathrm{BH^+}} - \log_{10}(C_{\mathrm{BH^+}}/C_{\mathrm{B}}) \qquad (3)$$

amines were plotted against perchloric acid concentration on a single graph and a smooth curve was drawn through the points. Values of H_0 at 0·5 mol kg^{-1} intervals of perchloric

TABLE 1

Values of $\log_{10}(C_{\mathrm{BH^+}}/C_{\mathrm{B}})$ as a function of perchloric acid concentration for six amine bases at four temperatures

m/mol kg^{-1}	288 K	298 K	308 K	318 K
(a) 4-Nitroaniline				
0·065	−0·09	−0·18	−0·26	−0·35
0·08	0·04	−0·04	−0·13	−0·21
0·14	0·21	0·13	0·05	−0·04
0·25	0·56	0·48	0·39	0·31
0·38	0·78	0·70	0·62	0·54
0·52	0·98	0·89	0·81	0·72
0·65	1·13	1·03	0·94	0·85
0·80	1·20	1·11	1·02	0·94
(b) 2-Nitroaniline				
0·38	−0·49	−0·57	−0·63	−0·69
0·52	−0·31	−0·40	−0·47	−0·54
0·80	−0·08	−0·17	−0·23	−0·30
1·10	0·10	0·03	−0·03	−0·11
1·40	0·21	0·16	0·09	0·03
1·70	0·35	0·29	0·23	0·17
1·98	0·51	0·44	0·37	0·30
2·30	0·62	0·56	0·49	0·43
2·60	0·78	0·70	0·63	0·55
(c) 2·5-Dichloro-4-nitroaniline				
1·70	−1·16	−1·20	−1·23	−1·27
1·98	−1·03	−1·07	−1·10	−1·16
2·30	−0·90	−0·94	−0·98	−1·03
2·60	−0·76	−0·82	−0·86	−0·91
3·50	−0·43	−0·49	−0·54	−0·58
4·10	−0·18	−0·24	−0·29	−0·34
4·75	0·03	−0·01	−0·05	−0·10
5·60	0·28	0·24	0·19	0·13
6·00	0·40	0·35	0·31	0·26
6·45	0·54	0·48	0·44	0·38
6·90	0·65	0·61	0·55	0·49
7·25	0·78	0·72	0·67	0·61
(d) 2,4-Dichloro-6-nitroaniline				
4·75	−1·24	−1·25	−1·25	−1·26
5·60	−0·97	−0·98	−0·99	−1·00
6·00	−0·84	−0·85	−0·86	−0·87
6·45	−0·70	−0·70	−0·73	−0·75
6·90	−0·54	−0·56	−0·58	−0·62
7·25	−0·37	−0·43	−0·45	−0·49
7·65	−0·23	−0·27	−0·31	−0·33
8·10	−0·10	−0·14	−0·18	−0·21
8·50	0·08	−0·01	−0·04	−0·07
9·00	0·23	0·15	0·11	0·05
9·45	0·36	0·30	0·22	0·16
9·95	0·53	0·45	0·38	0·31
10·40	0·70	0·63	0·57	0·51
10·90	0·87	0·78	0·70	0·62
(e) 2,4-Dinitroaniline				
9·45	−0·96	−0·97	−1·00	−1·01
9·95	−0·78	−0·80	−0·83	−0·85
10·40	−0·60	−0·69	−0·62	−0·66
10·90	−0·39	−0·41	−0·45	−0·50
11·50	−0·10	−0·17	−0·22	−0·30
12·07	0·10	0·03	−0·03	−0·11
12·60	0·30	0·23	0·17	0·10
13·25	0·50	0·42	0·36	0·28
13·90	0·73	0·63	0·56	0·45
14·55	0·94	0·83	0·75	0·63
(f) 2,6-Dinitroaniline				
11·50	−1·09	−1·12	−1·15	−1·17
12·07	−0·90	−0·93	−0·95	−0·99
12·60	−0·70	−0·74	−0·77	−0·80
13·25	−0·51	−0·55	−0·57	−0·62
13·90	−0·30	−0·35	−0·37	−0·42
14·55	−0·12	−0·16	−0·19	−0·23
15·25	0·14	0·05	0·00	−0·02
15·90	0·27	0·23	0·18	0·15
16·65	0·55	0·43	0·39	0·33

TABLE 2

Values of $\mathrm{p}K_{\mathrm{BH^+}}$ for the conjugate acids of six amines in water at four temperatures

Amine	288 K	298 K	298 K	308 K	318 K
4-Nitroaniline	1·08	1·00	0·99 [a]	0·92	0·83
2-Nitroaniline	−0·22	−0·28	−0·29 [a]	−0·34	−0·41
2,5-Dichloro-4-nitroaniline	−1·75	−1·78	−1·79 [b]	−1·81	−1·86
2,4-Dichloro-6-nitroaniline	−3·00	−3·00		−3·00	−2·99
2,4-Dinitroaniline	−4·31	−4·25	−4·26 [b]	−4·20	−4·16
2,6-Dinitroaniline	−5·33	−5·23	−5·25 [b]	−5·13	−5·03

[a] 'Best values' of Long and Paul [14] and of Rochester.[1]
[b] Values of Yates and Wai.[12]

TABLE 3

The H_0 acidity function for aqueous perchloric acid at four temperatures (figures are for $-H_0$)

m/mol kg^{-1}	288 K	298 K	298 K [a]	308 K	318 K
0·5	0·06	0·04		0·05	0·05
1·0	9·31	0·30	0·32	0·31	0·29
1·5	0·50	0·49	0·50	0·50	0·49
2·0	0·72	0·72	0·70	0·71	0·71
2·5	0·93	0·92	0·92	0·92	0·92
3·0	1·13	1·13	1·12	1·12	1·11
3·5	1·33	1·32	1·30	1·31	1·30
4·0	1·52	1·51	1·49	1·49	1·48
4·5	1·70	1·68	1·65	1·67	1·65
5·0	1·86	1·84	1·81	1·83	1·82
5·5	2·02	2·01	2·00	1·99	1·97
6·0	2·16	2·15	2·17	2·13	2·11
6·5	2·32	2·30	2·35	2·28	2·27
7·0	2·50	2·47	2·50	2·45	2·42
7·5	2·68	2·65	2·65	2·61	2·59
8·0	2·87	2·82	2·81	2·77	2·75
8·5	3·03	2·98	2·97	2·93	2·89
9·0	3·20	3·15	3·15	3·11	3·05
9·5	3·39	3·32	3·35	3·26	3·17
10·0	3·58	3·50	3·51	3·41	3·32
10·5	3·78	3·70	3·69	3·60	3·50
11·0	3·98	3·83	3·82	3·76	3·67
11·5	4·18	4·00	4·00	3·96	3·85
12·0	4·36	4·22	4·17	4·12	4·00
12·5	4·52	4·40	4·35	4·31	4·17
13·0	4·70	4·57	4·52	4·49	4·34
13·5	4·85	4·70	4·70	4·61	4·47
14·0	5·05	4·90	4·89	4·79	4·64
14·5	5·20	5·05	5·08	4·95	4·78
15·0	5·35	5·20	5·26	5·08	4·92
15·5	5·50	5·32	5·43	5·21	5·06
16·0	5·65	5·50	5·57	5·33	5·17
16·5	5·80	5·62	5·71	5·48	5·31

[a] H_0 Scale of Yates and Wai [12] for aqueous $HClO_4$ at 298 K.

acid concentration were read off from the curve. The H_0 scales at four temperatures are given in Table 3. The scale measured by Yates and Wai [12] for aqueous perchloric acid at 298 K is included in Table 3 for comparison with the present scale at the same temperature. At low concentrations of perchloric acid H_0 varied only slightly with changing temperature. However at high concentrations (> *ca.* 3 mol kg^{-1}) H_0 showed an appreciable increase with increasing temperature, and the temperature coefficient of H_0, ($\mathrm{d}H_0/\mathrm{d}T$), increased as the concentration of perchloric acid became greater.

Standard free energies, enthalpies, and entropies of ionization of the amine indicators in water (Table 4) were deduced *via* equations (4) and (5).[13] Plots of $\log_{10} K_{\mathrm{BH^+}}$ against $(1/T)$ were accurately linear over the range of temperature

$$\Delta G^\circ = 2{\cdot}303RT\mathrm{p}K_{\mathrm{BH^+}} \tag{4}$$

$$\log_{10} K_{\mathrm{BH^+}} = -(\Delta H^\circ/2{\cdot}303RT) + (\Delta S^\circ/2{\cdot}303R) \tag{5}$$

studied in accord with previous reports [10,13] that $\Delta C^\circ_{\mathrm{p}}$ equals zero or is very small for the dissociation of substituted anilinium ions in water. The slopes and intercepts of the plots were deduced by computer using the standard method of least squares analysis. The thermodynamic quantities deduced from the present study of the ionization of six amines in aqueous perchloric acid solutions are compared in Table 4 with the corresponding quantities which have been reported following studies involving aqueous solutions of other strong acids.

TABLE 4

Values of ΔG°, ΔH°, and $T\Delta S^\circ$ (all in kJ mol^{-1}) for the dissociation of six substituted anilinium ions in water at 298 K

Acid	ΔG°	ΔH°	$T\Delta S^\circ$	Reference
(a) 4-Nitroaniline				
$HClO_4$	5·69	14·60	8·91	This work
HCl	5·82	14·31	8·49	*a*
HCl	5·73	13·01	7·28	*a, b*
HCl	6·15	19·25	13·10	6
H_2SO_4	5·82	12·55	6·73	10
H_2SO_4	5·69	13·14	7·45	8 *
H_2SO_4	5·73	13·68	7·95	7 *
(b) 2-Nitroaniline				
$HClO_4$	−1·59	11·00	12·59	This work
HCl	−1·51	7·03	8·54	13, *b*
HCl	−1·21	14·23	15·44	6
HCl	−1·42	8·20	9·62	13
H_2SO_4	−1·72	7·66	9·38	8 *
H_2SO_4	−1·46	14·14	15·60	7 *
H_2SO_4	−1·05	14·06	15·11	6
H_3PO_4	−1·09	13·39	14·48	6
(c) 2,5-Dichloro-4-nitroaniline				
$HClO_4$	−10·17	6·40	16·57	This work
H_2SO_4	−10·00	1·59	11·59	8 *
H_2SO_4	−9·96	7·40	17·36	7 *
(d) 2,4-Dichloro-6-nitroaniline				
$HClO_4$	−17·11	−0·59	16·52	This work
H_2SO_4	−17·20	5·02	22·22	7 *
H_2SO_4	−16·95	7·03	23·98	6
P_2O_5	−16·78	−2·93	13·85	6
(e) 2,4-Dinitroaniline				
$HClO_4$	−24·26	−−8·70	15·56	This work
H_2SO_4	−24·35	−11·42	12·93	8 *
H_2SO_4	−24·39	0·92	25·31	7 *
H_2SO_4	−25·06	1·76	26·82	6
(f) 2,6-Dinitroaniline				
$HClO_4$	−29·83	−17·41	12·42	This work
H_2SO_4	−30·75	−19·16	11·59	8 *
H_2SO_4	−30·67	−6·82	23·85	7 *

* Data calculated using equations (4) and (5) from p$K_{\mathrm{BH^+}}$ values given in the references.

[a] P. D. Bolton and F. M. Hall, *J. Chem. Soc.* (*B*), 1969, 939.
[b] A. I. Biggs, *J. Chem. Soc.*, 1961, 2572.

Enthalpies of dissociation ΔH of the conjugate acids of the six amine indicators in perchloric acid solutions of finite strength (as opposed to infinite dilution for ΔH°) were deduced *via* equation (6).[10] The $\log_{10}$ ($C_{\mathrm{BH^+}}/C_{\mathrm{B}}$) values were

$$\Delta H = -2{\cdot}303R\ \mathrm{d}\log_{10}(C_{\mathrm{BH^+}}/C_{\mathrm{B}})/\mathrm{d}(1/T) \tag{6}$$

taken at constant molality of perchloric acid. The resulting ΔH values are listed as a function of perchloric acid concentration in Table 5.

TABLE 5

Enthalpies (kJ mol^{-1}) of dissociation at 298 K of six substituted anilinium ions as a function of the concentration of perchloric acid in the aqueous solutions in which the dissociation occurs

$m_{\mathrm{HClO_4}}$/ mol kg^{-1}	ΔH	$m_{\mathrm{HClO_4}}$/ mol kg^{-1}	ΔH	$m_{\mathrm{HClO_4}}$/ mol kg^{-1}	ΔH
(a) 4-Nitroaniline					
0·065	14·8	0·25	15·1	0·65	16·4
0·08	14·6	0·38	14·0	0·80	15·8
0·14	14·4	0·52	15·0		
(b) 2-Nitroaniline					
0·38	11·6	1·10	12·8	1·98	10·5
0·52	13·3	1·40	12·2	2·30	12·2
0·80	12·3	1·70	10·5	2·60	11·3
(c) 2,5-Dichloro-4-nitroaniline					
1·70	6·40	3·50	8·70	6·00	8·12
1·98	7·53	4·10	9·29	6·45	9·12
2·30	7·53	4·75	7·53	6·90	9·87
2·60	8·70	5·60	8·70	7·25	9·87
(d) 2,4-Dichloro-6-nitroaniline					
4·75	1·13	7·25	6·11	9·45	12·2
5·60	1·76	7·65	5·48	9·95	12·8
6·00	2·34	8·10	6·40	10·4	11·6
6·45	2·89	8·50	8·70	10·9	14·6
6·90	4·64	9·00	10·5		
(e) 2,4-Dinitroaniline					
9·45	3·47	11·50	11·6	13·25	12·8
9·95	4·35	12·07	12·2	13·90	16·2
10·40	5·36	12·60	11·6	14·55	18·0
10·90	6·40				
(f) 2,6-Dinitroaniline					
11·50	4·35	13·25	5·82	15·25	9·29
12·07	5·82	13·90	6·40	15·90	7·28
12·60	5·82	14·55	6·40	16·65	12·8

DISCUSSION

The present values of p$K_{\mathrm{BH^+}}$ for five of the amine indicators in water at 298 K are in excellent agreement either with previously quoted ' best ' values [1,14] or with the values deduced by Yates and Wai [12] from a similar study of the protonation of the amines in aqueous perchloric acid solutions (Table 2). The protonation of 2,4-dichloro-6-nitroaniline in aqueous perchloric acid has not been studied previously although figures of −3·01,[7]

---

[12] K. Yates and H. Wai, *J. Amer. Chem. Soc.*, 1964, **86**, 5408.
[13] P. D. Bolton and F. M. Hall, *J. Chem. Soc.* (*B*), 1969, 1047.
[14] F. A. Long and M. A. Paul, *Chem. Rev.*, 1957, **57**, 1.

$-3{\cdot}13$,[15] $-3{\cdot}16$,[16] $-3{\cdot}28$,[17] $-3{\cdot}79$,[18] and $-2{\cdot}98$ [19] for $\mathrm{p}K_{\mathrm{BH^+}}$ at 298 K have been deduced from measurements of the protonation of the amine in aqueous solutions of other strong acids.

The H_0 acidity function scale deduced for aqueous perchloric acid at 298 K is in close agreement with the scale measured by Yates and Wai [12] (Table 3). H_0 at a particular molality of perchloric acid increases with increasing temperature. A similar result has been observed for aqueous solutions of sulphuric acid [6-8] and phosphoric acid [6] although a decrease in H_0 with increasing temperature has been reported for hydrochloric acid.[6] For perchloric acid ($\mathrm{d}H_0/\mathrm{d}T$) is small or negligible up to $m_{\mathrm{HClO_4}} \simeq 3$ mol kg^{-1} but becomes appreciable, increasing with increasing acid concentration, in the range 3 mol kg$^{-1} < m_{\mathrm{HClO_4}} < 17$ mol kg^{-1}. In this range of concentration the sensitivity of H_0 to temperature was such that a linear graph with slope $1{\cdot}14$ was obtained when the H_0 values at 288 and 318 K for each molality of acid were plotted against each other. The magnitude of the slope is consistent with a previous suggestion [20] that the effect of temperature on medium effects in strongly acidic solutions is often not large enough to have a significant influence on criteria of reaction mechanism [21,22] which rely upon correlations of the rates of acid catalysed reactions with H_0 acidity function scales. Many correlations of kinetic data at one temperature with equilibrium data at a different temperature have been tested.[21,22] However, this conclusion has been shown to be not always true in particular for correlations involving rates of amide hydrolysis.[23]

Although there is reasonable consistency between the values deduced from different studies of ΔG° for the dissociation of the substituted anilinium ions studied here, the agreement between reported values of the standard enthalpy of dissociation for a particular ion is often poor (Table 4). The only amine for which agreement is reasonable (apart from one value [6]) is 4-nitroaniline for which $\mathrm{p}K_{\mathrm{BH^+}}$ at each temperature has been deduced by the standard extrapolation of $\log_{10}(C_{\mathrm{BH^+}}/C_{\mathrm{HClO_4}}C_{\mathrm{B}})$ to infinite dilution of perchloric acid. For the other amines the strict reference of $\mathrm{p}K_{\mathrm{BH^+}}$ values to pure water as standard state relies upon the validity of the stepwise comparison of the plots of $\log_{10}(C_{\mathrm{BH^+}}/C_{\mathrm{B}})$ against acid concentration for progressively more weakly basic amines. The assumption of parallel acidity function behaviour for two bases in the same range of acid concentration must be applicable for all the temperatures studied if the ΔH° values deduced are to equal the standard enthalpy changes for the acid–base equilibria in water. It follows that equation (7) must be obeyed.[10] ΔH_1 and ΔH_2 are the enthalpies of dissociation, given by equation (6), for any pair of anilinium ions in the same

$$\Delta H_1^\circ - \Delta H_2^\circ = \Delta H_1 - \Delta H_2 \qquad (7)$$

perchloric acid solution and ΔH_1° and ΔH_2° are the standard enthalpies of dissociation [equation (5)] of the same two anilinium ions in water. Boyd and Wang [10] pointed out that the validity of equation (7) requires that ΔH_1 and ΔH_2 are parallel functions of acid concentration. The parallel behaviour of enthalpies of dissociation of the conjugate acids of four weak bases in aqueous sulphuric acid was demonstrated, and was used as the basis of extrapolation of ΔH to ΔH° values at zero concentration of sulphuric acid.[10] The corresponding plots for the amines studied here are shown in Figure 1. The dashed lines represent the extrapolation of each curve to ΔH° which has effectively been carried out in the present treatment. The curves are not exactly parallel although there is evidence for approximately parallel behaviour for indicators protonated in overlapping ranges of perchloric acid concentration. An analysis of published results [7,8] for the protonation of amines in aqueous sulphuric acid showed that plots of ΔH against $m_{\mathrm{H_2SO_4}}$ were also approximately parallel. However the results of the two studies were not entirely consistent with each other. In view of the variations between $\mathrm{p}K_{\mathrm{BH^+}}$ values which have been reported by different workers for a given amine at a particular temperature it is hardly surprising that the temperature derivatives of $\log_{10}(C_{\mathrm{BH^+}}/C_{\mathrm{B}})$ and of $\mathrm{p}K_{\mathrm{BH^+}}$ should be difficult to measure reliably,

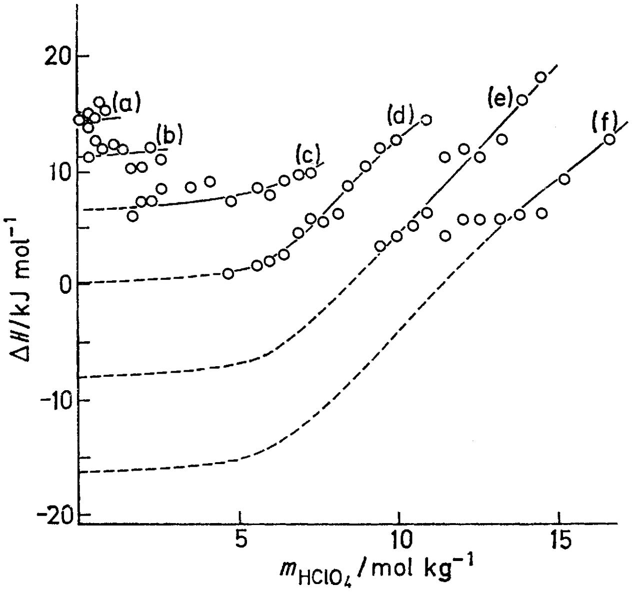

FIGURE 1 Variation of ΔH [equation (7)] with acid concentration for (a) 4-nitroaniline, (b) 2-nitroaniline, (c) 2,5-dichloro-4-nitroaniline, (d) 2,6-dichloro-4-nitroaniline, (e) 2,4-dinitroaniline and (f), 2,6-dinitroaniline

---

[15] J. L. Jenson and M. P. Gardner, *J. Phys. Chem.*, 1973, **77**, 1557.

[16] E. Hogfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, 1960, **82**, 15.

[17] R. S. Ryabova, I. M. Medvetskaya, and M. I. Vinnik, *Russ. J. Phys. Chem.*, 1966, **40**, 182.

[18] N. F. Hall and W. F. Spengeman, *J. Amer. Chem. Soc.*, 1940, **62**, 2487.

[19] E. Heilbronner and S. Weber, *Helv. Chim. Acta*, 1949, **32**, 1513.

[20] C. H. Rochester, *Progr. Reaction Kinetics*, 1972, **6**, 143.

[21] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956, 4968, 4973, 4978.

[22] J. F. Bunnett and F. P. Olsen, *Canad. J. Chem.*, 1966, **44**, 1917.

[23] K. Yates, *Accounts Chem. Res.*, 1971, **4**, 136.

particularly for the weaker amines, by standard acidity function methods.

The thermodynamic function $\Delta H - \Delta H^\circ$ has been evaluated from the data in Tables 4 and 5 and is plotted as a function of perchloric acid concentration in Figure 2. The relationship between $\Delta H - \Delta H^\circ$ and the variation of the H_0 acidity function with temperature follows from

$$\Delta H - \Delta H^\circ = 2{\cdot}303RT^2(\partial H_0/\partial T)_P \qquad (8)$$

equations (3), (5), and (6). If the curves in Figure 1 may be taken as parallel in overlapping ranges of acid concentration equation (7) is applicable for any pair of amines and therefore $\Delta H - \Delta H^\circ$ will also be a single smooth function of the concentration of perchloric acid.

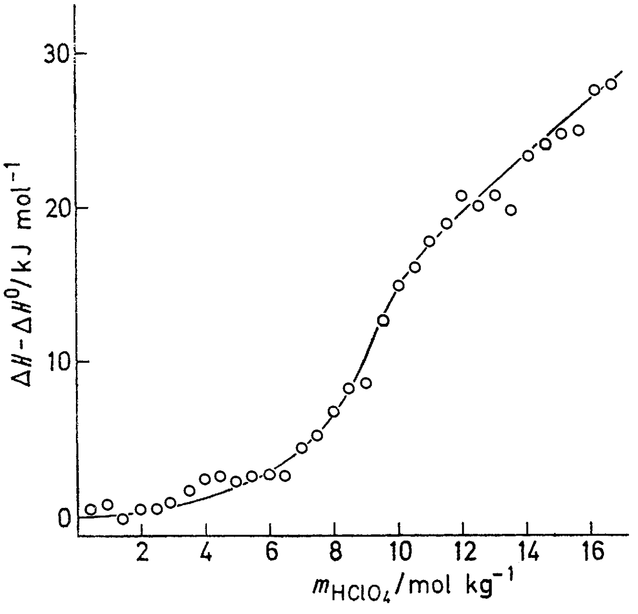

FIGURE 2 The variation of $\Delta H - \Delta H^\circ$ with perchloric acid concentration at 298 K. Curve calculated from equations (5) and (6). Points calculated from equation (8)

The $\Delta H - \Delta H^\circ$ curve in Figure 2 was calculated *via* equations (5) and (6) and is compared with the values (points) deduced from the smoothed H_0 acidity function scales (Table 3) *via* integration (constant molality) of equation (8). Knowledge of $\Delta H - \Delta H^\circ$ enables H_0 at one temperature to be calculated from H_0 at another temperature providing both temperatures are within the range over which $\Delta H - \Delta H^\circ$ may be taken as constant. It is now relevant to assess as follows whether the variation of $\Delta H - \Delta H^\circ$ with increasing concentrations of perchloric acid is consistent with theories which have been proposed to explain the free energy (H_0) data at a single temperature.

The protonation of a neutral base B in aqueous perchloric acid may be represented by equation (9) in which

$$\mathrm{B(H_2O)}_p + \mathrm{H(H_2O)}_q{}^+ \rightleftharpoons \mathrm{BH(H_2O)}_r{}^+ + n\mathrm{H_2O} \qquad (9)$$

p, q, and r are the hydration numbers of B, H^+, and BH^+ respectively and $n = (p + q - r)$.[2,3,21] The H_0 acidity function may now be written according to equation (10).

$$H_0 = -\log_{10} C_{H^+} + n \log_{10} a_w - \log_{10} (y_{H^+}y_B/y_{BH^+}) \qquad (10)$$

This equation is in a form first written by Bascombe and Bell[24] and with certain assumptions concerning the activity coefficient term gives a good account of acidity function behaviour for moderate (<*ca.* 7M) concentrations of strong acids. The steep rise in acidity of concentrated solutions of strong acids with increasing concentration is largely attributed to the term $n \log_{10} a_w$ in equation (10) where n is the number of water molecules of hydration liberated when one molecule of B is protonated to give BH^+. Several treatments have been presented in which the variation of n with acid concentration has been taken into account.[25-27] If the acid under consideration is incompletely dissociated at a stoicheiometric concentration C in water equation (11), in which α is the fraction

$$H_0 = -\log_{10} (\alpha C) + n \log_{10} a_w - \log_{10} (y_{H^+}y_B/y_{BH^+}) \qquad (11)$$

of acid dissociated, becomes applicable.[28] Hence the variation of H_0 with temperature is given by equation (12). The variation of C with temperature is given by

$$\frac{dH_0}{dT} = -\frac{d \log_{10} (\alpha C)}{dT} + n\frac{d \log_{10} a_w}{dT} - \frac{d \log_{10} (y_{H^+}y_B/y_{BH^+})}{dT} \qquad (12)$$

equation (13) where ρ is the density of the acid solution

$$(d \log_{10} C/dT) = (d \log_{10} \rho/dT) \qquad (13)$$

of concentration C. The term $(d \log_{10} a_w/dT)$ in equation (12) is related to the relative partial molal enthalpy of water $\bar{L}_w$ in the acid solution by equation (14).

$$(d \log_{10} a_w/dT) = (\bar{L}_w/2{\cdot}303RT^2) \qquad (14)$$

Hence combination of equations (8) and (12)—(14) leads to equation (15) for $\Delta H - \Delta H^\circ$. The magnitudes

$$\Delta H - \Delta H^\circ = -2{\cdot}303RT^2 \frac{d \log_{10} (\alpha\rho)}{dT} - n\bar{L}_w - 2{\cdot}303RT^2 \frac{d \log_{10} (y_{H^+}y_B/y_{BH^+})}{dT} \qquad (15)$$

of the contributions to $\Delta H - \Delta H^\circ$ of the terms on the right hand side of equation (15) have been assessed. The numerical data are given in Table 6.

Values of $[d \log_{10} (\alpha\rho)/dT]$ were calculated from published density data[29] and [equation (16)] from the fractions

$$(d \log_{10} \alpha/dT) = \log_{10} (\alpha_{40}/\alpha_{10})/30 \qquad (16)$$

α of perchloric acid dissociated at 10 and 40° determined by Haase *et al.*[30] The relative partial molal enthalpies of water $\bar{L}_w$ were deduced *via* equation (17)[31] from

$$\bar{L}_w = (\phi - \bar{L})m/55{\cdot}509 \qquad (17)$$

---

[24] K. N. Bascombe and R. P. Bell, *Discuss. Faraday Soc.*, 1957, **24**, 158.

[25] P. A. H. Wyatt, *Discuss. Faraday Soc.*, 1957, **24**, 162.

[26] E. B. Robertson and H. B. Dunford, *J. Amer. Chem. Soc.*, 1964, **86**, 5080.

[27] C. Perrin, *J. Amer. Chem. Soc.*, 1964, **86**, 256.

[28] J. G. Dawber, *Chem. Comm.*, 1966, 3.

[29] A. E. Markham, *J. Amer. Chem. Soc.*, 1941, **63**, 874.

[30] R. Haase, K-H. Dücker, and H. A. Küppers, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 97.

[31] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 1943, p. 224.

TABLE 6

Data used to test the validity of equation (15)

m_{HClO_4} / mol kg^{-1}	$\Delta H - \Delta H^\circ$ / kJ mol^{-1}	$RT^2(\mathrm{d}\ln\alpha p/\mathrm{d}T)$ / kJ mol^{-1}	$\bar{L}_w$ / kJ mol^{-1}	n [a]	Q [a] / kJ mol^{-1}	n [b]	Q [b] / kJ mol^{-1}	n [c]	Q [c] / kJ mol^{-1}
1	0·08	−0·33	0·008	19·8	0·17	14·0	0·22	41·9	−0·01
2	0·25	−0·46	0·025	12·0	0·16	7·16	0·28	27·9	−0·24
3	0·63	−0·50	0·042	10·7	0·05	6·73	0·22	22·4	−0·44
4	1·26	−0·54	0·000	9·65	0·54	6·31	0·54	18·6	0·54
5	1·97	−0·63	−0·213	8·44	2·43	5·63	1·83	15·6	3·95
6	3·10	−0·66	−0·339	7·47	3·19	5·08	2·38	13·3	5·17
7	4·52	−0·69	−0·498	6·76	4·06	4·73	3·05	11·6	6·47
8	6·82	−0·71	−0·707	6·30	5·16	4·60	3·96	10·4	8·06
9	10·5	−0·74	−0·979	5·82	6·44	4·38	5·03	9·3	9·84
10	15·0	−0·77	−1·314	5·47	7·96	4·23	6·33	8·5	11·9
11	17·8	−0·79	−1·732	5·13	9·68	4·06	7·82	7·8	14·3
12	19·9	−0·84	−2·243	4·91	11·9	3·96	9·72	7·2	17·0
13	21·8	−0·86	−2·858	4·67	14·2	3·81	11·7	6·8	20·3
14	23·6	−0·88	−3·594	4·44	16·8	3·67	14·1	6·3	23·5
15	25·5	−0·90	−4·473	4·21	19·7	3·51	16·6	5·9	27·3
16	27·4	−0·92	−5·494	4·01	23·0	3·37	19·4	5·6	31·7

The calculation of n and Q involved the use of [a] equation (18), [b] equation (19), [c] equation (20).

quoted[32] relative partial molal enthalpies $\bar{L}$ and apparent relative partial molal enthalpies ϕ of $HClO_4$ in aqueous perchloric acid solutions. The hydration numbers n were evaluated from equation (11) using published water activities[33] and values of α either ($m_{HClO_4} > 11$ mol kg^{-1}) given by Haase *et al.*[30] or ($m_{HClO_4} < 10$ mol kg^{-1}) estimated from plots given by Akitt *et al.*[34] At moderate to low concentrations of perchloric acid the data of Haase *et al.*[30] give lower values of α than those which have been deduced from several other independent studies.[34] Three separate estimates of n as a function of perchloric acid concentration were made and were based on three different assumptions embodied in equations (18)—(20)

$$\log_{10}(y_{H^+}y_B/y_{BH^+}) \sim 0 \qquad (18)$$

$$\log_{10}(y_{H^+}y_B/y_{BH^+}) \sim 0{\cdot}1\alpha C \qquad (19)$$

$$\log_{10}(y_{H^+}y_B/y_{BH^+}) \sim \log_{10} y_B \qquad (20)$$

concerning the behaviour of the activity coefficient term in equation (11). There is precedence for all these assumptions which have been chosen in order to give some impression of the sensitivity of the present calculations to the variation of ($y_{H^+}y_B/y_{BH^+}$) with acid concentration. Equation (19) relies on the observation that the effect of electrolyte concentration on activity coefficient ratios can sometimes be expressed by a Setschenow type of equation.[24,35,36] A Setschenow coefficient of 0·1 was chosen since it has previously been shown[24] that this figure is consistent with the fitting of equations (11) and (19) to the H_0 scale for aqueous perchloric acid. If $y_{H^+} = y_{BH^+}$ at all acid concentrations then equation equation (20) will be applicable. The present calculations used values of $\log_{10} y_B$ which were interpolated from the data of Yates *et al.*[36] for 2,4-dinitroaniline in aqueous perchloric acid solutions. There appears to be no way in which the final term in equation (15) can be estimated with any degree of reliability. The function (21) has therefore been evaluated and is compared with the experimental values of $\Delta H - \Delta H^\circ$ in Figure 3.

$$-2{\cdot}303RT^2(\mathrm{d}\log_{10}(\alpha\rho)/\mathrm{d}T) - n\bar{L}_w = Q \qquad (21)$$

The calculated values of Q have the same sign and are of approximately similar magnitude to the experimentally determined figures for $\Delta H - \Delta H^\circ$ The results therefore suggest that the enthalpy data are at least consistent with theories in which the H_0 acidity function is correlated with water activity either raised to some power or involved in a power series. The best agreement

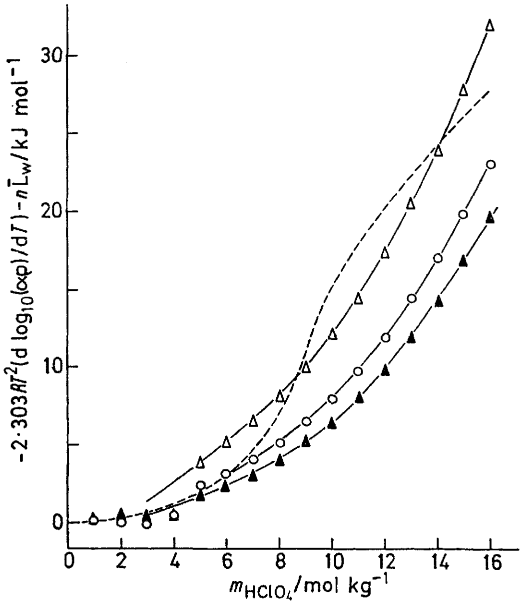

FIGURE 3 Variation of Q [equation (21)] with perchloric acid concentration. Curves are based on values of n calculated using equation (11) and ○ equation (18); ▲ equation (19); △ equation (20). The dashed line follows the experimental curve for $\Delta H - \Delta H^\circ$

---

[32] D. R. Didinosti and W. J. Biermann, *Canad. J. Chem.*, 1956, **34**, 1591.

[33] R. A. Robinson and O. J. Baker, *Trans. Roy. Soc. New Zealand*, 1946, **76**, 250; see also H. Wai and K. Yates, *Canad. J. Chem.*, 1969, **47**, 2326.

[34] J. W. Akitt, A. K. Covington, J. G. Freeman, and T. H. Lilley, *Chem. Comm.*, 1965, 349.

[35] F. A. Long and W. F. McDevit, *Chem. Rev.*, 1952, 51, 119.

[36] K. Yates, H. Wai, G. Welch, and R. A. McClelland, *J. Amer. Chem. Soc.*, 1973, **95**, 418.

between $\Delta H - \Delta H^\circ$ and Q for low concentrations of perchloric acid occurred when n was calculated from the combined equations (11) and (18). The close similarity of the two functions up to $m_{\mathrm{HClO_4}}$ *ca.* 7 mol kg^{-1} could be taken as indicating that the activity coefficient terms in both equations (11) and (18) are zero within this range of acid concentration and that the corresponding values of n truly represent the change in hydration number as given by equilibrium (9). Thus it is reasonable to expect that if the activity coefficient term in equation (11) is zero then its temperature coefficient should also be zero. However in view of the complexity and specificity of activity coefficient behaviour for ionic and neutral solutes in concentrated electrolyte solutions [36-38] and the simplicity of the present model which leads to equation (11) it is most unlikely that the activity coefficient terms may be neglected over wide ranges of perchloric acid concentration. At high concentrations Q and $\Delta H - \Delta H^\circ$ clearly deviate from each other (Figure 3). The magnitude of the deviation may, on the present model, be equated with the final term in equation (15). The three curves in Figure 3 correspond to cases where $\log_{10}(y_{\mathrm{H^+}}y_{\mathrm{B}}/y_{\mathrm{BH^+}})$ is positive [equation (19)], zero [equation (18)], or negative [equation (20)]. Comparison of the curves therefore gives some impression of the effect on Q of the magnitude and sign of the values of $\log_{10}(y_{\mathrm{H^+}}y_{\mathrm{B}}/y_{\mathrm{BH^+}})$. Data based on equation (20) for the activity coefficient term are unsatisfactory because the calculated values of n (Table 6) are too high to be consistent with the required interpretation of n in terms of hydration changes. It appears that the calculated values of n are unreasonably high for negative values of $\log_{10}(y_{\mathrm{H^+}}y_{\mathrm{B}}/y_{\mathrm{BH^+}})$ at all concentrations of perchloric acid. Only when $\log_{10}(y_{\mathrm{H^+}}y_{\mathrm{B}}/y_{\mathrm{BH^+}})$ is zero or positive are the estimated hydration parameters small enough to be interpreted in terms of equilibrium (9) and only then if species $\mathrm{H(H_2O)^+}_q$ with q up to *ca.* 10—12 are considered to exist in dilute acid solutions.[26] It follows from the deviation between Q and $\Delta H - \Delta H^\circ$ (Figure 3) and from equation (15) that $RT^2\mathrm{d}\ln(y_{\mathrm{H^+}}y_{\mathrm{B}}/y_{\mathrm{BH^+}})/\mathrm{d}T$ must be small (*ca.* 0 to -800 J mol^{-1}) for perchloric acid solutions up to *ca.* 6 mol kg^{-1} but becomes appreciable and negative at higher acid concentrations. Despite this trend the term $-n\bar{L}_{\mathrm{w}}$ in equation (15) makes the predominant contribution to $\Delta H - \Delta H^\circ$ at all but the lowest acid concentrations (where $RT^2\mathrm{d}\ln\rho/\mathrm{d}T$ becomes predominant). Thus the interpretation of the enthalpy data is consistent with solvation models for acidity function behaviour in which the involvement of water of hydration in chemical equilibria is considered to be a major cause of the high acidity of concentrated aqueous solutions of strong acids.

We thank the University of Tripoli for the financial assistance which supported this study.

[4/057 *Received*, 14*th January*, 1974]

---

[37] R. H. Boyd, 'Solute-Solvent Interactions,' eds. J. F. Coetzee and C. D. Ritchie, Dekker, New York, 1969, p. 97.

[38] T. R. Essig and J. A. Marinsky, *Canad. J. Chem.*, 1972, **50** 2254.