Dissociation and Liquid–Vapour Equilibria of Some Amines in Water at Elevated Temperatures

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Base dissociation constants and steam–water partition coefficients for the amines cyclohexylamine, piperidine, 2-amino-2-methylpropan-1-ol (AMP), and quinuclidine have been determined in the temperature range 100—300 °C from liquid–vapour equilibrium measurements. It has been shown that the temperature dependence of the dissociation constants of the conjugate acids (K_a) between 0 and 300 °C can be expressed, within experimental error, by an equation of the form:

$$\ln K_a = a_1 + a_2/T + a_3 \ln T$$

where a_1, a_2, and a_3 are independent of temperature and pressure. A similar equation involving steam density can be applied to partition coefficients.

Better concordance between low- and high-temperature dissociation data, particularly ΔC_p° values at 298 K, is obtained by using the four-term equation:

$$\ln K_a = a_1 + a_2/T + a_3 \ln T + a_4/T^2$$

The rate of decrease of base strength with temperature is less for quinuclidine than for the other bases, although the order of base strengths, quinuclidine > piperidine > cyclohexylamine > AMP, is similar at 25 and 250 °C. There does not appear to be a correlation between volatilities at 100—300 °C, where piperidine ≈ cyclohexylamine > quinuclidine > AMP, and basicities over the same temperature range.

Ionization and liquid–vapour equilibria of amines in aqueous solutions at 25 °C have been much studied over the years and a considerable body of data has been amassed.[1,2] However, there have been very few comparable studies for temperatures above 100 °C, even though amines, notably cyclohexylamine and morpholine,[3] have long been used for the treatment of boiler-water. Apart from any industrial applications, measurements of basicities in water over a wider temperature range may help towards a greater understanding of the effects of solvation on base strength, particularly when viewed in conjunction with gas-phase data.[4]

Here, we report measurements of base dissociation constants and partition coefficients between steam and water phases at 100, 200, 250, and 300 °C for four amines, namely, cyclohexylamine, piperidine, 2-amino-2-methylpropan-1-ol (AMP), and quinuclidine (1-azabicyclo[2.2.2]octane). All of these compounds have either been used, or proposed for use, in boilers.

Previously, the base dissociation constant (K_b) of cyclohexylamine has been determined up to 295 °C by a potentiometric method.[5] Values of K_b for piperidine up to 370 °C, obtained from conductivity measurements, have been reported,[6] but the reliability of this work has been questioned.[7] Otherwise, no dissociation data for this amine above 50 °C are available.[8] Potentiometric studies of the dissociation equilibrium of AMP up to 60 °C[9] have been made, whilst K_b values for quinuclidine and cyclohexylamine between 5—50 °C have been obtained using a conductance technique.[10]

The partition of cyclohexylamine between water and steam at temperatures of 100 °C and above has been the subject of a number of studies,[11–14] but the results are conflicting, especially at the lower end of this temperature range. The analogous equilibrium for AMP has been measured between 100—311 °C by Anerousis,[13] whose results seem rather erratic. Corresponding data on piperidine are extremely sparse, consisting of measurements at only three temperatures, 25 °C,[15] 180 °C,[16] and 243 °C.[17] Published results on quinuclidine cover only the temperature range 25—100 °C.[18]

Experimental

Apparatus and Techniques.—The experiments all involved measurements of the partition of amines between water and steam under static conditions in a closed autoclave. This autoclave, which was provided with three outlets of AISI Type 316 stainless steel, had an internal volume of *ca.* 1 250 cm^3 and was manufactured from Nimonic 80A alloy (major constituents: Cr, 20.5; Ni, *ca.* 70%). The vessel resided in a circulating-air oven, fitted with a temperature controller whose performance could be monitored to an accuracy of ±0.5 °C with a stainless steel sheathed, calibrated chromel–alumel thermocouple inside the autoclave. All the operations of washing, filling, and emptying of the autoclave were carried out at the working temperature and the system used for this is shown diagrammatically in Figure 1. Most of this system was of stainless steel, apart from the reservoir, R (Pyrex), and some Nylon, Perspex and silicone rubber tubing in the water purification circuit.

Between experiments, degassed water (O_2 < 5 μg kg^{-1}) from a modified Pyrex laboratory still was pumped continuously by the metering pump, M, at a rate of *ca.* 4 cm^3 min^{-1} through the partition autoclave A, exiting *via* the vapour sample line, V. A back-pressure valve (not shown), fitted on the outlet side of the vapour sample valve, was set at a pressure sufficient to ensure that the vessel remained full of liquid.

An experiment was started by isolating autoclave A and removing a quantity of water sufficient to create a steam space of *ca.* 500—600 cm^3 (750 cm^3 in the 100 °C experiments). A

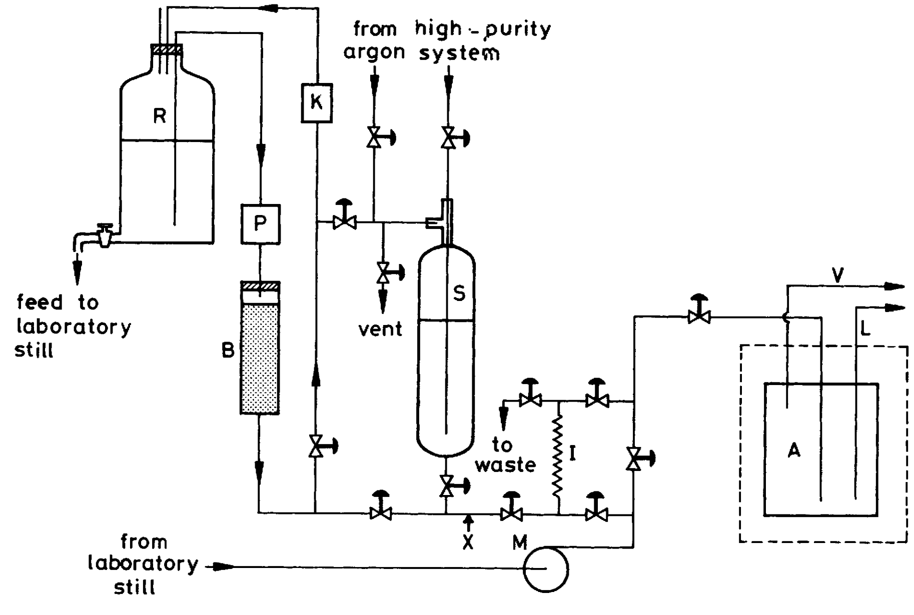

Figure 1. Injection and filling system for partition experiments (schematic) R, deionized water reservoir (Pyrex); P, peristaltic pump; K, conductivity cell; B, mixed-bed resin column (40 × 7 cm); S, amine solution reservoir; M, metering pump; I, injection loop; A, partition autoclave in air oven; X, temporary drain and filling connection; V, steam sample line; L, liquid sample line

quantity of amine solution which had been run from the storage vessel, S, into one of several interchangeable injection loops, I (0.5, 1, 1.5, or 4 cm^3 capacity), was then forced into the autoclave A using pump M.

In all experiments at 100 °C, and in some at higher temperatures, the solution thus produced was allowed to stand overnight before any samples were removed. Otherwise, sampling was begun about 1 h after amine injection.

Steam and liquid phases were normally sampled simultaneously at rates varying between 0.025—0.5 g min^{-1}, the lower rate only being achievable at 100 °C, when samples could be withdrawn using a peristaltic pump. All samples were collected into weighed volumetric flasks for analysis which was carried out within 1 h. Weights of sample taken were in the range 0.2—15 g, depending on concentration.

Materials and Methods of Analysis.—Samples of quinuclidine, obtained from Aldrich Chemical Co., seemed to be slightly discoloured, so were purified by sublimation under reduced pressure at 80—100 °C. Some piperidine samples from B.D.H. were purified by the method described by Bates and Bower,[8] but when results obtained with these and with unpurified material were compared, no significant differences were found. No purification of cyclohexylamine or AMP (B.D.H. AnalaR Biochemical Grade) was carried out.

Solutions for injection into the partition autoclave were prepared using deionized water and drawn into the storage vessel through the temporary pipework connection, X (Figure 1). They were then deoxygenated by three cycles of alternate evacuation and pressurization to *ca.* 7 MPa with high-purity argon ($O_2 < 4$ vpm). Trials showed that dissolved oxygen concentrations <5 μg kg^{-1} could be achieved with this procedure.

Vapour and liquid samples from the partition autoclave were analysed for amine content using an ion-chromatographic technique.[19] Cyclohexylamine, piperidine, and quinuclidine calibration standards were prepared by dilution from stock solutions whose concentrations had been determined acidimetrically. The concentration of the stock AMP solution had been determined by gas chromatography,[20] since an appreciable quantity of amine impurity was present, and separation of this from AMP is extremely difficult.

In trial experiments, the standard deviation obtained in repeated analyses of samples by the ion-chromatographic method was found to be ±3.5%.

Results

The equilibrium compositions of steam and liquid phases were measured at each temperature over a range of amine concentration. Molal units are used to express concentration throughout this work. The ratio of each pair of measured concentrations in steam and liquid, *i.e.* the relative volatility (r), was calculated and these values, together with the corresponding liquid-phase concentrations (c) are displayed in Tables 1—4. In some experiments, sodium hydroxide was added to suppress the ionization of amine. This gave a direct measure of the amine partition coefficient (K_p), defined as the ratio of concentrations of un-ionized base in steam and liquid.

Removal of samples from a closed autoclave will itself cause concentration changes in steam and liquid as the total quantity of amine falls and the relative amounts of liquid and steam phases alter. After some preliminary trials using ammonia, it was concluded that errors due to this effect would be minimized by withdrawing liquid and steam samples simultaneously. Usually, three such pairs of samples were taken in any particular experiment. All have been tabulated and, as can be seen from, as an example, the first three results at 100 °C in Table 1, the concentration changes may be quite considerable.

The amine AMP decomposed at an appreciable rate at 250 °C, particularly in the absence of sodium hydroxide. Ammonia was the only reaction product detectable by the ion-chromatography system used for these experiments and the concentrations found, which had to be taken into account in the calculation of K_a and K_p, are also given in Table 3. At 300 °C, AMP decomposed too rapidly for any partition measurements to be made in the absence of sodium hydroxide.

Slight decomposition of cyclohexylamine to ammonia was also observed at 300 °C in some experiments, but the other two

Table 1. Steam–water equilibrium results for cyclohexylamine

θ/°C							
100		200		250		300	
10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r
25.4[a]	20.9	104[b]	15.8	94.4[c]	8.64	70.5[c]	4.65
20.3[a]	21.4	98.6[b]	14.6	83.7[c]	8.43	66.4[c]	4.98
12.7[a]	22.4	86.7[b]	14.2	24.9[c]	9.00	65.8[c]	4.92
95.0	14.7	24.1[b]	15.6	24.1[c]	8.59	21.8[c]	4.91
85.4	13.0	23.2[b]	15.2	22.1[c]	8.64	21.1[c]	4.69
67.6	13.5	20.0[b]	15.2	5.66[c]	8.41	18.9[c]	4.72
50.8	12.9	4.97[b]	15.0	5.45[c]	8.77	4.36[c]	4.93
45.6	12.1	4.57[b]	15.3	4.65[c]	8.97	3.95[c]	5.09
41.9	12.1	3.89[b]	15.3	43.0	7.21	3.93[c]	5.06
28.4	10.7	42.4	11.5	41.3	7.29	10.3	4.31
26.8	9.93	37.6	11.5	39.4	7.21	10.2	4.15
23.3	9.14	33.4	11.7	21.4	7.80	9.66	4.02
24.3	9.47	17.1	11.1	18.6	6.99	5.17	4.45
22.3	9.42	16.3	10.7	18.2	7.36	4.80	4.46
19.6	8.52	15.1	10.5	10.7	6.17	4.57	4.27
14.2	8.31	7.20	8.42	10.2	6.47	2.54	4.09
13.4	7.35	6.43	8.32	10.2	6.21	2.02	4.29
12.1	7.17	6.31	7.69	4.43	5.67	2.45	4.41
8.23	6.05	3.63	7.00	3.88	5.67	2.31	4.32
7.68	5.82	3.38	7.31	3.80	5.26	2.06	4.13
7.08	5.56	3.32	6.78	3.42	5.41	0.924 (0.147)[d]	3.66
5.14	4.26			3.14	5.73	0.843 (0.190)[d]	3.57
5.02	4.20			3.09	5.31	0.718 (0.267)[d]	3.64
				1.31	4.38	0.864	3.72
				1.23	4.67	0.695	4.16
				1.19	4.20	0.586	4.10

[a] 10^{-2} mol kg^{-1} NaOH present. [b] 1.25×10^{-3} mol kg^{-1} NaOH present. [c] 5×10^{-4} mol kg^{-1} NaOH present. [d] Figures in brackets are ammonia concentrations.

Table 2. Steam–water equilibrium results for piperidine

θ/°C							
100		200		250		300	
10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r
310	12.1	367[a]	15.3	398[b]	9.32	345[b]	4.90
302	12.2	361[a]	14.5	365[b]	8.88	317[b]	4.95
271	12.1	330[a]	14.2	345[b]	8.87	288[b]	5.03
110	8.78	41.1[a]	13.7	40.8[b]	9.53	34.2[b]	5.03
110	8.25	37.2[a]	13.3	36.2[b]	9.48	31.2[b]	5.35
103	8.50	32.9[a]	13.8	34.5[b]	9.25	29.4[b]	5.27
34.6	5.55	4.45[a]	15.3	6.84[b]	8.74	5.42[b]	5.06
24.8	5.34	3.98[a]	14.5	6.16[b]	8.90	4.87[b]	5.26
36.0	4.86	3.37[a]	15.0	5.71[b]	8.84	4.60[b]	5.11
20.2	3.46	47.9	9.33	405	8.25	295	5.05
20.2	3.48	44.5	8.54	324	9.85	293	4.74
19.7	3.41	39.9	9.20	365	7.95	303	4.85
8.95	1.93	23.1	6.93	26.8	6.75	25.4	4.21
8.80	1.89	22.2	6.80	27.0	6.85	24.7	4.41
8.90	1.94	19.4	7.01	27.2	6.62	23.2	3.91
4.33	1.01	10.2	4.72	26.5	6.04	13.6	4.52
4.14	0.932	8.88	5.47	16.8	6.13	13.6	4.40
4.06	0.956	8.74	4.94	16.3	6.06	14.3	4.43
		5.11	3.46	19.4	5.10	4.21	3.56
		4.73	3.55	15.0	5.64	4.01	3.64
		3.91	3.68	5.71	3.78	3.64	3.46
				4.70	4.79		
				5.01	4.23		
				3.24	4.32		
				3.18	3.52		
				3.14	3.50		
				2.93	3.20		

[a] 5×10^{-3} mol kg^{-1} NaOH present. [b] 2.5×10^{-3} mol kg^{-1} NaOH present.

amines appeared to be completely stable over the 6—7 h period of experimental measurements.

In the absence of sodium hydroxide and ammonia, and for solutions sufficiently dilute to be considered ideal, the relationship between r, K_a, K_p and liquid-phase amine concentration (c) is given by the equation:

$$(K_p - r)^2(K_a{}^2K_p + K_arc) + K_wK_pr^2 = 0 \qquad (1)$$

Values of K_w, the ionic product of water, used in calculations were taken from the work of Sweeton *et al.*[21]

Equation (1) is obtained by expressing the charge balance equation:

$$[H^+] + [BH^+] = [OH^-] \qquad (2)$$

in terms of the experimentally measurable quantities, r and c, using the equations:

$$K_a = [B][H^+]/[BH^+] \qquad (3)$$

$$K_w = [H^+][OH^-] \qquad (4)$$

$$c = [BH^+] + [B] \qquad (5)$$

$$K_p = y/[B] \qquad (6)$$

and

$$r = y/c \qquad (7)$$

In equations (2)—(7), y is the concentration of base in the steam phase, all other concentrations (square brackets) referring to the liquid phase.

A similar analysis can be carried out for experiments where sodium hydroxide (assumed completely dissociated) or ammonia is present. In the latter case, values of K_b for ammonia obtained by Hitch and Mesmer[22] were used.

Values of K_a and K_p for the four amines at the various temperatures were calculated by carrying out a non-linear least-squares regression analysis on the appropriate data in Tables 1—4, fitting the experimental r and c values to equation (1) or its analogues. This analysis also yielded confidence intervals for the equilibrium constants.[23] The results of these calculations may be found in Table 5.

From equations (3)—(7), it can be shown that there should be a linear relationship between $1/r$ and $[H^+]$. If 'experimental' $[H^+]$ values are calculated from the experimental liquid-phase amine concentrations and the K_a values obtained in the regression analysis, the resulting plots show no signs of curvature. This suggests that the concentration range is sufficiently low that the equilibrium constants obtained can be regarded as true thermodynamic constants. Further evidence for this view comes from the observation that omission of all the results obtained in the presence of sodium hydroxide had no significant effect on K_a and K_p values obtained by the regression analysis.

Discussion

Amine Dissociation.—Results obtained in this and earlier work on these four amines are plotted against temperature in Figure 2. Only for cyclohexylamine are there suitable data with which the present work can be compared directly. It can be seen from Figure 2 that, except at 300 °C, there is a reasonable agreement between our results and the calculated curve obtained by Mesmer and Hitch,[5] which incorporated the data of Bergstrom and Olofsson.[24] The partition method for measuring base strength seems less satisfactory when a weak base, such as cyclohexylamine at 300 °C, is studied. Under these conditions, the change in relative volatility over the range of concentrations which it is possible to use becomes rather small, resulting in less precise values for the equilibrium constants.

For the other three amines, it was found that the temperature dependence of the acid dissociation constants could be expressed, within experimental error, by either of the following three-term equations:

$$\ln K = a_1 + a_2/T + a_3 \ln T \qquad (8)$$

$$\ln K = a_1 + a_2/T + a_3 T \qquad (9)$$

Values of the parameters a_1, a_2, and a_3, together with thermodynamic quantities for each of the three amines at 25 °C, were calculated from a least-squares regression fitting of all the appropriate data in Figure 2 to equations (8) or (9). The results of this analysis are shown in Table 6 (analyses a and b). Similar calculations had been carried out in the earlier reported work[8–10] at temperatures below 100 °C and these data are also presented in Table 6 (analyses c).

It can be seen from Table 6 that values of $\Delta G°_{298}$, $\Delta H°_{298}$, and ΔS_{298} calculated using all the data in Figure 2 do not differ significantly from the literature values. However, this does not apply to the quantity $\Delta C°_p$, where significant discrepancies are apparent. It should further be noted that the use of thermodynamic data obtained at 5—50 °C for predictive purposes[4,18] could give rise to large errors also; a study of Table 6 indicates that such a prediction of pK_a at 250 °C could be in error by as much as 0.35 pK units.

Whilst the previously reported dissociation data[8–10] on AMP, piperidine, and quinuclidine has been obtained at a pressure of 1 atm, the present work was carried out at pressures of 15.3 atm (200 °C), 39.3 atm (250 °C), and 84.8 atm (300 °C).[25] Calculations based on the correlations between ionization constants and pressure proposed by Marshall[26] and using data obtained by Mesmer *et al.*,[5,21,22] indicated that the effect on pK_a at the highest pressure would be *ca.* 0.003 units. Therefore, it was

Table 3. Steam–water equilibrium results for AMP

θ/°C							
100		200		250		300	
10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r
48.4^a	0.217	107^b	0.662	133^c	0.805	91.1^c	0.895
49.3^a	0.225	107^b	0.669	126^c	0.788	71.3^c	0.928
49.5^a	0.232	105^b	0.669	124^c	0.794	59.2^c	0.905
15.5^a	0.215	35.3	0.674	26.9^c	0.844	55.5^c	0.856
14.5^a	0.228	35.2^b	0.693	26.3^c	0.817	41.9^c	0.895
58.9	0.166	34.4^b	0.672	25.0^c	0.820	30.4^c	0.918
60.1	0.171	108	0.637	6.11^c	0.831		
61.4	0.169	114	0.619	6.13^c	0.814		
14.7	0.134	109	0.659	5.68^c	0.835		
15.0	0.141	17.8	0.556	21.6 (3.70)^d	0.759		
15.4	0.149	18.2	0.560	19.7 (6.31)^d	0.726		
5.06	0.100	17.9	0.581	16.0 (9.28)^d	0.712		
5.15	0.109	10.3	0.523	10.4 (2.17)^d	0.705		
5.13	0.112	10.6	0.520	7.41 (5.25)^d	0.735		
5.12	0.100	8.08	0.507	6.21 (6.42)^d	0.692		
4.96	0.106	7.98	0.541	5.41 (1.37)^d	0.673		
2.07	0.072	7.86	0.527	3.89 (2.75)^d	0.656		
2.17	0.069	6.04	0.492	2.99 (3.24)^d	0.629		
		5.96	0.495	1.62 (0.444)^d	0.604		
		6.05	0.507	1.20 (0.940)^d	0.608		

[a] 2.5 × 10^{-3} mol kg^{-1} NaOH present. [b] 5 × 10^{-4} kg^{-1} NaOH present. [c] 2.5 × 10^{-4} mol kg^{-1} NaOH present. [d] Figures in brackets are ammonia concentrations.

Table 4. Steam–water equilibrium results for quinuclidine

θ/°C							
100		200		250		300	
10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r	10^5c/mol kg^{-1}	r
268	5.49	37.9^a	10.9	144^b	6.78	123^b	3.89
252	5.75	36.4^a	10.1	146^b	6.15	126^b	3.82
257	5.49	35.1^a	9.60	140^b	6.29	116^b	4.17
93.3	3.40	26.2^a	9.47	52.0^b	6.23	42.4^b	3.77
90.5	3.51	23.0^a	10.7	48.4^b	6.16	40.1^b	3.94
91.2	3.61	23.2^a	10.0	47.2^b	6.12	38.9^b	3.93
29.1	1.63	42.5	4.92	4.58^b	6.46	3.60^b	4.03
30.0	1.66	45.5	4.59	4.13^b	6.88	3.45^b	4.14
28.7	1.65	44.5	4.74	3.94^b	6.42	3.13^b	4.22
12.7	0.898	23.2	3.59	37.8	4.47	37.8	3.44
13.4	0.933	23.7	3.45	40.9	4.13	41.1	3.14
13.3	0.917	22.8	3.56	37.7	4.30	20.3	3.10
7.27	0.528	9.81	2.27	20.8	3.75	21.1	2.92
6.90	0.548	10.3	2.21	21.0	3.53	20.5	2.90
7.07	0.526	10.0	2.27	19.9	3.72	9.00	2.71
4.98	0.380	3.38	1.11	6.63	2.32	9.58	2.53
4.80	0.385	3.68	1.04	7.11	2.26	8.40	2.57
5.06	0.383	3.62	1.14	6.73	2.41	5.17	2.26
5.01	0.363			3.04	1.58	5.41	2.26
				3.21	1.52	5.00	2.40
				3.02	1.60		

[a] 1.25 × 10^{-2} mol kg^{-1} NaOH present. [b] 2.5 × 10^{-3} mol kg^{-1} NaOH present.

Table 5. Equilibrium constants (with 95% confidence limits) calculated from experimental measurements in Tables 1—4

		θ/°C			
		100	200	250	300
Cyclohexylamine	pK_a	8.48 ± 0.03	6.69 ± 0.06	6.09 ± 0.07	5.22 ± 0.12
	K_p	21.8 ± 0.4	15.4 ± 0.3	8.70 ± 0.19	4.86 ± 0.12
Piperidine	pK_a	9.15 ± 0.03	7.37 ± 0.08	6.71 ± 0.10	6.01 ± 0.15
	K_p	19.9 ± 0.5	14.7 ± 0.5	9.24 ± 0.32	5.10 ± 0.12
AMP	pK_a	7.77 ± 0.07	6.10 ± 0.07	5.56 ± 0.08	
	K_p	0.224 ± 0.006	0.682 ± 0.009	0.821 ± 0.013	0.898 ± 0.063
Quinuclidine	pK_a	9.44 ± 0.02	7.76 ± 0.08	7.08 ± 0.07	6.53 ± 0.09
	K_p	11.7 ± 0.2	10.4 ± 0.3	6.59 ± 0.16	4.01 ± 0.10

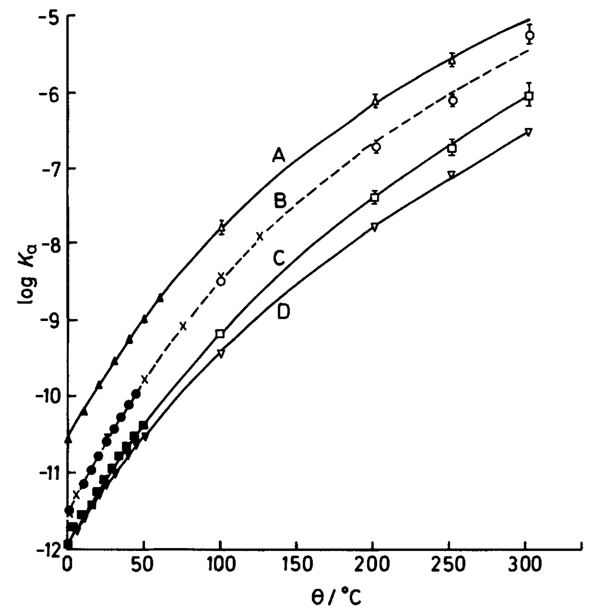

Figure 2. Dissociation of AMP (curve A), cyclohexylamine (B), piperidine (C), and quinuclidine (D) between 0—300 °C. Open symbols represent data obtained in this work, with 95% confidence limits shown. (▲), Ref. 9; (●), ref. 5; (×), ref. 24; (■), ref. 8; (▼), ref. 10. Broken curve, ref., 5. Solid curves were calculated from a least-squares fit of all the data to equation (8)

considered that no significant improvement would be achieved by adding terms in pressure to equations (8) and (9).

The use of more complex equations than (8) and (9) was then investigated in an attempt to resolve the discrepancies obtained with three-term expressions. A critical assessment of various equations used to express the dependence of equilibrium constants on temperature has recently been carried out by Blandamer *et al.*[27] Two of the more widely used of the equations mentioned in this review were examined. These are:

$$\ln K = a_1 + a_2/T + a_3 \ln T + a_4/T^2 \qquad (10)$$

and

$$\ln K = \ln K_\varphi + \frac{\Delta H^\circ_\varphi}{R}\left[\frac{1}{\varphi} - \frac{1}{T}\right] + \frac{\Delta C^\circ_p(\varphi)}{R}\left[\frac{\varphi}{T} - 1 + \ln\frac{T}{\varphi}\right] + \frac{\Delta^2 C^\circ_p(\varphi)}{R}\left[\frac{\varphi}{2}\right]\left[\frac{T}{\varphi} - \frac{\varphi}{T} - 2\ln\frac{T}{\varphi}\right] \qquad (11)$$

In equation (11), originally proposed by Clarke and Glew,[28] a reference temperature, φ, is chosen and the thermodynamic quantities $\ln K_\varphi$, ΔH°_φ, $\Delta C^\circ_p(\varphi)$ are readily obtained from the parameters of a least-squares regression. R is the gas content.

However, significant discrepancies in $\Delta G^\circ_p(298)$ values, comparable to or greater than those shown in Table 6, were still observed when four-variable regressions of the amine data to equations (10) and (11) were carried out.

Table 6. Temperature dependence of amine dissociation—results obtained with three-term fitting equations. Values in parentheses are standard errors

Amine	Analysis	a_1	a_2	a_3	ΔG°_{298} J mol^{-1}	ΔH°_{298} J mol^{-1}	ΔS°_{298} J mol^{-1} K^{-1}	$\Delta C^\circ_{p(298)}$ J mol^{-1} K^{-1}	ΔpK^a (523)
AMP	*c*	−7.3110	−6 230.21	1.0329	55 330	54 350	−3.3	8.6	0.02
					(40)	(480)	(1.6)	(6.0)	
	d	−1.1229	−6 433.51	0.001 272	55 330	54 420	−3.0	6.3	0.02
					(40)	(470)	(1.6)	(4.9)	
	e	14.609	−7 163.71	−2.2645	55 342	53 949	−4.60	−18.8	−0.20
					(<10)	(10)	(0.04)	(1.4)	
Piperidine	*c*	−58.040	−3 990.95	8.0413	63 480	53 110	−34.8	66.9	0.05
					(30)	(430)	(1.5)	(4.8)	
	d	−10.239	−5 500.98	0.010 34	63 460	53 380	−33.8	51.3	0.04
					(30)	(360)	(1.2)	(3.2)	
	e	−14.629	−4 848.32	0.017 70	63 488	53 390	−33.9	88	0.35
					(10)	(80)	(0.3)	(11)	
Quinuclidine	*c*	−69.925	−2 802.33	9.4155	63 650	46 630	−57.1	78.3	−0.02
					(30)	(390)	(1.3)	(4.2)	
	d	−13.731	−4 613.86	0.011 84	63 640	47 110	−55.4	58.7	−0.03
					(30)	(390)	(1.3)	(3.4)	
	e	−192.19[b]	9 786.16[b]	29.121[b]	63 668	46 639	−57.1	17.6	−0.30
					(20)	(400)	(1.2)	(2)	

[a] ΔpK = pK_a (measured) − pK_a (calculated). [b] Fitting parameters for ln K_b. [c] All data in Figure 2 fitted to equation (8). [d] All data in Figure 2 fitted to equation (9). [e] Literature data (temperatures below 100 °C) referring to equation (8) (AMP and quinuclidine) or equation (9) (piperidine).

Table 7. Temperature dependence of amine dissociation—four-term equation (10) fitted to 25 °C data

Amine	a_1	a_2	a_3	$10^{-5}a_4$	$\Delta C_p^\circ(298)$ J mol^{-1} K^{-1}	$\Delta C_p^\circ(523)$ J mol^{-1} K^{-1}	$\Delta C_p\Delta$pK^a (523)
AMP	79.907	−665.653	−10.869	5.8359	−18.8	54.9	0.03
Piperidine	9.3170	8 705.42	−1.464	−4.0542	88.0	36.8	0.06
Quinuclidine	188.646	−8 905.80	−25.402	10.349	17.6	148	−0.04

[a] ΔpK = pK_a (measured) − pK_a (calculated).

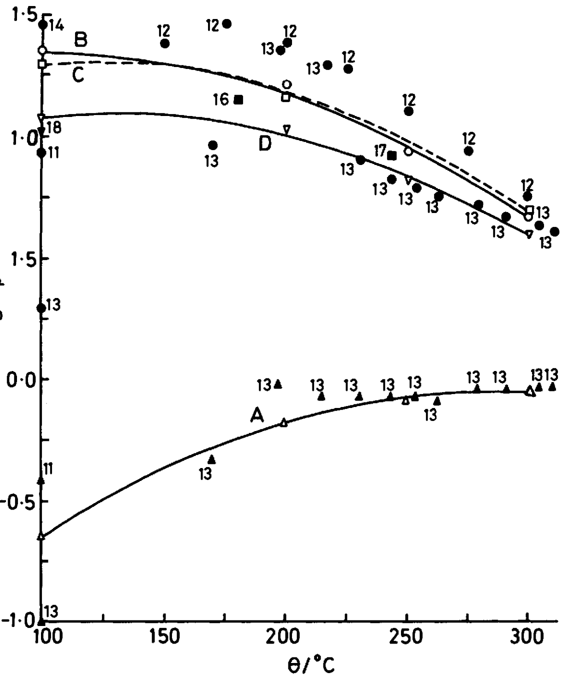

Figure 3. Volatility of amines between 100—300 °C. Open symbols represent data obtained in this work, filled symbols (with ref. no.) data from previous studies. (▲,△), Curve A, AMP; (●,○) curve B, cyclohexylamine; (■,□), curve C, piperidine; (▼,▽), curve D, quinuclidine. Curves were obtained from a least-squares fit of the data obtained in this work to equation (8)

The best-fit to both low- and high-temperature data was made on a trial-and-error basis, using equation (10), together with the existing literature data[8–10] for pK_a, $\Delta H°$, and $\Delta C°_p$ at 25 °C. Values of $\Delta C°_p$ at 250 °C were tried until a minimum in the quantity $\Sigma[pK_a(\text{measured}) - pK_a(\text{calculated})]^2$ was obtained.

The results of this calculation are given in Table 7. Although there are greater discrepancies between calculated and measured pK_a values at 250 °C when this method is used (*cf.* Table 6), the differences are still within the estimated experimental errors.

The order of base strengths, quinuclidine > piperidine > cyclohexylamine > AMP, is the same at 250 °C as at 25 °C, but the decrease in base strength with temperature is less for the tertiary amine, quinuclidine, than for the primary and secondary amines. Similar behaviour, though over a less extended temperature range, was noted in a study of four C_6 amines.[24]

As far as is known the only other nitrogenous bases whose dissociation in water has been measured up to 300 °C are ammonia[22] and morpholine.[5] Both are weaker than AMP over the whole temperature range, but whilst morpholine is the weakest of the six bases at 25 °C, ammonia becomes the weakest above *ca.* 225 °C.

Although only a small number of amines has so far been studied, these observations do suggest that solvation effects are weakened with increasing temperature, with the result that the order of base strength is tending more closely towards that found in the gas-phase.[4]

Liquid–Vapour Equilibria.—K_p Values obtained in this work are plotted in Figure 3. 95% Confidence limits, calculated from the data in Tables 1—4, were generally about 2% of the K_p values and could not be depicted on the scale of this Figure. Results obtained in previous studies on these four amines[11–14,16–18] are also shown in Figure 3. In some cases, where only relative volatility measurements were reported,[11,16] we have made corrections for base dissociation.

As can be seen, the results for cyclohexylamine are conflicting. However, it is considered that those obtained in the present work are the most reliable, because they originate from the same set of experimental measurements which yielded pK_a values in good agreement with independent determinations.[5,24]

The volatilities of piperidine and cyclohexylamine appear almost identical over a wide temperature range. Quinuclidine is somewhat less volatile than piperidine, both at 100—300 °C and at 25 °C.[15,18] Calculations made using the empirical correlations of Cabani *et al.*[2] would appear to indicate an opposite order of volatility for these two amines at 25 °C.

Results obtained for AMP at 250 and 300 °C are in good agreement with those of Anerousis *et al.*,[13] but diverge at lower temperatures. These workers' data for AMP, cyclohexylamine, and various other amines seem to lack self-consistency in the temperature range 100—225 °C, and it is therefore concluded that the K_p values obtained in the present work are the more reliable. Whichever set of data is taken, AMP is clearly the least volatile of the four amines, presumably due to the presence of a second hydrophilic group in the molecule.

Steam–water partition data are also available for ammonia[29] and morpholine,[11–13] in the temperature range 100—300 °C. The volatility of the latter base is slightly greater than that of AMP under these conditions; ammonia, the second most volatile base at 100 °C, becomes less volatile than quinclidine above *ca.* 135 °C.

To make any quantitative connection between base strength and steam volatility would require knowledge of the thermodynamics of hydration of ions in steam which is at present unavailable. However, it does appear that the substitution of $O<$ for $CH_2<$ in cyclic amines (*cf.* morpholine and piperidine) reduces both volatility and base strength.

Correlation of K_p with Temperature and Specific Volume.—There is evidence for the existence of a linear relationship between the logarithms of K_p and steam:water density ratio, applicable to a number of substances including NaCl, SiO_2, NH_3, and CO_2.[30] Difficulties arise in attempts to apply this rule to quinuclidine or piperidine, since K_p values for these amines appear to reach a peak at 100—150 °C.

The experimental K_p data as displayed in Figure 3 can be fitted to equations similar to (8), but greater concordance between low- and high-temperature results is obtained[18] by working with the Henry's Law coefficient, K_H, defined by the equation:

$$K_H = f_A/x_A \qquad (12)$$

In equation (12), f_A is the fugacity of amine in the steam phase in equilibrium with a mol fraction x_A in the liquid. Ellis[31] and Cobble[18] relate K_H to K_p by the equation:

$$K_H = PK_p/Z \qquad (13)$$

where P is the vapour pressure of water and Z the compressibility factor for steam. It follows from equations (12) and (13) that, for dilute aqueous solutions:

$$K_H = 55.55\ RTK_p/v \qquad (14)$$

where v is the specific volume of steam ($dm^3\ kg^{-1}$) at temperature T and pressure P.

Henry's Law coefficients for each amine were calculated from equation (14) and the data in Table 5, v being obtained from

Table 8. Temperature dependence of Henry's Law coefficients for amines. Values in parentheses are standard errors

Amine	a_1[a]	a_2[a]	a_3[a]	ΔG°_{298} J mol^{-1}	ΔH°_{298} J mol^{-1}	ΔS°_{298} J mol^{-1} K^{-1}	ΔC°_p J mol^{-1} K^{-1}
AMP	73.787	−10 275.8	−8.0591	16 400	65 500	165	−67
				(500)	(2 500)	(7)	(16)
Cyclohexylamine	159.17	−12 893.1	−20.519	2 440	56 300	181	−171
				(760)	(4 300)	(12)	(27)
							246.7[b]
Piperidine	171.95	−13 872.4	−22.255	3 430	60 160	190	−185
				(100)	(840)	(3)	(8)
				3 480[c]	65 410[c]	−207.5[c]	−318.5[c]
				(80)	(200)	(0.8)	
Quinuclidine	150.98	−12 791.5	−19.287	4 500	58 500	181	−160
				(600)	(3 600)	(10)	(23)

[a] $\ln K_H = a_1 + a_2/T + a_3 \ln T$. [b] Ref. 2. [c] Refs. 2 and 15.

Steam Tables.[25] The results were then fitted to equation (8) and values of the parameters thus obtained may be found in Table 8. Analysis of the piperidine data also took into account the results of Cabani *et al.*, at 25 °C.[15] Thermodynamic parameters at this temperature, calculated from the fitted curves, are also given in Table 8, together with literature data.[2,15]

Agreement between the ΔC°_p values obtained for piperidine seems rather poor, but because of the small amount of data available, investigation of this difference does not appear useful at present.

The curves shown in Figure 3 were calculated using the parameters in Table 8 and equation (14), in conjunction with Steam Tables.[25]

The approach outlined here appears to be satisfactory up to *ca.* 250—300 °C. However, it is not always consistent with the requirement that all K_p values should approach unity at the critical temperature (374.15 °C). This suggests that the relationship between K_H and K_p given in equation (13) is an over-simplification. A more accurate form of this equation would require extensive studies on pressure–volume–temperature relationships in amine–water mixtures.

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