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Heats of Solution of Five Substituted Pyridines in 2*N* Hydrochloric Acid

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The heats of solution of five substituted pyridines have been determined in 2*N* HCl: 4-ethylpyridine, 2-picoline, 3-picoline, 4-picoline, and 2,6-lutidine. The values are discussed and compared with pK$_a$ values.

WE HAVE RECENTLY investigated the thermochemistry of some Group 3 halide pyridine and substituted pyridine complexes (*6*). The methods used involved the determination of the heats of hydrolysis of the complexes, together with the heats of solution of the pure ligands in 2*N* HCl.

Since previous work (*5*) has involved determination of the heats of solution of the ligands at very low acid concentration, we feel it desirable to report the present results, since these are useful in determination of the heats of formation for the type of complexes described above.

EXPERIMENTAL

The substituted pyridines were dried by refluxing over potassium hydroxide, fractionally distilled, and transferred to a vacuum line. They boiled at: 2-picoline 129.2° (760 mm.), 3-picoline 144.1° (760 mm.), 4-picoline 145.3° (760 mm.), 2,6-lutidine 143.4° (749 mm.), 4-ethylpyridine 167.8° (762 mm.). The pyridines were transferred to fragile glass bulbs, which were evacuated and sealed under vacuum. The calorimeter (*2*) was checked by measuring the heat of reaction of 0.1*N* hydrochloric acid with tri(hydroxymethyl)aminomethane: $-\Delta H$ = 7.06, 7.12, 7.16 (av. 7.11 ± 0.05) kcal. per mole at 25.0° C. (literature value 7.104) (*3*).

RESULTS AND DISCUSSION

The results are presented in Table I.

ΔH_s is the heat of solution and is given by

$$B_{(\text{liquid})} + \text{excess } 2N\text{ HCl} \xrightarrow{\Delta H_s} BH^+ \text{ (in } 2N\text{ HCl)} + Cl^- \text{ (in } 2N\text{ HCl)}$$

The weights (in grams) of the base are shown; the temperature rise, ΔT, is expressed in microvolts and the electrical calibration, C, is in terms of the thermochemical calorie (4.1840 joules) per microvolt.

Table II compares heats of solution ($-\Delta H_s$), heats of ionization ($-\Delta H_i$), and pK$_a$ values.

There is an over-all increase in $-\Delta H_s$ as the base strength, pK$_a$, increases. However, this comparison is misleading, since pK$_a$ concerns the ionization equilibria:

$$B_{(aq)} + H_3O^+ = BH^+_{(aq)} + H_2O \qquad (1)$$

Table I. Heats of Solution of Bases in Excess 2*N* HCl

Base	Wt. of Base in 100 Ml. 2*N* HCl, G.	ΔT, μv.	C, Cal./μv.	$-\Delta H_s$, Kcal./Mole
2-Picoline	0.2978	187.0	0.1735	10.17 ± 0.04
	0.3919	246.0	0.1737	
	0.2726	172.0	0.1739	
3-Picoline	0.3407	195.0	0.1737	9.27 ± 0.05
	0.2502	142.0	0.1744	
	0.1968	113.0	0.1743	
4-Picoline	0.2821	167.0	0.1738	9.64 ± 0.06
	0.2358	141.0	0.1738	
	0.1796	107.0	0.1745	
4-Ethylpyridine	0.4116	213.0	0.1718	9.57 ± 0.04
	0.3116	162.5	0.1717	
	0.2614	136.0	0.1720	
	0.3793	197.0	0.1716	
2,6-Lutidine	0.3049	196.0	0.1741	11.99 ± 0.02
	0.3904	251.0	0.1740	
	0.2173	139.0	0.1746	

The low heat of ionization of 2,6-lutidine compared with pyridine has been ascribed to the lower heat of hydration of the BH^+ species (*4*); in the 2,6-lutidine ion the two alpha-methyl groups prevent strong solvation of the $N{-}H^+$.

Our heats of solution may be considered to occur via the following steps:

$$B_{(liquid)} + aq. = B_{(aq)} \qquad (2)$$

$$B_{(aq)} + 2N\ HCl = BH^+ + Cl^- \text{ in } 2N\ HCl \qquad (3)$$

Table II. Heats of Solution, Ionization (*5*), and pK_a Values (*1*) of Bases

Base	pK_a	$-\Delta H_s$, Kcal./Mole	$-\Delta H_i$, Kcal./Mole
Pyridine	5.17	8.41	5.70
3-Picoline	5.68	9.27	6.70
2-Picoline	5.97	10.17	6.95
4-Picoline	6.02	9.64	7.03
4-Ethylpyridine	6.02	9.57	...
2,6-Lutidine	6.75	11.99	6.15

The heat evolved in Equation 1 differs from that evolved in Equation 3 mainly by the heat of dilution and it is likely that this will be similar for all of the bases in $2N$ HCl considered. The main difference then lies in the heat change in Equation 2—i.e., the heat of hydration of liquid base. This would be expected to be greater for 2,6-lutidine because of the larger inductive effect produced by the two methyl groups. This would explain the high value of the heat of solution of 2,6-lutidine.

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Precision Densities of Dilute Aqueous Solutions of the Isomeric Butanols

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The densities of aqueous solutions of the four isomeric butanols in the molal concentration range $0.003 < m < 0.2$ have been determined at 0.5°, 5°, 25°, and 40° C. by means of a magnetic float technique, capable of a precision of better than 1 p.p.m. The solute apparent molal volumes have been evaluated.

THE VOLUMETRIC properties of aqueous solutions of nonelectrolytes are of interest in the elucidation of solute-water interactions. In conjunction with other thermodynamic properties, they provide information about the phenomena of hydrophobic hydration and specific hydrogen bonding (*2*). These properties are affected both by the steric configurations of alkyl groups and the relative strengths of the solute-water hydrogen bonds. The water-butanol systems were therefore selected for study, since both these effects could be examined.

To obtain the limiting solute partial molal volumes $\bar{V}_2^0$, density data on dilute solutions must be available. As the concentration is reduced, the uncertainties in $\bar{V}_2$, corresponding to a given experimental error in the solution density, rapidly increase, so that at concentrations below $0.1m$, density errors must not exceed ±1 p.p.m.

EXPERIMENTAL

The magnetic float technique was selected as being capable of producing data of the required precision, and details of the apparatus and its method of operation have already been described elsewhere (*3, 11*). Briefly, a quartz float, containing a small bar magnet of 100 c.g.s. unit pole strength, was weighted with platinum loops until it just sank in the solution under test. Different currents, i, were then applied to a solenoid wound around the outside of the solution cell and the times, t, taken by the float to rise through a given distance were determined. From the t^{-1} (i) relationship, the extrapolated current i_0 could be evaluated for which the electrical forces balanced those due to buoyancy. Thus;

$$i_0 = \frac{(1 - d/D)\,w}{f} + \frac{W - dV}{f}$$

where d and D are the densities of the solution and platinum, respectively, W and w are the weights of the float and the platinum loops, V is the volume of the float, and f is the solenoid constant.

The cell was constructed in such a manner that progressive solute additions could be made without disturbing the float. The apparatus was immersed in a double thermostat, the temperature of which could be controlled to ±0.001°, this being essential for measurements at 25° and above. Absolute temperatures were determined to ±0.002° with National Physical Laboratory calibrated thermometers. Values of i were obtained by measuring the potential drop across a standard 2-ohm resistance. Since no sufficiently accurate data exist for nonelectrolytes, the