Phase Relationships in the Pyridine Series. Part V. The Thermodynamic Properties of Dilute Solutions of Pyridine Bases in Water at 25° and 40°.

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Some thermodynamic properties of very dilute aqueous solutions of methyl- and ethyl-pyridines and of pyridine itself (solutions containing *ca.* 4 × 10^{-5} mole-fraction of base) have been measured at 25° and 40° by a transpiration technique.

The logarithms of the activity coefficients of the pyridine base components, at a given temperature, have been found to be additive functions of the groups making up the base molecule, so that the activity coefficients of many higher *n*-alkylpyridines can be predicted from the experimental data here presented. The activity coefficients at infinite dilution for nine of the bases at their respective lower consolute temperatures are the same, and by utilizing this fact, together with the above additivity rule, it is demonstrated that the lower consolute temperatures of many higher *n*-alkylpyridines can be calculated. By an examination of the excess partial molar functions and "hydration" functions, it is shown that pyridine homologues containing α-methyl or α-ethyl groups appear to be more extensively hydrogen-bonded with water than their β- or γ-isomers. Finally, the heats of hydration and the entropies of hydration are compared with these functions for other organic solutes. It is concluded that the structures of the aqueous solutions of the pyridine bases at 25° are in no way exceptional and that the closed solubility loops which appear in this series are solely a result of the delicate balance between hydrophobic and hydrophilic groups in the base molecules.

Some measurements of the thermodynamic properties of very dilute solutions of certain pyridine bases in water at 70°, 85°, and 100° were reported in Part III (*Discuss. Faraday Soc.*, 1953, **15**, 168). The present paper gives the results of a similar study of the properties of very dilute aqueous solutions of pyridine, of all the methylpyridines, and of all the pyridine homogues of formula C_7H_9N at 25° and 40°. As explained previously (Part III, *loc. cit.*) it was considered that the investigation of these dilute solutions might yield results which could be interpreted in terms of base–water interactions and in this way information might be obtained on the general conditions necessary for the formation of closed-loop solubility curves.

The equilibrium-still technique described earlier (Part III, *loc. cit.*) did not prove satisfactory at 25° and 40° on account of the low total vapour pressure, so Butler and Shaw's transpiration method (*Proc. Roy. Soc.*, 1930, *A*, **129**, 519), with suitable modification, was employed instead. In every instance the solutions were so dilute (*i.e.*, of the order of 4 × 10^{-5} mole-fraction) that the measured values of the volatility ratio (α) are indistinguishable from the limiting values at infinite dilution. The volatility ratio is defined in the general case by the equation $\alpha = y_1(1 - x_1)/(1 - y_1)x_1$, where y_1 and x_1 are the mole-fractions of the base in the vapour and liquid respectively. In the present work, however, α may be set equal to y_1/x_1, because y_1 and x_1 are so small that the function $(1 - x_1)/(1 - y_1)$ is very nearly unity.

Experimental

Solutions.—The pyridine bases were drawn from the same sources as those employed in Part I (*J.*, 1952, 4601) and Part IV (*loc. cit.*). Stock base solutions were made up in carbon dioxide-free distilled water to contain *ca.* 4 × 10^{-5} mole-fraction of base.

Apparatus.—Fig. 1 shows the essential features of the apparatus. Dry, carbon dioxide-free,

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* Part IV, preceding paper.

nitrogen from a cylinder entered the apparatus at *A* and bubbled through a base solution in the saturator unit *B*, which consisted of three tubes inclined to the horizontal as in Butler and Shaw's design (*loc. cit.*); *B* was charged with a stock solution of base through the port *F*. The rate of flow of nitrogen could be accurately controlled by a two-stage reduction valve fitted with a needle valve, and the rate was measured by a flow-meter. The gas was preheated to the temperature of the solution in the saturator *B* by passage through a coil of lead tubing immersed in the thermostatically-controlled tank *E*. The gas stream, after leaving the saturator, passed through two bubblers in series, then out of the apparatus at *D*. A constriction with a spherically-ground seating *C*, into which fitted a stainless steel ball-bearing, was situated between the saturator and the bubblers; the ball could be lifted magnetically and transferred to a small side limb, when necessary. The lower parts of the bubblers, which contained 0·1N-sulphuric acid to absorb the bases, were attached by standard taper joints as shown. The whole unit was placed in tank *E*. The gas stream from *D* passed into an aspirator equipped with means for controlling the rate of outflow of water. This device consisted of a long steel rod which fitted, with a small clearance, into a length of capillary tube *G*; the rod could be raised or lowered by means of a screw thread. Experiments were carried out in the following manner. First, the saturator unit and the absorbers were charged with the appropriate solutions and, with the ball valve *C* closed, the apparatus was lowered into tank *E*, and left for 1 hr.; then the aspirator, which was filled with water, was connected to *D* by rubber tubing and, with ball-valve *C* now open, a slow stream of nitrogen was passed through the apparatus. The tap of the aspirator was opened, and the outflowing water was collected in a measuring cylinder; the position of the rod in capillary *G* was regulated so that the water level in the barometer tube *H* remained as close as possible to the level in the aspirator. At the end of an experiment, these two water levels were made to coincide and the nitrogen stream was stopped. Ball-valve *C* was shut, the transpiration unit was removed from the bath, and the contents of the bubblers were analyzed as described below. The volume of water removed from the aspirator (*V* l.) and the temperature of the water and of the gas in the aspirator were recorded. The barometric pressure (P_a, mm. Hg) was measured.

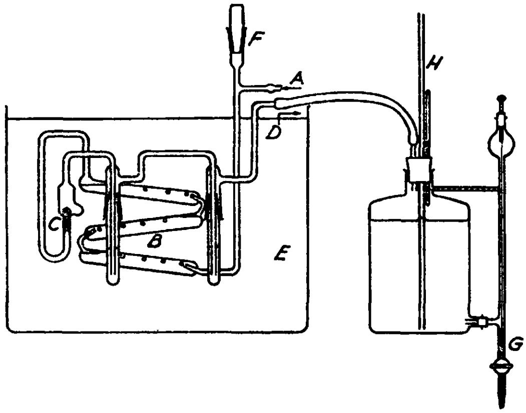


FIG. 1. *Transpiration apparatus.*

Analysis and Calculation.—The contents of the absorbers were transferred to volumetric flasks and made up to standard volumes with 0·1N-sulphuric acid. The resulting solutions were analyzed for their pyridine base content by ultra-violet spectroscopy. Aliquot portions of the original base solutions, after appropriate dilution with 0·1N-sulphuric acid, were analyzed in like manner. It should be noted that the amounts of base removed by transpiration never exceeded 0·5% of the amounts originally present in the stock solutions; it was therefore justifiable to consider the concentration of base in the saturator to be the same at the end of an experiment as at the beginning. Measurements of optical density were made by means of a Unicam SP 500 Spectrophotometer at five convenient wave-lengths (usually at $\lambda_{\max.}$, $\lambda_{\max.} - 4$, $\lambda_{\max.} - 2$, $\lambda_{\max.} + 2$, and $\lambda_{\max.} + 4$, mμ).

Now let the optical density of the original solution of the base, after having been diluted *l* times, be *m*, and let the optical density (at the same wave-length) of the solution prepared from the absorbing solutions be *n*. Suppose, further, that the vapour removed by transpiration from the base stock solution would have had a volume q ml. if it had been condensed and that the absorbing solution has been made up to r ml. Then $\alpha = nr/lmq$ and the only quantity on the right-hand side of this equation which is not immediately known is q; this may be calculated as follows.

Since in the present experiments the vapour always consisted predominantly of water (*i.e.*, the vapour contained more than 99·9% of water by weight) the condensed liquid from the vapour could be assumed to have the same density as water. This density was taken as unity for the present purposes. The volume, in c.c., of the vapour (corrected to that of a gas under 760 mm. pressure at 0° c) removed by transpiration is therefore $22{,}400q/18$ if it is assumed that the vapour behaves as an ideal gas. It can then be shown, by using Dalton's law, that:

$$q = [18 \times 273p_2V(P_a - p_3)]/[22{\cdot}4 \times 760T_1(P_a - p_2)]$$

where p_3 is the partial pressure of the water vapour within the aspirator and p_2 is the partial pressure of water vapour at the temperature of the saturator; T_1 is the temperature of the gas within the aspirator; V and P_a have been defined on p. 3189.

The effectiveness of the saturator was tested in a series of subsidiary experiments in which it was filled with distilled water while the absorbers were left empty. The gas stream after leaving D (Fig. 1) was led through a trap, cooled at −78°, which was placed between D and the aspirator; a glass connection between D and the trap was electrically heated to a little above the temperature of bath E to prevent condensation of vapour. A transpiration experiment was then carried out, and at the end of it, the condensate in the trap was transferred by high-vacuum distillation at room temperature into a trap, previously weighed; in this manner, the weight of water vapour removed by transpiration could be found directly and compared with the weight calculated from the equation given above. In two experiments in which the flow rate of nitrogen was 8 c.c./min., the ratios of found to calculated weight were 0·99 and 1·00, while in five experiments in which the rate of flow was 15 c.c./min., the ratios were 0·98, 1·00, 1·03, 1·04, 0·99. As a result of these experiments it was concluded that the gas stream became fully saturated with vapour when passed through B at 15 c.c./min., and this flow rate was adopted in all experiments with base solutions; in these latter experiments the quantity q was of course calculated from the equation given. One final preliminary experiment was carried out to check the effectiveness of the two absorbers. It was found that 96% of the base transpired was collected in the first absorber and the remaining 4% in the second, *i.e.*, no base could be detected in a third absorber.

Results.—The measured values of α for the dilute pyridine base solutions studied are recorded in Table 1; each value is the mean from at least three experiments. Also shown are the corresponding values of the activity coefficients of the base components, γ_1, calculated by the relation $\gamma_1 = Py_1/p_1x_1$, where P is the total vapour pressure of the base–water mixture and p_1 is the vapour pressure of the pure base, *i.e.*, the activity coefficients were calculated with reference to the pure liquid bases (at the same temperature) as the standard state. With very dilute solutions, P is indistinguishable from the vapour pressure of water at the temperature being studied, p_2, and since $\alpha = y_1/x_1$ (see above), we may write $\gamma_1 = \alpha p_2/p_1$. Values of p_2 were taken from the tables of Osborne and Meyers (*J. Res. Nat. Bur. Stand.*, 1934, **13**, 1), and wherever possible values of p_1 were calculated by use of the constants of the Antoine equations given by Herington and Martin (*Trans. Faraday Soc.*, 1953, **49**, 154). A direct comparison of calculated and observed values for the vapour pressures of certain of the bases near 25° could be made by use of the experimental measurements by Brown and Barbaras (*J. Amer. Chem. Soc.*, 1947, **69**, 1137). The relevant values are as follows: at 20°, pyridine 15·82 mm. (obs.) and 15·74 mm. (calc.), 3-methylpyridine 4·46 mm. (obs.) and 4·36 mm. (calc.), and 4-methylpyridine 4·29 mm. (obs.) and 4·15 mm. (calc.); at 20·3°, 2-methylpyridine, 8·55 mm. (obs.) and 8·49 mm. (calc.). The vapour pressures of the seven bases used in this work for which no vapour-pressure data exist, other than the normal b. p.s, were calculated by an empirical method. Use was made of Herington and Martin's observation (*loc. cit.*) that when the values of Antoine's constant B for six bases are plotted against the normal b. p.s a smooth curve is obtained. Hence by interpolation, or extrapolation, it was possible to deduce the Antoine constants B of the seven bases whose vapour pressures were required, since their normal b. p.s were known (Eguchi, *Bull. Chem. Soc. Japan*, 1928, **3**, 227; and Part IV, preceding paper). Examination of the published values showed that the Antoine constant C is close to 210 for the three monomethylpyridines and close to 208 for the two dimethylpyridines studied by Herington and Martin, so it was assumed that $C = 208$ for the seven bases in question. The Antoine constants A of these seven bases were then found by setting t in the Antoine equation equal to the b. p. (in °c) at 760 mm. Finally, the constants A, B, and C were used to calculate the vapour pressures, p_1, at 25° and 40° shown in Table 1. The validity of this procedure was tested by comparing the known vapour pressures of two bases with the calculated values, as follows : 2 : 3-dimethylpyridine at 81·2°, 55·8 mm. (obs.), 53·4 mm. (calc.); 3 : 4-dimethylpyridine at 111·0°, 98·3 mm. (obs.), 95·8 mm. (calc.).

TABLE 1. *Volatility ratios, α, and activity coefficients, γ_1, of the pyridine-base components of very dilute aqueous base solutions.*

	t (c)	α	σ_α *	p_1, mm.	γ_1	$\sigma_{\gamma,1}$ †	ln γ_1
Pyridine	25°	15·70	0·20	20·81	17·9	0·2	2·884
	40	17·29	0·08	45·10	21·2	0·1	3·054
2-Methylpyridine	25	17·65	0·10	11·22	37·4	0·2	3·622
	40	21·13	0·14	25·49	45·9	0·3	3·827
3-Methylpyridine	25	13·83	0·05	5·96	55·1	0·2	4·009
	40	16·52	0·11	14·15	64·6	0·4	4·168
4-Methylpyridine	25	10·54	0·15	5·68	44·1	0·6	3·787
	40	12·97	0·10	13·52	53·1	0·4	3·972
2-Ethylpyridine	25	29·21	0·15	4·69	147·9	0·8	4·997
	40	37·00	0·14	11·43	179·1	0·7	5·188
3-Ethylpyridine	25	18·43	0·13	2·19	199·9	1·4	5·298
	40	22·32	0·20	5·60	220·4	2·0	5·396
4-Ethylpyridine	25	14·72	0·17	2·22	157·5	1·8	5·060
	40	17·38	0·14	5·67	169·6	1·4	5·134
2 : 3-Dimethylpyridine	25	12·71	0·17	2·75	109·8	1·5	4·699
	40	16·77	0·07	6·92	134·1	0·6	4·899
2 : 4-Dimethylpyridine	25	11·90	0·13	3·12	90·6	1·0	4·507
	40	16·01	0·15	7·79	113·7	1·1	4·734
2 : 5-Dimethylpyridine	25	15·23	0·11	3·25	111·3	0·8	4·712
	40	20·47	0·14	8·10	139·8	1·0	4·940
2 : 6-Dimethylpyridine	25	18·57	0·14	5·58	79·0	0·6	4·370
	40	25·90	0·13	13·44	106·6	0·5	4·669
3 : 4-Dimethylpyridine	25	6·50	0·03	1·23	125·5	0·6	4·832
	40	8·40	0·03	3·18	146·1	0·5	4·984
3 : 5-Dimethylpyridine	25	12·34	0·08	1·69	173·4	1·1	5·156
	40	15·82	0·11	4·41	198·4	1·4	5·290

* Standard deviations of the mean values of α.

† Standard deviations of the mean values of γ_1 calculated from col. 4. These values of $\sigma_{\gamma,1}$ do not of course take into account possible errors in the estimation of the vapour pressures of the bases.

DISCUSSION

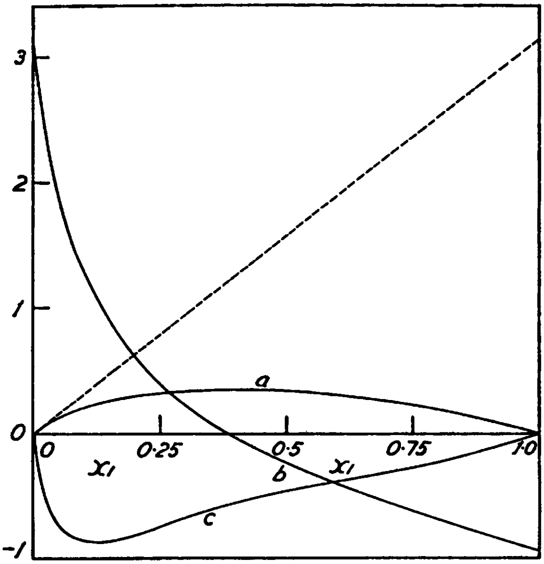
Table 1 shows that the volatility ratios, α, for all the bases in dilute aqueous solution at 25° and 40° are considerably greater than unity. Since pyridine and 2-, 3-, and 4-methylpyridine are miscible with water in all proportions (Part I, *J.*, 1952, 4601), and since the vapour pressures of the pure bases at a given temperature are less than the vapour pressure of water at that temperature, it follows from the data of Table 1 that the base–water binary systems containing these four bases must all exhibit homogeneous minimum boiling azeotropes at 25° and 40°.

As explained above, the values of ln γ_1 (component 1 being the base) listed in Table 1 refer to very dilute solutions, so that the values will be numerically indistinguishable from those for the infinitely dilute solution. Inspection of Table 1 reveals that the values of ln γ_1 at any temperature are additive functions of the groups within the pyridine base molecule, provided that due regard is paid to the positions of the substituents with respect to the nitrogen atom of the pyridine ring. For example, by combining the results for pyridine with those for the three methylpyridines at 25° it is found that the contributions of the α-, β-, and γ-methyl groups to ln γ_1 are 0·74, 1·12, and 0·90, respectively. By using these figures together with the value of ln γ_1 for pyridine itself it is possible, by assuming additivity, to compute the values of ln γ_1 for all the dimethylpyridines at 25°. Thus the following values were obtained: 2 : 6-dimethylpyridine 4·36; 2 : 3- or 2 : 5-dimethylpyridine 4·74; 2 : 4-dimethylpyridine 4·52; 3 : 5-dimethylpyridine 5·12; 3 : 4-dimethylpyridine 4·90. A very satisfactory measure of agreement is found between these figures and the experimental results for 2 : 6-, 2 : 3- or 2 : 5-, 2 : 4-, 3 : 5-, and 3 : 4-dimethylpyridine, respectively (Table 1). Analysis of the experimental results for 40° (Table 1) and for pyridine, 2-, 3-, and 4-methylpyridine, and 2 : 5- and 2 : 6-dimethylpyridine in the temperature range 70—100° (Part III, *loc. cit.*) shows that they also obey this additivity rule. There is approximately a constant difference, equal to 1·31 units, between the ln γ_1 values for the ethyl and methyl homologues at 25° (the actual differences are 1·38 units for the α-, 1·29 units for the β-, and 1·27 units for the γ-position) and an average difference of 1·25 units between the same quantities at 40°.

The discovery that ln γ_1 is an additive function enables the values of this quantity for higher *n*-alkylpyridine homologues (*e.g.*, the trimethylpyridines and ethylmethylpyridines) to be calculated, and this also allows an estimate to be made of the solubility properties of these bases.

When the values of ln γ_1 for the 2 : 5- and 2 : 6-dimethylpyridines reported in Table 1 and the values recorded in Table 1 of Part III (*loc. cit.*) were plotted against temperature, it was found that the values of ln γ_1 at the respective lower critical solution temperatures (Part IV, preceding paper) were 4·48 and 4·56, respectively; this treatment was next applied to the results at 25° and at 40° for 2 : 3- and 2 : 4-dimethylpyridine on the assumption that the curves had the same general shapes as those of the 2 : 5- and 2 : 6-isomers. Values of ln γ_1 equal to 4·54 and 4·49 at the lower critical solution temperatures were then obtained for 2 : 3- and 2 : 4-dimethylpyridine respectively. This procedure was also applied to the results for the five other relevant systems listed in Table 1. Here, however, the extrapolations were rather long and in consequence the estimated values of ln γ_1 at the lower critical solution temperatures were less reliable. Nevertheless, the graphs show that these values of ln γ_1 must lie between 4·35 and 4·65. Hence it follows that at the lower consolute temperatures of the nine partially miscible base–water mixtures studied, the values of ln γ_1 are all close to 4·5, *i.e.*, γ_1 is close to 90. If now the very reasonable assumption is made that this relation holds for binary mixtures of higher *n*-alkyl homologues of pyridine with water, it is possible to estimate the lower consolute temperatures by using the data presented in Table 1. Consider for instance 2 : 4 : 6-trimethylpyridine : the values of ln γ_1 over a range of temperatures may readily be calculated

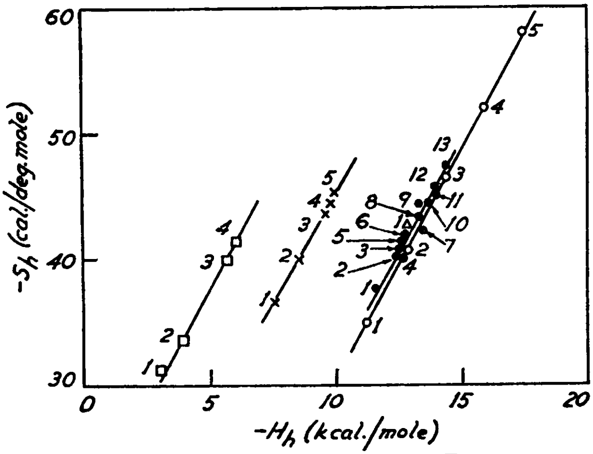
FIG. 2.



Curve *a* is the plot of G^E/RT against x_1.
Curve *b* is the plot of $[\partial(G^E/RT)/\partial x_1]_T$ against x_1.
Curve *c* is the plot of $x_1(1 - x_1)[\partial^2(G^E/RT)/\partial x_1^2]_T$ against x_1.

by the additivity rule given above. Extrapolation of the plot of ln γ_1 against temperature to ln $\gamma_1 = 4{\cdot}5$ then shows that the lower consolute temperature of this base with water should be at $+2° \pm 3°$, which is in agreement with Rothmund's measurement, *i.e.*, $+6{\cdot}4°$ (*Z. physikal. Chem.*, 1898, **26**, 433); recent experiments in this laboratory with an authentic sample of 2 : 4 : 6-trimethylpyridine have confirmed Rothmund's result. There is probably very little steric hindrance between the alkyl groups and the nitrogen atom, or between the alkyl groups themselves, in the compounds studied in the present work, because these alkyl groups contained at the most two carbon atoms. If, however, aqueous solutions of pyridine homologues with very bulky substituents (*e.g.*, 2 : 6-di-*tert.*-butylpyridine; cf. Brown and Kanner, *J. Amer. Chem. Soc.*, 1953, **75**, 3865) were studied it is probable that effects due to steric hindrance would appear. Predictions of solubility in such cases should obviously be made with caution.

FIG. 3.



□ 1, Methane. 2, Ethane. 3, Propane. 4, *n*-Butane.
(Calc. from the measurements of Claussen and Polglase, *J. Amer. Chem. Soc.*, 1952, **74**, 4817.)

× 1, Benzene. 2, Toluene. 3, *p*-Xylene. 4, Ethylbenzene. 5, *m*-Xylene.
(Calc. from the measurements of Bohon and Claussen, *ibid.*, 1951, **73**, 1571).

● 1, Pyridine. 2, 4-Ethylpyridine. 3, 3-Methylpyridine.
4, 4-Methylpyridine. 5, 2-Methylpyridine. 6, 3-Ethylpyridine.
7, 3 : 4-Dimethylpyridine. 8, 3 : 5-Dimethylpyridine. 9, 2-Ethylpyridine.
10, 2 : 3-Dimethylpyridine. 11, 2 : 4-Dimethylpyridine. 12, 2 : 5-Dimethylpyridine.
13, 2 : 6-Dimethylpyridine.

○ 1, Methanol. 2, Ethanol. 3, *n*-Propanol. 4, *n*-Butanol. 5, *n*-Pentanol.
(Butler, *Trans. Faraday Soc.*, 1937, **33**, 229.)

△ 1, Ethylamine (*idem, loc. cit.*)

Further implications of the finding that ln γ_1 equals 4·5 for all the bases at their lower consolute temperatures will now be considered. In Fig. 2, curve *a* is a plot for an imaginary system of $G^E/\boldsymbol{R}T$ against x, where G^E is the molar excess free energy of mixing. It follows from the properties of partial molar quantities that the tangent to this curve at $x_1 = 0$ cuts the ordinate $x_1 = 1$ at the point ln γ_∞. (As explained above, the values of γ_1 reported in the present paper will be indistinguishable from values at infinite dilution, *i.e.*, γ_∞.) Curve *b* is a plot of $[\partial(G^E/\boldsymbol{R}T)/\partial x_1]_T$ against x_1, and curve *c* is the plot of the function $x_1(1 - x_1)[\partial(^2G^E/\boldsymbol{R}T)/\partial x_1{}^2]_T$ against x_1. Since for any binary system $[\partial(G^E/\boldsymbol{R}T)\partial x_1]_T$ is equal to ln (γ_1/γ_2), it follows that curve *b* is also a plot of ln (γ_1/γ_2) against x_1, and curve *c* is also a plot of $x_1(1 - x_1)[\partial(\ln \gamma_1/\gamma_2)/\partial x_1]_T$ against x_1. Now it can be shown that at a consolute temperature, either upper or lower, the function $x_1(1 - x_1)[\partial^2(G^E/\boldsymbol{R}T)/\partial x_1{}^2]_T$ equals -1 (see, *e.g.*, Prigogine and Defay, " Thermodynamique chimique," Desoer, Liége, 1950), *i.e.*, the consolute temperature is the temperature at which the minimum of curve *c* lies at -1. Reference to Part IV (preceding paper) will show that the lower consolute compositions, expressed as the mole-fraction of base, of the partially miscible pyridine base–water mixtures studied, lie between 0·06 and 0·08. The *c* curves of all these systems at their consolute temperatures must therefore have minima at $x_1 \simeq 0{\cdot}07$; moreover, because of the functional relationship between the *c* and *b* curves it follows that the *b* curves must all have identical slopes at $x_1 \simeq 0{\cdot}07$.

Further, the limiting value of $\ln (\gamma_1/\gamma_2)$ as x_1 approaches zero (*i.e.*, $\ln \gamma_\infty$) is approximately 4·5 for each of the nine systems at their lower consolute temperatures, so it is almost certain that the *b* curves of these systems at their lower consolute temperatures will prove to be identical over the composition range $x_1 = 0$ to $x_1 = 0{\cdot}07$. Also, because $G^{\mathrm{E}}/\boldsymbol{R}T$ equals $\int_0^{x_1} \ln (\gamma_1/\gamma_2) \, . \, \mathrm{d}x_1$, it is very probable that the curves of $G^{\mathrm{E}}/\boldsymbol{R}T$ plotted against x_1 for these systems at their lower consolute temperatures are identical over the same composition range.

Since for the systems studied here, $\gamma_\infty = 90$ and $x_1 = 0{\cdot}07$ at the lower consolute point it follows that the relation between G^{E} and x_1 is not given by an equation of the form $G^{\mathrm{E}} = k_T x_1 (1 - x_1)$ because this equation requires that γ_∞ should equal 7·4 and x_1 should equal 0·50 at the consolute point (see Copp and Everett, *Discuss. Faraday Soc.*, 1953, **15**, 174, 268, for a discussion of this equation).

The results at 25° show that each additional methylene group increases the value of the activity coefficient of the base in dilute solution approximately 2·5-fold, as had previously been found for measurements made in the temperature range 70—100° (Part III, *loc. cit.*). In Part III it was remarked that the finer differences in the values of γ_∞ for isomers could be correlated with the basic dissociation constants of the pyridine homologues. If consideration of the α-homologues be excluded because of the possibility of an *ortho*-proximity effect (cf. Part IV, *loc. cit.*) then this correlation also exists at 25° in the sense that 3-methyl-, 3-ethyl-, and 3 : 5-dimethyl-pyridine have larger values of γ_∞ than, respectively, 4-methyl-, 4-ethyl-, and 3 : 4-dimethyl-pyridine. Unpublished results from this laboratory show that the dissociation constants can be arranged in the following order: 3-methyl- < 4-methyl-; 3-ethyl- < 4-ethyl-; 3 : 5-dimethyl- < 3 : 4-dimethyl-pyridine.

Two sets of thermodynamic functions were calculated from the results given in Table 1, namely, the excess partial molar functions and the "hydration" functions (Butler, "Chemical Thermodynamics," Macmillan, London, 1946, p. 389). The limiting values of the partial molar excess free energies of the base compounds ($\bar{G}^{\mathrm{E}}_{\infty}$) were calculated by means of the equation $\bar{G}^{\mathrm{E}}_{\infty} = \boldsymbol{R}T \ln \gamma_\infty$ (note that γ_∞ equals γ_1 in the present experiments) and the corresponding partial molar excess entropies ($\bar{S}^{\mathrm{E}}_{\infty}$) and partial molar heats of mixing ($\bar{H}^{\mathrm{M}}_{\infty}$) were calculated in the usual way from the equations $-\bar{S}^{\mathrm{E}}_{\infty} = (\partial \bar{G}^{\mathrm{E}}_{\infty}/\partial T)_p$ and $\bar{H}^{\mathrm{M}}_{\infty} = \bar{G}^{\mathrm{E}}_{\infty} - T(\partial \bar{G}^{\mathrm{E}}_{\infty}/\partial T)_p$.

The free energy of hydration (G_h) was calculated from the expression $G_h = \boldsymbol{R}T \ln \alpha p_2$. This free energy is the difference between the partial molar free energies of the base in two standard states. The initial state is that of a gas at 1 atm. pressure at the prevailing temperature, and the final state is a hypothetical one in which the mole-fraction of the base is unity but where certain thermodynamic properties are those of an infinitely dilute solution. The entropies (S_h) and enthalpies (H_h) of hydration were calculated by the usual equations $-S_h = (\partial G_h/\partial T)_p$ and $H_h = G_h - T(\partial G_h/\partial T)_p$.

In the evaluation of the expressions $(\partial \bar{G}^{\mathrm{E}}_{\infty}/\partial T)_p$ and $(\partial G_h/\partial T)_p$ it was assumed that $\bar{G}^{\mathrm{E}}_{\infty}$ and G_h both varied linearly with T over the temperature range 25—40°. Similar assumptions have invariably been made by other workers but it follows from the existence of closed solubility loops in the systems studied here that $\bar{S}^{\mathrm{E}}_{\infty}$ (and hence S_h) must vary with temperature; $\bar{G}^{\mathrm{E}}_{\infty}$ and G_h cannot, therefore, be true linear functions of T. Nevertheless, very little error in the estimations of $\bar{S}^{\mathrm{E}}_{\infty}$, S_h, $\bar{H}^{\mathrm{M}}_{\infty}$, and H_h will arise by assuming for the present systems that the plots of $\bar{G}^{\mathrm{E}}_{\infty}$ (or G_h) against T are linear over a range as short as

15°. The values of the functions so found are listed in Table 2. The only previously published value for any of the data of Table 2 is a calorimetric value of $\bar{H}^{M}_{\infty}$ (−2·27 kcal./mole) for pyridine (Baud, *Bull. Soc. chim.*, 1909, **5**, 1022), which may be compared with the value −2·0 kcal./mole reported in the Table.

TABLE 2. *Thermodynamic functions for some very dilute aqueous solutions, at 25°.*

Solute	$\bar{G}^{E}_{\infty}$ (kcal./mole)	$-\bar{S}^{E}_{\infty}$ (cal./deg. mole)	$-\bar{H}^{M}_{\infty}$ (kcal./mole)	G_h (kcal./mole)	$-S_h$ (cal./deg. mole)	$-H_h$ (kcal./mole)
Pyridine	1·709 ± 0·008 *	12·4 ± 0·5 *	2·00 ± 0·17 *	−0·423 †	37·6 †	11·65 †
2-Methylpyridine	2·145 ± 0·004	15·3 ± 0·4	2·42 ± 0·11	−0·355	41·2	12·64
3-Methylpyridine	2·374 ± 0·003	14·2 ± 0·3	1·87 ± 0·10	−0·498	40·6	12·60
4-Methylpyridine	2·243 ± 0·008	14·9 ± 0·6	2·19 ± 0·19	−0·659	40·8	12·82
2-Ethylpyridine	2·960 ± 0·003	17·5 ± 0·2	2·26 ± 0·06	−0·057	44·4	13·31
3-Ethylpyridine	3·138 ± 0·004	14·4 ± 0·5	1·15 ± 0·13	−0·328	41·8	12·78
4-Ethylpyridine	2·997 ± 0·007	13·0 ± 0·6	0·86 ± 0·17	−0·462	40·3	12·48
2 : 3-Dimethylpyridine...	2·783 ± 0·008	17·2 ± 0·5	2·35 ± 0·16	−0·549	44·4	13·79
2 : 4-Dimethylpyridine...	2·669 ± 0·007	17·9 ± 0·6	2·67 ± 0·17	−0·587	45·0	14·02
2 : 5-Dimethylpyridine...	2·791 ± 0·004	18·4 ± 0·4	2·68 ± 0·12	−0·441	45·5	14·00
2 : 6-Dimethylpyridine...	2·588 ± 0·005	20·5 ± 0·4	3·53 ± 0·11	−0·325	47·3	14·44
3 : 4-Dimethylpyridine...	2·862 ± 0·003	15·6 ± 0·2	1·78 ± 0·07	−0·945	42·2	13·54
3 : 5-Dimethylpyridine...	3·054 ± 0·004	15·6 ± 0·4	1·59 ± 0·11	−0·566	43·2	13·45
Benzene ‡	4·616	13·5	−0·59	3·385	36·7	7·56
Toluene ‡	5·337	15·9	−0·60	3·391	40·1	8·55
Ethylbenzene ‡	6·071	19·1	−0·38	3·476	44·6	9·83
m-Xylene ‡	6·112	19·2	−0·40	3·436	44·8	9·92
p-Xylene ‡	6·100	19·0	−0·45	3·456	44·4	9·79

* These standard errors were calculated from the standard errors given in Table 1.

† The standard errors attaching to G_h, $-S_h$, and $-H_h$ are respectively the same as those attaching to $\bar{G}^{E}_{\infty}$, $-\bar{S}^{E}_{\infty}$, and $-\bar{H}^{M}_{\infty}$ for the same solute.

‡ The thermodynamic functions for the aromatic hydrocarbons were calculated from Bohon and Claussen's measurements (*J. Amer. Chem. Soc.*, 1951, **73**, 1571) with the aid of vapour-pressure data calculated from Table 5k of A.P.I.–N.B.S. Project 44.

Inspection of the listed values of $\bar{S}^{E}_{\infty}$ and $\bar{H}^{M}_{\infty}$ for the pyridine series shows that these values are all negative and numerically large. Now the temperature to which these values refer, 25°, is fairly close to the lower consolute points of the dimethylpyridine and ethylpyridine systems with water. It is not surprising therefore that $\bar{S}^{E}_{\infty} < 0$ and $\bar{H}^{M}_{\infty} < 0$ since theory shows that it is necessary that $S^{E} < 0$ and $H^{M} \leqslant 0$ provided the plots of G^{E}, S^{E}, and H^{M} against x_1 maintain the same sign for all values of x_1 (see, *e.g.*, Copp and Everett, *loc. cit.*).

Comparison of the values of $\bar{H}^{M}_{\infty}$ at 25° with similar values at 85° (Part III, *loc. cit.*) shows that in every instance the values change with temperature by 2—3 kcal./mole in the direction indicating a large positive value for $\bar{C}^{E}_{p\infty}$. This is the expected behaviour for systems having closed solubility loops (Copp and Everett, *loc. cit.*).

The data in Table 2 indicate that an alkyl group in the α-position of the pyridine nucleus gives rise to much larger values of $-\bar{S}^{E}_{\infty}$ and $-\bar{H}^{M}_{\infty}$ than does the same group in the β- or γ-positions. Now it is known that the physical properties of the α-alkylpyridines are often very different from those of the isomers containing β- or γ-groups (*e.g.*, the b. p.s of α-, β-, and γ-methylpyridines are respectively 129°, 144°, and 145°), so it might be thought that the " α-effect " apparent in the $-\bar{S}^{E}_{\infty}$ and $-\bar{H}^{M}_{\infty}$ values noted above might be due to the choice of the pure liquid as the standard state. However, an examination of the $-S_h$ and $-H_h$ values of Table 2 shows that the " α-effect " persists even when the vapour at 1 atm. pressure is taken as the standard state. The " α-effect " in the $-S_h$ and $-H_h$ values is not very striking for the monomethylpyridines but can be seen readily in the results for the ethylpyridines and dimethylpyridines. The conclusion would therefore seem to be that the pyridine homologues containing α-methyl or α-ethyl groups are more extensively hydrogen-bonded to water at 25° than their β- or γ-isomers, since large negative excess entropies and negative heats of mixing are well known to result from hydrogen-bonding.

Finally, the properties of dilute aqueous solutions of the pyridine bases are compared with those of dilute aqueous solutions of other organic compounds, and for this purpose it is convenient to consider the values of $-S_h$ and of $-H_h$. A comparison of the properties of dilute solutions of the aromatic hydrocarbons with those of the pyridine bases is particularly instructive because the benzene series bears such a close structural relationship to the pyridine series. Appropriate values for the aromatic hydrocarbons have been calculated from the measurements of Bohon and Claussen (*J. Amer. Chem. Soc.*, 1951, **73**, 1571) and are set out in Table 2, which shows that, although the $-S_h$ values of analogues in the two series (*e.g.*, pyridine compared with benzene; methylpyridines compared with toluene) are closely similar, yet there is a striking difference in the $-H_h$ values. This marked difference arises chiefly from the fact that the pyridines dissolve in water at 25° with a considerable evolution of heat, owing to formation of hydrogen bonds, whereas the aromatic hydrocarbons dissolve in water at 25° with absorption of heat. Other workers have also observed that molecules of approximately the same size have closely similar values of S_h but may have very different values of H_h; thus Butler and Reid (*J.*, 1936, 1171) found such a relation for ethane, methyl chloride, and methyl alcohol. Butler (*op. cit.*, p. 396) has also drawn attention to the fact that $-S_h$ bears an approximately linear relation to $-H_h$ for solutions of the permanent gases in water and for solutions of the alcohols in water. Examination of the present measurements on the pyridine series shows that the same relation holds, as can be seen from Fig. 3, where $-S_h$ is plotted against $-H_h$ for a number of compounds at 25°. A feature of this diagram which does not seem to have been emphasized before is that it is made up of parallel lines of slope 0·0034 and that each homologous series occupies a separate line. The origin of this behaviour becomes evident if the equation is written as $-S_h = -H_h/T + G_h/T$. Now it happens that in the ascent of all the homologous series which have been studied at 25°, G_h changes very slowly (*ca.* 0·1 kcal. per methylene group) whereas $-H_h$ increases rapidly (*ca.* 1·5 kcal. per methylene group), and therefore to a first approximation G_h/T may be considered as a constant for a given T, so that $-S_h$ varies linearly with $-H_h$, the gradient of the line being equal to $1/T$, *i.e.*, 0·0034 when T equals 298° K.

The plot of $-S_h$ against $-H_h$ for aqueous solutions at 25° is thus made up of a series of parallel straight lines disposed in such a manner that the lines for solutes which are most hydrogen-bonded lie furthest to the right. It may be noted that the line for the pyridine bases at 25° is nearly coincident with that for the aliphatic alcohols; a single point for ethylamine also lies close to the line for the pyridine series. These measurements indicate, therefore, that the structures of aqueous solutions of the pyridines are not in any way exceptional, and it would appear that the reason why these bases form closed solubility loops while the alcohols do not, is to be found in the delicate balance between the hydrophobic and hydrophilic groups within the molecules of the pyridine bases. The result is that any small change in the system, such as that produced by altering the temperature, is sufficient to change markedly the solubility of these bases (cf. Part IV, and Copp and Everett, *locc. cit.*).

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