Table I. Density Equations for Organic Melts

Salt	Melting Point (° C.)	$\rho = \alpha - \beta t$ α (g./cc.)	 $\beta \times 10^4$ (g./cc./° C.)	Std. Dev. $\times 10^3$ (G./Cc.)	Temperature Range (° C.)
Tributylbenzylphosphonium chloride	162–163	1.021	5.48	0.2	178–240
Tributyl-2:4-dichlorobenzylphosphonium chloride	117–118	1.165	6.90	1.1	155–221
Tetra-*n*-butylammonium bromide	109–110	1.086	6.87	0.7	123–146
Tetra-*n*-butylammonium iodide	143–144	1.187	6.60	0.2	149–169
Tetra-*n*-hexylammonium iodide	103.5–104.5	1.093	7.30	0.6	122–150

The phosphonium chlorides were the most stable, their percentage weight loss being $<1\%$ after 20 hr., while the alkylammonium halides began to lose weight after about 8 hr. The vapor pressures of the molten salts and the absence of a stationary atmosphere above the melts can explain the weight losses.

(c) Melting points of samples of the salts after prolonged melting, but prior to slight decomposition, agreed well with those of the pure salts.

(d) Infrared spectra of the phosphonium chlorides and tetra-*n*-butylammonium iodide before and after prolonged melting showed little evidence of subsequent decomposition.

RESULTS

The density data were fitted to the equation $\rho = \alpha - \beta t$ by the method of least squares. In this equation, ρ is the density, α and β are constants and t is the temperature in ° C. The results are given in Table I which lists the melting point of the pure component, α and β in the density equation, the standard deviation from the least squares fit, and the experimental range in ° C. Densities were determined at approximately 5° intervals.

The experimental temperature range was often limited in the case of the alkylammonium salts since they usually had low boiling points, whereupon data points were taken at more frequent intervals.

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Basicities of Alkylamines and Substituted Pyridines in Fifty Volume–Per Cent Dioxane–Water

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Acid dissociation constants for the protonated species of certain alkylamines and substituted pyridines in 50 volume–per cent dioxane–water are reported and trends within a series of similar compounds are discussed. Differences in the basicities of the aminopyridines are attributed to electromeric effects. The constants determined for these compounds in aqueous solution are included for comparative purposes.

MEASUREMENTS of the dissociation constants for the conjugate acids of many organic bases have been made in order to study their coordination tendencies with metal ions, using both aqueous and nonaqueous media as solvents. Of special interest as a solvent system is 50 volume–per cent dioxane–water, which is being used extensively for compounds that are somewhat insoluble in water. Since the properties of this mixed solvent differ from those of water, the basicities of water-soluble organic bases which have not been studied in this system were determined.

In this investigation apparent pK values for a series of alkylamines and substituted pyridines in 50 volume–per cent dioxane–water are reported and discussed. The values obtained in aqueous solution are included for comparative purposes, Table I.

EXPERIMENTAL

The aminopyridines, pyridine-aldoximes and 2-pyridylcarbinol were obtained from Aldrich Chemical Co., Milwaukee, Wis. The alkylamines and pyridine were purchased from Eastman Organic Chemicals. 1-(2-Pyridyl)-urea was prepared according to the method of Gerchuks and Taits (*11*) and 1-(2-pyridyl)thiourea according to the method outlined by Fairfull and Peak, (*9*). All the compounds were purified immediately before use and the purity established by conformity to melting points or boiling points reported in the literature.

The acid dissociation constants were determined by the Calvin-Bjerrum method of potentiometric titration, (*3, 6*). A glass electrode was used since it is not subject to great error in mixed solvents in which the proportion of water is relatively large, (*8, 13*). Those compounds for which p*K* values in aqueous medium are available were studied only in 50 volume-per cent dioxane-water. All other compounds were studied both in aqueous solution and in dioxane-water. The titration apparatus and procedure are essentially the same as described by Freiser *et al.*, (*10*). Fifty ml. of dioxane and 50 ml. of o.01*N* perchloric acid were added to a weighed quantity of the compound studied. Measurements in water solution were obtained by adding 50 ml. of 0.32*M* $NaNO_3$ to a solution containing the organic base in 50ml. of 0.01*N* nitric acid. In all titrations the amount of organic base used was approximately 0.4mole. The standard base (0.1*N* NaOH) was added in small increments to the stirred solution.

For measuring the p*H*, a Radiometer p*H* meter 4 (Copenhagen), standardized with specially provided phosphate buffer solution (p*H* = 6.48 ± 0.02 at 25° C., corresponding to the American, British and French standards), was used. This allowed the p*H* to be read directly to two decimal places and estimated to the third, thus minimizing errors arising from inaccuracies in p*H* readings. A value of 0.10, 0.07, 0.04 and 0.01 was added (*18*) to all p*H* readings taken in 50 volume-per cent dioxane-water solutions at 35°, 25°, 15° and 0°, respectively, in order to convert p*H* meter readings to hydrogen ion concentrations. All volumes of the dioxane-water solutions were multiplied by 0.98 to correct for the partial molal volume of dioxane in water.

RESULTS AND DISCUSSION

The basicities of the ligands obtained in this study are reported in Table I. The values obtained by previous workers in aqueous media are also included in the table with appropriate references. The p*K* values are the negative logarithms of the dissociation constants obtained from the equations:

$$K_1 = \frac{[R][H^+]}{[RH^+]} \text{ and } K_2 = \frac{[RH^+][H^+]}{[RH_2^{++}]}$$

where $[R]$, $[RH^+]$, $[RH_2^{++}]$ and $[H^+]$ represent the concentration of the free ligand, the monoprotonated ligand, the diprotonated ligand and the free proton, respectively. Since activity coefficients were not determined, the values obtained are properly termed "apparent p*K* values."

The acid dissociation constant of protonated methylamine in 50 volume-per cent 1-4 dioxane at 25° C. is 10.25, Table I. This is about 0.5 p*K* unit lower than the value reported for the same compound in water. The p*K* values of 10.23, 9.83 and 9.82, Table I, for ethylamine, propylamine and butylamine, respectively, indicate that the replacement of these alkyl groups for the methyl does not increase the basicity of the nitrogen atom in these compounds. This is consistent with the results obtained by previous workers who studied the dissociation constants of these compounds in water, Table I. The lowering in p*K* value for propylamine and butylamine may be due to the blocking effect of the longer alkyl chains on the approach of solvated protons to the nitrogen atom. A similar decrease in basicity has been observed by Britton *et al.*, (*4*) in passing from dimethylamine to trimethylamine.

Pyridine has a p*K* value of 5.45 at 25° and 5.35 at 35° in water (*7*). In dioxane-water the p*K* values are 4.54, 4.36, 4.25 and 4.16 at 0°, 15°, 25° and 35°, respectively. Approximate thermodynamic functions at 25° C. were calculated from these data using the relations:

$$\frac{d\ln K}{dT} = \frac{\Delta H^\circ}{RT^2}$$

and

$$T\Delta S^\circ = \Delta H^\circ - \Delta F^\circ,$$

Table I. Basicities of the Ligands in Water and in 50 Volume-Per Cent Dioxane-Water at 25° C. Apparent pK Values.

	Dioxane-Water		Water	
	pK_1	pK_2	pK_1	pK_2
Methylamine	10.25		10.72(*2*)	
Ethylamine	10.23		10.81(*5*)	
n-Propylamine	9.83		10.58(*7*)	
n-Butylamine	9.82		10.61(*16*)	
Pyridine (0° C.)	4.54		...	
Pyridine (15° C.)	4.36		...	
Pyridine (25° C.)	4.25		5.45(*5*)	
Pyridine (35° C.)	4.16		5.35(*5*)	
2-Aminopyridine	1.74	6.11	2.17	6.84
3-Aminopyridine	1.55	5.41	2.00	6.08
4-Aminopyridine	1.97	8.50	2.49	9.26
2-Amino-4-methylpyridine	...	...	2.90	7.23
2-Amino-4,6-dimethylpyridine	2.63	6.98	2.90	7.67
Pyridine-2-aldoxime	2.80	11.63[a]	3.82	9.81[a]
6-Methylpyridine-2-aldoxime	3.38	11.84[a]	4.43	9.46[a]
1-(2-Pyridyl)-urea	3.55		4.48	
1-(2-Pyridyl)-thiourea	1.65		2.44	
2-Pyridylcarbinol	4.16	12.90[a]	4.99	11.08[a]

[a] Shows pK_{OH} where K_{OH} is the acid dissociation constant for the hydroxyl group.

where $-\Delta F^\circ = RT \ln K$. A comparison of the values obtained for 50 volume-per cent dioxane-water ($-\Delta H^\circ = 4.20$ kcal./mole; $-\Delta S^\circ = 5.37$ cal./deg.) with those for water ($-\Delta H^\circ = 4.13$ kcal./mole; $-\Delta S^\circ = 11.10$ cal./deg.) indicate that the difference in the basicity of pyridine in the two systems is primarily an entropy effect, probably due to differences in solvent interaction.

The aminopyridines have two nitrogen atoms, each of which is capable of accepting a proton. The titration curves obtained show two inflection points indicating that these compounds are actually diprotic. The lower of the two pK values in each case, Table I, is assigned to the basicity of the pyridine nitrogen while the higher pK value which is closer to the pK value (9.25) of ammonia (*15*) is assigned to the basicity of the primary amine. That these values are lower than the pK value of ammonia can be attributed to the electron withdrawing tendency of the pyridine ring.

The basicity of the pyridine nitrogen in these compounds increases in the order 3-amino < 2-amino < 4-amino. This is not in agreement with the results obtained for the methylpyridines (*1, 12*) for which the basicity of the pyridine nitrogen increases as the distance between the methyl group and the nuclear nitrogen becomes greater. It is, however, consistent with the greater mesomeric effect observed in the ortho and in the para positions of aromatic rings. The pyridine nitrogen in all the compounds under study is considerably less basic than that in unsubstituted pyridine. This may be explained by the fact that the protonation of the amino nitrogen results in the creation of a positive charge around this nitrogen atom which could exert a considerable electron withdrawing effect on the pyridine nitrogen thus lowering its proton affinity. The pK values for 2-amino-4-methylpyridine and 2-amino-4,6-dimethylpyridine show a slight increase from the 2-amino compound due to the electron releasing tendency of the methyl groups.

The weak basicity of the pyridine nitrogen in 1-(2-pyridyl)-urea and 1-(2-pyridyl)-thiourea can be attributed to the presence of the electron withdrawing oxygen and sulphur atoms, respectively.

In general, the basicities obtained for all the compounds studied are from 0.5 to 1 pK unit lower in 50 volume-per cent dioxane-water than in aqueous solutions indicating that the cationic acids are weaker in water. James and Knox (*17*) noted that in passing from water to 70 volume-per cent dioxane the conjugate acid of aniline became approximately one pK unit stronger. Harkins (*14*) observed a similar trend in his study of 2-(2-pyridyl)-imidazoline and 2,2′-bipyridine.

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CORRECTION

In the article entitled, "The Equilibrium Absorption of Oxygen by *p*-Xylene," by G.T. Fisher [J. CHEM. ENG. DATA 8, 206 (1963)]. Columns 5 and 6 in Table I were interchanged, so that the headings appear with the wrong number. The columns correctly placed read as follows:

Room Temp., ° C.	Henry's Law Constant Atm. O_2/Mole Fraction $O_2 \times 10^{-2}$
25.2	8.89
26.9	9.00
25.4	8.81
24.8	8.46
24.5	8.40
25.8	8.70