A Thermodynamic Analysis of Solvation Effects on the Basicities of Alkylamines. An Electrostatic Analysis of Substituent Effects

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Abstract: Gas-phase basicity data for alkylamines have been combined with known aqueous thermodynamic data to provide a complete set of data for the analysis of solvent effects on these acid–base equilibria. This analysis shows the gas-phase basicities to be altered in solution primarily as a result of compensating electrostatic solvation terms in the solvation of the alkylammonium ions. This causes a strong attenuation of the gas-phase basicities in solution, but the aqueous enthalpies of solution remain proportional to the proton affinities within the primary, secondary, and tertiary amine series. Small but significant entropy terms alter this order, such that changes in the aqueous free energies of protonation are small and somewhat irregular. Among the methyl, ethyl, and *n*-propyl substituted amines the enthalpy attenuation is larger and a little irregular as a result of larger electrostatic terms than within a series of primary, secondary, or tertiary amines. Such electrostatic enthalpy terms correlate well with charge density and with proton affinity as do the corresponding electrostatic entropy terms. Hydrophobic solvation in the neutral amines and ammonium ions is assumed to nearly cancel in its effect on the aqueous proton transfer equilibrium. A simple electrostatic approach is suggested for the analysis of solvent effects on proton transfer reactions using gas-phase equilibrium data. The key electrostatic solvation terms are approximately proportional to the proton affinity for proton transfer within a related series of molecules, such that the changes in enthalpies and free energies of protonation are attenuated in solution but remain proportional to the proton affinity changes. The attenuation factors for various classes of substituent effects can be qualitatively understood in terms of electrostatics. Alkyl substituent effects in aliphatic amines and alcohols are highly attenuated in solution, sometimes with reversals in basicity orders. Resonance and inductive effects in substituted amines, pyridines, phenols, and carboxylic acids are also attenuated. But the resonance and hybridization effects stabilizing the lone pairs in pyrrole, aniline, pyridine, and acetonitrile relative to alkylamines are not attenuated in solution, because the charge densities of the ions are not affected.

The availability of quantitative ion cyclotron resonance techniques for the measurement of gas-phase basicities[1] makes a thorough analysis of the effect of structural variation on intrinsic (gas-phase) basicities and solution basicities possible. In previous papers, the intrinsic effects associated with the gas-phase basicities of alkylamines have been described in terms of simple charge-induced dipole interaction models.[2-4]

The irregular order of the aqueous basicities (pK_a's) of alkylamines has been the subject of some confusion and concern for many years.[5] Among the several explanations for such behavior,[5] it is now clear from gas-phase basicity studies that the intrinsic basicities of alkylamines increase regularly with increasing substitution and that the anomalies in the pK_a's result from solvation effects rather than intrinsic effects in the alkylamines.[2-4,6] The quantitative gas-phase basicity data[2] can be combined with thermochemical measurements of the solution properties of alkylamines to provide a complete set of accurate thermodynamic data[2a,3a,6] for the analysis of solution basicities in fundamental terms.[7] We present here a detailed analysis of the relationships between gas-phase and aqueous basicities and the solvation effects that lead to differences between gas- and solution-phase basicities of alkylamines.

Results and Discussion

For protonation in the gas phase, the negative enthalpy of the reaction ($-\Delta H_{\text{prot,g}}°$) is defined to be the proton affinity (PA). Analogously, we have called the negative free energy for this reaction ($-\Delta G_{\text{prot,g}}°$) the gas-phase basicity (GB).[8] The gas-phase basicities (GB's) for a series of alkylamines have been measured by equilibrium ion cyclotron resonance techniques[1,2] and are summarized in Table I. The key index of basicity in aqueous solution is the free energy of protonation of the base in water, $\Delta G_{\text{prot,s}}°$, or the p$K_a$ of the conjugate acid ($\Delta G_{\text{prot,s}}° = -RT \ln K_a$). Free energies of protonation ($\Delta G_{\text{prot,s}}°$) from titrimetric studies and calorimetric enthalpies of protonation ($\Delta H_{\text{prot,s}}°$) of alkylamines in dilute aqueous solution are included in Table I with the corresponding gas-phase data, GB's and PA's.

An attempt to correlate $\Delta G_{\text{prot,s}}°$ and GB is shown in Figure 1. This plot illustrates the very poor correlation between these free energies of protonation in the gas phase and solution. The changes in $\Delta G_{\text{prot,s}}°$ are very much smaller than those in GB as seen by the deviation of the points from lines of unit slope. In fact, except for ammonia and trimethylamine, the solution basicities are nearly all the same (±0.5 kcal/mol). In contrast to the changes in gas-phase basicities, the changes in solution basicity ($\Delta G_{\text{prot,s}}°$) are irregular with the regular structural changes from NH_3 to primary, secondary, or tertiary amines or within a series of primary, secondary, or tertiary amines. This irregularity must be the result of a complex combination of solvation effects. The $\Delta G_{\text{prot,s}}°$ values are so similar that even simple entropy effects from symmetry changes on protonation can play a major role in the ordering of solution basicities.[8] For example, the order of basicity, $-\Delta G_{\text{prot,s}}°$ (kcal/mol) (NH_3 (12.61) < Me_3N (13.37) < $MeNH_2$ (14.53) < Me_2NH (14.70)) changes on subtraction of the symmetry effect to Me_3N (13.37) $\lesssim$ NH_3 (13.43) < Me_2NH (15.11) $\lesssim$ $MeNH_2$ (15.18). In view of the small changes in $\Delta G_{\text{prot,s}}°$, development of a theory of solvation capable of quantitatively explaining differences between GB and $\Delta G_{\text{prot,s}}°$ appears most difficult.[4b]

Because of the complexity of these solvation effects, we have found it helpful to analyze these free energies by a separate analysis of the $\Delta H°$ and $T\Delta S°$ state functions (see Table I). The enthalpies of protonation of alkylamines in the gas phase and in aqueous solution, in fact, correlate very well giving three nearly parallel lines for primary, secondary, and tertiary amines in Figure 2. Thus, the small and irregular structural effects in $\Delta G_{\text{prot,s}}°$ may be analyzed as the sum of more regular effects in $\Delta H_{\text{prot,s}}°$ and $T\Delta S_{\text{prot,s}}°$.

By use of the thermodynamic cycle in Scheme I, our

Table 1. Thermodynamic Properties of Amines at 25°^{a}

	GB^{a,s}	$-\Delta G_{\mathrm{prot,s}}{}^\circ$	$-\Delta G_{\mathrm{s}}{}^\circ$(B)	$-\Delta G_{\mathrm{s}}{}^\circ$(BH$^+$)^{d,s}	PA^{b,s}	$-\Delta H_{\mathrm{prot,s}}{}^\circ$	$-\Delta H_{\mathrm{s}}{}^\circ$(B)	$-\Delta H_{\mathrm{s}}{}^\circ$(BH$^+$)^{d,s}	$-T\Delta S_{\mathrm{prot}}{}^\circ$ (g)	$-T\Delta S_{\mathrm{prot,s}}{}^\circ$	$-T\Delta S_{\mathrm{s}}{}^\circ$(B)	$-T\Delta S_{\mathrm{s}}{}^\circ$-(BH$^+$)^d
NH_3	[198 ± 3]	12.61^e	2.41^f	78 ± 3	[207 ± 3]^c	12.49^e	8.42^e	84 ± 3	8.57	−0.12	6.01	6.6
$MeNH_2$	[210.0]^a	14.53^e	2.68^g	67.7	[218.4]^a	13.18^e	10.82^e	75.4	8.40	−1.35	8.14	7.7
$EtNH_2$	213.0	14.57^e	2.61^g	64.7	221.4	13.71^i	13.05^e	75.2	8.40	−0.86	10.44	10.5
n-$PrNH_2$	214.4	14.42^e	2.51^g	63.0	222.8	13.84^i	13.37^e	74.2	8.40	−0.58	10.86	11.2
n-$BuNH_2$	214.9	14.51^e	2.41^g	62.5	223.3	13.98^i	14.11^e	74.6	8.40	−0.53	11.70	12.1
i-$BuNH_2$	215.4	14.30^n			223.8	13.92^i	13.66^e	73.6	8.40	−0.38		
i-$PrNH_2$	215.3	14.56^n			223.7	13.97^i	13.37^e	73.4	8.40	−0.59		
s-$BuNH_2$	216.4	14.41^e			224.8	14.03^i			8.40	−0.38		
t-$BuNH_2$	217.3	14.58^e			225.7	14.35^e	14.10^e	72.6	8.40	−0.23		
Me_2NH	216.6	14.70^e	2.41^g	61.0	224.8	12.04^i	12.69^e	69.7	8.16	−2.66	10.28	8.8
Et_2NH	221.2	15.03^e	2.19^g	56.5	229.4	12.73^i	15.31^e	68.4	8.16	−2.30	13.12	12.0
n-Pr_2NH	223.2	15.01^j	1.76^g	54.1	231.4	13.17^i	17.26^e	68.8	8.16	−1.84	15.50	14.8
n-Bu_2NH	224.3	15.35^j	1.34^g	52.9	232.5	13.66^i	18.81^e	69.9	8.16	−1.69	17.55	17.0
i-Bu_2NH	224.8	14.32^i			233.0	13.38^i	15.56^e	65.7	8.16	−0.74		
i-Pr_2NH	225.0	15.28^i			233.2	13.55^i	16.81^e	67.0	8.16	−1.73		
s-Bu_2NH	227.0	14.88^i			235.2	14.03^i	17.81^e	66.4	8.16	−0.85		
Me_3N	220.8	13.37^e	1.34^g	54.4	228.6	8.82^e	13.23^e	63.3	7.75	−4.55	11.89	8.9
Et_3N	227.7	14.62^e	1.15^g	48.6	235.5	10.32^i	16.76^e	61.4	7.75	−4.30	15.61	12.9
n-Pr_3N	229.9	14.54^i	0.80^h	45.9	237.7	10.50^i			7.75	−4.04		
Pyrrolidine	220.4	15.42^j	1.21^l	56.7	228.6	12.82^k	15.19^e	69.2	8.16	−2.60	13.98	12.5
Piperidine	221.5	15.30^j	0.83^l	55.1	229.7	12.71^k	15.63^e	68.4	8.16	−2.59	14.80	13.4
N-Methyl-pyrrolidine	224.4	14.26^j	-0.30^l	50.1	232.2	9.05^l	15.16^e	61.8	7.75	−5.21	15.46	11.8
N-Methyl-piperidine	225.4	13.75^j	-0.38^l	48.5	233.2	9.44^l	15.22^e	61.8	7.75	−4.31	16.10	13.3
Cyclohexylamine	217.2	14.56^j			225.6	14.38^i			8.40	−0.18		
Aniline	207	6.27^i			216	7.24^i			8.40	0.97		
Pyridine	216.9	7.12^j	0.42^n	51.1	224.7	4.80^p	11.98^q	61.9	7.75	−2.25	11.56	10.9
Morpholine	215.7	11.58^i			223.9	9.33^i			8.16	−2.25		
Piperazine	218	13.41^j			226	10.17^i			8.16	−3.24		
1,4-Diazabicyclo-[2.2.2]octane	225	12.03^i			233	7.30^i			7.75	−4.73		
2,2,2-Trifluoro-ethylamine	196	7.65^m			205	8.30^m			8.40	+0.65		
Quinuclidine	227.9	15.21^j			235.7	11.14			7.75			
Pyrrole	205	-5.18^j			213				8.16	−2.6 (est)		
CH_3CN	180	-13.6^r			188							

[a] All values in kcal/mol. GB's measured relative to methylamine (210.0 kcal/mol). [b] PA's calculated from GB's by correction for symmetry and the entropy of H$^+$ [A. P. Altshuller, *J. Am. Chem. Soc.*, 77, 3480 (1955); see also ref 7]. [c] A plot of PA vs. IP was used to approximate ΔPA for NH_3 and CH_3NH_2. Absolute PA of NH_3 taken as 207 ± 3 kcal/mol [M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, 50, 2028 (1969)]. [d] Calculated using $\Delta G_{\mathrm{s}}{}^\circ(\mathrm{H}^+) = -260.5$ kcal/mol [R. M. Noyes, *J. Am. Chem. Soc.*, 84, 513 (1962)], and $\Delta H_{\mathrm{s}}{}^\circ(\mathrm{H}^+) = -269.8$ kcal/mol, ref 24c. [e] Reference 6b. [f] R. G. Bates and G. D. Pinching, *J. Res. Natl. Bur. Stand.*, 42, 419 (1949). [g] A. O. Christie and D. J. Crisp, *J. Appl. Chem.*, 17, 11 (1967). [h] Extrapolated from footnote *g* data. [i] J. J. Christenson, R. M. Izatt, D. P. Wrathall, and L. D. Hansen, *J. Chem. Soc. A*, 1212 (1969). [j] D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworths, London, 1965. [k] S. Cabani, G. Conti, and L. Lepori, *Ric. Sci.*, 38, 1039 (1968). [l] S. Cabani, G. Conti, and L. Lepori, *Trans. Faraday Soc.*, 67, 1933 (1971). [m] P. Love, R. Cohen, and R. W. Taft, *J. Am. Chem. Soc.*, 90, 2455 (1968). [n] R. J. L. Andon, J. D. Cox, and E. F. G. Herington, *J. Chem. Soc.*, 3188 (1954). [p] L. Sacconi, P. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, 82, 3831 (1960). [q] L. Sacconi, P. Paoletti, and M. Ciampolini, *ibid.*, 82, 3828 (1960). [r] I. M. Kolthoff and M.K. Chantooni, Jr., *ibid.*, 95, 4768, 8539 (1973). [s] Recent results indicate that PA(NH_3) = 202 kcal/mol and PA($MeNH_2$) = 211 kcal/mol. This lowers the values of GB and PA and raises the values of $\Delta G_{\mathrm{s}^\circ}$-(BH$^+$) and $\Delta H_{\mathrm{s}}{}^\circ$(BH$^+$) by ca. 7 kcal/mol for all of the other compounds except CH_3CN.

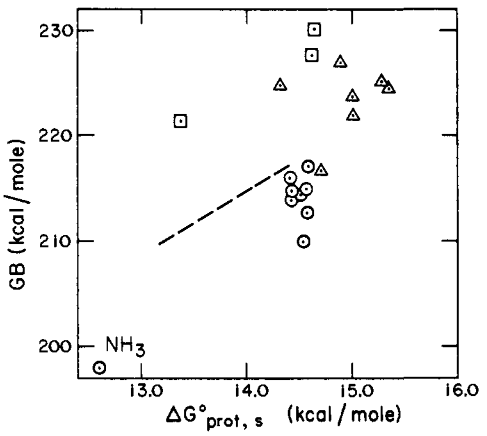

Figure 1. Plot of free energies of protonation in water, $\Delta G_{\mathrm{prot,s}}°(B)$ vs. gas-phase basicities, GB, of alkylamines at 25°. Primary amines are represented by ○, secondary amines by △, and tertiary amines by □. The dashed line represents the corresponding plot (Figure 2) of $\Delta H_{\mathrm{prot}}°$ vs. GB for the primary amines for comparison. (For the primary amines GB = PA − 8.40 kcal/mol for conversion of the ordinate axis values.)

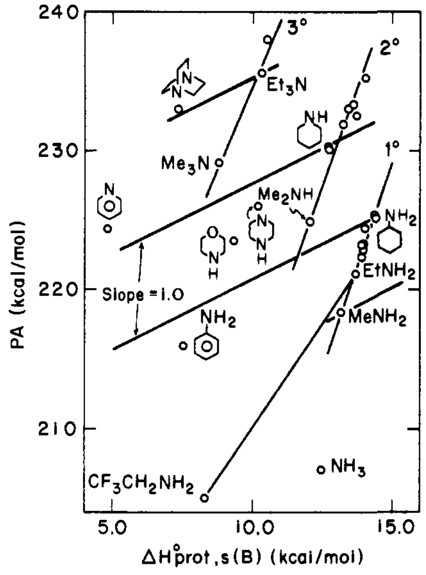

Figure 2. Plots of heats of protonation in water, $\Delta H_{\mathrm{prot,s}}°(B)$, vs. proton affinity, PA, of amines, at 25°.

Scheme I. Thermodynamic Cycle for Analysis of Solution Effects on Basicities

$$\begin{tikzcd}
B_g \arrow[d, "\Delta H_s^\circ(B)"] & + & H_g^+ \arrow[r, "\Delta H_{\mathrm{prot,g}}^\circ", "-PA"'] \arrow[d, "\Delta H_s^\circ(H^+)"] & BH_g^+ \arrow[d, "\Delta H_s^\circ(BH^+)"] \\
B_s & + & H_s^+ \arrow[r, "\Delta H_{\mathrm{prot,s}}^\circ"] & BH_s^+
\end{tikzcd}$$

$$\Delta H_{\mathrm{prot,s}}^\circ = -\mathrm{PA} + \Delta H_s^\circ(BH^+) - \Delta H_s^\circ(B) - \Delta H_s^\circ(H^+) \tag{1}$$

quantitative PA's together with heats of hydration $[\Delta H_s°(B)]$ of amines and heats of protonation in water $(\Delta H_{\mathrm{prot,s}}°)$ permit the calculation of heats of solvation for a large number of ammonium ions for the first time.[2a,3a] Corresponding free energies $[\Delta G_s°(BH^+)]$ and entropies $[\Delta S_s°(BH^+)]$ can be calculated as well from this cycle to give a complete set of these thermodynamic data.

These data provide the basis for an analysis of the differences between gas and solution basicities and an explanation of the solvation effects leading to these differences. It can be seen from the thermodynamic cycle in Scheme I that relative differences between PA and $\Delta H_{\mathrm{prot,s}}°$ can arise only from differences in the heats of solvation of the neutral amines, $\Delta H_s°(B)$, and the charged ammonium ions, $\Delta H_s°(BH^+)$. Thus, explanations of the differences between gas and solution basicities must be based on factors affecting $\Delta H_s°(B)$ and $\Delta H_s°(BH^+)$ and the corresponding $\Delta G_s°$ and $T\Delta S_s°$ parameters (Table I).

Within each series of primary, secondary, and tertiary amines, the PA's increase with increasing size and branching of the alkyl chain as described earlier,[2] and the solution heats $(\Delta H_{\mathrm{prot,s}}°)$ change in nearly the same way as the PA's. The linear plots in Figure 2 show slopes of 5-6 rather than unity, however, indicating that the changes in $\Delta H_{\mathrm{prot,s}}°$ are much smaller than those in PA. *Thus the effect of changing the structures of the alkyl groups on the aqueous heats of protonation of alkylamines runs remarkably parallel to the effect on the proton affinities in the gas phase, but the effect is dramatically attenuated (by five- to six-fold) in solution.*

The total increase in PA in a series of primary amines from methylamine to *tert*-butylamine is 7.3 kcal/mol, while the increase in $\Delta H_{\mathrm{prot,s}}°$ is only 1.2 kcal/mol. Nevertheless, the solvation effects are regular enough throughout the primary amines that $\Delta H_{\mathrm{prot,s}}°$ changes regularly and produces linear PA vs. $\Delta H_{\mathrm{prot,s}}°$ plots. Differences between PA and $\Delta H_{\mathrm{prot,s}}°$ result from changes in the relatively small heats of solvation of the neutral amines $[\Delta H_s°(B)]$ and the large heats of solvation of the ammonium ions $[\Delta H_s°(BH^+)]$. Within the series of primary amines, $-\Delta H_s°(B)$ increases by 3.3 kcal/mol, while $-\Delta H_s°(BH^+)$ decreases by 2.8 kcal/mol. These two effects add to give the overall 6.1 kcal/mol discrepancy between the changes in PA (δPA = 7.3 kcal/mol) and $\Delta H_{\mathrm{prot,s}}°$ ($\delta\Delta H_{\mathrm{prot,s}}°$ = 1.2 kcal/mol) (see eq 1).

The exothermicity of solvation of the alkylamines increases in direct proportion to the number of carbon atoms in the alkyl groups. This effect can be attributed to the well known hydrophobic interactions between alkyl groups and water (vide infra). An interpretation of the changes in the exothermicity of solvation of the ammonium ions, however, has no ready precedent, since such data have not previously been available.[2,3,6] We propose here a simple theoretical approach to this problem which can explain the major effects observed in alkylammonium ion solvation and shows promise in explaining the solvation of other organic ions.

The solvation of ions may be thought of as involving two distinct steps: (1) the introduction of a neutral molecule the same size as the ion into the solvent, and (2) the interaction of the charge on the ion with the solvent. The first step involves the formation of a cavity for the neutral molecule and the weak interactions between the neutral molecule and the solvent. For an alkylammonium ion, the most convenient model for the enthalpy associated with step 1 of solvation is the enthalpy of hydration of the alkylamine, $\Delta H_s°(B)$ (eq 2). This neutral solvation term in alkylamines appears to change primarily as a result of hydrophobic effects and will be loosely called a hydrophobic term in the following discussion. The remaining electrostatic term $\Delta H_s°(BH^+)^{\mathrm{el}}$ is then a hydrophobically corrected heat of hydration which may be *defined as an electrostatic term since it reflects those solvation effects that result from addition of a proton and its positive charge to the neutral amine.* Within the primary amines, the hydrophobic term, $\Delta H_s°(B)$, changes by 3.0 kcal/mol; so the electrostatic term would be 6.1 kcal/mol.[9] This electrostatic effect is qualitatively reasonable from the simple electrostatic theory of

$$\Delta H_s°(BH^+) = \text{neutral solvation term} + \text{electrostatic term} \simeq \Delta H_s°(B) + \Delta H_s°(BH^+)^{\mathrm{el}} \tag{2}$$

Born wherein ions of small size, e.g., Li^+ or $MeNH_3^+$, have larger heats of solvation than large ions, e.g., Cs^+ or t-$BuNH_3^+$. Support for the validity of this approach and the possibility that other factors, such as hydrogen bonding, may operate in alkylammonium ion solvation will be discussed in the following sections of this paper.

It is useful to note that in combining eq 1 and 2 the $\Delta H_s°(B)$ terms cancel, and the differences between gas-phase and aqueous enthalpies of protonation (e.g., 6.1 kcal/mol for primary amines) can, according to this model, be fully attributed to an electrostatic effect in the solvation of the alkylammonium ions (eq 3). It might further be pointed

$$-\Delta H_{\mathrm{prot,s}}° - \mathrm{PA} = \Delta H_s°(\mathrm{BH^+})^{\mathrm{el}} - \Delta H_s°(\mathrm{H^+}) \qquad (3)$$

out that the horizontal deviation of each primary amine point in Figure 2 from the line of unit slope through methylamine is equal to the difference between the change in PA and $\Delta H_{\mathrm{prot,s}}°$ relative to methylamine, which is attributed to an electrostatic effect on the enthalpies of hydration of the alkylammonium ions. From the linearity of these plots, it can be deduced that this electrostatic term, $\Delta H_s°(\mathrm{BH^+})^{\mathrm{el}}$, must be proportional to PA and $\Delta H_{\mathrm{prot,s}}°$ within each series.

Solvation of Neutral Amines. It is generally found in Table I that the heats of hydration in each series of alkylamines decrease in regular fashion as molecular size increases. Successive addition of carbon atoms to a chain appears to have a nearly additive effect on $\Delta H_s°(B)$. The difference between methylamine and *tert*-butylamine is 3.3 kcal/mol, representing average increments of 1.1 kcal/mol per methylene group. Similarly, the 3.5 kcal/mol difference in $\Delta H_s°(B)$ between trimethylamine and triethylamine corresponds to ca. 1.2 kcal/mol per methylene group. Significantly, these effects even account for differences in heats of hydration between primary, secondary, and tertiary amines. For example, the heat of hydration of ethylamine (13.05 kcal/mol) is close to that of dimethylamine (13.26 kcal/mol), so that changes in alkylamine hydration appear to depend primarily on the alkyl group interactions.

Such effects of alkyl groups on solvation are generally termed hydrophobic effects. These effects have been studied in much detail,[10,11] but they have been the subject of some controversy and appear not yet well understood. It is generally agreed, however, that, whatever theoretical model should apply, the hydration of nonpolar solutes occurs with a net structuring of the solvent and with characteristic closely correlated changes in enthalpies and entropies of hydration which nearly exactly compensate (see Figure 3).

That hydrophobic interactions can lead to enthalpy changes of the proper magnitude to account for the changes in heats of hydration for alkylamines is confirmed by comparison with the heats of hydration of alcohols and alkanes (see Figure 3).[10d,12-20] The 8 kcal/mol difference in the heats of hydration of the alkanes and similar amines must result from the favorable dipole-dipole interactions of the amines and water solvent. Comparable values and changes in the heats of hydration of aliphatic alcohols are also observed.[10d,14] Closely correlated changes in enthalpies and entropies of hydration can be seen in the parallel plots (slopes = 0.9) in Figure 3 for alkylamines, alkanes, and alcohols.[18] Ammonia and primary, secondary, and tertiary amines nearly fall on the same line in Figure 3 suggesting that solvation changes resulting from changes in numbers of hydrogen bonds are small.

Linear and parallel plots of partial molar heat capacities vs. carbon number for alkylamines, alcohols, amides, and carboxylic acids[17] further show that changes in the structure of water around the nonpolar portion of these molecules are nearly independent of the polar group. The observation of comparable hydrophobic effects for a variety of substituted alkanes of different polarity and further arguments in the following section support our use of $\Delta H_s°(B)$ for alkylamines as a model for the hydrophobic term in alkylammonium ion solvation (eq 2).

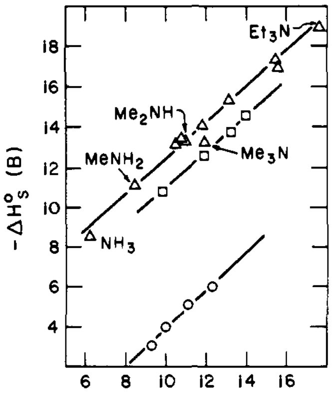

Figure 3. Plots of heats of hydration, $-\Delta H_s°(B)$, vs. entropy term for hydration of alkanes (○), alkylamines (△), and alcohols (□) at 25°.

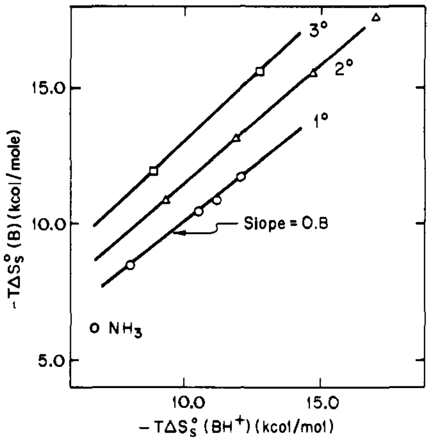

Figure 4. Plot of entropy terms for hydration of alkylamines, $-T\Delta S_s°(B)$, vs. entropy terms for hydration of protonated amines, $-T\Delta S_s°(BH^+)$, at 25°.

Solvation of Alkylammonium Ions. Examination of the enthalpies and entropies of hydration in Table I reveals significantly different behavior between neutral amines and ammonium ions. While the heats of hydration of the neutral amines become more exothermic through the series of primary amines of increasing size, the heats of hydration of the alkylammonium ions become less exothermic. The corresponding entropy terms, $-T\Delta S_s°(B)$ and $-T\Delta S_s°(BH^+)$, however, both increase in parallel fashion, with the rate of increase for the ammonium ions a little greater than that for the neutral amines as shown by slopes of ca. 0.8 in Figure 4. The close correlation between the entropies of hydration for the neutral amines and ammonium ions in Figure 4 suggests that the hydrophobic interactions in the hydration of neutral amines occur to a nearly equal extent in the hydration of the alkylammonium ions.[21,22]

A hydrophobically corrected set of heats of hydration, $\Delta H_s°(\mathrm{BH^+})^{\mathrm{el}}$, for alkylammonium ions has been calculated by subtraction of $\Delta H_s°(B)$ from $\Delta H_s°(BH^+)$ (eq 2) as shown in Table II.[23] Hydrophobic effects for the neutral amines and ammonium ions cancel each other in the thermodynamic cycle in Scheme I, so that the key factor in altering the proton affinities in aqueous solution is the electrostatic term, $\Delta H_s°(\mathrm{BH^+})^{\mathrm{el}}$, for alkylammonium ion solva-

Table II. Crystal Radii of Alkylammonium Ions as Determined from Partial Ionic Molar Volumes

Cation	$\bar{V}$, cm^3/mol	$r_{\bar{V}}$, Å	$-\Delta H_s°(BH^+)^{el,b}$ kcal/mol
NH_4^+	12.5	1.70 (1.63)^a	75^b (81)^c
$MeNH_3^+$	30.7	2.30	64.6
$EtNH_3^+$	47.5	2.66	62.1
n-$PrNH_3^+$	64.0	2.94	60.8
i-$PrNH_3^+$	(64.0)^d	2.94	60.0
n-$BuNH_3^+$	80.1	3.17	60.5
i-$BuNH_3^+$	(80.1)^d	3.17	59.9
t-$BuNH_3^+$	(80.1)^d	3.17	58.5
$Me_2NH_2^+$	49.2	2.69	57.0
$Et_2NH_2^+$	83.4	3.21	53.1
n-$Pr_2NH_2^+$	115.4	3.58	51.5
i-$Pr_2NH_2^+$	(115.4)^d	3.58	50.2
n-$Bu_2NH_2^+$	147.4	3.88	51.0
i-$Bu_2NH_2^+$	(147.4)^d	3.88	50.1
s-$Bu_2NH_2^+$	(147.4)^d	3.88	48.6
Me_3N^+H	67.3	2.99	50.1
Et_3N^+H	116.1	3.58	44.6
Me_4N^+	84.2	3.22	41^e
Et_4N^+	143.7	3.85	35^e

^{a}This crystal radius (see Appendix) is used in Figures 5 and 7. ^{b}Corrected for hydrophobic hydration from eq 2. ^{c}Corrected for hydrophobic hydration with interpolated heats of hydration of inert gases of comparable radius (ref 12). ^{d}Assumed. ^{e}See Appendix and ref 70 and 12b.

tion. The changes in $\Delta H_s°(BH^+)^{el}$ can be explained economically and potentially quantitatively within the framework of the simple classical electrostatic theory of Born.[24] The free energy of hydration of a charged sphere is inversely proportional to its radius from electrostatics. Application of this relationship to ions gives the Born equation:

$$\Delta G_s°(M^+) = -\frac{Nz^2e^2}{2r}(1 - (1/D)) = K\frac{1}{r} \tag{4}$$

where N is the number of ions, z is the charge number of the ion, e is the charge of the electron, D is the dielectric constant of the solvent, and r is the ionic radius. Differentiation of this equation with respect to T yields an expression for the entropy of hydration (eq 5).[24b] From eq 4 and 5, $\Delta H_s°$ can be readily obtained as in eq 6. All three thermodynamic functions are seen to be simply proportional to

$$\Delta S_s°(M^+) = \frac{Nz^2e^2}{2r}\frac{1}{D^2}\frac{\partial D}{\partial T} = K'\frac{1}{r} \tag{5}$$

$$\Delta H_s°(M^+) = \frac{Nz^2e^2}{2r}\left(\frac{1}{D} - 1 + \frac{T}{D^2}\frac{\partial D}{\partial T}\right) = K''\frac{1}{r} \tag{6}$$

$1/r$ at constant temperature and in a medium of fixed dielectric constant (at 25°, in water, $K = -163.9$ (kcal Å)/mol, $K' = -9.68$ (cal Å)/mol/deg, and $K'' = -166.8$ (kcal Å)/mol). A mechanism for this electrostatic effect involves delocalization of the charge onto the surrounding solvent. Ions with large effective ionic radii, i.e., ions which already benefit from a high degree of internal charge delocalization, interact less strongly with the solvent because further delocalization of the charge is energetically less effective.

As a test of the Born equation, the thermodynamics of hydration of alkali metal ions have been investigated in some detail as a function of crystal radius.[24] The variations of $\Delta G_s°$, $\Delta H_s°$, and $\Delta S_s°$ with respect to $1/r$ are all nicely linear as predicted, but with slopes somewhat different from those predicted theoretically.[25] This correlation is remarkably good considering the assumptions of uniform distribution of the charge over the surface of a sphere and of a continuous unstructured solvent of constant dielectric constant,[26] and the problems in the choice of proper ionic radii, which should ideally be gas-phase radii.[27] Nevertheless, a self-consistent set of crystal radii (see Appendix) gives a very good correlation with $\Delta G_s°$, $\Delta H_s°$, and $T\Delta S_s°$. This provides an *empirical* basis for the quantitative, or at least semiquantitative, analysis of the electrostatic terms, $\Delta H_s°(BH^+)^{el}$, in alkylammonium ion solvation as a function of ionic size.

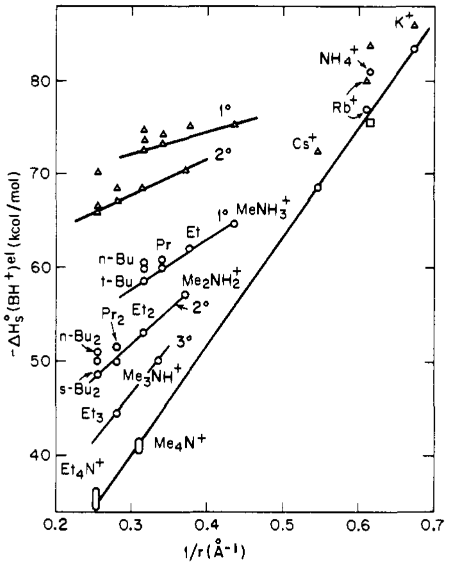

Figure 5. Plot of heats of hydration of alkali cations and alkylammonium ions vs. reciprocal ionic radius. Absolute heats of hydration, $\Delta H_s°(BH^+)$, are represented by △, and heats corrected for hydrophobic effects, $\Delta H_s°(BH^+)^{el}$, are represented by ○. Two points are shown for the corrected heat of hydration for NH_4^+; correction using NH_3 as a model (□) and using rare gas data (○) as for the alkali cations. Extrapolated heats of hydration of hydrocarbons were used to correct $\Delta H_s°$ of NMe_4^+ and NEt_4^+. The $\Delta H_s°$ of NMe_4^+ is accurate to ±1 kcal/mol and ca. ±2 kcal/mol for Et_4N^+ (see ref 70). The alkali cation line is a least-squares line including Na^+ and Li^+ points not shown (correlation coefficient = 0.9999). See Table II and Appendix for the heat and radius data.

We have estimated ionic radii of the alkylammonium ions (see Appendix) and compared the behavior of $\Delta H_s°(BH^+)$ for these ions to that of the alkali metal cations as a function of $1/r$ (see Table II and Figure 5). The values for $\Delta H_s°(BH^+)$ plotted △ in Figure 5 lie far above the corresponding alkali metal line, but correction of the alkylammonium ion and alkali metal ion heats for hydrophobic effects gives a new set of $\Delta H_s°(BH^+)^{el}$ and $\Delta H_s°(M^+)^{el}$ values ○ (see Table II) which lie reasonably close to the alkali metal line in Figure 5.[25] Significantly, the line through the alkali metal ions is nearly coincident with the spherically symmetrical ammonium ion and tetraalkylammonium ion points. The enthalpies of hydration of these symmetrical ammonium ions are quantitatively fit remarkably well by this electrostatic correlation with ionic radius. The heat of hydration of ammonium ion, when corrected for hydrophobic effects using inert gas data as for the alkali metals (○), is only 4 kcal/mol more exothermic than expected from the alkali metal line.[28] This deviation is within the estimated errors (ca. ±5 kcal/mol) in the absolute value of the proton affinity of ammonia[2b] and the heat of hydration of H_3O^+ used in calculation of $\Delta H_s°(NH_4^+)$. The heat of hydration of H_3O^+, itself, lies only 5 kcal/mol above the line.[29] The heats of hydration of the tetraethyl- and tetramethylammonium ions are also very close to the alkali metal line, although they cannot form hydrogen bonds like ammonium ion. Thus, it appears that, in spite of their unique ability to form hydrogen bonds to the solvent, H_3O^+ and NH_4^+ are exothermically hydrated with about the same energy as alkali metal ions of comparable size. We conclude therefore that, although ammonium ion probably does form such hydrogen bonds, the total enthalpic advantage of four such hydrogen bonds relative to hydration of an alkali metal of comparable size (Rb^+) is relatively small.[28,30,31]

In comparing heats of hydration of alkylammonium ions to ammonium ion, and to one another, the inaccurate absolute PA and $\Delta H_s°(H_3O^+)$ cancel to provide a more accurate set of relative heats of hydration. In comparison with alkylammonium ions, the point □ for ammonium ion corrected for the hydrophobic and polar effects of ammonia should be used.[28] The Born equation was derived for spherical particles with charge uniformly distributed on their surfaces. For alkali metal ions the charge is not on the surface of a sphere, and for most alkylammonium ions the particles are neither spherical nor uniformly charged. Nevertheless, we have used ionic radii calculated for spheres of volume equal to the volume of the ion, and, to a first approximation, the charge is assumed to be equally distributed over the ion. The assumption of uniform charge distribution should lead to heats of hydration higher than predicted from the alkali metal ion line as a result of higher local charge densities in asymmetrically charged ions. In fact, analysis of the structures of the ions within the primary ammonium ion series, for example, shows that the unbranched long-chain *n*-butyl- and *n*-propylammonium ion points show the largest deviations from a line through methylammonium ion parallel to the alkali metal line. It is just these ions which should have the positive charge most localized near the nitrogen atom, while the highly branched isopropyl- and *tert*-butylammonium ions would be expected to have more uniform charge distribution on the basis of the $1/r^4$ dependence of the polarizability model for charge delocalization.[2b] An analysis of the charge densities from CNDO/2 calculations on the alkylammonium ions also shows that branched amines have a more uniform charge distribution than unbranched amines.[2b] These calculations indicate that the positive charge localized on the $-NH_3^+$ moiety of methylammonium ion is only 0.72, while the other 28% of the charge is delocalized onto the hydrogens of the methyl group. In the series from methylammonium ion to ethyl-, *n*-propyl-, isopropyl-, *n*-butyl-, and *tert*-butylammonium ions, the charge density of nitrogen decreases regularly with increasing chain length and branching so that only 63% of the positive charge is localized at the $-NH_3^+$ moiety in the *tert*-butylammonium ion.[2b] So, while the nominal ionic radius of *tert*-butylammonium ion is the same as *n*-butylammonium ion, the effective radius of *tert*-butylammonium ion (+0.63 charge on $-NH_3^+$) is larger and the charge density lower than for *n*-butylammonium ion (+0.67 charge on $-NH_3^+$). The *tert*-butylammonium ion should then be less exothermically solvated than *n*-butylammonium ion. Among the isomeric alkylammonium ions, it is generally observed that the more highly branched isomers have smaller $-\Delta H_s°(BH)^{el}$ values (Figure 5, Table II).

The charge densities at $-NH_3^+$ decrease linearly with increasing proton affinity for the primary amines.[2b] Since charge densities appear to vary regularly with proton affinity for alkylamines, the proton affinity might be a good indicator of the charge density and "effective" ionic radius of the alkylammonium ions. Indeed, a plot of $\Delta H_s°(BH^+)^{el}$ vs. PA gives excellent correlations within primary, secondary, or tertiary series (Figure 6), much better than the correlations within these series shown by plotting the reciprocal nominal ionic radii vs. $\Delta H_s°(BH^+)^{el}$ in Figure 5. The linear dependence of $\Delta H_s°(BH^+)^{el}$ on PA within a series of primary, secondary, or tertiary amines is then reasonable in terms of simple electrostatic theory. This proportionality of $\Delta H_s°(BH^+)^{el}$ and PA leads to the observed proportionality of $\Delta H_{prot,s}°$ and PA in Figure 2, since it is this key $\Delta H_s°(BH^+)^{el}$ term which causes the solvent attenuation of PA's.

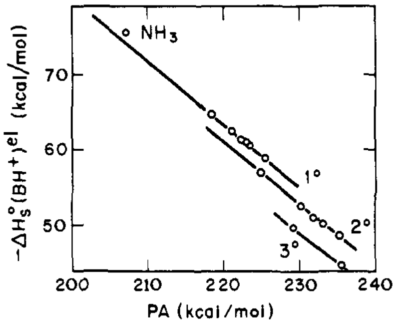

Figure 6. Plot of electrostatic heats of hydration, $\Delta H_s°(BH^+)^{el}$, of alkylammonium ions vs. proton affinities of the corresponding amines.

The electrostatic heats of hydration of secondary and tertiary alkylammonium ions are smaller than expected from their PA's in Figure 6. These 2-4 kcal/mol differences between the primary, secondary, and tertiary amine lines in Figure 6 might be attributed to differences in the number of hydrogen bonds to water that are available in the alkylammonium ions,[28] assuming that the PA correlation in Figure 6 should give a single line for all amines if only an electrostatic effect operates. Hydrogen bonding differences alone [up to 6-8 kcal/mol/H bond in $\Delta H_s°(BH^+)$] have previously been thought to explain the differences in the heats of solvation of the methylamines in water and their irregular basicity order.[2a,3a,5e,f,6,9] In considering electrostatic effects, however, it appears from the arguments presented above and in Figure 5 that most of these apparent hydrogen bonding differences can be explained by hydrophobic contributions to $\Delta H_s°(BH^+)$ and by electrostatic effects in $\Delta H_s°(BH^+)^{el}$.[9] The heat of hydration of NH_4^+ appears to be very well explained in terms of its ionic radius and electrostatic theory with little added stabilization from hydrogen bonding.[28,30,31] The methyl- and dimethylammonium ions are solvated about 9 kcal/mol more exothermically than predicted from their nominal ionic radii. This discrepancy could be accommodated, however, by considering the asymmetric charge delocalization of these ions which could make their effective ionic radii smaller than their nominal radii.[32] The more symmetrical trimethylammonium ion falls only 5 kcal/mol above the alkali cation line.[28]

Although a rigorous quantitative electrostatic treatment of these unsymmetrical alkylammonium ions is not yet possible, these arguments based on a consideration of charge density or "effective" ionic radius appear capable of explaining the enthalpy data.[33] The excellent empirical correlation of $\Delta H_s°(M^+)^{el}$ and $1/r$ for alkali metal ions provides a surprisingly successful basis for quantitative correlation of the nearly symmetrical alkylammonium ions (Figure 5). The empirical correlations of $\Delta H_s°(BH^+)^{el}$ and PA in Figure 6 provide a basis for quantitative prediction of $\Delta H_s°(BH^+)^{el}$ for the unsymmetrical alkylammonium ions as well. Both of these empirical correlations are consistent with electrostatic predictions based on charge density in the ion. The small (2-4 kcal/mol) differences between the primary, secondary, and tertiary amine lines in Figure 6 and what could be as large as a 5-10 kcal/mol deviation of the NH_4^+ point[28] in Figure 5 might be explicable in terms of differences in the numbers of hydrogen bonds available. We believe, however, that any larger special hydrogen bonding or "steric" effects[32] are not required *in addition* to electrostatic charge density effects to explain the available data and appear inconsistent with the near normal $\Delta H_s°(BH^+)^{el}$ values for NH_4^+ and H_3O^+ in Figure 5.[34,35] We conclude then that the number of hydrogen bonds is less important than the total strengths of these bonds, which can be correlated with charge density.

That the strengths of hydrogen bonds can vary dramatically and that these electrostatic charge density arguments are useful in making predictions about the solvation of ions other than alkylammonium ions are illustrated in the following examples. The inductive lowering of the basicity of 2,2,2-trifluoroethylamine relative to ethylamine is greater in the gas phase (16 kcal/mol) than in solution (6.9 kcal/mol in $\Delta G°$ and 5.4 kcal/mol in $\Delta H°$) (see Table I). This difference between gas-phase and solution basicity can be analyzed in terms of an increased heat of hydration of the trifluoroethylammonium ion relative to the ethylammonium ion. Although the heat of solution of trifluoroethylamine has not been measured, we can still evaluate an electrostatic term, $\Delta H_s°(BH^+)^{el}$. For trifluoroethylamine $\Delta H_s°(BH^+)^{el}$ is -73 kcal/mol, 11 kcal/mol more exothermic than that for ethylamine.[36] This change in solvation energy can result from an increased charge density relative to the ethylammonium ion. Such effects on charge density are seen in the results of CNDO/2 calculations, where the charge on the $-NH_3^+$ group in ethylammonium ion is +0.69 and that in the trifluoroethylammonium ion is +0.73. This solvation effect is illustrated graphically in Figure 2 where the trifluoroethylamine point lies on a line of slope 3.0 through ethylamine and deviates from a slope of unity by the 11 kcal/mol electrostatic effect in $\Delta H_s°(BH^+)^{el}$. This attenuation effect of 3.0 in solution is smaller than the five- to sixfold attenuation factor characteristic of the alkylamine polarizability effects. Morpholine and piperazine show attenuation factors of 2.0 and 1.7, respectively, relative to piperidine (see Table I and Figure 2). The inductive and resonance effects in ortho-, meta-, and para-substituted pyridines likewise show an attenuation factor of ca. 3.[37]

A Kirkwood-Westheimer[38] approach to the analysis of these attenuation factors appears to explain the differences qualitatively. The effective dielectric constant of the medium between the substituent and the charged nitrogen might be expected to be lower for morpholine or piperazine than for trifluoroethylamine because solvent cannot approach and intervene as effectively. Interestingly, 1,4-diazabicyclo[2.2.2]octane shows virtually no attenuation at all in its solution basicity relative to triethylamine (see Table I and Figure 2). This may be because of the lack of solvent penetration between the two nitrogens in the ammonium ion. Similarly, the attenuation factor within the tertiary alkylamines is smaller than for secondary or primary amines (Figure 2), perhaps for this reason.

The success of the correlations of $\Delta H_s°(BH^+)^{el}$ with PA for alkylamines in Figure 6 suggests that this correlation may be more generally applicable, but the variations in attenuation factors noted above complicate such plots. In fact, in some cases, the attractive notion that more strongly acidic ammonium ions should form stronger hydrogen bonds and be more exothermically solvated fails completely. The decrease in the gas-phase basicity of aniline relative to cyclohexylamine (10 kcal/mol) is little larger than the decrease in $\Delta H_{prot,s}°(B)$ (7.1 kcal/mol). In spite of a large PA difference, the ions have nearly identical values of $\Delta H_s°(BH^+)^{el}$. This is nicely explained, however, in terms of charge densities since the cyclohexane and benzene rings have nearly identical polarizabilities and should therefore be equally effective in delocalizing the charge at nitrogen. Thus, the charge densities and electrostatic heats of solution of the cyclohexylammonium ion and the anilinium ions should be about the same, leading to an almost unattenuated solution basicity difference.[39,40] Similarly, the ionic charge densities in pyrrole vs. pyrrolidine, pyridine vs. piperidine, or acetonitrile vs. ethylamine are expected to be similar, and in each case there is little attenuation of basicity changes between these pairs in solution (Table I, Figure 2).[41,42]

Some principles based on this electrostatic enthalpy analysis, which appear to be generally applicable, can now be identified. (1) When inductive effects operate to lower the PA of an amine by destabilization of the ammonium ion, the ion usually has a higher charge density at nitrogen and should be better solvated than normal, thus leading to an attenuation of the $\Delta H_{prot,s}°$ in solution. (2) Conversely, when resonance and polarizability effects raise the PA by stabilizing the ammonium ion through charge delocalization the ion should be less exothermically solvated than normal, again leading to an attenuated effect in $\Delta H_{prot,s}°$ because of this compensating electrostatic term. For these compounds, the electrostatic heats of hydration of the ions generally become increasingly exothermic as the proton affinity decreases, i.e., the more acidic ammonium ions are better solvated. (3) For amines whose PA's are low because of stabilization of the lone pair in the neutral amine (by resonance in aniline and pyrrole or through hybridization effects in pyridine and acetonitrile), rather than by changes in the charge delocalization of the ion, one would expect the effective ionic radius to be about the same as in model compounds of comparable size and polarizability. It is in just these cases that we observe the nearly unattenuated solution basicity changes expected when the electrostatic heats of solution of the ions remain essentially unchanged with changing PA.

Entropy Effects. It now appears that $\Delta H_s°(BH^+)$ values can be reasonably well explained on the basis of hydrophobic and electrostatic effects, but the free energies of protonation (and pK_a's) of amines are sometimes quite different from the enthalpies, $\Delta H_{prot,s}°(B)$, because of the entropy term, $-T\Delta S_{prot,s}°(B)$. Changes in this entropy term must result almost entirely from the solvation terms, $-T\Delta S_s°(B)$ and $-T\Delta S_s°(BH^+)$, since the gas-phase entropy change on protonation is nearly the same for all alkylamines except for symmetry changes.[2,3c,7]

As in our treatment of $\Delta H_s°(BH^+)$, the entropy term, $-T\Delta S_s°(BH^+)$, can be divided into a hydrophobic term equal to $-T\Delta S_s°(B)$ and a remaining electrostatic term, $-T\Delta S_s°(BH^+)^{el}$. The hydrophobic term will become an increasingly unfavorable one as the size of the alkyl group increases and causes more ordering in the surrounding solvent. The electrostatic term, $-T\Delta S_s°(BH^+)^{el}$, should be small, but would become more favorable as the size of the ion increases and the solvent around the ion is less electrostricted on the basis of Born theory and alkali metal ion behavior.[32c,43]

As discussed earlier, $-T\Delta S_s°(B)$ correlates well with $\Delta H_s°(B)$ (Figure 3) as expected for predominant hydrophobic interactions of the alkyl group and the water solvent. At the same time, the $-T\Delta S_s°(BH^+)$ term shows a very similar variation with the size of the alkyl group, except that the changes are slightly larger in $-T\Delta S_s°(BH^+)$ than in $-T\Delta S_s°(B)$ (Figure 4). Values for $-T\Delta S_s°(BH^+)^{el}$ are shown in Table III. Unlike the corresponding electrostatic enthalpies (Table II), the corrected entropy terms in the primary amine series show almost no variation. The electrostatic entropy terms, $-T\Delta S_s°(BH^+)^{el}$, in the series NH_3, $MeNH_2$, Me_2NH, Me_3N show changes in the opposite direction of the $-T\Delta S_s°(BH^+)$ or $-T\Delta S_s°(B)$ term, as expected from the Born eq 5 and from the trends shown in alkali metal plots of $1/r$ vs. $-T\Delta S_s°(M^+)^{el}$ (Figure 7). These electrostatic entropy effects are small, however, and they are nearly swamped out by the larger hydrophobic entropy changes. In fact, *within* a series of primary, secondary, or tertiary amines the small variation of $-T\Delta S_s°(BH^+)^{el}$ is

Table III. Entropies for Hydration and Protonation of Alkylamines at 25°[a]

	$-T\Delta S_{\text{prot,s}}°(\text{B})$[b]	$-T\Delta S_s°(\text{BH}^+)^{\text{el}}$[b]	$RT \ln (\sigma_{\text{BH}^+}/\sigma_{\text{B}})$[b]
NH_3	−0.12	+0.6 (−2.7)[c]	0.82
$MeNH_2$	−1.35	−0.4	0.65
$EtNH_2$	−0.86	0.1	0.65
n-$PrNH_2$	−0.58	0.3	0.65
n-$BuNH_2$	−0.53	0.4	0.65
Me_2NH	−2.66	−1.6	0.41
Me_3N	−4.55	−3.0	0.0

[a] All values in kcal/mol. [b] $T\Delta S_{\text{prot,s}}°(\text{B})$ = constant term − $T\Delta S_s°(\text{BH}^+)^{\text{el}} + RT \ln (\sigma_{\text{BH}^+}/\sigma_{\text{B}})$; where the constant term = $-T\Delta S_{\text{prot,g}}°(\text{B}) - RT \ln (\sigma_{\text{BH}^+}/\sigma_{\text{B}}) + T\Delta S_s°(\text{H}^+)$ = 2.25 kcal/mol, and $-T\Delta S_s°(\text{BH}^+)^{\text{el}} = -T\Delta S_s°(\text{BH}^+) + T\Delta S_s°(\text{B})$ (see Table II). [c] Calculated as in eq 2 using interpolated entropies of hydration of inert gases of comparable radius (ref 12).

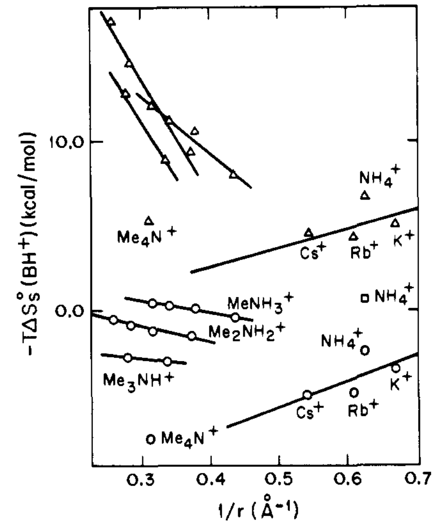

Figure 7. Plot of entropy terms of hydration of alkali cations and alkylammonium ions vs. reciprocal ionic radius at 25°. Absolute entropies of hydration, $-T\Delta S_s°(\text{BH}^+)$, are represented by △, and entropy terms corrected for hydrophobic effects, $-T\Delta S°(\text{BH}^+)^{\text{el}}$, are represented by ○. Two points are shown for the corrected entropy of hydration for NH_4^+; correction using NH_3 as a model (□) and using rare gas (○) data as for the alkali cations. The value for NMe_4^+ was corrected for hydrophobic effects by using extrapolated values from hydrocarbon entropies of solution. The alkali metal lines are drawn to include the Na^+ and Li^+ not shown here. See Tables II and III and Appendix for the entropy and radius data.

opposite to that expected for an electrostatic effect. This appears to be a result of the fact that the hydrophobic effects have not been fully subtracted out of the electrostatic term $-T\Delta S_s°(\text{BH}^+)^{\text{el}}$. This is expected from the slopes of ca. 0.8 in Figure 4, suggesting that hydrophobic effects are about 25% larger in the alkylammonium ions than in the alkylamines.

Although this 25% hydrophobic effect in $-T\Delta S_s°(\text{BH}^+)$ is small, it is just this effect which causes the linear plots of PA vs. $\Delta H_{\text{prot,s}}°(\text{B})$ (Figure 2) to become vertical and irregular when entropy effects are included (see the GB vs. $\Delta G_{\text{prot,s}}°$ plot in Figure 1). This entropy effect almost exactly cancels the attenuated base strengthening effect of the larger alkyl groups on $\Delta H_{\text{prot,s}}°(\text{B})$ (Figure 2), giving nearly identical $\Delta G_{\text{prot,s}}°(\text{B})$ or pK_a values throughout the series of primary or secondary amines.[44] Within the series of methylamines, however, the $T\Delta S_s°(\text{BH}^+)^{\text{el}}$ effects appear to be electrostatic in origin.[45]

The Irregular Order of Solution Basicities of the Methyl Amines. In comparing the solution basicities of the methyl- (or ethyl or propyl) substituted amines, their irregular order has been a problem of much interest.[2-6] The origin of this order can be understood from gas-phase basicity data and enthalpy and entropy effects on solvation. The attenuation of the gas-phase basicity effects on the enthalpies of protonation in solution, $\Delta H_{\text{prot,s}}°(\text{B})$, is stronger in the series of methylamines than within each series of primary, secondary, or tertiary amines because of large electrostatic enthalpy terms, $\Delta H_s°(\text{BH}^+)^{\text{el}}$. On looking at Figure 2, the order of solution enthalpies has completely reversed for trimethylamine vs. ammonia (slope = −6.0), the methylamine and dimethylamine enthalpy effects are attenuated to about slope = 1 with their enthalpies of protonation nearly identical with that of ammonia. The $\Delta H_s°(\text{BH}^+)^{\text{el}}$ terms (Table IV) for these methylamines do not vary linearly in the $1/r$ plots (Figure 5) or in the PA plots (Figure 6), and as a result their attenuation factors differ to produce an irregular order in $\Delta H_{\text{prot,s}}°$. The nonlinearity in Figures 5 and 6 was attributed earlier to the fact that the methylammonium ion and dimethylammonium ion have their charges less symmetrically delocalized over their ionic volumes than the ammonium ion or the trimethylammonium ion. The Trotman-Dickenson explanation[5e] for the irregular order of $\Delta H_{\text{prot,s}}°(\text{B})$ for methylamines is based simply on the number of hydrogen bonds available for solvation. It neglects hydrophobic effects and electrostatic effects which we have shown to be important in $\Delta H_s°(\text{BH}^+)$ in the foregoing discussion. While it is possible that effects based on the number of hydrogen bonds may play a role in determining the enthalpies of protonation in solution,[28] it appears that the major effect is an electrostatic one resulting from changes in charge density at nitrogen.[32]

The order of basicity from the $\Delta H_{\text{prot,s}}°(\text{B})$ term, $MeNH_2 > NH_3 > Me_2NH \gg Me_3N$, is therefore the result of competition between the intrinsic base strengthening effect of methyl substituents and the larger base weakening effect of methyl substituents on $\Delta H_s°(\text{BH}^+)^{\text{el}}$ because of an increasing effective ionic radius and decreasing ionic charge density. Hydrophobic effects on $\Delta H_s°(\text{BH}^+)$ and $\Delta H_s°(\text{B})$ appear to approximately cancel. This order is altered, however, in looking at $\Delta G_{\text{prot,s}}°(\text{B})$ by a significant base strengthening electrostatic entropy term, $-T\Delta S_s°(\text{BH}^+)^{\text{el}}$ (Table IV). This electrostatic entropy term and a small, but still significant, symmetry entropy term, $RT \ln (\sigma_{\text{BH}^+}/\sigma_{\text{B}})$,

Table IV. An Analysis of the Dominant Terms in the Solution Basicities of Alkylamines at 25°: [a] $NH_4^+ + R_3N \rightleftharpoons NH_3 + R_3NH^+$

R_3N	$\delta\Delta G_{\text{prot,s}}°(\text{B})$	=	$\delta(-\text{PA})$	+	$\delta\Delta H_s°(\text{BH}^+)^{\text{el}}$	+	$\delta T\Delta S_s(\text{BH}^+)^{\text{el}}$	+	$\delta RT \ln (\sigma_{\text{BH}^+}/\sigma_{\text{B}})$
Me_3N	−0.8		−21.6		+25.2		−3.6		−0.8
Me_2NH	−2.1		−17.8		+18.3		−2.2		−0.4
$MeNH_2$	−1.9		−11.4		+10.7		−1.0		−0.2
Et_3N	−2.0		−28.5		+30.7		−3.3		−0.8
Et_2NH	−2.4		−22.4		+22.2		−1.7		−0.4
$EtNH_2$	−2.0		−14.4		+13.2		−0.5		−0.2
n-Pr_3N	−1.9		−30.7		+32.7[c]		−(3.1)[b]		−0.8
n-Pr_2NH	−2.4		−24.4		+23.8		−1.3		−0.4
n-$PrNH_2$	−1.8		−15.8		+14.5		−0.3		−0.2

[a] All values in kcal/mol. [b] Assumed from Me_3N and Et_3N. [c] Calculated.

are both base strengthening as one increases the number of methyl substituents on nitrogen. They oppose the strong base-weakening effect of the electrostatic enthalpy term, $\Delta H_s°(BH^+)^{el}$, such that the final order of $-\Delta G_{prot,s}°(B)$ at 25° is $NH_3 < Me_3N \ll MeNH_2 < Me_2NH$. Various enthalpy and entropy terms have so nearly canceled, however, that these free energies differ by only 2.1 kcal/mol. The subtle interplay of these competing effects is illustrated in the analysis of the terms contributing to the basicities of the methyl-, ethyl-, and *n*-propylamines relative to ammonia in Table IV. For trimethylamine the two electrostatic terms exactly cancel the change in PA, leaving only the entropy term from the difference in the symmetries to control the equilibrium with ammonia. Because of the unsymmetrical charge delocalization in $MeNH_3^+$ and $Me_2NH_2^+$, the electrostatic terms, $\Delta H_s°(BH^+)^{el} - T\Delta S_s°(BH^+)^{el}$, are not quite large enough to offset the increase in PA so that the solution basicities of methylamine and dimethylamine are about 2 kcal/mol greater than ammonia. The ethylamines and *n*-propylamines show trends similar to the methylamines except that triethylammonium ion and tri-*n*-propylammonium ion appear to have a less symmetrical charge distribution than trimethylammonium ion (see deviations from lines in Figure 5) and smaller electrostatic terms so that their solution basicities are close to the other alkyl amines (2.1 ± 0.3 kcal/mol higher than ammonia for all the ethyl- and *n*-propylamines).

Generalizations and Conclusions. In a general treatment of solvent effects in acid-base equilibria between related pairs of molecules A and B in solution, Hepler[46,5a] has considered the enthalpy, $\Delta H°$, and entropy, $\Delta S°$, terms for such reactions to be composed of internal (gas-phase) effects and external (solvent) effects (eq 7 and 8). The $\Delta S_{int}°$ term should be negligible,[7] so $\Delta S°$ should equal $\Delta S_{ext}°$.[46]

$$\text{for } AH^+ + B \rightleftarrows A + BH^+ \text{ in solution}$$

$$\Delta H° = \Delta H_{int}° + \Delta H_{ext}° \tag{7}$$

$$\Delta S° = \Delta S_{int}° + \Delta S_{ext}° \tag{8}$$

$$\Delta G° = \Delta H_{int}° + (\beta - T)\Delta S° \cong \Delta H_{int}° \tag{9}$$

$$\text{where } \beta \cong T$$

In early versions of this treatment (eq 9), it was suggested that $\Delta G°$ should closely approximate the internal or intrinsic basicity (PA) order.[46-48] Equation 9 is not generally applicable, however, because the assumed cancellation of $\Delta H_{ext}°$ and $-T\Delta S_{ext}°$ is often incomplete.[48] For hydrophobic solvation effects, $\Delta H_{ext}°$ and $-T\Delta S_{ext}°$ nearly cancel with $-T\Delta S_{ext}°$ usually about 10% larger (Figure 3). For electrostatic solvation of ions, however, the entropy term is only about 10% of the enthalpy term and provides very little compensation (Figure 7).[25] Modification of eq 9 to include a term that puts the uncompensated $\Delta H_{ext}°$ term proportional to $\Delta H_{int}°$ with a proportionality constant γ (eq 10)

$$\Delta G° = (1 + \gamma)\Delta H_{int}° + (\beta - T)\Delta S° \cong (1 + \gamma)\Delta H_{int}° \tag{10}$$

$$\text{where } \beta \cong T$$

has been suggested by Hepler.[47c,d] This approach properly accounts for the proportionality between $\Delta H_{int}°$ and $\Delta G°$ observed in many cases.[37,49-54] Since $\Delta S°$ is proportional to $\Delta H_{int}°$ for various families of alkylamines,[55] and in the other compounds[37,50-52] where data are available, we propose a simplification of these equations wherein external enthalpies and entropies are both assumed to be proportional to $\Delta H_{int}° = \delta PA$ with proportionality constants h and s (eq 11-13). From these equations and eq 7 and 8 the solution enthalpies, $\Delta H°$, and free energies, $\Delta G°$, are predicted to both be proportional to $\Delta H_{int}° = \delta PA$.[56]

$$AH^+ + B \rightleftarrows A + BH^+ \tag{11}$$

$$\Delta H_{ext}° = h\Delta H_{int}° \tag{12}$$

$$-T\Delta S_{ext}° = Ts\Delta H_{int}° \tag{13}$$

$$\Delta H° = (1 + h)\Delta H_{int}° \tag{14}$$

$$\Delta G° = (1 + h + Ts)\Delta H_{int}° \tag{15}$$

With the availability of intrinsic gas-phase basicities, it is now possible to test the generality of these relationships for a variety of acid-base equilibria (eq 11). Indeed, it appears that these equations hold for such diverse structural types as pyridines,[37] fluorinated alkylamines,[49] phenols,[50] benzoic acids,[51] aliphatic carboxylic acids,[52] aliphatic alcohols,[53] and the halogen acids.[54] Quite diverse values of h and s are found in these systems, however. The sign of h is generally negative but its value varies. For a series of primary, secondary, or tertiary alkylamines, the value of h is −0.83 to −0.80 reflecting the five- to sixfold attenuation ($1 + h = \frac{1}{5}$ to $\frac{1}{6}$) of $\Delta H_{int}°$ by the compensating $\Delta H_{ext}° = \delta\Delta H_s°(BH^+)^{el}$ term. In this case, the sign of Ts is also negative and ca. −0.15 such that $\Delta G° \approx 0$. Usually s is positive so that $-T\Delta S_{ext}°$ compensates for $\Delta H_{ext}°$, but the incomplete cancellation of hydrophobic effects in $\Delta H_s°(B)$ and $\Delta H_s°(BH^+)$ causes s to be negative here as discussed earlier.

Polarizability effects tend, then, to be very strongly attenuated in solution, leading to many of the reversals that make gas-phase and solution basicities so different.[6] For negative ions it appears that this attenuation is even stronger. For the alcohols from methanol to *tert*-butyl alcohol the compensating solvent effect, $\Delta H_{ext}°$, is twice as strong as $\Delta H_{int}°$, so that $\Delta H°$ is *inversely* proportional to $\Delta H_{int}°$ with a slope of $1 + h \simeq 1$.[53] Arnett reports a good correlation of $\Delta H_{ext}°$ with $1/r$ for the alcoholate anions as expected from the Born equation.[53]

Inductive and resonance effects in aliphatic amines and substituted pyridines show reasonably good correlations of $\Delta H_{prot,s}°$ and PA and a threefold attenuation ($h \simeq -0.75$). For pyridines the entropy term $-T\Delta S_{ext}°$ is quite small ($Ts < 0.1$) except for the ortho substituents.[37] Such inductive effects in negative ions (phenolate,[50] benzoate,[51] and carboxylate[5]), however, are fully attenuated, such that $\Delta H° \simeq 0$ ($h \simeq -1.0$). In these cases the free energies, $\Delta G°$, are, nevertheless, linearly related to $\Delta H_{int}°$, since the entropy terms are approximately linear in $\Delta H_{int}°$ with $Ts \simeq 0.2$ for phenols and aliphatic carboxylic acids, and $s \simeq 0.1$ for substituted benzoic acids.

As noted in the earlier discussion, there are some cases in which changes in hybridization or resonance stabilization of the neutral molecules play a larger role in determining $\Delta H_{int}°$ than stabilization effects in the ions, e.g., aniline vs. cyclohexylamine or pyridine vs. piperidine. In these instances, the PA's are unattenuated in solution ($h \simeq 0$) and $\Delta S°$ is small because the ionic radii are nearly the same in the two ions.

It has often been suggested,[40,46,47a,57] that free energies, $\Delta G°$, of proton transfer reactions (eq 11) in solution should more closely approximate the internal energy of reaction, $\Delta H_{int}° \simeq \Delta E_{int}°$, than the enthalpies, $\Delta H°$, of proton transfer in solution.[58] This conclusion has, in large part, been based on analyses of entropy controlled negative ion equilibria of the type above, where $\Delta H°$ does not vary appreciably, but $\Delta G°$ behaves as expected on the basis of internal effects. For pyridinium ions, however, there is little difference between $\Delta G°$ and $\Delta H°$. Moreover, for primary, secondary, and tertiary alkylamine series, just the opposite is observed; $\Delta H_{\mathrm{prot,s}}°(\mathrm{B})$ correlates better with PA than does $\Delta G_{\mathrm{prot,s}}°(\mathrm{B})$. In fact, both $\Delta H°$ and $\Delta G°$ usually correlate with $\Delta H_{\mathrm{int}}°$ in a linear fashion as in eq 14 and 15, but $\Delta G°$ is often closer to $\Delta H_{\mathrm{int}}°$ because of the compensating entropy term $-T\Delta S_{\mathrm{ext}}°$.

In conclusion, we have suggested an analysis of solution basicities of alkylamines which well accommodates the available data within the framework of hydrophobic and electrostatic solvation. We have shown (1) that the hydrophobic and small polar solvation effects in the neutral amine cancel similar effects in the ammonium ions and (2) that the remaining solvation terms causing the attenuation of proton affinities in solution may be considered to be electrostatic in origin and to correlate with ΔPA, i.e., the internal enthalpy change, $\Delta H_{\mathrm{int}}°$. These attenuation factors (expressed in the h and s parameters in eq 11-15) vary for different types of substituent effects in a manner qualitatively consistent with electrostatic theory. A more rigorous and quantitative understanding of these different substituent effects for both positive and negative ions and in solvents other than water remains a problem for more sophisticated theoretical approaches. The electrostatic correlations presented here, however, appear reasonable theoretically, and they provide an attractively simple and predictive method for the analysis of solvation effects on ionic equilibria.

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Appendix

Ionic Radius Assignments of Alkylammonium Ions. In order to compare hydration energies and ionic radii of alkali metal ions and protonated amines, assignment of a consistent set of radii to both sets of cations is desirable. Ideally gas-phase ionic radii should be used for the Born treatment. Such radii are only available for alkali metal ions,[26] but they correlate well with the more available crystal radii, so crystal radii have been used here. While a number of methods[59] have been used to estimate crystal ionic radii of the alkali cations, we have chosen to use the recent values of Morris[60] obtained by analysis of electron density maps from x-ray crystallography. A good correlation is observed between Morris radii and the crystal lattice cell dimensions[61] of the respective halides. A radius of 1.63 Å for NH_4^+ on the Morris scale is thus calculated from Wyckoff's[61] crystal data of ammonium halides. This is in good agreement with other estimates[59b,d-f] of the crystal radius of NH_4^+ relative to the alkali metal ions.

We have found that a good approximation to the size of alkylammonium ions is provided by their partial ionic molar volumes in water.[62,24c] These partial molar volumes are very nearly equal to the best estimates of ionic volumes as calculated from some known crystal radii,[63] or from the molar volumes of isoelectronic hydrocarbons[64] for the larger alkylammonium ions. The radii determined from partial molal volumes are calculated for spheres of equal volume according to eq 16. In a plot of these radii, $r_{\bar{V}}$, vs. known

$$\bar{V} = {}^{4}\!/_{3}\pi N o r_{\bar{V}}^{3} \qquad (16)$$

crystal radii, the smaller alkali cations do not fall on the same straight line that is determined from the amines. Electrostriction causes the small alkali metal ion partial molal volumes to be abnormally small. There is a good correlation, however, between estimates of ionic radius based on known crystal radii,[63] partial molar volumes of amines[65] and of alkylammonium ions,[66] molar volumes of analogous hydrocarbons, molar volumes of corresponding neutral amines,[64] and polarizabilities determined from indices of refraction of the neutral amines.[64,66] The maximum deviation of estimates of these radii is only ca. ±0.2 Å. We have chosen to use partial molar volumes as the basis of the radii chosen (except for the alkali metal ions) because a rather complete and self-consistent set of experimental values are available. The radii used in Figure 6 were Morris'[60] crystal radii for the alkali metal ions. The alkylammonium ion radii are derived from conventional[67] partial ionic molal volumes[68] adjusted to absolute volumes using Zana and Yeager's[69] value of $-5.4\ \mathrm{cm^3/mol}$ for the absolute partial molal volume of the proton.

The heats of hydration in Figure 6 have been corrected for hydrophobic effects in both the ammonium ion and alkali cation data. For corrections to the tetraalkylammonium ions,[70] extrapolated heats of hydration based on the hydrocarbon data of Wauchope[12b] were used.

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NOTE ADDED IN PROOF. The absolute proton affinity of ammonia appears to be ca. 202 kcal/mol on the basis of recent work (see footnote 12 in the preceding paper in this issue). These changes in absolute PA's lower all of the alkylamine GB's and PA's in Table I by ca. 7 kcal/mol. This raises the $\Delta G_s°(BH^+)$, $\Delta H_s°(BH^+)$, and $\Delta H_s°(BH^+)^{el}$ values in Tables I and II by ca. 7 kcal/mol for the alkylamines and by ca. 5 kcal/mol for ammonia. This also raises all the alkylammonium ion data points in Figure 5 except for Me_4N^+ and Et_4N^+. Such a change in Figure 5 puts the ammonia point (○) 9 kcal/mol above the line and the point □ 3 kcal/mol above the line, indicating that the hydrogen-bonding interaction in NH_4^+ is ca. 9 kcal/mol, and only ca. 3 kcal/mol more than in NH_3. This 9 kcal/mol hydrogen bonding term on top of the large electrostatic term for $\Delta H_s°(BH^+)^{el}$ is remarkably consistent with the 2–4 kcal/mol differences between the lines in Figure 6 attributed to hydrogen-bonding effects. Of the 27 kcal/mol difference in $\Delta H_s°(BH^+)^{el}$ between NH_3 and Me_3N, however, only ca. 3 kcal/mol can be attributed to hydrogen-bonding effects not present in the neutral amines. A 32 kcal/mol difference would be expected in heats of hydration simply from radius effects in Figure 5, but this effect is apparently diminished by 12 kcal/mol because of the asymmetry of Me_3NH^+.

(29) The $\Delta H_s°(H_3O^+)^{el} = -100$ kcal/mol (see footnote *d*, Table I) is calculated from eq 3 using $PA(H_2O) = 168$ kcal/mol [S. R. Chong, R. A. Meyers, and J. R. Franklin, *J. Chem. Phys.*, **56**, 2427 (1973)] and a small inert gas hydrophobic correction. The ionic radius (1.31 Å) is calculated to the approximation that the ion is spherical from x-ray data: G. D. Carpenter, *Acta Crystallogr.*, **12**, 17 (1959).

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(33) The simple electrostatic arguments presented here are based on a macroscopic view of the solvent and therefore are limited in quantitative application. Hopefully, other approaches such as that of Kirkwood and Westheimer and more quantitative microscopic approaches can be developed. For example, hydration of ammonium ions can be analyzed at a microscopic level by considering individual heats of association for the first several waters, and then using the macroscopic electrostatic Born theory for the remaining hydration energy of this larger, partially hydrated ion. For $NH_4^+ \rightarrow NH_4^+(H_2O)_4$ $\Delta G° = -29.6$ kcal/mol (ref 31) and for $Me_3NH^+ \rightarrow Me_3NH^+(H_2O)$ $\Delta G° = -7.3$ kcal/mol [P. Kebarle, private communication]. This difference of 22.3 kcal/mol compares well with the overall difference in $\Delta G_s°(BH^+)$ between NH_4^+ and Me_3NH^+ of 24 kcal/mol, since the ions $NH_4^+(H_2O)_4$ and $Me_3NH^+(H_2O)$ should have comparable sizes and hydration energies. A comparison of $\Delta G°$'s for association of the first five water molecules with NH_4^+ and Me_3NH^+ shows a total of −32.6 kcal/mol for NH_4^+ and ca. −16 kcal/mol for Me_3NH^+. Even for the first water, $\Delta G°(NH_4^+) = -11.4$ and $\Delta G°(Me_3NH^+) = -7.3$ kcal/mol, showing that these hydration energies depend on ion size.

(34) It has been suggested that hydrogen bonding effects account for solvation effects of alkylammonium ions, but that they are less important for phosphonium and sulfonium ions (ref 6). The $\Delta G_s°(BH^+)^{el}$ terms for H_3O^+, NH_4^+, Me_3NH^+, PH_4^+, and Me_3PH^+ calculated from PA's and pK_a's in ref 6 correlate well with reciprocal ionic radii. The phophonium ionic radii are based on correlations showing P–H and P–C bonds 0.40 Å longer than N–H and N–C bonds; "Tables of Interatomic Distances and Configuration in Molecules and Ions", L. E. Sutton, Ed., The Chemical Society, London, Burlington House, W.1, 1958. This plot is coincident with the alkali metal ion plot of $\Delta G_s°(M^+)^{el}$ (ref 25), with a correlation coefficient of 0.97 for these five ions and the alkali metal ions. Similarly, $\Delta H_s°(BH^+)^{el}$ terms in fluorosulfuric acid (ref 6) correlate fairly well with $1/r$ for these ions, with a slope one-half that of alkali metal ions in water.

(35) Some small pK_a effects in nonaqueous solvents for alkylamines have been interpreted in terms of hydrogen bonding effects, but possible ambiguities in ion pairing, solvent effects, and entropy effects make these data difficult to interpret (see discussion in ref 6b).

(36) The $-T\Delta S_{prot,s}°(B)$ for $CF_3CH_2NH_2$ is somewhat more positive (by 1.52 kcal/mol) than for $CH_3CH_2NH_2$. This may be the result of an unfavorable electrostatic entropy term for $CF_3CH_2NH_3^+$, assuming that hydrophobic and polar effects in neutral amine solvation can be subtracted from the effects in the ion (see discussion of entropy effects).

(37) D. H. Aue, H. M. Webb, M. T. Bowers, C. L. Liotta, C. J. Alexander, and H. P. Hopkins, in press.

(38) See K. B. Wiberg, "Physical Organic Chemistry", Wiley, New York, N.Y., 1964, p 282 ff. The Kirkwood–Westheimer field model provides a useful alternative to the Born electrostatic theory for the treatment of solvent effects in molecules showing inductive effects and will be developed further elsewhere.

(39) The small (22%) attenuation of $\Delta H_{prot,s}°(B)$ for aniline may be the result of an attenuated inductive effect of the sp^2 ring carbon. This inductive effect is estimated to be about equal to the effect of resonance stabilization of aniline: B. M. Webster, *Recl. Trav. Chim. Pays-Bas*, **71**, 1171 (1952).

(40) It has been noted that the changes in entropy terms, $-T\Delta S_{prot,s}°(B)$, for aniline cause the $\Delta G_{prot,s}°(B)$ changes to approach the PA changes somewhat more closely than the $\Delta H_{prot,s}°(B)$ changes do (ref 9). This may in some cases be explained in terms of small electrostatic entropy terms, $-T\Delta S_s°(BH^+)^{el}$, which partially compensate for the attenuation by the electrostatic enthalpy term $\Delta H_s°(BH^+)^{el}$ (see ref 36).

(41) The deviation of the pyridine point in Figure 2 from the line of unit slope through piperidine can be explained as a result of the resonance delocalization in pyridine which should make pyridinium ion less exothermically solvated than piperidinium ion. Similarly, pyrrole has a negative attenuation in $\Delta G_{prot,s}°$ relative to pyrrolidine, which may result from such charge delocalization in the ion. Pyrrole appears to protonate on carbon: D. H. Aue, W. R. Davidson, and M. T. Bowers, unpublished work.

(42) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **97**, 4137 (1975).

(43) Since the Born entropy is a derivative (eq 5), it should not be as quantitatively reliable as the free energy. Since the entropy effect is small, however, the Born enthalpy should be as reliable as the free energy (ref 25).

(44) The tertiary amines show this cancellation to a lesser degree. The $\Delta G_{prot,s}°(B)$ for isobutylamine appears unusual. More complete data for $\Delta G_s°(B)$ would be desirable in analyzing these effects.

(45) Heat capacities of protonation of alkylamines are known in several cases and have been observed to correlate with the corresponding

$\Delta S_{\mathrm{prot,s}}^\circ$ values reasonably well: see D. H. Everett, in ref 10b, p 1 ff; F. M. Jones, Ph.D. Thesis, University of Pittsburgh, 1970, p 354 ff; ref 6b; and ref 24c. Using the same approach as for the entropy terms here, the hydrophobic heat capacities of solution of the free bases can be assumed to cancel the corresponding hydrophobic terms in the ammonium ions, leaving $\Delta C_{\mathrm{p,prot,s}}^\circ$ equal to the electrostatic $\Delta C_{\mathrm{p,s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$ term in $\Delta C_{\mathrm{p,s}}^\circ(\mathrm{BH^+})$ (see ref 7). In the series NH_3, $MeNH_2$, Me_2NH, and Me_3N the values of $\Delta C_{\mathrm{p,s}}^\circ(\mathrm{BH^+})^{\mathrm{el}} = \Delta C_{\mathrm{p,prot}}^\circ$ vary from +1.1 to −41.1 cal mol^{-1} deg^{-1}, as expected empirically from alkali metal ion heat capacities (note that these changes are of opposite sign expected for electrostatic effects, however, ref 24c). As in the case of the electrostatic entropy terms, however, the series of primary or secondary amines show only small changes (−5.0 to −3.1 cal mol^{-1} deg^{-1} from $MeNH_2$ to *t*-$BuNH_2$), suggesting residual hydrophobic effects.

(46) L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, **65**, 811 (1961).

(47) (a) C. D. Ritchie and W. F. Sager in "Progress in Physical Organic Chemistry", Vol. 2, Wiley-Interscience, New York, N.Y., 1969; (b) J. W. Larson and L. G. Hepler in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969; (c) L. G. Hepler and E. M. Wooley, ref 24c, Chapter 3; (d) J. W. Larson and L. G. Hepler, *J. Org. Chem.*, **33**, 3961 (1968).

(48) It can be seen from Figure 1 that eq 9 is not applicable to alkylamines.

(49) D. H. Aue, H. M. Webb, W. R. Davidson, and M. T. Bowers, to be published.

(50) R. T. McIver, Jr., and J. H. Silvers, *J. Am. Chem. Soc.*, **95**, 8462 (1973).

(51) R. Yamdagni, T. B. McMahon, and P. Kebarle, *J. Am. Chem. Soc.*, **96**, 4035 (1974).

(52) R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, **95**, 4050 (1973); R. Yamdagni and P. Kebarle, *Can. J. Chem.*, **52**, 861 (1974); K. Hiraoka, R. Yamdagni, and P. Kebarle, *ibid.*, **95**, 6833 (1973).

(53) E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96**, 5638 (1974); R. T. McIver, Jr., J. A. Scott, and J. M. Riveros, *ibid.*, **95**, 2706 (1973).

(54) J. I. Brauman, J. R. Eyler, L. K. Blair, M. J. White, M. B. Comisarow, and K. C. Smyth, *J. Am. Chem. Soc.*, **93**, 6360 (1971).

(55) The proportionality of $\Delta H_{\mathrm{ext}}^\circ = \Delta H_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$ and $\Delta H_{\mathrm{int}}^\circ = \delta \mathrm{PA}$ for alkylamines is illustrated in the plot in Figure 6. A similar plot of $-T\Delta S_{\mathrm{ext}}^\circ = -T\Delta S_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$ vs. PA is linear within the primary, secondary, or tertiary amine series.

(56) The approach in eq 11–15 is attractive because of its simplicity and because it derives all of the solvation effects from a single internal property of the acid–base reaction, $\Delta H_{\mathrm{int}}^\circ$.

(57) R. P. Bell, "The Proton in Chemistry", Cornell University Press, Ithaca, N.Y., 1959, pp 70–73.

(58) A related suggestion has been made by Bell (ref 57) and by Coetzee and Ritchie (ref 46a) that, in solution, the free energy, ΔG°, should be closer than ΔH° to the enthalpy or energy at absolute zero, $\Delta H_0^\circ \simeq \Delta E_0^\circ$. This is the quantity calculated from quantum mechanical or electrostatic models. In the gas phase, $\Delta H_{\mathrm{g}}^\circ$ should equal $\Delta G_{\mathrm{g}}^\circ$ since $\Delta S_{\mathrm{g}}^\circ \simeq 0$, and $\Delta H_{\mathrm{g}}^\circ \simeq \Delta H_{0,\mathrm{g}}^\circ$ since $\Delta C_{\mathrm{p,g}}^\circ \simeq 0$ and $\Delta(PV)_{\mathrm{g}} \simeq 0$ for reaction 11. The argument in solution is that the second heat capacity integral in eq ii will probably partially cancel the first integral, making ΔG° closer to ΔH_0° at 25° than ΔH°. Some confirmation of this suggestion

$$\Delta H^\circ = \Delta H_0^\circ + \int_0^T \Delta C_{\mathrm{p}}^\circ \, \mathrm{d}T \tag{i}$$

$$\Delta G^\circ = \Delta H_0^\circ + \int_0^T \Delta C_{\mathrm{p}}^\circ \, \mathrm{d}T - T\int_0^T \frac{\Delta C_{\mathrm{p}}^\circ}{T} \, \mathrm{d}T \tag{ii}$$

comes from our analysis of the alkylamine thermodynamic data in terms of electrostatic contributions. In considering the $\Delta G_{\mathrm{s}}^\circ(\mathrm{B})$ data in Table II, the changes are minimal. As expected for hydrophobic interactions, $\delta\Delta G_{\mathrm{s}}^\circ(\mathrm{B})$ could be equal to $\delta\Delta H_{0,\mathrm{s}}^\circ(\mathrm{B})$ for reaction 11, since the interaction energy should be very small between the hydrocarbon and solvent at absolute zero. For $\delta\Delta G_{\mathrm{s}}^\circ(\mathrm{BH^+})$ the hydrophobic term in $\delta\Delta H_{\mathrm{s}}^\circ(\mathrm{BH^+}) \simeq -T\delta\Delta S_{\mathrm{s}}^\circ$ $(\mathrm{BH^+})$ has been approximately subtracted from $\delta\Delta H_{\mathrm{s}}^\circ(\mathrm{BH^+})$, so that $\delta\Delta G_{\mathrm{s}}^\circ(\mathrm{BH^+}) \simeq \delta\Delta H_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$ (see Tables II and III). This electrostatic term represents an electrostatic interaction energy which should persist at absolute zero, again in accord with the suggestion that $\delta\Delta H_{0,\mathrm{s}}^\circ(\mathrm{BH^+}) \simeq \delta\Delta G_{\mathrm{s}}^\circ(\mathrm{BH^+})$. The $\delta\Delta G_{\mathrm{prot,g}}^\circ(\mathrm{B})$ term approximates the energy of proton transfer at absolute zero in the gas phase as expected. Finally the $\delta\Delta G_{\mathrm{prot,s}}^\circ(\mathrm{B})$ term is approximately the sum of the electrostatic interaction term and the intrinsic gas-phase basicity term (which should have the symmetry entropy term removed) at absolute zero. The small changes in $\delta\Delta G_{\mathrm{prot,s}}^\circ(\mathrm{B})$ are again the result of a near cancellation between the gas-phase basicity terms and the electrostatic terms. While this analysis of energy terms at absolute zero is in accord with our treatment of the alkylamine basicities, it should be noted that this analysis does *not* imply that the change in free energy, $\delta\Delta G_{\mathrm{prot,s}}^\circ$, is equal to the intrinsic basicity change at absolute zero, $\delta\Delta H_{0,\mathrm{prot,g}}^\circ(\mathrm{B})$. This would only be true if the electrostatic entropy term, $-T\delta\Delta S_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$, were to fully compensate the electrostatic enthalpy term, $\delta\Delta H_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$, as initially postulated by Hepler (eq 9). In fact, $-T\Delta S_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$ is only a small fraction of $\Delta H_{\mathrm{s}}^\circ(\mathrm{BH^+})^{\mathrm{el}}$, as noted previously.

(59) (a) V. M. Goldschmidt, *Skr. Nor. Vidensk.-Akad. Oslo*, *1*, 21 (1926); (b) L. Pauling, "Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960; (c) B. S. Gourary and F. J. Adrian, *Solid State Phys.*, **14**, 127 (1960); (d) T. C. Waddington, *Trans. Faraday Soc.*, **62**, 1482 (1968); (e) M. F. C. Ladd, *Theor. Chim. Acta*, **12**, 333 (1968); (f) H. F. Halliwell and S. C. Nyburg, *Trans. Faraday Soc.*, **59**, 1126 (1963).

(60) D. F. C. Morris, *Struct. Bonding (Berlin)*, **4**, 63 (1968). Morris' radii are virtually identical with those of ref 59c using the same technique.

(61) R. W. G. Wyckoff, "Crystal Structures", Vol. 1, 2nd ed, Interscience, New York, N.Y., 1963, see also T. R. R. McDonald, *Acta Crystallogr.*, **13**, 113 (1960).

(62) J. E. Desnoyers and C. Jolicoeur, "Modern Aspects of Electrochemistry", No. 5, J. O'M. Bockris and B. E. Conway, Ed., Plenum Press, New York, N.Y., 1969.

(63) For Et_4N^+, $r_{\bar{V}} = 3.85$ Å and $r_{\mathrm{crystal}} = 3.47$ Å [see E. Watt and H. M. Powell, *J. Chem. Soc.*, 1872 (1958)] from an electron density projection of Et_4NI. For *n*-Pr_4N^+, $r_{\bar{V}} = 4.35$ Å and $r_{\mathrm{crystal}} = 4.25$ Å [see A. Zalkin, *Acta Crystallogr.*, **10**, 557 (1957)] from an electron density projection of *n*-Pr_4NBr. For Me_4N^+, $r_{\bar{V}} = 3.22$ Å and $r_{\mathrm{crystal}} = 3.22$ Å from a packing diagram and a_0 cell dimensions [see R. W. G. Wyckoff, "Crystal Structures", Vol. 1, Interscience, New York, N.Y., 1963].

(64) (a) Calculated from densities from "The Handbook of Chemistry and Physics", 50th ed, R. C. Weast, Ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1970. (b) Density of *n*-Pr_4C is assumed to be 0.77 cm^3/g. (c) Density of *n*-Bu_4C is 0.7945 cm^3/g [G. Desgrandchamps, A. Dehryarche, and A. Maillard, *Bull. Soc. Chim. Fr.*, 264 (1961)].

(65) M. V. Kaulgud and K. J. Patel, *J. Phys. Chem.*, **78**, 714 (1974).

(66) R. F. Gould, Ed., *Adv. Chem. Ser.*, **No. 29** (1961).

(67) The term conventional refers to values relative to the $\bar{V}$ of H^+ taken to be zero.

(68) See ref 24, p 67.

(69) R. Zana and E. Yeager, *J. Phys. Chem.*, **71**, 521 (1967).

(70) Heats of hydration of tetraalkylammonium ions are taken from M. F. C. Ladd, *Z. Phys. Chem.* (*Frankfurt am Main*), **72**, 91 (1970), and are based on calculations of crystal energies of the halide salts. A prior study [R. H. Boyd, *J. Chem. Phys.*, **51**, 1470 (1969)] incorporated nonelectrostatic potentials in a similar calculation resulting in generally higher and less regularly changing heats of hydration in going from Me_4N^+ to *n*-Pr_4N^+. The estimated accuracies in these heats of hydration were ±1 kcal for Me_4N^+ and at least ±2 kcal/mol for Et_4N^+ and *n*-Pr_4N^+ (ref 12b).