

THE LOCAL REACTION FIELD (LRF) MODEL OF SOLVENT EFFECTS AS THE BASIS FOR THE ANALYSIS OF THE BASICITY OF ALKYLAMINES IN AQUEOUS SOLUTION

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ABSTRACT

The Local Reaction Field (LRF) model of solvent effects, implemented within the SCF-CNDO/2 approximation, has been applied to the study of the acid-base equilibrium of alkylamines in aqueous solution. Semi-quantitative results concerning the thermodynamics of ammonium ion solvation have been obtained. These results, combined with gas phase proton affinities (P.A.) are used to discuss the solution equilibria of protonation of alkylamines. The use of a convenient partition for the free energy of the solute-solvent system allows us to separate the intrinsic (gas phase) contributions from those due exclusively to solvation. The results are in qualitative agreement with experimental data. Finally the relevance of the entropic contribution to the protonation process in solution in these systems is discussed.

1. INTRODUCTION

The irregular order of the aqueous basicities of alkylamines has been the subject of increasing attention over the years [1-4]. The main conclusion issued from several experimental studies devoted to this problem, suggest that the observed order ($\text{NH}_3 < \text{primary} < \text{secondary} < \text{tertiary}$), cannot be explained on the basis of any single cumulative substituent effect such as inductive effect [4,5].

The recently developed ion-cyclotron resonance technique for the measurement of quantitative gas-phase basicities has introduced a crucial element in the study of this anomaly; indeed, these studies have shown that the intrinsic (gas phase) basicity of alkylamines increases regularly with increasing substitution thus suggesting that the observed anomalies in pKa result from solvation effects rather than from intrinsic effects [3-5]. Furthermore, the difference between gas phase and solution basicities in these systems appear to be strongly related to entropies and enthalpies of solvation [4-6].

From a theoretical point of view, it was found that quantum mechanical calculations reproduce quite well the experimental trends of the gas phase basicity of amines [7,8]. However, very little theoretical work has been devoted to the study of such acid-base equilibria in solution.

Recently, the Virtual Charge Model (VCM) of solvent effects proposed by Constanciel and Tapia [9] has been applied to the study of the relative protonation energies of alkylamines in aqueous solution [10]. In that work, the

solvation energies of the neutral (B) and protonated (BH^+) species have been calculated on that basis of the generalized Born formula (GBF). The calculated solvation energies (which represent, within the GBF approach, a *free energy* of solvation) have been compared with the experimental enthalpies of solvation reported by Aue et al. [4]. This procedure implies complete neglect of the entropy of solvation which, in this case, is not well justified. In fact, as it was concluded by Aue et al. [4], the free energy of protonation (and pKa) of amines are sometimes quite different from their enthalpy because the entropic contribution $-\Delta S_{s,\text{prot}}(\text{BH}^+)$ is not negligible. The change in the entropy term results almost entirely from the electrostatic solvation term, $\Delta S_s(\text{BH}^+)$, of the protonated species [4,5]. Thus, the conclusions suggested in reference [10] are to be taken with care because they follow from the comparison between two distinct thermodynamic functions.

Within the continuum models of solvent effects, based on the GBF, the calculation of the electrostatic entropy of solvation for both, monoatomic and molecular ions, is often greatly overestimated [11,12]. This problem is mainly traced to the fact that dielectric saturation effects are neglected and as a result, the solvent polarization contribution is considered to be completely orientational in nature [12,13]. An extension of the GBF approach that allows local dielectric effects to be taken into account has been shown to work reasonably well in the calculation of free energies [12] and entropies of solvation [13] of molecular ions. As a result, a complete calculation of the thermodynamics of ion solvation is actually possible and we would like to show here its utility in the study of the acid-base equilibria of aliphatic amines.

In this work, we present a detailed theoretical analysis of the gas and aqueous phase basicities of a series of alkylamines and discuss the solvation effects that is apparently responsible for the observed differences.

2. THEORY

In the absence of other solvent effects than those due to electrostatic forces, the total free energy of the solute-solvent system, $A_T(\epsilon_B, P)$, formed by a molecule (or a molecular ion) immersed in a polarizable environment can be written as a function of the temperature-dependent bulk dielectric constant ϵ_B and the one-particle density matrix P as follows:

$$G_T(\epsilon_B, P) = E(1, P) + \Delta G_S(\epsilon_B, P) \quad (1)$$

where $E(1,P)$ represents the total energy of the molecular system in vacuum and $\Delta G_S(\epsilon_B,P)$ is the electrostatic solvation energy which corresponds to the free energy variation of the solute-solvent system when the solute is inserted isothermally into the solvent [14]. Thus, the solvation term $\Delta G_S(\epsilon_B,P)$ results from the sum of two contributions:

$$\Delta G_S(\epsilon_B,P) = E_{\Sigma-S}(\epsilon_B,P) + E_{\Sigma}^{pol}(\epsilon_B,P) \quad (2)$$

where $E_{\Sigma-S}(\epsilon_B,P)$ is the electrostatic solute-solvent interaction energy and $E_{\Sigma}^{pol}(\epsilon_B,P)$ is the solvent polarization energy.

The partition is such that, based on statistical arguments [14], it may be concluded that roughly, the first term in Equation (2) is thermodynamically consistent with an enthalpic contribution to the free energy of solvation whereas the second one is related to the electrostatic entropy of solvation [13]. However, as we discussed in previous publications [12,13], the solvent molecules may polarize in two distinctly different ways: Indeed it may be that the solvent molecules more closely bound to the solute (i.e. the first solvation shells), are highly influenced by the orientating effect of the reaction field and almost independent of the temperature-induced effects due to the coupling with the thermostat. On the other hand, the solvent molecules placed beyond the first solvation shells (i.e. the bulk solvent), can be expected to be electronically relaxed with respect to the reaction field but dependent on the temperature averaging effects. As a result, the polarization of the solvent molecules in the vicinity of the ion is mainly electronic, whereas the bulk solvent polarization is essentially orientational. From a dielectric point of view, the difference between these two different and opposite effects induced by the reaction field and the thermostat should manifest itself by a different value of the dielectric constant. Thus dielectric saturation may be regarded as a system characterized by two dielectric constants: ϵ_L in the neighborhood of the solute and ϵ_B , in the bulk region. Based on this argument, an improved version of the GBF method for the computation of the free energy of solvation in molecular systems was presented recently [12]. The results obtained in the case of ammonium ions solvation were quite encouraging. Nevertheless, the entropy of solvation was not derived rigorously in our previous paper; rather it was equated to the orientational polarization energy of the solvent [13]. This problem is solved here, by using the direct differentiation of the free energy of solvation, which is expressed within the SCF-CNDO/2 approach as follows:

$$\Delta G_S(\epsilon_L,\epsilon_B,P) = -\frac{1}{2} \left(1 - \frac{1}{\epsilon_L}\right) \sum_{AB} \sum Q_A(P) Q_B(P) \gamma_{AB} \quad (3)$$

with respect to temperature T , according to the classical expression

$$\Delta S = -\left(\frac{\partial \Delta G}{\partial T}\right)_{V,D} \quad (4)$$

where V is the volume of the dielectric and D , the dielectric displacement vector. Since the only temperature-dependent variable in Equation (3) is ϵ_B , one obtains, after applying relation (4):

$$T\Delta S^o = -\frac{1}{2} \frac{(T\partial L\epsilon_B)}{\partial T} \sum_{AB} \sum Q_A(P) Q_B \Gamma_{AB}^e(R_S) \quad (5)$$

where $\Gamma_{AB}^e(R_S)$ is the external polarization charge-electron interaction integral, which depends only on the parameter R_S measuring the extent of the dielectric saturation effects. (See references [12] and [13] for further details).

Finally, by combining Equations (3) and (5), the following expression for the enthalpy of solvation is obtained:

$$\Delta H_S^o(\epsilon_L,\epsilon_B,P) = -\frac{1}{2} \left(1 - \frac{1}{\epsilon_L}\right) \sum_{AB} \sum Q_A(P) Q_B(P) \gamma_{AB}^i \quad (6)$$

It is important to stress the fact that the minimization energy procedure involves the free energy of the solute-solvent system, while the entropy and enthalpy of solvation terms are calculated at the end of the SCF cycle, using the density matrix compatible with the minimum of $G(\epsilon_B,\epsilon_L,P)$.

3. DETAILS OF THE CALCULATION

All calculations were done with a standard CNDO/2 program, with modifications to include solvent effects. In order to make reliable comparisons with previous studies in gas phase and solution [5,10], all tetrahedral bond angles were set as 109.47° . The following bonds lengths were used: $d_{C-C} = 1.53$ A, $d_{C-N} = 1.47$ A, $d_{C-H} = 1.09$ A and $d_{N-H} = 1.0$ A.

The integrals γ_{AB}^i and $\Gamma_{AB}^e(R_S)$ were calculated according to the following parametrization [13]: for A.O.'s associated with the same atomic center of the corresponding internal polarization charge, γ_{AA} is given by $1/r_A$, where r_A is the Pauling's Van der Waals radius of the particular atom. If the A.O.'s and the internal polarization charges are associated with different atomic centers A and B say, the internal solute-solvent interaction integrals are calculated as

$$\gamma_{AB}^i = 1/(R_{AB} + r_B) \quad (7)$$

where R_{AB} is the interatomic distance.

The external solute-solvent interaction integrals, $\Gamma_{AB}(R_S)$, were calculated as in our previous work [13], in terms of the r_{AB} integrals as follows

$$\Gamma_{AA}(R_S) = \gamma_{AA}^i / (1 + R_S * \gamma_{AA}^i) \quad (8)$$

and

$$\Gamma_{AB}(R_S) = (R_{AB} + 0.5(\Gamma_{AA}^{-1} + \Gamma_{BB}^{-1}))^{-1} \quad (9)$$

respectively.

The parameter R_S measuring the extent of the local dielectric region, was taken as the diameter of a water molecule (i.e. 2.80 Å). Finally, as suggested in reference [12] and based on previous calculations [13], the values $\epsilon_L = 5.0$ and $\epsilon_B = 78.5$ were used.

4. RESULTS AND DISCUSSION

Calculations of the thermodynamic functions of solvation of some ammonium ions were performed using the LRF model described in section 2.

Table I shows, for the primary, secondary and tertiary ammonium ions the experimental and calculated gas phase proton affinities (PA). The calculation of PA's is performed by taking the difference of the total energy of the protonated (BH^+) and neutral species:

$$-PA = E_T(BH^+) - E_T(B) \quad (10)$$

In our calculations, the same standard geometries as those reported in reference [5] have been used. In accord with previous results in the literature [7], the basicity order tertiary > secondary > primary > NH_3 for $R = Me, Et, n-Pr$ and $n-Bu$, is qualitatively reproduced by CNDO/2 calculations. Even though the qualitative trend is well reproduced within this approximation, the calculated values systematically overestimate the experimental gas phase PA by about 100 kcal/mol. This overestimation often causes the solvation properties to lose their meaning when they are combined to analyze acid-base equilibria in solution. The consequences of these results are discussed below.

In Table II, the calculated free energies, enthalpies and entropies of solvation for the series of ammonium ions in water are compared with the experimental values reported by Aue et al. [1]. Examination of the calculated free energies of solvation reveals a significant agreement with experimental data: within the primary ammonium ions series, the alkylation of NH_4^+ results in a decrease of ΔG_S as the alkyl group size increases. This is of course due to the trivial relationship between ΔG_S and the ionic radii. The calculated entropies of solvation, displayed in the last column of Table 2, are also in qualitative agreement with the experimental values. For instance, the observed trend $NH_4 > MeNH_3 > Me_2NH_2 > Me_3NH$ has been reasonably accounted for on the basis of Equation (3). This is also the case for the series of primary ammonium ions: $MeNH_3 < EtNH_3 < n-PrNH_3 < n-BuNH_3$. As a result, the variations of ΔH_S within the series, is also in good qualitative agreement with the observed trends. It is also worth emphasizing that the values displayed in Table II provide a better description of the entropic contributions, $T\Delta S_S$, than those reported previously [13]. This improvement is probably related to the more rigorous description of the temperature-dependent orientational polarization of the solvent introduced in this paper.

Experimental and calculated enthalpies of solvation are not directly comparable (the same is true for the free energy and entropy of solvation). For instance, Equation (5) only includes the electrostatic contribution to the heat of solvation. In actuality, the cavitation energy and

the non-electrostatic weak solute-solvent interactions also contribute to the measured values. Nevertheless, following a procedure analogous to that proposed in reference [1], it becomes possible to obtain an estimation of an "experimental" electrostatic enthalpy of solvation as follows:

$$\Delta H_S^{el}(BH^+) = \Delta H_S(BH^+) - \Delta H_S(B) \quad (11)$$

where $\Delta H_S(BH^+)$ and $\Delta H_S(B)$ are the measured solvation enthalpies of the ammonium ions and the corresponding amine respectively. With Equation (11) in mind, the protonation enthalpy in solution, $\Delta H_{s,prot}$, for the acid-base process may be partitioned according to:

$$\begin{aligned} -\Delta H_{s,prot}(\epsilon_L, \epsilon_B, P) &= \Delta E(1, P) + \Delta H_S(\epsilon_L, \Delta_B, P) + C \\ &= -PA + \Delta H_S^{el}(\epsilon_L, \epsilon_B, P) + C \end{aligned} \quad (12)$$

where C is the solvation enthalpy of the proton.

From Equation (12), it may be seen that the solution enthalpy of protonation depends on both the gas phase PA, and the electrostatic solvation enthalpy of the intervening ammonium ion. As we stated before, the calculated PA's suffer from large errors, making the solvation contribution meaningless and precluding any attempt to separate the intrinsic and solvent effects. For instance, if we compare the calculated and experimental values of $\Delta H_{s,prot}$ of alkylamines in water-at 25°C, (second column, first three entries of Table III) the large deviations in the gas phase PA's are causing significant errors in $\Delta H_{s,prot}$ in spite of the almost quantitative agreement obtained for the solvation enthalpies displayed in column 4 of Table III. These results thus show that even though excellent solvation properties are obtained with increasingly refined models of solvent effects, the description of solution equilibrium properties remain highly dependent on the quality of the gas phase calculations. This conclusion is not only true for semiempirical calculations like the present one, but also for more sophisticated wave functions, especially in the case where anions are involved.

Our current model seems to work best with unbranched alkylamines, although acceptable results are also obtained for the effect of branching on $\Delta H_{s,prot}$ (see for instance, the variations of $\Delta H_{s,prot}$ within the series $MeNH_3, Me_2NH_2, Me_3NH$). The problems associated with the description of the equilibrium properties of molecules containing bulky substituents seem to be caused by steric hindrance effects upon solvation which are not accounted for in the present model.

In Table IV, the calculated and experimental entropies of protonation, $T\Delta S_{s,prot}$, of alkylamines in water are shown. As in the case of $\Delta H_{s,prot}$ the following partition of $T\Delta S_{s,prot}$ is possible:

$$-T\Delta S_{s,prot} = -T\Delta S(BH^+) + RT \ln(\sigma_{BH^+} / \sigma_B) \quad (13)$$

where, $T\Delta S_S(BH^+)$ is the electrostatic solvation entropy of the corresponding ammonium ion computed by using Equation (5). The second term, which is expressed in terms

of the symmetry number of the protonated and neutral amines, σ_{BH^+} and σ_{B} respectively, corresponds to the intrinsic entropy variations and the third one is a constant contribution due to the solvation of the proton [1]. In this case, the description of the gas phase contribution only depends on the variation of the degree of freedom of reagents and products. The entropic contributions are then free of the problems discussed in connection with the calculated gas phase PA's and their influence on the $\Delta H_{\text{s,prot}}$ values. The order for $T\Delta S_{\text{s,prot}}$ is found to be (Table 4). $\text{MeNH}_2 < \text{EtNH}_2 < \text{n-PrNH}_2 < \text{n-BuNH}_2$.

This is consistent with the experimental data. The same good agreement is found for the R_2NH and R_3N series. To our knowledge, no previous theoretical results concerning equilibrium entropies in solution have been reported.

It is interesting to notice that the theoretical problems encountered with the gas phase calculations and their influence on the solution acid-base equilibria under study, almost parallels the developments of the experimental methods for the determination of the thermodynamic properties in solution which only recently, with the introduction of modern techniques like ion-cyclotron resonance (ICR) spectroscopy, has become possible.

Having in mind the limitations discussed above, we propose an empirical procedure to estimate the thermodynamic functions for the acid-base equilibrium in solution. In this method, the experimental gas phase PA's are combined with the calculated solvation properties to provide theoretical estimates of the solution equilibrium properties. The third entry of the second column of Table III shows the results obtained. It may be seen that the absolute values of $\Delta H_{\text{s,prot}}$ are reasonably well described by such a procedure.

As it has been previously established in the literature [1-3], the discussion of acidity or basicity properties of any system in solution may only be done in terms of variations of the free energy. In the present case, the free energy protonation appears to be quite different from the enthalpies of protonation because of the entropic term $T\Delta S_{\text{s,prot}}$. Thus, there is no justification, at least for the alkylamines basicity problem, to compare theoretical free energy values with experimental enthalpies [10]. In order to illustrate this argument, we write the free energy of protonation of NH_3 in solution, as follows:

$$\Delta G_{\text{s,prot}}(\epsilon_{\text{L}}, \epsilon_{\text{B}}, \text{P}) = -\Delta \text{PA} + \delta \Delta H(\text{BH}^+) + \delta T\Delta S_{\text{S}}(\text{BH}^+) + d\text{RTLn}(\sigma_{\text{BH}^+} / \sigma_{\text{B}}) \quad (14)$$

The results of the calculation of $\Delta G_{\text{s,prot}}$ are shown in Table 5. At first glance, one is tempted to neglect the entropic contribution to $\Delta G_{\text{s,prot}}$ because of their small values compared to $\Delta H_{\text{s}}(\text{BH}^+)$. However, the full partition of $\Delta G_{\text{s,prot}}$ as proposed in Equation (14), permits to observe that the enthalpic effects almost cancels out the intrinsic contributions, giving special relevance to the electrostatic entropy of solvation of the corresponding

ammonium ion. This conclusion is consistent with that suggested by Aue et al. [1] and opposed to the working hypothesis used in reference [10]. The calculated $\Delta G_{\text{s,prot}}$ shown in Table V are in reasonable agreement with the absolute experimental values. Let stress that here again, the calculated values for the bulkier substituted alkylamines deviate most from the experimental ones.

5. CONCLUDING REMARKS

The anomalous solution basicity of alkylamines, as compared to the gas phase values, is a classical problem in physical organic chemistry. This is a well known non trivial system which we selected as a "case study" because it offered the opportunity to characterize aspects of the acid-base solution equilibrium.

The following general conclusions may be drawn from the present work:

- i) We have shown that the LRF model significantly improves the calculation of the thermodynamic characteristics of ion solvation. Particular emphasis is made concerning the description of entropy of solvation using rigorous thermodynamic relationships.
- ii) There is no way, at present, to perform a complete theoretical analysis of the acid-base equilibria in these systems in solution because the crude gas phase calculations provided by semiempirical methods do not yield a sufficiently accurate framework. The other alternative open to the theoretical study of these systems, are ab-initio calculations combined with simulation techniques of the liquid state (like Monte Carlo method).
- iii) Taking into account the above problem, we have proposed an empirical procedure which represents a compromise between the fair gas phase calculations and the quality of the solvation properties obtained by the LRF model. This procedure allowed us to identify the relevant contributions to the solution basicity of alkylamines and particularly those contributions arising from entropy effects.
- iv) From a formal point of view, we have used the *free energy* minimum criteria for the discussion of the solution acid-base equilibrium. We have shown that any procedure which *a priori* neglects entropy effects is questionable, even though good numerical results may be obtained.

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TABLE I

Experimental and calculated gas phase proton affinities (PA) of alkylamines at 25° C.^a

B	Experimental ^b		Calculated	
	PA	δ (-PA)	ΔE (1, P)	$\delta \Delta E$ (1, P)
NH ₃	207.0	(0.0)	294.6	(0.0)
MeNH ₂	218.4	-11.4	307.9	-13.3
EtNH ₂	221.4	-14.4	313.0	-18.4
n-PrNH ₂	222.8	-15.8	315.6	-21.0
n-BuNH ₂	223.3	-16.3	317.1	-22.5
Me ₂ NH	224.8	-17.8	317.7	-23.1
Et ₂ NH	229.4	-22.4	326.6	-32.0
n-Pr ₂ NH	231.4	-24.4	329.8	-35.2
n-Bu ₂ NH	232.5	-25.5	331.7	-37.1
Me ₃ N	228.6	-21.6	325.0	-30.4
Et ₃ N	235.5	-28.5	336.3	-41.7

^aAll values in Kcal/mol. All values relative to NH₃.

^bFrom reference [1].

TABLE II

Thermodynamic Functions of Solvation of Alkylammonium Ions in water ^a.

Solute	Experimental ^b			Calculated		
	ΔG	ΔH	$-T\Delta S$	ΔG	ΔH	$-T\Delta S$
NH ₄	75.0	75.6	0.6	71.9	72.9	1.0
MeNH ₃	65.0	64.6	-0.4	61.8	62.7	0.9
EtNH ₃	62.0	62.1	0.1	60.5	61.8	1.3
n-PrNH ₃	60.5	60.8	0.3	58.8	60.2	1.4
n-BuNH ₃	60.1	60.5	0.4	58.4	60.0	1.6
Me ₂ NH ₂	58.6	57.0	-1.6	54.6	55.4	0.8
Et ₂ NH ₂	54.3	53.2	-1.1	53.3	54.8	1.5
n-Pr ₂ NH ₂	52.3	51.6	-0.7	50.6	52.2	1.6
n-Bu ₂ NH ₂	51.6	51.0	-0.6	49.9	51.8	1.9
Me ₃ NH	53.1	50.1	-3.0	49.5	50.2	0.7
Et ₃ NH	47.3	44.6	-2.7	50.1	52.6	2.4

^aAll values in Kcal/mol.

^bFrom reference [1].

TABLE III

Calculated and Experimental Enthalpies of Protonation of Alkylamines in water at 25°C. ^a

B	$-\Delta H_{s,prot}$	= $\Delta E(1,P)^b$	+ $\Delta H^{el}(\epsilon_L, \epsilon_B, P)$	+ C^c
NH ₃	97.7	294.6	72.9	-269.8
	12.5	207.0	75.6	
MeNH ₂	100.8	307.9	62.7	-269.8
	13.2	218.4	64.6	
	11.3			
EtNH ₂	105.0	313.0	61.8	-269.8
	13.7	221.4	62.1	
	13.4			
n-PrNH ₂	106.0	315.6	60.2	-269.8
	13.8	222.8	60.8	
	13.2			
n-BuNH ₂	107.3	317.1	60.0	-269.8
	14.0	223.3	60.5	
	13.5			
Me ₂ NH	103.3	317.7	55.4	-269.8
	12.0	224.8	57.0	
	10.4			
Et ₂ NH	111.6	326.6	54.8	-269.8
	12.7	229.4	53.2	
	14.4			
n-Pr ₂ NH	112.2	329.8	52.2	-269.8
	13.2	231.4	51.6	
	13.8			
n-Bu ₂ NH	113.7	331.7	51.8	-269.8
	13.7	232.5	51.0	
	14.5			
Me ₃ N	105.4	325.0	50.2	-269.8
	8.8	228.6	50.1	
	9.0			
Et ₃ N	119.1	336.3	52.6	-269.8
	10.3	235.5	44.6	
	18.3			

^aFirst value corresponds to the calculated enthalpy of protonation, the second one corresponds to the experimental value from ref. [1], the third entry corresponds to the estimated values calculated by using experimental PA's and calculated properties (see the text). All values are in Kcal/mol.

^bIn the row corresponding to the experimental enthalpies of protonation, this value corresponds to the PA.

^cThis value is a constant contribution representing the solvation enthalpy of the proton.

TABLE IV

Calculated and Experimental Entropies of Protonation of Alkylamines in water at 25°C.^a

B	$-T \Delta S_{s,prot} = -T \Delta S(BH^+) + RT \ln(\sigma_{BH}/\sigma_B) + C'$			
NH ₃	0.27	1.0	0.82	-1.55
	-0.13	0.6		
MeNH ₂	0.0	0.9	0.65	-1.55
	-1.35	-0.4		
EtNH ₂	0.40	1.3	0.65	-1.55
	-0.86	0.1		
n-PrNH ₂	0.50	1.4	0.65	-1.55
	-0.58	0.3		
n-BuNH ₂	0.70	1.6	0.65	-1.55
	-0.53	0.4		
Me ₂ NH	-0.34	0.8	0.41	-1.55
	-2.66	-1.6		
Et ₂ NH	0.36	1.5	0.41	-1.55
	-2.30	-1.1		
n-Pr ₂ NH	0.46	1.6	0.41	-1.55
	-1.84	-0.7		
n-Bu ₂ NH	0.76	1.9	0.41	-1.55
	-1.69	-0.6		
Me ₃ N	-0.85	0.7	0.0	-1.55
	-4.55	-3.0		
Et ₃ N	0.85	2.4	0.0	-1.55
	-4.30	-2.7		

^aFirst value corresponds to the calculated entropy of protonation, the second one is the experimental value as given in ref. [1]. All values are in Kcal/mol.

TABLE V

An analysis of the dominant terms in the solution basicity of Alkylamines at 25°C.^a

B	NH ₄ (aq) +	B(aq)	→	NH ₃ (aq) +	BH ⁺ (aq).
	$-\delta \Delta G_s^{\text{prot}}$	$= \delta (-PA)$		$+ \delta \Delta H^{\text{el}}(\text{BH}^+) + \delta T \Delta S^{\text{el}}(\text{BH}^+) + \delta \text{RTL}n(\sigma_{\text{BH}} + / \sigma_{\text{B}})$	
NH ₃	(0.0)	(0.0)	(0.0)	(0.0)	(0.0)
MeNH ₂	-1.9	-11.4	10.7	-1.0	-0.2
	-3.4	-13.3	10.2	-0.1	
	-1.5				
EtNH ₂	-2.0	-14.4	13.2	-0.5	-0.2
	-7.2	-18.4	11.1	0.3	
	-3.2				
n-PrNH ₂	-1.8	-15.8	14.5	-0.3	-0.2
	-8.1	-21.0	12.7	0.4	
	-2.9				
n-BuNH ₂	-2.5	-16.3	14.2	-0.2	-0.2
	-9.2	-22.5	12.9	0.6	
	-3.0				
Me ₂ NH	-2.1	-17.8	18.3	-2.2	-0.4
	-6.2	-23.1	17.5	-0.2	
	-0.9				
Et ₂ NH	-2.2	-22.4	22.2	-1.7	-0.4
	-13.8	-32.0	18.1	0.5	
	-4.2				
n-Pr ₂ NH	-2.4	-24.4	23.8	-1.3	-0.4
	-14.3	-35.2	20.7	0.6	
	-3.5				
n-Bu ₂ NH	-2.3	-25.5	24.4	-1.2	-0.4
	-15.5	-37.1	21.1	0.9	
	-3.9				
Me ₃ N	-0.8	-21.6	25.2	-3.6	-0.8
	-8.8	-30.4	22.7	-0.3	
	0.0				
Et ₃ N	-2.0	-28.5	30.7	-3.3	-0.8
	-20.8	-41.7	20.3	1.4	
	-7.6				

^aFirst value is the experimental free energy of protonation. The second one is the calculated quantity and the third entry is the estimated value obtained by using the experimental PA's with the calculated solvation property. All values in Kcal/mol.

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