# A Study of Nitrogen-15 Nuclear Magnetic Resonance Shifts in Liquid $^{15}NH_3$–Solvent Mixtures[1a]

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**Abstract:** In nmr studies of hydrogen bonding, relatively little has been done to determine the influence of hydrogen bonding on the nmr shift of the atom which donates the electron pair in forming the hydrogen bond. As an approach to this problem, we have chosen to investigate the $^{15}N$ nmr shift for the $^{15}NH_3$ molecule in various environments. The $^{15}N$ nmr shift relative to gaseous $^{15}NH_3$ was measured as a function of concentration for $^{15}NH_3$ in 13 solvents. Utilizing high-resolution techniques, the $^{15}N$ shifts could be measured to ±0.2 ppm at $^{15}NH_3$ concentrations as low as 2 mole %. Extrapolation to zero $^{15}NH_3$ concentration yields a set of "infinite-dilution" shifts which are well interpreted on the basis of a simple model describing the interactions between the $^{15}NH_3$ molecule and solvent molecules. The model assumes that the observed infinite-dilution shifts are the sum of contributions due to two general types of interactions: (1) the interaction of the ammonia nitrogen lone-pair electrons with solvent–molecule groups and (2) hydrogen bonding between solvent–molecule unshared electron pairs and $^{15}NH_3$ protons. The results indicate that interactions involving the nitrogen lone-pair electrons make a rather large paramagnetic contribution to the $^{15}N$ shift in $^{15}NH_3$ while the hydrogen bonding of $^{15}NH_3$ protons by solvent electron pairs makes a much smaller diamagnetic contribution. These results are discussed in terms of the Ramsey chemical-shift formulation, and possible implications with regard to electronic displacements produced by the various types of interactions are noted.

The application of nmr techniques to studies of hydrogen bonding has produced a large volume of work dealing mainly with the nmr shift of the proton in various types of hydrogen bonds. Relatively little attention has been given to the influence of hydrogen bonding on the nmr shift of the atom which donates the electron pair to the hydrogen bond. In some recent work[2,3] we have observed that the $^{17}O$ resonance in pure liquid $H_2{}^{17}O$ and the $^{15}N$ resonance in pure liquid $^{15}NH_3$ both occur at significantly lower applied fields than the respective resonances in the gaseous molecules. Moreover, both resonances move to lower fields with decreasing temperature in the pure liquids. It has also been observed[4] that the shift of the $^{17}O$ resonance in $H_2{}^{17}O$ at low concentration in a liquid solvent is dependent upon the nature of the solvent. In this work we report the results of a rather extensive study of $^{15}N$ nmr shifts for $^{15}NH_3$ in a number of different solvents as a function of concentration.

We anticipated that such a study might serve to enhance our understanding of the interactions which influence the nmr shifts of atoms which commonly serve as electron-pair donors in hydrogen bonding.

## Experimental Section

The $^{15}N$ used in this work was obtained from a low-temperature nitric oxide distillation process which provides material with up to 100% $^{15}N$.[5] In processing the $^{15}NO$, the $^{15}N$ is recovered as $Ca_3{}^{15}N$ which is then hydrolyzed to yield the $^{15}NH_3$ used in this study.

The $^{15}NH_3$–solvent mixtures were prepared directly in nmr sample tubes by condensing measured amounts of gases (by pressure change in a known volume) or liquids (by weight) into 5-mm o.d. tubes prepared from standard-wall (~1 mm) Pyrex tubing. The total sample volume was kept at ~0.5 ml and samples were sealed under vacuum. In samples containing small concentrations of $^{15}NH_3$ it was sometimes advantageous to add very small amounts of $NH_4Cl$ which, by accelerating proton exchange, ensured a single $^{15}N$ resonance peak. In a few cases, where the added $NH_4^+$ was ineffective in producing a sharp averaged line, small amounts of KOH were added to suppress any averaging so that observation of a sharp $^{15}N$ quartet was possible. Although the $^{15}N$–H coupling constant could then be observed, the primary purpose of observing the multiplet was to obtain sharp peaks which then could be used to obtain an accurate chemical shift value. In all series of solutions except the $^{15}NH_3$–$H_2O$ and $^{15}NH_3$–$NH_4Cl$ systems, a very small amount of TMS was added as an internal standard for the proton shift measurements which were also made on most of these solutions.

The $^{15}N$ nmr measurements were made on a modified Varian D-60A spectrometer utilizing an external water-proton lock-on system. The Varian 8.13-MHz radiofrequency components (normally used for $^{17}O$ nmr) were modified to operate at 6.08 MHz which is the frequency required for $^{15}N$ at a field of ~14 kG. The external lock-on system was used to keep the magnetic field constant by maintaining the water proton in resonance at a fixed frequency of 60 MHz. This 60-MHz lock signal was supplied by a harmonic of the 5-MHz output of a General Radio Model GR 1163 frequency synthesizer. This same source also furnished a constant intermediate frequency of 11.08 MHz to provide the required 5-MHz difference frequency for the 6.08-MHz receiver. The $^{15}N$ resonances were then recorded by a frequency sweep utilizing a Hewlett-Packard Model 5100 frequency synthesizer and Model 5110 driver. The frequency synthesizer was swept either by the x-pot of the Varian flat-bed recorder or by the ramp output of the Varian C-1024 time-averaging computer. Bias for the frequency sweep was supplied by a Model ABC-40-0.5 M Kepco power supply.

The $^{15}N$ shifts were measured at 29.6 ± 0.5° relative to pure liquid $^{15}NH_3$ sealed in a 5-mm o.d. Pyrex tube similar to those used for the $^{15}NH_3$–solvent mixtures. Preliminary experiments demonstrated that the $^{15}N$ resonant frequency in this reference sample could be reproduced to better than 0.05 ppm on repeated removal and replacement in the probe. Thus the $^{15}N$ shift in an $^{15}NH_3$–solvent mixture was made by simply measuring its resonant frequency and comparing it with the $^{15}N$ resonant frequency in the liquid $^{15}NH_3$ reference sample. Susceptibility corrections were made by measuring the volume susceptibilities of all samples and applying the correction for cylindrical geometry.[6] The shift of

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[2] A. E. Florin and M. Alei, *J. Chem. Phys.*, 47, 4268 (1967).

[3] W. M. Litchman, M. Alei, and A. E. Florin, *ibid.*, **50**, 1031 (1969).

[4] M. Alei and A. E. Florin, *J. Phys. Chem.*, 73, 863 (1969).

[5] We are indebted to Dr. B. B. McInteer and Mr. R. M. Potter of this laboratory for providing us with this material.

**Table I.** $^{15}$N Shifts[a] in $^{15}NH_3$–Solvent Mixtures

| Solvent | Mole % $NH_3$ 95 | 90 | 80 | 70 | 68 | 60 | 50 | 45 | 40 | 30 | 20 | 10 | 5 | 2 | 0[b] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $H_2O$ | | −17.09 | −17.99 | −18.66 | | −19.24 | −19.46 | | −19.56 | −19.53 | −19.51 | −19.47 | | | −19.4 |
| $Me_2O$ | | −14.67 | −13.57 | −12.68 | | −11.76 | −10.93 | | −10.19 | −9.47 | −8.91 | −8.35 | | | −7.7 |
| $Me_3N$ | | −14.89 | | −13.28 | | | −12.02 | | | −11.02 | −10.59 | −10.29 | | | −10.0 |
| $Me_4C$ | | | | | | | | −12.07 | | −11.67 | −11.47 | −11.26 | | | −11.1 |
| $MeNH_2$ | | −15.33 | | −14.13 | | | −13.56 | | | −12.85 | | | | | −12.3 |
| MeOH | | | | −15.10 | | | −14.46 | | | −13.89 | | −13.61 | | | −13.4 |
| EtOH | | −15.82 | | −15.99 | | | −16.21 | | | −16.48 | | −16.55 | | −16.63 | −16.6 |
| $Me_2NH$ | | −14.97 | | −13.53 | | | −12.31 | | | −11.21 | | −10.45 | | | −10.1 |
| $EtNH_2$ | | | | | −14.70 | | −14.33 | | | −13.98 | | −13.73 | | | −13.7 |
| $Et_2O$ | | | | | | | −12.48 | | | −11.79 | | −11.13 | | | −10.8 |
| $Et_3N$ | | | | | | | −13.49 | | | −13.05 | | | | | −12.4 |
| $Et_2NH$ | | | | | | | −13.57 | | | −13.15 | | −12.83 | | | −12.7 |
| $NH_3$ | | | | | | | | | | | | | | | −15.9 |
| $CCl_4$ | | | | | | | −15.88 | | | | −15.97 | −15.79 | −15.76 | | |
| $NH_4Cl$ | −20.74 | −24.90 | −31.99 | −35.44[c] | | | | | | | | | | | |

[a] All shifts paramagnetic (downfield) relative to $^{15}NH_3$(g). Units are ppm. [b] Shifts derived by extrapolation of plotted data (Figure 1). [c] Shift actually corresponds to 72 mole % $NH_3$ which represents nearly the saturation solubility of $NH_4Cl$ in $NH_3$ at room temperature.

$^{15}NH_3$(l) relative to $^{15}NH_3$(g) was also determined and corrected for susceptibility assuming a vapor susceptibility of zero. Finally all $^{15}$N shifts were calculated relative to the $^{15}$N resonance in gaseous $^{15}NH_3$ as zero. It is estimated that the over-all uncertainty in the reported shifts does not exceed ±0.2 ppm.

The reported proton spectra were obtained in the usual way on the Varian D-60A spectrometer with external lock-on and internal TMS as reference. The proton shifts are probably accurate to ±1 Hz in 60 MHz.

## Results

1. **$^{15}$N Chemical Shifts**. Table I and Figure 1 display the measured $^{15}$N shifts for $^{15}NH_3$ as a function of concentration in each of the solvents used in this work. The shifts are relative to the $^{15}$N resonance of gaseous $^{15}NH_3$. All measurements are at 29.6 ± 0.5° and the data are corrected for liquid volume susceptibilities. Since the data fall on smooth curves and since, in each case, the change in shift decreases with decreasing $NH_3$ concentration, we assume that each curve may be extrapolated to zero $NH_3$ concentration to yield an "infinite dilution shift" characteristic of the $^{15}$N environment when a single $^{15}NH_3$ molecule is surrounded by solvent molecules. These infinite dilution shifts obtained by extrapolation of the experimental data are listed under zero $NH_3$ concentration in Table I.

Since small concentrations of $NH_4^+$ were used to promote rapid proton averaging in some solutions, we were interested in quantitatively measuring the $^{15}$N shift produced by addition of $NH_4^+$ to $^{15}NH_3$. The measured $^{15}$N shifts for $^{15}NH_3$ with varying amounts of added $NH_4^+$ (as $NH_4Cl$) are listed in Table I and the first two points plotted in Figure 1. The lower limit of 72 mole % $NH_3$ is near the saturation solubility of $NH_4Cl$ in liquid $NH_3$ at room temperature. Although these data demonstrate that addition of $NH_4^+$ produces a large downfield shift, the roughly $10^{-3}$ mole % $NH_4^+$ used to promote proton averaging in some of the $NH_3$–solvent systems does not significantly affect the $^{15}$N shifts in those systems.

2. **Proton Data.** Although we are mainly concerned with $^{15}$N shifts in this work, we have also measured $^{15}NH_3$ proton shifts in most of the same $^{15}NH_3$–solvent systems. For solvents with no protons capable of rapid averaging with $^{15}NH_3$ protons, such shifts may be directly indicative of interactions between the solvent molecules and $^{15}NH_3$ protons. Table II and Figure 2 summarize the measured $^{15}NH_3$ proton shifts in such solvents.

## Discussion

The data presented here display several important features. With regard to the $^{15}$N shifts, we note that in none of the solvents studied does the shift for $^{15}NH_3$ at infinite dilution appear to be the $^{15}$N resonance position in gaseous $^{15}NH_3$. Moverover, the infinite dilution shifts are not determined solely by the solvent functional group. In fact, for solvents with the same functional group, solvent ethyl groups lead to infinite dilutions shifts which are consistently downfield of those in solvents with methyl groups. We also note a trend which appears to be related to a contribution by solvent functional-group protons. Thus the infinite dilution shifts in MeOH and EtOH are downfield of the shifts in

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(6) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 81.

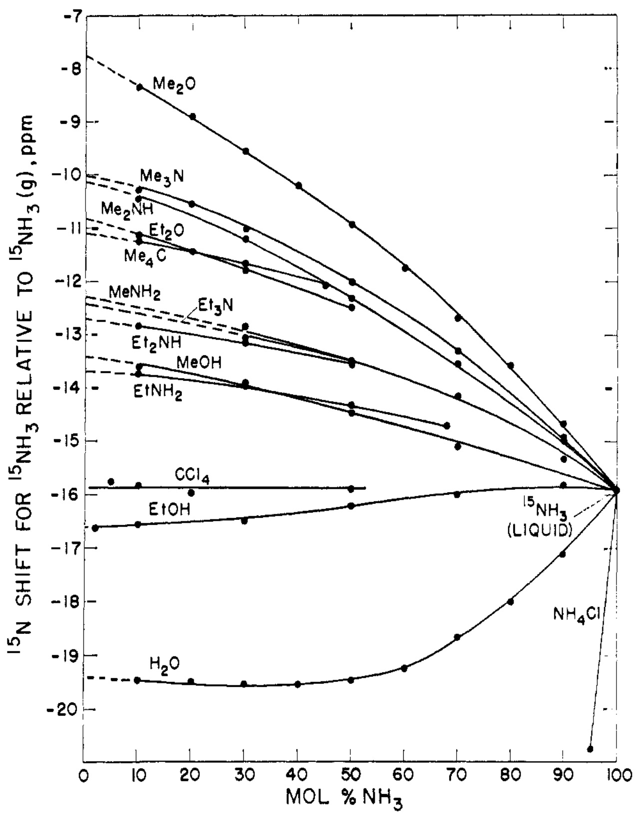

Figure 1. $^{15}N$ nmr shifts in $^{15}NH_3$–solvent systems at 29.6 ± 0.5°.

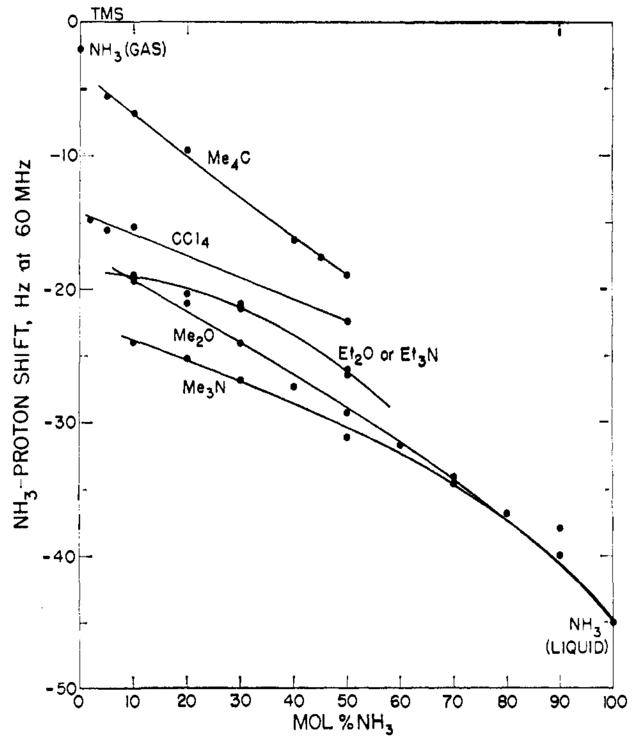

Figure 2. $NH_3$ proton nmr shifts in $NH_3$–solvent systems at 29.6 ± 0.5°.

$Me_2O$ and $Et_2O$, respectively. Similarly for the amine–solvent series $Me_3N$, $Me_2NH$, $MeNH_2$, and $Et_3N$, $Et_2NH$, $EtNH_2$, there is, in each case, a progressive shift downfield with increasing number of solvent, functional-group protons.

**Table II.** $NH_3$ Proton Shifts in $NH_3$–Solvent Mixtures[a]

| Solvent | Mole % $NH_3$ | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 90 | 80 | 70 | 60 | 50 | 45 | 40 | 30 | 20 | 10 | 5 | 2 |
| $Me_2O$ | −37.9 | −36.8 | −34.1 | −31.7 | −29.3 | | −27.3 | −24.1 | −21.1 | −18.9 | | |
| $Me_3N$ | −39.9 | | −34.5 | | −31.1 | | | −26.8 | −25.2 | −24.0 | | |
| $Me_4C$ | | | | | −18.9 | −17.7 | −16.3 | | −9.6 | −6.8 | −5.6 | |
| $Et_2O$ | | | | | −26.4 | | | −21.5 | | −19.3 | | |
| $Et_3N$ | | | | | −26.0 | | | −21.1 | | | | |
| $CCl_4$ | | | | | −22.4 | | | | −20.4 | −15.3 | −15.6 | −14.8 |

[a] All shifts in Hz at 60 MHz relative to internal TMS.

The above observations suggest that the measured infinite dilution shifts may be the results of interaction of the $^{15}NH_3$ molecule with specific solvent–molecule sites and that each such interaction may be relatively independent of the over-all composition of the solvent molecule. We thus consider the possibility that the observed shifts may be derived by appropriate summation of a relatively small number of "interaction parameters" which are constant over the entire group of solvents studied. For this purpose, we assume a simple model in which the ammonia molecule is entirely surrounded by solvent molecules. We consider two general types of interactions to be responsible for the observed $^{15}N$ shifts.

(1) The interaction of the ammonia nitrogen lone-pair electrons with a solvent molecule. This interaction may be either hydrogen-bond formation with solvent functional-group protons or some sort of interaction between the nitrogen lone pair and solvent R groups. We thus assume that the nitrogen lone pair is always associated with either a solvent proton or solvent R group (*i.e.*, $CH_3$ or $C_2H_5$) and does not interact in any way with solvent basic sites (*i.e.*, oxygen or nitrogen). In solvents with more than one site (*i.e.*, solvents containing both functional-group protons and R groups) available for interaction with the nitrogen lone pair, we simply assume that the probability of interaction with a particular solvent site is directly proportional to the relative abundance of that site in the solvent molecule. This interaction is assumed to contribute $\sigma_{A_x}$ ppm to the $^{15}N$ shift relative to gaseous $^{15}NH_3$.

(2) Hydrogen-bond formation between solvent electron-donor sites and the $NH_3$ protons. We assume the $NH_3$ protons are always associated with solvent oxygen or nitrogen and do not interact in any way with other solvent groups. This effect is assumed to operate through the $^{15}N$–H bond to alter the shielding at the $^{15}N$ nucleus and to contribute $\sigma_{B_x}$ ppm to the $^{15}N$ shift relative to gaseous $^{15}NH_3$.

We now assume that the infinite dilution shifts in all the solvents studied (except $CCl_4$ which will be discussed separately) will be given as a linear combination of six interaction parameters each of which makes a contribution to the $^{15}N$ shift due to the indicated interaction:

| | |
|---|---|
| $\sigma_{AOH}$ | hydrogen bonding between the $^{15}NH_3$ nitrogen lone pair and a solvent OH proton |
| $\sigma_{ANH}$ | hydrogen bonding between the $^{15}NH_3$ nitrogen lone pair and a solvent NH proton |
| $\sigma_{AMe}$ | interaction between the $^{15}NH_3$ nitrogen lone pair and a solvent methyl group |
| $\sigma_{AEt}$ | interaction between the $^{15}NH_3$ nitrogen lone pair and a solvent ethyl group |
| $\sigma_{BO}$ | hydrogen bonding between solvent oxygen lone pairs and $^{15}NH_3$ protons |
| $\sigma_{BN}$ | hydrogen bonding between solvent nitrogen lone pairs and $^{15}NH_3$ protons |

We assume that each of the above parameters is a constant, independent of the solvent molecule in which the particular solvent site is located. Thus $\sigma_{ANH}$ has the same value whether the solvent be $MeNH_2$, $Et_2NH$, etc., and $\sigma_{BO}$ is the same in $Me_2O$, EtOH, etc.

On the basis of this model and the indicated assumptions, we write for the infinite dilution shift for $^{15}NH_3$ in EtOH as solvent

$$\delta_{EtOH} = {}^1/_2\sigma_{AEt} + {}^1/_2\sigma_{AOH} + \sigma_{BO}$$

In $EtNH_2$

$$\delta_{EtNH_2} = {}^1/_3\sigma_{AEt} + {}^2/_3\sigma_{ANH} + \sigma_{BN}$$

The scheme of coefficients for each of 13 such equations, one for each solvent used, is listed in Table III. A least-squares treatment of the 13 equations yields a set of interaction-parameter values which gives the best fit to the experimentally determined infinite dilution shifts. Table IV lists these best values for the interaction parameters and compares the experimental infinite dilution shifts with the shifts calculated from the best parameter values. Although some of the discrepancies between calculated and experimental values (as great as 1.2 ppm in the case of EtOH as solvent) lie outside our experimental uncertainty, the agreement is surprisingly good when one considers the underlying assumptions. In particular, the assumption of constancy of the interaction parameters from one solvent to another must certainly be an oversimplification. We must also emphasize that in order to get the unique set of best parameter values listed in Table IV, the value for $\sigma_{AMe}$ must be fixed at the $^{15}N$ infinite dilution shift for $^{15}NH_3$ in neopentane. This, in effect, assumes that in neopentane the only interaction is one which is characteristic of the interaction between the $^{15}NH_3$ nitrogen lone pair and a solvent methyl group.

**Table III.** Scheme of Coefficients

| Solvent | $\sigma_{AMe}$ | $\sigma_{AEt}$ | $\sigma_{ANH}$ | $\sigma_{AOH}$ | $\sigma_{BN}$ | $\sigma_{BO}$ |
|---|---|---|---|---|---|---|
| $H_2O$ | | | | 1 | | 1 |
| $Me_2O$ | 1 | | | | | 1 |
| $Me_3N$ | 1 | | | | 1 | |
| $Me_4C$ | 1 | | | | | |
| $MeNH_2$ | $^1/_3$ | | $^2/_3$ | | 1 | |
| MeOH | $^1/_2$ | | | $^1/_2$ | | 1 |
| EtOH | | $^1/_2$ | | $^1/_2$ | | 1 |
| $Me_2NH$ | $^2/_3$ | | $^1/_3$ | | 1 | |
| $EtNH_2$ | | $^1/_3$ | $^2/_3$ | | 1 | |
| $Et_2O$ | | 1 | | | | 1 |
| $Et_3N$ | | 1 | | | 1 | |
| $Et_2NH$ | | $^2/_3$ | $^1/_3$ | | 1 | |
| $NH_3$ | | | 1 | | 1 | |

In the light of the assumptions involved in the foregoing treatment, we can only offer it as a simple interpretation which gives a good fit to the experimental observations. That it is the correct interpretation is certainly open to question. If we accept it, we are led to believe that an $^{15}NH_3$ nitrogen lone pair is just as likely to interact with a solvent methyl or ethyl group as it is with a solvent functional-group proton. Moreover, the effect on the $^{15}N$ shift is not much greater for the latter interaction than for the former (compare, for example, $\sigma_{ANH}$ and $\sigma_{AEt}$). Since protons attached to carbon are not generally considered to enter into hydrogen bonding, we presume that the interaction between the nitrogen lone pair and methyl or ethyl groups may be of the van der Waals type. Hindman, Svirmickas, and

**Table IV.** Values of Parameters and Calculated Results

| Best parameter values, ppm | Infinite dilution shifts | | | |
|---|---|---|---|---|
| | Solvent | Exptl | Calcd | Dif |
| $\sigma_{AOH}$ −23.1 | $H_2O$ | −19.4 | −19.8 | −0.4 |
| | $Me_2O$ | −7.7 | −7.8 | −0.1 |
| $\sigma_{ANH}$ −17.0 | $Me_3N$ | −10.0 | −9.0 | +1.0 |
| | $Me_4C$ | −11.1 | −11.1 | 0.0 |
| $\sigma_{AEt}$ −14.4 | $MeNH_2$ | −12.3 | −12.9 | −0.6 |
| | MeOH | −13.4 | −13.8 | −0.4 |
| $\sigma_{AMe}$ −11.1 | EtOH | −16.6 | −15.4 | +1.2 |
| | $Me_2NH$ | −10.1 | −10.9 | −0.8 |
| $\sigma_{BO}$ +3.31 | $EtNH_2$ | −13.7 | −14.0 | −0.3 |
| | $Et_2O$ | −10.8 | −11.1 | −0.3 |
| $\sigma_{BN}$ +2.13 | $Et_3N$ | −12.4 | −12.3 | +0.1 |
| | $Et_2NH$ | −12.7 | −13.1 | −0.4 |
| | $NH_3$ | −15.9 | −14.9 | +1.0 |

Dixon[7] have shown that such interactions can make significant contributions to proton liquid-association shifts in certain systems. It is not inconceivable that such interactions could produce even larger effects at the $^{15}N$ nucleus if the $^{15}N$ lone pair were directly involved.

The assumed model also produces the interesting result that the $\sigma_{A_x}$ parameters are considerably larger in magnitude than the $\sigma_{B_x}$ parameters and of opposite sign. The much larger effect of the lone-pair interactions seems intuitively reasonable since these are directly associated with the $^{15}N$ nucleus while the interactions at the $NH_3$ protons are further removed. The direction of the $\sigma_{A_x}$ shift, however, is not simple to interpret. On the basis of the generally accepted hypothesis that changes in chemical shift of nuclei other than protons are dominated by the effects of bonding on the paramagnetic term in the Ramsey chemical-shift formulation,[8] our results would indicate that hydrogen bonding or other interactions involving the nitrogen lone pair result in an increase in the paramagnetic term. Such an increase could result from a decrease in $\Delta E$, the average excitation energy for the lone-pair electrons, or an increase in $\langle 1/r^3 \rangle_{av}$. Stevenson, Coppinger, and Forbes[9] have shown that ultraviolet absorption band for $NH_3$ dissolved in $H_2O$ is shifted to higher frequency relative to its position when dissolved in dry $Et_2O$. This indicates that hydrogen bonding *increases* $\Delta E$ and hence, if the change in $\Delta E$ were the predominant effect, the shift of the $^{15}N$ resonance for $^{15}NH_3$ in $H_2O$ should be *upfield* of that for $^{15}NH_3$ in $Et_2O$. This is clearly not so. Thus, if the paramagnetic term dominates, the observed shifts would require that hydrogen bonding produce a contraction of the lone-pair orbital such that the increase in $\langle 1/r^3 \rangle_{av}$ would more than offset the increase in $\Delta E$. On the other hand, Lambert, Binsch, and Roberts[10] have proposed that the paramagnetic term is at a minimum for the $^{15}N$ shift in the spherically symmetric $NH_4^+$ ion. They further state that the $^{15}N$ shift in $^{15}NH_4^+$ relative to $^{15}NH_3$ "is downfield because protonation removes shielding by the unshared pair." This would imply that changes in the *diamagnetic* term of the Ramsey formulation dominate the $^{15}N$ chemical shift between $^{15}NH_3$ and $^{15}NH_4^+$. On this basis, a paramagnetic shift would be due to a decrease in the diamagnetic term. This would require a decrease in $\langle 1/r \rangle_{av}$ which implies an *expansion* of the lone-pair orbital as a result of hydrogen bonding or van der Waals interactions. The diamagnetic nature of the $\sigma_{B_x}$ parameters would furthermore suggest that elongation of the $^{15}N$–H bond by hydrogen bonding of the $^{15}NH_3$ protons causes a small displacement of the bonding electrons toward the $^{15}N$ nucleus. These conclusions are consistent with the proposals of Burawoy[11] concerning the effects of hydrogen bonding on electron displacements about the oxygen nucleus in phenolic substances. However, it is also possible that the nmr shifts may be due to changes in bond hybridization rather than electron displacements.

That there is indeed an interaction between solvent–molecule unshared electron pairs and the $^{15}NH_3$ protons giving rise to the $\sigma_{B_x}$ contributions to the $^{15}N$ shift is substantiated by the proton shift data in Figure 2. Only in neopentane as solvent does it appear that the $^{15}NH_3$ proton shift at infinite dilution may be essentially the same as in gaseous $^{15}NH_3$. For all other solvents, the $^{15}NH_3$ proton resonance at infinite dilution appears to be paramagnetically shifted relative to gaseous $^{15}NH_3$. This would be consistent with hydrogen bonding between solvent–molecule electron pairs and $^{15}NH_3$ protons. Moreover, the apparent lack of any relationship between the proton shifts and $^{15}N$ shifts for $^{15}NH_3$ in those solvents where both were measured is consistent with the result that the interaction responsible for the proton shift ($\sigma_{B_x}$ type) plays a relatively unimportant role in determining the $^{15}N$ shift.

The effect of $NH_4^+$ on the $^{15}N$ shift in $NH_3$ is interesting. Lambert, Binsch, and Roberts[10] report the $^{15}N$ shift in aqueous $^{15}NH_4^+$ to be −24 ppm relative to the $^{15}N$ resonance in pure liquid $NH_3$. If we assume that the $^{15}N$ shift produced by adding $NH_4^+$ to liquid $^{15}NH_3$ is simply due to the averaging of the shift of the $^{15}N$ nucleus in the liquid $^{15}NH_3$ environment with its shift in the $^{15}NH_4^+$ environment, we obtain a shift of −85 ppm for the $^{15}N$ shift in $^{15}NH_4^+$ relative to $^{15}NH_3$. At first glance, this might suggest that surrounding the $^{15}NH_4^+$ ion by $NH_3$ molecules instead of $H_2O$ molecules produces a strong downfield shift in the resonance of the $^{15}N$ nucleus in the $^{15}NH_4^+$ ion. However, in liquid $NH_3$ with added $NH_4^+$, the very rapid proton exchange causes the $^{15}N$ resonance to represent an average overall $^{15}N$ environment. If we focus attention on the $^{15}NH_3$ molecules in the first sphere about an $^{15}NH_4^+$ ion, we would expect, on the basis of our earlier arguments, that the interaction between the lone pairs of these $^{15}NH_3$ molecules and the $^{15}NH_4^+$ ion would cause a strong downfield shift in the $^{15}N$ resonance of the first-sphere $^{15}NH_3$ molecules. It is thus conceivable that the discrepancy between the $^{15}N$ shift in aqueous $NH_4^+$ and the shift produced by adding $NH_4^+$ to liquid $NH_3$ is not due to any large solvent effect on the $^{15}N$ resonance in the $^{15}NH_4^+$ ion itself, but rather is the result of the large downfield shift produced in the $^{15}N$ resonance of the $^{15}NH_3$ molecules which surround the $NH_4^+$ ion in liquid $^{15}NH_3$.

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(7) J. C. Hindman, A. Svirmickas, and W. B. Dixon, *J. Chem. Phys.*, 47, 4658 (1967).

(8) N. F. Ramsey, *Phys. Rev.*, 78, 699 (1950); C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 40, 1714 (1964).

(9) D. P. Stevenson, G. M. Coppinger, and J. W. Forbes, *J. Am. Chem. Soc.*, 83, 4350 (1961).

(10) J. B. Lambert, G. Binsch, and J. D. Roberts, *Proc. Natl. Acad. Sci. U. S.*, 51, 735 (1964).

(11) A. Burawoy in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, pp 259–276.

The $^{15}N$ nmr shift for $^{15}NH_3$ dissolved in $CCl_4$ is especially interesting in that it coincides almost exactly with the $^{15}N$ shift in pure liquid ammonia and is essentially independent of solution composition. This would suggest that either the $^{15}NH_3$ molecules dissolved in $CCl_4$ tend to remain in aggregates with structures similar to those in pure liquid ammonia (even down to 2 mole % $NH_3$ in $CCl_4$) or that the interaction between an $^{15}NH_3$ molecule and surrounding $CCl_4$ molecules produces an $^{15}N$ shift (relative to gaseous $^{15}NH_3$) of almost exactly the same magnitude as that due to hydrogen bonding between ammonia molecules in pure liquid ammonia. The fact that the proton shifts in the $^{15}NH_3$–$CCl_4$ system move to significantly higher fields (relative to liquid $^{15}NH_3$) with decreasing $^{15}NH_3$ concentration indicates that the liquid ammonia structure is being broken. We would thus conclude that the interaction of $^{15}NH_3$ with $CCl_4$ produces a rather large downfield shift of the $^{15}N$ resonance. In terms of our model, an interaction between the nitrogen lone-pair electrons and the $CCl_4$ molecule contibutes $\sigma_{A_{CCl_4}}$ to the $^{15}N$ shift where $\sigma_{A_{CCl_4}}$ is negative and comparable in absolute magnitude to $\sigma_{A_{NH}}$. Clearly $\sigma_{A_{CCl_4}}$ represents a sizable shift which cannot be ascribed to hydrogen bonding. If we assume that the interaction is of the dipole-induced dipole type, the magnitude of $\sigma_{A_{CCl_4}}$ may be attributable to the large polarizability of the C–Cl bond (four times as large as for the C–H bond) or of the $CCl_4$ molecule as a whole. This interpretation is, however, purely speculative and other self-consistent interpretations of the experimental observations could, no doubt, be given. In any case, it seems probable that $^{15}NH_3$–solvent interactions other than hydrogen bonding may produce large shifts of the $^{15}N$ resonance. If this is so, the $^{15}N$ shift as a measure of hydrogen bonding in amine systems may be of limited utility.

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# Microcalorimetry. Thermodynamics of the Reaction of an Anionic Detergent with a Cationic Detergent[1]

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**Abstract:** The heat of reaction of sodium dodecyl sulfate and cetylpyridinium chloride was measured at 37° with a Beckman microcalorimeter. The critical micelle concentration of each detergent was determined in distilled water, 0.0001 *M* NaCl, and 0.145 *M* NaCl, and heats of dilution were measured at several concentrations of each detergent. In all but two cases, this heat of dilution was a composite including the dilution of monomers, the dilution of micelles, and the heat of micellization. Since the product micellizes, the enthalpy reported includes the $\Delta H^\circ$ of interaction plus the $\Delta H^\circ$ of the mixed micelle formation. Two approaches were used in an attempt to interpret the data. The first disregarded the micellization of the product, giving rise to a $\Delta H^\circ$ of $\sim -18$ kcal/mol, an equilibrium constant of $2 \times 10^6$, a $\Delta G^\circ$ of $\sim -9$ kcal/mol, and a $\Delta S^\circ$ of $\sim -30$ eu. The second considered the micellized products as a pseudophase and the unmicellized portion as having constant activity. In this instance, an equilibrium constant of $\sim 3 \times 10^{10}$, a $\Delta G^\circ$ of $\sim -15$ kcal/mol, and a $\Delta S^\circ$ of $\sim -11$ eu were obtained. The $\Delta H^\circ$ is the same in both cases. These results are discussed in terms of the nature of the product and precipitate, effect of pH, and the plausibility of the thermodynamic parameters.

This paper describes an attempt to extend the thermodynamic treatment of microcalorimetric data to reactions of the general type $A + B \rightleftharpoons C$. Similar work has already been described by Benzinger[2] for other systems. This system is of interest because certain biological reactions are of this type. It was hoped that this study could serve as an entree to the investigation of such biological interactions.

The use of oppositely charged detergents as reactants was suggested by the paper of vanOss.[3] He demonstrated the reaction by precipitation in an agar double diffusion study.

Although the reaction of charged detergents with one another has been utilized in analytical titrations for some time,[4] there appears to have been little work directed toward the definition of the reaction parameters and the nature of the product. Scowen and Leja[5] have studied the product spectroscopically, and Hua and Chao[6] have measured the surface activity of mixed detergent micelles. Letsinger and Wagner[7] used an anionic detergent to counter the supressor activity of a cationic detergent in a hydrolysis reaction.

In this paper, measurements of the heat evolved during the interaction of sodium dodecyl sulfate (DSS) and cetylpyridinium chloride[8] (CPC) are described. The reaction is expected to be of the type $A + B \rightleftharpoons C$, but complicated by aggregation of the monomers and the product.

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(1) Presented in part at the 2nd Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., 1968, and at the 23rd Annual Calorimetry Conference, Midland, Mich., 1968.

(2) T. H. Benzinger, *Proc. Natl. Acad. Sci. U. S.*, **42**, 109 (1956).

(3) C. J. vanOss and Y. S. L. Heck, *Z. Immunitaetsforsch.*, **122**, 44 (1961).

(4) W. B. Smith, *Analyst*, **84**, 77 (1959).

(5) R. V. Scowen and J. Leja, *Can. J. Chem.*, **45**, 2821 (1967).

(6) H. Hua and K. Chao, *Chem. Abstr.*, **62**, 7146*b* (1965).

(7) R. L. Letsinger and T. E. Wagner, *J. Am. Chem. Soc.*, **88**, 2062 (1966).

(8) 1-Hexadecylpyridinium chloride.