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Adsorption of Atmospheric Gases at the Air−Water Interface. 3: Methylamines

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The surface-bound state of methylamines adsorbed at the air−water boundary has been studied using a combination of equilibrium surface tension measurements and ab initio quantum calculations. Methylamine, dimethylamine, and trimethylamine all adsorb at the water surface, with saturated coverages roughly corresponding to the average concentration of “free” surface hydrogens. The standard enthalpies of adsorption from the gas phase show a correlation with the standard enthalpies of solvation, implying that partial solvation takes place at the air−water boundary. Comparison of experimental adsorption enthalpies and ab initio amine−water binding enthalpies suggests that the binding at the surface consists primarily of a single hydrogen bond to a surface water molecule possessing a “free” hydrogen.

Introduction

The uptake of trace gases onto the surfaces of atmospheric particles is of fundamental importance. Many key atmospheric processes have been found to be heterogeneous in nature, occurring on particles of dust, salts, ice, organic material, or aqueous droplets.[1,2] Halogen processing in the stratosphere, tropospheric aqueous-phase redox reactions, and human exposure to atmospheric pollutants all depend on the transport of gas-phase species to the condensed-phase medium of the particle. Because this transport necessarily involves passage through, or capture by, an interfacial region, the chemical and physical processes that take place at this interface are of great interest.

The chemical physics of interfacial regions is a well-established field of study.[3−5] Recently, Davidovits and co-workers[6,7] have developed a model for uptake that involves the participation of a surface state. In this model, atmospheric species are adsorbed at the air−water interface until the species has become partially solvated, at which time it may be incorporated into the bulk. Solvation at the surface takes place by the growth of clusters, comprising the species of interest and several water molecules. These clusters grow by addition of increasing numbers of water molecules until such time as a “critical cluster” is formed and the adsorbed species dissolves into the bulk solution.

In previous work from one of our laboratories the adsorption of SO_2,[8,9] NH_3 (hereinafter **I**),[10] and several partially oxidized organics (hereinafter **II**)[11] at the air−water interface has been investigated using a combination of surface second-harmonic generation spectroscopy, equilibrium and nonequilibrium surface tension measurements, and ab initio quantum calculations. Some important conclusions of these studies may be summarized: (1) the saturated coverage of the species that participate in hydrogen bonding with water at the surface is approximately given by the number of “free” hydrogens at the surface; (2) the standard enthalpy of adsorption to the surface from the gas phase is strongly correlated with the standard enthalpy of solvation but is not correlated with the standard enthalpy of vaporization; (3) in the case of ammonia, there are at least two and perhaps several water molecules associated with each surfacial ammonia, most likely in a cyclic hydrogen-bonded structure. This result seems to hold for ammonia adsorbed on ice as well.[12] A tilted geometry of NH_3 at the air−water interface, consistent with a cyclic hydrogen bond,[10] has recently been inferred in a surface sum−frequency generation study.[13] These points are strongly suggestive of a partial solvation process occurring at the surface, analagous to the “critical clusters” suggested by Davidovits and co-workers.[6,7]

The present work extends the work reported in **I** and **II** to another class of molecules expected to have strong hydrogen-bonded interactions with water: the methylamines. In the following we present results of equilibrium surface tension measurements at three temperatures for the aqueous solutions of methylamine (MA), dimethylamine (DMA), and trimethylamine (TMA) in equilibrium with their vapors. Following **I** and **II,** the gas-to-water adsorption thermochemistry for these molecules is extracted from these measurements. Ab initio calculations of complexes of the amines with one and two water molecules are used to help understand the nature of the binding at the surface.

Adsorption Thermochemistry of Volatile Solutes. Here the thermodynamic treatment presented in **I** and **II** is summarized. To understand the thermodynamics of adsorption at the air−water interface of a species that is both soluble and volatile, the chemical potentials of the molecule of interest in all three of the phases present—vapor, surface, and solution—must be known.

The chemical potential of species i in each of the two bulk phases is

$$\mu_i^{g} = \mu_i^{0,g} + RT\ln(p_i/p^0)$$

$$\mu_i^{aq} = \mu_i^{0,aq} + RT\ln(a_i/a^0)$$

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where p^0 and a^0 are the standard pressure (1 bar) and standard activity (which is taken as 1 M), respectively. The solution activity, a_i, is: $a_i = \gamma_i M_i$, where the γ_i are concentration-dependent activity coefficients and M_i represents the solute concentration in mol L^{-1}. Here ideal gas behavior of the vapor is assumed, which is quite reasonable in atmospheric applications.

By analogy with the bulk phases, in the surface phase

$$\mu_i^{\sigma} = \mu_i^{0,\sigma} + RT \ln(\gamma_i^{\sigma} \pi_i/\pi^0)$$

where nonidealities at the surface are included by use of a surface activity coefficient, γ_i^{σ}. In this expression π^0 (= 0.06084 dyne cm^{-1}) represents the standard state proposed by Kemball and Rideal[14] for the surface phase, which is the two-dimensional analogue to the 1 bar pressure standard state in the gas phase. It is expressed in terms of the surface pressure, π, defined as $\pi = \sigma^* - \sigma$, where σ^* is the surface tension of the pure solvent, and σ gives the surface tension of the solution.

At equilibrium among all three phases the chemical potentials are equal, $\mu_i^{g} = \mu_i^{\sigma} = \mu_i^{aq}$, and from the Gibbs equation,[5] the relative surface excess of species i over water may be written as

$$\Gamma_{H2O,i} = (\partial\sigma/\partial\mu_i)_{T,\mu j\neq 1} = -(a_i/RT)(\partial\sigma/\partial a_i)$$

for adsorption from solution. An analogous expression holds for adsorption from the vapor phase. (In the following, $\Gamma_{H2O,i}$ will be abbreviated to Γ). A plot of Γ as a function of solution activity can often be fit to a Langmuir adsorption isotherm, to obtain adsorption parameters

$$\Gamma = \Gamma^{sat} c/(b + c)$$

where c represents the concentration in solution, b is a parameter related to the rate constants for adsorption and desorption from both bulk phases,[10] and Γ^{sat} gives the saturated surface coverage.

The experiments described below measure the surface tensions of aqueous solutions of the methylamines under conditions such that equilibrium holds among all phases present. Γ is determined from the above expression; under our conditions this quantity is essentially equal to the surface concentration of adsorbate.

The free energy for transferring 1 mol of species i from the gas phase to the surface (the molar free energy of adsorption) is

$$\Delta G_{g\rightarrow\sigma} = \mu_i^{\sigma} - \mu_i^{g} = (\mu_i^{0,\sigma} - \mu_i^{0,g}) + RT \ln[(\gamma_i^{\sigma}\pi_i/\pi^0)/(p_i/p^0)]$$

At phase equilibrium $\Delta G_{g\rightarrow\sigma} = 0$ and so from the above,

$$\Delta G^0_{g\rightarrow\sigma} = -RT \ln[(\gamma_i^{\sigma}\pi_i/\pi^0)/(p_i/p^0)]_{eq}$$

The surface activity coefficients are unknown functions of the surface coverage (and hence, surface pressure, π). However, they are defined such that all of the $\gamma_i^{\sigma} \rightarrow 1$ as $\pi_i \rightarrow 0$. Therefore, a plot of $RT \ln[(\pi_i/\pi^0)/(p_i/p^0)]_{eq}$ versus (p_i/p^0) extrapolated to zero pressure will yield the "ideal gas" value of $\Delta G^0_{g\rightarrow\sigma}$, which is independent of the concentration of i in any of the phases.

Over a reasonable temperature range the standard entropy and standard enthalpy of adsorption are essentially constant, so may be calculated from the temperature dependence of $\Delta G°$ as $\Delta S^0 = -(\partial\Delta G^0/\partial T)$, and then $\Delta H^0 = \Delta G^0 + T\Delta S^0$.

TABLE 1: Henry's Law Parameters

amine	K_H (298 K) (mol L^{-1} atm^{-1})	$\Delta H^0_{solv.}$ (=$\partial \ln K_H/\partial(1/T)$) (kJ mol^{-1})
MA	90	21.6
DMA	56	33.2
TMA	10	33.2[a]

[a] Assumed to be the same as DMA.

Experimental and Theoretical Methods

Equilibrium static surface tension measurements were performed at 278, 298, and 313 K using the capillary rise method.[15] A capillary of inner diameter 0.0496 cm was used in a sealed sample vessel of diameter 5 cm. Commercial samples of 99.95−99.99% MA, DMA, and TMA, all provided as 40 wt % aqueous solutions, were used as supplied. Solutions were prepared volumetrically using these stock solutions and diluting with HPLC-grade water. To our knowledge, activity coefficients as a function of concentration for aqueous solutions of the MAs are not tabulated; in their absence we take the activities of the solutions to be equivalent to their concentrations. Essentially, we assume that the activity coefficients do not vary (a lot) over the concentration ranges we are studying. Solution concentrations were transformed to equilibrium vapor pressures using Henry's law parameters given by Sander;[16] these are listed in Table 1.

Ab initio calculations were performed using the GAUSSIAN 98 suite of programs.[17] To provide the same level of calculation for all the species of interest, the calculations were done at the MP2 level, using a 6-31+G(d,p) basis set. Geometry optimizations were carried out for all species; the calculated minimum energy geometries were accepted only if they gave rise to no imaginary vibrational frequencies in a harmonic frequency calculation. The vibrational frequencies obtained in that calculation were scaled[18] by a factor of 0.9427; the scaled frequencies were then used to calculate the zero-point energies of all species. The binding energy of each complex was calculated as the difference between the electronic energy of the complex and the electronic energies of the water and MA partners. This difference was corrected for zero-point energy differences (ZPC) and for basis set superposition error (BSSE), which was estimated using the full counterpoise correction.[19] This approach has been used effectively in our previous work.[9,10]

Results and Discussion

Figure 1 illustrates the variation of the surface tension of 298 K aqueous solutions of the three amines as a function of their concentration. The rapid decrease in surface tension with increasing concentration is indicative of partitioning of the amines to the surface. The propensity to partition to the surface clearly increases in the series MA < DMA < TMA; that is, as one "end" of the amine becomes increasingly hydrophobic. The surface tension decrease may be fit to a polynomial function and the instantaneous slope used in the Gibb's expression to obtain the surface excess as a function of amine concentration. Figure 2 displays this result for MA at 298 K, as well as a fit to a Langmuir adsorption isotherm. The fits for all three amines are similar, yielding saturated surface coverages, Γ^{sat}, of (2−3) × 10^{14} molecules cm^{-2}, given in Table 2. The major source of uncertainty lies in the somewhat different results obtained by using different functions to fit the surface tension versus

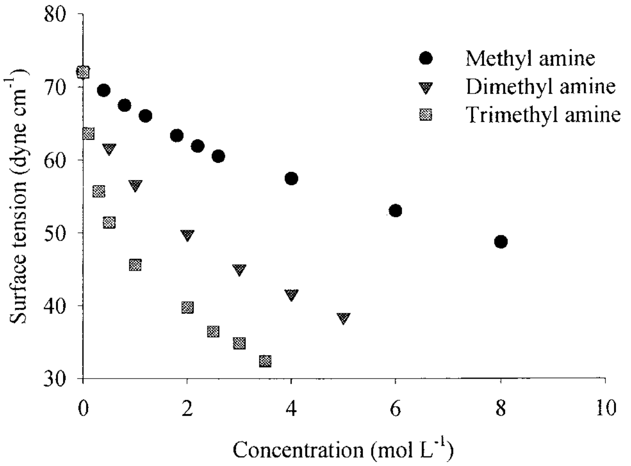

Figure 1. Surface tensions of aqueous solutions of methylamines as a function of amine concentration.

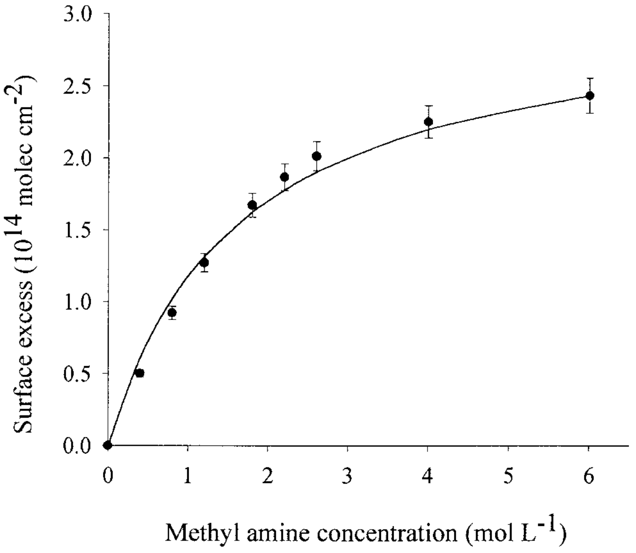

Figure 2. Gibbs surface excess of methylamine in aqueous solution as a function of its concentration (points). Error bars show the variation of Γ obtained by using different functions to fit the surface tension vs concentration data. The line illustrates a fit of these points to a Langmuir isotherm.

TABLE 2: Experimental Results for Adsorption of Amines at the Air−Water Interface

amine	Γ^{sat} ($\times 10^{-14}$ molecules cm^{-2})	$\Delta G^0_{g\to\sigma}$ (kJ mol^{-1})	$H^0_{g\to\sigma}$ (kJ mol^{-1})
NH_3[a]	1.2 ± 0.2	−19.1 ±0.5	−41 ± 5
MA	2.4 ± 0.3	−22.3 ± 1.0	−28 ± 3
DMA	2.8 ± 0.4	−23.7 ± 1.0	−37 ± 3
TMA	2.4 ± 0.3	−23.2 ± 1.0	−34 ± 3

[a] From ref 7.

concentration data. These Γ^{sat} values are roughly equivalent to the concentration of "free" (nonhydrogen bonded) OH groups present at the air−water interface,[20] estimated to be at least 2.7 × 10^{14} molecules cm^{-2}.

In Figure 3, $\Delta G^0_{g\to\sigma}$ determined as given above for DMA is plotted at 278, 298, and 313 K. A linear variation of $\Delta G^0_{g\to\sigma}$ with the calculated amine vapor pressure is seen at pressures below about 0.2 atm in all cases. This same basic behavior is also observed for ammonia[10] and partially oxidized organics.[11] Some curvature in the plots is observed at higher solution concentrations, presumably due to treating the activity coefficients as constant. The temperature dependence of ΔG^0_{ads} gives ΔS^0_{ads} and ΔH^0_{ads} from the gas phase. Table 2 displays the free energies and enthalpies of adsorption from the gas phase derived from plots such as that shown in Figure 3.

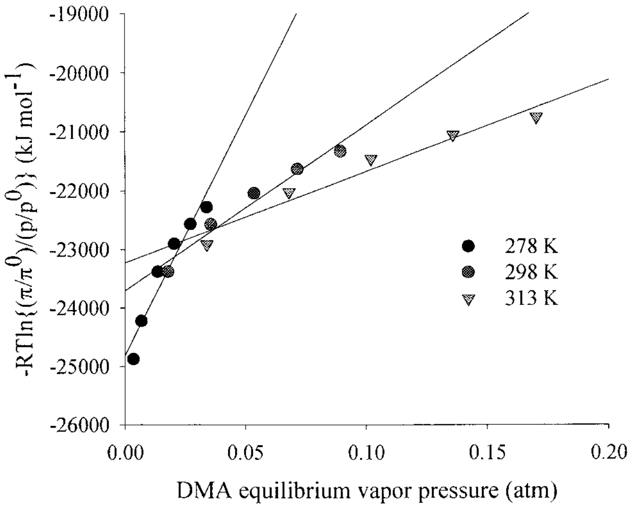

Figure 3. Plots of $-RT\ln[(\pi/\pi^0)/(p/p^0)]$ as a function of dimethylamine (DMA) equilibrium vapor pressure at three temperatures. DMA vapor pressures are calculated from the aqueous concentrations using the Henry's law parameters in Table 1. Intercepts of the best-fit lines through the points are reported as $\Delta G^0_{g\to\sigma}$ in Table 2.

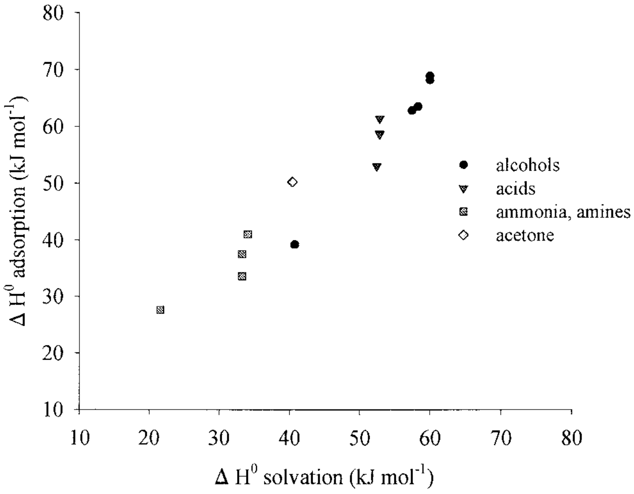

Figure 4. Standard enthalpy of adsorption, $\Delta H^0_{g\to\sigma}$, calculated from the temperature dependence of $\Delta G^0_{g\to\sigma}$ plotted vs the standard enthalpy of solvation (from the temperature dependence of the Henry's law constants) for several atmospheric gases. The absolute values of the enthalpies are plotted.

One of the primary motivations for this work was to determine whether the strong correlation between the standard enthalpy of adsorption and the standard enthalpy of solution reported in **II** holds for other molecules than partially oxidized organic species. Figure 4 shows that this correlation holds for all the molecular species tested so far: alcohols, acids, amines, and acetone. Figure 5 illustrates that there is no simple relation between the standard enthalpies of adsorption and vaporization. We conclude that adsorption of the amines to the aqueous surface involves specific chemical forces—the formation of a nascent solvation shell—rather than being a simple condensation process.

To gain some further insight into the nature of the forces acting at the surface, we performed ab initio calculations of the complexes expected to play a role in the surface binding. Similar calculations on the ammonia−water system[10] indicated that two or more water molecules per adsorbed ammonia molecule are

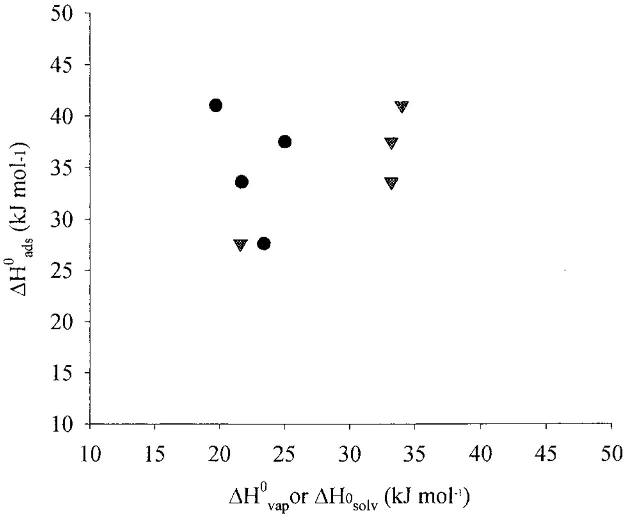

Figure 5. The (negative) $\Delta H^0_{g\rightarrow\sigma}$ of ammonia and the methylamines plotted as a function of the (negative) standard enthalpy of solvation (triangles; as in Figure 4) and the standard enthalpy of vaporization (circles). No simple relation between $\Delta H^0_{g\rightarrow\sigma}$ and ΔH^0_{vap} is observed for these molecules.

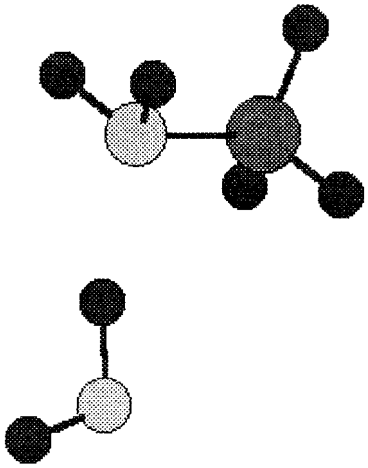

Figure 6. Calculated minimum energy structure of the 1:1 methylamine–water complex.

likely to be important in understanding the surface binding. For the calculated binding enthalpy to approximate the experimental standard adsorption enthalpy, an ammonia molecule must be bound to at least two, and perhaps three, water molecules at the surface. Therefore, in the present work we performed calculations on the (1:1) and (1:2) complexes of the amine: water complexes. To allow a direct comparison of these calculations with those done on ammonia, we performed a further calculation of the 1:1 ammonia:water complex at the same level of theory. The full results of these calculations will be presented elsewhere;[21] here we give the relevant results only.

At the present level of calculation, there is good agreement with experiment in the geometry of uncomplexed MA.[22] The oxygen–nitrogen separations in the DMA-H_2O and TMA-H_2O complexes also reproduce experimental values quite well: 2.87 Å (ab initio) versus 2.82 Å (experiment) for DMA-H_2O[23] and 2.84 Å (ab initio) versus 2.85 Å (experiment) for TMA-H_2O.[24] The calculated structure of the MA-H_2O 1:1 complex is illustrated in Figure 6. Similar hydrogen-bonded structures are obtained for DMA-H_2O and TMA-H_2O.

All of the 1:1 complexes of water with amines exhibit moderately strong hydrogen bonds. Tables 3 and 4 present the (corrected) calculated binding energies and the hydrogen bonding parameters, respectively. As shown in Table 4, the hydrogen bond strength increases and the hydrogen bond length decreases monotonically with increasing methylation, from ammonia through TMA. This behavior matches that of the gas-phase basicities,[25] also shown in Table 4, which also increase in the same order.

TABLE 3: Energetics of the 1:1 Amine–Water Complex

X =	MA	DMA	TMA
E_X (hartree)	−95.55741	−134.72990	−173.91101
E_{H2O} (hartree)	−76.23311	−76.23311	−76.23311
E_{X-H2O} (hartree)	−171.80561	−210.97895	−250.15863
ΔE (kJ mol^{-1})	−39.62	−41.85	−38.10
ZPC (kJ mol^{-1})	+8.65	+8.11	+8.14
BSSE (kJ mol^{-1})	+10.25	+12.91	+8.45
ΔE^0_0 (kJ mol^{-1})	−20.21	−20.83	−21.50

TABLE 4: Ab Initio Results for 1:1 Amine–Water Complex

amine	$R_{N\cdots H}$ (Å)	$-\Delta H^0_{0,complex}$ (kJ mol^{-1})	gas-phase basicity (kJ mol^{-1})
NH_3	1.99	15	198
MA	1.92	22	210
DMA	1.90	23	217
TMA	1.87	24	221

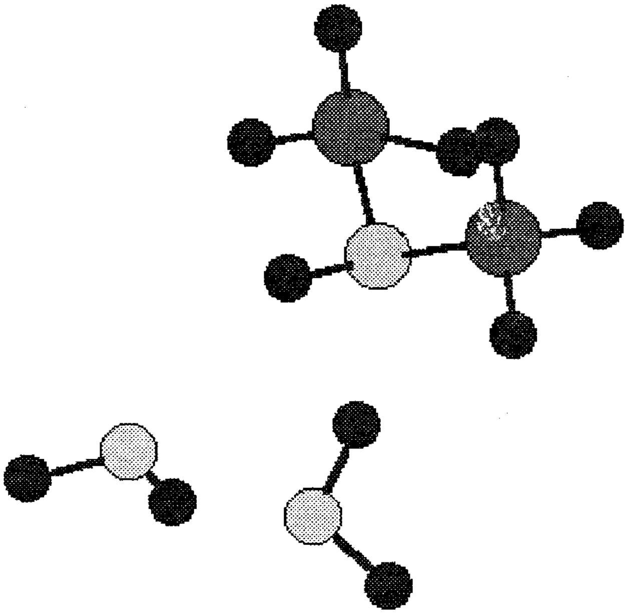

Figure 7. Calculated minimum energy structure of the (1:2) dimethylamine–water complex. A cyclic structure is observed, with the amine acting as both hydrogen bond donor and acceptor.

As shown in Table 4, the ammonia–water hydrogen bond enthalpy, corrected for zero-point differences and BSSE, is smaller than that given in **I,** which was calculated at a much higher level of theory [MP4/6-311++G(3df,2dp)]. The present result gives an enthalpy of −15.0 kJ mol^{-1} versus −18.4 kJ mol^{-1}, given in **I**. We expect that the water–amine binding energies are also underestimated at the MP2/6-31+G(d,p) level (mainly by overestimation of the BSSE correction),[21] making the present results a lower limit to the true binding energies.

Complexes formed from one amine (MA or DMA) molecule and two water molecules show the same type of cyclic hydrogen bonding as calculated[10] for $(H_2O)_2$-NH_3, with the amine acting as both a hydrogen bond donor, to one of the water molecules, and hydrogen bond acceptor with the other water.[21] Figure 7 illustrates the calculated geometry of the DMA-$(H_2O)_2$ complex. The binding energy of each amine to a water dimer is roughly

TABLE 5: Hydrogen Bond Enthalpies Calculated for (1:1) and (1:2) Amine−Water Complexes

amine	experimental $\Delta H^0{}_{g\rightarrow\sigma}$ (kJ mol^{-1})	ab initio $\Delta H^0{}_0$ (1:1) (kJ mol^{-1})	ab initio $\Delta H^0{}_0$ (1:2) (kJ mol^{-1})
NH_3	−41	−15 (−18)[a]	(−30)[b]
MA	−29	−22	−43
DMA	−34	−23	−45
TMA	−36	−-24	/

[a] From ref 10.

twice that of the binding to a single water molecule. This was also the case in ammonia,[10] where the calculated binding enthalpy increased from 18.4 kJ mol^{-1} in the 1:1 complex to 29.8 kJ mol^{-1} for ammonia to the water dimer. For the reasons stated above, we take the water dimer−amine binding energies calculated here to represent lower limits to their true values.

Table 5 compares the experimental standard enthalpies of adsorption with the binding enthalpies calculated for the 1:1 and 1:2 complexes. Although in the case of ammonia it is clear that the 1:1 complex does not adequately describe the binding involved at the surface and that two or more water molecules must be involved, the situation is not so clear for the other amines. Considering the probable underestimation of the complex binding energy calculated here, the present results are most consistent with a primary hydrogen-bonded interaction at the surface involving one (or at most, two) water molecules only.

Conclusions

A combination of equilibrium surface tension measurements and ab initio calculations has been used to characterize the adsorption of methylated amines at the air−water interface. Like ammonia and partially oxidized organic molecules, the primary interaction at the surface seems to be hydrogen bonding to surfacial water molecules. Only one (or perhaps, two) water molecule(s) is (are) involved in binding these amine molecules at the surface. The measured standard enthalpy of adsorption from the gas phase shows the same strong correlation with the standard enthalpy of solvation as is displayed by ammonia and partially oxidized organics. We conclude that the methylated amines are partially solvated at the surface, and that this surface solvation most likely involves hydrogen bonding to the “free” hydrogen of a single surface water molecule.

Of course, the air−water interface is a dynamic entity, with molecules exchanging with the vapor, diffusing into the bulk and reorienting on very fast time scales. For example, in **I** the lifetime of an individual ammonia molecule on the water surface is estimated to be in the nanosecond range. The results reported here (and elsewhere)[8,10,11] should be understood to correspond to the average features of the dynamic interface.

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