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Adsorption of Atmospheric Gases at the Air−Water Interface. 2. C_1-C_4 Alcohols, Acids, and Acetone

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Measurements of the temperature- and concentration-dependent surface tensions of aqueous solutions of methanol, 1- and 2-propanol, 1- and 2-butanol, acetic, propionic, and butanoic acids, and acetone were used to determine the standard free energies, enthalpies, and entropies of adsorption from the vapor phase onto a water surface. The saturated surface coverage of all these species is approximately 10^{14} molecules cm^{-2}. The standard enthalpies of adsorption are correlated to the enthalpies of solution, suggesting that these molecules are partially solvated in the adsorbed state. These results further suggest that atmospheric water droplets could be coated with an organic layer.

Introduction

The uptake of gas-phase trace species into (or onto) atmospheric droplets has received much attention lately. (See refs 1−4 for recent reviews of work in this area.) This interest is due to the importance of heterogeneous chemical reactions, both in the stratosphere and in the troposphere. Stratospheric heterogeneous chemistry is responsible for transforming halogen-containing species from nonphotochemically active forms (such as HCl or $ClONO_2$) to photolabile species (Cl_2, HOCl), which may participate in ozone-destroying cycles. In the troposphere, oxidation reactions often take place in the aqueous phase, within fogs, and cloud droplets; as well, the atmospheric lifetimes of soluble species are influenced by their partitioning into these droplets and subsequent "raining out".

Several techniques have been developed to study uptake (both reactive and nonreactive) of gas-phase species in the laboratory.[1] Though different in detail, they all investigate uptake as a kinetic process, looking at the time dependence of the concentration of a trace gas in the presence of the bulk phase, which is present as a liquid surface, as a droplet stream, or as an aerosol mist. Analysis of the results yields the uptake coefficient, either time dependent or steady state, depending on the particular experiment. For nonreactive uptake, the integrated value of the time-dependent uptake coefficient is simply related to the total amount of gas absorbed by the liquid, i.e., the Henry's law constant. Since the equations governing the gas-phase transport and solution diffusion and reaction are fairly well-known, deviations from the expected behavior may be interpreted as indicating other processes, for instance, a surface reaction.

On the basis of a large body of such kinetic results, Davidovits, Worsnop, and co-workers[5−7] proposed a model for gas uptake into the aqueous phase. In this model, a gas molecule impinges on a liquid surface; if it "sticks" (is accommodated), it may either desorb back into the gas phase or be incorporated into the bulk liquid. The latter process is postulated to occur via formation of a "critical cluster" of solvent about the molecule. The "critical cluster" is defined as one that has no free energy barrier for its transport between the interfacial and the bulk regions. It is formed because of the dynamic nature of the air−water interface; solvent molecules are continually departing from and returning to the surface of the liquid. Those that strike the adsorbed solute species may help form the "critical cluster", which is the surface analogue of a solvation shell. Until such a critical cluster is formed, however, a free energy barrier along the path connecting the adsorbed and the bulk-dissolved species is postulated.[5−7] The existence of such a barrier and its interpretation has recently been questioned,[8,9] at least for some systems, on the basis of molecular dynamics simulations of ethanol uptake onto water. There is therefore a need for further experiment to establish the presence and thermochemistry of adsorbed trace gases at the air−water interface.

In the first paper of this series[10] (hereinafter denoted by Part 1), we presented an experimental and theoretical study of the adsorbed state of ammonia on water surfaces. In that work, a thermodynamic and kinetic framework for analyzing the adsorption of volatile, soluble species on solvent interfaces was developed. Here, we extend that treatment to a series of small (C_1-C_4) organic molecules, some of which have been studied by Davidovits, Worsnop, and co-workers.[5]

Adsorption Thermochemistry of Volatile Solutes

Here we summarize the treatment presented in Part 1. We are interested in the thermodynamics of adsorption at the air−water interface of a species that is both soluble and volatile. To treat the system correctly, then, we must know the chemical potentials of the molecule of interest in all three of the phases present: vapor, surface, and solution.

The chemical potentials for species "i" in the vapor and solution phases are

$$\mu_i^{g} = \mu_i^{0,g} + RT\ln(p_i/p^0) \qquad (1a)$$

$$\mu_i^{aq} = \mu_i^{0,aq} + RT\ln(a_i/a^0) \qquad (1b)$$

where p^0 and a^0 are the standard pressure (1 atm) and standard activity (which we shall take as 1 M), respectively. The activity, a_i, is given by $a_i = \gamma_i M_i$, where the γ_i are concentration-dependent activity coefficients and M_i represents the solute concentration in mol L^{-1}. We have assumed ideal gas behavior of the vapor, which is quite reasonable in atmospheric applications.

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As outlined in Part 1, for the surface phase,

$$\mu_i^{\sigma} = \mu_i^{0,\sigma} + RT\ln(\gamma_i^{\sigma}\pi_i/\pi^0) \qquad (1c)$$

where any nonidealities are included by use of a surface activity coefficient, γ_i^{σ}. Here, π^0 represents the standard state proposed by Kemball and Rideal[11] for the surface phase. This choice of the standard state is the exact two-dimensional analogue to the 1 atm 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 represents the surface tension of the solution. The numerical value of this standard state is $\pi^0 = 0.060\,84$ dyne cm^{-1}, and it is independent of temperature, just as is the gas-phase standard state.

At phase equilibrium, the chemical potentials are all equal; $\mu_i^{g} = \mu_i^{\sigma} = \mu_i^{aq}$. So from the Gibbs equation,[12] the relative surface excess of species "i" may be expressed as

$$\Gamma_{H_2O,i} = (\partial\sigma/\partial\mu_i)_{T,\mu j\neq 1} = -(a_i/RT)(\partial\sigma/\partial a_i) \qquad (2)$$

for adsorption from solution, with an analogous expression for adsorption from the vapor phase. (Hereinafter, $\Gamma_{H_2O,i}$ will be abbreviated to Γ). In the experiments reported here, we measure the surface tensions of aqueous solutions of the molecule of interest under conditions such that equilibrium holds among all phases present. By making the measurements over a range of concentrations, Γ is determined from the slopes of surface tension vs solute activity plots; under our conditions, this quantity is essentially equal to the surface concentration of adsorbate.[10]

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

$$\Delta G_{aq\rightarrow\sigma} = \mu_i^{\sigma} - \mu_i^{aq} = (\mu_i^{0,\sigma} - \mu_i^{0,aq}) + RT\ln\{(\gamma_i^{\sigma}\pi_i/\pi^0)/(a_i/a^0)\} \qquad (3)$$

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

$$\Delta G^0_{aq\rightarrow\sigma} = -RT\ln\{(\gamma_i^{\sigma}\pi_i/\pi^0)/(a_i/a^0)\}_{eq} \qquad (4a)$$

A plot of $RT\ln\{(\gamma_i^{\sigma}\pi_i/\pi^0)/(a_i/a^0)\}_{eq}$ vs (a_i/a^0) extrapolated to zero concentration will yield the "ideal gas" value of $\Delta G^0_{aq\rightarrow\sigma}$. Alternatively, the free energy of adsorption onto the surface from the vapor phase may be determined by transforming the solution activities to equilibrium vapor pressures via the Henry's Law constant, K_H; $p_i/p^0 = (a_i/a^0)/K_H$ so that

$$\Delta G^0_{g\rightarrow\sigma} = -RT\ln\{(\gamma_i^{\sigma}\pi_i/\pi^0)/(p_i/p^0)\}_{eq} \qquad (4b)$$

Over a reasonable temperature range, the standard entropy and standard enthalpy of adsorption may be considered constant and are calculated from the temperature dependence of ΔG^0 determined above as

$$\Delta S^0 = -(\partial\Delta G^0/\partial T) \text{ and } \Delta H^0 = \Delta G^0 + T\,\Delta S^0$$

Experimental Methods

Equilibrium surface tensions of aqueous solutions of the C_1-C_4 solutions were measured at 278, 298, and 318 K using the capillary rise method.[13] A capillary of inner diameter 0.0392 cm was used in a sealed vessel of diameter 2.8 cm. Measurements were performed in a commercial recirculating water bath with a stated temperature stability of ±0.2 K.

TABLE 1: Henry's Law Constants Used in This Work[a]

species	K_H (M atm^{-1})	δH_{sol} (kJ mol^{-1})
methanol	220	−40.7
1-propanol	150	−59.9
2-propanol	130	−59.9
1-butanol	130	−57.4
2-butanol	110	−58.2
acetic acid	5000	−52.8
propionic acid	6000	−52.8
butanoic acid	4700	−52.8
acetone	30	−40.3

[a] From ref 16. Values of ΔH_{sol} for the acids were assumed to be equal.

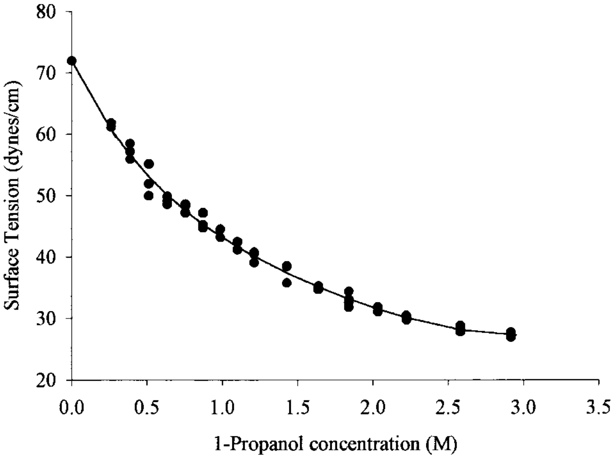

Figure 1. Surface tension of aqueous solutions of 1-propanol at 298 K as a function of the alcohol concentration. The line shows a fit to the data using the function described in the text.

Solutions were prepared volumetrically, using analytical grade organics and high-purity water. The surface tensions of all pure compounds were measured and agreed with published values. The activity coefficients for each species at each concentration used were calculated using the van Laar[14] parameters tabulated in Gmehling and Onken.[15] These varied less than about 20% over the concentration ranges used here, so solution concentrations were used rather than activities. Henry's Law constants and their temperature dependence were taken from the compilation of Sander.[16] They are listed in Table 1.

Results

Figures 1 and 2 show representative plots of surface tension vs solution concentration at 298 K for 1-propanol and butanoic acid solutions, respectively. Similar quality data is obtained for all the solutions studied. An exponential-polynomial function of the form

$$\sigma = \sigma_0\,e^{-a_1c} + a_2c + a_3c^2 + a_3c^3$$

where "c" represents the solution concentration in molarity and σ_0 is the surface tension of pure water ($\sigma_0 = 72.0$ dyne cm^{-1}) was used to fit each 298 K data set. The derivative of this function was then used to calculate the relative surface excess, via the Gibbs equation. Figures 3 and 4 show the resulting relative surface excess as a function of the concentration of 1-propanol and butanoic acid, respectively. Since these are equilibrium measurements, these may readily be converted to Γ vs p plots, with the equilibrium vapor pressure calculated using the Henry's Law constants given in Table 1. Table 2 presents the values of the saturated surface coverage for all species considered here. These were determined by fitting the

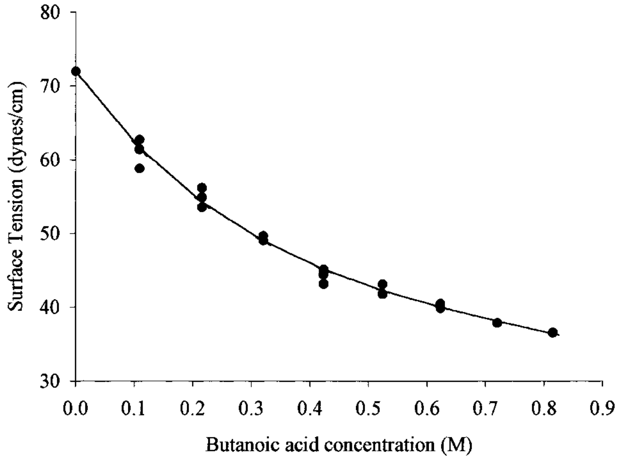

Figure 2. Surface tension of aqueous solutions of butanoic acid at 298 K as a function of the acid concentration. The line shows a fit to the data using the function described in the text.

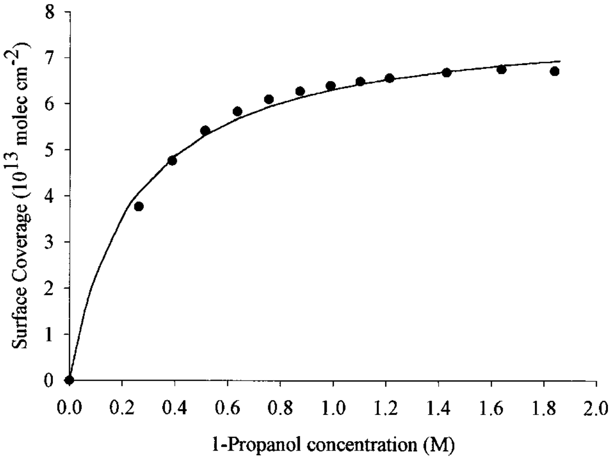

Figure 3. Surface excess of 1-propanol in aqueous solution as a function of its concentration at 298 K. The line shows a fit to the data of a Langmuir adsorption isotherm.

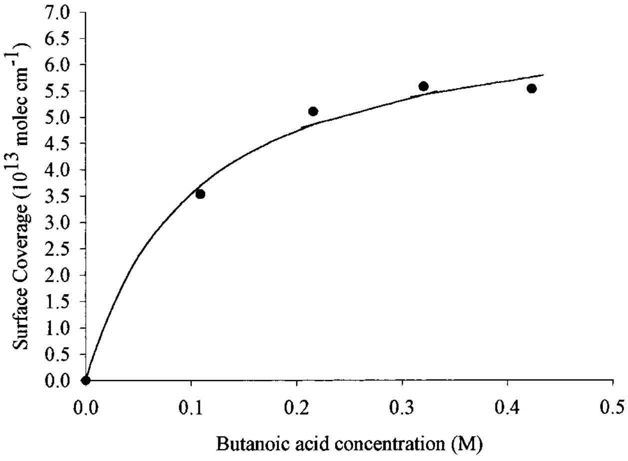

Figure 4. Surface excess of butanoic acid in aqueous solution as a function of its concentration at 298 K. The line shows a fit to the data of a Langmuir adsorption isotherm.

Γ vs c plots to a Langmuir isotherm,[12]

$$\Gamma = \Gamma^{\mathrm{sat}} c/(b + c) \tag{5}$$

where Γ^{sat} gives the surface coverage at saturation and b is a parameter related to the rate constants for adsorption and desorption from the surface into the two bulk phases.[10]

TABLE 2: Saturated Coverages and Adsorption Thermodynamic Parameters[a]

species	Γ^{sat} ($\times 10^{-13}$ molec cm^{-2})	$\Delta G^0_{g\to\sigma}$ (kJ mol^{-1})	$\Delta H^0_{g\to\sigma}$ (kJ mol^{-1})	$\Delta S^0_{g\to\sigma}$ (J K^{-1} mol^{-1})
methanol	9.2	-24.5 ± 0.5	-39.2 ± 2.0	-50 ± 6
1-propanol	7.8	-28.7 ± 0.5	-68.2 ± 1.0	-133 ± 3
2-propanol	6.5	-28.8 ± 0.5	-68.9 ± 2.0	-135 ± 6
1-butanol	10.1	-31.3 ± 0.5	-62.8 ± 1.2	-105 ± 4
2-butanol	7.0	-30.3 ± 0.5	-63.5 ± 1.3	-111 ± 4
acetic acid	7.4	-33.9 ± 0.5	-58.8 ± 2.5	-82 ± 8
propionic acid	7.7	-37.7 ± 0.5	-61.4 ± 1.2	-80 ± 4
butanoic acid	7.1	-39.4 ± 0.5	-58.6 ± 1.0	-64 ± 2
acetone	6.7	-22.5 ± 0.5	-50.3 ± 1.7	-94 ± 6

[a] At 298 K.

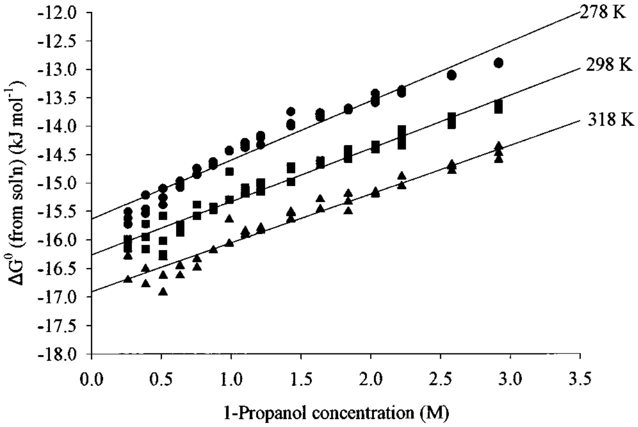

Figure 5. Standard adsorption free energy from solution of 1-propanol at the air−water interface as a function of its concentration at three temperatures. The lines show linear fits to the data sets. Extrapolation of the data to zero concentration yields the “ideal” standard adsorption free energy from solution. See the text for details.

The acid constants of all three acids studied here are about 1.5×10^{-5} M. We estimate $\leq 5\%$ of the acid is ionized in solution in the least concentrated solutions used here. Because adsorption of soluble ionic species at the air−water interface is energetically unfavorable with respect to full solvation, we assume that the coverages and energetics measured here for the acids represent those of the neutral species.

The standard free energies of adsorption of the organic molecules from the gas phase were calculated using the ideas presented above. Plots of $\Delta G^0_{\mathrm{aq}\to\sigma} = -RT \ln\{(\pi_i/\pi^0)/(c_i/c^0)\}_{\mathrm{eq}}$ as a function of solution concentration were made; the $c = 0$ M intercept yields the “ideal”ΔG^0 for adsorption from solution. Application of Henry’s Law then provides the corresponding value for adsorption from the gas phase. Figures 5 and 6 illustrate such plots for the 1-propanol and butanoic acid data, respectively. In every case studied here, a linear dependence of $\Delta G^0_{\mathrm{aq}\to\sigma}$ on concentration was obtained. Linear dependencies were also obtained for the adsorption free energy from the gas phase as a function of equilibrium vapor pressure. The slopes were very much greater for the latter plots, however, leading to larger uncertainties in the extrapolations to the $p = 0$ intercept.

Figure 7 displays a plot of ΔG^0 from the gas phase as a function of temperature for 1-propanol and butanoic acid. The slopes of the plots yield the respective entropies of adsorption from the gas phase. The adsorption enthalpies were calculated from $\Delta H^0 = \Delta G^0 + T\Delta S^0$, assuming negligible temperature dependencies of $\Delta H°$ and $\Delta S°$ over the 278−318 K range. Table 2 presents the adsorption free energies at 298 K, as well as the adsorption enthalpies and entropies, all from the gas phase, of all the species investigated here.

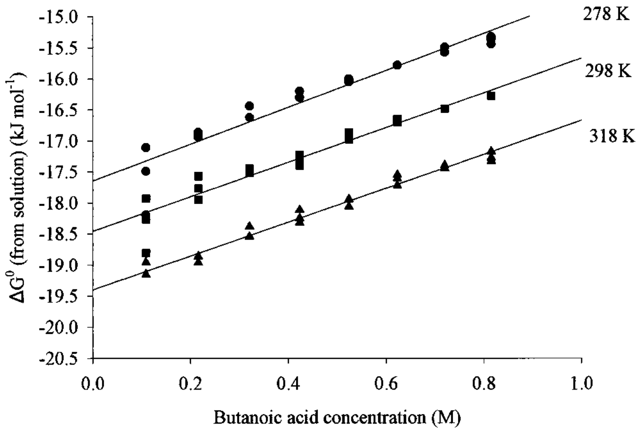

Figure 6. Standard adsorption free energy of butanoic acid at the air−water interface as a function of its concentration at three temperatures. The lines show linear fits to the data sets. Extrapolation of the data to zero concentration yields the "ideal" standard adsorption free energy. See the text for details.

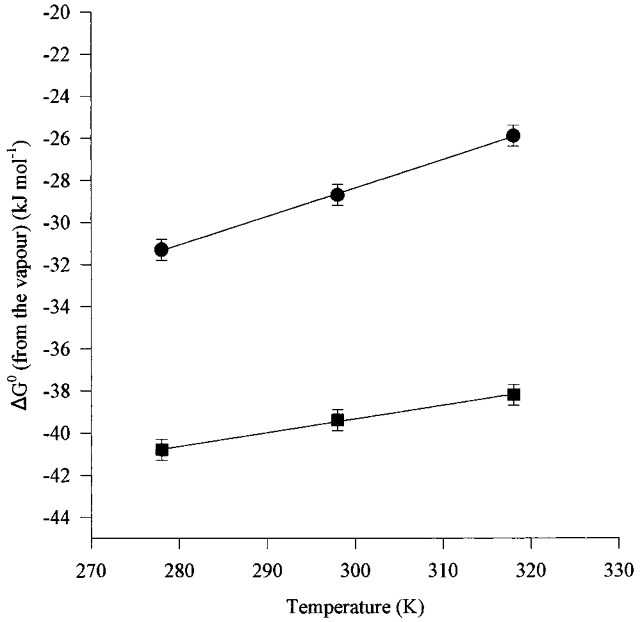

Figure 7. Standard free energies of adsorption from the gas phase shown as a function of temperature for 1-propanol (circles) and butanoic acid (squares).

Discussion

A. *Thermochemistry of Adsorption.* The saturated coverage at 298 K for all of the molecules studied here is similar, about 10^{14} molecules cm^{-2}. On the basis of the variation in this parameter on the exact function used to fit the surface tension vs concentration data, we estimate an uncertainty of about ±50% in the Γ^{sat} values presented in Table 2. This result suggests that at surface saturation these small organic molecules have a surface concentration that is approximately 10% of that of the underlying water, assuming the water surface concentration is given by its bulk density.

The magnitude of the standard Gibbs energy of adsorption from the gas phase generally increases as the hydrocarbon chain becomes longer. In the alcohols, it approaches −30 kJ mol^{-1}; $\Delta G^0_{g\rightarrow\sigma}$ for the acids decreases monotonically from acetic acid to butanoic acid, with no obvious leveling off. The Henry's law constants for the organics also decrease as the hydrocarbon chain length increases. This means that binding of the organic molecule to the water surface becomes more and more favorable compared to full solvation as the hydrocarbon chain length increases. The result is exactly as expected intuitively; as the hydrocarbon chain length increases, both the volatility and the solubility in water of organic compounds decreases. The presence of a hydrophilic group in the molecules studied here gives rise to their hydrogen bonding to water at the surface. The present data do not allow any conclusion to be drawn concerning the presence of any free energy barrier lying between the surface-adsorbed state and the fully solvated state. However, we note that in Part 1 it was shown that for ammonia any such barrier must be smaller than the free energy difference between the adsorbed and the vapor states.

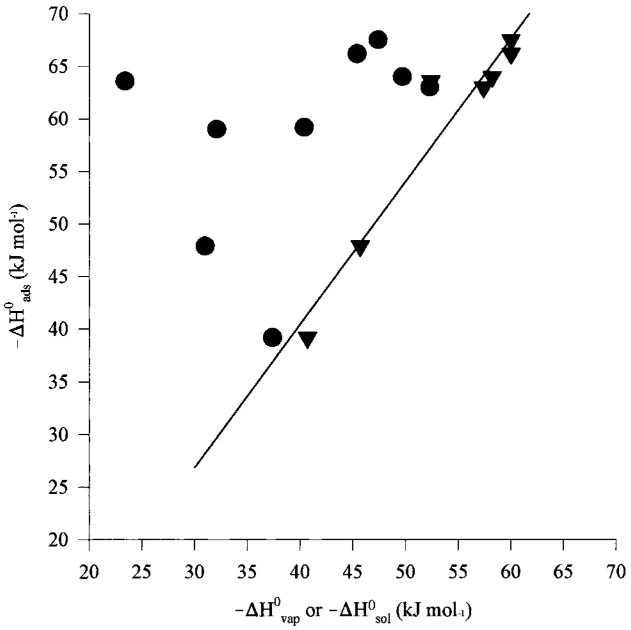

Figure 8. Standard enthalpies of adsorption from the gas phase (calculated as described in the text) plotted as a function of the standard enthalpies of vaporization (squares) and the standard enthalpies of solution from the gas phase (triangles).

The enthalpy of adsorption from the gas phase is of some interest since it indicates the nature of the surface forces operating. For many insoluble species, including hydrocarbons, the enthalpy of adsorption is equal to or slightly less than the enthalpy of vaporization.[17,18] This is expected when the major intermolecular interactions responsible for adsorption are between the adsorbate molecules, rather than between the adsorbate and substrate molecules. The circles in Figure 8 display the dependence of ΔH^0_{ads} on $\Delta H^0_{vap.}$ The adsorption enthalpy generally lies above the enthalpy of vaporization, and no clear correlation between the two quantities is present. By contrast, also shown in Figure 8 by triangles is ΔH^0_{ads} plotted as a function of ΔH^0_{sol}, the enthalpy of solution extracted from the temperature dependence of the Henry's law constant. Here, a much stronger dependence is obvious, indicating that there is a preferential interaction with water, rather than coadsorbed molecules. This result suggests that these soluble organic species become solvated to some degree at the interface, in accord with the ideas concerning the formation of critical clusters at the interface.[5−7]

B. *Atmospheric Implications.* Field measurements have shown that a significant mass fraction of tropospheric aerosols can consist of organic compounds.[19−22] The solubilities, optical properties, and surface activities of these compounds will play an important role in the reactivity and radiative transfer properties of atmospheric aerosols.[19,21,23−25] The present results allow an estimate to be made of the extent of coverage of an aqueous aerosol surface under typical atmospheric conditions.

For any reasonably soluble organic compound, under normal atmospheric conditions, the aqueous phase will never become saturated and the partitioning from the bulk aqueous phase to the surface will remain minor. However, this will not be the case for insoluble species containing some hydrophilic groups, C_6-C_{10} alcohols, aldehydes, and acids for example. Such species have been measured in abundance in Los Angeles rainwater.[20]

We can estimate the steady-state coverage of water droplets by such insoluble (or very slightly soluble) organic species. Following the kinetic derivation of the Langmuir isotherm,[12] we assume steady-state coverage and equate the rate of adsorption from the gas phase with the rate of evaporation of the adsorbed organic species from the droplet surface. Expressed in terms of the relative coverage, Θ, given by

$$\Theta = \Gamma/\Gamma^{\text{sat}} = [X^{\sigma}]/N$$

where $[X^{\sigma}]$ is the concentration of adsorbed species and N represents the concentration of adsorption sites, this condition is

$$k_{\text{ads}}[X^{g}](1 - \Theta) = k_{\text{evap}}\Theta \tag{6}$$

where $[X^{g}]$ represents the gas-phase concentration. Then,

$$\Theta_{\text{ss}} = \frac{k_{\text{ads}}[X^{g}]}{k_{\text{ads}}[X^{g}] + k_{\text{evap}}} \tag{7}$$

Note that this expression is given by eq 14 of Part 1, assuming X to be insoluble and setting k_{ads} and k_{evap} to be k_2 and k_{-1}, respectively.

The adsorption rate constant is taken to be the product of the gas-kinetic rate coefficient for collisions between X and a droplet of radius r, multiplied by an accommodation coefficient, α; $k_{\text{ads}} = \alpha\pi r^2 v_{\text{rel}}$, where v_{rel} is the relative collision velocity at the temperature of interest. Assuming that evaporation is a first-order activated process whose rate constant may be estimated by transition state theory, we may say that

$$k_{\text{evap}} = \frac{k_{\text{B}}T}{h}\, e^{\frac{-\Delta G^{\ddagger}}{k_{\text{B}}T}} \tag{8}$$

where $\Delta G^{\ddagger}$ represents the activation free energy and k_{B} and h are Boltzmann's and Planck's constants, respectively. In Part 1, it was determined that $\Delta G^{\ddagger}$ for the evaporation of ammonia from the water surface is equivalent to the adsorption free energy; that is, there is no free energy barrier to evaporation other than the endothermicity. Since we expect that the binding of partially oxidized organic species to a water surface is primarily due to hydrogen bonds (as in the case of ammonia), we assume that $\Delta G^{\ddagger}$'s for evaporation of these species are also given by their adsorption free energies.

At 273 K and taking an adsorption free energy of −35 kJ mol^{-1}, the predicted evaporation rate constant is $1.1 \times 10^6\ \text{s}^{-1}$. This is considerably less than that given for ammonia,[10] reflecting the larger adsorption free energies of the organic species considered here. For droplets of diameter 1 μm and a concentration of 1 ppb for the trace organic species, the calculated value of $k_{\text{ads}}[X^{g}]$ is $6.34 \times 10^6\alpha\ \text{s}^{-1}$. The steady-state coverage becomes

$$\Theta_{\text{ss}} = \frac{6.34 \times 10^6\alpha}{6.34 \times 10^6\alpha + 1.1 \times 10^6}$$

For $\alpha = 1$, the surface coverage is predicted to be about 85% of its saturated value; the prediction for $\alpha = 0.1$ is $\Theta_{\text{ss}} = 0.36$.

This amount of surface coverage may have important effects. The surface tension will be decreased, though for droplets in the micrometer size range this will not affect the water vapor pressure in equilibrium with the droplet to any significant extent. However, the lowered surface tension and more hydrophobic nature of the surface could affect the growth and reactivity of droplets in this size range.[23−25] Two particularly interesting effects could be (1) the possibility of accreting fat-soluble species that would not adsorb on a bare water interface and (2) the alteration of oxidation pathways and kinetics due to the presence of soluble oxidizing agents in the droplet to which the organic is adsorbed. We are continuing to investigate effects such as these and other consequences of adsorbed organic layer on heterogeneous atmospheric chemistry.[26]

Conclusions

We have determined the standard free energies, enthalpies, and entropies for adsorption of a series of small, soluble organic species from the vapor phase onto a water surface. The values are consistent with a surface-bound species mediating transport between the gas and solution phases. Atmospheric water droplets could very likely be coated with an adsorbed layer of organic molecules.

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