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Adsorption to Ice of *n*-Alcohols (Ethanol to 1-Hexanol), Acetic Acid, and Hexanal

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The gas-to-ice uptakes of a variety of small organic molecules (C2 to C6 n-alcohols, acetic acid and hexanal) have been measured in a coated-wall flow tube coupled to an electron-impact mass spectrometer. The ice films are prepared by freezing liquid water and the temperature range covered is between 213 and 245 K. With the exceptions of 1-hexanol and high partial pressures of 1-pentanol, the surface coverages at 228 K are adequately described by a standard Langmuir adsorption isotherm model consistent with a saturated surface coverage of 2 to 3 × 10^{14} molecules/cm^2, where the area is the geometric surface area of the film. For similar partial pressures, 1-hexanol exhibits very much larger uptakes than the other species, an indication that multilayer adsorption is occurring. The equilibrium constant for the partitioning between the gas-phase organic and its adsorbed form has been measured from the linear dependence of the surface coverage on pressure at low partial pressures. The temperature dependence of these equilibrium constants is used to derive the following heats of adsorption to ice at temperatures close to 228 K (in kcal/mole): -17.5 ± 2.8 for acetic acid, -17.1 ± 1.6 for 1-pentanol, -16.2 ± 0.9 for 1-butanol, -14.8 ± 0.4 for ethanol, and -15.5 ± 1.4 for hexanal. The gas-to-surface equilibrium constants at 228 K correlate closely with the free energy change for gas-to-liquid condensation, indicating that polar organics adsorbing to ice participate in H-bonding interactions analogous to those in the pure liquid. The 228 K equilibrium constants do not correlate well with the aqueous Henry's Law constants, an indication that dissolution into a liquidlike layer of water on the surface has a minor impact on the uptakes.

Introduction

Although ice is one of the most prevalent condensed phases present in the Earth's atmosphere, there still remain significant gaps in our understanding of how atmospheric trace gases interact with ice surfaces. A large number of studies have been performed with HNO_3 and HCl, which indicate that a very strong interaction takes place on the surface, most probably driven by the dissociation of the strong acids.[1−7] The large uptake that results from this interaction may lead to efficient gas-to-particle scavenging in ice cloud regions and, in the case of HCl, the adsorbed species becomes highly reactive with molecules such as $ClONO_2$, HOCl, and HOBr. These studies promote a model involving strong chemical interaction of the water molecules on the ice surface with the adsorbing species. In particular, although strong acids will first adsorb to the ice surface by a H-bonding interaction, it is the dissociation of the acids and their subsequent hydration that ultimately leads to high surface coverages. This model has been supported by high-level molecular dynamics calculations of the intermolecular interactions that take place with HCl on an ice surface.[8] It is also consistent with laboratory studies that indicate SO_2 also adsorbs to ice surfaces via a reaction with water and the formation of surface phase hydronium and bisulfite ions.[9,10]

Molecules that do not have the capability to interact in this manner adsorb to a considerably smaller degree, relying upon H-bonding interactions and weak van der Waals interactions. Hydrogen peroxide is an example of such a species, exhibiting an uptake orders of magnitude smaller than nitric acid for the same partial pressure.[9] For molecules of this type, it is interesting to investigate whether the ice surface interacts in a static manner akin to the behavior of a low volatility solid or whether the uptake is similar to that which occurs when a molecule interacts with a liquid water surface. Previous studies involving critical angle and vapor adsorption measurements of small, nonpolar hydrocarbons to ice have implied that the latter case is prevalent, where the adsorbents drive a fair degree of surface restructuring at temperatures as low as 243 K and the uptakes resemble those to liquid water.[11−14] However, the extent to which a liquidlike layer of water on the surface of ice at high temperatures affects the uptake of polar molecules from the gas phase is not known.

To address issues of this nature and to better assess the extent to which volatile organic compounds may be scavenged by ice clouds in the atmosphere, we have measured the gas-to-ice uptakes of a variety of polar organic molecules. Hudson et al. have investigated the low temperature (<200 K) behavior of a set of two-carbon organics—acetone, acetaldehyde and acetic acid—and found that uptake is atmospherically significant, occurring at the 0.001 monolayer level for temperatures above 180 K.[15] Acetic acid was found to bind most strongly to the surface and acetaldehyde least strongly. In this work, we extend measurements of this type to temperature conditions of the free troposphere, between 213 and 245 K. The suite of molecules that we have chosen to study includes a set of five alcohols, ethanol through to 1-hexanol, to investigate the effect which molecular size has on the uptake within a homologous series of molecules with the same functional group. We have also studied acetic acid and hexanal to determine the nature of the interaction of other functional groups relative to that of an alcohol. By working with these species, we are particularly interested to see whether there is a single model which quantitatively describes the uptake across a range of molecular types. A model of this type would provide a convenient framework to estimate the interactions with ice undergone by

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the very wide range of volatile organic carbon species present in the atmosphere. We pay particular attention to quantifying the unsaturated portion of the adsorption isotherms given that atmospheric surface coverages exist in this regime for most small volatile organics. The coverage of the surface as it approaches saturated conditions is used to determine the surface areas of the films at the molecular level.

Experimental Section

Experiments were conducted in a low-pressure, coated-wall flow tube using the approach used previously in this laboratory to measure the uptake of gases by thin films of ice formed by freezing liquid water.[4,9] Briefly, the inner walls of a 2.34-cm-i.d. Pyrex tube were coated with distilled water at room temperature. The tube was inserted into the cold, double-jacketed flow tube and allowed to sit for 10 min until the water froze to form a transparent ice film. A flow of between 100 and 300 sccm helium carrier gas was established over the ice film at a pressure of about 0.7 Torr. By passing a fraction of the carrier gas through a room-temperature water bubbler, we operated in a mode where the film at the upstream end of the flow tube is experiencing net water vapor condensation. This ensures that the helium passing down the remainder of the flow tube was conditioned to contain water vapor at the vapor pressure of ice at the flow tube temperature. At the highest temperatures of this work (248 K), the flow of water vapor was roughly equal to the flow of helium. Uptake experiments were not conducted over the ice at the back of the flow tube that may have been experiencing net condensation. Trace organic species were added to the flow tube through a movable injector initially positioned with its tip beyond the downstream end of the ice film.

A differentially pumped electron-impact mass spectrometer was used to sample the composition of the gas phase by monitoring the following ion signals in the mass spectrum of the organic: mass 60 for acetic acid, 56 for hexanal, 46 for ethanol, 59 for 1-propanol, 41 or 56 for 1-butanol, 55 for 1-pentanol and 56 for 1-hexanol. Detection limits for these species were between 10^{-7} and 10^{-6} Torr for a 3-second integration time and a S/N of 1. In all cases, commercially available chemicals were purified of air by freeze−pump−thaw cycles. The partial pressure of the organic species in the flow tube was determined from the drop in pressure with time from a glass reservoir of known volume which contained a mixture of the species in helium. For acetic acid, the effects of gas-phase dimerization were taken into account by using the literature equilibrium constant to calculate the relative proportions of monomers and dimers in the glass reservoir at the measured pressure.[16] The total flow of acetic acid molecules from the reservoir was then determined by taking into account that each dimer contributed two acetic acid molecules to the flow tube.

Uptake experiments were conducted by pulling the injector back over the ice film a distance of between 3 and 10 cm, the exact value being determined by the need to see a sufficiently large change in signal indicative of partitioning to the surface via adsorption. The injector was then pushed back in to its starting position. A number of uptake experiments was performed on each film. A limit to the largest partial pressures that we could study was set by the vapor pressure of the organic at the temperature of the experiment. In particular, the partial pressures were kept considerably below the point at which condensation of the organic would occur in the cold injector.

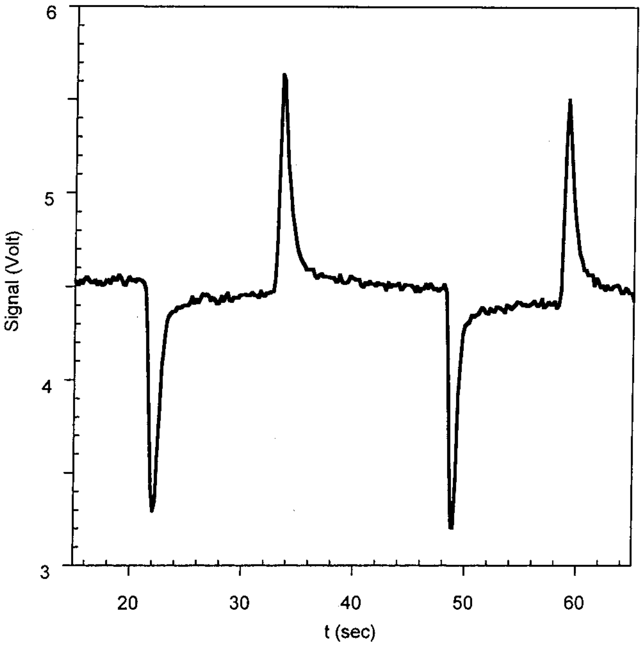

Figure 1. Mass spectrometer signal as a function of time during a sequence of two uptake experiments of 1-butanol on an ice film at 233 K. The partial pressure of 1-butanol was 2.2×10^{-4} Torr and the average uptake measured for the two experiments is 1.8×10^{14} molecules/cm^2.

Results and Discussion

Typical uptake profiles for 1-butanol at 228 K are shown in Figure 1, where the injector is withdrawn and pushed back in to its starting position two times. The signal declines sharply when the injector is pulled out because gas-phase molecules partition to the fresh ice surface. The signal then recovers as the surface approaches equilibrium with the partial pressure of the gas-phase organic. We integrate the short-term loss of signal associated with pulling the injector out, as described previously.[4] Knowing the flow rate of the organic down the flow tube, we can convert this quantity into a surface uptake, which we then reference to the geometric area of the exposed ice surface to calculate a surface coverage. It should be noted that, as shown in Figure 1, there is a tendency for the signal to not recover fully to its starting value in some experiments. This effect is not nearly as pronounced as it was in our work with nitric acid and may be indicative of a slow diffusion of the organic into the upper layers of the ice film.[4]

In a previous publication,[9] we described how it is necessary to account for a momentary decline in the trace gas signal that accompanies pulling the injector back, even when adsorption is not occurring. This effect arises because the injector is being withdrawn into a flow of carrier gas which is free of trace gas. Compared to the uptakes attributed to adsorption, this loss of signal due to this effect is minor, with the exception of molecules that exhibit very small uptakes. In particular, for the species studied in this work, the effect is only significant for the hexanal uptakes at 226 K, where it represents roughly 15% of the uptake.

When the injector is pushed back to its starting position, the signal momentarily surges indicative of desorption of organic molecules from the surface. The rapid signal increase indicates that the lifetimes of the molecules on the ice surface are less than the time it takes to push the injector back in, i.e., a second or so. This leads us to believe that the ice surface readily reaches equilibrium with the gas phase over the exposure time scales. For all of the experiments conducted in this work, the area under

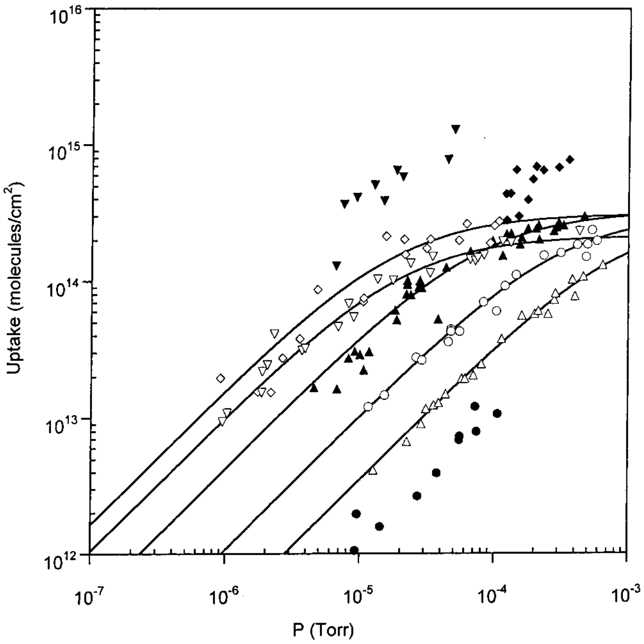

Figure 2. 228 K uptakes for all gases, except for hexanal where the uptakes were measured at 226 K: ● − hexanal, △ − ethanol, ○ − 1-propanol, ▲ − 1-butanol, ▽ − acetic acid, ◇ − 1-pentanol (low pressure), ◆ − 1-pentanol (high pressure), ▼- 1-hexanol. The solid lines are Langmuir adsorption isotherm fits to the experimental data. For 1-pentanol, the "high pressure" points are those which occur at higher pressures than the breakpoint between the plateau region indicative of monolayer coverage and the larger uptake region indicative of multilayer growth. Only the "low pressure" points were used to determine the fit (see Results and Discussion). Each point represents the average of between two and four uptakes measured on the same ice film.

the curve indicative of desorption from the surface was equal to the uptake area within experimental uncertainties. This is an indication that the uptake was reversible on the time scale of the experiment. This behavior is quite different from that reported for HNO_3, where a large fraction of the uptake is irreversible on the time scale of the experiment.[4] Repeated uptakes on the same film were similar to each other with a typical precision of ±15%. It was noted that the molecules which exhibited larger uptakes exhibited considerably more scatter in their adsorption isotherms than molecules which were less surface active. We attribute this behavior in part to a more variable mass spectrometer background signal, arising from the sticking of the more surface-active molecules to vacuum line and mass spectrometer surfaces. As an example, in the dependence of the uptakes on partial pressure presented below, the scatter in the data for 1-pentanol is considerably higher than that for ethanol. It is also true that the precision of the uptakes from film to film was poorest when low partial pressures were used.

For all species except hexanal, we concentrated on precisely measuring the uptakes at a common temperature, 228 K, as a function of partial pressure. For hexanal, the uptakes were so small that 226 K was chosen to perform a detailed study. To make a ready comparison between the adsorption behavior of the different molecules under these temperature conditions, the results for all the molecules studied are shown in Figure 2 where the uptakes are plotted versus the partial pressure.

There are a number of features to address in Figure 2. Starting with the species that exhibits the smallest uptakes, hexanal, it is seen that there is a linear dependence of the uptake on the partial pressure for all pressures studied. The uptakes are considerably smaller than those of a monolayer coverage, which is about 5×10^{14} molecules/cm^2 assuming small molecules (~0.5 nm diameter) stacked side-by-side on the surface. Thus, it is clear that the surface coverages are unsaturated in this regime. For the other species, which all exhibit considerably larger surface coverages, there is also an unsaturated portion of the adsorption isotherm at low partial pressures but the surface coverage begins to saturate at higher partial pressures. For ethanol and 1-propanol, this saturation is not complete for the partial pressures studied but for 1-butanol, 1-pentanol and acetic acid, the surface coverages approach a distinct plateau region in the adsorption isotherm at coverages of 2 to 3×10^{14} molecules/cm^2, i.e., at a large fraction of the monolayer value assuming the surfaces are smooth at the molecular level.

To be more quantitative, we have fit the uptake data as a function of partial pressure to a standard Langmuir adsorption isotherm[17]

$$\theta/\theta_o = K_P P/(K_P P + 1) \tag{1}$$

where θ is the surface coverage (in molecules/cm^2), θ_o is the saturated surface coverage (in molecules/cm^2), K_P is the equilibrium constant that describes the partitioning from the gas phase to the surface (Torr^{-1}) and P is the partial pressure of the organic (Torr). The fits are shown graphically in Figure 2, and the fit parameters are given in Table 1. As can be seen from the fit parameters, the saturated surface coverages consistent with the data are remarkably constant from molecule to molecule varying for the alcohols by less than ±10% from the mean value of 3.1×10^{14} molecules/cm^2, even for ethanol which was studied at surface coverages far from saturation. Given that

TABLE 1: Fit Parameters for Langmuir Adsorption Isotherms

Ethanol	T (K)		228			
	θ_o (molecules/cm^2)		2.9×10^{14}			
	K_P (Torr^{-1})		1.22×10^3			
1-Propanol	T (K)		228			
	θ_o (molecules/cm^2)		3.1×10^{14}			
	K_P (Torr^{-1})		3.5×10^3			
1-Butanol	T (K)	221	228	233		
	θ_o (molecules/cm^2)	3.4×10^{14}	3.2×10^{14}	3.4×10^{14}		
	K_P (Torr^{-1})	4.6×10^4	1.34×10^4	5.2×10^3		
1-Pentanol	T (K)		228	233	238	245
	θ_o (molecules/cm^2)		3.1×10^{14}	3.4×10^{14}	3.0×10^{14}	2.2×10^{14}
	K_P (Torr^{-1})		5.4×10^4	3.2×10^4	1.45×10^4	8.0×10^3
Acetic Acid	T (K)	222	228	233	238	245
	θ_o (molecules/cm^2)	2.8×10^{14}	2.2×10^{14}	2.8×10^{14}	2.7×10^{14}	4.2×10^{14}
	K_P (Torr^{-1})	5.4×10^4	4.9×10^4	1.11×10^4	6.1×10^3	2.33×10^3

an ethanol molecule is considerably shorter than one of 1-pentanol, the fact that both exhibit the same saturated surface coverage is probably an indication that when the surface is saturated the molecules are oriented in a similar manner with the hydroxyl group binding to the ice surface and the alkyl chain at right angles to the surface.

For acetic acid, the saturated surface coverage is similar to that of the alcohols but somewhat lower, 2.2×10^{14} molecules/cm^2. However, it should be noted that the acetic acid adsorption isotherm is considerably complicated by the fact that a sizable fraction of the molecules in the cold flow tube will have dimerized under the partial pressure conditions which give a saturated surface. Given that we do not know whether the adsorption isotherm of acetic acid monomers is the same as that of the dimers, coupled to the fact that the ratio of monomers to dimers changes as a function of partial pressure, in Figure 2 we have simply plotted the partial pressure assuming that all the acetic acid molecules in the flow tube are in the monomeric form. To give some idea of the extent of dimerization at 228 K, we calculate that the fraction of acetic acid molecules in the monomer form is 80% at a reported partial pressure of 1×10^{-4} Torr and 98% at 8×10^{-6} Torr.[16]

Given that the saturated surface coverage of 2 to 3×10^{14} molecules/cm^2 is calculated using the geometric surface area of the ice film is a strong indication that the film is smooth at the molecular scale. In a previous publication, we have pointed out that uptakes of HCl measured on vapor-deposited ice films can be substantially larger than those on films formed by freezing liquid water.[4] However, with the frozen water films the uptakes for both HNO_3 and HCl are measured to be about 2×10^{14} molecules/cm^2 for partial pressures of about 10^{-6} Torr at temperatures close to 210 K. Both gases have a very weak dependence on partial pressure from 10^{-7} to 10^{-6} Torr indicating that the surfaces are saturated in this regime.[2,4,7] Finally, although the films are polycrystalline to some extent, we do not believe that this affects the measured surface coverage because the uptake of HNO_3 by submicron-sized ice single crystals formed by homogeneous freezing of liquid water droplets has been shown to be within a factor of 2 of the uptake on the macroscopic ice films.[6] All of these studies together provide strong evidence that the ice surfaces used in this and previous studies from our laboratory, which are formed by freezing liquid water, are smooth at the molecular level. Compared to BET measurements involving N_2 or Kr, the use of a molecule such as 1-butanol or 1-propanol is a preferable method to measure the specific surface area of high-temperature ice because the experiments can be conducted at the temperature of interest and not at 77 K.

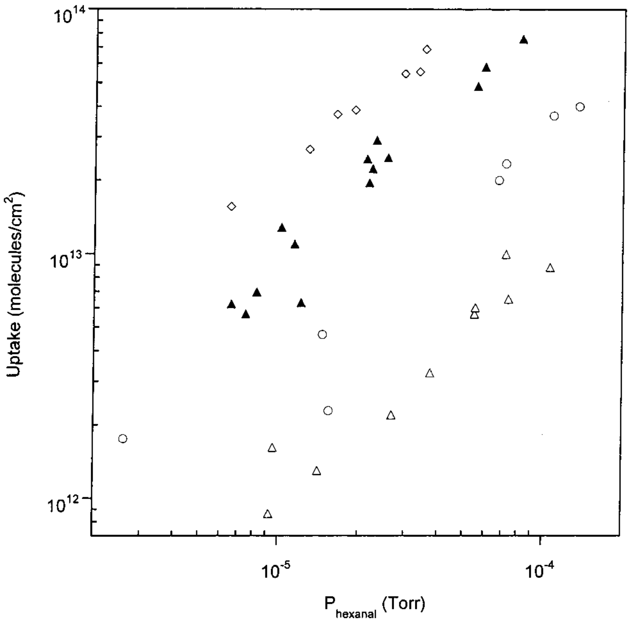

Figure 3. Uptakes for hexanal as a function of partial pressure at a variety of temperatures: △ − 226 K, ○ − 221 K, ▲ − 213 K, ◇ − 209 K.

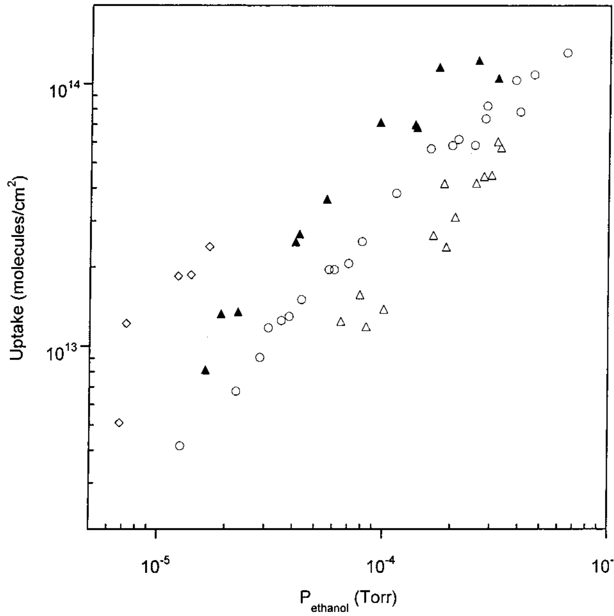

Figure 4. Uptakes for ethanol as a function of partial pressure at a variety of temperatures: △ − 233 K, ○ − 228 K, ▲ − 223 K, ◇ − 218 K.

Although this was not the primary focus of this paper, we performed a few studies with 1-pentanol at partial pressures considerably higher than the break in the adsorption isotherm indicative of monolayer coverage. These data are shown in Figure 2 as solid filled diamonds. The Langmuir fit parameters given in Table 1 were determined using only the data marked by open diamonds. We believe this propensity for multilayer growth is the reason that for the partial pressures used 1-hexanol exhibits surface coverages which are somewhat higher than those for a saturated monolayer. To test this hypothesis, we performed a few uptake experiments with 1-hexanol at slightly higher temperatures, 233 K, hoping to measure an adsorption isotherm which sampled the transition region to saturated coverage. These data (not shown) clearly indicate a transition from submonolayer coverages at partial pressures below 1×10^{-5} Torr and a plateau region of 3×10^{14} molecules/cm^2 at higher pressures. It is important to point out that the multilayer growth exhibited by both 1-hexanol and 1-pentanol is occurring at partial pressures which are well below the partial pressures of the liquid at 228 K, 1×10^{-3} and 3×10^{-3} Torr respectively.[18] That is, simple condensation of the gases is not occurring, as indicated by the fact that the shape of the uptake profiles is similar in the multilayer regime to that in the submonolayer regime.

To gain more insight into the thermodynamics of the adsorption, we studied the temperature dependence of the uptakes of five molecules, as shown in Figures 3 through 7 for hexanal, ethanol, *n*-butanol, *n*-pentanol, and acetic acid, respectively. For both ethanol and hexanal, the adsorption isotherms remain largely in the unsaturated regime for the temperature ranges studied. For *n*-butanol, *n*-pentanol and acetic acid, the transition from the unsaturated to the saturated regime occurs

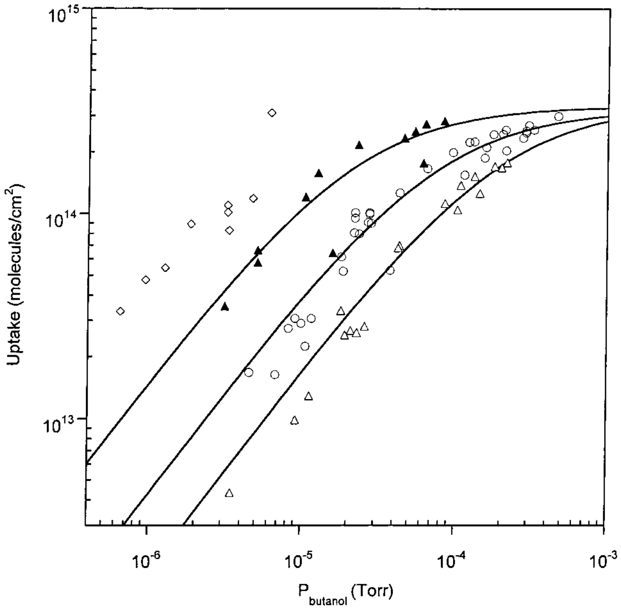

Figure 5. Uptakes for 1-butanol as a function of partial pressure at a variety of temperatures: △ − 233 K, ○ − 228 K, ▲ − 221 K, ◇ − 213 K. The solid lines are Langmuir adsorption isotherm fits to the experimental data.

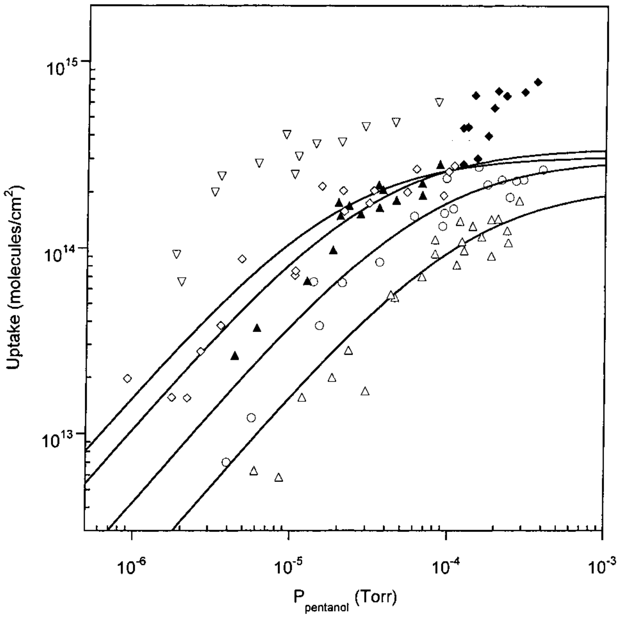

Figure 6. Uptakes for 1-pentanol as a function of partial pressure at a variety of temperatures: △ − 245 K, ○ − 238 K, ▲ − 233 K, ◇ − 228 K (low pressure), ◆ − 228 K (high pressure), ▽ − 221 K. The solid lines are Langmuir adsorption isotherm fits to the experimental data. At 228 K, only the low pressure points were used to determine the fit because the high pressure points represent multilayer coverage experiments (see Results and Discussion).

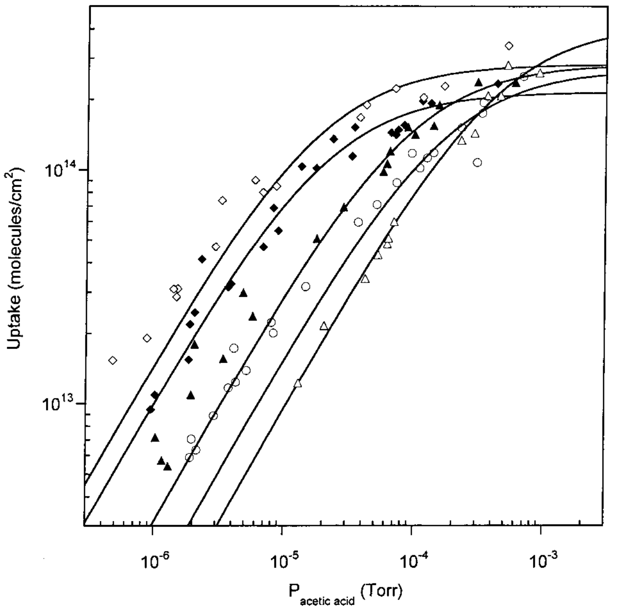

Figure 7. Uptakes for acetic acid as a function of partial pressure at a variety of temperatures: △ − 245 K, ○ − 238 K, ▲ − 233 K, ◆ − 228 K, ◇ − 222 K. The solid lines are Langmuir adsorption isotherm fits to the experimental data.

at lower partial pressures for lower temperatures, as expected for exothermic processes such as adsorption. For 1-pentanol, it appears that at 221 K the surface coverages are in the multilayer regime for partial pressures around 1×10^{-5} Torr and higher.

For these three species, Langmuir fits are shown in the Figures and the fit parameters are given in Table 1. It should be noted that the quality of the fits at higher temperatures is somewhat poor for both 1-pentanol and acetic acid. For acetic acid this may be related to the complications arising from the varying fraction of dimers in the flow tube as the partial pressure is varied. The saturated surface coverages derived from the fits at temperatures different from 228 K are very similar to the value of 2 to 3 × 10^{14} molecules/cm^2, indicating that there is not a substantial temperature dependence to the surface area of the ice on the molecular scale. The one exception to this is the fit for acetic acid at 245 K, which has a value of 4 × 10^{14} molecules/cm^2. It is unclear why the surface coverage is particularly high at this temperature. One possibility is that the liquidlike layer of water that is known to exist on the surface of water at temperatures close to the melting point is sufficiently thick at 245 K such that there is an appreciable degree of full solvation of acetic acid occurring, as opposed to an interaction which is fully adsorptive. Acetic acid would show a considerable effect in this regard because its Henry's Law constant is so high compared to the other molecules studied in this work. Clearly, however, this is simply a suggestion without strong experimental support.

The slopes of the unsaturated portion of the adsorption isotherm have been plotted in Figure 8 in a log-linear manner versus the inverse temperature. In most cases, the data for an individual molecule fall along straight lines close to the experimental uncertainties. One exception is for acetic acid, where we have not included the lowest temperature point in the line-of-best-fit because we believe that acetic acid may be undergoing appreciable dissociation on the surface at this temperature. In particular, for all four of the higher temperature data sets, the dependence of the uptake on the partial pressure is strongly linear, with slopes in a log−log sense of close to unity. For the lowest temperature point the uptakes scale more closely with the square root of the partial pressure with the slope of the log−log plot being 0.6. A square root dependence would be an indication that acetic acid is dissociating on the surface.[9] We do not include these data points in our analysis because the adsorption thermodynamics may be different for a dissociating molecule than for an undissociating molecule.

The enthalpy of adsorption of the organics to ice can be determined using a van't Hoff analysis of the slopes of the fits in Figure 8. The results are the following (in kcal/mole): −17.5 ± 2.8 for acetic acid, −17.1 ±1.6 for 1-pentanol, −16.2 ± 0.9 for 1-butanol, −14.8 ± 0.4 for ethanol, and −15.5 ± 1.4 for

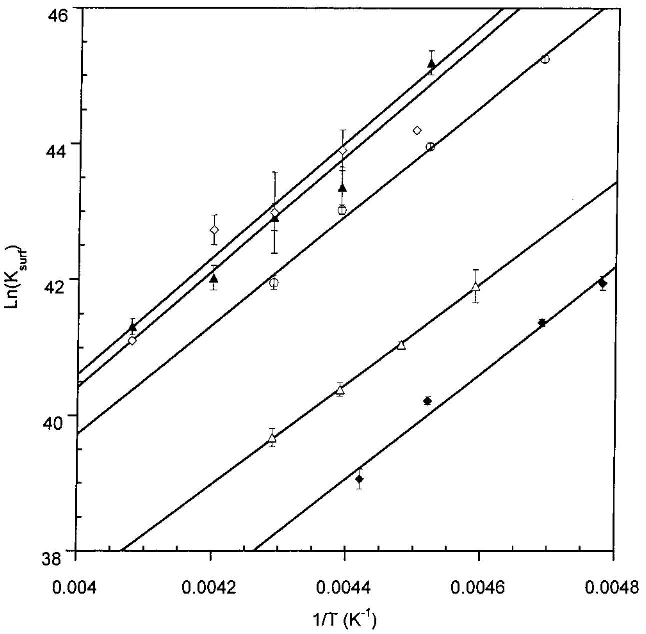

Figure 8. Van't Hoff plot of the experimental gas-to-surface equilibrium constants, K_{surf}, as a function of inverse temperature for five species: ◆ − hexanal, △ − ethanol, ○ − 1-butanol, ▲ − 1-pentanol, ◇ − acetic acid. For reasons described in the text, the line-of-best-fit does not include the lowest temperature point for acetic acid. The error bars represent 1-σ precision uncertainties in slopes of uptake versus partial pressure plots. If not shown, they are smaller than the size of the point.

hexanal, where the uncertainties are 1-σ precisions. As expected, the corresponding heats of condensation are significantly smaller (in kcal/mole): −12.4 for acetic acid, −13.6 for 1-pentanol, −12.2 for 1-butanol, −10.3 for ethanol, and −10.3 for hexanal.[19] It is interesting that the heats of adsorption are quite similar to those inferred from surface tension measurements for the heat of adsorption of organic species to liquid water. In particular, for 1-propanol, 1-butanol and acetic acid, Donaldson and Anderson report heats of adsorption of −16.3, − 15.0, and −14.1 kcal/mol, respectively.[22] This quantity is clearly larger than would arise from a single H-bond which would account for perhaps 5 kcal/mol or so. Instead, for both water and ice, the adsorption enthalpies imply interactions with a number of water molecules on the surface. Donaldson et al. were able to correlate their heats of adsorption to liquid water to the standard enthalpy of solvation but not to the standard enthalpy of vaporization. We find that although we obtain a somewhat tighter correlation to the heat of vaporization, we do not have enough data points or precision in each point to make a strong claim in this regard.

The entropies of adsorption were also derived from the *y*-intercepts in Figure 8, where we have employed the standard state of Kemball and Rideal.[23] In particular, this standard state corresponds to the same standard volume per molecule as in a gas at one atmosphere pressure, except that the thickness of the 'two-dimensional' ideal gas is specified to be 0.6 nm. The values that we determine are similar to each other (in cal/(K mole)): −30 ± 12 for acetic acid, −30 ± 8 for 1-pentanol, −28 ± 4 for 1-butanol, −27 ± 1 for ethanol, and −36 ± 7 for hexanal, where the uncertainties are 1-σ precisions. These entropies are all very close to the values for gas-to-liquid condensation, indicating that a highly ordered state is not being formed (in cal/(K mole)): −29 for acetic acid, −34 for 1-pentanol, −33 for 1-butanol, −29 for ethanol, and −34 for hexanal.[19]

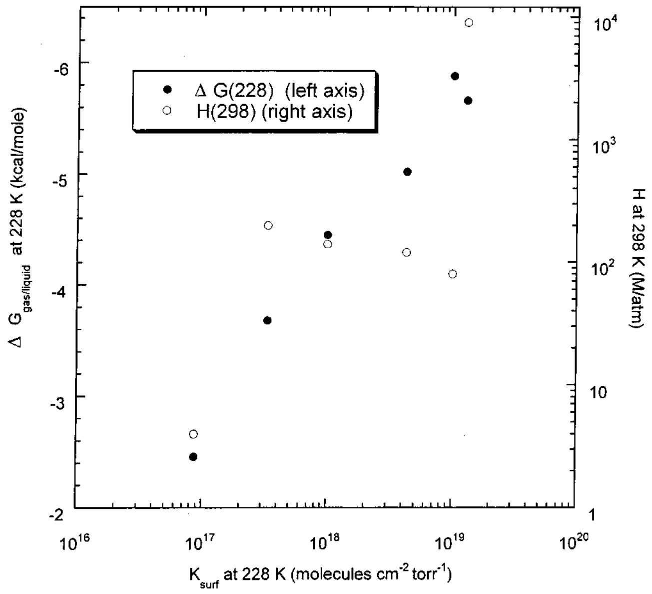

Figure 9. Plot of the logarithm of the experimental gas-to-surface equilibrium constant at 228 K, K_{surf}, with the change in free energy at 228 K for the condensation of the gas to a pure liquid, $\Delta G_{\mathrm{gas/liquid}}$ (left axis, ●) and with the 298 K aqueous Henry's Law constant (right axis, ○).

A goal of this work was to determine the mode of interaction with the ice surface from the uptake behavior exhibited by the different organics. To do so, we have attempted to find a good correlation between the gas-to-surface 228 K equilibrium constants, K_{surf}, and standard thermodynamic quantities.[24] As shown in Figure 9, a striking correlation arises when the logarithm of the experimental equilibrium constants are plotted versus the free energy change at 228 K calculated for the condensation of organic vapor to the pure organic liquid, $\Delta G_{\mathrm{gas/liquid}}(228)$. $\Delta G_{\mathrm{gas/liquid}}(228)$ is calculated from $\Delta H^{\mathrm{o}}_{\mathrm{gas/liquid}} - 228\Delta S^{\mathrm{o}}_{\mathrm{gas/liquid}}$, where the standard enthalpy and entropy of condensation are taken from the literature.[19] This correlation encompasses not only all the alcohols, but also the aldehyde (hexanal) and the carboxylic acid (acetic acid). Also plotted in Figure 9 is the poor correlation with the aqueous room-temperature Henry's Law constant.[20]

In most cases, the vapor pressure of the organic liquid is directly related to the quantity $\Delta G_{\mathrm{gas/liquid}}$ through the following relationship for gas-to-liquid condensation

$$\mathrm{VP}_{\mathrm{liquid}}(T) = \exp(\Delta G_{\mathrm{gas/liquid}}/RT) \tag{2}$$

where $\mathrm{VP}_{\mathrm{liquid}}$ is the vapor pressure in atmospheres. From eq 2, one might expect that an equally tight correlation should exist with the experimental vapor pressures of the organic species. However, as shown in Figure 10, this is not fully true in our case with both acetic acid and hexanal lying significantly off the trend. For both of these molecules, the vapor pressure calculated using eq 2 and tabulated thermodynamic values does not agree with the literature values for the vapor pressure (which are extrapolated from higher temperature measurements),[18] whereas the agreement for all the alcohols is very good. For acetic acid, the reason for this is likely that the dimerization of acetic acid significantly affects the experimental vapor pressure. For hexanal, the cause of the discrepancy is not clear. It is possible that either the tabulated thermodynamic values or the 228 K vapor pressure is in error.

The correlation in Figure 9 implies that the adsorption of small polar organic molecules proceeds via interactions which

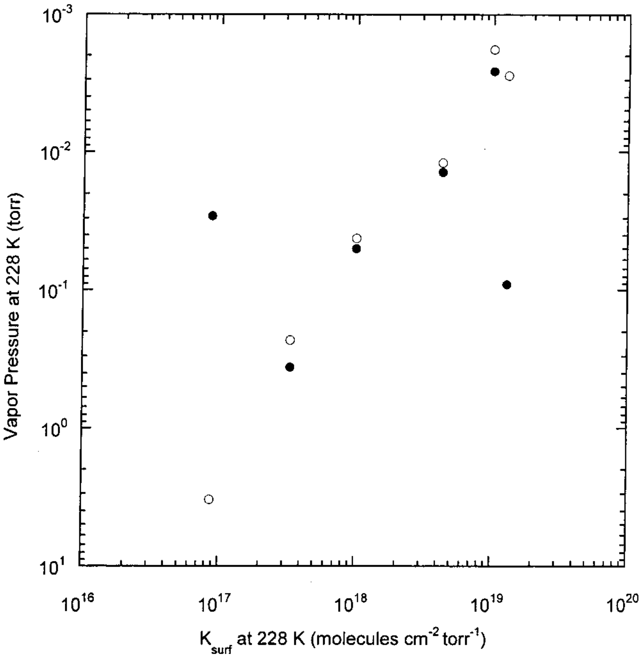

Figure 10. Plot of the logarithm of the experimental gas-to-surface equilibrium constant at 228 K, K_{surf}, with the logarithms of both the literature vapor pressures of the pure organic liquids at 228 K (●) and the values calculated from eq 2 (○).

are thermodynamically similar to those undergone during condensation to the liquid state. In particular, H-bonding to the ice surface will occur, as it does in the pure organic liquid between organic molecules. Note, however, that this is not to say that condensation of the pure liquid is occurring except perhaps in the form of organic 'islands' on the surface. If islands are indeed forming, there is also a sizable interaction of the individual organic molecules with the water molecules on the ice surface because the enthalpies of adsorption are considerably larger than the enthalpy of condensation (see above).

The somewhat poor correlation with the Henry's Law constants (see Figure 9) is an indication that full solvation of the adsorbing molecule does not occur upon adsorption. To elaborate, the Henry's Law constants within the *n*-alcohol series monotonically decrease from 200 M/atm for ethanol to 80 M/atm for 1-pentanol because the free energy cost of solvating an alkyl chain grows as the chain grows longer whereas the enthalpic benefit arising from H-bonding in solution remains constant in that series. For adsorption to an ice surface, where the alkyl chain is not solvated, there is no equivalent thermodynamic penalty. If there is a quasi-liquid layer of water on the surface of ice at the temperature of this study, it does not appear to significantly affect the uptake of polar organics by fully dissolving them.

Although we believe this is the first report of the thermodynamics of the adsorption of these polar organics to ice at high temperatures, analogous studies involving urban air particulate surfaces have been documented for the adsorption of larger, less volatile species such as the PAHs and organochlorines. A model, derived from the Langmuir adsorption isotherm in the unsaturated regime, which quantitatively describes the behavior seen in these studies has been developed where the gas-to-surface partition coefficient, *K*, is expressed in the following manner[25]

$$K = AT(-\Delta H_{ads} - \Delta H_{vap})/RT)/\mathrm{VP}_{liquid} \qquad (3)$$

where ΔH_{ads} is the enthalpy of adsorption, ΔH_{vap} is the enthalpy of vaporization, and *A* is a constant. The partition coefficient scales with VP_{liquid} because the nature of the adsorbed molecules more resembles the state of the molecule in the pure liquid state than, for example, in a solid state. For the alcohols at least (see Figure 10), our data appear to be consistent with this model.

Atmospheric Implications

From numerous previous studies, it is known that precipitating ice contains appreciable levels of organic matter. In particular, the study of Gill et al. systematically documented the levels and types of organic species that are found on ice and snow, along with other particulate types, and they used this evidence to propose that a surfactant-like organic layer exists on the surface of atmospheric particles.[26] The measurements made in this paper support the suggestion that there may be a significant organic surface component associated with ice because there is a relatively strong bonding interaction made between the ice surface and an adsorbing molecule at temperatures close to 228 K. Our results are in qualitative agreement with those of Hudson et al. which also demonstrated significant uptakes of small organics, such as acetic acid, albeit at somewhat lower temperatures.[15]

To quantitatively assess the possible atmospheric implications for this interaction we can estimate the fraction of organic adsorbed to an ice surface relative to the total amount in the gas phase

$$\begin{aligned}\text{Fraction adsorbed} &= N_{surf}/N_{gas} \\ &= \mathrm{SA}\ \theta/N_{gas} \\ &= 1.04 \times 10^{-19}\,\mathrm{T\ SA}\ K_{surf}\end{aligned} \qquad (4)$$

where N_{surf} is the number of molecules adsorbed on ice in a gas-phase unit volume (molecules/cm^3), N_{gas} is the number of organic molecules in the gas-phase per unit volume (molecules/cm^3), SA is the total ice surface area per unit volume (cm^2/cm^3), θ is the specific surface coverage prevalent at the gas-phase organic partial pressure (molecules/cm^2), K_{surf} is the experimental gas-to-surface partitioning coefficient (molecules cm^{-2} Torr^{-1}) and the 1.04×10^{-19} T term accounts for the conversion from concentration to pressure units. Note from eq 4 that the fraction adsorbed is dependent in the unsaturated region on only the ice surface area and not the partial pressure of the organic species.

The surface area of ice clouds is essentially unmeasured on the molecular scale. BET adsorption isotherm measurements on snow give specific surface areas of between 5×10^2 and 1×10^4 cm^2/g.[27,28] Ice clouds frequently have a water content of 1×10^{-7} g/cm^3.[29] Combining these two values gives a specific surface area of between 5×10^{-5} and 1×10^{-3} cm^2/cm^3, i.e., values equal to or slightly larger those frequently used for thick cirrus clouds.[30]

Taking the upper limit of 1×10^{-3} cm^2/cm^3, our data at 228 K imply that the potential effects of gas-to-particle scavenging on the gas-phase composition of polar organics range from being insignificant to highly significant. For example, for hexanal and ethanol the adsorbed fraction for each is less than 1%. However, for acetic acid the fraction adsorbed is roughly 25%. For heavier carboxylic acids and alcohols, such as 1-hexanol, the fraction scavenged from the gas phase will be even larger, approaching the state where scavenging is effectively complete. Once the clouds evaporate, it is predicted that the organics will reversibly desorb unless they have a strong affinity for any involatile trace species that were part of the ice particle. These predictions are for 228 K only and it should be reiterated that the surface area of ice clouds on the molecular scale is very poorly known.

The impact of this chemistry will be felt in regions where molecules with relatively low volatility coexist with ice clouds. Molecules with short gas-phase lifetimes will tend to be present only close to their source regions in the atmospheric boundary layer. On the other hand, molecules such as ethanol and acetic acid are found ubiquitously throughout the atmosphere. That is, longer-lived molecules that have the potential to be transported to the free troposphere will most likely be affected by ice scavenging processes by the type described in this paper. It is also likely that snow in the polar boundary layer, where temperatures can often be quite low, may contain a significant number of scavenged polar organic molecules.

Conclusions

At 228 K, the uptakes of polar organic molecules on ice are adequately described by a standard Langmuir adsorption isotherm model up to the point where multilayer growth occurs. In the unsaturated regime the logarithm of the gas-to-surface partition coefficient correlates closely with the free energy for condensation at the temperature of the experiment, i.e., with the molecules' volatility. This implies that the chemical interactions involved in the adsorption process are analogous to those experienced in the pure liquid, but not that condensation of the pure liquid is occurring. The heats of adsorption are similar to those measured for the adsorption of polar organics to liquid water surfaces and sufficiently large that a number of water molecules on the surface must be involved in the interaction. In this manner, the surface behaves in a manner more similar to that of liquid water than an involatile solid. However, we have no need to invoke an aqueous layer on the surface of the ice to explain the observations.

Compared to strong acids such as HNO_3 and HCl, the saturated surface coverages for the polar organic molecules are the same, between 2 and 3×10^{14} molecules/cm^2, but the unsaturated portion of the adsorption isotherm prevails at much higher partial pressures. For example, the surface coverages for HNO_3 show no systematic dependence on partial pressure from 10^{-7} and 10^{-6} Torr,[4] whereas we believe that all the molecules studied in this work are in the unsaturated portion of the adsorption isotherm in this partial pressure regime. The stronger adsorption of HNO_3 and HCl is most likely due to their ability to dissociate on the ice surface.

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