

Reactive Uptake of N₂O₅ on Aqueous H₂SO₄ Solutions Coated with 1-Component and 2-Component Monolayers

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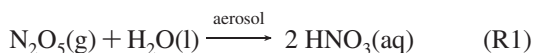
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Reactive uptake of N₂O₅ on aqueous sulfuric acid solutions was studied in the presence of 1-component (octadecanol) and 2-component (octadecanol + phytanic acid) monolayers. In the 1-component monolayer experiments, the reactive uptake coefficient depended strongly on the molecular surface area of the surfactant. Also, the 1-component monolayer showed significant resistance to mass transfer even when the fractional surface coverage of the surfactant was less than 1. For example, a monolayer of 1-octadecanol with a fractional surface coverage of 0.75 decreased the reactive uptake coefficient by a factor of 10. This is consistent with previous studies. In the 2-component monolayer experiments, the reactive uptake coefficient depended strongly on the composition of the monolayer. When the monolayer contained only straight-chain molecules (1-octadecanol), the reactive uptake coefficient decreased by a factor of 42 due to the presence of the monolayer. However, when the monolayer contained 0.20 mole fraction of a branched surfactant (phytanic acid) the reactive uptake coefficient only decreased by a factor of 2. Hence, a small amount of branched surfactant drastically changes the overall resistance to reactive uptake. Also, our results show that the overall resistance to reactive uptake of 2-component monolayers can be predicted reasonably accurately by a model that assumes the resistances to mass transfer can be combined in parallel.

Introduction

Heterogeneous reactions between aerosol particles and gas phase species can play a key role in the atmosphere.^{1–11} One heterogeneous reaction that has been studied extensively is the reaction between N₂O₅ and aqueous particles:



Modeling studies have demonstrated that the rate for this reaction needs to be known accurately to predict tropospheric concentrations of NO_x, O₃, and OH.^{2,6,12}

Often the efficiency of N₂O₅ heterogeneous reactions is described by the reactive uptake coefficient (γ), which is defined as the fraction of collisions with a surface that leads to the irreversible loss of the gas-phase species due to a reaction. Since the initial modeling studies that demonstrated the atmospheric importance of the N₂O₅ heterogeneous reaction, there has been extensive laboratory investigations of the reactive uptake coefficient of N₂O₅ on aqueous inorganic solutions and particles.^{13–24} These studies have shown that N₂O₅ reactive uptake is large (γ is between 0.02 and 0.15) on aqueous inorganic particles.

In addition to inorganic material, tropospheric particles can also contain a significant fraction of organic surfactants.²⁵ These surfactants can form organic monolayers at the air–aqueous interface,^{26–36} and depending on the composition and degree of compression of these organic monolayers, they may limit the transfer of molecules across the air–aqueous interface.^{26–28,37–51}

Possibly related, recent field measurements over the northeast United States by Brown et al.⁵² showed that the reactive uptake coefficient of N₂O₅ can decrease significantly (by a factor of

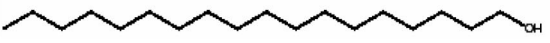
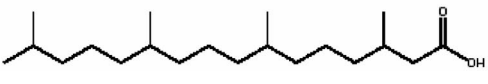
≥ 10) when particles contain a large amount of organic material in addition to inorganic material. One possible explanation for these results is that the organic material formed a coating on the aqueous droplets, and this coating limited the transfer of N₂O₅ molecules across the air–aqueous interface.⁵²

Recently, several research groups have investigated the effect of organic monolayers on reactive uptake of N₂O₅ on aqueous solutions or particles.^{37,38,44–46,51} Park et al.⁴⁵ studied N₂O₅ uptake on H₂SO₄ solutions and showed that γ decreased by a factor of 2.5 in the presence of hexanol monolayers and decreased by a factor of 1.5 in the presence of butanol monolayers. Thornton and Abbatt⁴⁴ investigated N₂O₅ uptake on sea salt aerosols and determined that the uptake coefficient decreased by a factor of 3–4 in the presence of hexanoic acid monolayers. McNeill et al.,³⁸ studied uptake of N₂O₅ on aqueous salt aerosols, and they observed a decrease in γ by a factor of 7.5 in the presence of monolayers formed from sodium dodecyl sulfate³⁷ and a factor of 20 in the presence of monolayers formed from sodium oleate.³⁸ More recently, we measured the reactive uptake of N₂O₅ on H₂SO₄ solutions coated with 1-octadecanol, 1-hexadecanol, and stearic acid and observed a decrease in the reactive uptake coefficient by a factor of 61, 55, and 17, respectively.⁵¹ In contrast, we found that an insoluble, branched monolayer containing 16 carbon atoms (phytanic acid) did not have an effect on γ within our experimental error.⁵¹ The structures of 1-octadecanol and phytanic acid are shown in Table 1.

Related to the above, Folkers et al.⁴¹ investigated the uptake of N₂O₅ on aqueous NH₄HSO₄ particles coated with organics produced by the ozonolysis of α -pinene. In these studies, it was observed that an organic film approximately 15 nm thick reduced the reaction probability of N₂O₅ by approximately a factor of 5. Also, Badger et al.⁵³ investigated N₂O₅ uptake on aqueous ammonium sulfate aerosols containing humic acid (a surfactant). For aerosols containing only 6% humic acid by dry mass, a

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TABLE 1: Structure of Organic Molecules Used in This Study^a

Organic compound	Melting points ^a (°C)	Structure
1-octadecanol	67-72	
phytanic acid (3,7,11,15- tetramethylhexadecanoic acid)	< 20	

^a Melting point for 1-octadecanol was obtained from Sigma-Aldrich. The melting point for phytanic acid has not been reported, but it is a liquid at room temperature.

decrease in reactivity of more than a factor of 2 was observed compared with the case for single-component ammonium sulfate. Analysis of the uptake coefficients using the water concentration data showed that the change in reactivity could not be explained by the change in water content alone. The authors attributed the larger than expected change in reactivity to the formation of organic films by the humic acid surfactants.⁵³

Despite the recent progress on the effect of organic monolayers on N_2O_5 reactive uptake, much remains to be done. For example, in most of the previous studies only single-component monolayers were investigated. More work on multicomponent monolayers (monolayers containing more than one type of organic surfactant) is needed. Also, much remains to be learned to understand the mechanism by which monolayers and films affect N_2O_5 uptake. Uptake studies as a function of molecular surface area of the surfactant, the two-dimensional (2D) phase of the organic monolayer, and temperature would be useful to better understand the physical chemistry. This type of information is also necessary to accurately extrapolate laboratory data to atmospheric conditions.

As mentioned above, we recently studied N_2O_5 reactive uptake on aqueous sulfuric acid solutions coated with 1-octadecanol, 1-hexadecanol, stearic acid, and phytanic acid.⁵¹ In these studies, we only investigated 1-component monolayers, and for each organic monolayer we only measured the reactive uptake at one surface pressure, which corresponds to one molecular surface area of the surfactant (i.e., packing density of the surfactant). Experiments as a function of molecular surface area with the same surfactant were not carried out. The current paper is an extension of our previous work and consists of two series of measurements. In the first series of measurements, we investigate the uptake of N_2O_5 on aqueous sulfuric acid solutions coated with a 1-octadecanol monolayer (a 1-component monolayer) as a function of the molecular surface area of the surfactant. This allows us to isolate the effect of molecular surface area on the reactive uptake coefficient. In addition, the results from this study allow us to investigate whether or not the 2D phase of the surfactant monolayer has a large impact on uptake. Monolayers can go through a series of 2D phase transitions (see below), and in the 1-octadecanol experiments as a function of molecular surface area mentioned above the monolayer undergoes a phase transition. This allows us to observe how the 2D phase alters the reactive uptake coefficient. Below, we present these results and also discuss the results in terms of the Accessible Area Theory,⁵⁴ which has been used in the past to predict the effect of organic monolayers on water evaporation.^{48,55,56}

In the second series of measurements, we focus on a 2-component monolayer consisting of 1-octadecanol (a straight-

chain surfactant) and phytanic acid (a branched surfactant). This mixed monolayer is of atmospheric relevance because monolayers in the atmosphere may consist of more than one type of surfactant. It is also reasonable to expect that some atmospheric monolayers will consist of mixtures of straight-chain and branched surfactants. Prior to our uptake measurements, we first determine if 1-octadecanol–phytanic acid monolayers are miscible or immiscible, which is necessary for understanding our uptake data.⁵⁷ To determine the miscibility, we measure the surface pressure–area isotherms of the 2-component monolayer. The analysis of this data allows us to show that 1-octadecanol–phytanic acid monolayers are immiscible. After proving this 2-component monolayer is immiscible, we study the uptake coefficient of N_2O_5 on aqueous H_2SO_4 solutions in the presence of these monolayers as a function of the composition of the monolayer (i.e., mole fraction of phytanic acid in the 2-component monolayer). The results from these studies are presented below and compared to predictions based on two different models used to describe mass transfer across the air–aqueous interface in the presence of a 2-component monolayer. The atmospheric implications of these results are also discussed.

Experimental Section

Rectangular Channel Flow Reactor and Determination of Reactive Uptake Coefficients. A rectangular channel flow reactor^{46,51} coupled to a chemical ionization mass spectrometer⁵¹ is used to measure heterogeneous reaction rates for the uptake of N_2O_5 on aqueous solutions coated with organic monolayers. The strength of the rectangular channel flow reactor configuration is that we can determine the surface pressure and molecular surface area (i.e., packing density) of the organic monolayer before and after each kinetic measurement.

Figure 1 is a schematic of the rectangular channel flow reactor (RCFR). A detailed description of the flow reactor and flow dynamics in the reactor can be found in our previous work.^{46,51} Our flow reactor builds on earlier experiments, where a Langmuir trough was used for heterogeneous studies.^{58,59} Our flow reactor is made entirely from aluminum and is temperature controlled by circulating coolant through open channels in the body of the reactor. All interior aluminum walls are coated with halocarbon wax to minimize loss of N_2O_5 to the walls. A glass trough is located on the bottom surface of the reactor, which is filled with the aqueous solution. The reactive surface is 7.5 cm in width and 22 cm in length. This aqueous solution can be coated with an organic monolayer. The height of the headspace above the liquid surface (Figure 1b) is in most cases less than 1 cm. As shown in Figure 1a, N_2O_5 enters the flow cell through a stainless steel, T-shaped injector that slides just above the

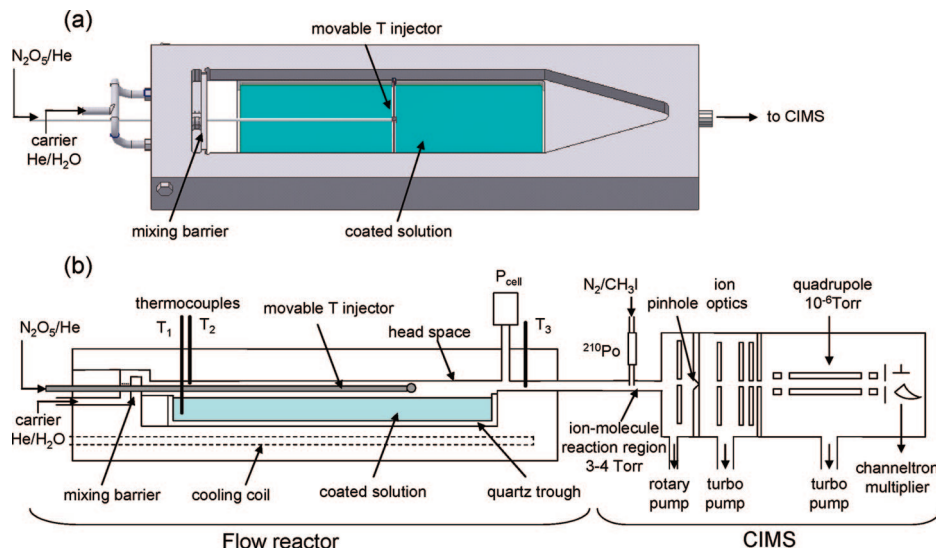


Figure 1. (a) A top view sketch of the rectangular channel flow reactor without the aluminum cover. The liquid solution is placed in a quartz trough, which fits smoothly inside the flow reactor. (b) A side view of the rectangular channel flow reactor coupled to a CIMS.

surface of the liquid. The T-shaped injector is equipped with six exit holes (0.2 mm in diameter) facing the top of the reactor, which distribute N₂O₅/He evenly along the width of the flow cell. The carrier gas (He) enters the flow reactor through inlets at the back of the flow cell. The gas stream within the reactor first flows against a barrier to ensure mixing before reaching the liquid surface. The temperature of the liquid and the gas above the liquid are measured using thermocouples, and in all cases the liquid and the gas are within ± 0.5 K of each other. The pressure inside the flow cell is measured using an MKS baratron at the exit of the flow reactor (see Figure 1b).

Prior to entering the flow reactor, the carrier gas was passed through a carbon filter (Supelco, Supelcarb HC) and a Drierite (W.A. Hammond Drierite Co. Ltd.) trap cooled with liquid nitrogen to remove any possible organic contamination. The carrier gas then passed over a water reservoir held at a fixed temperature to adjust the relative humidity (RH) of the carrier gas. The RH was adjusted so that it matched the relative humidity over the aqueous 60 wt % sulfuric acid solution, calculated using the AIM model.^{60–62} The RH of the carrier gas was verified with a dew point hygrometer.

The open channel above the liquid surface has a rectangular geometry. The flow dynamics of our system have been characterized in our previous publication using computation fluid dynamics simulations.⁴⁶ These calculations show that the carrier gas reaches a fully developed laminar flow in less than 1.5 cm, which is much shorter than the length of the reactive surface. See our previous publication for further discussion on the gas flow dynamics in the system.⁴⁶

N₂O₅ was produced by reacting a small flow of NO₂ with an excess of O₃. O₃ was generated by passing a flow of O₂ over an ultraviolet source (Jelight, model 600). To remove water vapor from the O₂ carrier gas, a Drierite trap was placed immediately before the UV lamp. NO₂ was passed through a P₂O₅ trap to remove trace amounts of water prior to reaction with O₃. N₂O₅ produced by this reaction flowed through an additional P₂O₅ trap to reduce the concentration of nitric acid and was then collected and stored in a glass trap immersed in an ethanol bath cooled to 193 K. N₂O₅ condensed as white crystals inside the glass trap.

A saturated flow of N₂O₅ between 7–8 cm³ min^{−1} at standard temperature and pressure (STP) was mixed with 70–80 cm³

min^{−1} at STP of dry He prior to entering the flow reactor through the T-shaped injector. Total mass flow rates inside the flow reactor ranged from 260 to 360 cm³ min^{−1} at STP and total pressures were between 2.6 to 3 Torr. Laminar flows were achieved under these conditions as Reynold's numbers ranged from 0.4 to 0.8.

A chemical ionization mass spectrometer (CIMS) was connected to the exit of the flow cell, which was used to measure the change in the gas phase reactant concentration as a result of reactive uptake at the liquid surface.^{46,51,63,64} N₂O₅ was detected as NO₃[−] after its chemical ionization by I[−].^{15,21,65} Trace amounts of CH₃I diluted in 1250–1500 cm³ min^{−1} at STP of N₂ were passed through a polonium-210 source (NRD, model Po-2031) to form I[−]. For N₂O₅ detection in the presence of H₂O, the chemical ionization region was biased to −122 V to decluster weakly bound ion-H₂O clusters.^{15,21} N₂O₅ concentrations ranged from 2.1×10^{10} to 1.1×10^{11} molec cm^{−3} in these experiments. N₂O₅ concentrations were based on the I[−] + N₂O₅ chemical ionization reaction rate that has been reported in the literature.⁶⁵

The reactive uptake coefficients were determined from the irreversible removal of N₂O₅ as a function of injector position in the RCFR. Shown in Figure 2 are plots of the natural logarithm of the N₂O₅ signal as a function of reaction time for the loss of N₂O₅ on coated and uncoated aqueous 60 wt % sulfuric acid solutions at 273 ± 1 K. The data for each uptake experiment is represented with a linear fit, which yields the observed first-order rate constant (k_{obs}) from the slope of each data set. The first order wall loss rate (k_w) was calculated from k_{obs} using a procedure developed by Knopf et al.⁴⁶ This procedure corrects for any concentration gradients that can develop in the flow reactor as a result of a fast heterogeneous reaction at the surface.

The determination of k_w from k_{obs} requires diffusion coefficients for N₂O₅ in He ($D_{\text{N}_2\text{O}_5\text{-He}}$) and N₂O₅ in H₂O ($D_{\text{N}_2\text{O}_5\text{-H}_2\text{O}}$). The values used for $D_{\text{N}_2\text{O}_5\text{-He}}$ and $D_{\text{N}_2\text{O}_5\text{-H}_2\text{O}}$ at 273 K were 289 and 72 Torr cm² s^{−1}, respectively. These values were taken from Knopf et al.⁴⁶ and were calculated based on molecular parameters.^{66–68} The diffusion coefficient (D) for N₂O₅ in a binary mixture of helium and water is then given by⁶⁹

$$\frac{1}{D} = \frac{P_{\text{He}}}{D_{\text{N}_2\text{O}_5-\text{He}}} + \frac{P_{\text{H}_2\text{O}}}{D_{\text{N}_2\text{O}_5-\text{H}_2\text{O}}} \quad (1)$$

where P_{He} and $P_{\text{H}_2\text{O}}$ are the partial pressures of helium and water vapor in the flow cell, respectively.

The reactive uptake coefficient (γ) was determined from k_w using^{70,71}

$$\frac{1}{\gamma} = \frac{c}{4k_w} \cdot \frac{S}{V} + \frac{1}{2} \quad (2)$$

where c is the mean molecular velocity of N_2O_5 , S is the reactive surface area inside the flow cell, and V is the volume above this area.

Preparation of 1-Component Monolayers for the Reactive Uptake Measurements. The first set of experiments involved N_2O_5 uptake experiments on 1-component monolayers (specifically 1-octadecanol) as a function of molecular surface area of the surfactant (i.e., packing density of the surfactant). We prepared monolayers with various molecular surface areas by varying the amount of organic surfactant added to the surface. Because the total area of the surface was known accurately and the total amount of organic surfactant added to the surface was known accurately, the molecular surface area of the surfactant molecules could be accurately calculated. The molecular surface area of the surfactant was also verified by measuring the surface tension of the films before and after the reactive uptake measurements (see below). More details on preparation of the monolayers are as follows: first, the surface of the aqueous acid was thoroughly cleaned using a PTFE nozzle aspirator to remove any organic contamination on the surface prior to preparing an organic monolayer. Second, solutions of 1-octadecanol were prepared by dissolving the surfactant in chloroform ($\sim 1 \text{ mg cm}^{-3}$) to make organic solutions. Finally, monolayers were prepared by depositing a known volume of the organic solution on a clean aqueous sulfuric acid surface. The chloroform was allowed time to evaporate, leaving behind an organic monolayer with a known molecular surface area of the surfactant.

To verify the molecular surface area of the surfactants, we measured the surface tension of the prepared films using the Wilhelmy plate method prior to and after the uptake measurements. From the surface tension, we calculated the surface pressure, and then from the surface pressure we determined the molecular surface area of the surfactant molecules from the pressure-area isotherm of octadecanol on aqueous sulfuric acid solutions. The pressure-area isotherm for 1-octadecanol, which was determined in previous experiments⁵¹ using a commercial Langmuir film balance, is illustrated in Figure 3a (solid curve). The isotherm shows the relationship between the surface pressure of the film and the molecular surface area of the surfactant, so once the surface pressure is known, the molecular surface area can be determined. The molecular surface areas determined from the surface tension measurements were always within a few percent of the molecular surface areas calculated from knowledge of the mass of organic surfactant added to the surface. Also shown in Figure 3a are the molecular surface areas at which reactive uptake coefficients were determined in this study (open symbols). The solid symbol represents the conditions used in our previous study for 1-octadecanol monolayers.⁵¹

More details on the surface tension measurements are as follows:⁵¹ surface tension measurements were carried out with a platinum Wilhelmy plate (23.32 mm perimeter) connected to a tensiometer (NIMA Technology, model PS4). The platinum plate was cleaned using a 1:1 solution of H_2SO_4 and HNO_3

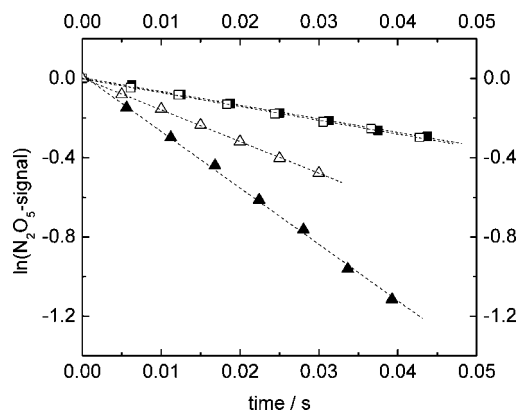


Figure 2. Natural logarithm of the observed N_2O_5 signal as a function of reaction time. Symbols show representative data for a series of 1-octadecanol monolayers with varying molecular surface area. Solid squares, a molecular surface area of $20.7 \text{ Å}^2 \text{ molec}^{-1}$; open squares, $21.2 \text{ Å}^2 \text{ molec}^{-1}$; open triangles, $22.6 \text{ Å}^2 \text{ molec}^{-1}$; and solid triangles, $24.2 \text{ Å}^2 \text{ molec}^{-1}$. The dashed lines represent the corresponding linear fits to the data.

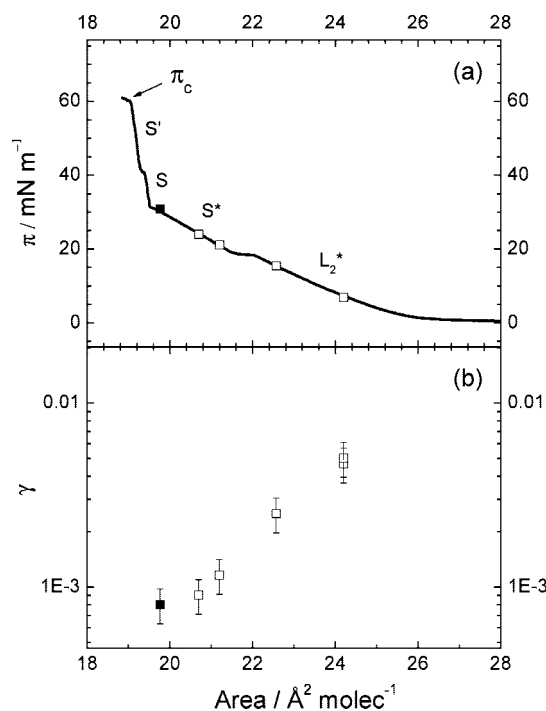


Figure 3. Surface pressure-area isotherm for 1-octadecanol⁵¹ (panel a) and reactive uptake coefficients (γ) for N_2O_5 on organic coated aqueous 60 wt % sulfuric acid at $273 \pm 1 \text{ K}$ plotted as a function of molecular surface area of 1-octadecanol (panel b). The solid line in panel a represents the variation of surface pressure (π) with a change in molecular surface area. S' , S , S^* , and L_2^* represent the different 2D phases of the monolayer (see text for further details).⁷⁶ Also shown is the collapse pressure (π_c) of the 1-octadecanol monolayer. The open symbols in panel a represent the experimental conditions (surface pressures and molecular surface areas) at which reactive uptake experiments were performed for N_2O_5 on aqueous 60 wt % H_2SO_4 at $273 \pm 1 \text{ K}$ coated with 1-octadecanol. The solid square in panel a represents experimental conditions used previously by Cosman et al.⁵¹ for 1-octadecanol monolayers.

prior to each measurement, followed by thorough rinsing with purified water. The Wilhelmy plate was hung from the tensiometer and was immersed in the aqueous acid solution contained in the temperature controlled flow cell. The force on the Wilhelmy plate was measured while the plate was immersed and detached from the liquid solution contained in the quartz

trough. The surface tension was calculated from the maximum difference in the force on the plate between immersion and separation from the solution.^{51,72,73} The surface tension in the presence of the film was measured before and after each kinetic experiment and used to calculate the surface pressure.

Measurements of Surface Pressure-Area (π -A) Isotherms of the 2-Component Monolayers. The second set of experiments involved N₂O₅ uptake experiments on a 2-component monolayer (consisting of 1-octadecanol and phytanic acid) as a function of mole fraction of phytanic acid in the monolayer (x_{phytanic}). First, in order to characterize these monolayers, which was necessary for interpreting the uptake results, we measured surface pressure-area isotherms⁵⁷ as a function of mole fraction of phytanic acid in the monolayer, using a commercial Langmuir film balance (NIMA Technology, model 611). The main point of these experiments was to determine if the 2-component monolayer was immiscible or miscible.

The Langmuir film balance consisted of a PTFE trough (with dimension of 20 by 30 cm), two movable barriers, and a surface pressure sensor (NIMA Technology, model PS4) with a platinum plate. The experimental procedure that was followed is described in detail by Myrick and Franses.⁷⁴ Briefly, the trough was filled with an aqueous sulfuric acid solution, and the surface of the acid solution was cleaned thoroughly using an aspirator. A known volume of an organic solution (containing 1-octadecanol and phytanic acid dissolved in chloroform) was added to the clean H₂SO₄-H₂O surface. The chloroform was allowed to evaporate leaving behind a known number of surfactant molecules on the surface. The surface pressure was then recorded as the moveable barriers reduced the available surface area, resulting in a surface pressure-area isotherm.⁵⁷ Surface pressure-area isotherms for 2-component monolayers were measured at a constant compression rate of 20 cm² min⁻¹.

Preparation of the 2-Component Monolayers for the Reactive Uptake Measurements. After characterizing the 1-octadecanol-phytanic acid monolayers, we then investigated the reactive uptake of N₂O₅ on aqueous 60 wt % H₂SO₄ solutions in the presence of these monolayers. Measurements were carried out as a function of the mole fraction of phytanic acid in the monolayer. For these experiments, the surface pressure of the films was kept 21 ± 2 mN m⁻¹, which is less than the first collapse pressure of the 2-component monolayer (see below for more details). Monolayers with a surface pressure of 21 ± 2 mN m⁻¹ were prepared by dissolving a known amount of 1-octadecanol and phytanic acid (with a fixed ratio) in chloroform. Drops of this solution were then added to a clean aqueous sulfuric acid surface until the desired surface pressure was reached, which was verified by measuring the surface tension of the solution. The surface tension was measured with the procedure discussed above.

Chemicals. Helium (Praxair, 99.999% Purity), nitrogen (Praxair, 99.999%), nitrogen dioxide (Matheson, 99.5%), oxygen (Praxair, 99.5%), diphosphorus pentoxide (Aldrich, 97%), 1-octadecanol (Sigma-Aldrich, 99%), phytanic acid (Sigma-Aldrich, 96%), chloroform (Fischer, 99+%), and sulfuric acid (Fischer, 95+%) were all used as supplied.

Results and Discussion

N₂O₅ Reactive Uptake in the Presence of a 1-Component Monolayer (1-Octadecanol). The reactive uptake of N₂O₅ on aqueous H₂SO₄ was measured in the presence of a monolayer of 1-octadecanol at varying molecular surface areas of the surfactant. The surface pressure-area isotherm for 1-octadecanol is shown in Figure 3a.⁵¹ The solid line in Figure 3a illustrates

the isotherm for 1-octadecanol on 60 wt % H₂SO₄ at 273 K,⁵¹ and the symbols represent the surface pressures and molecular surface areas at which reactive uptake experiments were performed. Figure 3a illustrates that as the molecular surface area decreases, the monolayer undergoes a series of phase transitions shown by a change in the slope of the isotherm.^{57,75} These phase transitions correspond to different degrees of ordering of the organic surfactants on the surface.^{75,76} At large molecular surface areas (greater than approximately 40 Å² molec⁻¹) the films exist as a 2D gas on the aqueous acid surface, with molecules on the surface exerting relatively little force on each other due to sufficient separation.⁵⁷ For decreasing molecular surface areas the monolayers undergo several phase transitions until they reach their collapse pressure, π_c (which occurs at approximately 19 Å² molec⁻¹ for 1-octadecanol).⁵⁷ In Figure 3 the different phase regions (defined by discontinuities in the slope of the isotherm) are labeled as S', S, S*, and L₂*, based on previous studies of 1-octadecanol monolayers on water.⁷⁶ The different phases correspond to different orientations of the organic chains and also different unit cells. Traditionally, S' and S would be classified as a condensed solid phase and S* and L₂* would be classified as a liquid condensed phase.⁵⁷ In our experiments, we studied N₂O₅ uptake in the presence of S* and L₂* phases. The main difference between these two phases is a change in the tilt angle of the hydrocarbon chains in the monolayer.⁷⁶

Figure 3b shows the reactive uptake coefficients (γ) in the presence of 1-octadecanol monolayers determined in our studies using different molecular surface areas. The error bars for γ take into account reproducibility in the kinetic experiments and a 20% uncertainty in the diffusion coefficients.

Figure 3 shows that the reactive uptake coefficient depends strongly on the molecular surface area of the organic monolayer with the reactive uptake coefficient decreasing as the molecular surface area was decreased. This observation is consistent with previous studies of the rate of water evaporation through organic monolayers.^{56,57,77} In these previous studies, it was generally observed that the resistance to evaporation increased as the molecular surface area of the surfactant decreased.

Figure 3 also suggests that the reactive uptake coefficient does not change drastically when the phase of the monolayer converts from S* to L₂*. The γ values shown in Figure 3b increase smoothly with increasing molecular surface area of the surfactant with no apparent step function change observed upon transition between monolayer phases S* and L₂*. This is also generally consistent with studies of the rate of water evaporation through organic monolayers. For example, La Mer et al.⁷⁷ showed that the resistance to water evaporation increased smoothly (i.e., no apparent step function change in the evaporation resistance was observed) as monolayers underwent phase transitions from condensed liquid to solid phases. Our results are also not surprising as the surface pressure changes relatively smoothly between S* to L₂*, and the structural differences between S* to L₂* are thought to be relatively minor. Because of experimental constraints, we were not able to compress the monolayer to molecular surface areas beyond that at equilibrium. Hence, we were not able to monitor the change in reactive uptake coefficient when going from the phase S* to S, where the surface pressure changes most steeply.

In Figure 3, we have plotted γ versus the molecular surface area of the organic monolayer. Another way to present the reactivity data is versus the fractional surface coverage. Here, we define the fractional surface coverage as the molecular surface area of the surfactant normalized to the molecular surface

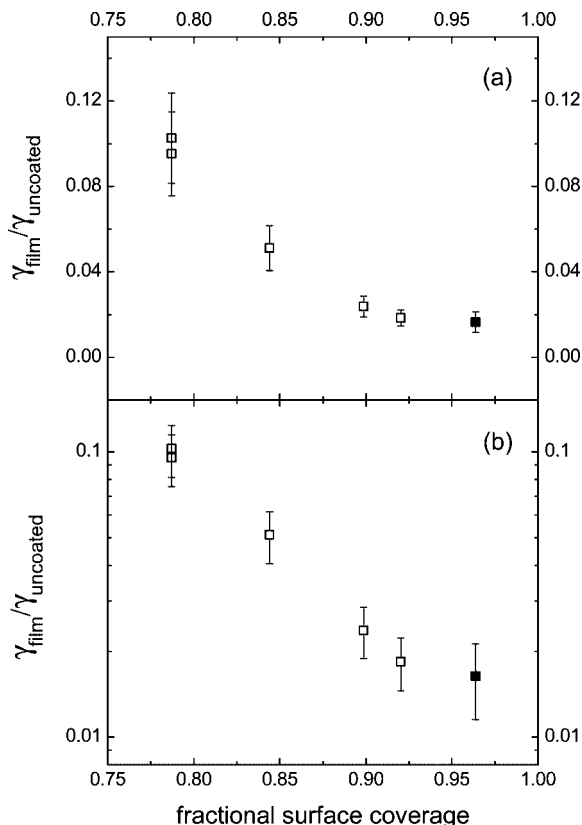


Figure 4. Reactive uptake coefficients for N_2O_5 on organic coated aqueous 60 wt % sulfuric acid at 273 ± 1 K plotted as a function of the fractional monolayer surface coverage. In this figure, the reactive uptake coefficient in the presence of the organic monolayer (γ_{film}) is normalized to reactive uptake coefficient for the uncoated solution (γ_{uncoated}) to illustrate the change in reactive uptake coefficient due to the presence of the monolayer. Open squares, 1-octadecanol (this study); solid square, 1-octadecanol (Cosman et al.).⁵¹ Panel a gives the ordinate in a linear scale whereas panel b shows the ordinate in a log scale.

area of the surfactant at the collapse pressure, π_c . Shown in Figure 4 is the reactive uptake coefficient in the presence of the organic monolayer (γ_{film}) normalized by the uptake coefficient for the uncoated case (γ_{uncoated}) as a function of this fractional surface coverage. Figure 4 shows that the fractional surface coverage does not have to be 1 to significantly decrease the reactive uptake coefficient. Even at 0.75 of the maximum surface coverage (i.e., fractional surface coverage = 0.75), the monolayer still decreases the reactive uptake coefficient by a factor of 10. Park et al.⁴⁵ and McNeill et al.,³⁸ also performed a similar analysis to the above (although they defined the fractional surface coverage slightly differently). Our conclusion mentioned above is similar to the conclusions reached by these authors previously. For example, McNeill et al.³⁷ observed a significant decrease in γ (approximately a factor of 3 decrease) even when the fractional surface coverage was 0.08 for a NaCl aerosol coated with sodium dodecyl sulfate monolayers.

In Figure 5, we compare our 1-octadecanol results with previous measurements of N_2O_5 reactive uptake measured for aqueous sulfuric acid solutions coated with 1-component monolayers. For this comparison we use the molecular surface area on the x -axis, since in our previous work we have shown that the uptake results for coated aqueous sulfuric acid solutions correlate better with the molecular surface area of the surfactant compared to other parameters such as surface pressure.⁵¹ Panel a displays γ_{film} and panel b displays the ratio of γ_{film} to the reactive uptake coefficient of the uncoated solution (γ_{uncoated}).

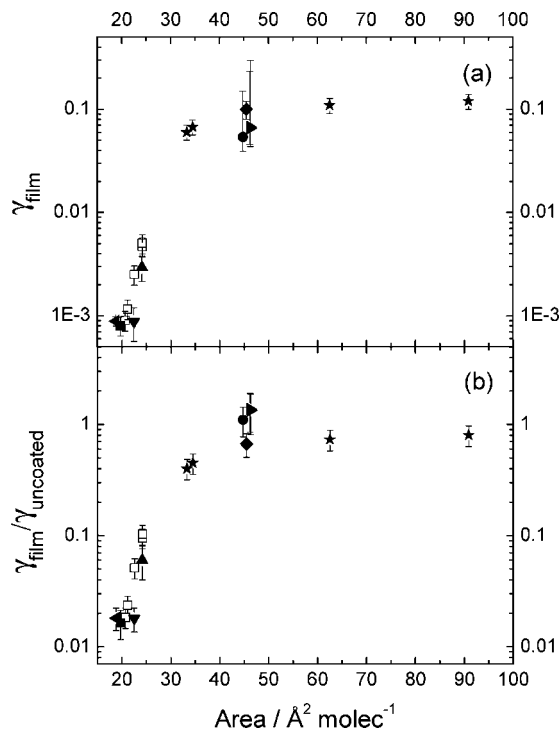


Figure 5. Reactive uptake coefficients for N_2O_5 on aqueous sulfuric acid in the presence of organic monolayers as a function of molecular surface area. Open squares, 1-octadecanol (this study); solid right facing triangles, phytanic acid (this study); solid squares, 1-octadecanol (Cosman et al.);⁵¹ solid triangles, stearic acid (Cosman et al.);⁵¹ solid circles, phytanic acid (Cosman et al.);⁵¹ solid left facing triangles, 1-hexadecanol (Cosman et al.);⁵¹ solid diamonds, butanol (Park et al.);⁴⁵ solid stars, hexanol (Park et al.);⁴⁵ and solid inverted triangles, 1-octadecanol (Knopf et al.).⁴⁶ In panel a, the ordinate is the reactive uptake coefficient in the presence of the organic film (γ_{film}), and in panel b the ordinate is γ_{film} normalized to reactive uptake coefficient for the uncoated solution (γ_{uncoated}).

Our current data for 1-octadecanol is represented with open symbols, and all the other data (obtained with soluble and insoluble monolayers) is represented by solid symbols. First, our current data generally fits well the trend observed with all the previous data.^{45,46,51} Second, considering all the data, there appears to be a strong correlation between the reactive uptake coefficient and the molecular surface area. This trend was observed in our previous publication,⁵¹ and our current data adds more support to this conclusion.

The fact that the data in Figure 5 correlates well with the surface area is broadly consistent with the Accessible Area Theory.⁵⁴ The Accessible Area Theory has previously been used to predict the effect of organic monolayers on the evaporation rate of water. This theory captures well the general trends in evaporation of water in the presence of several long-chain alcohols. However, the agreement between theory and experiments is not quantitative.^{48,56} The Accessible Area Theory suggests that transport occurs only through open sections of the surface. Such sections may be formed through random fluctuations or by incomplete packing of the film. One limitation of this theory is that it does not consider the effect of chain length on the mass transport of gases.⁵⁴

Note that Figure 5 should not be considered as a rigorous test of the Accessible Area Theory because the figure largely separates the short chain molecules (right hand side in Figure 5) from the long chain molecules (left hand side in Figure 5) with the exception of phytanic acid). More work is needed to fully test the Accessible Area Theory. Studies of the reactive

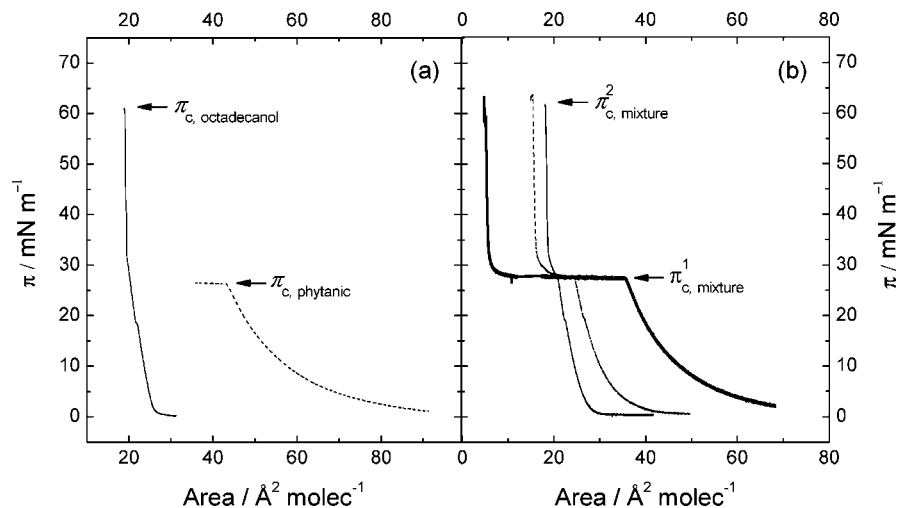


Figure 6. Surface pressure-area isotherms for organic monolayers on aqueous 60 wt % sulfuric acid at 273 ± 1 K. Panel a: the isotherm for 1-octadecanol⁵¹ ($x_{\text{phytanic}} = 0$) represented by the solid line and phytanic acid⁵¹ ($x_{\text{phytanic}} = 1$) shown as the dashed line. $\pi_{\text{c, octadecanol}}$ and $\pi_{\text{c, phytanic}}$ represent the surface pressure at which monolayers of pure 1-octadecanol and pure phytanic acid collapse, respectively. Panel b: the isotherm for 2-component monolayers of 1-octadecanol and phytanic acid. The solid line, dashed line, and bold solid line represent the isotherms for compositions of $x_{\text{phytanic}} = 0.05, 0.2$, and 0.7 , respectively. Isotherms for $x_{\text{phytanic}} = 0.1$ and 0.4 have been omitted for clarity.

uptake of N₂O₅ in the presence of long-chain molecules with large molecular surface areas would be useful. From Figure 5, we conclude that the trend in reactive uptake coefficient of N₂O₅ with molecular surface area is broadly consistent with the Accessible Area Theory (i.e., a correlation between the reactive uptake coefficient and the molecular surface area is observed). More work is needed to determine if the theory is quantitative. Also, note that in Figure 5 we have only plotted data measured with aqueous sulfuric acid solutions. As we discussed in our previous manuscript,⁵¹ data measured with a sea salt or NaCl subphase are not consistent with the trend shown in Figure 5. More work is needed to understand this apparent conflict.

Surface Pressure-Area Isotherms of 2-Component Monolayers and the Miscibility of These Monolayers. A 2-component monolayer may be miscible or immiscible. An immiscible monolayer can be thought of as made up of two separate monolayers, whereby one component forms patches of a monolayer distributed within a monolayer of the second component.⁵⁷ The main point of this section is to determine if the 2-component system we studied (1-octadecanol-phytanic acid monolayer) is immiscible.

Shown in Figure 6 are the pressure-area isotherms for the 1-octadecanol-phytanic acid monolayers (with various x_{phytanic} values) as well as the isotherms for the pure components (i.e., pure 1-octadecanol and phytanic acid). The π -A isotherm for 1-octadecanol (see Figure 6a) shows several “kinks” in the isotherm due to 2D phase transitions, as discussed above.^{57,75,76} As the molecular surface area decreases, the monolayer undergoes several phase transitions until it reaches its collapse pressure (labeled in Figure 6 as $\pi_{\text{c, octadecanol}}$),⁵¹ and a further compression of the film results in the formation of a new bulk phase on the surface.⁵⁷

The behavior for the branched surfactant, phytanic acid, is significantly different than for the straight-chain surfactant, 1-octadecanol (see Figure 6a). Between $45 \text{ \AA}^2 \text{ molec}^{-1}$ and approximately $80 \text{ \AA}^2 \text{ molec}^{-1}$, the branched-chain monolayer is in a liquid expanded state.^{51,57} At a surface pressure of 26 mN m^{-1} the monolayer collapses (labeled $\pi_{\text{c, phytanic}}$ in Figure 6a), and further compression of the film results in the formation of liquid lenses in equilibrium with a monolayer at a molecular surface area of $44.5 \text{ \AA}^2 \text{ molec}^{-1}$.⁵¹

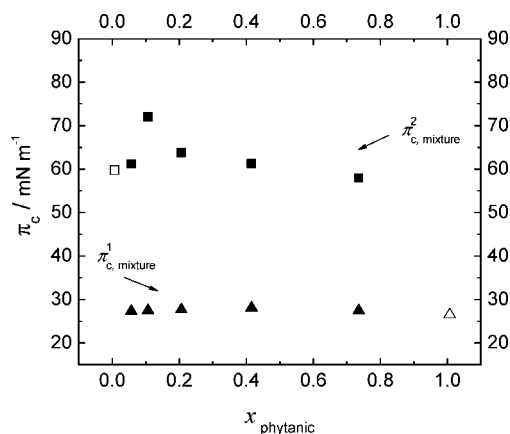


Figure 7. The collapse pressures of 1-octadecanol-phytanic acid monolayers on aqueous 60 wt % sulfuric acid at 273 ± 1 K as a function of composition (x_{phytanic}). Solid triangles and solid squares represent the first collapse pressure ($\pi_{\text{c,mixture}}^1$) and second collapse pressure ($\pi_{\text{c,mixture}}^2$) for the 2-component monolayers, respectively. The open triangle and open square represent the collapse pressure of pure phytanic acid and pure 1-octadecanol monolayers, respectively.

Panel b of Figure 6 illustrates the π -A isotherms for the 2-component monolayers. The isotherms for the mixtures appear to be intermediate between the pure component isotherms and also exhibit two discontinuities that we assign as collapse pressures of the monolayers, labeled $\pi_{\text{c,mixture}}^1$ and $\pi_{\text{c,mixture}}^2$. The π -A isotherms for $x_{\text{phytanic}} = 0.1$ and 0.4 have been omitted for clarity.

One useful tool for establishing the miscibility of a 2-component monolayer is the interfacial phase rule.^{57,78,79} According to this phase rule, when a monolayer is immiscible it will exhibit two separate collapse events that correspond to the collapse pressures of the individual pure components, independent of monolayer composition.⁵⁷ If, however, the two components of the monolayer at the interface are miscible, the surface pressure at which the monolayer collapses is dependent on the monolayer composition.⁵⁷ Figure 7 shows the collapse pressure for the 2-component monolayers of 1-octadecanol and phytanic acid as a function of monolayer composition (i.e., x_{phytanic}), as well as the collapse pressures for the single component monolayers. The solid symbols represent the collapse pressures for the

2-component monolayer and the open symbols represent the collapse pressures for the 1-component systems. Figure 7 shows that the 1-octadecanol-phytanic acid monolayers exhibit two collapse pressures that are consistent with the collapse pressures of the pure component systems and are roughly independent of composition, as one would expect for an immiscible monolayer. The scatter in $\pi^2_{c,mixture}$ as a function of $x_{phytanic}$ is not surprising. $\pi^2_{c,mixture}$ corresponds to the collapse pressure of 1-octadecanol in the 2-component monolayer. In this case, the 1-octadecanol is in a 2D solid phase just before collapse. It is well known that the collapse pressure of a 2D solid phase can vary significantly from experiment to experiment and is sensitive to trace levels of impurities in the monolayer because the collapse of a 2D solid phase is a nucleation event with a large kinetic barrier.⁵⁷ Also the scatter observed in Figure 7 is typical for immiscible monolayers.⁸⁰

Another useful tool for investigating the miscibility of a monolayer is the average molecular surface area in the 2-component monolayer and the excess area in the 2-component monolayer. If the 2-component monolayer is completely immiscible, then the average molecular surface area of the surfactant molecules in this monolayer should be related to the molecular surface area in the 1-component monolayers at the same surface pressure, according to the following equation:⁵⁷

$$A_{12,predicted} = A_1x_1 + A_2x_2 \quad (3)$$

where $A_{12,predicted}$ is the average molecular surface area predicted for an immiscible 2-component monolayer. A_1 and A_2 are the molecular surface areas in the 1-component monolayers 1 and 2, respectively, and x_1 and x_2 are their respective mole fractions. For eq 3 to apply, $A_{12,predicted}$, A_1 , and A_2 need to be evaluated at the same surface pressure. In Figure 8a, we plot $A_{12,predicted}$ as well as the measured average molecular surface area in the 2-component monolayer, $A_{12,measured}$, evaluated at a surface pressure of 21 mN m⁻¹. $A_{12,measured}$ was determined from the surface pressure-area isotherms shown in Figure 6b. In Figure 8a, symbols represent $A_{12,measured}$ and the line represents $A_{12,predicted}$. The good agreement between the two gives more support for an immiscible monolayer. To further explore this point, we also calculated the excess area, A_{ex} , as a function of monolayer composition (evaluated at 21 mN m⁻¹) for the 2-component monolayer. The excess area is a measure of nonideality of the monolayer, and is given by^{80,81}

$$A_{ex} = A_{12,measured} - A_{12,predicted} \quad (4)$$

where $A_{12,measured}$ and $A_{12,predicted}$ are as defined above. 2-Component monolayers that are completely immiscible have $A_{ex} = 0$.⁸⁰ Positive or negative values for the excess area indicate nonideal mixing in the 2-component systems.⁸¹ Figure 8b shows the excess areas as calculated using eq 4. The values of A_{ex} do not appear to vary in any systematic way from zero. In fact, the error bars for all data points overlap zero except for one.

A final way we explored the miscibility of the monolayer was by comparing our measured pressure-area isotherms with predictions. If the monolayers are completely immiscible, then the isotherms of the 2-component monolayer should be a linear combination of the 1-component monolayers, scaled to the mole fractions of the single components. In Figure 9, we have shown two of our measured isotherms, along with predictions (shown as dashed lines) assuming the monolayers were immiscible. The good agreement gives further support that our monolayers are immiscible.

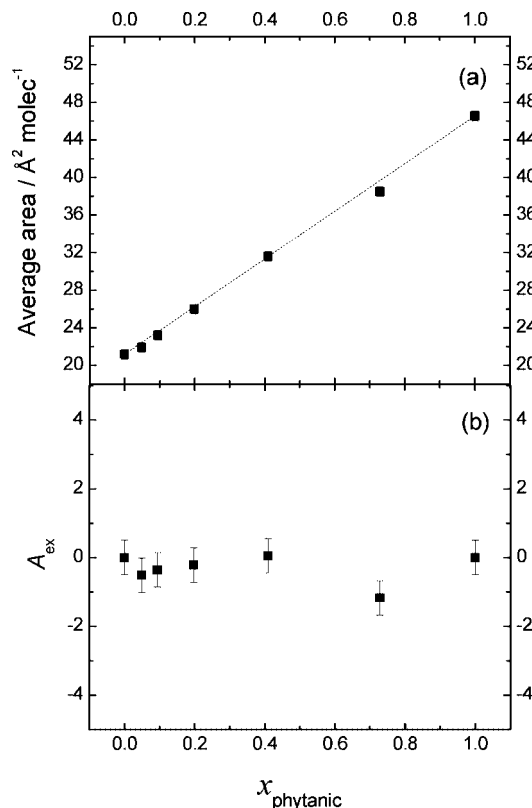


Figure 8. Panel a shows the measured molecular surface area (solid symbols) and the predicted molecular surface area (dashed line) for 2-component monolayers with $\pi = 21 \pm 2$ mN m⁻¹ as a function of composition ($x_{phytanic}$). Panel b displays the excess area (A_{ex}) as a function of composition for 1-octadecanol-phytanic acid monolayers. See text for further details.

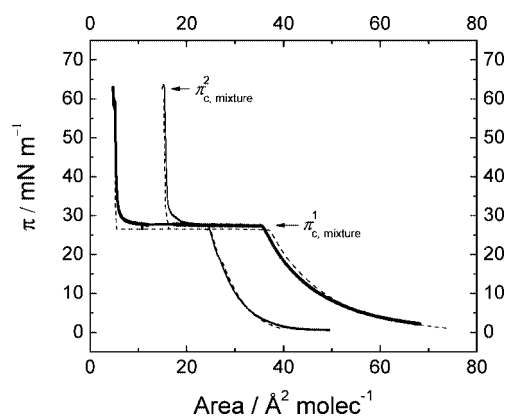


Figure 9. Surface pressure-area isotherms for binary mixtures of 1-octadecanol and phytanic acid performed on aqueous 60 wt % sulfuric acid at 273 ± 1 K. Examples of experimentally measured isotherms for 2-component monolayers containing $x_{phytanic} = 0.1$ (bold solid line) and $x_{phytanic} = 0.7$ (solid line) are shown. The dashed lines are the predicted isotherms based on a linear combination of the isotherms for pure 1-octadecanol⁵¹ and pure phytanic acid.⁵¹

The above evidence gives strong support that the 1-octadecanol-phytanic acid monolayers are completely immiscible and hence one can think of the monolayers as forming patches of phytanic acid distributed within a monolayer of 1-octadecanol (or vice versa). At the first collapse pressure ($\pi^1_{c,mixture}$), phytanic acid is squeezed out resulting in a monolayer that contains only 1-octadecanol until the second collapse pressure ($\pi^2_{c,mixture}$) at which the 1-octadecanol collapses as well. Because at the first collapse pressure all the phytanic acid is squeezed out of the monolayer, we performed all our uptake measurements using a

TABLE 2: Measured Reactive Uptake Coefficients for N₂O₅ on 60 Wt % Aqueous Sulfuric Acid Solutions at 273 ± 1 K Coated with 1-Octadecanol–Phytanic Acid Monolayers at 21 ± 2 mN m^{-1a}

x_{phytanic}	π (mN m ⁻¹)	molecular surface area (Å ² /molec)	γ	lower limit	upper limit
0	21.1	21.3	0.00116	0.00091	0.00141
0.05	19.7	22.1	0.00579	0.00405	0.00752
0.1	21.7	23.5	0.0109	0.00761	0.0141
0.2	20.1	26.3	0.0217	0.0174	0.0261
0.4	21.4	32.2	0.0352	0.0246	0.0457
0.7	21.9	38.1	0.0625	0.0410	0.0841
1	21.5	47.2	0.0663	0.0439	0.0894

^a The average molecular surface areas for each 2-component monolayer (determined from the pressure-area isotherms) are also included.

surface pressure of 21 ± 2 mN m⁻¹. This ensures that we still had two components in the monolayer.

N₂O₅ Reactive Uptake in the Presence of a 2-Component Monolayer. The reactive uptake of N₂O₅ on aqueous 60 wt % H₂SO₄ solutions at 273 K was measured in the presence of 1-octadecanol–phytanic acid monolayers. 2-Component monolayers with a mole fraction of phytanic acid (x_{phytanic}) equal to 0, 0.05, 0.1, 0.2, 0.4, 0.7, and 1 were studied. Reactive uptake coefficients and average molecular surface areas for each binary mixture studied are reported in Table 2. The upper and lower limits for γ in Table 2 take into account 20% error in the diffusion coefficients.

The reactive uptake coefficients determined in these studies are also shown in Figure 10. This figure shows that γ increases as x_{phytanic} increases. This was expected as the uptake coefficient on a H₂SO₄–H₂O solution coated with a phytanic acid monolayer (at a surface pressure of 21 ± 2 mN m⁻¹) is much larger than for the same solution coated with a 1-octadecanol monolayer (at a surface pressure of 21 ± 2 mN m⁻¹). As discussed in our previous publication,⁵¹ the reason phytanic acid has a smaller effect on the reactive uptake coefficient is because of the branched structure of the molecule, which prevents the surfactant from packing densely on the surface (or achieving a small molecular surface area).

Two different models have been suggested to explain the mass transfer of species across a 2-component organic monolayer. Gaines⁵⁷ suggests that for 2-component immiscible monolayers the resistance to mass transfer of patches of unmixed monolayers might be expected to combine as resistances in parallel. This model can be expressed with the following equation:⁵⁷

$$\gamma_{12} = x_1\gamma_1 + x_2\gamma_2 \quad (5)$$

where x_1 and x_2 are the mole fractions of component one and component two in the 2-component monolayer, and γ_{12} , γ_1 , and γ_2 represent the reactive uptake coefficients for the 2-component and 1-component monolayers, respectively (all evaluated at the same surface pressure).

In contrast, Barnes and LaMer⁸² used the Energy Barrier Theory^{82–84} to predict the resistance to mass transfer through an ideal, miscible monolayer. In terms of reactive uptake coefficients, this model can be expressed with the following equation:⁸²

$$\ln\left(\frac{1}{\gamma_{12}}\right) = x_1 \ln\left(\frac{1}{\gamma_1}\right) + x_2 \ln\left(\frac{1}{\gamma_2}\right) \quad (6)$$

The dashed lines in Figure 10 are the result of plotting eq 5, whereas the dash-dot lines in Figure 10 are the result of plotting

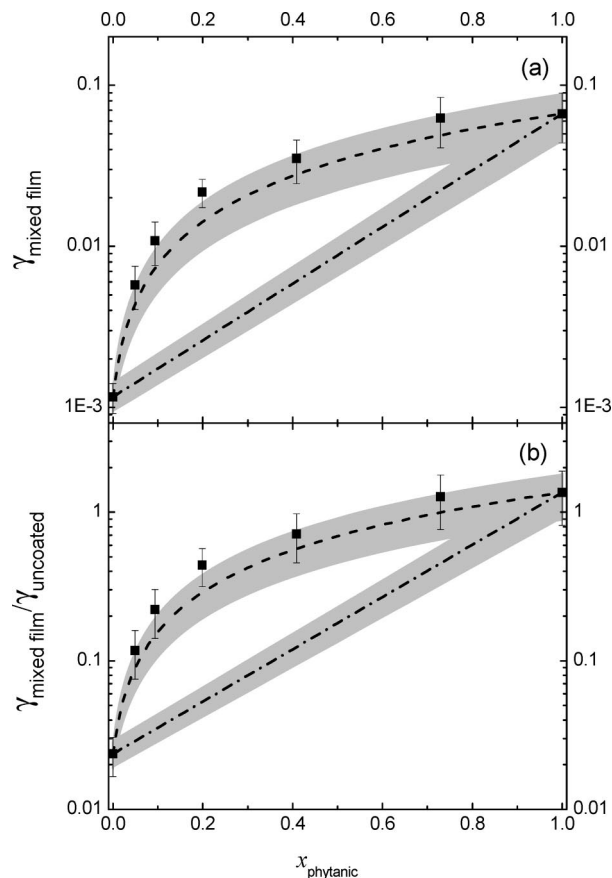


Figure 10. The reactive uptake coefficient for N₂O₅ on aqueous sulfuric acid in the presence of 1-octadecanol–phytanic acid monolayers ($\gamma_{\text{mixed film}}$) as a function of mole fraction of phytanic acid in the monolayer, x_{phytanic} . Solid squares represent the average γ value for each corresponding monolayer. The error bars represent 2 σ . The bold dashed line represents the prediction based on eq 5 whereas the bold dash dot line represents the prediction based on eq 6.⁵⁷ The shaded regions reflect the uncertainty in the predictions based on the uncertainty in γ_1 ($x_{\text{phytanic}} = 0$) and γ_2 ($x_{\text{phytanic}} = 1$). In panel a, the ordinate is the reactive uptake coefficient in the presence of the organic film ($\gamma_{\text{mixed film}}$), and in panel b the ordinate is $\gamma_{\text{mixed film}}$ normalized to reactive uptake coefficient for the uncoated solution (γ_{uncoated}).

eq 6 for our experimental conditions. The shaded regions in Figure 10 reflect the uncertainty in the model predictions based on the uncertainty in γ_1 and γ_2 . Our data is consistent with the model for reactive uptake in the presence of an immiscible monolayer presented by Gaines⁵⁷ (eq 5). However, our data does not agree well with the model prediction for a miscible monolayer (eq 6). Our data is the first case where the results for an immiscible monolayer are consistent with eq 5. More on this is included below.

Related to this discussion, several researchers have investigated the evaporation of water coated with 2-component organic monolayers.^{55,77,84–90} Researchers have generally found that the resistance to water evaporation due to an ideal, miscible monolayer can be explained with eq 6.^{77,90} For immiscible monolayers, none of the water evaporation studies could be explained by eq 5 (or eq 6).^{48,56,85,87,89} For example, several studies have investigated the evaporation resistance of 1-octadecanol–cholesterol monolayers (which are expected to be immiscible) and have shown resistances that are appreciably lower than those predicted by eq 5.^{85,89} For example, deviations from model predictions by up to a factor of 2.2 were observed by Barnes et al.⁸⁵ Possible explanations for why evaporation resistance measurements through immiscible monolayers are not

consistent with eq 5 include partial miscibility or mass transfer occurring mainly at grain boundaries.⁴⁸

The difference in structure between cholesterol and octadecanol seems to be greater than the difference between octadecanol and phytanic acid. This may also be related to why eq 5 fits our octadecanol–phytanic acid data and not the previous octadecanol–cholesterol data. Note that the reactive uptake coefficient of N₂O₅ on aqueous sulfuric acid solutions coated with 1-octadecanol–phytanic acid monolayers may also deviate slightly from the predictions based on eq 5, but our work shows that this deviation is less than the uncertainty in our measurements as illustrated by Figure 10.

In addition to water evaporation studies, Gilman and Vaida⁴² studied the uptake of acetic acid in the presence of mixed monolayers consisting of 1-triacontanol and *cis*-9-octadecanol, which are expected to form immiscible monolayers. These authors studied equimolar mixtures and observed that the mixed films had permabilities that were between that of the single-component films that comprise the mixture, which is consistent with our findings. However, the applicability of eqs 5 and 6 to their results were not studied.

Because the transfer of molecules across 2-component monolayers is an important step toward a complete understanding of the mechanism of mass transfer across the air–aqueous interface in the presence of monolayers, more work in this direction is required. Further experiments that would be beneficial could include studies of N₂O₅ uptake on the same 2-component immiscible monolayers studied in the water evaporation experiments where the results deviated significantly from eq 5.

Summary and Conclusions and Atmospheric Implications

The first part of this manuscript focused on the reactive uptake of N₂O₅ on aqueous sulfuric acid solutions coated with a 1-component monolayer (1-octadecanol). Our results showed that the reactive uptake coefficient depends strongly on the molecular surface area of the surfactant in the monolayer. We also observed no step function increase in γ when transitioning between 2D phases. We also demonstrated that when the fractional surface coverage was less than 1, the monolayer still showed significant resistance to mass transfer, consistent with previous studies of N₂O₅ reactivity on aqueous particles in the presence of surfactants.^{37,38,45} For example, even at 0.75 of the maximum surface coverage, the monolayer still decreased the reactive uptake coefficient by a factor of 10. This observation may be of atmospheric relevance, because monolayers in the atmosphere are not expected to always have a fractional surface coverage of 1.

When we compared all previous measurements of reactive uptake of N₂O₅ on aqueous sulfuric acid solutions coated with a 1-component monolayer, we observed a strong correlation between the reactive uptake coefficient and the molecular surface area of the surfactant. This observation is broadly consistent with the Accessible Area Theory for permeation through monolayers.

The second part of the manuscript focused on 2-component monolayers consisting of a mixture of a straight-chain surfactant (1-octadecanol) and a branched surfactant (phytanic acid). These studies may be of more atmospheric relevance because monolayers in the atmosphere probably consist of more than one component and a combination of straight-chain and branched surfactants. The 2-component monolayers were first shown to be immiscible through a series of pressure–area isotherm measurements. Then we focused on measurements of the N₂O₅

reactive uptake. These measurements showed that when the monolayer contained 100% straight-chain molecules, the decrease in the reactive uptake coefficient was approximately a factor of 42 due to the presence of the monolayer. However, our results showed that when the mole fraction of branched surfactant was only 0.20 the decrease in the reactive uptake coefficient was only a factor of 2 (down from 42). Hence, a small amount of branched surfactant drastically changes the overall resistance to reactive uptake on aqueous sulfuric acid solutions. This highlights the importance of understanding the composition of mixed organic monolayers in acidic atmospheric particles. Also, our results showed that the overall resistance to reactive uptake of immiscible monolayers can be predicted reasonably accurately using eq 5, which assumes the resistances to mass transfer can be combined in parallel. This equation may be useful for making predictions of reactive uptake of aqueous particles coated with multicomponent monolayers in the atmosphere.

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