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on a swelling clay**

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Heterogeneous uptake of the C₁ to C₄ organic acids on a swelling clay mineral

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Abstract

Mineral aerosol is of interest due to its physiochemical impacts on the Earth's atmosphere. However, adsorbed organics could influence the chemical and physical properties of atmospheric mineral particles and alter their impact on the biosphere and climate. In this work, the heterogeneous uptake of a series of small organic acids on the swelling clay, Na-montmorillonite, was studied at 212 K as a function of relative humidity (RH), organic acid pressure and clay mass. A high vacuum chamber equipped with a quadrupole mass spectrometer and a transmission Fourier transform infrared spectrometer was used to detect the gas and condensed phases, respectively. Sub-monolayer coverage of organic acid on montmorillonite was observed under dry conditions and relevant organic acid pressures. However, the organic acid content increased significantly with increasing humidity. Additionally, while the initial uptake efficiency was found to be independent of organic acid pressure, it increased linearly with increasing clay mass. Thus, the small masses studied allow access to the entire surface area of the clay sample with minimal effects due to surface saturation. Results from this study show that the initial uptake efficiency for n-butyric acid on the clay increases by an order of magnitude as the RH is raised from 0% to 45% RH at 212 K while the uptake of formic, acetic and propionic acids increase only slightly at higher humidities. Additionally, the presence of organic acids was found to slightly enhance the water content of the clay above 45% RH. Our results indicate that heterogeneous uptake of organic acids on swelling clay minerals provides an important heterogeneous sink for these species and may modify the cloud forming potential of the clay particles.

1 Introduction

Mineral aerosol in the Earth's atmosphere is of interest because of its direct and indirect effect on climate as well as its potential importance for heterogeneous chemistry (Sokolik et al., 1998; Tang et al., 2004; Zhang and Carmichael, 1999). Mineral aerosol

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components are variable depending on the mineralogy of the source region and atmospheric processing during transport. Recent field measurements have shown that atmospheric mineral aerosol is predominantly composed of layered silicates. For example, Reid et al. (2003) found that 70% of all mineral particle mass originating from Africa consisted of layered silicates such as illite, kaolinite and montmorillonite clays. Montmorillonite is of particular interest because it has a unique ability to accommodate an aqueous environment and provide a large reactive surface area for adsorption. Additionally, this clay is known to contain comparable quantities of water to common deliquescent species, such as ammonium sulfate (Frinak et al., 2005). Thus, the hygroscopic nature of montmorillonite may provide an excellent platform for uptake of gas phase species in the Earth's troposphere and may make it a good cloud nucleus.

As mineral particles are transported through the atmosphere, the particles encounter many environments. Mineral aerosol is generally emitted from dry regions where humidity is low. However, the emitted particles may be entrained in the troposphere for days to weeks (Bauer et al., 2004). For example, an estimated 50% of airborne mineral particles from Chinese deserts are transported long distances (Zhang et al., 1997). As the mineral aerosol moves out of the source region it can pass through semi-arid regions where biomass burning often occurs, providing a substantial source of organics to the atmosphere. Additionally, transport over urban regions can result in the mixing of pollution with dust plumes (Maxwell-Meier et al., 2004; Sun et al., 2005; Wang et al., 2005). Mineral particles en route through these regions could have a significant impact on the gas phase abundance of species such as nitric acid, sulfuric acid and organics and may help transport these species over longer distances. Further, swelling clays, such as montmorillonite, can provide a reactive environment for heterogeneous chemistry under more humid conditions as the particles are transported out of the arid source region.

Field measurements have shown that mineral particles entrained in the atmosphere often contain organic components. Single particle analysis of mineral aerosol has shown that oxygenated organic compounds are found in the same particles as min-

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eral species, including aluminosilicate clays (Falkovich et al., 2004; Haderlein and Schwarzenbach, 1993; Lee et al., 2002; Lee et al., 2003). Russell et al. (2002) used soft X-ray spectromicroscopy to map adsorbed components on atmospheric aerosol particles. This study found a strong interaction between mineral aerosol and carbonyl species, possibly aldehydes, ketones and organic acids. Additionally, Falkovich et al. (2004) studied dust samples collected over an urban region in Israel's coastal plain. Scanning electron microscopy coupled with an energy dispersion system (SEM/EDS) revealed that some of the collected particles were agglomerates of aluminosilicates containing heterogeneous organic coatings. Falkovich et al. (2004) also found that carboxylic acids adsorbed more efficiently to Saharan mineral aerosol particles at higher relative humidity (RH) with respect to liquid water. Thus, heterogeneous uptake of organic acids appears to play a role in the atmospheric processing of mineral aerosol and may be enhanced under humid conditions. However, very little is known about the kinetics and mechanisms of these interactions.

A few laboratory studies have begun to explore the heterogeneous chemistry of organic compounds with various types of minerals (Al-Abadleh and Grassian, 2003; Al-Hosney et al., 2005; Carlos-Cuellar et al., 2003; Li et al., 2001). Previous studies probing the uptake of acetic acid at 295 K on minerals such as Al_2O_3 , $\alpha\text{-Fe}_2\text{O}_3$ and SiO_2 and formic acid at 295 K on CaCO_3 have been reported (Al-Hosney et al., 2005; Carlos-Cuellar et al., 2003). Al-Hosney et al. (2005) found that addition of a small amount of water vapor enhanced the affinity of CaCO_3 for formic acid but quantification of the heterogeneous uptake efficiency under humid conditions has not been reported. These laboratory studies have shown that some minerals representative of airborne dust may have a sizable capacity to adsorb small organic acids. However, previous studies have not yet quantified the heterogeneous uptake of organic acids under typical upper tropospheric temperatures and atmospherically relevant RH values, nor have they explored the aqueous environment of a swelling clay which may impact gas-to-particle conversion of organic acids in the atmosphere.

Previous studies in our laboratory have explored the heterogeneous adsorption of

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water and nitric acid on Na-montmorillonite clay (Frinak et al., 2005; Mashburn et al., 2006). These studies have suggested that swelling clays may be important cloud condensation nuclei because of their large water adsorption capacities. Additionally, in the presence of nitric acid, montmorillonite can accommodate even more water at RH values greater than 30% (Mashburn et al., 2006). Thus, in addition to the potential effects on gas phase concentrations of organic acids, the hygroscopic properties of these clays may also be altered in the presence of organics. These previous studies have allowed for a detailed characterization of Na-montmorillonite as a function of RH. The present study explores the heterogeneous uptake of the C₁ to C₄ organic acids, including formic, acetic, propionic and n-butyric acids, at upper tropospheric temperatures on Na-montmorillonite clay as a function of RH, organic acid pressure and clay mass.

2 Experimental methods

2.1 Vacuum chamber

The Knudsen cell flow chamber used for the present study has been described in detail previously and is briefly discussed here (Mashburn et al., 2006). A high vacuum flow reactor equipped with a UTI 100C quadrupole mass spectrometer and a Nicolet 740 Fourier transform infrared (FT-IR) spectrometer in transmission mode are used to simultaneously monitor the gas and condensed phases, respectively. The stainless steel chamber is evacuated through an escape orifice, 0.16 cm², by a 210 L/s turbomolecular pump (Pfeiffer) reaching baseline pressures near 2×10^{-7} Torr. The gas phase organic acid and water vapor are introduced through two separate leak valves backed by the vapor pressure above the liquid phase held at 0°C in an ice bath. The organic acids are housed in glass bulbs and are degassed by daily freeze-pump-thaw cycles. The design of this vacuum chamber allows for isolation of the reactive surface from the gas phase flow by covering the sample with a retractable Teflon cup that seals against the

chamber walls with an O-ring. Thus, a steady-state flow of gas phase reactants may be established prior to exposure of the clay.

An MKS Baratron capacitance manometer and an ionization gauge measure the total chamber pressure while the absolute pressure of the organic acid is monitored by mass spectrometry. Prior to each experiment, the mass spectrometer signal for the organic acid is calibrated to the partial pressure of the acid measured by the Baratron and ionization gauge. The partial pressure of the acid is obtained from the mass spectrometer signal after equilibration with the water vapor at the experimental temperature and prior to exposure to the clay sample. The partial pressure of water, obtained by subtracting the partial pressure of the organic acid from the total chamber pressure, is used to determine the relative humidity at the temperature of the sample (Flatau et al., 1992). The water pressure is maintained below the saturation vapor pressure with respect to water ice for all experiments reported here.

The clay sample is deposited onto an infrared-transparent silicon wafer and the wafer is attached to a gold-coated copper mount with stainless steel clips. Indium foil is placed between the sample and mount to improve thermal contact. Upper tropospheric temperatures are reached using a liquid nitrogen-cooled cryostat. The temperature is controlled by a Eurotherm temperature controller and monitored by two type T thermocouples attached to either side of the sample mount. The temperature of the thermocouple is calibrated by performing ice frost point calibrations (Marti and Mauersberger, 1993) and is held at 212 K for all experiments reported here.

2.2 Sample preparation

The chemical composition, surface area and infrared analysis of Na-montmorillonite, SWy-2, clay obtained from the Clay Mineral Society's Clay Source Repository, have been reported previously (Frinak et al., 2005; Madejova and Komadel, 2001; Van Olphen and Fripiat, 1979). The clay sample is prepared by depositing a well-mixed slurry of 100 mg SWy-2 in 25 mL water (Fisher Scientific, HPLC grade) on the silicon wafer. The deposited slurry is allowed to dry under ambient conditions and is then

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dried further by evacuation in the vacuum chamber for 24 to 48 h or until a background pressure of approximately 2×10^{-7} Torr is reached. This method results in consistent sample masses near 1.5 mg and geometric surface areas near 2 cm^2 .

Transmission (TEM) and scanning electron microscopy (SEM) were used to examine the SWy-2 particle size and surface characteristics. Figure 1a shows a representative TEM image of the SWy-2 clay, where the particles are observed as the dark regions. This sample was prepared with a very dilute solution of the clay in water and yielded much smaller total masses than those used in the experiments. As shown, the clay particles are approximately $2 \mu\text{m}$ in diameter and are non-spherical. Figure 1b shows an SEM image of SWy-2 prepared in a similar manner as described for the uptake experiments. This image shows the rough surface morphology of the clay particles under experimental conditions.

2.3 Experimental procedure

During an experiment, an FT-IR background scan of the dry clay is first collected at the experimental temperature. The Teflon cup is then closed and the flow of organic acid is established through a leak valve. The chamber walls are passivated until a steady flow is achieved, approximately 45 min. For experiments performed under humid conditions, water vapor is added using a separate leak valve after sufficient passivation of the walls with the organic vapor. The experimental partial pressure of the organic species is obtained from the mass spectrometer after equilibration with the water and organic vapors for approximately 45 additional minutes. Once a constant flow of the acid and water vapor is established, the initial uptake is measured by opening the cup and exposing the sample to the gas phase for 200 s. Independent experiments at longer exposure times allowed for characterization of the condensed phase by FT-IR spectroscopy as the clay fully expands upon water adsorption.

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2.4 FT-IR data analysis

Infrared spectra of the clay upon exposure to the gas phase were obtained when the Teflon cup was open by averaging 32 scans at 4 cm^{-1} resolution and were ratioed to the background spectrum of the clay collected prior to each experiment. For each RH, the adsorbed products were monitored by transmission FT-IR spectroscopy as a function of time until the condensed phase was no longer observed to change, typically for three to five hours. Blank experiments, in which no clay sample was present, were performed for the same conditions and exposure times as experiments where the clay was present. No changes were observed in the infrared spectra for blank experiments under all conditions studied. FT-IR measurements allowed for quantification of adsorbed water as described in previous papers (Frinak et al., 2005; Mashburn et al., 2006).

2.5 MS data analysis

2.5.1 Uptake efficiency measurements

Mass spectrometer measurements with two second time resolution allowed for direct observation of changes in the gas phase organic acid concentration during each experiment. The initial drop in the mass spectrometer signal of the organic acid upon exposure to the sample is used to quantify heterogeneous uptake efficiency, γ_o . The uptake efficiency is defined as the ratio of the number of gas phase molecules lost to the surface per unit time to the total number of collisions with the surface per unit time. The γ_o is obtained from mass spectrometer data in the same manner as was determined previously for nitric acid uptake on SWy-2 and shown below (Mashburn et al., 2006):

$$\gamma_o = \frac{A_h}{(\text{SSA}_{\text{BET}} \times m)} \left(\frac{I_o - I_t}{I_t} \right) \quad (1)$$

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In Eq. (1), SSA_{BET} is the specific surface area (cm^2/mg) of SWy-2, A_h is the effective area of the escape orifice, $A_h=0.16\text{ cm}^2$, calibrated using nitrogen gas and m is the mass of the SWy-2 sample. I_o is the initial mass spectrometer signal of the organic acid before opening the Teflon cup to expose the sample and I_t denotes the mass spectrometer signal of organic acid immediately after exposure, corrected for blank experiments performed under the same conditions. For all experiments reported here, initial uptake on the blank silicon wafer is significantly less than uptake observed when the SWy-2 sample is present. Additionally, independent mass spectrometer measurements scanned the gas phase for potential products during exposure of the organic acids to SWy-2. Under all conditions studied, the evolution of gas phase products during exposure was not observed.

2.5.2 Clay surface area

The swelling properties of montmorillonite clay have been studied for many decades and a more detailed description of water adsorption and swelling may be found in the literature (Anderson et al., 1978; Cases et al., 1992; Frinak et al., 2005; Hall and Astill, 1989; Mooney et al., 1952). In the absence of water vapor, only the external surfaces of montmorillonite are available for adsorption. Water begins to penetrate the interlayer space of the clay above 16% RH and reaches monolayer coverage of water, both internal and external, near 48% RH (Cases et al., 1992; Hensen and Smit, 2002; Newman, 1983). Water begins adsorbing in multiple layers at higher humidities. Upon swelling, access to both internal and external surfaces results in the availability of a significantly larger surface area compared to the dry external surface area (Brunauer et al., 1938; Cases et al., 1992; Frinak et al., 2005).

To determine γ_o , the appropriate surface area is needed. As shown in the SEM image of the SWy-2 particles, the rough morphology of the clay particles implies that the geometric surface area, assuming a flat surface, is a significant underestimate of the available surface area. Non-polar molecules, such as nitrogen, are known to

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only adsorb to the external surfaces of montmorillonite and thus provide a direct measurement of the external surface area including clay microstructure (Hendricks et al., 1940; Mooney et al., 1952; Pennell et al., 1992). The BET surface area for SWy-2 is $318.2(\pm 2.2)$ cm²/mg (Dogan et al., 2006), as reported by the Clay Mineral Society and independently confirmed by the authors. However, when swollen, the available surface area of SWy-2 can increase as much as 25 times that of the external surface area obtained from BET measurements (Frinak et al., 2005; Mashburn et al., 2006).

Previous studies have determined the surface area of the swollen clay at various RH values using gravimetric (Cases et al., 1992) and FT-IR techniques (Frinak et al., 2005) to probe water adsorption. Frinak et al. (2005) found that saturation of adsorbed water on SWy-2 at low water pressures required fairly long exposure times at sufficiently low water pressures. For example, reducing the water pressure from 10 to 3 mTorr increases the 1/e loading time by a factor of four, from approximately 10 minutes to 40 min. The measurements reported here were conducted under low water pressure conditions; therefore, we expect long exposure times to be required for the SWy-2 clay to become swollen and the internal surfaces accessible. Thus, the interlayer space of the clay is not accessible to the organic acids at the early time of two seconds and only the external surfaces are available for adsorption during initial uptake (Frinak et al., 2005; Mashburn et al., 2006). As discussed below, the availability of the entire BET surface area is confirmed by studying the mass dependence of the heterogeneous uptake of formic, acetic, propionic and n-butyric acids on SWy-2 at 212 K and 29% RH.

2.6 Quantification of adsorbed organic acid

Mass spectrometer measurements may also be used to quantify the total amount of organic acid adsorbed to SWy-2 (Frinak et al., 2004). The organic acid content adsorbed to SWy-2 is determined by integrating the area under the mass spectrometer signal while the sample is exposed after correction for loss to the sample mount by subtraction. The mass spectrometer signal was first converted to a flow (molecules/sec) using

the Knudsen effusion relation:

$$F = \frac{\rho_{\text{org}} A_h}{(2\pi M_w kT)^{1/2}} \quad (2)$$

where A_h is the effective area of the escape orifice, 0.16 cm^2 , to the turbomolecular pump, M_w is the molecular weight of the organic acid, k is the Boltzmann constant and T is the temperature of the gas phase, defined as room temperature. The flow of organic acid during exposure to the clay is then offset and inverted so that the area under a double exponential fit through the uptake data gives the number of organic acid molecules adsorbed to the surface (Frinak et al., 2004). The number of organic acid molecules adsorbed at steady-state, n_{org} , is obtained by extrapolating the data collected during a 200 s experiment to 5000 s and correcting for uptake on the silicon wafer when the clay sample was not present. Finally, n_{org} can then be converted to a mass and divided by the mass of the clay sample resulting in a mass ratio in units of $\text{mg}_{\text{org}}/\text{g}_{\text{clay}}$. Alternatively, the number of adsorbed organic acid molecules can be divided by the surface area of the SWy-2 clay to estimate the acid coverage (molec/cm^2). Isothermal desorption is also measured to determine the reversibility of the interaction.

3 Results

3.1 FT-IR measurements of condensed products

FT-IR measurements revealed that under dry conditions, even after five hours of exposure to organic acids, no adsorbed species were observed in the infrared spectra. This suggests that the organic acids do not have a strong affinity for SWy-2 when water vapor is not present and the clay is not swollen. However, in the presence of water vapor, there is evidence for organic uptake. Figure 2 shows the FT-IR spectra collected before and after exposure of acetic acid to SWy-2 at 212 K and 29% RH. FT-IR peak assignments based on previous studies are shown in Table 1 (Bishop et al., 1994; Grassian,

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2001; Shilling et al., 2006; Shilling and Tolbert, 2004). In the presence of acetic acid and water vapor, the most prominent features observed after exposure are the stretch and bend of adsorbed water at 3350 cm^{-1} and 1640 cm^{-1} , respectively (Bishop et al., 1994). Additionally, a small change in the structural OH stretching region at 3624 cm^{-1} is observed. All of these features are typical of an experiment in which SWy-2 is exposed only to water without any organic acid present (Frinak et al., 2005). However, since the dominant feature of carbonyl species, the carbonyl stretch, is normally found near 1700 cm^{-1} , an overlap with the water bending peak would occur.

Previous studies have shown that adsorbed water is completely reversible upon warming the SWy-2 sample to room temperature (Frinak et al., 2005). Thus, following each experiment, adsorbed water was removed by warming to room temperature and the resulting infrared spectrum is shown in Fig. 2. Upon removal of adsorbed water, a broad feature, from 1350 to 1470 cm^{-1} , and a peak near 1615 cm^{-1} remain. These peaks are observed for all organic acids studied at experiments performed at 29% and 45% RH after warming to room temperature. The broad feature near 1400 cm^{-1} is attributed to the methyl deformation of adsorbed organic species (Grassian, 2001). The peak near 1615 cm^{-1} is not apparent in the infrared spectrum collected when water is present, probably due to overlap with the water bend. Additionally, this peak was not observed in previously reported water only measurements (Frinak et al., 2005) nor was it observed in the infrared spectrum of dry SWy-2 reported by the Clay Mineral Society (Madejova and Komadel, 2001). Previous studies showing adsorption of the C_1 to C_4 organic acids to ammonium nitrate found that the organic acid ionizes on the surface and the carbonyl peak, normally observed near 1700 cm^{-1} , shifts to lower wavenumbers near 1580 cm^{-1} based on literature spectra of sodium acetate (Kubicki et al., 1999; Max and Chapados, 2004; Shilling et al., 2006; Shilling and Tolbert, 2004). This result is also in agreement with bulk studies of acetic acid on montmorillonite clay (Kubicki et al., 1999). Thus, the infrared peak near 1615 cm^{-1} is probably due to carboxylate species on the surface of the clay, such as formate and acetate. Additionally, a previous study of nitric acid uptake on SWy-2 suggested that the interlayer cation

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appears to influence uptake under humid conditions (Mashburn et al., 2006). Since the peak near 1615 cm^{-1} was only observed in the infrared spectra under conditions in which the clay is expected to be swollen; the interlayer cation may also play a critical role in the uptake and dissociation of organic acids on SWy-2 when the interlayer space of the clay is accessible. Results from infrared analysis suggest that the aqueous-like nature of the clay under humid conditions may induce ionic dissociation and irreversible adsorption of organic acids under humid conditions.

Infrared measurements also allowed us to probe the effect of organic acids on water adsorption by the clay. The water content, in units of $g_{\text{H}_2\text{O}}/g_{\text{clay}}$, at steady-state is determined by FT-IR spectroscopy, as in previous studies (Frinak et al., 2005; Mashburn et al., 2006), using the optical constants for bulk water (Downing and Williams, 1975). Figure 3 shows the steady-state water content of SWy-2 at 212 K in the presence of the organic acids at 29% and 45% RH compared to water only measurements performed at 222 K as a function of RH (Frinak et al., 2005). The error bars represent the variability in the data based on multiple experiments performed under similar conditions. Only the OH stretching region observed near 3350 cm^{-1} was used for this calculation due to possible interference of the carbonyl stretch with the water bend at 1640 cm^{-1} . Figure 3 shows that, at 29% RH, the water content does not appear to deviate from the value obtained when no organic is present. A previous study of water adsorption in the presence of nitric acid observed similar results (Mashburn et al., 2006). However, this study also found that nitric acid only influenced the water content above 30% RH. Similar to the nitric acid study, Fig. 3 also shows that, at 45% RH, a significant enhancement in the water content is observed in the presence of the organic acids compared to studies where only water vapor is present. Experiments performed with propionic and n-butyric acids show an increase in water content by almost a factor of two compared to water only measurements (Frinak et al., 2005). This result suggests that adsorption of organic acids may influence the optical properties and cloud nucleating capabilities of smectite clays above 45% RH.

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3.2 MS measurements

3.2.1 Isothermal desorption to test for reversibility

5 Isothermal desorption measurements were performed to probe the reversibility of the heterogeneous interaction of organic acids with SWy-2. Upon completion of each uptake experiment, while the cup was still closed, the flow of organic acid was discontinued and the vacuum chamber was evacuated to the baseline pressure. Once a stable baseline pressure was established, the Teflon cup was retracted and isothermal desorption of the organic acid from SWy-2 was monitored by mass spectrometry. Integration of the area under the desorption peak resulted in the number of desorbed molecules. Upon comparing to the number of molecules adsorbed during the experiment we found that less than 20% of the adsorbed organic acid desorbed upon opening the cup for all of the organic acids and under all conditions studied. This result suggests irreversible adsorption of organic acids on SWy-2 clay, in agreement with the observation of the dissociated carbonyl stretch by FT-IR observed for experiments performed under humid conditions upon removal of adsorbed water.

3.2.2 Uptake as a function of clay mass

20 Mass spectrometry was used to directly monitor loss of the organic acid to the clay surface as a function of clay mass. Figure 4 shows the raw uptake curves obtained from the mass spectrometer during exposure of 1.6, 5.7, 7.8 and 17.1 mg SWy-2 samples to approximately 1×10^{-4} Torr propionic acid at 212 K and 29% RH. Similar traces are observed for the other organic acids studied. These curves show that organic acid uptake on small sample masses results in saturated adsorption within the 200 second time scale of the measurement indicated by complete recovery of the mass spectrometer signal to the original value before the cup is closed and exposure is halted. In contrast, uptake on larger sample masses results in unsaturated adsorption, indicated by incomplete recovery to the baseline signal. This observation is probably due to

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the longer time scale required for diffusion into and adsorption on the underlying clay layers at large masses. Longer exposure times are required to accurately determine the organic acid coverage at steady-state for larger sample masses. Thus, the organic acid content is only reported for the small sample masses used in the RH and pressure studies, discussed below.

To determine the appropriate surface area for quantification of γ_o , the heterogeneous uptake of the C₁ to C₄ organic acids was studied as a function of SWy-2 mass at 212 K, 29% RH and approximately 1×10^{-4} Torr organic acid, 1×10^{-5} Torr for n-butyric acid. Figure 5 shows $(I_o - I_t)/I_t$ as a function of SWy-2 mass for each of the organic acids studied. As expected from previous reports, $(I_o - I_t)/I_t$ values appear to increase linearly for small sample masses (Al-Hosney et al., 2005; Carlos-Cuellar et al., 2003; Mashburn et al., 2006). Sample masses less than 5 mg were considered to lie within the linear mass dependent regime. For masses larger than 5 mg, $(I_o - I_t)/I_t$ appears to saturate, suggesting that all of the underlying clay layers are not accessible by the adsorbate. Thus, the entire sample mass is available for adsorption on the time scale of the measurement if the samples remain smaller than 5 mg, such as those used in the RH and pressure studies (~1.5 mg). Thus, the BET surface area is used to determine γ_o for these studies. The slope obtained from a linear fit through the linear mass dependent region is used to calculate an average initial uptake efficiency, γ_o^{avg} , over the mass range studied as follows:

$$\gamma_o^{\text{avg}} = (\text{slope}) \frac{A_h}{\text{SSA}_{\text{BET}}} \quad (3)$$

As shown in Table 2, we find γ_o^{avg} values of $1.7(\pm 0.3) \times 10^{-5}$, $2.0(\pm 0.4) \times 10^{-5}$, $3.2(\pm 0.2) \times 10^{-5}$ and $4.0(\pm 0.1) \times 10^{-5}$ for the heterogeneous uptake of formic, acetic, propionic and n-butyric acids, respectively, on SWy-2 at 212 K and 29% RH from the data shown in Fig. 5.

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3.2.3 Uptake as a function of organic acid pressure

Results from the mass study are based on organic acid pressures near 1×10^{-4} Torr to maximize signal. This value is much higher than the partial pressure of organic acids found in the troposphere. Previous studies have shown that γ_o can vary significantly with pressure (Underwood et al., 2000). Thus, the γ_o values for the C₁ to C₄ organic acids on SWy-2 were measured as a function of organic acid pressure from 6×10^{-6} to 1×10^{-4} Torr at 212 K and 0% RH. The initial uptake efficiency was determined using Eq. (1). Figure 6 shows γ_o obtained from mass spectrometer data for organic acid uptake on approximately 1.5 mg SWy-2 at 212 K and 0% RH as a function of organic acid pressure. Error in the data represents deviation from multiple experiments performed under similar conditions. The horizontal lines represent the average γ_o obtained over the range of pressures studied. Similar to a previous study of acetic acid on α -Fe₂O₃ (Carlos-Cuellar et al., 2003), we find γ_o to be independent of organic acid pressure for all of the acids studied. Therefore, gas phase adsorption of organic acids is a first-order process within the range of pressures studied. The average γ_o for heterogeneous uptake of formic, acetic, propionic and n-butyric acids on approximately 1.5 mg SWy-2 at 212 K and 0% RH are $1.7(\pm 0.9) \times 10^{-5}$, $1.3(\pm 0.5) \times 10^{-5}$, $5.4(\pm 1.5) \times 10^{-5}$ and $2.2(\pm 0.8) \times 10^{-5}$, respectively. These values are also reported in Table 2.

Organic acid coverage on SWy-2 is determined from the mass spectrometer data as described previously and corrected for blank experiments performed under the same conditions. Figure 7 shows the steady-state coverage of formic, acetic, propionic and n-butyric acids on 1.5 mg SWy-2 at 212 K and 0% RH as a function of organic acid pressure. We find that the amount of adsorbed organic acid increases with acid pressure. Sub-monolayer coverages of formic, acetic and propionic acids are found to increase linearly with organic acid pressure, never reaching saturation within the range of pressures studied. However, n-butyric acid appears to saturate at approximately one monolayer for pressures greater than 2×10^{-5} Torr. Thus, under dry conditions, sub-monolayer coverage of organic acid is expected at relevant vapor pressures on

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atmospheric mineral aerosol surfaces.

3.2.4 Uptake as a function of relative humidity

Previous studies have shown that the C₁ to C₆ carboxylic acids favor the particle phase under humid conditions based on the Henry's law constant for these acids in water (Khan et al., 1995). Thus, under humid conditions, it is probable that swelling clay minerals may be a significant sink for organic acids. The heterogeneous uptake of the C₁ to C₄ organic acids on 1.5 mg SWy-2 samples was measured as a function of RH from 0% to 45%, at 212 K and approximately 1 × 10⁻⁴ Torr organic acid, 1 × 10⁻⁵ Torr for n-butyric acid. The measured γ_o values are summarized in Table 2 and shown graphically in Fig. 8a. At 0% RH, γ_o is independent of pressure and thus the average values obtained from the pressure study are reported here. The γ_o values at 29% RH represent γ_o^{avg} determined from the mass study. Assuming that the organic acids have access to the entire sample mass over the range of humidities studied, γ_o at 45% RH was also determined. Figure 8a shows that γ_o does not appear to vary significantly at RH values less than 29%. However, we find that the initial uptake efficiency of n-butyric acid increases by nearly an order of magnitude as the RH was raised from 0% to 45%. This may be due to enhanced acid dissociation on the clay surface under humid conditions, as suggested by infrared analysis. However, the uptake of formic, acetic and propionic acids increase only slightly with increasing RH. Thus, adsorbed water appears to influence the uptake of some organic acids more so than others, particularly near 45% RH. Higher humidities may result in even larger uptake. This represents the first report of the γ_o for small organic acids on smectite clay under tropospherically relevant humidities and temperatures.

Organic acid uptake was found to vary with the type of organic acid studied. Under all conditions, formic acid was found to have the lowest reactivity with the SWy-2 surface. To help understand these results, Table 3 shows the number of carbon atoms, molecular weight, boiling point and enthalpy of vaporization for each acid studied (Lide, 2004). Additionally, the γ_o values at 45% RH are also shown in Table 3. The γ_o ap-

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pears to follow general trends in molecular weight, boiling point, vapor pressure and the number of carbon atoms in the hydrocarbon chain; all of which influence the initial interaction between the clay surface and gas phase organic acid.

Previous studies of nitric acid uptake on SWy-2 clay as a function of RH found that the γ_o was not measurable below 16% RH (Mashburn et al., 2006). However, above 16% RH, the γ_o for nitric acid uptake on SWy-2 at 221 K increased dramatically with RH. In contrast to nitric acid uptake, measurable uptake was reported here for all of the organic acids at 0% RH. We find that the behavior of n-butyric acid with increasing RH is very similar to that observed for nitric acid uptake on the same clay. However, under humid conditions, the γ_o from organic acid uptake is smaller by a factor of two to an order of magnitude from the values observed for nitric acid. Thus, organic acid uptake on smectite clays is less efficient than nitric acid uptake under humid conditions.

The organic acid content at saturation was also determined as a function of RH at 212 K and approximately 1×10^{-4} Torr organic acid, 1×10^{-5} Torr for n-butyric acid. Figure 8b shows the organic acid content, $\text{mg}_{\text{org}}/\text{g}_{\text{clay}}$, of formic, acetic, propionic and n-butyric acids on approximately 1.5 mg SWy-2 samples at 212 K as a function of RH. It can be seen that, as the RH is increased, the organic acid content increases significantly for all organic acids studied. The propionic acid shows the largest increase in adsorbed mass with RH, increasing by a factor of five from 0.3% to almost 2% propionic acid by mass from 0% to 45% RH. Thus, while the uptake kinetics are not significantly increased, the equilibrium organic acid content does increase with increasing water vapor.

4 Discussion

Although no direct comparison of the data reported here can be made to previous studies due to different adsorbates, some statements can be made comparing uptake on other minerals found in the troposphere. Similar to findings from previous studies of formic and acetic acids on carbonate and other mineral oxides (Al-Hosney et al., 2005;

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Carlos-Cuellar et al., 2003), our results suggest that the organic acids dissociate on the montmorillonite clay under humid conditions. However, differences are apparent in the measured uptake efficiencies. One previous study investigated the heterogeneous uptake of acetic acid on a series of minerals under dry conditions at room temperature (Carlos-Cuellar et al., 2003). That study found irreversible uptake of acetic acid and reported γ_o values of 2×10^{-3} , 2×10^{-3} and 2×10^{-4} for α -Fe₂O₃, α -Al₂O₃ and SiO₂, respectively, at 6×10^{-6} Torr. These values are one to two orders of magnitude larger than the γ_o for acetic acid on SWy-2, $\gamma_o = 1 \times 10^{-5}$, reported here under dry conditions. The pressure-independent uptake measurements indicate that this difference is not due to the different pressures used in each study. Additionally, independent measurements of acetic acid uptake on SWy-2 at room temperature and dry conditions give a γ_o of 3×10^{-6} ; a factor of four lower than the value obtained at 212 K. Thus, temperature dependence is not responsible for the difference in measured uptake efficiencies. We conclude that the discrepancy in measured uptake efficiencies is a result of the different reactivity of the substrates studied. This result suggests that mineralogy of the reactive surface strongly influences the heterogeneous uptake of organic acids on mineral aerosol in the troposphere and should be considered in atmospheric models.

Previous studies have also reported the surface coverage for acetic acid on α -Al₂O₃ and SiO₂ to be approximately 8×10^{13} and 7×10^{11} molec/cm², respectively (Carlos-Cuellar et al., 2003). Based on our results shown in Fig. 7b, we estimate the steady-state coverage of acetic acid on SWy-2 at 6×10^{-6} Torr to be near 4×10^{12} molec/cm²; on the same order as adsorbed acetic acid observed on other minerals at room temperature.

5 Atmospheric implications

The heterogeneous removal of organic acids from the atmosphere by uptake onto mineral aerosol will only be competitive if this mechanism counters or exceeds other dominant removal processes (Ravishankara, 1997). The dominant removal process of many

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carboxylic acids is through wet and dry deposition. Considering the initial uptake efficiencies for formic, acetic, propionic and n-butyric acids on SWy-2 at 212 K and a mineral aerosol loading of $150 \mu\text{m}^2/\text{cm}^3$ (de Reus et al., 2000), typical of a dust storm, the lifetime, τ (s), for removal by mineral aerosol in the kinetic limit, assuming the dust plume is entirely composed of montmorillonite, is determined as follows:

$$\tau = \frac{4}{\gamma_o \langle v \rangle SA} \quad (4)$$

where $\langle v \rangle$ (cm/s) is the average velocity of the organic molecule and SA (cm^2/cm^3) is the surface area density of the dust event. We estimate the atmospheric lifetime of these organic acids resulting from heterogeneous removal on swelling clay minerals at 29% RH to be longer than one month at upper tropospheric temperatures. At 45% RH, the atmospheric lifetimes for removal of formic, acetic and propionic acid are reduced to two weeks, while n-butyric acid may be removed within six days. However, the true lifetime for removal is likely to be shorter because the estimated mineral aerosol surface area is based on the diameter of smooth atmospheric mineral spheres.

To account for the differences between the surface area we used to obtain the initial uptake efficiency and the surface area reported in field studies, we convert our uptake efficiencies to a value based on the SA_{sphere} . Assuming spherical clay particles with a particle diameter of $2 \mu\text{m}$, the SA_{sphere} is estimated using the clay mass and a density of 2.2 g/cm^3 . As shown in Table 3, using SA_{sphere} , we estimate the initial uptake efficiencies, γ_o^{sphere} , for organic acid uptake on SWy-2 to be 4.0×10^{-4} , 3.0×10^{-4} , 1.3×10^{-3} and 5.1×10^{-4} for formic, acetic, propionic and n-butyric acids, respectively, at 0% RH and 212 K. Estimated values of γ_o^{sphere} at 45% RH and 212 K are also shown in Table 3. These values are probably more relevant for use in atmospheric models where spherical particles are often assumed. Using the same method as described above, the lifetime of the organic acids due to heterogeneous removal by mineral aerosol can be obtained using the calculated γ_o^{sphere} values. We find that atmospheric removal of all the organic acids studied is reduced to less than four days at 0% RH and loss is faster

as the RH is raised. Additionally, assuming an organic acid concentration of 1 ppbv at 5 km altitude, monolayer coatings of organic acids on mineral aerosol would be expected in less than two hours. Thus, based on these values, heterogeneous uptake of organic acids on mineral aerosol may be a significant removal mechanism for carboxylic acids in troposphere. Additionally, we find that the presence of the organic acid appears to enhance the water content at RH values greater than 45% RH compared to when the organic acid is not present (Frinak et al., 2005). Thus organic acid adsorption to smectite clays can modify the cloud forming potential and optical properties of these minerals in the troposphere.

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Peak Position (cm ⁻¹)	Assignment
~1620	Dissociated carbonyl species ^{a,b}
1350–1475	Deformations of CH ₃ groups ^a
3624	Structural OH stretch ^c
3350	OH stretch ^c
1640	HOH bend ^c

^a from Grassian (2001)^b from Max et al. (2004) and Kubicki et al. (1999)^c from Bishop et al. (1994)

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Table 2. The initial uptake efficiencies for uptake of formic, acetic, propionic and n-butyric acids on SWy-2 at 212 K as a function of RH from 0% to 45% RH.

Organic	0% RH	29% RH	45% RH
Formic acid	1.7×10^{-5}	1.7×10^{-5}	2.3×10^{-5}
Acetic acid	1.3×10^{-5}	2.0×10^{-5}	6.0×10^{-5}
Propionic acid	5.4×10^{-5}	3.2×10^{-5}	6.2×10^{-5}
n-Butyric acid	2.2×10^{-5}	4.0×10^{-5}	2.2×10^{-4}

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Table 3. Properties of the C₁ to C₄ carboxylic acids, including number of carbon atoms, molecular weight, boiling point and enthalpy of vaporization compared to the heterogeneous initial uptake efficiency for the organic acids on SWy-2 at 212 K.

Organic Acid	# of C atoms	M _w (g/mol)	BP* (K)	ΔH _{vap} * (kJ/mol)	γ _o at 45% RH	γ _o ^{sphere} at 0% RH	γ _o ^{sphere} at 45% RH
Formic	1	46	374	20	2.3x10 ⁻⁵	4.0x10 ⁻⁴	5.4x10 ⁻⁴
Acetic	2	60	391	23	6.0x10 ⁻⁵	3.0x10 ⁻⁴	1.4x10 ⁻³
Propionic	3	74	414	32	6.2x10 ⁻⁵	1.3x10 ⁻³	1.5x10 ⁻³
n-Butyric	4	88	437	41	2.2x10 ⁻⁴	5.1x10 ⁻³	5.1x10 ⁻³

* Handbook of Chemistry and Physics, 73rd Ed. (Lide, 2004)

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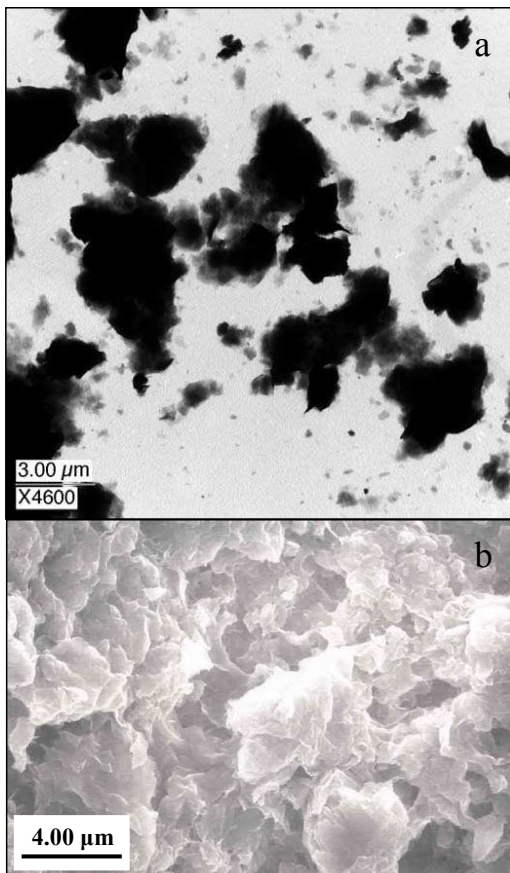


Fig. 1. (a) TEM and **(b)** SEM images of SWy-2 particles.

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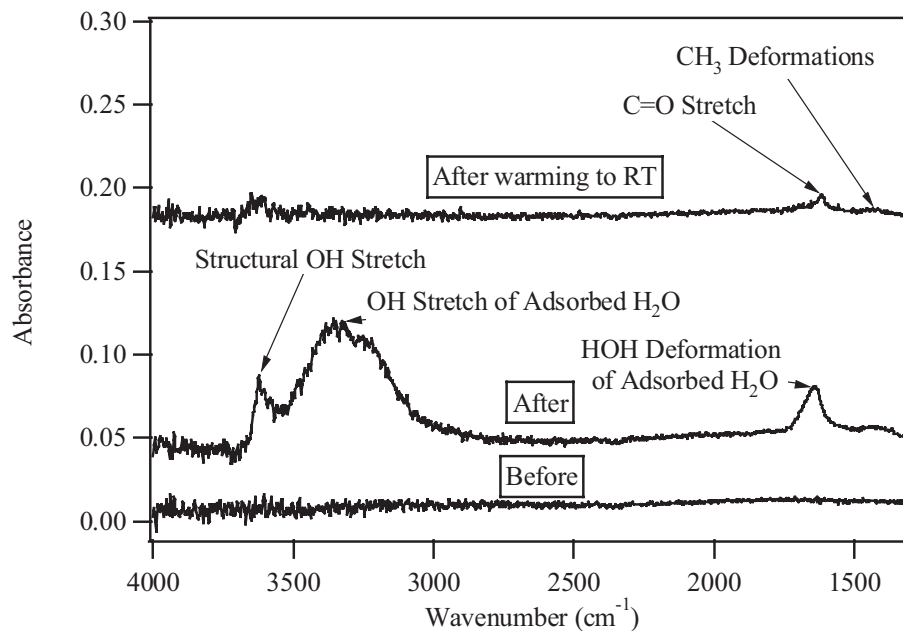


Fig. 2. FT-IR spectra collected (a) before and (b) after exposure of a 1.2 mg SWy-2 sample to 1×10^{-4} Torr acetic acid at 212 K and 29% RH. (c) Also shown is the infrared spectrum collected after warming the sample to room temperature to drive off adsorbed water. All spectra are ratioed to a background spectrum of the clay collected prior to exposure at the same temperature.

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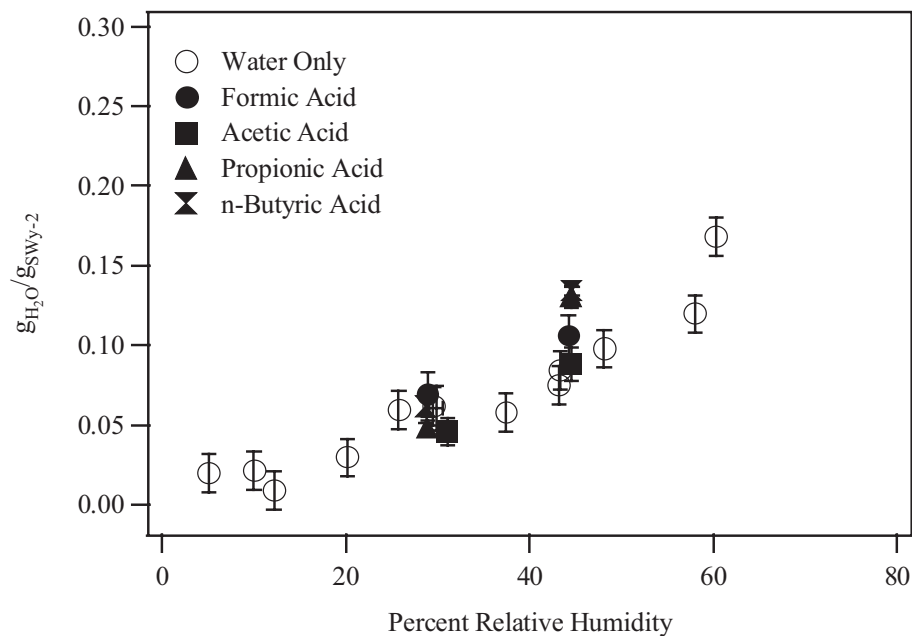


Fig. 3. Steady-state water content of SWy-2 as a function of relative humidity. The open circles represent water only experiments performed at 222 K (Frinak et al., 2005) and the closed symbols represent the water content adsorbed on SWy-2 at 212 K in the presence of the organic acids.

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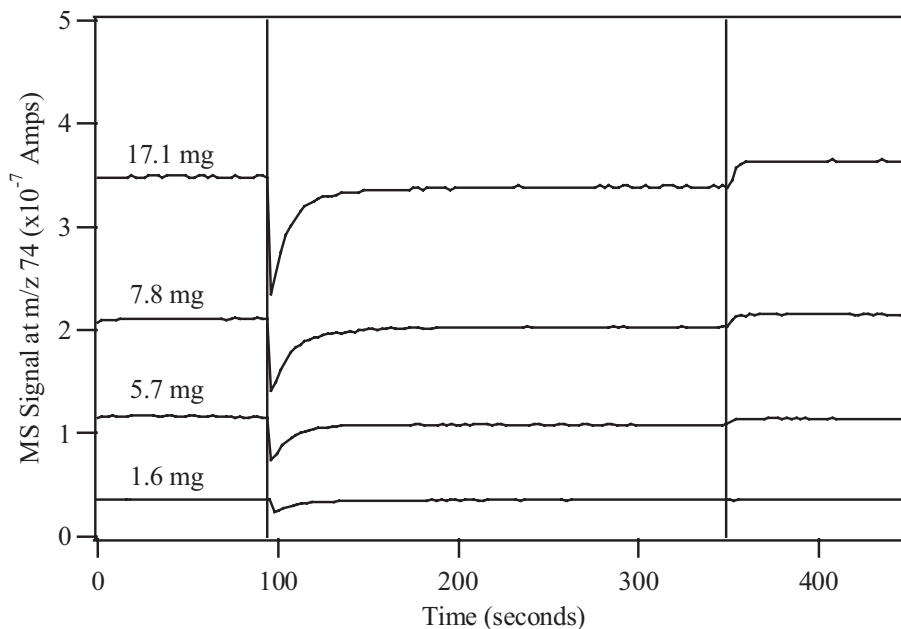


Fig. 4. Raw uptake curves of propionic acid on 1.6, 5.7, 7.8 and 17.1 mg SWy-2 samples at 212 K, 29% RH and approximately 1×10^{-4} Torr propionic acid. The vertical lines represent the time SWy-2 was exposed to the gas phase. The traces are offset for clarity.

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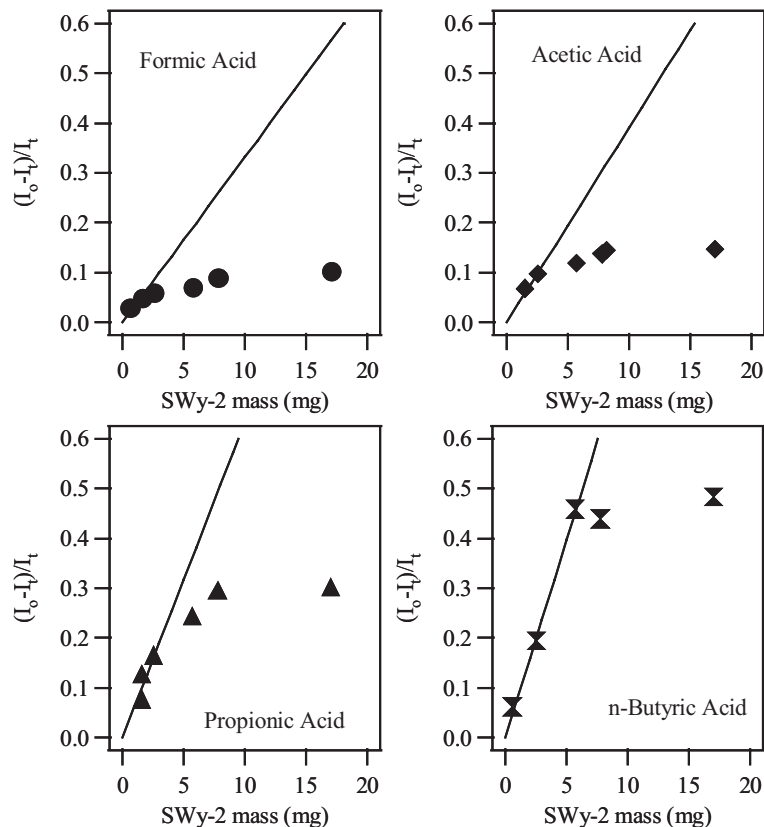


Fig. 5. $(I_o - I_t)/I_t$ obtained from organic acid uptake measurements at 212 K and 29% RH as a function of SWy-2 mass. Formic, acetic and propionic acid uptake experiments shown here were performed in the presence of approximately 1×10^{-4} Torr acid while n-butyric acid uptake measurements were performed in the presence of approximately 1×10^{-5} Torr n-butyric acid.

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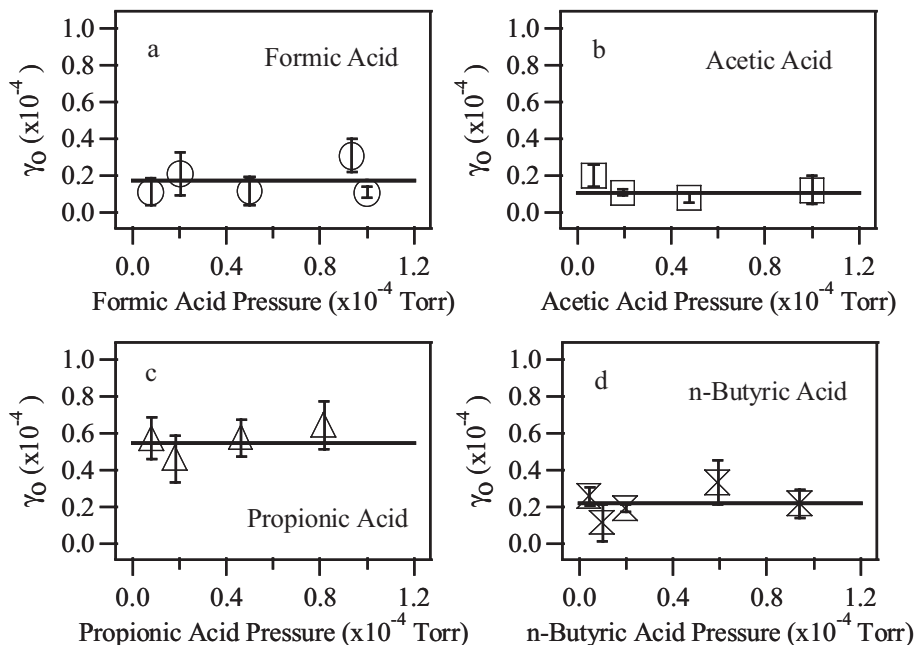


Fig. 6. Initial uptake efficiencies for **(a)** formic, **(b)** acetic, **(c)** propionic and **(d)** n-butyric acid uptake on approximately 1.5 mg SWy-2 at 212 K and 0% RH as a function of organic acid pressure. The horizontal lines represent the averaged γ_0 value obtained over the range of partial pressures studied.

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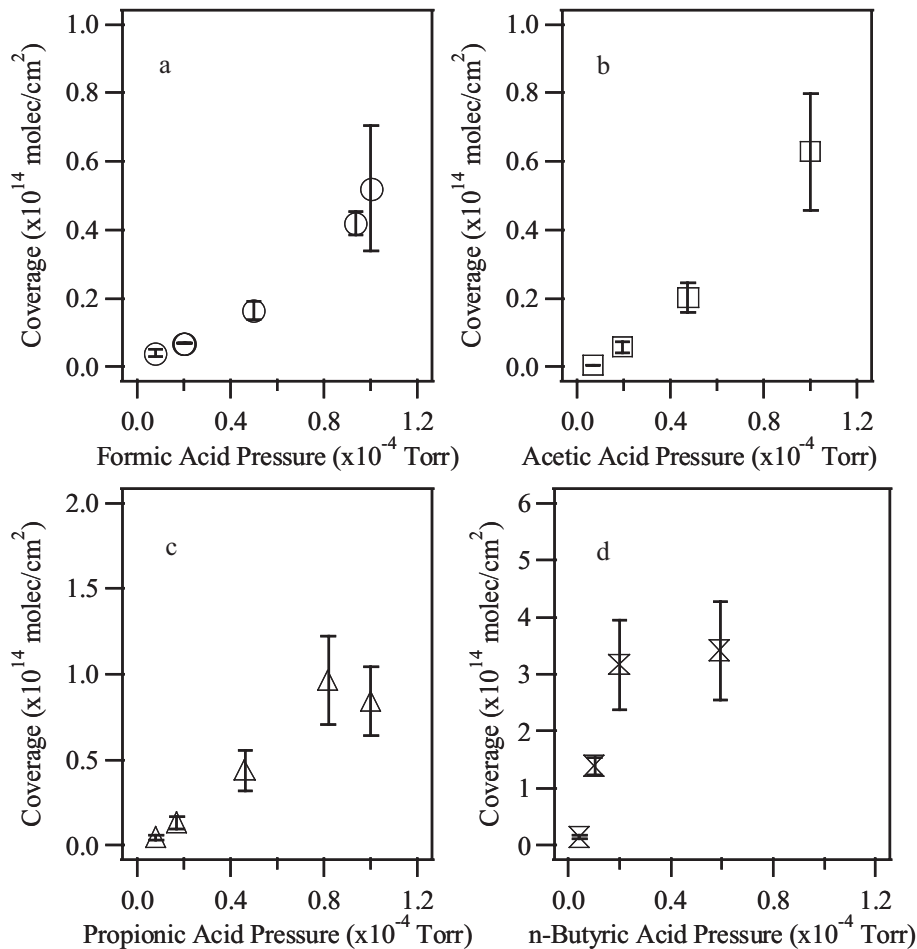


Fig. 7. The steady state coverage of (a) formic, (b) acetic, (c) propionic and (d) n-butyric acids on 1.5 mg SWy-2 at 212 K and 0% RH as a function of organic acid pressure.

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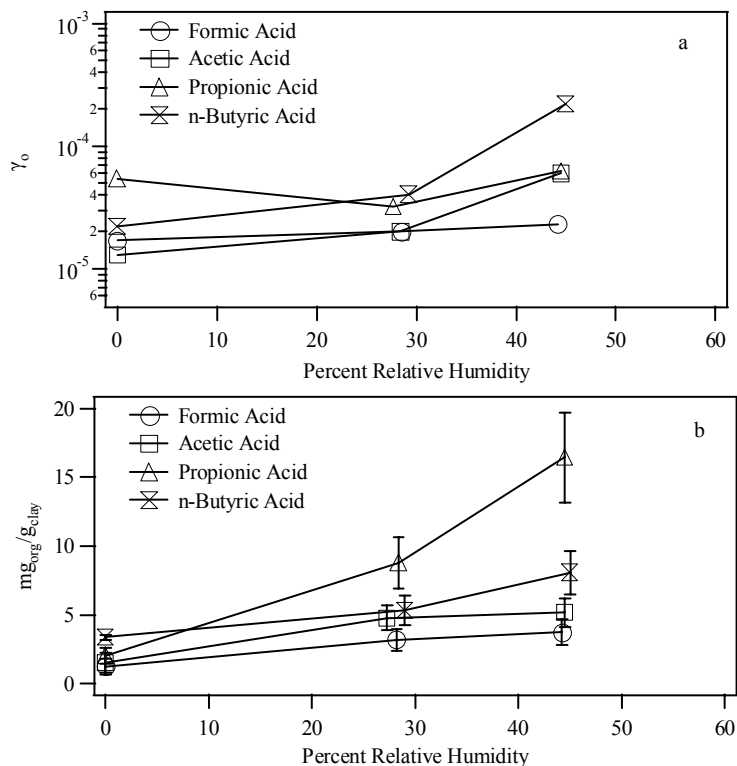


Fig. 8. (a) The initial uptake efficiencies on a log scale for the uptake of formic, acetic, propionic and n-butyric acids on approximately 1.5 mg SWy-2 at 1×10^{-4} Torr organic acid pressure, 1×10^{-5} Torr n-butyric acid and 212 K as a function of RH. (b) The organic acid content, $\text{mg}_{\text{org}}/\text{g}_{\text{clay}}$, of adsorbed formic, acetic, propionic and n-butyric acids on approximately 1.5 mg SWy-2 at 212 K as a function of RH. Lines are drawn to guide the eye.

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