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The Influence of Organic Films at the Air−Aqueous Boundary on Atmospheric Processes

D. J. Donaldson*,† and Veronica Vaida*,‡

Department of Chemistry and Department of Physical and Environmental Sciences-UTSC, University of Toronto, Toronto, Ontario M5S 3H6, Canada, and Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder, Colorado 80309-0215

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1. Introduction

Over the temperature and pressure ranges found on Earth and in its atmosphere, water in its different phases plays an important role in determining the climate and significantly contributes to the chemistry of the planet. The temperatures and pressures characteristic of the Earth's atmosphere sample the region around the triple point ($P = 0.006$ atm, $T = 273.16$ K) on the water phase diagram providing a mechanism for fine-tuning of phase transitions and associated latent heat effects.[1,2] Oceans cover a substantial area of the planet; consequently water vapor, aerosols, liquid water, and ice partition between the surface and the atmosphere according to geophysical conditions. Of particular interest in this review are water−air interfaces (e.g., the sea surface and aqueous atmospheric aerosols), which provide interesting and unique reaction environments in any planetary atmosphere, including the present and prebiotic Earth. In organic monolayers at the surfaces of bodies of water, amphiphilic molecules are exposed both to an aqueous phase containing dissolved inorganic chemical species and polar organic molecules and to the atmosphere containing reactive radicals and solar

James Donaldson attended Carleton University, where he obtained a B.Sc. in 1979 and Ph.D. in 1984. Following postdoctoral work at JILA (as an NSERC Postdoctoral Fellow) and in the Chemistry Department of the University of Colorado, he joined the University of Toronto in 1988 as an NSERC University Research Fellow. He is now a Professor of Chemistry at the University of Toronto.

Veronica Vaida obtained her undergraduate training at the University of Bucharest, Romania, and at Brown University, receiving a B.S. from Brown in 1973. She received an M.S. and a Ph.D. degree (1977) from Yale University and was then a Xerox postdoctoral fellow at Harvard University. Her independent career started at Harvard, where she was an assistant then associate professor from 1979 to 1984, at which time she moved to the University of Colorado, Boulder, where she is now Professor of Chemistry. She has held an appointment on the faculty in the Program in Atmospheric and Oceanographic Sciences since 1992, and has been a Fellow of the Cooperative Institute for Research in Environmental Sciences since 2000.

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* E-mail addresses: jdonalds@chem.utoronto.ca; vaida@colorado.edu.
† University of Toronto.
‡ University of Colorado.

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radiation. Chemical reactions within organic layers and at interfaces between organic films and an aqueous phase or the atmosphere often exhibit different reactivity than organics in bulk solution or the bulk phase.

Aqueous−air interfaces are found in the Earth's atmosphere at the boundaries of oceans, lakes, and atmospheric aerosols. The latter form an important class of atmospheric interface due to their extremely large surface/volume ratios. Aerosols are small (approximately micrometer diameter) solid or liquid suspensions in air, globally distributed in the atmosphere of Earth. Any rotating planet will be heated differentially by the Sun, giving rise to winds. Wind action on the surface of a liquid ocean, sea, or lake generates bubbles, which upon breaking form sea spray.[3,4] Some of the drops thus formed become airborne aerosols. Atmospheric particles are also formed over continents in urban and rural environments. Particularly important continental sources of aerosols are fires and urban pollution.

Aerosols have important roles to play in determining the temperature and therefore the climate of a planet and in promoting heterogeneous chemistry.[5,6] The properties of atmospheric aerosols relevant to climate and chemistry are highly nonlinear. Their size and number density are strongly dependent on small temperature fluctuations in the atmosphere of a planet. Attempts to model the effects of atmospheric aerosols in climate have so far been very limited, with uncomfortably large uncertainties in the magnitude and sign of aerosol effects.[7]

To complicate this already difficult problem, atmospheric measurements are finding that aerosols have a large organic content.[8−22] To the extent that molecular speciation of collected aerosols is possible, surface active amphiphilic organics (alcohols, acids, amines, etc.) are found to be important contributors to the organic mass found on atmospheric aerosols. In a 1983 review, Gill, Graedel, and Weschler[23] discussed the formation and potential consequences of organic films on atmospheric particles. Over a decade later, Ellison et al.[24] reexamined the effects of organic films on atmospheric aerosols and pointed out that atmospheric "processing" of the film compounds by atmospheric oxidants would alter the surface properties of the particle and thus perhaps its reactivity. The idea is illustrated in Figure 1. These seminal papers have motivated considerable and increasing research effort in recent years. The present review aims to point to the current state of knowledge as we embark on more sensitive and sophisticated field and laboratory work.

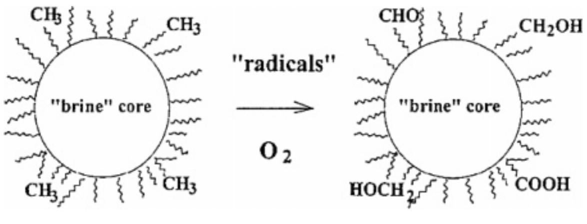


Figure 1. Heterogeneous oxidative processing of atmospheric aerosols with an organic coating. Reactions of species at the air−water interface with gas-phase oxidants may alter the film properties and may give rise to different gas-phase and aqueous products than the corresponding homogeneous (gas- or aqueous-phase) processes. Reproduced by permission of American Geophysical Union from ref 24. Copyright 1999 American Geophysical Union.

The review is organized as follows. We start with a brief overview of the physicochemical nature of surface films, with particular emphasis on newer results of relevance to atmospheric processes. This is followed by a discussion of the evidence available from field measurements for the occurrence of such films in the real atmosphere. Next, the physical and chemical effects arising from the presence of such films are described, with most attention paid to atmospherically relevant processes. This is followed by a section that presents some novel ideas about how organic-coated aerosols might have played some role in prebiotic biochemistry. We end with a short summary and suggestions for where future work might be directed.

There is a vast body of literature concerning organic films and organic partitioning to the aqueous−air interface, spanning a century. We have specifically chosen to limit this review to work and results that have some reasonably direct relevance to atmospheric processes. Even culling the literature to that extent leads to an enormous body of knowledge; we have restricted this review further to (fairly) recent results to maintain some degree of focus. Excellent coverage of spectroscopic probes of the air−water interface is given in several recent reviews,[25−27] as well as in the present issue. Benjamin[28] gives a thorough review of the important features of reaction dynamics at this interface from a computational viewpoint. Other papers in this issue cover atmospheric aspects of interfacial chemistry. A recent review by Rudich[29] deals especially with chemistry involving organic aerosol particles. Interested readers are directed to these sources for more information. We apologize in advance to all those authors whose work we have not mentioned here.

2. The Nature of the Coated Interface

2.1. General Principles

There is an extensive body of literature and many textbooks that deal with the adsorption of organic compounds at the air−water interface (e.g., refs 30−32). This review will concentrate on some more recent concepts and studies of particular relevance to atmospheric heterogeneous processes. The presence of such films could give rise to very different surface properties and heterogeneous reactivity; hence, it is important to understand what such films might "look like" to potential atmospheric reagents.

The strong hydrogen bonds associated with water give rise to a very high surface energy at the liquid−air interface. This quantity, which is measured as the surface tension, expresses the work required for a unit increase in the interfacial area (at constant volume and temperature). The high surface energy may be reduced if surface-active species are present at the interface; this occurs spontaneously if the decrease in surface energy is sufficient to overcome the loss of full solvation by the surfactant species. Amphiphilic compounds, such as long-chain carboxylic acids and phospholipids, are good examples of this principle, since the hydrophilic headgroups may be well solvated by surfacial water molecules, whereas the hydrophobic tails point into the air phase. However, even quite soluble compounds such as DMSO or ethanol can be surface active; that is, may spontaneously partition to the air−water boundary in a proportion greater than that present in the bulk aqueous phase.

As we shall discuss in section 4, there are a large number of organic compounds that have been identified in atmospheric particulate matter—water-soluble and insoluble, volatile and nonvolatile, biogenic and anthropogenic. Most attention has been paid to two different situations: the properties of (relatively) insoluble, nonvolatile films of biogenic amphiphiles (such as fatty acids and phospholipids) and the uptake of volatile, soluble species by aqueous surfaces (also discussed elsewhere in this issue).

2.2. Insoluble Surfactant Films

Insoluble (nonvolatile) surfactants exist exclusively at the interface, and the film properties may be expressed in terms of a film equation of state. The equation of state of a 2-D (insoluble) film on a liquid surface, such as a film formed by a long chain fatty acid, is generally expressed using variables of state π, the surface pressure (given by the difference in surface tension between the pure liquid substrate and that of the film), and A, the surface area occupied per adsorbed molecule. These are used as direct analogies to gas-phase variables p and V_m. $\pi-A$ isotherms may be measured,[32] which describe the film behavior; as with gases, they are approximated using various assumptions regarding interadsorbate interactions. For long-chain acids and similar compounds, a van der Waals-type equation is often appropriate:

$$(\pi - \pi_c)(A - A_0) = k_B T \qquad (1)$$

Here, π_c represents the "cohesion pressure", a measure of attractive interadsorbate forces, A_0 represents the minimum area occupied by a single adsorbate molecule, and k_B is the Boltzmann constant.

Figure 2 illustrates a $\pi-A$ isotherm for stearic acid, which at low surface pressures is well approximated using the van der Waals model. These sorts of data are generally obtained by measurements of the surface tension of the coated interface as its surface area is decreased.[32] Water-insoluble films are introduced to the interface by applying a small volume of an organic solution of the surfactant (generally in hexanes or methanol) onto the aqueous surface and allowing the organic solvent to evaporate. The isotherm displayed in Figure 2 shows several "kinks", noted by the arrows in the figure, corresponding to 2-D phase transitions (gas, expanded liquid, compressed liquid, solid) taking place in the film. On a molecular scale, these phase transitions correspond to differing degrees of ordering of the surfactant molecules on the surface: gas phase molecules are widely dispersed and noninteracting (as shown by the independence of π on the area occupied per molecule); with increasing compression, interadsorbate interactions govern the isotherm. For long-chain amphiphiles such as stearic acid, the final stage of compression gives a "solid" phase, in which the hydrocarbon tails are all aligned, pointing out of the aqueous phase, and the hydrophilic headgroups are close packed. The relationship between the observed two-dimensional phase behavior and interadsorbate interactions has been elucidated spectroscopically.[33−36]

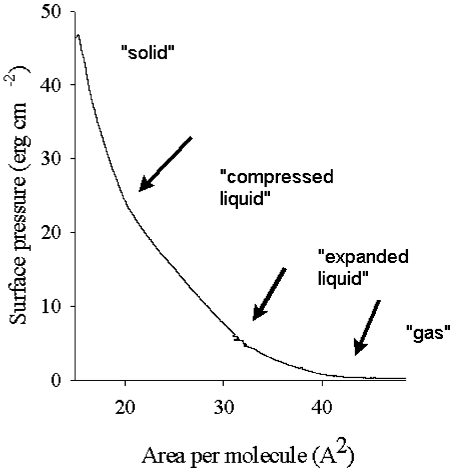


Figure 2. A typical $\pi-A$ isotherm for long-chain fatty acids, in this case, stearic acid. The arrows indicate "kinks" in the isotherm due to phase transitions; the two-dimensional phases are labeled. Adapted from Donaldson et al.[320] Reproduced by permission of the PCCP Owner Societies.

Many relevant properties of such interfacial films have been studied, with particular attention being given to the effect of the carbon chain lengths, the nature of the polar headgroup, the pH of the subphase, and temperature.[37−44] The acidity of amphiphilic adsorbates has been shown to be significantly different from the bulk-phase value.[45] It is seen that more soluble organic surfactant species appear to form less compact films that do not undergo the phase transitions to compact structures characteristic of long-chain molecules.[39] Recent reports from the Eisenthal group show that aqueous solvation at the interface depends on the charge of the surfactant.[46,47] The polarity of the interface[48] influences its ability to solvate hydrophobic[48−50]and hydrophilic[51] species there. Elegant surface spectroscopic studies of the vibrational spectra of molecules at the liquid−air interface of aqueous solutions have been used to probe not only partitioning to the surface but also the orientation of organics at the interface.[52−55] These studies confirm that the surfactant compounds are oriented with the alkyl tails away from the aqueous subphase.

2.3. Soluble Surfactants

In studies of soluble surfactants, it is generally the surface excess, rather than the surface concentration, of adsorbate that is measured. This quantity is defined as the adsorption to the surface of component i relative to that undergone by the solvent, water in this case. It may be shown[56] that the relative surface coverage may be given by the Gibbs equation:

$$\Gamma_i = (\mathrm{d}\sigma/\mathrm{d}\mu_i)_T \qquad (2)$$

which relates the relative surface excess to the dependence of surface tension (σ) on the bulk activity of solute i (a_i) through the chemical potential:

$$\mu_i = \mu_i^0 + RT \ln(a_i) \qquad (3)$$

Often, activity coefficients are ignored, and solute concentration is used in place of activity. The surface tension as a function of solute activity is fitted to a convenient functional form (arbitrary, but preferably with as few parameters as possible), and the derivative of this function is used to determine $\Gamma_i(a_i)$ via eq 2. By fitting Γ to a model for surface adsorption, adsorption isotherms may be obtained.[32] It should be remembered that this procedure gives the surface excess, which is not necessarily identical to the true surface concentration.

For soluble surfactants, the concentration (or activity) dependence of the surface excess at solute concentrations below phase separation has generally been described by a Langmuir adsorption isotherm:[32]

$$\Gamma_i = \Gamma_i^{\max}[i]/(B + [i]) \qquad (4)$$

where $\Gamma_i^{\max}$ gives the saturated surface excess (or coverage) and B represents a ratio of rate coefficients for adsorption and desorption from the surface.[57] In the case of an insoluble gas-phase adsorbate or a nonvolatile solution-phase adsorbate, B reduces to the equilibrium constant for adsorption from the bulk phase.[32] This type of adsorption behavior implies that there exists a finite number of independent adsorption sites at the water surface, with a single enthalpy of adsorption, independent of surface coverage. Figure 3 displays sample data for butanoic acid solutions.[58]

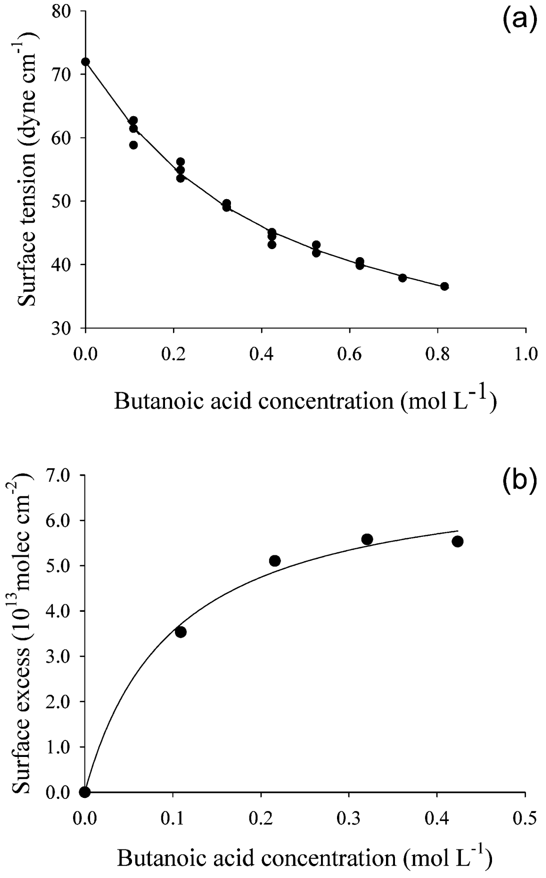


Figure 3. (a) Surface tension vs solution concentration of butanoic acid at room temperature. The solid line shows a fit to the data using an arbitrary polynomial function. (b) The surface excess of butanoic acid vs its solution concentration, calculated from the surface tension data given in panel a. Both images taken from Donaldson and Anderson[58] with permission. Copyright 1999 American Chemical Society.

True surface *concentrations* may, in principle, be obtained through spectroscopic measurements. Adsorption isotherms have been measured using surface second harmonic generation (SHG),[26,59−61] sum-frequency generation (SFG),[27,53,55,62] and fluorescence[49,63] techniques. It is very difficult, however, to relate such measurements to absolute surface concentrations. Consequently, such spectroscopically obtained isotherms are often normalized against surface-excess-derived isotherms.[59] Often, but not always, the two methods give thermochemical results in reasonably good agreement, such as that reported for DMSO solutions.[59,60] Interestingly, such good agreement is not always obtained in the same system using different spectroscopic techniques.[60,62] This is most likely due to different sensitivities toward surface interactions among adsorbates offered by the different nonlinear surface spectroscopic techniques.

The work discussed above is primarily concerned with nonvolatile adsorbates. There is only a fairly small body of literature on studies of gas adsorption onto water surfaces, much of which has described the adsorption behavior of vapors of organic liquids onto water. The idea that soluble gases could adsorb onto a water−air interface, reducing the surface tension, was advanced in 1928 by O. K. Rice,[64] who measured the surface tension vs concentration for solutions of ammonia. This idea received little attention until fairly recently.[13,57,59,65−97] The propensity for an organic (or any other) compound to adsorb at the air−aqueous interface is indicated by a negative free energy of transfer of the compound from a bulk phase (either atmosphere or solution) to the surface. Thermochemical measurements relating to this transfer are most often determined at equilibrium, yielding a standard free energy of adsorption, $\Delta G°$. Almost always, this quantity has been determined by measurements of an equilibrium constant for the partitioning of the compound of interest to the interface, measured chromatographically[13,79] or via an adsorption isotherm determined using the concentration dependence of the solution surface tension in conjunction with the Gibbs equation,[32] using eqs 2 and 4.

Atmospheric gases that adsorb at the air−water interface are generally also soluble in aqueous solution. Donaldson[57] treated the general case of the adsorption thermodynamics of volatile, soluble species onto the water surface. He showed that the free energy for transferring 1 mol of species i from bulk phase X (either gas or solution) to the surface, the molar free energy of adsorption, is given by

$$\Delta G_{\mathrm{X}-\sigma} = \mu_i^{\sigma} - \mu_i^{\mathrm{X}} = (\mu_i^{\circ,\sigma} - \mu_i^{\circ,\mathrm{X}}) + RT \ln[(\gamma^{\sigma}\pi/\pi^{\circ})/(a_{\mathrm{X}}/a^{\circ,\mathrm{X}})]$$

where the μ represent the chemical potentials, $a°$ gives the standard activity (1 mol kg^{-1} in solution; 1 atm in the gas phase), the solution- and gas-phase activities are $a_i = \gamma_i m_i$ and $a_i = \gamma_i p_i$, respectively, where the γ_i are concentration-dependent activity coefficients, and π represents the film pressure, defined above. The standard state of the adsorbed species was taken to be that proposed by Kemball and Rideal: a film with the same number density as would be present in an ideal gas at 1 atm in a container of thickness 6 Å. In terms of film pressure, this choice of standard state gives $\pi° = 0.060\,84$ dyn cm^{-1}. Other recent works have chosen different standard states.[96,98,99] The choice of standard states is arbitrary but will affect the numerical values of any thermochemical parameters derived from equilibrium measurements.

At phase equilibrium, $\Delta G_{\mathrm{X}-\sigma} = 0$, so $\Delta G^{\circ}_{\mathrm{X}-\sigma} = -RT \ln[(\gamma^{\sigma}\pi/\pi^{\circ})/(a_{\mathrm{X}}/a^{\circ,\mathrm{X}})]_{\mathrm{eq}}$. By plotting the quantity $-RT \ln[(\gamma^{\sigma}\pi/\pi^{\circ})/(a_{\mathrm{X}}/a^{\circ,\mathrm{X}})]$ against the activity of the bulk phase and extrapolating to zero bulk phase concentration, one could obtain "ideal gas" surface adsorption standard free energies. Several organic surface-active solutes were treated this way at several temperatures, yielding values of $\Delta G°$, $\Delta H°$, and $\Delta S°$ for adsorption to the air−water interface.[57,58,71,83] The standard enthalpies of adsorption thus obtained were proportional to the standard enthalpies of solvation, which the authors took as support for the "surface solvation" model of Davidovits and co-workers.[100,101] A dependence of $\Delta G^{\circ}_{\mathrm{X}-\sigma}$ on bulk phase concentration was noted, indicating that the activity coefficients were not constant with concentration.

The issues of surface standard states and activity coefficients for species adsorbed on water surfaces have been raised in only a handful of other studies to date.[99,102,103] The choice of standard state will influence the importance and magnitude of the activity coefficients, which quantify the departure from the "ideal" mixture, expressed in the dimensions of the standard state. Common choices (either explicit or implicit) for the surface standard state are (in addition to that given above) the "unit concentration" standard state, 1 mol m^{-2}, the "unit surface pressure" standard state (1 mN m^{-1}) and the "unit mole fraction" standard state, in which the surfactant surface coverage $\theta = 1$. Regardless of which is used, it is important to be aware that this choice will affect the values of the thermochemical parameters derived, so direct comparisons are not always possible between the various reports in the literature.

That being said, the standard enthalpy of adsorption is less sensitive to the choice of standard state (for compounds exhibiting Langmuir adsorption isotherms or in the low-coverage regime) than the standard free energy or entropy of adsorption, so some comparisons may be made. There is generally good agreement among various groups on the enthalpies of adsorption of alkane and aromatic hydrocarbons. These tend to increase with molecular size yet are smaller than the corresponding vaporization enthalpies.[65,69,70,81,94,104,105] For compounds that are expected to be better solvated by water, the standard enthalpies of adsorption are again different from those of vaporization but are related to the infinite-dilution solvation enthalpies.[73,83] These observations suggest that adsorption of gases to the water surface involves specific interactions there, rather than the surface merely providing a site for condensation.[69,73,83]

2.4. Effects of Subphase Composition

In studies of the uncoated water surface, both the orientation and the ratio of "free" to hydrogen-bonded OH groups of surficial water molecules are reported to change with changes in solution pH. The addition of acids apparently disrupts the first layer of surface water molecules, allowing ions to approach the surface more easily.[106] Recent molecular dynamics studies suggest that in acidic solutions *both* the anion and the hydronium ion may reside at or near the interface,[107] in contrast with basic or neutral salt solutions, in which only strongly polarizable ("soft") anions reside at the surface.[51] This could have important consequences with respect to the reactivity of organic species adsorbed there. The influence of bulk pH on films of fatty acids has been recognized for close to a century. In 1917 Langmuir[41] showed how the addition of trace amounts of inorganic acids could dramatically alter the shapes of isotherms such as that illustrated in Figure 2. Decreasing the solution pH lowers the extent of ionic dissociation of the surficial fatty acids, allowing the now-neutral hydrophilic headgroups to approach one another more closely. Thus the solution pH can control the packing density of insoluble films at the interface. The solvation dynamics at the interface are also affected by the degree and the sign of the charge on the surfactant headgroup.[46,47,108]

The presence of salts in aqueous solution may affect the ability of organic molecules to dissolve through the salting-out effect.[109] The salting-out effect refers to the decrease in aqueous solubility and increase in the activity coefficient of aqueous neutral nonpolar compounds by inorganic salts. Ions in solution tightly bind several water molecules into hydration shells, resulting in a reduction of the volume of the aqueous solution (electrostriction). A smaller aqueous volume means that there is less available water to form cavities to accommodate organic molecules; consequently, their aqueous solubility decreases. This, in turn, changes the thermochemistry related to equilibrium surface adsorption. Demou and Donaldson[71] reported that both hexanoic acid and 1-propanol display a reduction in their propensities to partition from the gas phase to the surface as the salt concentration is increased. At the same time, the maximum surface excess of organic, Γ_i^{max}, determined for salt solutions was larger than that for pure water and increased with increasing salt concentration.

3. Laboratory Techniques

The methods used in laboratory studies of air–aqueous interfacial film properties are, for the most part, by now standard. Experiments involving insoluble surfactants are often carried out in modified Langmuir troughs,[32] to vary and monitor the state of the film. These devices allow the film surface area to be altered without changing the system volume. Generally, the surface tension is monitored as the surface area is changed. For example, Gilman et al.[110] describe GC-MS measurements of the time dependence of the surface composition in mixed organic films using such a setup. Likewise, both Wadia et al.[111] and Mmereki et al.[50] used Langmuir troughs to study heterogeneous reaction kinetics in films. The group of Unwin has coupled a Langmuir trough with scanning electrochemical microscopy in studies of interfacial transfer across surfactant films.[112,113] A great deal of the spectroscopic work mentioned above has also been performed in such devices. A novel approach has recently been documented by Borden and Longo[114] in which the coated surface lies at the interior of microbubbles, rather than at the top of a Langmuir trough.

For soluble surfactants, the degree of partitioning to the interface is generally determined via surface tension measurements (discussed above) or spectroscopically. Here, one relies upon bulk–surface equilibrium being rapidly achieved and maintained. Experiments may be done using flat surfaces, droplets[70] or jets,[115] and bubbles.[116] Spectroscopic, electrochemical, or even molecular beam[117] probes may be used to follow the interfacial processes of interest, with standard analytical techniques used in the bulk phases.

An interesting experimental challenge is to develop methods for creating reproducible, well-characterized aqueous aerosol particles that are coated with an organic film. Both soluble and insoluble surfactants present problems in bubbler or nebulizer type aerosol generators, the former due to surface tension lowering effects and the latter due to its lack of solubility. Consequently, not much work has been reported on coated aqueous particles in aerosol flow tubes. One approach that avoids these issues is to form aqueous salt particles and then introduce the surfactant from the gas phase. This often requires heating the surfactant, so dry particles are utilized; these are later deliquesced. Both soluble[118] and insoluble[119,120] surfactants have been studied in this manner.

An exciting new approach is to utilize optical trapping of single particles in these studies. Trapping times of several hours may be achieved in a controlled environment with spectroscopic probing of surficial and bulk components possible.[121] One report to date has hinted at this method's potential;[122] one might anticipate many more to come.

4. Field Measurements

The presence of organic films at the air−water interface is not just a laboratory curiosity but has been verified at "real" atmospheric boundaries as well. In this section, we outline what has been learned about such films from field measurements.

4.1. The Sea–Surface Microlayer

The Earth's surface is mostly water-covered; essentially all bodies of marine and fresh water are covered by an organic film (the "surface microlayer") of 1−1000 μm thickness. Two recent monographs review the current state of knowledge of the physical, chemical, and biological properties of these films.[123,124] The microlayer is generally sampled using one of three techniques:[124] a rotating drum collector, in which a cylinder with a hydrophilic surface rotates at the water surface collecting the microlayer, which is scraped off into a collection vessel; a fine-mesh screen, which is dipped repeatedly into the water and drained; and a glass plate collector, which is based on those used to collect Langmuir−Blodget films.[32] The three methods sample different microlayer thicknesses: 10−80, 150−450, and 22−125 μm, respectively. The collected sample may then be analyzed using standard analytical techniques.

Chemical analysis of the organics at the sea surface[14,123,125−132] has shown that amphiphiles derived from oceanic biota (fatty acids, fatty alcohols, sterols, amines, etc.) are enriched in the microlayer and also in interfacial bubble samples at the sea surface.[133] Its amphiphilic nature implies that the sea-surface microlayer can act both as a sink and as a source for a range of pollutants. Indeed, it is found to be highly contaminated in many parts of the world.[134,135] Also, the unique environment afforded by the microlayer gives rise to specialized microorganisms ("neustrons"), which inhabit it. Chemical processes taking place in this region clearly do so in a veritable soup of chemical and biochemical components. This daunting complexity might be responsible for the almost complete lack of attention paid to surface microlayers by the atmospheric chemistry community.

4.2. Aerosol Measurements

Marine aerosols are generated by wind action on the sea surface,[3,4] which, as discussed above, is covered by an organic "oil slick".[123] The nascent marine aerosol is thus generated with a surfactant concentration from the organic pool segregated at the top of the ocean; these compounds have been identified in marine aerosols.[9−11,136−145] The concentrations of marine bacteria and viruses in natural aerosols have also been evaluated.[146] Comparison with their concentration in the sea-surface microlayer and subsurface water has found a 15−25-fold enrichment during transport from subsurface water into the atmosphere. These observations point to significant surfactant enrichment in marine aerosol particles.

Continental aerosols of both biogenic and anthropogenic origin have been observed to contain soluble and insoluble organics.[20,22,136−138,147−151] Secondary organic aerosols result from gas-phase oxidation of volatile organics, followed by condensation of partially oxidized organic compounds onto an aqueous or a nonaqueous substrate.[6] Because of the high concentration of water vapor in the troposphere, even fairly hydrophobic substrates will take up some water[29,152−154] and should give rise to surfactant compounds at the interface.

Field missions have been undertaken to target the various organic constituents in aerosol particles, using both ground-based and air-borne platforms.[136,140,155−166] Most studies attempting molecular speciation of organics have relied on investigating bulk samples collected at the site of interest and analyzed by GC/MS, HPLC, and NMR techniques.[167,168] GC/MS is the most widely used analysis method, with the recent promising modifications for separation of complex mixtures such as thermal desorption, orthogonal gas chromatography, and fast acquisition.[161,168−170]

Few simultaneous measurements are available of structure and composition of atmospheric aerosol particles; accordingly, much of the field evidence for the existence of surface films at the water−air interface of such particles is indirect or circumstantial. Obtaining molecular speciation of the organic surface films in the atmosphere is a daunting task because the organic composition varies with the source, the altitude, and the latitude of the measurement, providing a challenging analytical sampling and analysis problem.[160,161]

Atmospheric aerosols can be measured in real time optically, by light scattering,[171] but composition of individual particles is much more difficult to obtain. Real time monitoring techniques have been under development for about three decades[172−178] and have been used successfully for direct atmospheric sampling and analysis.[164,165,179−189] Such methods are able to provide information about the size, number density, and composition with great sensitivity and fewer artifacts than analysis of bulk samples.[190−194] However, these real-time approaches, while extremely sensitive, often fail to obtain molecular speciation of the individual organic molecules on the particle, especially when the sample contains large, polar organic compounds. In addition, single-particle methods fail to obtain the near-surface composition, a potentially important parameter in predicting the optical and chemical properties of atmospheric particles. These problems can be somewhat alleviated by the use of combined individual particle and bulk aerosol analysis.[195−199] Real-time measurements have been performed successfully not only in the troposphere but also in the lower stratosphere, which is accessible by specialized high-altitude aircraft.[181]

Despite the difficulties outlined above, field measurements have contributed some evidence for the existence of surface organic films on atmospheric particles. Surface films have been inferred by a decrease in surface tension with respect to pure water in rain and fog waters and cloud droplets.[9,200−204] Electron microscopy images of haze particles collected in Los Angeles showed a "wrinkled bag" of nonvolatile organics left behind when the particles were evaporated under vacuum.[205] Atomic force microscopy (AFM) and transmission electron microscopy (TEM) of aerosol particles collected over the North Atlantic ocean showed "halos" around the particle whose content measured by energy-dispersive spectrometry (EDS) was rich in S, O, and C.[206] This was interpreted as evidence for the presence of organic surfactant compounds in the aerosols.

These earlier studies have been supplemented recently by direct evidence for hydrophobic organic surfactant films on atmospheric aerosols[145,207−209] of marine and continental origin. The predominant organic compounds detected at the surface of aerosols collected in Finland and analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS) are fatty acids. Marine samples contained fatty acids with C_{14}−C_{18}, while continental aerosols contained fatty acids with longer carbon chains ranging from C_{14}−C_{30} with a maximum distribution at about C_{22} and a strong even to odd carbon number alternation. These compounds are consistent with known sources of organics in marine and continental environments.[210,211]

As shown in Figure 4, further evidence for the existence of the surface fatty acid films in these experiments was obtained from sputtering of the surface layer.[145,209] Sputtering the sample reduces the fatty acids, with a commensurate increase in the signal due to sea salt (in the case of marine samples) or sulfate (in the case of continental samples). Such direct evidence complements functional group analysis studies of bulk samples and leads to the conclusion that organic surfactant films on marine and continental aerosols are more common than previously believed and could therefore possibly affect the optical and chemical properties of atmospheric particles.[15,101,212−214]

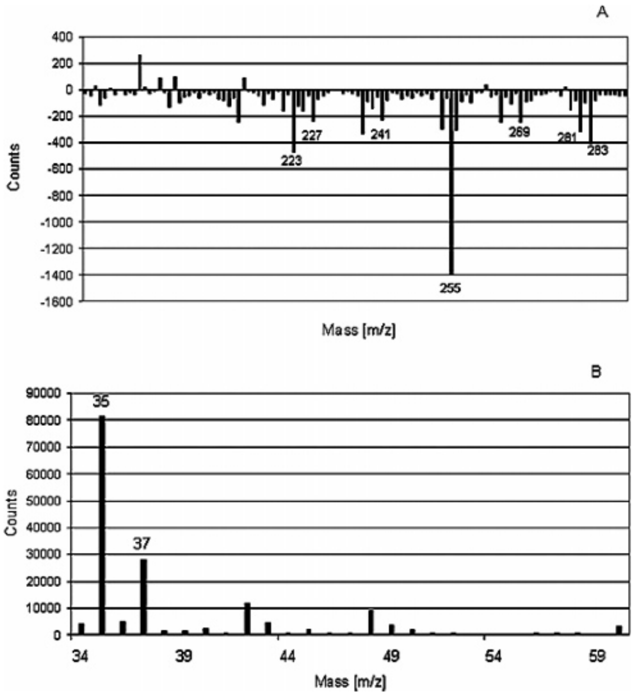


Figure 4. TOF−SIMS difference spectra showing how the chemical composition of a particular marine aerosol particle changed upon sputtering of its outer layer. Panel A shows a decrease in the masses associated with palmitic acid, while panel B indicates an increase in the chloride (sea salt) concentration. Taken together these offer strong evidence for the claim that the palmitic acid resides exclusively at the air−aqueous interface. Reproduced by permission of American Geophysical Union from ref 336. Copyright 1999 American Geophysical Union.

Significant recent attention has been given as well to supercooled sulfuric acid particles, given their role in heterogeneous reactions in the Earth's atmosphere.[215] Field measurements have shown that upper tropospheric aerosols, composed primarily of sulfuric acid containing particles, also contain organic molecules. However, these field studies lack the ability to investigate the particle structure and obtain the molecular speciation needed to quantify the surface partitioning of the organic material.[181,216,217] In general, the collection of field data and interpretation of field results on ambient particles remains an important yet extremely challenging area of research.

5. Physical and Chemical Consequences of Interfacial Films

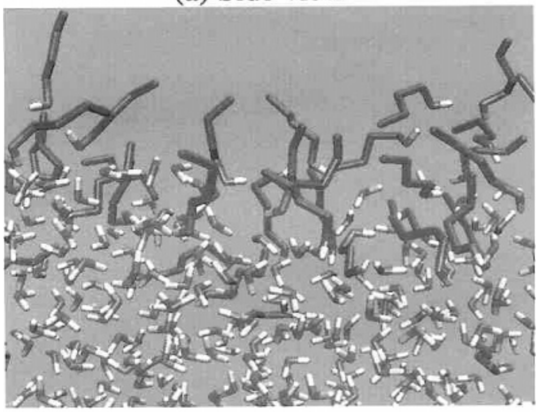
The presence of an organic film at the water surface may have several potential physical and chemical effects. First, the film may act as a barrier to transport across the interface, inhibiting uptake into solution or reaction there. It may, alternatively, act as a more soluble medium than water for hydrophobic gas-phase species, concentrating them at the interface. The film itself, or compounds concentrated in it, may react with gas- or solution-phase reagents; here the film may act to concentrate one or both reagents at the interface. Finally, the film or compounds dissolved within it may undergo photochemical reactions; here the different (from water and air) physicochemical properties of the film may play an important role.

5.1. Nonreactive Interactions

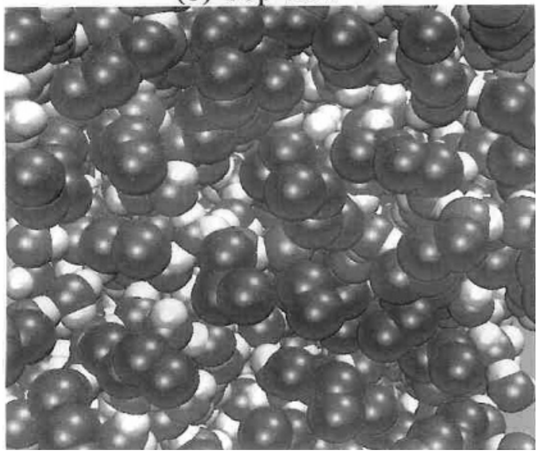
The rate of water evaporation and the more general issue of gas transport through surfactant films has been of great interest for some time and has significant consequences for environmental water−air interfaces.[37,38,42,44,218−222] Processes such as carbon transport across the air−sea interface, water uptake, and evaporation from atmospheric aerosols are critical to the climate system. The interfacial transport of halides, HX (X = Cl, Br), O_2, O_3, NH_3, acids, alcohols, and other atmospheric gases and trace species is especially relevant to atmospheric aerosols.[73,90,223−229] The effects of surfactant hydrophilic group and hydrophobic carbon chain lengths have been investigated for monolayers of fatty acids, alcohols, and phospholipids.[114,229,230] There are clearly large differences in the behavior of soluble and insoluble surfactants. While the former form "porous" films, which do not alter or even enhance the gas uptake under conditions relevant in the atmosphere,[115,231−234] the latter are able to significantly retard evaporation of water and penetration of atmospheric gases through the interface.[38,39,42,44,218,220,235−237]

These different effects follow from the different surfactant properties of the two types of film. Soluble surfactants undergo equilibrium partitioning between the bulk and the interface, governed by a minimization of the free energy by so doing. With increasing surface pressure (as surface coverage increases), this equilibrium may be altered, with more solute partitioning to the bulk (or giving rise to phase separation and lens formation), rather than close packing of the surfactant. Some recent molecular dynamics calculations[238,239] do suggest that liquidlike and gaslike phases may coexist in such systems, however. The case of DMSO, mentioned above, is a good example: the surface achieves "saturation" at concentrations well below the solubility limit. Ethanol or propanol are similar. Figure 5[232] illustrates a molecular dynamics simulation of the resulting porous nature of a monolayer of a soluble surfactant, butanol, at the air−water interface.

This porous nature is of some importance in understanding the potential for atmospheric particles to "activate", forming cloud droplets. Abbatt and co-workers show that surface-active organic compounds do not promote or inhibit activation of aqueous aerosols, outside of changes expected due to size or concentration effects, except in the case of a thick coating of stearic acid.[240] Similarly, Wagner et al.[241] report a slowing of the deliquescence rate of salt particles of 50−60 μm size when these are coated by a thick layer of octanoic acid. Deliquescence was not prevented, however. Small



(a) Side view



(b) Top view

Figure 5. Side (a) and top (b) views of a Monte Carlo simulation of a full monolayer of butanol on water at 298 K. United-atom methyl and methylene groups, water oxygens, and hydrogens are shown as black, gray, and white balls and sticks, respectively. Simulations by B. Chen, J. I. Siepmann, and M. L. Klein reported in Lawrence et al.[338] and reproduced with permission. Copyright 2005 American Chemical Society.

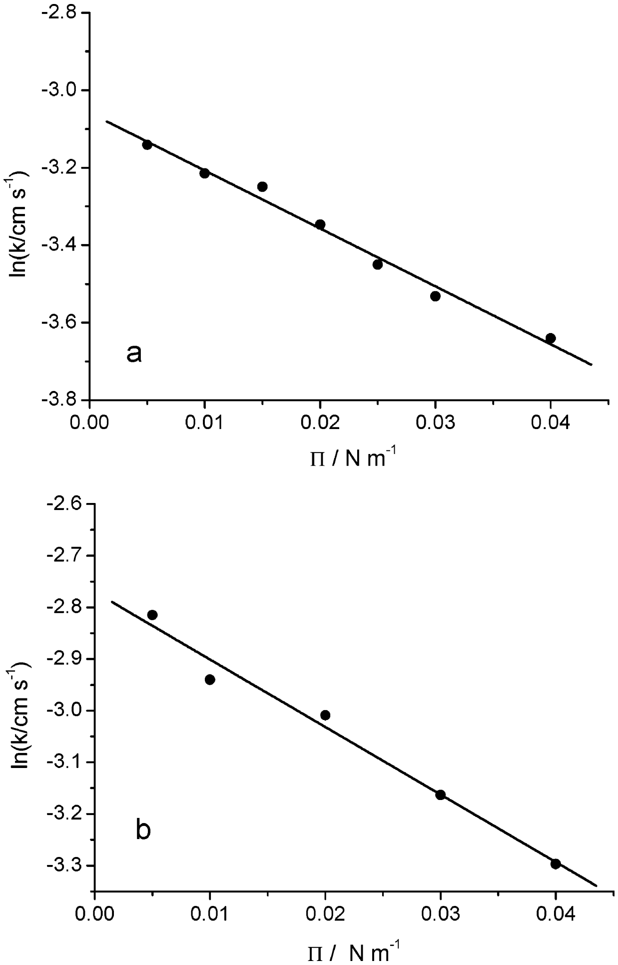


Figure 6. Pseudo-first-order rate constant for transfer of oxygen across monolayers of (a) 1-octadecanol and (b) the phospholipid L-*R*-dipalmitoyl phosphatidic acid at the air−water interface, plotted as a function of the film surface pressure. The points show measured data and the solid lines indicate fits to a barrier penetration model. Used with permission from ref 113. Copyright 2004 American Chemical Society.

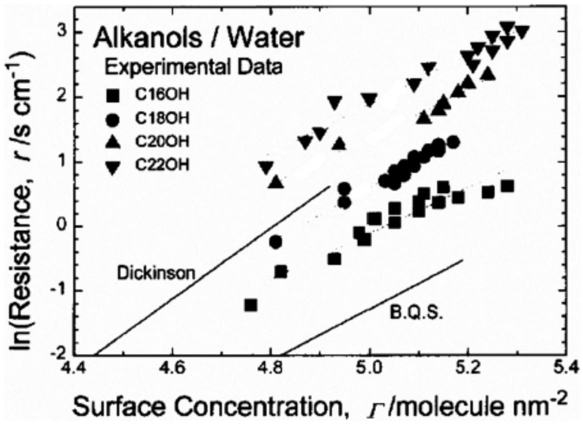


Figure 7. The resistance to transfer across the air−water interface is shown as a function of the concentration of surfactant for several long-chain alcohols, shown as points. The solid lines give predictions of two “available area”-type models. Reprinted from ref 38, copyright 1997, with permission from Elsevier Ltd.

changes to the water uptake behavior without preventing deliquescence have also been reported by other authors.[120,242,243] Jefferson et al.[119] showed a decrease in the mass accommodation of sulfuric acid onto a polydisperse (nanometer size range) population of $(NH_4)_2SO_4$ and NaCl aerosol particles when these were coated with stearic acid. Again, uptake was not halted for the coated particles.

For insoluble surfactants there are several models, in two basic classes, for understanding the inhibition of gas transport.[38] The first type of model treats interfacial transport as an activated, barrier-crossing process. Here, increasing the film density on the surface raises the barrier to transport; this barrier is given by the surface energy. Consequently, the degree of compression of such films is found to be important to the retardation effect. Figure 6[113] shows a clear dependence of the rate of oxygen passage through two different surfactant films on the film surface pressure. This dependence is well modeled by a “surface barrier” model, shown as the solid lines in the figure. A second class of models 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. Figure 7[38] displays the surface resistance to evaporation as a function of surface concentration for several long-chain alcohols, as well as the predictions of two “accessible surface area” models. The general trends are certainly well captured, though agreement is not quantitative. A variation on these ideas is that transport may take place at surfacial “grain boundaries”. There is some evidence to support this viewpoint as well.[38]

As well as blocking or inhibiting interfacial transport, organic surface films can "dissolve" nonpolar organic hydrocarbons at the interface. There is clear effect of the surfactant film on the solubility of hydrophobic organic compounds at atmospheric water−air interfaces.[49,63,244−247] Lo and Lee[245] suggested that an organic coating could enhance adsorption of more hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs) in fog droplets, perhaps explaining the observed non-Henry's law concentrations measured in field samples. In a subsequent paper, enhanced aqueous solubilities were reported for naphthalene in the presence of the surfactant sodium dodecyl sulfate (SDS). Most of this enhancement was due to dissolution of the naphthalene in SDS micelles, however. Wistus et al.[248] and Kozarac et al.[244] reported that pyrene (a hydrophobic PAH compound) dissolves in a monolayer of fatty acid at the air−water interface, forming a mixed film there. Mmereki et al.[49,63,249] showed that soluble surfactants (hexanoic acid and 1-octanol) also enhance hydrophobic partitioning to the air−aqueous interface, even at submonolayer coverage, and that the magnitude of the enhancement is larger for less polar interfacial environments. Figure 8[49] illustrates how the surface concentration of pyrene depends on the surfactant concentration, increasing through monolayer coverage of the surface by hexanoic acid. These effects have been modeled successfully by Djikaev and Tabazudeh,[250] who used a thermodynamic formulation and showed how the apparent Henry's law is increased for surface-active compounds, yielding higher-than-predicted concentrations of organics in cloud droplets.

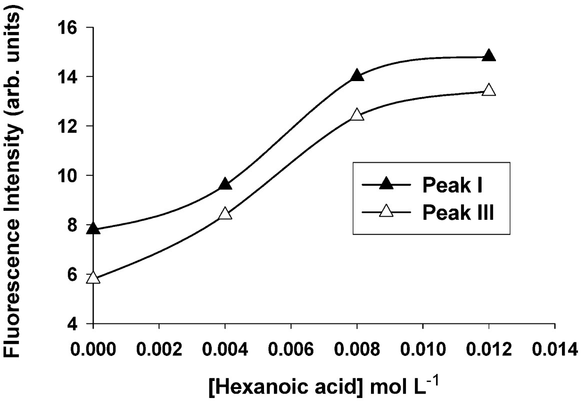


Figure 8. The fluorescence intensity from two different vibronic bands of pyrene adsorbed at the air−aqueous interface following excitation at 337 nm is plotted as a function of the hexanoic acid concentration in the bulk solution. Monolayer surface coverage of the acid corresponds to roughly 0.004 M bulk concentration.[71] Reproduced from ref 49 by permission of the PCCP Owner Societies. Copyright 2002.

This surface concentration effect may play an important role in interfacial transport in aerosols and also at the surfaces of oceans and lakes. Sadiki et al.[251,252] show that lead nitrate readily coadsorbs at aqueous surfaces coated with benzene or cyclohexane. Aerosol generation at such an interface, by wind or wave action, could eject high concentrations of lead. This mechanism could well be important for injecting pollutants such as polychlorinated biphenyls (PCBs) and PAHs, which are enriched in the sea-surface microlayer, into the marine atmosphere.

A final, somewhat more subtle, effect due to soluble surfactants is by their surface-tension-lowering property. Aerosol formation in wave-breaking and bubble-bursting events will be affected by changes in the surface tension, as well as surface composition. The activation of atmospheric aerosol particles to form cloud droplets depends on their ability to increase in size above some critical diameter. The Kelvin equation[32] describes how the equilibrium vapor pressure above a spherical droplet depends on the radius and the surface tension. Surface-tension-lowering solutes were predicted[253] to depress the "critical supersaturation", the local supersaturation of water vapor that is thermodynamically required to bring about spontaneous condensation of water onto a growing droplet. A recent modeling study also indicates a large influence of this parameter, especially for aqueous droplets.[254] Very recent works by Sorjamaa et al.[255] and by Abbatt et al.[240] come to opposite conclusions concerning the surface tension effect. The former group reports an effect of surface tension lowering, as predicted, though those experiments were done with quite insoluble surfactants. As mentioned above, the experiments reported by Abbatt et al.[240] showed no such influence using soluble surfactants. Clearly, more experimental work is required in this area.

5.2. Chemical Reaction at the Interface

The possibility that a surface film might inhibit heterogeneous reactions follows from the possibility of hindering transport through the interface. This effect has been studied in a few systems. Daumer et al.[223] studied the reaction of gas-phase ammonia with sulfuric acid aerosol particles. Submicrometer acid particles were generated and then exposed to the vapor of various organic compounds in a flow tube system. Two straight chain compounds, *n*-hexadecane and *n*-hexadecanol; a branched compound, 1-(hydroxymethyl)-adamantane; and three terpenes, camphene, limonene, and α-pinene, were used as coating materials. Particle diameters were determined before and after the coating step and were seen to increase following exposure to the organic vapor; neutralization results were given for coatings of 3−5 nm thickness and two relative humidities. The reaction was followed by determining the fraction of original acidic mass, which had reacted as a function of exposure time to ammonia. For all coatings but the branched compound, the neutralization reaction was slowed considerably (by up to two orders of magnitude) when the acid particles were coated; the effect was larger for thicker coatings and lower relative humidities. These observations were interpreted as indicating the formation of tightly packed surface films in the case of the straight chain hydrocarbons and more loosely packed coatings when the branched compound was used.

The heterogeneous hydrolysis reaction, $N_2O_5 + H_2O \rightarrow 2HNO_3$, is a key atmospheric process, redistributing nitrogen oxides among NO_x and NO_y. It is responsible for removal of active nitrogen via dissolution of the nitric acid product in the particle aqueous phase. Consequently, it has been the subject of considerable laboratory study over the past decade.[256−264] Using aerosol droplets of aqueous sulfuric acid,[256−261,265,266] sodium or ammonium sulfate or bisulfate,[259,261,262] sodium chloride,[264,265] or malonic acid[263] at relative humidities above about 50%, researches have obtained reaction probabilities of a few (1−3) percent. The results from several laboratories suggest a strong near-surface component to the reaction with reacto-diffusive depths of a few molecular layers inferred from the uptake kinetics.[256,263,266]

Folkers et al.[267] used a 256 m^3 aerosol smog chamber to investigate the N_2O_5 reaction taking place on organic-coated particles. They exposed aqueous ammonium bisulfate particles to the ozonolysis products of α-pinene inside the chamber, then introduced NO_2 to form N_2O_5 from residual ozone. Hydrolysis uptake coefficients onto the particles were obtained via modeling of the time-dependent N_2O_5 concentration using a box model, which reproduced well the experimental concentrations for all species in the absence of organic coatings. A decrease in the hydrolysis uptake coefficient was observed that depended on the inferred organic content of the resulting aerosols. For particles thought to have a thin (several nanometer) coating of organic, the reaction probability dropped by a factor of 3−6. This was interpreted as being due to a diminished solubility of N_2O_5 in the organic film, rather than the film acting as a barrier to access into the droplet.

Similar results have also been obtained by Thornton and Abbatt,[118] who exposed deliquesced aqueous sea-salt particles to hexanoic acid vapor prior to reaction with N_2O_5 in an aerosol flow tube reactor. Assuming equilibration of the particles with the organic vapor, the results of Demou and Donaldson[71] on the vapor−surface−solution equilibrium partitioning of hexanoic acid in salt solutions were used to estimate hexanoic acid surface coverages. Two different relative humidities, corresponding to different salt concentrations were used: 50% (giving a surface coverage of 1×10^{13} molecules cm^{-2}) and 70% (1×10^{14} molecules cm^{-2}). At the higher surface coverage, N_2O_5 hydrolysis was slowed by a factor of 3−5 compared to the uncoated value.

A very different situation seems to hold in the case of HX proton exchange reactions at the sulfuric acid surface. Lawrence et al.[268] have shown that a near-monolayer coating of 1-butanol on the surface of 60−68 wt % D_2SO_4 solution at 213 K enhances the H → D exchange of an impinging molecular beam of HBr by about a factor of 3 and that of HCl by about 1.5−2 over the case with no butanol. Figure 9[268] shows that as the butanol concentration is increased in the bulk, the fraction of collisions undergoing exchange increases, following almost exactly the surface excess of butanol at the interface. No such enhancement (or a decrease) of H → D exchange is observed in scattered beams of CF_3CH_2OH upon coating the acid surface. It was concluded that the presence of butanol at the surface aids in the HX solvation there, increasing the likelihood that HX enters the bulk phase acid and undergoes subsequent proton exchange. Interestingly, these same authors[232] saw no effect of surfacial butanol on water evaporation (vide supra).

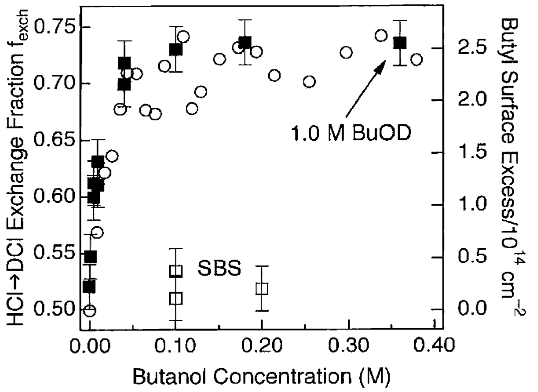


Figure 9. The HCl → DCl exchange fraction for collisions of molecular beams of HCl with deuterated sulfuric acid are plotted vs butanol concentration (filled squares) for 60 wt % D_2SO_4 solutions at 213 K. The exchange fraction values for 0.10 and 0.20 M sodium 1-butanesulfonate (SBS) solutions are shown as open squares. On the right axis, the open circles show the butyl surface excess, calculated from surface tension measurements of butanol in 58 wt % H_2SO_4 at 294 K. Taken from ref 339 with permission. Copyright 2005 American Chemical Society.

Another way in which a film might influence heterogeneous reactivity is for a chemical reaction to take place between a gas (or solution)-phase reactant and the film itself. Recently, there has been a surge of interest in the reactive uptake of OH and O_3 by organic aerosols, films, and organized monolayers, motivated largely by a need to understand changing hygroscopic properties of organic-containing particles during their atmospheric lifetimes.[29,153,154,269−284] Considerable recent effort has been directed toward the reaction of gas-phase ozone with particle-bound oleic acid. The heterogeneous kinetics, reaction products, and changes in water uptake have been reported for this benchmark system, as well as a few similar unsaturated systems. In general, it is found that the reaction probability is considerably enhanced over the corresponding gas-phase rate, presumably through solvent trapping or caging effects.[111,227] Consistent with this idea, the reaction products are not strictly those expected for gas-phase ozonolysis but can be rationalized by invoking ozone-induced radical chain reactions taking place in the organic phase.

Despite this interest, very little work has been reported on reactions taking place in films adsorbed on a water surface. Finlayson-Pitts and co-workers[111,285] have investigated the reaction of ozone with monolayers of unsaturated phospholipids at the air−water interface. Lai et al.[285] exposed monolayers of phosphocolines coated on an aqueous subphase in a Langmuir trough to ozone/oxygen mixtures of varying concentration for varying times. The surface pressure−molecular area (π−A) isotherms were measured and showed dramatic changes following exposure to ozone. The specific nature of these changes depended upon the pH of the subphase and were interpreted as being due to formation of acidic surfactant product(s), which competed for surface area with the original compound. In later work, Wadia et al.[111] used an atmospheric pressure ionization mass spectrometer coupled to the Langmuir trough to identify the gas-phase products of the reaction with one of the unsaturated phospholipids studied previously. By measuring the time for reaction to be complete, they estimated the reaction probability (per collision) to be at least an order of magnitude larger than the corresponding gas-phase value. No clear trend was observed in the reaction time as a function of the degree of film compression over the range 40−158 $Å^2$ $molecule^{-2}$ on the surface.

Molecular dynamics calculations carried out in conjunction with the experimental work[111] and later[227] were used to explain the increased reaction probability in the film. Figure 10[227] illustrates how the ozone average residence times in a liquid hydrocarbon or a phospholipid monolayer are both enhanced by a factor of 3 over those found for the uncoated water surface or a self-assembled monolayer, due to the possibility of uptake into the organic medium. Even when strictly surface residence times are compared, the more “liquid” substrates give a factor of 2 increase in ozone residence over the water or self-assembled monolayer (SAM) surfaces. The looser structures and higher solubility combine to yield a more effective trapping (or surface solvation) of ozone at the interface. This same effect is probably operative for other more hydrophobic gases at the surface as well.

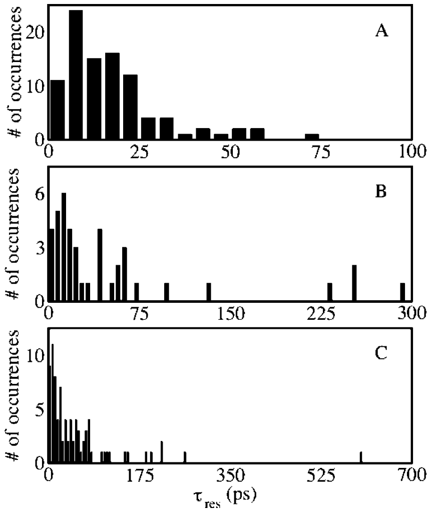


Figure 10. Results of molecular dynamics simulations showing the average lifetime of an ozone molecule at the interface between vacuum and (A) a self-assembled monolayer of 1-octenethiolate molecules adsorbed on a gold surface, (B) liquid 1-tetradecene, and (C) a monolayer of 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine molecules adsorbed at the water liquid/vapor interface. Note the very different time scales for the three cases. Reproduced from ref 227 with permission. Copyright 2004 American Chemical Society.

King et al.[122] reported a growth in particle size (thought to be due to water uptake) when aqueous sea-salt particles coated with oleic acid were exposed to gas-phase ozone. A laser Raman tweezers apparatus trapped micrometer-sized droplets and interrogated composition and size. Figure 11 displays nicely how, as the droplet size evolves, the oleic acid concentration decreases and product nonanal and nonanoic acid concentrations increase. Although the presence of oleic acid as a coating was not confirmed in these experiments, its lack of aqueous solubility implies this structure. The thickness of this film was not determined.

George and co-workers[286] reported a measurement involving reaction between a film coating the water surface and an aqueous reagent. Cl_2^- radical anion was generated using a laser flash photolysis method, and its reaction with ethanol at the air−water interface was followed via UV diffuse reflectance spectroscopy. Ethanol is somewhat, though not strongly, surface active; reaction in the bulk aqueous phase was differentiated from reaction at the interface by the linear dependence on ethanol concentration of the former and Langmuir-type dependence of the latter, as shown in Figure 12. The extracted surface reaction rate coefficient was found to be about two times larger than the corresponding value in solution. These results, although not of great atmospheric importance in themselves, serve to demonstrate that surface films may influence atmospherically important heterogeneous processes through their reactions with the subphase components, as well as gas-phase reactants.

This point is made again in a study by Kuznetsova and Lee,[287] who showed that extracellular peptide hydrolysis reactions occur more rapidly in the sea-surface microlayer than in the underlying subphase. In a controlled, laboratory setting, these authors doped samples of sea-surface microlayer and of its underlying bulk water with a synthetic, fluorescence-labeled peptide and observed the hydrolysis rate in each. A seasonal variation in the hydrolysis rates was seen; the ratio of the pseudo-first-order rate coefficients (microlayer/bulk) also varied seasonally, being largest (about a factor of 2) in the winter months. This enhancement in reaction rates was also correlated with an enhancement of total hydrolyzable amino acids in the microlayer.

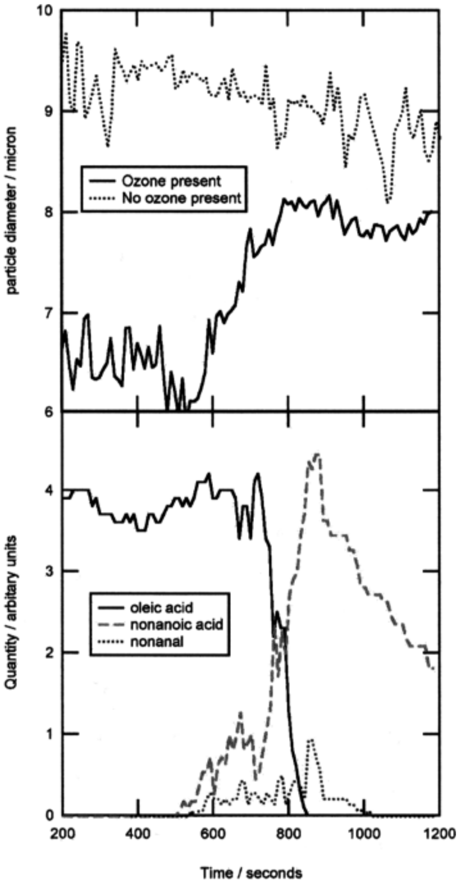


Figure 11. Real-time Raman spectroscopic study of the reaction of gas-phase ozone with oleic acid adsorbed at the water interface of micrometer-sized particles suspended in a laser tweezers trap. The upper panel shows the growth in particle size following processing; this is probably due to water vapor uptake by the processed aerosol. The lower panel displays the decrease in oleic acid concentration and the simultaneous growth in concentration of the expected products of its ozonation reaction. Taken from ref 122 with permission. Copyright 2004 American Chemical Society.

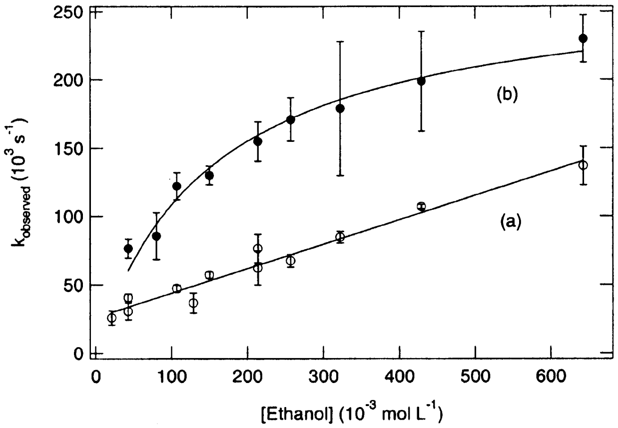


Figure 12. Measured pseudo-first-order rate coefficients for the loss of Cl_2^- by reaction with ethanol (a) in bulk aqueous solution and (b) at the air−aqueous interface are shown as points. The lines illustrate fits to a linear (for the bulk reaction) and Langmuir−Hinshelwood (for the surface reaction) kinetic behavior in the two instances. Reproduced from ref 286 with permission. Copyright 2003 American Chemical Society.

Another role that surface films may play is to provide a different medium in which reaction might occur. Reactions may be affected by increasing the solubility of one or both reagents or by providing a different physicochemical environment (polarity, hydrogen-bonding capacity, viscosity, etc.), which may alter reaction pathways or energetics. Recent papers from the Donaldson group illustrate the effect that the physical and chemical nature of the film might have on heterogeneous reaction.[50,249,288] These authors used a fluorescence technique to examine the reaction of gas-phase ozone with anthracene or pyrene adsorbed at aqueous surfaces that were coated with monolayer quantities of various organic compounds. The results are summarized in Figure 13. In all cases, adsorbed anthracene reacted with gas-phase ozone following a Langmuir−Hinshelwood mechanism, implying rapid equilibration of ozone between gas and surface phases, followed by reaction in two dimensions. At low ozone partial pressures, the kinetics depend both upon the surface reaction rate and the surface uptake; at higher ozone concentrations, the surface becomes saturated and the reaction rate is independent of ozone pressure. A similar mechanism is also reported for the reaction of ozone with pyrene at coated and uncoated aqueous surfaces[288] and for benzo[*a*]pyrene adsorbed onto solid soot[289]and salt[290] surfaces.

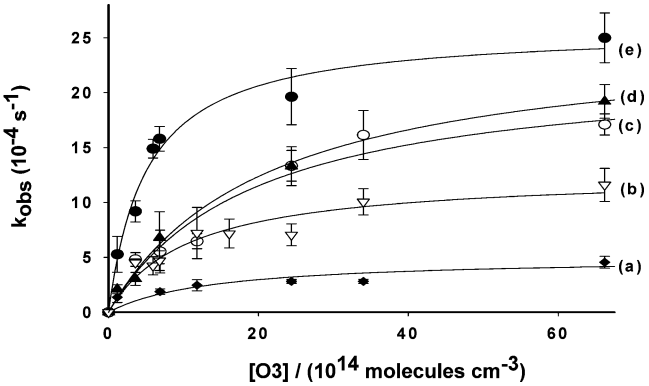


Figure 13. Measured pseudo-first-order rate coefficients for the loss of anthracene adsorbed at the air−aqueous interface, as a function of gas-phase ozone concentration for monolayers of several surfactants: (a) hexanoic acid; (b) octanoic acid; (c) uncoated water interface; (d) uncompressed film of stearic acid; (e) 1-octanol. The solid lines give fits to Langmuir−Hinshelwood kinetic models. Reprinted from ref 50, copyright 2004, with permission from Elsevier Ltd.

Compared to results at the bare water surface, the two-dimensional rate coefficient inferred from the kinetics measured under surface-saturated conditions is considerably diminished when the oxidation occurs on a "bare" Teflon surface or at an aqueous interface coated with monolayer amounts of short-chain (C_6 or C_8) carboxylic acids. The 2-D rate constants for reaction at a monolayer of 1-octanol or an uncompressed monolayer of stearic acid are essentially the same as those of an uncoated water surface; upon compression of the stearic acid film, the reaction rate is slowed somewhat. Interestingly, ozone uptake is enhanced on the organic-coated surfaces over that seen on uncoated water, though to different extents depending on the coating. This enhanced uptake of ozone by organic-coated surfaces is consistent with the results discussed above for reactions in phospholipid monolayers.

6. Optical and Photochemical Effects of Surface Films

6.1. Optical Properties

In the real atmosphere the presence of organic films, composed of either soluble or insoluble surfactants, is unlikely to have direct effects on the optical properties of the aerosol particles due to the low absolute numbers of absorbers at the surface. In the sea-surface microlayer, however, the situation may be somewhat different: satellite observations of the ocean surface sample just the surface;[291] hence the optical properties of the microlayer and how they change with chemical reactions need to be understood to take full advantage of remote sensing measurements. In addition, the microlayer constituents could change the intensity and spectral distribution of sunlight that penetrates into the near-surface ocean water, changing the aqueous photochemistry there. This effect could play a role, as yet unexplored, in aerosol aqueous photochemistry as well.

A possible indirect optical effect of surface coatings on aerosol particles arises from the different reactivity and solvating ability of such layers from those of uncoated aqueous solution. Noziere and Esteve[292] have measured dramatic color changes in sulfuric acid solutions following the uptake of several partially oxidized organic compounds, due to condensation-type reactions. Michelson et al. report low solubility of acetaldehyde in sulfuric acid but remark that "small amounts of organic content in a sulfate particle may increase the uptake of more organics."[293] In section 5, we discuss how an organic coating on particles may enhance the uptake and reaction of atmospheric species at the surface. If such reactions yield products with significantly different (stronger or weaker) optical absorption than the reagent species, the optical properties of the particle itself could be affected. This possibility awaits experimental verification.

6.2. Photochemistry

There has been little or no attention paid to date on atmospherically relevant photochemistry taking place at the air−water interface, in contrast to ice surface photochemistry, which has drawn some recent interest. Given the results presented above, one might well expect photochemical processes taking place in an organic surfactant film to proceed with different rates, yield different products, or both, compared to those processes in the aqueous or atmospheric phases. In natural water surface microlayers, it is speculated[294] that some photochemical processes could be enhanced, but there is little experimental evidence of this to date.[134,294]

7. Possible Role of Water–Air Interfaces in Prebiotic Chemistry

An intriguing possibility that has recently been proposed is that organic-coated interfaces could have played some role in prebiotic biochemistry.[295−298] Atmospheric interfaces have been considered by other authors, as well, in different origin of life scenarios.[299−301] In this section, we outline some of the arguments for considering organic films at the air−water interface in this context.

In a prebiotic atmosphere, it is accepted that synthesis of simple organic compounds (hydrocarbons, amino acids, cyanides, purines, pyrimidines, etc.) from inorganic precursors could occur by several mechanisms with energy supplied from lightning discharges, UV radiation, hydrothermal vents, volcanoes, geothermal sources, and other sources. Simple organic molecules have been discovered in interstellar space and extracted from meteorites, suggesting in addition the possibility of synthesis elsewhere and subsequent transport to Earth.[302−307] There is thus little question that compounds that might exhibit partitioning to the aqueous surface could have been present in the early Earth.

The role of prebiotic surfactant films has been discussed in various "Lipid World" scenarios for the origin of life,[301,308−313] scenarios involving vesicles in liquid environments. Organic films acting as membranes at the water−air interface were originally proposed by Goldacre,[40] who suggested that organic films at the sea surface could collapse to form surfactant-surrounded aqueous folds. Atmospheric aerosols were mentioned in a prebiotic context independently by Shah,[314] Lerman,[315−318] and Dobson et al.[296]

The water−air interface has been shown to concentrate and select organics, properties that can be postulated to select from the available chemical space the precursors and reactions needed for biology.[319] We have discussed in the previous sections the likelihood of uptake and concentration of hydrophobic organic compounds by such films. Other concentration mechanisms are possible in aerosols, such as the evaporation of water through the film during the aerosol's atmospheric journey in low humidity regions[318] and the coagulation of aerosols in the atmosphere;[320] whatever the exact mechanism or mechanisms, concentration of organics at the water−air interface is an important effect.[296−298]

The way in which atmospheric aerosols could be actors in early biochemical transformations is through this concentration effect. By concentration of the building blocks of biochemistry at the air−water interface and their presentation with propitious circumstances for reaction (through exposure to solar radiation and atmospheric reagents), it is possible that early versions of present-day biomolecules could be formed. These building blocks do partition to some extent to the aqueous surface and exhibit some interesting specific properties there.

The conformation, orientation, and chiral enrichment of amino acids and polypeptides at the air−water interface and at the organic−water interface has been studied using elegant surface-sensitive techniques.[321−324] Sum-frequency vibrational spectroscopy has been used to study amino acids in monolayers at the oil−water and air−water interfaces.[322,325,326] The arrangement of hydrophobic peptide helices at the air−water interface was investigated to show that helical peptide rods spontaneously arrange at the air−water interface.[327,328] Furthermore, long α-helical peptides have been shown to form closed-packed domains, which partially cover the surface even at low surface pressure.[329−331] Glucose oxidase monolayers on aqueous solutions could be enriched using Langmuir−Blodgett techniques in the α-helix vs the β-sheet form. The relative enzyme activity became higher as the content of the α-helix increased. These studies[322,326−332] document the ability of the aqueous interface to control the configuration and orient amino acids and peptides that would have been important in biomolecular synthesis in a prebiotic scenario.

The effective concentration of organic reagents can be greatly increased at the surface, and as we discuss above, in organic surface films, reaction rates are accelerated and mechanisms and products modified by comparison with their solution counterparts.[333,334] It could be that reactions that are not favorable in bulk solution may occur at atmospheric aqueous interfaces (aerosols, lakes, oceans), and these may have contributed to biopolymer formation in nonenzymatic, prebiotic scenarios.[295,297] Elegant studies[333,334] have recently shown that surface monolayers are ideal models for amino acid condensation. The experiments used long-chain hoisters of amino acids, which reacted with amphiphilic nucleophiles when these were together in a surface monolayer film. In these studies, peptide bond formation could be induced with control over the orientation, pressure, and intermolecular distance, as well as subphase pH and temperature.

Condensation reactions of this type, while implicated in biopolymer formation, are handicapped on both thermodynamic and kinetic grounds. Aqueous solutions are the preferred reaction medium for biology. However, these reactions are unfavorable in bulk water because they involve elimination of H_2O. Attempts to form proteins and nucleic acids in the absence of enzymes have only been successful in water-restricted environments. In the work mentioned above,[333] kinetic analysis of amide bond formation at the water−air interface showed accelerated rates in the surface monolayer, rates comparable to the corresponding reactions in enzymes. While the mechanism that controls the reactivity in monolayers is not well understood, surface films are proving effective nonenzymatic models of ribosomal and nonribosomal peptide synthesis. In essence, the hydrophobic effect in the surface film provides an environment with the low water activity necessary for the condensation reactions that eliminate water to form peptide bonds and nucleoside oligomers.

As a final, rather provocative point, it has been suggested that spontaneous division of atmospheric aerosol particles covered in a compressed surface film, unlike their uncoated counterparts, is thermodynamically possible.[320] Atmospheric aerosols that are coated by an insoluble organic film can certainly coagulate, presumably sharing their contents. In conditions auspicious for film collapse, they may also change shape away from spherical and form "buds". The result is the possible formation of two daughter particles (one large, bacterial sized, and one small, viral sized), or formation of vesicles and micelles within the larger particle.[320,335] The conclusion is that thermodynamics would allow coagulation and fission, which could have provided an early form of replication.[295,297]

8. Summary and Outlook for Future Work

Although organic films at the air−water interface have been studied for the best part of a century, their role(s) in atmospheric chemistry is really only now being explored in detail. Recent work has shown several ways in which the different physicochemical nature of an organic-coated water surface may influence properties such as transport of atmospheric gases through the interface, activation of cloud nuclei, uptake of hydrophobic compounds, transport of pollutants through the interface, and chemical reaction rates, mechanisms, and products. Biogenic fatty-acid coatings of the kind reported by Tervahattu et al.[22,336] appear to be more effective at inhibiting mass transport across the air−water interface than shorter, more soluble organic surfactants. This has implications for aqueous-phase heterogeneous chemistry, as well as for the uptake and loss of water and nonreactive trace gases. However, there seems to be little effect of their presence at the interface on the activation of aqueous aerosol particles to cloud nuclei, unless a very thick (several molecular layers) coating is present. Both short-chain and longer surfactants can affect the rates of surfacial chemical reactions; for the reactions studied to date, this effect is primarily through enhancing solvation of reagents at the surface. A recent result[50] suggests that there could be important chemical effects that depend on the chemical nature of the surfactant as well.

There is clearly much work yet to be done. The presence of surfactant species at the surface of tropospheric aqueous particles seems now to be established; just how common are such particles? Given the reactivity of these types of coating toward OH and ozone, how long do they survive in the atmosphere? How significant is interfacial processing at the sea surface microlayer and does this affect pollutant concentrations there? What sorts of photochemistry are possible in interfacial films?[134] Could, for example, photoreduction of metals such as Pb(II),[251,252] and by extension, Hg(II), take place in such a highly reduced environment? Given the presence of organics in stratospheric sulfate particles, could the presence of an organic surface film influence chlorine activation chemistry?

One must also ask how generally may laboratory results, scarce as they are at present and almost exclusively confined to single-component films, be applied to the real atmosphere? These questions are of fundamental importance to atmospheric heterogeneous chemistry and have only now started to be asked.[337] The next few years promise to be rich with new explorations along these lines.

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