

Adsorption parameters of atmospherically relevant organic species: Determination and applications

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Abstract

We report adsorption parameters for methanol, a water miscible organic molecule, and sodium laurate, a colloid-forming organic surfactant. Adsorption parameters were extracted by using composition-dependent surface tension measurements in the Szyszkowski equation. This equation is based on assumptions used to derive the Langmuir adsorption isotherm. Per unit mole sodium laurate is considerably more surface-active than methanol. Adsorption parameters derived for sodium laurate are used to show that organic films on atmospheric particles are most likely condensed rather than crystalline in nature. The latter type is commonly used in laboratory and modeling studies to mimic surface properties of organic-containing particles in the atmosphere. We also show that the mass of organic matter in condensed films can only account for a negligible amount of organic matter measured in submicron aerosol particles in the atmosphere. Surface tension of Aldrich humic acid is presented and compared against that of methanol and sodium laurate. From these comparisons we show that surface properties of humic substances or humic-like material in atmospheric aerosols are much closer to colloid-forming surfactants than water miscible organics.

Submitted to Journal of Geophysical Research-Atmospheres, April 2007

1. Introduction

Surface tension plays an important role in the activation of aerosol particles into cloud droplets [eg. *Seinfeld and Pandis*, 1998; *Facchini et al.*, 1999; *Raymond and Pandis*, 2003]. In addition, recent studies indicate that crystallization of ice in a supercooled drop may also initiate at its surface both in homogeneous [*Tabazadeh et al.*, 2002; *Lu et al.*, 2005; *Sastry*, 2005; *Vrbka and Jungwirth*, 2006] and heterogeneous freezing [*Shaw et al.*, 2004; *Durant and Shaw*, 2005, *Sastry*, 2005] modes, highlighting the role of particle surface in ice formation in the atmosphere. Trace amounts of highly surface-active molecules in aerosols, such as organic surfactants, can effectively partition to the droplet surface, dominating the surface composition of particles in the atmosphere. *Djikaev and Tabazadeh [2003]* have shown that highly surface-active organics, even at low molalities (< 0.001 m), can fully saturate the surface of an aqueous drop in the atmosphere.

The submicron dry aerosol mass in the troposphere is often 50% or more organic by weight [eg. *Decesari et al.*, 2005; *Cavalli et al.*, 2004; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002]. Further, chemical analysis of filter samples of submicron aerosols [e.g. *Facchini et al.*, 1999, 2000; *Decesari et al.*, 2005; *Havers, et al.*, 1998; *Zappoli et al.*, 1999; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Cavalli et al.*, 2004] indicate that organics in particles come in three broad categories; (1) small water miscible compounds (identified chemically as small diacids, sugars, alcohols, etc.), (2) water-soluble surfactants (identified generally as humic-like substances), and (3) hydrophobic matter (lipids like fatty acids or hydrocarbons).

Category 1+2 compounds are soluble in water and upon dissolution can partition to the surface, displacing water molecules at the air/solution interface. This displacement lowers the surface tension of an aqueous particle. In contrast, category 3 compounds, which are insoluble in water, are recently proposed to disperse on the surface of aqueous solutions either as solid clumps or insoluble oil drops [*Aumann and Tabazadeh*, 2007]. *Aumann and Tabazadeh* show that the spreading rate of lipids, like stearic acid, on an aqueous surface is a relatively slow process, preventing formation of crystalline stearic acid coats on most types of aerosol surfaces in the atmosphere. In the absence of lipid

coats on particles, the surface tension of aerosols in the atmosphere is primarily controlled by water-soluble organic components, namely category 1+2 compounds listed above. Category 1 and category 2+3 compounds are shown to comprise a few percent and over 90% of the total fine dry organic aerosol mass, respectively [e.g. *Facchini et al.*, 1999, 2000; *Decesari et al.*, 2005; *Havers, et al.*, 1998; *Zappoli et al.*, 1999; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Cavalli et al.*, 2004]. Since category 1 compounds are present at low aqueous concentrations (less than a few percent) and category 3 compounds are insoluble in water, it is reasonable to assume that category 2 compounds (water-soluble surfactants) are mainly responsible for lowering the surface tension of aqueous particles in the atmosphere.

Category 2 compounds are shown to be humic-like in character [*Decesari et al.*, 2005; *Havers, et al.*, 1998; *Zappoli et al.*, 1999; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Cavalli et al.*, 2004]. Humic materials are known to form colloids or micelles in solution at very low aqueous concentrations [*Stevenson*; 1994; *Yates and von Wandruszka*, 1999; *Tabazadeh*, 2005]. A “micelle” is an organic aggregate often composed of 100 or so individual molecules [e.g. *Myers*, 1999]. Molecules in a micelle unit are arranged in such a way that the aggregate surface is hydrophilic (that can interact with water), whereas its core is hydrophobic (that can solubilize hydrophobic organic matter in an aqueous solution). To our knowledge no laboratory or modeling studies has yet been conducted to examine how typical surfactant molecules, which are colloid-forming in aqueous solutions, are mass partitioned in atmospheric aerosol solutions and how such partitioning may affect their surface properties.

2. Surface Tension Measurements

We measured surface tension over a wide spectrum of solution compositions for two types of binary aqueous systems, namely methanol-water and sodium laurate-water solutions. We also measured surface tension of Aldrich humic acid. The results for the latter measurements are discussed in the atmospheric application section.

Methanol and sodium laurate (NaL) were chosen to represent category 1 (a small water-miscible organic molecule) and category 2 (a water-soluble, colloid forming surfactant) compounds in aerosol particles, respectively. NaL, which is a typical soap

molecule, has a chemical formula of $C_{12}H_{23}NaO_2$. We used NaL instead of sodium stearate ($C_{18}H_{35}NaO_2$), used by other investigators as a typical surfactant molecule in aerosol particles [e.g. *Ellison et al.*, 1999], because the latter is insoluble in water at room temperature. Surface tension was measured with a Krüss K11 tensiometer using the Wilhelmy Plate Method.

Solutions were prepared in the tensiometer's glass vessel. The tensiometer measures the force acting on the plate when it is partially submerged in solution. The vessel, containing the aqueous solution, is raised by the automated stage until the point of maximum force acting on the plate is reached upon contact with solution. From maximum force, the surface tension is determined from the following equation:

$$\sigma = \frac{F}{L \cdot \cos \theta} \quad (1)$$

where σ is the solution surface tension in dyne cm^{-1} , F is the measured force in dyne, L is the wetted length of the probe (40.2 mm for our instrument), and θ is the contact angle. At the point of maximum force $\cos \theta = 1$. At this point the surface tension is simply the ratio of exerted force divided by the wetted length. The tensiometer was regularly calibrated by measuring the surface tension of pure MilliQ deionized water. Before each individual measurement, the probe was rinsed with acetone and/or water and torched to remove trace amounts of organic contaminants.

Methanol-water solutions were prepared by dissolving Sigma-Aldrich Reagent Plus $\geq 99\%$ pure methanol in MilliQ deionized water. Sodium laurate-water solutions were prepared by dissolving solid Sigma $\geq 99\%$ pure sodium laurate. A watch glass was placed over solutions to prevent evaporation. The sample vessel, containing the solutions, was placed in a thermal jacket. Temperature was controlled by a circulating water bath and surface tension was measured when solutions reached thermal equilibrium.

The left panel in Fig. 1 shows the variation of surface tension with composition for aqueous solutions of methanol over the entire range of solution compositions, where methanol mole fraction varied from zero (pure water) to one (pure methanol). Also shown are previous measurements of aqueous methanol surface tension by *Vazquez et al.* [1995]. The comparison of our data against previously published work indicates that our

apparatus is well calibrated, registering high quality surface tension data. The right panel in Fig. 1 shows the variation of surface tension for aqueous solutions of NaL. We note large differences in the surface tension lowering ability between the two systems.

First, per unit mole NaL is about 200 times more efficient in lowering the surface tension of water than methanol. For example, the surface tension of water is lowered from 72 to 25 dyne cm^{-1} when mole fractions of NaL and methanol in solution are 0.004 and 0.8, respectively. This difference in surface activity implies that the surface tension of atmospheric particles cannot be simply determined by the mass content of organic materials in aerosols as commonly assumed [e.g. *Facchini et al.*, 1999]. It is evident that the chemical composition of organic materials in particles may play a more important role in determining their surface properties than the absolute amount of organic mass in particles. For example, a very small amount of a highly surface active component, like NaL, can effectively reduce the surface tension of an aqueous particle. Thus it is not the amount of organic material in particles but rather their surface activity per unit mass or mole that should be used in atmospheric models to determine the surface tension lowering ability of organic-containing aerosol particles in the atmosphere.

Second, the surface tension of aqueous NaL levels off at around a mole fraction of about 0.004, whereas that of methanol steadily declines until the surface tension of pure methanol is reached. NaL in an aqueous solution forms organic colloids or micelles at a fixed solution composition [e.g. *Myers*, 1999], known as the critical micelle concentration (cmc). Once the cmc point of a colloid-forming organic solution is reached, the surface is saturated with the surfactant molecule. Additional amounts of surfactant, pass the cmc point, contributes only to formation of more micelles or aggregates in solution. All water-soluble organic surfactants, with molecular weights above 200 amu, are known to be colloid forming in aqueous solutions [e.g. *Myers*, 1999]. Molecular weight analysis of category 2 compounds (water-soluble surfactants) show that the amu of most organic molecules in aerosols are often greater than 300 amus [e.g., *Kiss et al.*, 2003]. Thus we propose that the dissolution of this high molecular weight surfactant mass in pure water, observed during chemical analysis of filter samples [*Facchini et al.*, 1999, 2000; *Decesari et al.*, 2005; *Havers, et al.*, 1998; *Zappoli et al.*, 1999; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Cavalli et al.*, 2004], must occur via formation of

micelles. Micelle formation limits the ability of organic surfactants in aerosols to lower the surface tension of solution beyond a set point. This point, marked in Fig. 1 as the cmc point, is about 25 dyne cm⁻¹ for NaL. Water-soluble colloid-forming surfactants cannot lower the surface tension of a particle beyond their cmc limits in solution. This implies that the surface tension of aerosols in the atmosphere may often be independent of the total organic mass content of particles.

3. Determination of Adsorption Parameters

Variation of surface tension with composition can be used to extract adsorption constants for organic molecules in aqueous solutions. The partitioning of an organic molecule from the bulk to the aqueous surface can be determined by the Langmuir adsorption isotherm:

$$\Gamma = \frac{\Gamma_{\infty}x}{b + x} \quad (2)$$

Where Γ , b , Γ_{∞} , and x represent the surface excess, the Langmuir adsorption constant, the surface coverage at maximum saturation in units of moles per cm² of surface, and the bulk aqueous mole fraction of the organic molecule, respectively. The Langmuir adsorption isotherm is shown to fit experimental data for many adsorption processes in the atmosphere, including adsorption of inorganic acids on ice surfaces [e.g. *Tabazadeh and Turco*, 1993; *Tabazadeh et al.*, 1999], organic molecules on ice surfaces [*Hudson et al.*, 2002; *Sokolov and Abbatt*, 2002] and organic alcohols at aqueous surfaces [*Donaldson and Anderson*, 1999].

Surface excess (Γ), which gives the excess number of organic molecules at the surface relative to that of water, relates to surface tension (σ) by the Gibbs-Duhem relation [*Adamson and Gast*, 2000],

$$d\sigma = -\Gamma d\mu \quad (3)$$

where μ is the chemical potential of the organic molecule in the bulk solution, given by;

$$\mu = \mu^{\circ} + RT \ln(\gamma \cdot x) \quad (4)$$

where γ is the activity coefficient that tends to one in an ideal solution, μ^o is the chemical potential of the pure solution, R is the gas constant and T is temperature in kelvin. We assume γ is one initially and discuss how this assumption will affect the derivation of adsorption parameters for the methanol-water system later on.

Assuming γ is one for the NaL solution is reasonable since the aqueous concentration of laurate monomers in solution is low below the cmc point of solution (see Fig. 1). From equations 2 and 3 the surface tension can be expressed as:

$$\sigma(x) = \sigma_0 - RT\Gamma_\infty \ln\left(1 + \frac{x}{b}\right) \quad (5)$$

The above substitution yields the well-known Szyszkowski equation for the surface tension of a binary solution, where σ_0 is the surface tension of pure water.

We extracted adsorption parameters, namely b and Γ_∞ using equation (5). To do so we fit the data shown in Fig. 1 for methanol and NaL using a Levenburg-Marquardt nonlinear least-squares regression. Equation (5) can be used only over a concentration range, where surface tension decreases monotonically with x . For methanol-water system, equation (2) can be used for the entire range of concentrations shown in Fig. 1. Thus we used the entire data range shown in Fig. 1 to extract the adsorption parameters for methanol. For NaL, equation (5) only holds for concentrations below the cmc point, where surface tension declines steadily with increasing x . For NaL we extracted adsorption parameters using the range of data where x is below the cmc point marked in Fig. 1. The adsorption parameters derived for both systems are given in Table 1.

Fig. 2 shows the variation of surface excess (Γ) with composition using the parameters derived in Table 1 in equation (2). As expected, surface saturation occurs at a very low aqueous concentration ($x \sim 0.004$) for NaL. For methanol, surface saturation is reached near about $x \sim 0.6$. However, at high aqueous concentrations methanol behavior in water is no longer ideal and therefore adsorption parameters (given in Table 1) at high concentrations are invalid for the methanol-water system.

For the methanol-water system, we also used the van Laar activity relation to account for solution nonideality. This relation is given by;

$$\ln \gamma = A \left[\frac{B(1-x)}{Ax + B(1-x)} \right]^2 \quad (6)$$

Where A and B are empirical constants given in *Lavi and Marmur* (2000). We determined new values for b and Γ_∞ by substituting equation (6) in (4) and repeating the least-squares procedures outlined above. The new values for adsorption parameters differed from the values given in Table 1 by no more than 15%. However, *Lavi and Marmur* show that at high methanol aqueous concentrations ($x > 0.2$), the Langmuir adsorption isotherm fails to adequately represent the adsorption behavior of methanol in water.

Water miscible organic compounds, like methanol, only comprise a small mass fraction of organics found in atmospheric particles (e.g. *Facchini et al.*, 1999, 2000; *Decesari et al.*, 2005; *Havers, et al.*, 1998; *Zappoli et al.*, 1999; *Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002; *Cavalli et al.*, 2004). The adsorption parameters reported here for methanol (Table 1), based on the Langmuir assumption, are valid for mole fractions below about 0.2 [*Lavi and Marmur*, 2000]. The mass fraction of water miscible organic compounds in aerosols is often below 5%, according to the references cited above, which is less than 0.2 in mole fraction units. Thus, we suggest that adsorption parameters for water-miscible organics in particles, such as methanol, sugar molecules, diacids, etc., can be derived using the above relations and assuming $\gamma = 1$ in equation (4).

4. Atmospheric Applications

The Γ_∞ parameter given in Table 1 specifies the total number of surface sites per unit area. From this parameter we can determine the total area occupied by an individual molecule on the surface. For NaL, the area occupied by an individual laurate ion on the surface is about $3.42 \times 10^{-7} \mu\text{m}^2$. The area of a carboxylate head group is measured to be $2.1 \times 10^{-7} \mu\text{m}^2$ [*Myers*, 1999]. When fatty acids, such as stearic or lauric acid, are spread on a water surface each molecule occupies a cross sectional area of about $2 \times 10^{-7} \mu\text{m}^2$ at its maximum packing density [*Myers*, 1999; *Aumann and Tabazadeh*, 2007]. These types of films, which are crystalline in nature, are rigid structures. Crystalline organic films can effectively prevent exchange of molecules between the surface and the aqueous solution.

Our calculated area per molecule for a laurate ion (Table 1) is about twice the area occupied by a crystalline carboxylic head group at its maximum packing density [Myers, 1999; Aumann and Tabazadeh, 2007]. Thus we conclude that the laurate ion surface film is condensed rather than a crystalline in nature. In a condensed film, laurate ions are constantly exchanged between the surface and the aqueous phase, whereas in a lauric acid crystalline film the carboxylic head group is permanently anchored in an upward direction on the surface [Seidl, 2000; Voss *et al.*, 2007].

Many laboratory and modeling studies assume that organic films on atmospheric aerosols are of the crystalline type [e.g., Seidl, 2000; Rudich, 2003; Eliason *et al.*, 2004; Voss *et al.*, 2007]. In a recent study, Aumann and Tabazadeh show that the spreading rate of an organic crystal on an aqueous particle is a very slow process. Based on Aumann and Tabazadeh's work and our results here, we conclude that organic films on atmospheric particles are most likely condensed rather than crystalline in nature. The former film cannot interfere with water transport in and out of a particle, whereas the latter film can. Also, organic chains (or hydrophobic portions of an organic molecule that partitions into the surface) in condensed films are not oriented in a perpendicular direction as they are in a crystalline film [Myers, 1999]. Therefore, oxidation rates reported for many kinetic studies [Rudich and references therein; Eliason *et al.*, 2004; Voss *et al.*, 2007], which make use of self-assembled organic monolayers as substrates, such as a crystalline stearic or oleic acid films, are not directly applicable to the atmosphere.

Below we present relations to calculate the amount of organic mass required to form a condensed monolayer film on a particle surface as a function of its size. The site area per molecule (Table 1, last column) gives the surface density σ_{\max} of the surfactant molecule at its saturation limit. Given σ_{\max} (last column in Table 1), we calculate the mass fraction of organic molecules required to form a complete coat on the surface of a particle of radius r . We begin with the following relation:

$$N_{\max} = \sigma_{\max} \cdot 4\pi r^2 \quad (7)$$

where N_{\max} is the maximum number of surfactant molecules that can adsorb onto the surface. The mass of adsorbed molecules as a percentage of total particle mass is given by the following:

$$Mass\% = 100 \times \frac{N_{\max} \cdot MM}{\frac{4}{3}\pi r^3 \cdot \rho \cdot N_A + N_{\max} \cdot MM} \quad (8)$$

where MM is the molar mass of the organic molecule, N_A is Avogadro's number, and ρ is the volume density, which we assume to be that of pure water (1 g cm^{-3}). Combining these two equations gives:

$$Mass\% = 100 \times \frac{3\sigma_{\max} \cdot MM}{N_A \cdot r \cdot \rho + \sigma_{\max} MM} \quad (9)$$

Fig. 3 shows the mass fraction of organic material required to form a condensed monolayer film based on equation (9). We assumed a molar mass of laurate ion for the organic material. The mass fraction to coat a particle is relatively large for a small particle (25% by weight organic if $r = 0.01 \text{ }\mu\text{m}$), but it becomes negligible for micron-sized particles (below 1% by weight). Almost all the organic mass found in atmospheric aerosols is in the submicron range near $r \sim 0.1 \text{ }\mu\text{m}$ [Seinfeld and Pandis, 1998]. In this size range the amount of organic mass required to form a condensed monolayer film is about a few percent (Fig. 3). Given that particles in this size range are often 50% or more organic by weight [e.g. Facchini et al., 1999, 2000; Decesari et al., 2005; Havers, et al., 1998; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Cavalli et al., 2004], we propose that almost all the organic mass in submicron particles must reside in the bulk rather than on the surface of particles. Thus, organic oxidation processes in atmospheric particles are perhaps more influenced by bulk rather than surface oxidation pathways. At the current time, surface processes are assumed to be a major pathway by which organic molecules in particles are oxidized in the atmosphere [Rudich, 2003 and references therein; Eliason et al., 2004; Voss et al., 2007].

As mentioned above organic materials in atmospheric particles are mostly humic-like in character. In Fig. 4 we show a comparison between surface tension lowering ability of methanol, NaL and Aldrich humic acid (AHA). Per unit mass AHA exhibits yet

a different surface tension behavior than either methanol or NaL. This comparison shows that different types of organic materials exhibit different surface-active behavior in solution. However, a few important similarities are noted between the NaL and AHA. Colloid formation in the AHA sample occurs at a cmc point of about 10 g L^{-1} . The surface tension at the cmc point is about 51 dyne cm^{-1} , which is much higher than the surface tension of solution ($\sim 25 \text{ dyne cm}^{-1}$) at the NaL cmc point. Thus humic materials per unit mass are much less surface active than strong surfactants like NaL. We speculate that the numbers of individual molecules that are present at the limit of surface saturation are lower for AHA than that given in Table 1 for NaL. Fewer numbers of molecules on the surface per unit area implies that AHA surface films are less condensed than NaL films. We suspect that the packing density of condensed films formed by water-soluble surfactant molecules in atmospheric particles are somewhere between NaL and AHA films.

We are unable to determine the adsorption parameters for AHA from the producers outlined above since the AHA sample is a mixture of many surfactant molecules. In the future we plan to fractionate the AHA (also Fulvic Acid) to determine how surface tension of humic materials varies as a function of molecular weight of their many components. This will allow us to report adsorption parameters for humic substances as a function of molecular weight of organic components that comprise each sample. We also plan to determine how solution pH, inorganic electrolytes and temperature affect the surface tension behavior of organic-containing aerosols in the atmosphere. For example, Fig. 4 shows that NaL at room temperature forms a gel when its aqueous concentration is only about 10 g L^{-1} . Gel formation of surfactants in aqueous solutions is known to amplify at colder temperatures [Myers, 1999]. Thus it is likely for surfactant materials in atmospheric aerosols, particularly at higher altitudes, to exist primarily in a gel rather than an aqueous phase in the atmosphere. Indeed, gel type materials have been observed on filter samples of submicron particles in the atmosphere [Mikhailov *et al.* 2004]. Such phase separations may not only affect the surface properties of organic-containing particles in the atmosphere, but also their hygroscopic and optical properties as well [Tabazadeh, 2005].

5. Conclusions

We outlined a procedure to determine adsorption parameters of organic molecules in aqueous solutions from composition-dependent surface tension measurements. We used the adsorption parameters to show that organic films on atmospheric particles are condensed rather than crystalline in nature. The latter assumption is often used in laboratory and modeling studies to mimic the surface composition of organic-containing particles in the atmosphere. Further, we calculated that most of the organic mass in submicron aerosols resides in the bulk rather than the surface of particles. This finding implies that oxidation of condensed phase organic matter in atmospheric aerosols is most likely controlled by bulk-phase oxidation pathways rather than surface processes. Finally surface activity of organics can vary over a wide range depending on their chemical composition. Therefore, it is unlikely for aerosol surface activity to be simply a function of the organic mass content of particles as generally assumed to be the case.

Acknowledgements

Funding for this project came mostly from the School of Earth Sciences discretionary funds at Stanford University. The undergraduate research advanced program (URAP) at Stanford University provided support for Jeremy Hiatt and Ben Cline.

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Table 1. Methanol and Sodium Laurate Adsorption Parameters

Solute	b	Γ_{∞} (mole cm ⁻²)	σ_{max} (μm^2 molecule ⁻¹)
Methanol	$.0202 \pm 6.50\%$	$5.12 \times 10^{-10} \pm 1.95\%$	3.24×10^{-7}
NaL	$.00426 \pm 3.76\%$	$4.85 \times 10^{-10} \pm 1.67\%$	3.42×10^{-7}

b and Γ_{∞} are the Langmuir adsorption constants determined at 20 °C. The adsorption parameters for methanol and NaL are valid below a mole fraction of 0.2 and 0.004, respectively. Methanol above a mole fraction of 0.2 forms a nonideal solution in water. NaL above a mole fraction of 0.004 forms colloids in water. The last column gives the surface area occupied by an individual molecule at surface saturation.

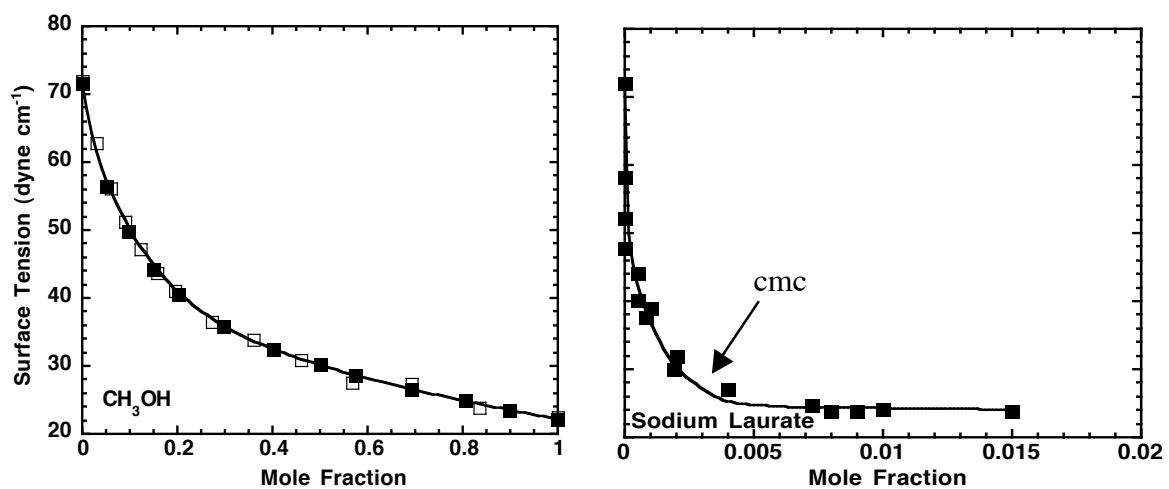


Figure 1. The left panel shows a comparison of surface tension measured in our laboratory, shown as filled symbols, against previous data [Vazquez *et al.*, 1995], shown as open symbols. The right panel shows surface tension of aqueous sodium laurate. The cmc of this solution is marked on the plot.

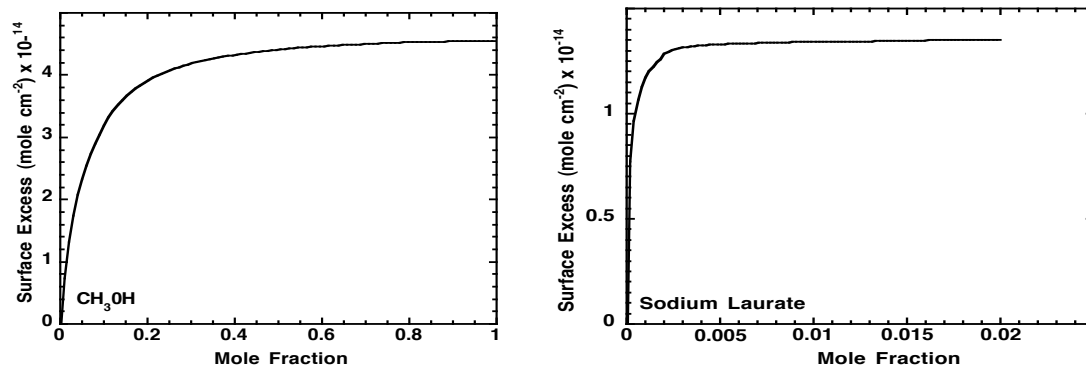


Figure 2: Surface excess as a function of mole fraction fitted into a Langmuir adsorption isotherm. The adsorption parameters used are given in Table 1.

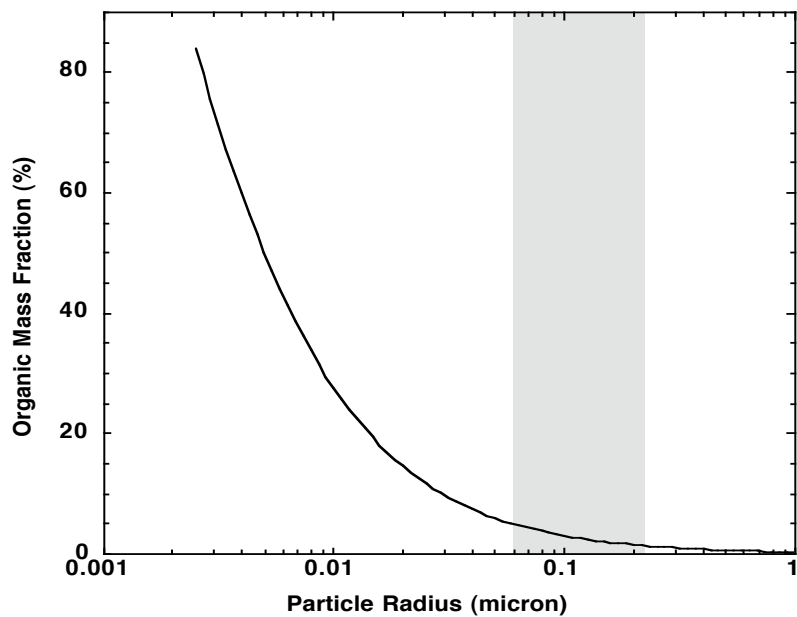


Figure 3. Variation of the organic mass content of an aerosol particle, confined to its surface, as a function of aerosol size. The line is obtained using equation (9). The area shaded gives a typical size range for organic aerosols [Seinfeld and Pandis, 1998]. In this range the organic mass on the surface, in the form of a condensed film, contributes only a few percent to the overall particle mass.

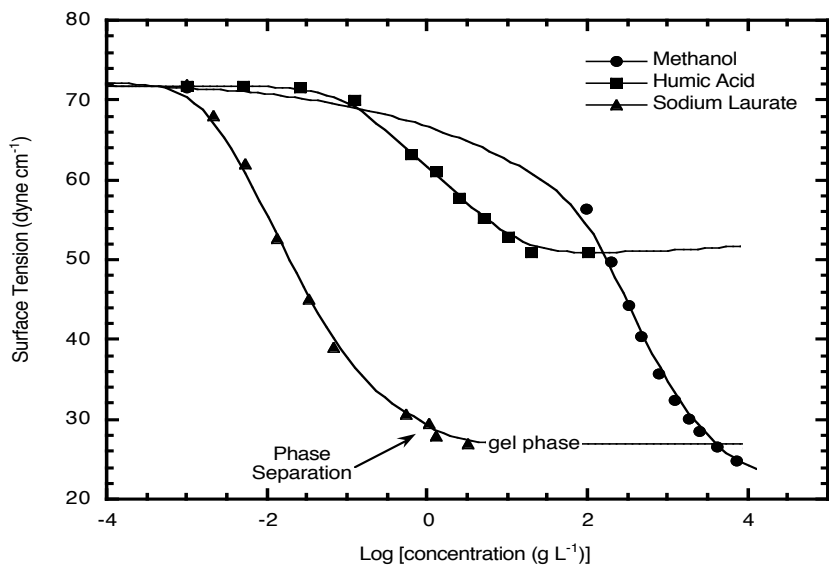


Figure 4. Variation of surface tension as a function of solute composition and concentration at 20°C. For sodium laurate a phase separation at the surface was noted when aqueous concentration was slightly above 1 g L⁻¹. For concentrations above 10 g L⁻¹ sodium laurate formed a gel in solution. Humic acid samples were allowed to equilibrate for 6 hours before surface tension was measured.