Organic aggregate formation in aerosols and its impact on the physicochemical properties of atmospheric particles

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Abstract

Fatty acid salts and “humic” materials, found in abundance in atmospheric particles, are both anionic surfactants. Such materials are known to form organic aggregates or colloids in solution at very low aqueous concentrations. In a marine aerosol, micelle aggregates can form at a low fatty acid salt molality of $\sim 10^{-3}$ m. In other types of atmospheric particles, such as biomass burning, biogenic, soil dust, and urban aerosols, “humic-like” materials exist in sufficient quantities to form micelle-like aggregates in solution. I show micelle formation limits the ability of surface-active organics in aerosols to reduce the surface tension of an atmospheric particle beyond about 10 dyne cm$^{-1}$. A general phase diagram is presented for anionic surfactants to explain how surface-active organics can change the water uptake properties of atmospheric aerosols. Briefly such molecules can enhance and reduce water uptake by atmospheric aerosols at dry and humid conditions, respectively. This finding is consistent with a number of unexplained field and laboratory observations. Dry electron microscope images of atmospheric particles often indicate that organics may coat the surface of particles in the atmosphere. The surfactant phase diagram is used to trace the particle path back to ambient conditions in order to determine whether such coatings can exist on wet ambient aerosols. Finally, I qualitatively highlight how organic aggregate formation in aerosols may change the optical properties and chemical reactivity of atmospheric particles.

Keywords: Organic aerosol; Micelle; Organic coats; Water uptake; Surface tension

1. Introduction

Polar organic molecules, which are capable of forming colloids in aqueous solutions, are important in many scientific and technological areas, including biological systems, medicine, detergency, crude-oil recovery, foods, pharmaceutical, and cosmetics (Myers, 1999; Lange, 1999). The atmosphere is an oxidizing medium and most condensable organics in aerosols are composed of polar oxygenated compounds (Facchini et al., 1999; Decesari et al., 2005; Graham et al., 2002; Mayol-Bracero et al., 2002; Russell et al., 2002; Cavalli et al., 2004), some of which are capable of forming colloids in solution. The results presented in this paper suggest that organic aggregates may play an important, yet unaccounted for, role in altering the basic physical and chemical properties of atmospheric particles.

The fine dry aerosol mass in the troposphere is often 50% or more organic by weight (Decesari et al., 2005; Cavalli et al., 2004; Graham et al., 2002; Mayol-Bracero et al., 2002). Hundreds of organic compounds have been identified in atmospheric aerosols (Rogge et al., 1993; Saxena and Hildemann, 1996; McMurry, 2000).

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However, this 5–10% known fraction is often limited to low molecular-weight species, which are readily identifiable by standard analytical techniques, using gas chromatography coupled with mass spectrometry (McMurry, 2000). To date a significant fraction of the organic mass in tropospheric aerosols, which is comprised of high molecular weight, oxygenated species, remains unidentified (Facchini et al., 1999, 2000; Deecesari et al., 2005; Russell et al., 2002; Graham et al., 2002; Mayol-Bracero et al., 2002; Cavalli et al., 2004). Recent analytical techniques have shown that some high molecular weight species found in atmospheric aerosols may be polymeric in character (Kalberer et al., 2004).

What is known and interesting about this unidentifiable organic mass fraction is that often a good fraction of it (30–80% by weight) is water-soluble (Havers et al., 1998; Zappoli et al., 1999; Gelencsé r et al., 2000; Cavalli et al., 2004; Graham et al., 2002; Mayol-Bracero et al., 2002). What types of known organic macromolecules are soluble in water and how do these large molecules dissolve in aqueous media? Here, I identify two mechanisms by which organic molecules and/or macromolecules can dissolve in large amounts in aqueous aerosol solutions, forming colloidal systems in atmospheric particles. The first is micelle formation in surfactant solutions found in marine particles. The second is formation of micelle-like structures by intra and/or intermolecular processes (Yates III and von Wandruszka, 1999; Rag le et al., 1997) in dissolved humic material found in marine, soil dust, biomass burning, biogenic and urban aerosols (Mukai and Ambe, 1986; Facchini et al., 1999, 2000; Deecesari 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 effects of colloid formation in aerosols on various physicochemical properties of atmospheric aerosols are discussed.

2. Aggregate formation in marine aerosols

Gill et al. (1983) first proposed the concept of organic molecules affecting the hygroscopic properties of atmospheric aerosols in 1983. They hypothesized that an organic film must cover the surface of most aerosol, fog and cloud droplets in the atmosphere, influencing their water uptake properties. Ellison et al. (1999) later developed Gill et al.’s hypothesis for a marine particle. Below I will briefly describe the main elements of the Ellison et al. model.

Biological degradation in ocean produces large amounts of fatty acids. The most common forms are stearic (C18) and palmitic (C16) acids. Fatty acids have a pKa in the range of 4.5, and therefore, in the ocean (pH ~8) they mainly exist in the ionic form. Based on the presence of large concentrations of fatty acids on the ocean surface, Ellison et al. suggested that an organic film, composed of stearate ions, might cover the surface of a marine particle, forming an “inverted micelle”. In an “inverted micelle” model, according to Ellison et al., a hydrophobic organic layer encapsulates the inorganic sea-salt solution (Fig. 1).

Ellison et al. presented the first model to describe how organic matter is physically distributed in an atmospheric particle, mainly in the form of a coating on the surface. Because the stearate ion is micelle forming in an aqueous solution (Myers, 1999; Lange, 1999), the formation of such aggregates, not accounted for in the Ellison et al. study, may prevent an enclosed film from developing on a marine particle surface. Fig. 1 shows the difference between a “micelle” model and an “inverted micelle” model in terms of the physical distribution of organic matter. Below I will use thermodynamics of aggregate formation (Myers, 1999) to investigate if stearate ion micelles can form in a marine particle, and how their formation may prevent organic coats from developing on the surfaces of marine particles. Before presenting arguments on the likelihood of micelle formation in a marine aerosol, I will briefly review some basic information on the properties of surfactant materials in aqueous solutions.

It is well known that salts of fatty acids, commonly found in seawater, are fine surfactants (Myers, 1999; Lange, 1999). To date surfactants have been assumed to only lower the surface tension of atmospheric particles by forming a complete or partial coating of organic molecules at the air–solution interface. However, in addition to lowering the surface tension, surfactants have other important colloidal properties, as illustrated in Fig. 2 (Myers, 1999, pp. 363–368). At a low molality, known as the critical micelle concentration (cmc), micelle aggregates form in a surfactant–water solution (Fig. 1). In Fig. 2 the effect of micelle formation on

![Fig. 1. An illustration of “micelle” (on the left) and an “inverted micelle” model (on the right) for the physical distribution of organic matter in a marine aerosol. The polar head group is shown as gray and the hydrophobic tail as black. Note that in the micelle model the organic molecule is water-soluble, whereas in the inverted micelle model it is assumed to be insoluble.](image-url)
various properties of atmospheric significance are highlighted and discussed briefly in the caption.

The cmc for fatty acid salts \((\text{CH}_3(\text{CH}_2)_n\text{COONa})\) in units of molality can be simply calculated from:

\[
\log_{10}\text{cmc} = 1.85 - 0.3n,
\]

where \(n\) is the number of carbons in the chain (Myers, 1999, p. 381). For example sodium stearate has a cmc of \(5.6 \times 10^{-4}\) m \((n = 17\) for sodium stearate) according to the above relation. Following the suggestion of Ellison et al., I assume the organic surfactant matter in a marine solution is made of stearate ions. This is a simplified assumption, however, aggregate formation is often enhanced in a mixture of surfactants (Myers, 1999, p. 387). For example, in a mixture of two fatty acid salts, the cmc is lower than the cmc of each individual component. Therefore in a marine particle, which most likely contains a complex mixture of many surfactants, the real cmc of solution is perhaps lower than that calculated here for sodium stearate. I will later extend the analysis to humic substances, which are comprised of a complex mixture of many surfactant molecules.

Table 1 gives inferred stearate ion molalities based on marine aerosol composition measurements off the West coast of Ireland in spring 2002 (O’Dowd et al., 2004). The organic mass fraction from these measurements is divided into two categories of water-soluble organic carbon (WSOC) and water-insoluble organic carbon (WIOC). I make the simple assumption that the WSOC and WIOC in the marine aerosol are water-soluble micelle-forming stearate ions and insoluble stearic acid, respectively. Later, I will extend this assumption to “humic-like” substances. From this assumption the stearate ion molality in solution is about 0.08–0.15 m (Table 1). This molality exceeds the cmc of sodium stearate \((5.6 \times 10^{-4}\) m) by over two orders of magnitude, indicating that the ions will aggregate up in solution to form micelles. Thus, over 99% of the stearate ion or the WSOC in the marine aerosol solution should be in the micelle form. Estimated numbers of micelles in solution for different size marine particles are given in Table 1.

The amount of organic matter measured in marine particles (Table 1) is inconsistent with an “inverted micelle” model (Ellison et al., 1999), which limits the organic mass content of a particle to just a monolayer

![Fig. 2. The range of cmc is shaded for anionic surfactants (Myers, 1999, p. 381). The atmospheric effect of each physical property is noted in parentheses. The change in surface tension arises because additional surfactant yields aggregates in solution pass the cmc point. This will affect the Kohler curve of an atmospheric particle (Seinfeld and Pandis, 1998, pp. 784–788). The change in conductivity arises due to increase in the mass per unit charge of the conducting species, which can affect the water uptake by an aerosol particle according to the ZSR relation since the ionic composition of a particle will change when aggregates form in solution (Seinfeld and Pandis, 1998, p. 535). The solubilization when micelles form is due to dissolution of hydrophobic matter in the hydrophobic cores of micelles in solution (see the illustration in Fig. 1). The turbidity arises because aggregates may scatter or absorb light more efficiently than a clear solution.](http://example.com/image)

### Table 1

<table>
<thead>
<tr>
<th>Size (μm)</th>
<th>WSOC</th>
<th>WIOC</th>
<th>OC\text{IM}</th>
<th>Molality</th>
<th>Micelle #</th>
<th>HULIS (g L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.060–0.125</td>
<td>23</td>
<td>60</td>
<td>&lt;30</td>
<td>0.15</td>
<td>8.4 \times 10^{-3} – 7.6 \times 10^{-2}</td>
<td>36</td>
</tr>
<tr>
<td>0.125–0.250</td>
<td>18</td>
<td>45</td>
<td>&lt;18</td>
<td>0.11</td>
<td>5.8 \times 10^{-3} – 4.6 \times 10^{-3}</td>
<td>27</td>
</tr>
<tr>
<td>0.250–0.500</td>
<td>18</td>
<td>44</td>
<td>&lt;15</td>
<td>0.11</td>
<td>4.6 \times 10^{-3} – 3.7 \times 10^{-3}</td>
<td>27</td>
</tr>
<tr>
<td>0.500–1.000</td>
<td>12</td>
<td>29</td>
<td>&lt;8</td>
<td>0.08</td>
<td>2.5 \times 10^{-3} – 2.0 \times 10^{-3}</td>
<td>18</td>
</tr>
</tbody>
</table>

Data in the first 3 columns are taken from O’Dowd et al. (2004), which represent the measured dry weight % of each component. The OC\text{IM} gives the total allowable organic mass (WSOC + WIOC) in wt% based on the “inverted micelle” model assumption as calculated by Ellison et al. (1999). The molality column gives the stearate ion molality assuming all the WSOC was made of stearate ions. The micelle column gives the number of stearate ion micelles needed to bring the stearate ion molality down to the cmc value of \(5.6 \times 10^{-4}\) m. For these calculations I assumed all the WSOC mass was made of stearate ions and each micelle contained 100 stearate ion molecules, which is at the higher end for anionic surfactants (Myers, 1999, p. 379). For the last column, I assumed all the WSOC mass was HULIS and its aqueous concentration in the particle is given in units of g L\(^{-1}\). All calculations were performed assuming a standard sea-salt model in which the particle is 85% by mass water (Andreas, 1992).
(Fig. 1). For example, during bloom period marine particles in the size range of 0.5–1 μm are 41% by mass organic, whereas the “inverted micelle” or coat model allows for less than 8% of total organic mass in a given particle (Table 1). Based on large organic mass fractions measured in marine particles and the fact that the cmc for sodium stearate is <10⁻³ m (see above), the stearate ion “inverted micelle” model for a marine aerosol is highly unlikely. Instead large mass fractions of organics in marine aerosols are possible according to the “micelle” model, where WSOC forms micelles and the WIOC can be solubilized, at least to some extent in micelles dissolved in solution. The solubilization process is identical to the removal of oil stains by soap particles. Soap in water forms micelles, similar to the ones formed in marine particles, and hydrophobic material can dissolve in the core of soap or marine aerosol micelles (Figs. 1 and 2).

### 3. General phase diagram for anionic surfactants

Fig. 3 shows a typical binary phase diagram for an anionic surfactant–water solution such as sodium stearate found in seawater. A standard model for a marine particle at 80% relative humidity is about 85% water by mass (Andreas, 1992). For this high water content, the surfactant–water solution is in the micelle regime and there is enough surfactant matter in the marine aerosol, as calculated above, to form micelles in the particle. When the aerosol is collected and dried for analysis, the surfactant–water mixture can form a liquid crystalline phase, which is a highly viscous liquid state (Fig. 3). This material may contribute to some of what is classed as humic-like substances (HULIS) collected on filter samples of marine and other types of atmospheric aerosols (Facchini et al., 1999, 2000; Deecesari et al., 2005; Havers et al., 1998; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Cavalli et al., 2004).

I note that at low relative humidity, the liquid crystalline phases can still absorb a substantial amount of water as evident in Fig. 3. For example at 50% RH, a standard marine aerosol (or NaCl solution) is about 40% water by mass (Andreas, 1992). Under these conditions, the surfactant–water system is in the liquid crystalline (Fig. 3). This water-absorbing property of a liquid crystal, which differs from that of a solid crystal, may help to explain why surface-active organics at low relative humidity appear to absorb more water relative to inorganics (Dick et al., 2002; Brooks et al., 2004; Carrico et al., 2005), which tend to form solid crystals under dry conditions and lose their hygroscopicity. Also laboratory studies (Mikhailov et al., 2004) show that aerosol surface-active organic species appear to form a gel-like phase when dried, which lends support to formation of liquid crystalline phases in atmospheric particles under dry conditions.

It is important to account for the water content of the aerosol in the real atmosphere to determine the actual phase of the organic surfactant matter in solution. Many sampling and analysis techniques are conducted at high temperatures and/or dry conditions (Jacobson et al., 2000), which could shift the state and the physical distribution of surfactant organic matter in the particle in different dimensions (Fig. 3). For example, if the sample is heated to high temperatures and/or dried off relative to its ambient state, viscous liquid crystalline states may phase separate and coat the inorganic salts crystallized in the sample under more extreme conditions than those prevalent in the atmosphere. In a real ambient particle, at higher relative humidities and lower temperatures, both inorganics and organics may be dissolved in solution. Thus, the apparent coating reported (Husar and Shu, 1975; Pósfai et al., 1998; Tervahattu et al., 2002; Russell et al., 2002; Rudich,
Using the phase diagram, I now return to the subject of “inverted micelles” or organic coats on atmospheric particles. For anionic surfactants “inverted micelles” form at high surfactant concentrations and high temperatures (see Fig. 3). In other words, “inverted micelles” form in anionic surfactant solutions when the surfactant becomes the solvent and the water becomes the solute. Also, the high temperatures (>150 °C) needed to form inverted micelles are inaccessible in the atmosphere. The “inverted micelle” term as used in the Ellison et al. (1999) study is different than the one depicted in Fig. 3, which is the term used for such a system in colloidal science. The “inverted micelle” term used by Ellison et al. (1999) is basically a particle with a hydrophobic coat immersed in air, whereas the standard “inverted micelle” is a small aggregate formed when micelles shown in Fig. 1 invert in solution at high surfactant concentrations and high temperatures. In the atmosphere temperatures are relatively low (<30 °C). Thus the ideal phase for an anionic surfactant is the micelle and not the “inverted micelle” phase. Once micelles form the concentration of free surfactant molecules in solution is very low (cmc values in Fig. 2 for anionic surfactants are below 0.6 m), making it difficult for a full organic coat to develop on the particle surface (Djikaev and Tabazadeh, 2004).

When surfactants or amphiphiles form a full coat on water the surface tension of water is known to drop from its pure value at ~72 dyne cm⁻¹ to a range of between 20 and 40 dyne cm⁻¹ (Lange, 1999, p. 16). Thus, full coatings of amphiphiles can reduce the surface tension of pure water by about 30–52 dyne cm⁻¹. On the contrary, surface tension measurements, using surface-active organics found in atmospheric aerosols, indicate that such materials can only lower the surface tension of water by about 18 dyne cm⁻¹ (Facchini et al., 2000) or even less according to more recent and accurate measurements (Decesari et al., 2003). These observations indicate that full coatings of organic surfactants, as proposed by Gill et al. (1983) and Ellison et al. (1999), are unlikely to be present on ambient particles in the atmosphere since the magnitude of surface tension reduction measured for field samples (Facchini et al., 2000; Decesari et al., 2003) is well below the expected level for complete coatings of known amphiphiles.

4. Aggregate formation in HULIS-containing aerosols

The stearate ion “micelle” model proposed above for a marine aerosol is highly simplified because many other high molecular-weight organic components, including WSOC and WIOC, are also present in a marine aerosol (Cavalli et al., 2004). One such component is humic-like materials, which are comprised of high molecular-weight polycarboxylic acids (Cavalli et al., 2004 and references therein). Briefly, humic substances are pigmented polymers and come in three broad categories; fulvic acid, humic acid and humin, and are formed by degradation of biological matter in soil and water (Yates III and von Wandruszka, 1999). Fulvic acid has a molecular weight in the range of 500–5000 amu; it is light yellow to yellow brown and is soluble in water at all pH values. Humic acid has a molecular weight in the range of 5000 to about a million amu; it is dark brown to gray-black and is soluble in water at pH >2. Humin has a molecular weight larger than a million amu; it is black and insoluble in water at all pH values.

Many observations of fine tropospheric aerosols show that humic-like substances (HULIS) are present in large amounts not only in marine aerosols but also in soil dust, biomass-burning, biogenic, and urban aerosols (Mukai and Ambe, 1986; 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). An approximate aqueous concentration range (18–36 g L⁻¹) for HULIS is quoted in Table 1 for fine marine aerosols. Because marine aerosols are dilute samples (>85% by mass water), I suspect HULIS aqueous concentration to be larger (>36 g L⁻¹) in other types of atmospheric particles. In addition to HULIS contained in natural particles, such as marine, soil dust, and biomass burning aerosols, a number of studies show that HULIS can form in biogenic (Limbeck et al., 2003) and urban (Havers et al., 1998) aerosols through secondary organic aerosol (SOA) formation mechanisms. There is also indication for in situ formation of HULIS in fog and cloud droplets through cloud processing of ambient aerosols (Gelencsér et al., 2003). The HULIS material formed in situ in the atmosphere has chemical characteristics (aromatic rings, carboxylic groups, phenol groups, alkyl moieties, etc.) very similar to that of natural humic matter, but has a relatively lower molecular weight as compared to natural forms (Kiss et al., 2003).

Aqueous solutions of both fulvic and humic acids show surface-active properties very similar to those shown for anionic surfactants in Figs. 2 and 3 (Yates III and von Wandruszka, 1999; Ragle et al., 1997). Fig. 4 shows the variation in surface tension of dilute aqueous solutions of fulvic and humic acids as a function of solution pH. In the atmosphere, the pH of particles can vary over a wide range. For example, recent measurements in Southwest China show a range of pH variations in urban aerosols from about 4 to 9 (Xiao and Liu, 2004). Thus, the ranges of variation in pH shown in Fig. 4 are applicable to the atmosphere.
Surface Tension (dyne cm\(^{-1}\))

Fig. 4. Variation in surface tension as a function of pH (shown in black) for solutions of fulvic and humic acids. Also shown in gray is variation in surface tension as a function of sodium ion concentration for humic acid solutions at pH of 6. Symbols are raw data taken from Yates III and von Wandruszka (1999). The fulvic acid solutions were SRFA (Suwannee River fulvic acid) and the humic acid solutions were LSLHA (Latahco silt loam humic acid). Yates III and Wandruszka present data for a number of different humic acid and humic acid–metal ion solutions. I chose only LSLHA for illustrative purposes since similar conclusions are drawn from all different humic samples studied. Acid concentrations for all cases were 0.5 g L\(^{-1}\). Solid lines are polynomial fits to the data. Dashed-line marks the surface tension of pure water at 25 °C.

The lowest surface tension point in Fig. 4 is \(\sim 62\) dyne cm\(^{-1}\), which is about \(10\) dyne cm\(^{-1}\) below the surface tension of pure water. Since aggregates are already present in such a dilute solution, I suggest that for humic substances the cmc must be below 0.5 g L\(^{-1}\), which was used in the experiments shown in Fig. 4. In atmospheric particles HULIS is present at concentrations above 36 g L\(^{-1}\) (see above). From Fig. 2 any additional HULIS above the cmc limit must form aggregates in solution. Thus, I suggest the HULIS component in atmospheric aerosols may only reduce the surface tension of a particle by about 10 dyne cm\(^{-1}\), which is consistent with what is inferred from field observations (Facchini et al., 2000; Deccesari et al., 2003). Nevertheless, as shown by Facchini et al. (1999) such changes in surface tension, even if they are about 10 dyne cm\(^{-1}\), can still have a large influence on cloud activation in the atmosphere.

The aqueous concentration of HULIS, which comprises the main fraction of WSOC in atmospheric particles (Facchini et al., 1999, 2000; Deccesari et al., 2005; Havers et al., 1998; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Cavalli et al., 2004) is significantly larger (\(> 36\) g L\(^{-1}\), see above) than those used (0.5 g L\(^{-1}\)) in the experiments shown in Fig. 4. Thus, in aerosols, which contain small amounts of metal ions, humic-like colloidal aggregates are very likely to be present in large amounts in aqueous solutions. Aggregate formation in HULIS-containing atmospheric particles will have an effect on the particle surface tension (Fig. 2). In fact the range of variations in surface tension measured (\(\sim 10\) dyne cm\(^{-1}\)) for field samples (Facchini et al., 2000; Decceresari et al., 2003) are in agreement with variations in surface tension changes measured for humic substances in the laboratory (Fig. 4). Decesari et al. (2003) has also noted that measured surface tensions for field samples show similar variations in surface tension as those determined in the laboratory for fulvic acid.

In a recent laboratory study, a 10 g L\(^{-1}\) solution of humic acid has been shown to reduce the surface tension of water by 15 dyne cm\(^{-1}\) (Tuckerman and Cammenga, 2004), which is somewhat higher than the cmc limit I set above for HULIS. This limit indicates that the

When metal ions are added to aqueous solutions of fulvic and/or humic acids micelle-like aggregates are known to form by intermolecular aggregation and/or intermolecular coiling (Yates III and von Wandruszka, 1999; Ragle et al., 1997). The effect of adding metal ions to a humic acid solution is shown in Fig. 4. As sodium ion is added it will cause rearrangement of functional groups in macromolecules of fulvic and/or humic acids.
maximum reduction in surface tension by HULIS in atmospheric particles is about 10 dyne cm\(^{-1}\). However, the samples studied by Tuckermann and Cammenga were devoid of metal ions, which are known to induce aggregate formation in humic acid solutions (Yates III and von Wandruszka, 1999; Ragle et al., 1997). When aggregates form an upper limit for surface tension, reduction can be set for a given amphiphile according to Fig. 2, and for HULIS in the presence of metal ions that may be around 10 dyne cm\(^{-1}\), as explained above.

Field and laboratory observations indicate that at high relative humidity some organics, probably HULIS, can reduce the ability of a particle to uptake water (Saxena and Hildemann, 1997; Brooks et al., 2004; Carrico et al., 2005). This may be due to entrapment of metal ions or cations by humic aggregates in solution. The uptake of water by free metal ions in solution is well understood and modeled. According to the ZSR method (Seinfeld and Pandis, 1998, p. 535), each free ion in solution has a given amount of water associated with it, which varies as a function of water activity in solution. Ironically, the cause of water uptake (Saxena and Hildemann, 1997; Carrico et al., 2005) reduction by some WSOC may be due to removal of cations from the aqueous solution and not the physical attachment of the WSOC to the particle surface as currently hypothesized (Gill et al., 1983; Ellison et al., 1999). The latter assumes that a full organic coat on the particle surface can slow down the rate of water transport to the particle. As suggested above, it is unlikely for anionic surfactants to form complete coats on ambient particles in the atmosphere due to aggregate formation. Thus, the cause of water uptake reduction by surface-active organics at high relative humidity may be related to complex interactions between the humic-like aggregates and inorganic cations in solution. If inorganic ions in solution form thermodynamically stable complexes with humic aggregates, which are anionic in character, then they are not free, as assumed by the ZSR relation, to uptake water from the atmosphere with increased humidity.

In many classes of atmospheric particles, ranging from purely natural to highly urbanized and polluted, metal ions are often abundant (Seinfeld and Pandis, 1998, pp. 440–444). Thus humic and fulvic acid-like molecules, measured in large amounts in atmospheric particles (Facchini et al., 1999, 2000; De cesari et al., 2005; Havers et al., 1998; Zappoli et al., 1999; Graham et al., 2002; Mayol-Bracero et al., 2002; Cavalli et al., 2004), are most likely present in colloidal systems in aerosol solutions. It is important to account for this colloidal nature because it will not only affect the particle surface tension and its hygroscopicity, as suggested above, but also the ability of the aerosol as a whole to solubilize volatile and hydrophobic organic matter in solution. For example, humic acid-aggregates formed in aqueous solutions are shown to have strong ability to solubilize hydrophobic (Ragle et al., 1997) and slightly soluble toxic organic compounds such as polycyclic aromatic hydrocarbons (Cho et al., 2002). The latter is primarily emitted from anthropogenic sources, and its aqueous concentration in atmospheric aerosols can be enhanced by uptake in humic aggregates.

5. Discussion

A recent study (Maria et al., 2004), based on analysis of field observations, provides circumstantial support for the presence of micelles in atmospheric aerosols. The study suggests that the rate of oxidation of organics in atmospheric aerosols may be a factor of 3 slower than that assumed by current models. The reason for this difference may relate to micelle formation. Micelles in solution can sweep hydrophobic organic matter off the surface and solubilize hydrophobic and volatile organic matter in solution (Ragle et al., 1997; Cho et al., 2002). Both factors can shield and prevent organic molecules from participating in known reaction pathways involving bulk or surface mechanistic steps.

Formation of micelles and/or micelle-like aggregates in an aerosol solution can also alter its scattering efficiency. Experimental studies show that when cmc of a surfactant–water solution is reached the bulk solution becomes turbid and milky (Myers, 1999, pp. 363–368). As more surfactant is added to the solution, pass the cmc point, the turbidity in the solution increases due to increase in the number of aggregates formed in solution (Fig. 2). The fact that the bulk solution becomes turbid and milky indicates that aggregates can scatter or absorb light more efficiently than a clear solution. As discussed above both fatty acid salts and humic materials are present in sufficient quantities in atmospheric particles to yield organic aggregates in solution. Once aggregates form, the resulting particle may become more or less reflective of solar radiation than a particle with the same chemical composition, but lacking organic aggregates in solution.

I note that the turbidity observed in a bulk sample, when micelles form, may not occur in atmospheric particles. The number of micelles in one m\(^3\) of bulk solution is at least a million times larger than those found in 1 m\(^3\) of air, which contains less than one gram of condensed solution. Thus, for knowledge no radiative transfer algorithm is currently available to treat a system of spherical micelles internally mixed in spherical particles immersed in air. Therefore, at this point, the
net effect of organic aggregate formation in aerosols on radiative transfer through the atmosphere remains uncertain and requires further investigation.

In this study, I presented a model to describe how soluble organic matter is physically distributed in atmospheric aerosols. I showed that the WSOC in solution exists mainly as micelles or micelle-like aggregates. Formation of such aggregates increases the solubility of both WSOC and WIOC in aqueous solutions of atmospheric particles. Colloidal materials in solution can influence important chemical and radiative properties of atmospheric aerosols. For example, I qualitatively highlighted how organic aggregates may alter the basic properties of aerosols, such as their reflectivity and reactivity. Organic aggregates also provide favorable conditions for complex interactions to take place in solution between organics and inorganics, making the use of the standard ZSR method to calculate the aerosol water content somewhat problematic. Surely there are many more subtle effects, such as CCN activation, ice nucleation, solubilization of both volatile and hydrophobic organic matter, light extinction, visibility, etc., which need to be explored by undertaking experimental and modeling studies to account for the colloidal nature of atmospheric particles.

In conclusion, it is very desirable to determine the factors that control the concentration and composition of organic aggregates in aqueous solutions in order to isolate and better understand how condensable organics can affect the physicochemical properties of atmospheric particles. Studies are underway to determine the effects of inorganic salts and pH on the onset of aggregate formation in different types of atmospheric particles.

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