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Enrichment of surface-active compounds in coalescing cloud drops

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[1] Surfactants often found in tropospheric aerosols, can affect the onset and development of clouds. Due to high dilution during droplet growth, the effects of surfactants on cloud microphysical processes have been mostly neglected. However, while cloud growth by coalescence conserves the combined volume of all cloud droplets, it reduces the combined surface area. This could lead to enrichment of water-insoluble surfactants (WIS) and to reduced surface tension of droplets forming in warm processes. Measurements of individual raindrops reveal the presence of water insoluble surfactants. Our field and laboratory studies as well as simple theoretical arguments suggest that by causing varying and size-dependent surface tension, WIS can affect cloud microphysics. Citation: Taraniuk, I., A. B. Kostinski, and Y. Rudich (2008), Enrichment of surface-active compounds in coalescing cloud drops, Geophys. Res. Lett., 35, L19810, doi:10.1029/2008GL034973.

1. Introduction

[2] Clouds, aerosols and their mutual interactions are recognized as a major uncertainty in our understanding of and ability to predict climatic changes [Solomon et al., 2007]. The difficulty arises because processes that occur on microscopic scales, namely aerosol activation, condensational growth, and finally the coalescence of cloud drops, eventually determine the macroscopic properties of clouds such as their lifetime, precipitation efficiency, and albedo [Baker, 1997; Baker and Peter, 2008]. Diffusional growth of cloud droplets occurs via activation of aerosols serving as cloud condensation nuclei (CCN) followed by the subsequent condensation of water vapor. Surfactants (soluble and insoluble), often abundant in CCN aerosols [Charlson et al., 2001; Ervens et al., 2005; Facchini et al., 2000, 1999; Feingold and Chuang, 2002; Latif and Brimblecombe, 2004], can dissolve in the forming droplet, reduce its surface tension and lower the water vapor concentration required for the activation. This possibility for promoting the onset of clouds has prompted considerable research on the role of water-soluble organic surfactants in CCN activation [Asa-Awuku and Nenes, 2007; Broekhuizen et al., 2004].

[3] In contrast, neither the later stage of droplet growth nor the possible effects of water-insoluble surfactants (WIS) have received much attention in this context. This appears reasonable as a factor of 20 or so increase in droplet radius (from ~0.5 to 10 μm) during the diffusional growth stage dilutes the original CCN material by about 10^3–10^4, implying negligible surfactant concentrations in the formed droplets. However, where water insoluble species are concerned, it is the surface concentration that affects surface tension, not the bulk concentration. While conserving the total volume of cloud water and the mass of surfactants in the cloud, the coalescence process decreases the total surface area of the cloud drops, and the total surface area of cloud drops scales as their inverse radius. Therefore, coalescence can enrich the WIS surface concentration and hence, lower surface tension of some of the coalescing drops. An important question in this respect is: can coalescence occasionally compensate for the high dilution of surfactants during the diffusional growth and restore their importance as drizzle or rain develops? Our field observations and laboratory experiments demonstrate that under some circumstances it does.

[4] Consider, for clarity, cloud drops of a single diameter d_0 whose surfactant surface concentration is c_0 ∼ m/d_0^2, where m is the amount of the surfactant and d_0 is on the order of 1 μm. Next, let the droplets grow by diffusion so that the surface concentration decreases as d^-2 during the diffusional growth stage. At some size (typically about 20–40 μm, denoted d_1), cloud drops start to grow by collisions and coalescence. At this point the WIS surface concentration reaches its minimum c_{min} = c_0(d_0/d_1)^2 but then begins to increase linearly with the droplet diameter. Eventually, this growth period terminates as the falling drizzle or raindrop leaves the cloud. Denoting the final size d_2, the final surfactant concentration is given by c_{final} = c_0 d_2^2/d_1^4. Note that the final concentration depends cubically on d_1, thus containing a memory of the transition from diffusion to coalescence mode of growth.

[5] In reality, the initial conditions as well as the coalescence history are random [Kostinski and Shaw, 2005], so that strongly fluctuating distribution of c_{final} is expected to occur. Taking average values of d_0 = 1 μm, d_1 = 20 μm, d_2 = 10^3 μm = 1 mm gives d_2^2/d_1^4 ≈ 0.125, so that the average final surface concentration is much lower than the original surface concentration. However, the final concentration is very sensitive to growth history. For example, doubling the initial droplet size (e.g., giant nucleus) and halving d_1 results in the final concentration reaching the initial one on a 250-micron drizzle drop. Such calculations suggest strong fluctuations in warm rain (no ice growth by diffusion) that could marginally produce a weak signal in bulk rainwater [Seidl and Hanle, 1983]. To overcome the difficulty of detecting such a weak signal, we examined the surface tension behavior of individual raindrops. We complemented these experiments by laboratory measurements of the surface tension of droplets containing water soluble...
and water insoluble surfactants during several coalescence events.

2. Experimental

2.1. Procedure of Surfactants Isolation From Aerosol Samples

[Aerosol particles were collected in the Rehovot, Israel during a nation-wide intensive wood burning event (May 5, 2007), with average PM10 mass concentration of 300–400 µg m$^{-3}$. The particles were sampled on a pre-heated quartz fiber filter by a high-volume sampler with a flow rate of 70 m$^3$ h$^{-1}$ for 6 hours.]

The filters were extracted by water 3 times for 24 hours by 150 ml of DDW. After decanting, water-soluble humic like substances (HULIS) were extracted from the supernatant as described by Dinar et al. [2006]. Following extraction of the water soluble HULIS, water-insoluble alkaline-extractable material was isolated. The filter was extracted three times by 150 ml of 10 mM NaOH solution in a shaker. The alkaline extract was filtered through 0.45 µm hydrophilic polyethersulfone membrane filter and its pH was adjusted to 1 by 6 M HCl. The precipitated material was centrifuged and washed three times by HCl and HF (1:1) mixture to remove SiO$_2$. Residuals of inorganic and small organic acids were washed with water until a neutral pH was achieved. The resulting material was freeze-dried.

2.2. Coalescence Experiments

To mimic coalescence, a pendant drop (pre-loaded with surfactants) was released onto a sessile drop. The surface tension of the pendant drop, formed at the tip of a syringe needle with micrometer dosage, was determined by axial-symmetric drop shape analysis (ADSA) [Dukhin et al., 1995] and [Hoofar and Neumann, 2006], using a Rame-Hart goniometer. Upon detachment from the needle, the drop collided with a sessile drop located 0.1 cm below without splashing and material loss. The sessile drop was placed in a 0.5 mm deep Teflon well of 18.2 mm diameter. The initial sessile drop volume of 500 µl was increased by 2.0 ± 0.1 µl with each addition of the pendant drop. The surface tension of the sessile drop was measured with a DeltaPi tensiometer (Kibron Ltd.) by the Wilhelmy method. After each measurement, the probe was cleaned from organic material in a flame to avoid accumulation of organic material.

2.3. Deposition Procedures for Generating Drops With WIS and WS

2.3.1. Drops With Water-Soluble HULIS Surfactants

[Aqueous solution (2.5 g L$^{-1}$, surface tension of ~37 mN m$^{-1}$) of the water-soluble HULIS extracts was used for generating drops. High concentrations were used to minimize the equilibration time after collisions.]

2.3.2. Drops With Water-Insoluble Surfactants

[Stearic acid was directly deposited on the drop surface as follows: n-hexane solution (0.67 × 10$^{-4}$ M, 0.5 µl) of stearic acid was dispensed on the pendent droplet’s surface using a micro-syringe. Following hexane evaporation, a droplet covered by stearic acid formed. The insoluble surfactants studied here are soluble in a basic medium but not in neutral or an acidic one. For deposition of the surfactants, a new procedure was developed. 0.5 µl of a 1 g L$^{-1}$ solution containing surfactants in 0.1 M NaOH was dispensed using a micro-syringe onto a 1.0 µl pendant drop containing 0.1 M HCl. The surfactants concentration is comparable to total surfactant concentrations found in real samples at 50–60 mN m$^{-1}$. The volumes of the pendant drop and the added solution were adjusted so as to neutralize the deposited alkaline solution but still maintain a slightly acidic pendant drop. The neutralized organics are insoluble in the acidic pendent drop and hence segregate to the droplet’s surface. The initial surface tension value after neutralization was 50–60 mN m$^{-1}$. Then, by increasing the drop volume to 2.0 µl, the surface tension increased to that of pure water and the droplet detached from the needle.]

2.4. Raindrop Surface Tension Measurements

Individual raindrops were collected by impaction into a liquid nitrogen dewar, instantly freezing upon impact [Bachmann et al., 1993] and preserving any existing surface film. Individual frozen drops were selected attached to the tip of a water-filled needle by freezing of the water inside the needle. The drops thaw (turbidity vanishes) ~1 minute so that their surface tension can be measured. To minimize loss of surface material, we used the axisymmetric drop shape analysis (ADSA) of a pendant drop for measuring surface tension. Using the syringe, varied amounts of the rain drop water were withdrawn and its volume decreased. The presence of WIS was deduced from observed decrease of the surface tension with the raindrop surface area.

3. Results and Discussion

Figure 1 presents surface tension measurements of individual raindrops collected in a warm rain event in Rehovot, Israel on Nov. 21, 2007. We measured the surface tension (in a pendant drop goniometer) of individual drops versus their surface area. Surface area was varied by withdrawing interior water with a syringe. The upper trace (open circles) represents the behavior of laboratory-made drops containing pure water. As the surface area decreased, the surface tension remained essentially constant (aside from an artifact of the surface tension retrieval algorithm for nearly spherical pendant drops that leads to some increase of ST; see Figure 1 caption). Natural raindrops were examined next. Remarkably, there are two distinct groups: 6 out of the 36 drops examined show a striking decrease of surface tension with decreasing surface area (solid squares in Figure 1). This behavior is typical of drops covered by insoluble surfactants and is similar to the behavior of drops covered by stearic acid: a well-known surfactant. The remaining 30 raindrops behave as the pure water reference drops (open squares in Figure 1 (top)) indicating that they either contain no surface-active material at all or water-soluble surfactants only. This finding reveals the presence of insoluble surfactants on some of the raindrops (about 12%) and confirms the predicted strong drop-to-drop fluctuations. Because this rain was stratiform, raindrops larger than 5 mm were not observed; therefore raindrop break-up was not significant.

Our observations suggest that water-insoluble surfactants are present in ambient atmospheric aerosols. To that end, we tested for the “coalescence enrichment” effect in laboratory experiments with soluble and insoluble surfac-
Two distinct groups: 6 WIS-containing raindrops evidenced by the decrease in surface tension with decreasing surface area (solid symbols), and 30 WIS-free raindrops are evidenced by overlapping with the pure water reference drops (open symbols). Despite undetectable average WIS concentration in this rainwater, WIS presence is detected in some individual raindrops. WIS cannot leave the drop surface so that the increasing surface concentration of the shrinking drop decreases surface tension (ST), thus providing WIS signature (solid squares). WIS-free raindrops, in contrast, maintain constant surface tension (open symbols). Behavior consistent with presence of water-insoluble-species was observed on 6 individual raindrops by decreasing the drop volume after drawing water from its interior with a syringe (6 symbols for the 6 drops measured).

containing water-soluble HULIS show that the surface tension is independent of coalescence events since the bulk concentration remains constant (Figure 2, solid circles). These experiments demonstrate surface tension reduction upon coalescence of droplets containing insoluble atmospheric surfactants due to their enrichment at the surface.

The discovery of insoluble organics on some collected raindrops reveals the importance of water insoluble surfactants and the associated fluctuations and size dependence of surface tension during the coalescence growth regime. This can set off a chain of implications in cloud microphysics. Surface tension via the Weber number may effect the size distribution of cloud drops and warm rain initiation [Brown, 1986; Ryan, 1976; Testik and Barros, 2007]. It affects the terminal speed and oscillation frequencies of drops [Brown, 1986; Donaldson et al., 2001; Ryan, 1976]. Surface tension values similar to those measured in our experiments for the atmospheric insoluble species (~52 mN m\(^{-1}\)) would reduce the size for the onset of instability by about 30% compared to drops with the surface tension value of water [Brown, 1986] and would promote fragmentation [Ryan, 1976]. In addition, WIS films may limit water evaporation rates from raindrops [Ervens et al., 2005]. Evaporation of falling raindrops would decrease surface and compress the film to the semi-solid state, thereby preventing further evaporation [Donaldson and Vaida, 2006]. The coalescence enrichment mechanism can operate only when water-insoluble surfactants are present, and may affect cloud properties in clouds forming in biomass burning plumes or over oceans. Finally, it remains to be studied how would such evaporated droplets, with enriched concentration of non-soluble organic surfactants, behave once they enter a second (or later) cloud cycle.

The insoluble organic fraction of aerosol can constitute 50–60% of the organic component, which can be
substantial in some aerosol types such as secondary organic aerosols, biomass burning, sea spray and pollution aerosols [Feczko et al., 2007; O’Dowd et al., 2004]. While the major sources of WIS surfactants are probably direct emissions of such compounds from vegetation, ocean spray, wood and fuel burning, it has been suggested that aerosol and cloud drops may themselves be the place of formation of such insoluble species. For example photo-polymerization of small molecular weight organics can lead to formation of oligomers [Gao et al., 2004; Kalberer et al., 2004; Mancinelli et al., 2006; McFiggans et al., 2006] which could be surface active and water insoluble. Acidification of raindrops by NOx and CO2 uptake can decrease the solubility of water-soluble surfactants initially present in a drop solution.

[16] Organic films at the air/water interface have also been suggested as key players in enabling the beginning of life. Dobson et al. [2000] suggested that drops covered by organic films could act as possible prebiotic reactors by isolating and concentrating chemicals in small drops. The formation of such drops requires the presence of compressed layers of surfactants, completely covering the drop surface. Our study suggests that WIS surfactants containing cloud drops can provide a complementary mechanism. Small organics existed in the early Earth atmosphere, and could have dissolved in cloud drops. Photochemical reactions could then have formed higher molecular weight insoluble organics which could form the films by collision and coalescence.

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References


