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The effect of fatty acid surfactants on the uptake of ozone to aqueous halogenide particles

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Abstract

The reactive uptake of ozone to deliquesced potassium iodide aerosol particles coated with linear saturated fatty acids (C_9 , C_{12} , C_{15} , C_{18} and C_{20}) as surfactants was studied. The experiments were performed in an aerosol flow tube at 293 K and atmospheric pressure. The uptake coefficient on pure deliquesced KI aerosol was $\gamma = (1.10 \pm 0.20) \times 10^{-2}$ at 72–75% relative humidity. In presence of organic coatings, the uptake coefficient decreased significantly for long straight chain surfactants ($>C_{15}$), while it was only slightly reduced for the short ones (C_9 , C_{12}). We linked the kinetic results to the monolayer properties of the surfactants, and specifically to the phase state of the monolayer formed (liquid expanded or liquid condensed state). We also investigated the effect of organic films to mixed deliquesced aerosol composed of a variable mixture of KI and NaCl, which allowed determining the resistance exerted to O_3 at the aqueous surface by the two longer chained surfactants pentadecanoic acid (C_{15}) and stearic acid (C_{18}). Finally, the effect of two-component coatings, consisting of a mixture of long and short chained surfactants, was also studied.

1 Introduction

Atmospheric aerosols contain a complex mixture of inorganic and organic compounds. It has been determined that organic species represent a significant percentage (20–90%) of the total mass fraction of the submicron aerosol varying with source and location (Zhang et al., 2007; Day et al., 2009; Kanakidou et al., 2004; O'Dowd et al., 2004; Putaud et al., 2004).

Some studies have shown the presence of fatty acids in marine aerosol and the predominance of saturated C_{12} – C_{19} straight chain fatty acids (Mochida et al., 2002; Cavalli et al., 2004). Fatty acids come from both anthropogenic (cooking, combustion, traffic emission, ...) and biogenic sources (forests, plants, biomass burning, ...) (Cheng et al., 2004; Hou et al., 2006; Huang et al., 2006; Pio et al., 2001; Robinson et al.,

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2006; Schauer et al., 2001; Simoneit and Mazurek, 2007). They are known to act as surfactants in the atmosphere (Rudich, 2003; Ellison et al., 1999; Gill et al., 1983), and they contribute significantly to the organic coating of sea salt particles (Mochida et al., 2002, 2007; Tervahattu et al., 2002a, b; 2005). Tervahattu et al. (2002), have provided evidence that fatty acids are actually located at the surface of sea salt particles.

Recently, several studies have focused on the influence of organic surfactant films at the air/water interface in order to determine their impact on atmospheric chemistry (Donaldson and Vaida, 2006; Smoydzin and von Glasow, 2007; Gilman et al., 2006). It turns out that the most important aspect of organic coatings is to reduce the mass transfer between the gas and particle phases. Organic coatings on aqueous aerosol particles can also affect the process of CCN formation and growth (Andrews and Larson, 1993; Chuang, 2003; Chan and Chan, 2005). In view of its importance to the ozone and halogen budgets in the marine boundary layer, several studies have focused on the reactive uptake of N_2O_5 and shown a decrease of the reactive uptake of N_2O_5 in presence of monolayers surfactants (Badger et al., 2006; Cosman and Bertram, 2008; Cosman et al., 2008; Knopf et al., 2007; McNeill et al., 2006, 2007; Park et al., 2007; Riemer et al., 2009; Stewart et al., 2004). For example Thornton and Abbatt (2005) demonstrated that the presence of a monolayer of hexanoic acid inhibits N_2O_5 uptake by a factor of 3 to 4 on deliquesced sea salt aerosol. McNeill et al. (2007) found that the presence of sodium dodecyl sulfate (SDS) decreases the N_2O_5 reaction probability on deliquesced NaCl particles. Stemmler et al. (2008) studied the effect of surfactants on the uptake of nitric acid HNO_3 to deliquesced NaCl aerosol. They showed that the uptake coefficient was reduced by a factor of 5–50 when the aerosol was coated with fatty acids. The effect was most pronounced with pentadecanoic acid and stearic acid, which they ascribed to the ability of these fatty acids to spontaneously form relatively well ordered, dense films. This indicates the importance of the surface phase state of surfactants in determining the phase transfer properties, an observation also made in conjunction with N_2O_5 uptake (Bertram and Thornton, 2009; Knopf et al., 2007) and with acetic acid uptake (Gilman and Vaida, 2006).

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However organic coatings can also promote the phase transfer. Experiments by Glass et al. (2006), Burden et al. (2009) and Park et al. (2009) have shown that soluble surfactants such as butanol or hexanol can enhance the uptake of HCl into sulfuric acid through specific interactions of the alcohol head groups with chloride ions. Many uncertainties remain with respect to the structure and the phase state of surfactant films on atmospheric particles and the changes to the properties of the aqueous surface and to what degree these properties affect the transfer of trace gases from the gas to the liquid phase. One way to explore these is to extend the range of gas molecules to a less soluble species, one of the motivations to study the reactive uptake of ozone to deliquesced KI and mixed NaCl/KI particles coated with fatty acids.

So far, the effect of surfactant layers on the phase transfer of O₃ to deliquesced aerosols has not been investigated. Recently, the heterogeneous reaction of ozone with aqueous iodide has been studied in presence of aqueous organic species such as phenols (Hayase et al., 2010), where, however, phenols interacted with ozone as a competing reactant rather than as inhibitor of phase transfer. Studies of ozone reacting with oleate covered deliquesced NaCl particles (McNeill et al., 2007) were related to the reaction with the double bond at the surface in contrast to similar studies with pure oleic particles (Smith et al., 2002; Zahardis and Petrucci, 2006) and not of direct relevance to the present investigation focusing on the transfer across a layer of saturated fatty acids. Recently, we studied the reactive uptake of O₃ to deliquesced potassium iodide and mixed sodium chloride/potassium iodide aerosol particles (Rouvière et al., 2010). From these results, we obtained an average initial uptake coefficient of $\gamma = (1.10 \pm 0.20) \times 10^{-2}$ and a bulk accommodation coefficient of $\alpha_b = 0.6 \pm_{0.5}^{0.4}$. Iodide provides a substantial aqueous phase sink to drive uptake of ozone and is thus ideally suited for the present investigation. This reaction is also important in halogen activation processes of the marine boundary layer, as it may initiate halogen activation (Enami et al., 2008). Of some relevance to the present study is the fact that surfactants may affect the interfacial distribution of halogenide ions near the interface (Tobias and Hemminger, 2008; Krisch et al., 2007; Latif and Brimblecombe, 2004).

2 Experimental section

A schematic representation of the experimental setup is given in Fig. 1, which has been described in detail by Rouvière et al. (2010). Potassium iodide particles were produced by nebulising an aqueous solution containing 5 g/L of potassium iodide salt into 5 L/min dry N₂. The aerosol particles emitted were dried in a silica gel diffusion dryer, exposed to a bipolar ion source (⁸⁵Kr) to obtain an equilibrium charge distribution and then passed through an electrostatic precipitator to remove all charged particles. For hygroscopic characterization experiments and to quantify the amount of fatty acid condensed on the particles (see below), a first DMA (Differential Mobility Analyzer) could be placed after the ion source to obtain a monodispersed aerosol. Experiments were performed at 75% RH (above the deliquescence humidity of 67%; Woods et al., 2007), which leads to a diameter growth factor of 1.3 for KI particles. Under the conditions of the present experiments thus a pure aqueous KI aerosol contains around 7.3 M KI. Ozone was generated by irradiating a flow of a mixture of O₂ and N₂ in a quartz tube with an ultra-violet lamp (Pen-Ray 3SC-9, UV Products Ltd., USA), which has a resonance line at a wavelength of 185 nm. Then the O₃/O₂/N₂ flow was introduced to the aerosol flow tube through a movable injector and diluted by the aerosol flow or N₂ (ratio 1/1). In absence of particles, the ozone concentration in the reactor was normally 90 ppb. The aerosol flow tube reactor was a pyrex tube, 85 cm long, with an inner diameter of 2.5 cm. The ozone injector, which was kept in the center of the flow tube by means of three PFA legs, could be moved to vary the reaction time from 2 to 25 s to obtain kinetic information. After the reactor, the aerosol surface concentration was measured with a Scanning Mobility Particle Sizer (SMPS) consisting of a DMA (3071, TSI) and a condensation particle counter (CPC, 3022, TSI, USA) collecting the aerosols at the exit of the flow tube. The concentration of ozone was measured with a photometric ozone analyzer (model ML 9810, Monitor Labs Inc, USA) after separating ozone from the particles by diffusion in an annular coflow device. This separation was necessary, because the aerosol interferes with the photometric ozone detection due to scattering

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and absorption.

In order to investigate the effects of surfactants on the ozone uptake, varying amounts of a specific fatty acid were condensed on the dry particles. Straight chain C_9 – C_{20} fatty acids (FA) were used as surfactants in the experiments. The effectiveness of the surfactant coatings will be related to their properties, as provided in Gabler and Heumann (1993). The procedure to get a reproducible amount of fatty acid on the particles has already been described by Stemmler et al. (2008). An organic vapor was generated by heating 0.5 g of surfactants in a temperature controlled reservoir. The coating took place after removing charged particles from the aerosol flow and before their humidification (Fig. 1). The aerosol flow passed over the reservoir through the heated zone and thereby got into contact with the surfactant vapor. In the condenser tube downstream of the warm zone, the gas gradually cooled and the vapor condensed onto the surface of the particles. The amount of fatty acid condensed on the particles was controlled by changing the evaporator temperature. For the example of lauric acid, Fig. 2a demonstrates the increasing particle size of monodispersed KI particles (particle mode diameter) coated with increasing amounts of lauric acid (C_{12}) with increasing temperature. The mass ratio of surfactant was derived from the associated change in particle volume for each temperature. The volume of fatty acid (V_{FA}) was obtained from the difference of the volume of coated particles (V_{KI+FA}) calculated from the corresponding measured diameter (D_c) and the volume of the dry particles with diameter $D_0(V_{KI})$. Using the densities of KI and the fatty acid of interest, respectively, we determined the mass ratio of fatty acid ($m_{FA}/(m_{FA} + m_{KI})$). The mass ratios obtained for C_9 , C_{12} , C_{15} , C_{18} and C_{20} as a function of the temperature of the evaporator are shown in Fig. 2b. We do not know whether the organics formed a homogeneous coating on the dry particles or condensed as a separate droplet or crystal attached to the particle. We therefore associate a significant uncertainty with these values, as we do not take into account any shape effects. It serves reasonably well to compare among the different fatty acids. Once deliquesced, we assumed that fatty acids spontaneously form a monolayer with the excess accumulating a lens at the aqueous surface, as described

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in the next section.

2.1 Assessment of monolayer properties

The monolayer properties of the fatty acids of interest here were explored using the model developed by Seidl (2000). These monomolecular films can exist in three different states: gaseous, expanded and condensed liquid state. The corresponding π -A isotherms are shown in Fig. 3a, where the film pressure is represented as a function of the area per molecule. This figure indicates also two essential values for the π -A isotherms that are the location of the phase transition from the expanded to the condensed liquid phase state (F_j , phase transition film pressure) and the Equilibrium Spreading Pressure (ESP). The ESP is defined as the pressure of the film in equilibrium with its condensed phase. It corresponds to the point where the monolayer can not be compressed more without that a separate solid (or liquid) phase would precipitate. It may be compared to the solubility of a compound in solution as the 3-D analog in that if more of this compound is added to the solution than given by the solubility the excess salt forms a solid phase in equilibrium with the solution. Compounds exhibiting an $ESP > 0$ mN/m spread spontaneously over the aqueous surface. Data concerning F_j and ESP are also reported in Table 1. We assume that if we have deposited fatty acids in amounts more than the equivalent of the corresponding monolayer at the ESP on the wet particles, the phase state of this monolayer is given by the ESP, while the rest remains as excess solid or liquid fatty acid attached to the aqueous solution. With smaller amounts of a fatty acid we assume that they form a more dilute monolayer with homogeneous surface density over the particle. To make this quantitative, from the mass fractions plotted in Fig. 2b we calculated the area per molecule (i.e., inverse surface density) as a function of evaporator temperature plotted in Fig. 3b. The surface density was calculated as the ratio of the number of fatty acid molecules per particle (n_{FA}) divided by the surface area per particle as obtained from the SMPS. Then, knowing the ESP of each FA from the corresponding π -A isotherm shown in Fig. 3a, the area per molecule in the monolayer was assumed to remain constant with further increasing

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mass fraction and represented as a solid line in Fig. 3b. This figure should demonstrate that for higher mass fractions, the monolayer density and structure remained constant, while the excess material formed a separate phase increasing the overall particle surface area but not affecting the monolayer properties above the aqueous solution. As already pointed out by Stemmler et al. (2008), we do not expect formation of micelles for these fatty acids.

3 Results and discussion

The effects of fatty acids to the ozone uptake on deliquesced KI particles or on mixed NaCl/KI particles were investigated in order to see if these amphiphilic surfactants promote or inhibit the mass transfer of ozone to the bulk phase.

The uptake coefficient, γ , of gases to an aerosol can be defined as the number of gas molecules being taken up by the particles divided by the number of gas molecules impinging onto their surface (Pöschl et al., 2007). The rate of ozone loss from the gas phase is described as a pseudo-first order process Eq. (1), where k_{g,p,O_3} is the first order rate coefficient, and t is the exposure time between the gas and the aerosol surface (Liu et al., 2001). Then, the rate coefficient can be related to the uptake coefficient, γ , on the aerosol using Eq. (2), where S is the aerosol surface area per volume of gas (m^2/m^3) and ω is the mean molecular velocity of O_3 in the gas phase (m/s).

$$\frac{d[O_3]}{dt} = k_{g,p,O_3}[O_3] \quad (1)$$

$$k_{g,p,O_3} = \frac{S\omega\gamma}{4} \quad (2)$$

In absence of an organic coating, the study of uptake of ozone to deliquesced potassium iodide aerosol particles showed that the uptake was both influenced by the bulk accommodation coefficient (α_b) and the bulk reactivity (Γ_b).

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In presence of a coating and under appropriate steady state approximations, the uptake coefficient of gas molecules from the gas-phase into a liquid can be expressed in terms of a sequence of resistances as shown in Eq. (3). In absence of an elementary picture of the detailed processes we replace the bulk accommodation coefficient, the probability that a gas phase molecule hitting the surface enters the liquid in solvated form, by an overall inverse resistance at the surface, $1/\beta$, for transport across the surfactant layer including also transfer into the liquid. The inverse resistance due to the bulk liquid phase reaction is expressed by $1/\Gamma_b$. In Eq. (3), T is the temperature, H is the Henry's law coefficient of O_3 , D_{b,O_3} is the diffusion coefficient of O_3 in the liquid phase, R is the universal gas constant, and k_b the second order loss rate constant of O_3 in the liquid phase:

$$\frac{1}{\gamma} = \frac{1}{\beta} + \frac{1}{\Gamma_b} \quad \text{with} \quad \Gamma_b = \frac{4HRT \sqrt{D_{b,O_3} k_b [I^-]}}{\omega} \quad (3)$$

Note that in our previous study we explicitly kept track of the iodide content as a function of reaction time to take into account its significant depletion, depending on particle size, during the residence time in the flow reactor and the coflow device. In the present study we used a simplified first order treatment as the coated particle exhibited significantly less ozone uptake, so that iodide in the aerosol phase remained in excess. After having established first order conditions for a number of representative cases, the reactive uptake coefficients were determined from the removal of O_3 at a fixed maximum interaction time (41 s, including the residence time in the coflow device) as a function of the amount of fatty acid deposited at the particle surface, which is related to the temperature in the evaporator as mentioned above. This allowed to directly compare uptake to coated particles with that to uncoated particles and reduced uncertainties related to day to day variations in flows, humidity and aerosol properties. The initial concentration of O_3 in absence of particles was around 2.2×10^{12} molecules/cm³. A typical decay of ozone after admission of deliquesced coated particles in the reactor is shown in Fig. 4 as a function of the coating temperature for the example of lauric acid

(C₁₂). The ozone signal returned to its initial value within about 2 min after exchanging the particle flow with a flow of pure N₂, consistent with the residence time distribution of the particles in the flow tube and the coflow separation device and the response time of the O₃ analyzer. Evidently, the ozone depletion was decreasing with increasing amounts of lauric acid.

Uptake coefficients of ozone to deliquesced potassium iodide coated by several fatty acids (C₉, C₁₂, C₁₅, C₁₈ and C₂₀) were measured. Figure 5a shows the ratio ($\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$) of the uptake coefficient to coated particles to that of neat deliquesced KI particles, covering the range of mass ratios of 0–70% of surfactants. For C₉ and C₁₂, the changes were relatively weak, with $\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$ dropping to about 50%. For the C₉ acid exhibiting the highest water solubility of the fatty acids investigated, less than 1% of a monolayer amount is soluble in a pure aqueous particle of the size as used in our experiments. So For C₉, we may rather suspect some losses due to evaporation as already discussed by Stemmler et al. (2008). However, as discussed below, it is more likely the phase state that determines the permeability of the C₉ and C₁₂ films. The saturated C₁₅, C₁₈ and C₂₀ acids lead to a strong depletion of the reaction rate of O₃ with aqueous KI particles. Overall, it appears that there is a trend of increasing degree of reduction in γ with the length of the hydrocarbon chain, although there is an exception with the C₁₅. Therefore, the first apparent conclusion is that also for O₃ organic surfactant coatings can have significant effects on interfacial mass transfer. Another way to interpret these results and to relate them to the monolayer properties is to plot the ratio $\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$ as a function of the area per molecule of surfactant as shown in Fig. 5b. On this scale, the low evaporator temperatures that led to low surfactant mass ratios now plot at the high area per molecule end, i.e., the area per molecule decreases with increasing mass ratio for all fatty acids C₉-C₂₀. Reiterating the assessment of the monolayer properties above, once the calculated area per molecule hits the position of the ESP in the phase diagram, values below that reflect virtual average properties only, but in reality, the area per molecule in the monolayer does not decrease further with increasing mass ratio, as indicated by

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the lines shown in Fig. 3b. The additional surfactant molecules form a separate phase as discussed above. In Fig. 5b the open squares represent the position of the ESP. These data were only available for C_{12} to C_{20} . From that we can deduce a decrease of the uptake coefficient by 30% for C_{12} , 85 % for C_{15} and 50% for C_{18} in presence of a monolayer of FA under ESP conditions at the air/water interface. We suspect that the further decrease of $\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$ with increasing mass ratio or decreasing effective area per molecule is not due to further compression of the monolayer but rather due to the extension of the separate fatty acid phase. At high mass ratios, the compound particle may be dominated by the fatty acid phase in volume and surface area, and only the aqueous subphase with the monolayer at ESP contributes to O_3 uptake. For the C_{18} fatty acid, adding the excess of fatty acid beyond the ESP as a separate sphere leads to about a doubling of the surface area, which should lead to a maximum decrease of the uptake coefficient by a factor of 2. The uptake coefficient decreased by more than a factor of two beyond the ESP. This may indicate that nevertheless further compression of the film due to the geometric constraints of the spherical droplet occurs or that a significant part of the droplet surface area is in contact with the excess solid phase and thus effectively reduces the surface area exposed to O_3 .

Figure 6 represents the ratio of the reactive uptake coefficient in presence of organic monolayer to the uptake coefficient of the uncoated particles ($\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$) as a function of the carbon chain length for three different mass ratios. While the mass ratio dependence is already contained in Fig. 5a, this plot makes the complex interplay between phase state, coverage, mass transfer properties and carbon chain length strikingly apparent. From Figs. 2b and 3b we note that we form a monolayer at the ESP for a mass ratio of 6, 10 and 15% for C_{12} , C_{15} and C_{18} , respectively. Therefore, in Fig. 6, the lowest mass ratio for lauric acid (C_{12}) is slightly below the position of the ESP, corresponding to a more dilute monolayer. The uptake coefficient responds slightly to an increase in mass ratio. A similar behavior is observed for the C_9 compound. In striking contrast, for C_{15} we observed a very strong decrease already for a mass ratio of 6%. Increasing the mass ratio to 20%, for which we expect the monolayer

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at its ESP with already a slight excess fatty acid phase, leads to a further drop of the uptake coefficient. Further increasing the mass ratio to 30% leads to no further change in the uptake coefficient. For C_{18} , with a mass ratio of 6%, the monolayer formed is quite more dilute than expected for the ESP, and the major drop in the uptake coefficient of ozone occurs with increasing the mass ratio to 20%, above the ESP, and a small further drop for the mass ratio increasing to 30%. Although we observe similar behavior for the C_{20} compound, we note that the model by Seidl returns a negative ESP, which means that it may eventually not spread spontaneously over the aqueous surface. Similar to the C_{18} case the reduction of the uptake coefficient could be partially explained by the increased surface area of the mixed phase particle. Again, the reduction of the uptake coefficient is more than expected based on the larger surface area due to the excess organic phase. Therefore, the formation of a monolayer also for the C_{20} may be feasible in spite of the negative ESP estimated by the model of Seidl (2000).

After deconvoluting the observations in Figs. 5a and 6 to take into account the mass fraction for each compound at which a monolayer at the ESP can be formed leads to a consistent picture of increasing inhibition of O_3 uptake with increasing mass ratio up to the point, where the monolayer exists at its ESP. A further decrease of the uptake coefficient may be related to the increasing surface area of an excess unreactive fatty acid phase. However, the most striking difference between the degree of uptake reduction for monolayers at the ESP among the different compounds is rooted in the different phase states the monolayers exist at the ESP. We therefore indicate the position of the phase transition from an expanded to a condensed liquid state, F_j , in Fig. 5b. It is immediately apparent that when going from higher to lower area per molecule or from lower to higher mass fraction, the C_{15} hits this phase transition first. Thus, for C_{15} , the state of the film at the ESP is condensed liquid, which has a substantially higher degree of ordering than in the expanded state, which in turn obviously leads to its increased resistance towards transfer of O_3 across the monolayer. In contrast, the C_{12} remains in its expanded state up to the ESP, associated with an only small effect on

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O₃ uptake. Higher compression would be necessary to bring a C₁₂ monolayer to its condensed liquid state, for which no driving force is available under the conditions of the present experiments. Also for the C₁₈ film, we expect the phase transition to the liquid condensed state just before the ESP, but at substantially higher mass fractions than for the C₁₅ explaining the delayed response of the uptake coefficient to increasing mass fractions beyond those expected by the different molecular weight.

Uptake coefficients obtained for aerosols containing a mixture of sodium chloride and potassium iodide in presence of fatty acids are shown as a function of the iodide concentration in Fig. 7a for the C₁₅ and Fig. 7b for the C₁₈ compound. To calculate the iodide concentrations we used the same procedure as described by Rouvière et al. (2010). For the mixed solution particles, we considered the solute mole fraction of iodide and chloride in the nebulized solution (x_{Cl}^- , x_{I}^-). Then, by first measuring the size distribution under dry conditions for each experiment, we obtained the dry particle diameter (D_0) and the dry particle volume, from which we deduced the total number of moles (iodide and chloride, n_{T0}) in the mixed particles by taking into account the density and the mole fraction of each salt. Under humid conditions, where particles were deliquesced, we obtained a wet diameter and a wet volume (D, V), and we calculated the total concentration of solutes for the mixed aqueous particles ($C_T = n_{T0}/V$). Finally, to obtain the iodide concentration we applied the mole fraction (x_{Cl}^- , x_{I}^-) to this concentration. The uptake coefficients presented in Fig. 7 are time averaged uptake coefficients calculated from the total ozone loss at the maximum residence time. As we have established earlier, O₃ uptake is driven by bulk reaction in the particle phase, and thus the uptake coefficient scales linearly with the square root of the iodide concentration Eq. (3). Note that this linear relation is not granted, if significant depletion of iodide occurs during the course of the residence time in the reactor as discussed in detail with a larger data set by Rouvière et al. (2010).

From Fig. 5a and b we could determine that we are forming a monolayer at the ESP for C₁₅ and C₁₈ as soon as we obtain a mass ratio of surfactant of 10 and 15%, respectively. From Fig. 7a and b we observed for both FA that the slope of increase

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of the uptake coefficient with iodide concentration decreases with increasing organic mass fraction. In both cases, for mass ratios of 30% and above, the uptake coefficient was insensitive to the iodide concentration. The changing slope is a direct result of the increasing contribution of the term $1/R$ to overall uptake Eq. (3). The rate of uptake shifts from being mostly reaction limited in presence of low amounts of organics to phase transfer limited at higher organic loadings. In accordance with the observations made with pure KI particles, this change in kinetic regime occurs at lower mass ratios for the C_{15} than for the C_{18} fatty acid. In both cases, for the highest mass ratios we expect a monolayer at its ESP, which is in the condensed liquid state. Since, obviously, the uptake is not influenced by the bulk reactivity (Γ_b) anymore for this case, γ can be expressed by $\frac{1}{\gamma} = \frac{1}{\beta}$. To estimate the resistance of the fatty acids for the transfer of O_3 at the interface we used the results from Fig. 7 for the highest mass ratio of surfactant: $\beta_{C_{15}} = 6.8 \times 10^{-4}$ and $\beta_{C_{18}} = 3.3 \times 10^{-4}$. Therefore, in spite of the slightly stronger compression of the C_{15} film, the resistance ($1/\beta$) for O_3 to cross this monolayer is about a factor two lower than for the C_{18} film. This might be related to the structure of these films and the longer chain length of the C_{18} fatty acid.

In an attempt to assess the inhibiting effects of mixed component surfactant layers we made a few rather qualitative experiments with C_{12}/C_{15} and C_{12}/C_{18} mixtures each containing a short and a long chained surfactant. Based on the results presented so far, C_{12} behaves substantially different than C_{15} or C_{18} , as it should not be able to form a liquid condensed film under our experimental conditions. Therefore, the intention of these experiments was to assess whether addition of the C_{12} fatty acid could significantly change the inhibitory effect of the C_{15} or the C_{18} monolayers. While Cosman and Bertram (2008) were able to control the composition of two component films, we mixed the two components in the evaporator in the same configuration as for coating the particles with one component alone described above. The amount of fatty acid condensing on the particles is related to its vapor pressure in the evaporator and to the temperature gradient in the condenser tube. The vapor pressure of one of the components in the evaporator should not depend strongly on the presence or

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not of an additional component in absence of mass transport limitations. We therefore assumed that the relative composition of the coated particles roughly scales with the mass ratios obtained for each component individually. Figure 8a and b presents the ratio $\gamma_{\text{mixed film}}/\gamma_{\text{uncoated}}$ for the two individual components C_{12} and C_{15} and C_{12} and C_{18} , respectively, as well as the mixtures thereof, in a format similar to Fig. 6. In Fig. 8, however, we do not use the measured mass ratio of organic but rather the evaporator temperature to categorize different levels of coatings. In Fig. 8a, the addition of some amount of C_{15} to the C_{12} in the evaporator leads to a strong change in the reduction of the uptake coefficient and a response more closely to that of the pure C_{15} case. The relative proportion of C_{15} to C_{12} in the evaporator does not strongly affect the results, since the vapor pressure in the evaporator of each component does not depend on the relative composition of the condensed phase. The dominating role of C_{15} in inhibiting the transfer of O_3 in the mixed film is likely because at the same temperature, the mass ratio of a C_{15} coating is by far higher than that of a C_{12} coating (Fig. 2b). This is also the case for the mixture between the C_{12} and the C_{18} , where the mixed coating is likely also dominated by the C_{18} . This would then be consistent with the observed O_3 uptake reduction being comparable to the pure C_{18} case (Fig. 8b), and again with little difference between the two different mixtures in the evaporator.

Therefore, in absence of experiments with a wider range of well controlled relative compositions, the only conclusion we can draw from the present results is that the addition of a small amount of a surfactant, which is in its expanded state, does not strongly affect the resistance of a concomitantly present condensed liquid monolayer towards the phase transfer of O_3 .

3.1 General discussion

Summarizing this discussion, we have observed a substantial reduction in uptake coefficient of O_3 to deliquesced KI aerosol in presence of fatty acid surfactants and that the efficiency of the barrier towards transfer of O_3 is strongly related to the phase state of the monolayer formed on the aqueous solution. It seems that only a monolayer in its

condensed liquid state is able to inhibit transfer of O_3 by more than an order of magnitude. Under such conditions, the monolayer likely exposes a hydrophobic interface to the adsorbing gases, from which O_3 rather desorbs than diffuses across.

In our case we studied a linear saturated fatty acid. We observed in all cases a decrease of the uptake due to the presence of these surfactants. However we obtained a stronger effect to impede the mass transfer for long chain surfactant as C_{15} , C_{18} and C_{20} due to the formation of a liquid condensed film, with a stronger deactivation by the C_{15} coating related to its more compressed monolayer at the equilibrium spreading pressure. For shorter chain FA as C_9 and C_{12} , they are able to form an expanded film but not a condensed film which can explain their only limited ability to inhibit phase transfer of O_3 .

In general, our results with the rather little soluble O_3 are in line with previous studies. Xiong et al. (1998) showed that a C_{18} coating reduced the hygroscopic growth rate of sulphuric acid aerosol, while a coating of oleic acid (nonlinear and unsaturated) had no effect, likely related to the fact that oleic acid does not form condensed liquid films at pressures, where the saturated straight chain C_{18} fatty acid does. Similarly, Gilman and Vaida (2006) related the permeability of the films to the molecular properties and pressure-area isotherms and demonstrated that the uptake of acetic acid through monolayers of saturated C_{18} and C_{30} alcohols into an aqueous phase was strongly reduced, but not affected by oleic acid.

Most studies on dinitrogen peroxide uptake (N_2O_5) to sulfuric acid, or to NaCl or sea salt aerosol in presence of organic surfactants have shown an inhibition of the uptake (McNeill et al., 2006; Park et al., 2009; Stewart et al., 2004; Thornton and Abbatt, 2005). More particularly Cosman and Bertram (2008) with the N_2O_5 uptake study on aqueous H_2SO_4 solutions coated with 1 or 2 component monolayers, have shown that the reactive uptake coefficient depend on the molecular surface area of the surfactant and also that a small amount of a branched surfactant could affect the overall resistance to the reactive uptake. Since these mixed component films were well defined in composition, these results cannot be directly compared to our qualitative

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results on mixed films. Some other studies have related the effectiveness of FA to act as barriers to the nature of the head group (polarity), the pH and the temperature (Barnes, 1997; Johann and Vollhardt, 1999; Latif and Brimblecombe, 2004).

4 Conclusions

The effects of amphiphilic fatty acids on the reaction of ozone with deliquesced potassium iodide aerosol particles were investigated with an aerosol flow tube experiment. This is the first time that this system has been investigated under aerosol conditions. From the previous study in absence of organic coating, we determined an initial uptake coefficient of $\gamma=(1.10\pm 0.20)\times 10^{-2}$. The presence of a long chain surfactant coating adds a significant resistance to the transfer of O_3 to deliquesced aerosol particles, similar to the case of more reactive trace gases. The results showed that, especially for the C_{15} - C_{20} , the amphiphilic surfactant limit the mass transfer of ozone to the aqueous phase. Through varying the iodide concentration in mixed chloride/iodide particles we could directly determine the resistance exerted at the aqueous surface by two longer chained surfactants: pentadecanoic acid and stearic acid. The effectiveness of C_{15} to inhibit the ozone uptake from the gas phase is higher than for the C_{18} . This could be explained by the monolayer properties of the fatty acids and also by the state of the monolayer formed at the equilibrium spreading pressure (in expanded or condensed liquid state). Concerning the short chained surfactant C_9 and C_{12} , the monolayers formed are in the liquid expanded state, known to be not well ordered and are only slightly hindering ozone uptake. This study highlights the effectiveness of immiscible films of long-chain organics (C_{15} - C_{20}) to have an effect on the mass transport across the air-water interface by acting as a barrier and impede the transport of gases and other volatile species across the interface.

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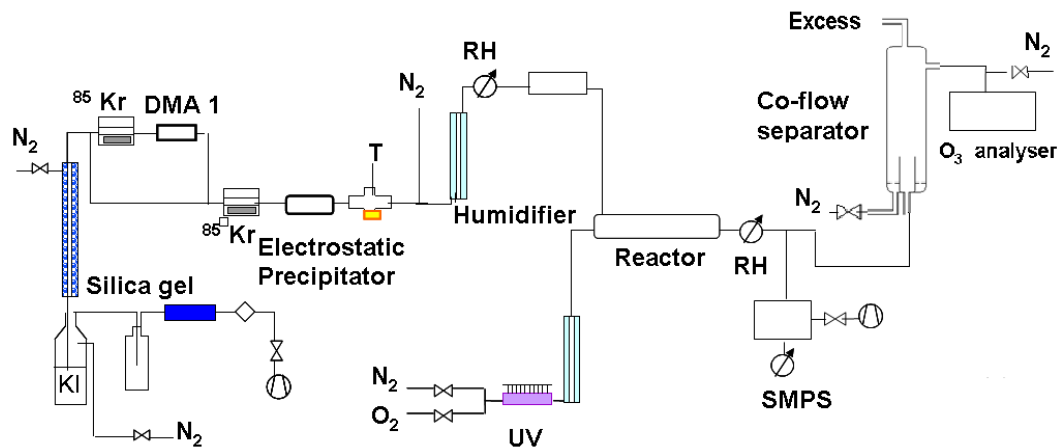
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Table 1. Properties of the surfactants.

Name	Formula	Molecular weight g/mol	Density g/cm ³	Aqueous solubility g/100g of water at 20 °C	Melting °C point	Vapor pressure at 25 °C	ESP mN/m ^a	Fj mN/m ^a
Nonanoic acid	C ₉ H ₁₈ O ₂	158.24	0.900	0.0284	12.4	9 × 10 ⁻²		
Lauric acid	C ₁₂ H ₂₄ O ₂	200.32	0.880	0.0055	43.8	2.9 × 10 ⁻³	23.4	43.5
Pentadecanoic acid	C ₁₅ H ₃₀ O ₂	242.40	0.8423	0.0012	52.3	1.1 × 10 ⁻⁴	21.0	6.2
Stearic acid	C ₁₈ H ₃₆ O ₂	284.48	0.847	0.00029	69.3	5.6 × 10 ⁻⁷	3.7	-23.9
Arachidic acid	C ₂₀ H ₄₀ O ₂	312.54	0.8240	–	76.5	4.4 × 10 ⁻⁸	-1.6	-57.9

^a ESP: Equilibrium spreading pressure; Fj phase transition film pressure from the expanded to the condensed liquid phase state. The values were calculated from the model of Seidl (2000).

The effect of fatty acid surfactants on the uptake of ozoneA. Rouvière and
M. Ammann**Fig. 1.** Overview of the experimental setup.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

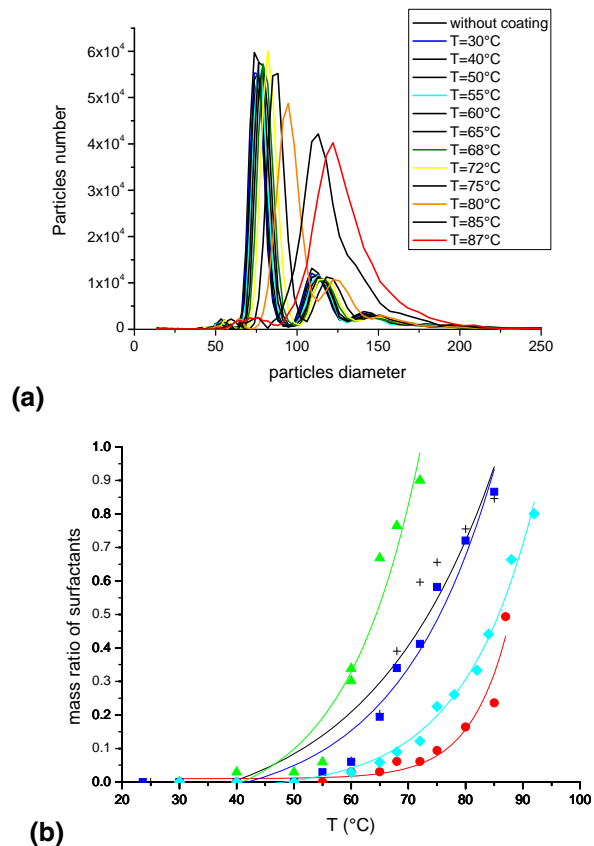
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Fig. 2. (a) Particle size distributions of a monodisperse dry aerosol (KI) exposed to Lauric acid (C_{12}) in the evaporator at different temperatures. (b) Evolution of the mass ratio of surfactants as a function of the evaporators temperature (black crosses: C_9 , red circles: C_{12} , green triangles: C_{15} , blue squares: C_{18} and turquoise diamonds: C_{20}).

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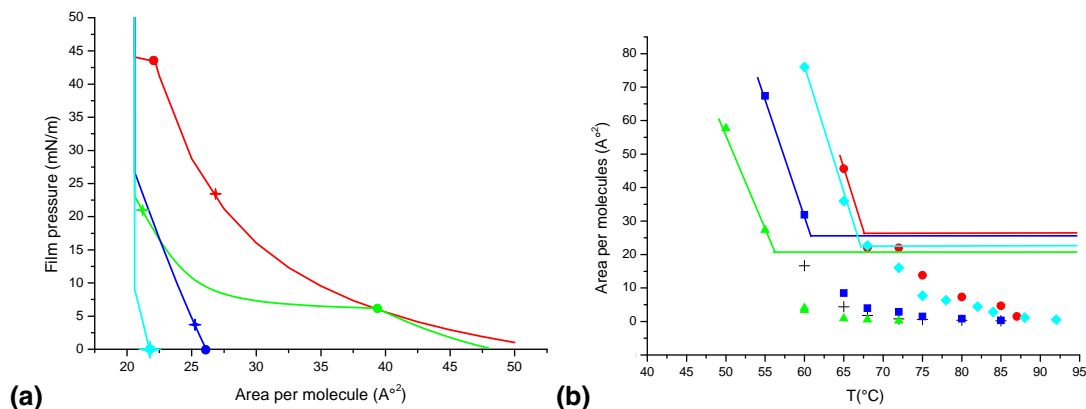


Fig. 3. (a) π -A isotherms of lauric acid (red line), pentadecanoic acid (green line), stearic acid (blue line) and arachidic acid (turquoise line), according to the model of Seidl (2000). The crosses represent the Equilibrium spreading Pressure of an excess bulk phase of the individual fatty acids and the circles illustrate the phase transition film pressure between the expanded and condensed phases. (b) Area per molecules of the fatty acids as a function of the evaporator's temperature (black crosses: C₉, red circles: C₁₂, green triangles: C₁₅, blue squares: C₁₈ and turquoise diamonds: C₂₀).

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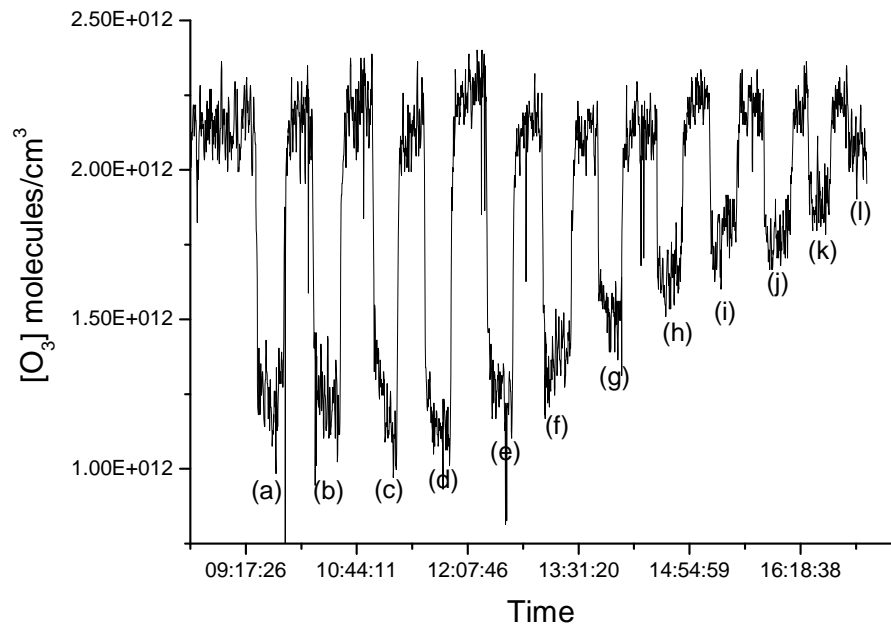
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Fig. 4. Experimental profile of the O_3 concentration in presence of lauric acid (C_{12}) for different coating temperature in the evaporator ((a) without coating, (b) $T=23.6^\circ\text{C}$, (c) $T=30^\circ\text{C}$, (d) $T=40^\circ\text{C}$, (e) $T=50^\circ\text{C}$, (f) $T=60^\circ\text{C}$, (g) $T=65^\circ\text{C}$, (h) $T=68^\circ\text{C}$, (i) $T=72^\circ\text{C}$, (j) $T=75^\circ\text{C}$, (k) $T=80^\circ\text{C}$, (l) $T=90^\circ\text{C}$).

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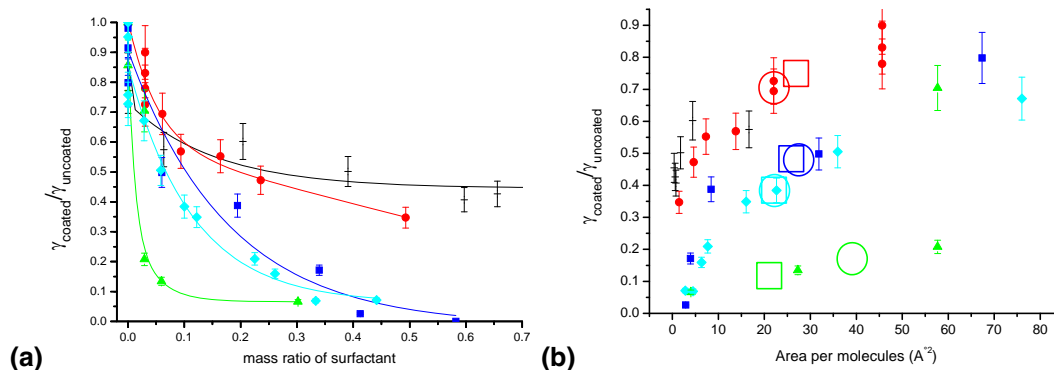


Fig. 5. (a) Ratio of coated uptake to neat uptake ($\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$) on deliquesced KI aerosol containing mass ratio of 0–70% of surfactants for different fatty acids (black crosses: C₉, red circles: C₁₂, green triangles: C₁₅, blue squares: C₁₈ and turquoise diamonds: C₂₀). (b) Ratio $\gamma_{\text{coated}}/\gamma_{\text{uncoated}}$ as a function of the area per molecules of surfactant (black crosses: C₉, red circles: C₁₂, green triangles: C₁₅, blue squares: C₁₈ and turquoise diamonds: C₂₀). The rectangles represent the position of the equilibrium spreading pressure ESP and the circles represent the phase transition film pressure F_j.

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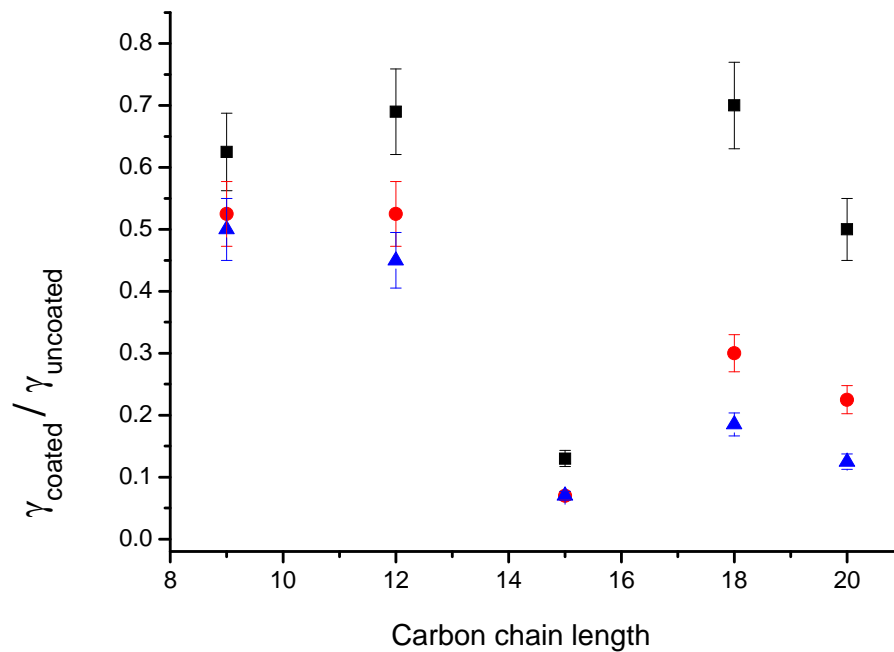
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Fig. 6. Ratio $\gamma_{\text{coated}} / \gamma_{\text{uncoated}}$ as a function of the carbon chain length for three different mass ratio of organic (black squares: 6%, red circles: 20%, blue triangles: 30%).

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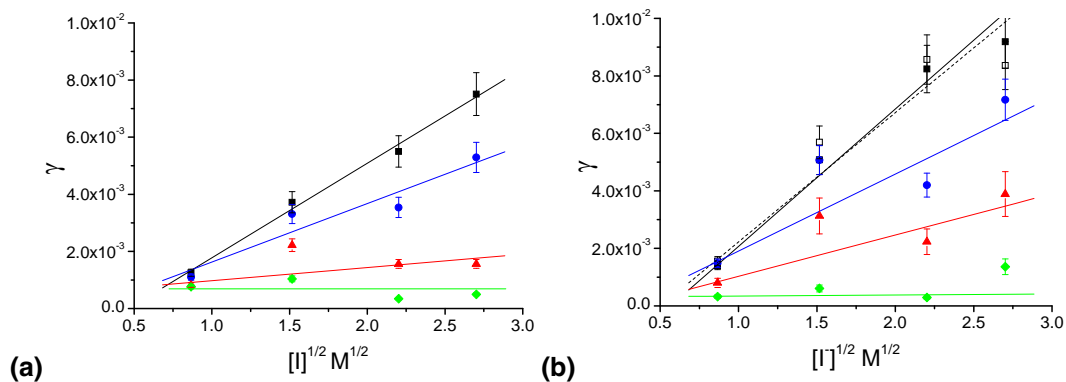


Fig. 7. Plot of the uptake coefficient vs. the iodide concentration $\sqrt{[I]}$ as a function of the mass ratio of surfactant ((a) for C_{15} and (b) for C_{18}). Different mass ratio are represented. For C_{15} black squares: no coating, blue circles: 3%, red triangles: 4% and green diamonds: 30%. For C_{18} black squares: no coating, empty black square: 0%, blue circles: 2%, red triangles: 6% and green diamonds: 37%.

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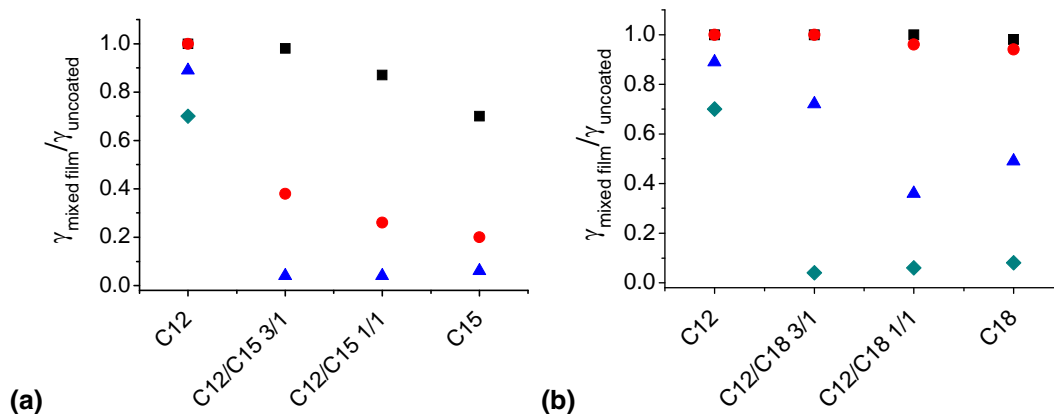


Fig. 8. Evolution of the ratio $\gamma_{\text{mixed film}} / \gamma_{\text{uncoated}}$ for two-component coatings **(a)** C₁₂/C₁₅ and **(b)** C₁₂/C₁₈ at different temperatures of the evaporator ($T=40\text{ }^{\circ}\text{C}$: black squares, $T=50\text{ }^{\circ}\text{C}$: red circles, $T=60\text{ }^{\circ}\text{C}$: blue triangles and $T=70\text{ }^{\circ}\text{C}$: green diamonds).

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