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Original Research

Structural Characterization of Fatty Acid Films on Rain Water: a Scaling Approach Using Physical Attributes

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Abstract

A complete compositional or structural description of naturally-occurring surfactants on rain water is not currently feasible. A main limitation of previous work has been the lack of means for correlating force-area characteristics with the chemical makeup of the films. Instead of analyzing the chemical composition of rain water film-forming organics, it is postulated here to introduce the novel scaling procedures (2D virial equation of state and 2D polymer film scaling theory) applied to the surface pressure-area (π-A) isotherms and surface pressure-temperature (π-T) isochors and resulting from generalized physical formalisms modified to a multicomponent surfactant film. A set of the introduced structural film state parameters (π, Γ, A_{lim}, E_{isoth}, y, R, M_w, β_s) could become sensitive indicators for surface-active source-specific organic matter pathway tracing, where the measurement of surfactant concentration and chemical analyses are avoided. The concept is quantified using the Langmuir trough film and disdrometer data on a set of rain water events observed in Gdańsk, Poland in May 2002.

Keywords: source-specific surfactants, rain water film, isotherm scaling, structural parameters, film structure quantification

Introduction

Measurements of atmospheric water samples have demonstrated the occurrence of surface films on fog, cloud droplets and raindrops, as well as on aerosols [1-3]. A complex mixture of many inorganic and organic substances with different physicochemical properties can accumulate at interfaces influencing mass energy and gas transfer between such modified surfaces. However, recent fieldwork has shown that much of the organic matter present in atmospheric aerosols is water insoluble [4-7]. Organic compounds comprised of a long hydrocarbon chain and polar group, e.g. organic acids, alcohols or esters, can form monomolecular films at the air-water interface. Single film-forming components have been detected quantitatively in samples in rain water in a number of studies [8-14]. Among the organic compounds analyzed in these studies, mostly n-alkanoic acids (fatty acids) with 12-18 carbon atoms have been found as film-forming compounds. Other surface-active substances, e.g. alcohols, had in general smaller concentrations [15, 16]. Sources of fatty acids in the atmosphere may be the ocean surface [17-22], primary biological material [23], and a number of anthropogenic sources like automobile exhaust [24], road dust [25], biomass burning [26] or meat cooking [27]. Since surface films can change the physico-chemical properties of humid aerosol particles, cloud droplets and raindrops can also affect the rain-forming process in a number of ways. It is of great importance to quantify the surface film structure and concentration and follow their evolution at different environmental conditions. At present, a complete compositional or structural description of surfactant films on natural waters

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is not available. Instead of analyzing the chemical composition of rain water film-composing organics (unknown in general) it could be possible to scale the film surface pressure-area isotherms and surface pressure-temperature isochores in terms of the structural parameters that reflect in a sensitive way the natural film morphology, and result from the generalized physical formalisms modified to a multicomponent surfactant film [28-30]. A set of the structural film parameters appears to be a quantitative measure of the film physicochemical composition, film molecule mobility, film material solubility and the miscibility of its film-forming components. The structural state of natural water surfactant films, which can be incorporated with source-specific surface-active components (so called "end members") of biogenic or anthropogenic origin, can be assessed through the quantification of parameter variability. They can be useful for tracking organic matter dynamics, as already established factors in atmospheric investigations such as the formic to acetic acid concentration ratio (F/A) [31] or the fractional acidity (FA) [32] describing the material dissolved in bulk samples of hydrometeors. A principal limitation of previous work was the inability to compare force-area isotherms and elastic properties of rain water films measured at different rain rates. In the present state the model describes the film-forming properties of fatty acids only. However, fatty acids appeared to be important film-forming compounds on rain water. Many other substances also have film-forming properties including polyacidic constituents of high molecular mass [2, 33] with a certain amount of nonpolar components capable of forming mixed films with the fatty acids. For model considerations the measurements of fatty acids in Bloomington, Indiana, USA [9], and in Bensheim, Germany [11] have been used. Finally, the rain water film structural parameters were evaluated in model Langmuir trough studies and corrected according to the scaling concept using the disdrometer data on a set of rain water events observed in Gdańsk, Poland, in May 2002. The main aim of this work was to provide a basis for systematically comparing force-area characteristics of rain water films collected at different rain event regimes and to relate the elastic structural properties to chemical composition and origin of source-specific compounds in future studies. We also evaluate the reproducibility of the concept and provide examples of its application to a wide range of differentiated organic films present at marine, inland and atmospheric water interfaces.

Theoretical Background

In this report we discuss some of the structural film properties which may be derived from the surface pressure-area $(\pi\text{-}A)_T$ isotherm measured at a number of temperatures and the surface pressure-temperature $(\pi\text{-}T)_A$ isochore. The selected rheological surface parameters reflect in a quantitative and sensitive way the natural multicomponent film morphology. The simplest equation of state to describe surface films is the 2D analog of the ideal gas law [34]:

$$\pi A_m = kT \tag{1}$$

where k is the Boltzmann constant, π the surface pressure of the film, A_m the area per film molecule related to Gibbs' adsorption Γ, $A_m = 1/\Gamma N_A$, N_A the Avogadro number and T is the temperature in Kelvin.

For the natural films, whose isotherms differ significantly from the ideal-gas behaviour, the following quadratic equation of state, e.g. the 2D virial equation, was proposed and scaled according to specific area [35]:

$$\pi A = C_0 + C_1\pi + C_2\pi^2 \tag{2}$$

where C_0, C_1, C_2 are the virial coefficients, and A is the film-covered area (in cm^2).

It is possible to interpret the virial coefficients obtained from the best-fit procedure applied to the registered π-A isotherms, in terms of the mean number of moles n_m present in the film, specific limiting area A_{lim}, and mean molecular mass M_W of the film-forming surfactant mixture as described in detail elsewhere [28-30].

In particular, the description of the 2D film state depends on the dilational elasticity modulus (or Gibbs' modulus) E_{isoth} expressing the static, compressional response of a film to compression or dilation corresponding to the isotherm registration at its thermodynamic equilibrium [34]:

$$E_{isoth} = -A(d\pi/dA)_T \tag{3}$$

In particular, the expression of elasticity is generalized to have both shear and dilational components. It is assumed that the shear components can be neglected for natural water surface films [36]. Moreover, the establishment of thermodynamic equilibrium in the film is not trivial, the most real natural surfactant systems are viscoelastic and the surface dilational viscoelastic modulus is a complex quantity composed of real E_d (dilational elasticity) and imaginary E_i (= i $\omega\eta_d$, dilational viscosity) parts: $E = E_d + i\,\omega\eta_d$ also=$E_0\cos\theta + i\,E_0\sin\theta$, where η_d is the surface dilational viscosity, ω – the angular frequency of periodic oscillations, E_0 (= $-\Delta\pi/(\Delta A/A)$) represents the amplitude ratio between surface stress and strain, and θ is the loss angle of the modulus [29]. The relaxation process in monolayers may affect the shape of isotherms and consequently the recovered film parameters. The effect depends on the dimensionless parameter – Deborah De number defined as the ratio of the film relaxation process time τ to the "time of observation " (a reciprocal of the strain rate of a film: $t_{obs} = [(dA/A)/dt]^{-1}$, as argued in [30]. Our stress-surface pressure relaxation measurements performed on natural sea surface films revealed a two-step relaxation process with characteristic times τ_1 (1.1-2.8) and τ_2 (5.6-25.6) seconds. The surface rheokinetic parameters collected in Tab. 2 of [29] demonstrate that we are concerned with elastic films ($E_d \gg E_i$) at sufficiently low film area compression rates. If the De number is much less than unity, as adopted in these studies, the interfacial system is in its quasi-equilibrium thermodynamic state, and the dilational viscoelasticity modulus can be approximated by E_{isoth}. It is supposed that the above considerations can be expanded to rainwater films of comparable surface characteristics.

In general, the expansion π-A curves do not retrace the compression curves. It can be assumed that the difference in the shape (hysteresis) of the compression and dilatation curves may be attributed to different arrangements of the molecules in the compression and dilation cycles. Since different organizations must be concerned with entropy (S), the hysteresis of the compression/expansion curves is correlated presumably with a change of entropy (ΔS) of the film-adjacent water layer system. According to the fundamental laws of thermodynamics applied to the isothermal compression–expansion cycle of a 2D film system (T=const, dS=dQ/T; dQ=dW, where Q and W are the heat provided and work done, respectively). Our ΔS_c (= ΔW/T, where $\Delta W = W_{dil} - W_{com}$ is the difference in the work derived from integration of the expansion and compression isotherm plots i.e.,

$$W_{com} = -\int_{A_i}^{A_f} \pi \, dA$$

between the initial A_i and final A_f film areas) is rather an entropy-related parameter than state function ΔS, since the work function is defined to be dependent on the way the process takes place [28]. A vertically organized interfacial system, consisting of multicomponent surfactant structures in a form of 2D domains and aggregates, during a compression-expansion cycle evolves into a new structural state with a certain loss of the system degrees of freedom leading to a larger entropy parameter ΔS_c change than expected for a homogeneous structureless film sample. The surface concentrations for these films were not measured, therefore it is not possible to determine whether such a loss to an actual loss of material from the film or to changes in conformation or intermolecular associations. Losses from the film could occur via desorption, micelle formation or collapse to a multilayered phase.

The isotherm reversibility R:

$$R = 100(W_{dil}/W_{com})\% \tag{4}$$

gives a measure of the entropy effect of surface films of different chemical structure depending on the film-forming material solubility, as already shown for natural seawater film samples [29, 37].

The characterization of the miscibility or phase separation of the monolayer-forming components can be expressed in terms of the 2D polymer film scaling theory via y – scaling exponent derived from the relation $E_{isoth} = y\pi$ applicable to the high-frequency limit of the surface dilational modulus, as shown in [38]. In the limit of fast enough area dilation/compression, the interchange of film molecules between the surface and the bulk becomes negligible and the film acts like "insoluble" monolayers. The advantage of such an approach is that measurement of the surface concentration is avoided. Moreover, it was postulated that the concept of the structural arrangements of molecules in a three-component system (an insoluble polymer spread on a surfactant solution), as illustrated in Fig.1 of [38], closely related to the value of y can also be extended to differentiated natural organic films (see Tab. 3 in [38]). Low values of y (< 3.5) stand for a homogeneous mixed film ("good" solvent condition), higher y ≈8 ("theta" solvent case) lead to less film homogeneity observed as patches or domains of film-forming components. The highest y values (> 10-16; "poor" solvent condition) indicate the vertical segregated film structures forming nearly separate layers at the interface (sandwich-like) with the most insoluble (hydrophobic) compound on the top of this layered system.

The thermodynamic analysis is based on a virial expansion of the ideal gas law. This is not recommended, since the Langmuir surface film behaviour and the characteristic parameters are related to the van der Waals law, which produces self consistent parameters for the characterization of the surface film. However, for the purpose of intercomparing films, we arbitrarily fit the isotherms within the interval 0-5 mN m^{-1}, to derive the structural and thermodynamic parameters, where a surface film can be assumed to exhibit the ideal gas behaviour. While interpretation of the extrapolated parameters using this method is uncertain, curve fitting with a virial expression nevertheless may provide a useful means for condensing isotherm and isochore data in order to explore systematic differences.

Considering the Langmuir film to represent a van der Waals liquid the equation may be written as [39]:

$$(\pi - \pi_c) = T\beta^s$$

where $\pi_c = (\partial U/\partial V)_T$, and (5)

$$\beta^s = (\partial \pi/\partial T)_A = E^s/K^s_T = \alpha^s_\pi/\kappa^s_T$$

where π_c relates to the cohesive surface pressure representing the van der Waals forces of attraction between the hydrocarbon chains. The cohesive pressure is thus a differential property and related to the integral cohesive energy $C = \sqrt{(\Delta U/V)} = \sqrt{(\Delta H - RT/V)}$, where U is internal energy, H is enthalpy, and V is volume. For long chain surfactants it has been empirically found that $\pi_c \approx -400\, m_m A_m^{-3/2}$, for $A_m > 1$ nm², where m_m denotes the number of methylene groups in the hydrocarbon chain and A_m is expressed in Å² [40]. π_c is a sensitive measure of the subphase pH effect on ionic surfactant molecules interactions [41]. The higher values of π_c are evidence for stronger cohesion between the molecules. Further information on intermolecular interaction of film compounds can be derived from the surface pressure-temperature isochore $(\pi\text{-}T)_A$. The surface pressure-temperature coefficient β_s is related to the relative thermal (kinetic) mobility of the film molecules expressed by the kinetic surface pressure $\pi_k = \beta_s T$ [39]. Furthermore, the surface pressure coefficient β_s relates to surface expansivity (E^s) or isobaric expansion coefficient (α^s_π) over the surface isothermal compressibility coefficient (κ^s_T) to each other. The isoarea process (studied here) should be clearly distinguished from the isochoric (V=const) process, since Gibbs surface thermodynamics is defined for a surface alone without volume. Isoarea temperature β(T) dependence can exhibit the inflection points coinciding with the presence of certain critical phenomena (partial film collapse, 2D-phase transitions of higher orders, compression-induced structural changes) not evidenced in compression $(\pi\text{-}A)_T$ isotherms [39]. Moreover, the total pressure of the film should be: $\pi = \pi_k + \pi_c + \pi_r$, where π_r is responsible for the electrostatic forces of repulsion between charged head groups of monolayers [41]. The latter term is assumed to be negligible for surfactants of neutral character. It should be borne in mind that the chemistry of the fatty acids is not evaluated in detail here. Contribution of π_r, changing with compression (surface charge density) for ionized fatty acids, should be compared to the π_c – contribution provided by the van der Waals surface film relationships. In further studies the π_k contribution must be defined as an integral property.

Experimental Methodology

Sampling of rain water was carried out on the terrace of the Physics, Mathematics and Informatics Department building (University of Gdańsk, Poland) about 1 m above the surface in May, 2002. The winds near the ground were breezy, averaging 2–4 m s^{-1} as measured with a cap anemometer.

Rain water was collected using a V-shaped polypropylene collector with a 50 cm diameter (the tray collection area is 1,434 cm^2) and drained into a brown glass bottle (5 l) and a measuring burette for the rain rate evaluations.

Automatic drop-size measurements were made with a lab-built instrument in a form of teflon plate (hydrophobic material–water static contact angle $\theta \approx 124°$) having an area of 30×30 cm^2. It should be noticed that adsorption of the rainwater film forming material at the solid surface can leave the film behind the drop leading to the contact angle hysteresis=($\Delta\theta = \theta_a - \theta_r$, where θ_a and θ_r are the advancing and receding contact angles) playing a certain role in raindrop shape evaluations based on dynamic methods [42]. Pictures of the raindrop tracers at the measuring plate are accumulated for a set period, typically 20-60 s (depending upon the rain rate), magnified by a long-focus microscope 40 times and taken using a CCD camera connected to a computer for further image processing and raindrop size spectra evaluations. Before undertaking field measurements the disdrometer was calibrated under laboratory conditions to assess the relation between the diameter of a distilled water drop from the micropipette, carefully introduced on the hydrophobic plate (teflon) surface of the instrument, and its sessile drop diameter. Disdrometer data for 10 rainfall events were available for the study. The information included 1-min. drop counts of equivalent-volume diameters (D, mm) quantized in size categories of 0.1 mm. The range in tabulated drop diameters was 0.1-5.0 mm.

In order to perform surface pressure-area $(\pi\text{-}A)_T$ isotherm measurements of the rain water films, an initial trough area (1.200 cm^2) of the conventional rectangular Langmuir trough (30×40×0.8 cm) is compressed, with an average deformation speed ΔA/Δt chosen arbitrarily to be 0.60 cm^2 s^{-1}, by moving stepwise every 30 s two barriers towards each other symmetrically around the film pressure sensor. The film deformation rate adopted in these Langmuir trough studies leads to De number values as low as 0.009, fulfils the condition of isotherm registration in its equilibrium. As shown in Table 2 of [29] the static surface modulus E_{isoth} is useful in describing the compressional behaviour of a natural sea water film under very low compression rates assuming a two-step relaxation process with characteristic times τ_1 (1.1–2.8) and τ_2 (5.6-25.6) seconds revealed in stress-surface pressure relaxation measurements. Surface pressures were measured with a Wilhelmy plate technique using a piece of filter paper (Whatman No1, Madstone, England; 5- cm wide) attached to the arm of a force sensor (GM2+UL5, Scaime, France); they were accurate to within 0.1 mN m^{-1}. After equilibrating the rain water sample in the trough for 30 min, i.e. the standard period chosen for practical purpose, π-A isotherms were recorded in the temperature interval 5-35°C. Temperature of the subphase was controlled within ± 0.2 K by water circulation from a thermostat on the bottom of the trough and measured using a thermocouple located just below the air-water interface. The reported surface isotherm π-A and isochore π-T plots stand for an average over 3-4 measuring runs performed from the given sample. The Langmuir trough isotherm studies of rain water films were completed within a 1 hour period after sample collection. Further details on the Langmuir trough studies can be found elsewhere [28, 29, 37]. In the next section, mean value of each parameter is used in discussion.

Results and Discussion

Chemical analyses of the rain water samples pointed to a group of long-chain fatty acids as basic surfactants determining the rheology of surface films [11]. The isotherm scaling procedure already applied to the $(\pi\text{-}A)_T$ isotherms of natural water surfactants being a mixture of unknown makeup and concentration of components can also be modified for rain water films. Mean molecular masses M_w of the film-composing material on rain water samples range from 261 to 270 Daltons as appears from a concentration distribution of particular rain water fatty acids shown in Table 6 in [3], assuming the mean $M_w = \sum x_i M_i$, where M_i is the molecular mass of i-th component entering the mixture with the molar ratio x_i. The isotherm of the fatty acid having M_w in the middle of the established range at the water sub-surface of pH 4.6 (the mean value evidenced in the studied rain water samples) at T=19°C is used in the scaling procedure of the experimental π-A plot shown in Fig. 1. Applying the best-fit approximation to the data, the virial coefficients are determined first. Then, the film area A_{20} (at π=20 mN m^{-1}) is obtained from Eq.(2). The mass m, which produces a surface film of a surface pressure 20 mN/m is equal to 29.1 μg and results from taking A_m=0.215 nm^2 $molec.^{-1}$ at π=20 mN m^{-1} from the reference isotherm [43]. Apart from the basic Langmuir trough area scale A (cm^2), the lower scale corresponding to the Langmuir trough area referred to a volume of 1-liter rain water is also presented in Fig. 1. The bottom area per molecule scale was constructed according to the scaling concept. The points corresponding to each other on the first and third scales are C_1=769.5 cm^2 and A_{lim}=1.57 nm^2 $molec.^{-1}$. Values of the remaining structural parameters derived from the model isotherm using Eqs. (3-4), and E_{isoth}=y π dependence obtained in [38] are: E_{isoth}=30.10 mN m^{-1}; M_w=269 Da; $\Delta S_c = -1.33 \times 10^{-5}$ J m^{-2} K^{-1}; R=73.9% and y=16.5. They point to a surface film of liquid-expanded (LE) type formed from slightly soluble material (large R values comparable to crude oil-derivative films spread at the air/water interface as discussed in [37]), and being a mixture of surfactants creating segregated molecular structures. The obtained y value confirms the assumption made on complete 2D immiscibility of rain water surfactants [38]. The exemplary isotherm shows the kink at 10 mN m^{-1} caused by the breakdown of palmitic acid, which is forced out of the film at its equilibrium surface pressure (ESP), as indicated in nearly all the measurement curves of [44]. Palmitic acid had the highest concentrations among the fatty acids evidenced in rain water (see Table 6 of [3]), which is why its ESP is so clearly marked. The other kink, at around 30 mNm^{-1}, is likely caused by the breakdown of oleic acid but such a feature was not found in our studies since it lies over the surface pressure isotherm range registered in the experiment reported here.

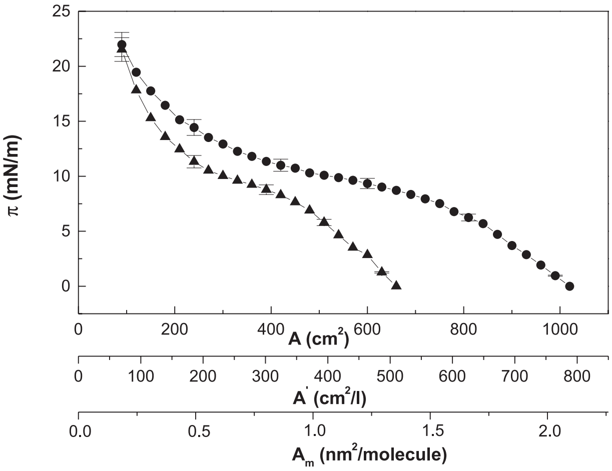

Fig. 1. Surface pressure-area $(\pi\text{-}A)_T$ isotherm of rain water sample collected on 28 May 2002. Compression (●) and expansion (▲) curves. The basic scale corresponds to the Langmuir trough area (cm^2), the lower one (area/liter) represents the Langmuir area referred to a 1 liter rain water volume. The bottom scale (area/molecule) was constructed according to the scaling concept. The points corresponding to each other on both scales are C_1 = 769.5 cm^2 and A_{lim} = 1.57 nm^2 $molec.^{-1}$.

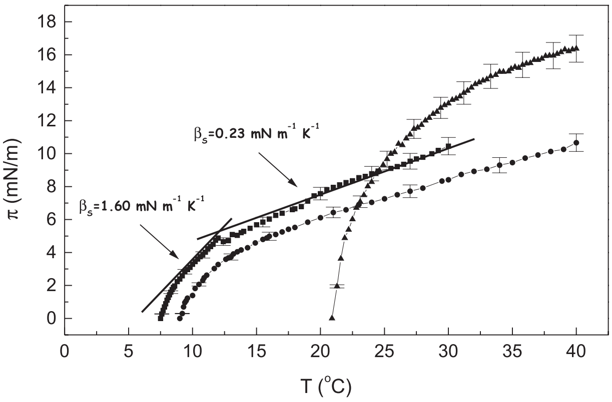

Fig. 2. Surface pressure-temperature $(\pi\text{-}T)_A$ isochores of rain water sample (▲) collected on 28 May 2003 and snow-melted waters sampled at Sopot (■) (21.03.2003) and Gdańsk (●) (06.03.2003), for comparison. The surface pressure-temperature coefficient β_s is evaluated from a slope of the straight line tangent to the experimental plot below and above a cusp point, as shown for 21.03.2003 registration.

Such a critical phenomenon within the film structure is also reflected in the surface pressure-temperature isochore $(\pi\text{-}T)_A$ plot presented in Fig. 2 as a cusp point at $\pi \approx 12.2$ mN m^{-1} at T=24°C. It should be borne in mind that ESP increases with the film temperature as depicted in Fig. 5 of [3]. Furthermore, β_s coefficient demonstrates a significant drop from 2.20 to 0.27 mN m^{-1} K^{-1} (see Fig. 2) that is attributed to a certain loss of the surfactant molecule mobility around the same π. The corresponding cohesive surface pressure π_c changes from -40.30 to -1.02 mN m^{-1}. Theoretically predicted values of π_c, for fatty acids C_{16}-C_{18} assuming A_m (=157 Å^2) taken from the model isotherm at the same π are much lower -7.00 to 7.87 mN m^{-1} but obtained if monolayers are considered to be neutral films. By changing the pH of the water sub-phase, the fatty acid monolayer can be neutral or negatively charged, due to ionization of the acid OH groups [45]. At very low pH (pH≈2) the monolayer is neutral and hydrogen bonding is the dominant interaction between monolayer head-groups and water molecules. At high pH values (pH≥7.0), the fatty acid OH groups should be significantly deprotonated, leaving the monolayer negatively charged. That creates a surface electric field and induces an ordered ("ice-like") hydrogen-bonding network. It appears that the pH of the rain water sub-phase has a major influence on the structure of fatty acid monolayers since pH values of rain/snow water were found to be > 4.0 (mean 4.4; [46]) whereas in natural sea water they are equal to 8.4, for instance. Cohesive surface pressure has an inverse relationship with the pH of the sub-phase, i.e. more negative π_c is obtained as pH increases. This implies that the interaction between molecules is stronger when the monolayer is spread over an alkaline sub-phase than over an acidic sub-phase.

Two isochore plots, for surface films formed from snow-melted water collected at Gdańsk and Sopot in March 2003 are also depicted in Fig. 2 for comparison. The same shape of the snow water isochors can be noticed with the cusp points at T=12°C and π=5.0 mN m^{-1} (Sopot), and T=13°C with π=4.3 mN m^{-1} (Gdańsk). It suggests a similar makeup of the film-forming material in snow-derived water apparently different from the rain water one. Values of β_s for both mentioned registrations are almost the same before (= 1.60 (Sopot) and 1.51mN $m^{-1}K^{-1}$ (Gdańsk)) and beyond (= 0.23 (Sopot) and 0.22 mN $m^{-1}K^{-1}$ (Gdańsk)) the isochore critical point. The corresponding π_c changes from -14.20 to -2.24 mN m^{-1} (Sopot) and from -15.33 to -1.44 mN m^{-1} (Gdańsk) at the isochore critical point that suggests the pH of the snow water is lower in comparison to the rain water considered above, assuming similarity of the film-forming material in the both samples. The higher concentration of the surface-active substances in the Sopot-collected sample can be deduced from the fact that the plot lies over the curve obtained from Gdańsk sample ($\Gamma \approx \pi / kN_AT$) since snow collection at Sopot took place after 14 days elapsed from the precipitation event, whereas at Gdańsk snow was sampled immediately.

It is interesting to compare the structural parameters of snow water films (derived from the isotherms not shown here), although the rain water scaling concept is not valid here. The isotherm-derived parameters from the sampling event (fresh snow) at Gdańsk on 6.03.2003 are: E_{isoth}=28.46 mN m^{-1}; ΔS_c=-0.69 x 10^{-5} J m^{-2} K^{-1}; R=80.9% and y=14.3 and are comparable to these evidenced in samples collected at Sopot on 21.03.2003: E_{isoth}=27.26 mN m^{-1}; ΔS_c= –0.24 x 10^{-5} J m^{-2} K^{-1}; R=88.3% and y=20.7. It appears that the surface-active material of snow water is less soluble (higher R) of similar chemical nature (similar values of E_{isoth} and y) if compared to the surfactants evidenced in rain water.

It is worth comparing surface rheology of natural organic films on marine water obtained by means of the same scaling procedures applied to the surface pressure-area isotherms and studied in neighboring coastal areas (Gulf of Gdańsk, Baltic Sea) where rain and snow water sampling took place. The limiting specific area A_{lim} (2.68-31.57 nm^2 $molec.^{-1}$), elasticity modulus E_{isoth} (19.31- 42.69 mN m^{-1}), molecular mass M_w (0.65-9.7 kDa), change in entropy ΔS_c (-0.09- 7.04 x 10^{-5} Jm^{-2} K^{-1}) and scaling exponent y (3.3-13.9) were found, for sea surface films [29, 30]. It should be pointed out that the structure of rainwater films is not a simple function of fatty acid composition but also depends on several environmental factors not controlled in the present study. The variability of the parameters introduced here rather than their absolute values is postulated to be a useful tool for rainwater surfactant pathways tracing and reflecting the film state spatial and temporal signatures, as recently shown in source-specific surfactant film studies performed for the Dead Vistula river, its tributaries and the adjacent coastal area [47]. Since natural films are composed of a range of surfactants each having unique adsorption and desorption rate constants, competitive adsorption takes place. For mixtures, relative rates of adsorption and desorption favor enrichment of certain components. For films under compression in Langmuir trough isotherm studies, the preferential desorption of hydrophilic components can leave behind the more hydrophobic species resulting ultimately in changes toward higher elastic moduli and other structural parameters in time, for instance. In addition, discontinuities in the isotherm plots attributed to phase transitions can also result from non-Newtonian surface rheologies, more complex interactions like gelation or aggregation. Other related mechanisms e.g., film polymerization and intermolecular bonding can cause similar film states. To sum up, more thorough discussion on the surface film 2D phase identification and formation awaits additional comprehensive experiments including surface potential measurements and Brewster angle microscopy direct film state inspection foreseen to be performed in future studies.

A more detailed description of the rain water film structure requires additional mechanisms taking place at the rain drop-film covered surface (evaporation and resulting shrinkage of the rain drop controlled by the film compression state [48], and the reaction of gaseous O_3 with a surface layer of surfactants at the air-water interface [49], for instance) to be accounted for in further studies. A large variability of the selected film parameters observed while comparing natural organic films present on atmospheric, inland and marine waters points to an opportunity to create a novel method for ecosystem quality assessment based on surface rheology studies.

Conclusions

The rain water film structural parameters derived from the force-area isotherms using the novel scaling concept established the highly-organized molecular morphology of slightly soluble immiscible components of mean molecular masses within 261-270 Daltons in agreement with chemical analysis findings.

Further information on the rain water film morphology can be gained from the $(\pi\text{-}T)_A$ isochore plots with the isoarea surface pressure temperature coefficient β_s related to thermal molecule mobility, intermolecular cohesive forces, and other critical phenomena in the interfacial system. The pH of the water sub-phase appears to be an important factor affecting the organic film structure on atmospheric particles.

The quantification of the structural parameters variability can be a universal measure of the surface elastic properties evolution applicable to a wide diversity of natural films present at natural water interfaces and developed to a new method for organic matter dynamics tracking.

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References

1. CAPEL, P. D., GUNDE, R., GIGER, W. Carbon speciation and surface tension on fog. Environ. Sci. Technol. **24**, 722, **1990**.
2. FACCHINI, M. C., MIRCEA, M., FUZZI, S., CHARLSON, R. J. Cloud albedo enhancement by surface-active organic solutes in growing droplets. Nature **401**, 257, **1999**.
3. SEIDL, W. Model for a surface film of fatty acids on rain water and aerosol particles. Atmos. Environ. **34**, 4917, **2000**.
4. CECINATO, A., MABILIA, R., MARINO, F. Relevant organic components in ambient particulate matter collected at Svalbard Islands (Norway). Atmos. Environ. **34**, 5061, **2000**.
5. GELENCSER, A., MESZAROS, T., BLAZSO, M., KISS, G., KRIVACSY, Z., MOLNAR, A., MESZAROS, E. Structural characterization of organic matter in fine tropospheric aerosol by pyrolysis-gas chromatography-mass spectrometry. J. Atmos. Sci. **37**, 173, **2000**.
6. GRAHAM, B., GUYON, P., TAYLOR, P., ARTAXO, P., MAENHAUT, W., GLOVSKY, M., FLAGAN, R., ANDREAE, M. Organic compounds present in the natural Amazonian aerosol: Characterization by gas chromatography-mass spectrometry. J. Geophys. Res. **108**, D4766, **2003**.
7. TERVAHATTU, H., JUHANOJA, J., VAIDA, V., TUCK, A. F., NIEMI, J., KUPIAINEN, K., VEHKAMAKI, K. M., VEHKAMAKI, H. Fatty acids on continental sulfate aerosol particles. J. Geophys. Res. **110**, D06207, **2005**.
8. GAGOSIAN, R. B., ZAFIRIOU, O. C., PELTZER, E. T., ALFORD, J. B. Lipids in aerosols from the tropical north Pacific: Temporal variability. J. Geophys. Res. **87C**, 11133, **1982**.
9. MEYERS, P. A., HITES, R. A. Extractable organic compounds in Midwest rain and snow. Atmos. Environ. **16**, 2169, **1982**.
10. GILL, P. S., GRAEDEL, T. E., WESCHLER, C. J. Organic films on atmospheric aerosol particles, fog droplets, cloud droplets, raindrops, and snowflakes. Rev. Geophys. Space Phys. **21**, 903, **1983**.
11. POLZER, J., BÄCHMANN, K. Determination of fatty acids in atmospheric samples via GC/MS. Fresenius Journal of Analytical Chemistry **340**, 555, **1991**.
12. MAZUREK, M., MASONJONES, M. C., MASONJONES, H. D., SALMON, L. G., CASS, G. R., HALLOCK, K. A., LEAITCH, M. Visibility-reducing organic aerosols in the vicinity of Grand Canyon National Park: Properties observed by high-resolution gas chromatography. J. Geophys. Res. **102D**, 3779, **1997**.
13. ROGGE, W. F., MAZUREK, M. A., HILDEMANN, L. M., CASS, G. R., SIMONEIT, B. R. T. Quantification of urban organic aerosols at a molecular level: Identification, abundance and seasonal variation. Atmos. Environ. **27A**, 1309, **1993**.
14. ZHENG, M., WAN, T. S. M., FANG, M., WANG, F. Characterization of the non-volatile organic compounds in the aerosol of Hong Kong: Identification, abundance and origin. Atmos. Environ. **31**, 227, **1997**.
15. DECESARI, S., FACCHINI, M. C., FUZZI, S., TAGLIAVINI, E. Characterization of water-soluble organic compounds in atmosphere aerosol: A new approach. J. Geophys. Res. **105**, 1481, **2000**.
16. FUZZI, S., DECESARI, S., FACCHINI, M. C., MATTA, E., MIRCEA, M., TAGLIAVINI, E. A simplified model of the water soluble organic component of atmospheric aerosols. Geophys. Res. Lett. **28**, 4079, **2001**.
17. BARGER, W. R., GARRETT, W. D. Surface active organic material in the marine atmosphere. J. Geophys. Res. **75**, 4561, **1970**.
18. MOCHIDA, M., KITAMORE, Y., KAWAMURA, K., NOJIRI, Y., SUZUKI, K. Fatty acids in the marine atmosphere: Factors governing their concentration and evaluation of organic films on sea-salt particles. J. Geophys. Res. **107**, 4325, **2002**.
19. RUSSELL, L. M., MARIA, S. F., MYNENI, S. C. B. Mapping organic coatings on atmospheric particles. Geophys. Res. Lett. **29**, 16, **2002**.
20. TERVAHATTU, H., HARTONEN, K., KERMINEM, V.-M., KUPIAINEN, K., AARNIO, P., KOSKENTALO, T., TUCK, A. F., VAIDA, V. New evidence of an organic layer on marine aerosols. J. Geophys. Res. **107**, D7, **2002**.
21. TERVAHATTU, H., JUHANOJA, J., KUPIAINEN, K. Identification of an organic coating on marine aerosol particles by TOF-SIMS. J. Geophys. Res. **107**, D16, **2002**.
22. MOCHIDA, M., KAWAMURA, K., UMEMOTO, N., KOBAYASHI, M., MATSUNAGA, S., LIM, H. –J., TURPIN, B., BATES, T., SIMONEIT, B. Spatial distribution of oxygenated organic compounds (dicarboxylic acids, fatty acids, and levoglucosan) in marine environments over the western Pacific and off the coast of East Asia: Continental outflow of organic aerosols during the ACE-Asia campaign. J. Geophys. Res. **108**, D23, **2003**.
23. SIMONEIT, B. R. T., MAZUREK, M. A. Organic matter of the troposphere – II. Natural background of biogenic lipid matter in aerosols over the rural western United States. Atmos. Environ. **16**, 2139, **1982**.
24. ROGGE, W. F., HILDEMANN, L. M., MAZUREK, M. A., CASS, G. R., SIMONEIT, B. R. T. Sources of fine organic aerosol. 2. Noncatalyst and catalyst-equipped automobiles and heavy-duty diesel trucks. Environ. Sci. Technol. **27**, 636, **1993**.
25. ROGGE, W. F., HILDEMANN, L. M., MAZUREK, M. A., CASS, G. R., SIMONEIT, B. R. T. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: Roads as sources and sinks. Environ. Sci. Technol. **27**, 1892, **1993**.
26. SIMONEIT, B. R. T. Biomass burning: A review of organic tracers for smoke from incomplete combustion. Appl. Geochem. **17**, 129, **2002**.
27. ROGGE, W. F., HILDEMANN, L. M., MAZUREK, M. A., CASS, G. R. Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations. Environ. Sci. Techol. **25**, 1112, **1991**.

28. POGORZELSKI, S. J. Structural and thermodynamic characteristics of natural marine films derived from force-area studies. Colloids Surfaces A: Physicochem. Eng. Aspects **189**, 163, **2001**.
29. POGORZELSKI, S. J., KOGUT, A. D. Structural and thermodynamic signatures of marine microlayer surfactant films. J. Sea Res. **49**, 347, **2003**.
30. POGORZELSKI, S. J., KOGUT, A. D. Adsorptive properties of natural water surfactant films. Dead Vistula catchment water studies. Oceanologia **45**, 373, **2003**.
31. KIEBER, R. J., PEAKE, B., WILLEY, J. D., BROOKS AVERY, G. Dissolved organic carbon and organic acids in coastal New Zealand rainwater. Atmos. Environ. **36**, 3557, **2002**.
32. BALASUBRAMANIAN, R., VICTOR, T., CHUN, N. Chemical and statistical analysis of precipitation in Singapore. Water, Air and Soil Pollut. **130**, 451, **2001**.
33. FACCHINI, M. C., FUZZI, S., ZAPPOLI, S., ANDRACCHIO, A., GELENCER, A., KISS, GY., KRIVÁCSY, Z., MÉSZÁROS, E., HANSON, H. C., ALSBERG, T., ZEBÜHR, Y. Partitioning of the organic aerosol component between fog droplets and interstitial air. J. Geophys. Res. **104**, 26821, **1999**.
34. ADAMSON, A. W. Physical Chemistry of Surfaces, Wiley, New York, **1982**.
35. BARGER, W. R., MEANS, J. S. Clues to the structure of marine organic material from the study of physical properties of surface films. In A.C. Sigleo and A. Hattori (eds.), Marine and Estuarine Geochemistry, Levis Publishers: Chelsea, pp. 47-67, **1985**.
36. BOCK, E. J., FREW, N.M. Static and dynamic response of natural multicomponent oceanic surface films to compression and dilation: Laboratory and field observations. J. Geophys. Res. **98**, 14599, **1993**.
37. POGORZELSKI, S. J., STORTINI, A. M., LOGLIO, G. Natural surface film studies in shallow coastal waters of the Baltic and Mediterranean Seas. Cont. Shelf. Res. **14**, 1621, **1994**.
38. POGORZELSKI, S. J. Application of 2D polymer film scaling theory to natural sea surface films. Colloids Surfaces A: Physicochem. Eng. Aspects **114**, 297, **1996**.
39. ROSENHOLM, J. B., IHALAINEN, P., PELTONEN, J. Thermodynamic characterization of Langmuir monolayers of thiolipids: A conceptual analysis. Colloids Surfaces A: Physicochem. Eng. Aspects **228**, 119, **2003**.
40. DAVIES, J. T., RIDEAL, E. K. Interfacial Phenomena, Academic Press, New York, Chapter 5, **1961**.
41. GONG, KE., FENG, SI.- S., GO, M. L., SOEW, P. H. Effects of pH on the stability and compressibility of DPPC/cholesterol monolayers at the air-water interface. Colloids Surfaces A: Physicochem. Eng. Aspects **207**, 113, **2002**.
42. CHIBOWSKI, E. Surface free energy of a solid from contact angle hysteresis. Adv. Colloid Interface Sci. **103**, 149, **2003**.
43. HARKINS, W. D. The Physical Chemistry of Surface Films, Reinhold, New York, **1952**.
44. SEIDL, W., HÄNEL, G. Surface-active substances on rainwater and atmospheric particles. Pure and Applied Geophysics **121**, 1077, **1983**.
45. MIRANDA, P. B., DU, Q., SHEN, Y. R. Interaction of water with a fatty acid Langmuir film. Chem. Phys. Lett. **286**, 1, **1998**.
46. BRIDGES, K. S., JICKELLS, T. D., DAVIES, T. D., ZEMAN, Z., HUNOVA, I. Aerosol, precipitation and cloud water chemistry observations on the Czech Krusne Hory plateau adjacent to heavily industrialized valley. Atmos. Environ. **36**, 353, **2002**.
47. POGORZELSKI, S. J., KOGUT, A. D., MAZUREK, A. Z. Surface rheology parameters of source – specific surfactant films as indicators of organic matter dynamics. Hydrobiologia **554**, 67, **2006**.
48. FROST, A. E., SEAVER, M. Ionic effects on solid phase formation in 1-octadecanol films on levitated water drops. Thin Solid Films **247**, 184, **1994**.
49. LAI, C. C., YANG, S. H., FINLAYSON-PITTS, B. J. Interactions of monolayers of unsaturated phosphocholines with ozone at the air-water interface. Langmuir **10**, 4637, **1994**.