

Original Research

The Surface Rheological Properties of Organic Films on Rain Water: Rain Rate Correction

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Abstract

The presented procedure allows one to recover the film properties present originally at the raindrop surface from the Langmuir trough data supplemented with simultaneously taken rain event characteristics (rain rate and rain drop diameter distribution). It requires the partitioning effect of the surfactant molecules between the surface and bulk phases to be estimated where the entering quantities are: the partitioning coefficient $K_p = \Gamma/c$ and a degree of the rain water interfacial system area development A_r/V_r evaluated here using fatty acid concentrations as model input data. The latter parameter depends on particular rain event signatures. The concept is quantified using the Langmuir trough film and disdrometer data on a set of rain water events observed at Gdańsk, Poland in May 2002.

Keywords: source-specific surfactants, rain water film, structural parameters, surfactant partitioning correction, rain rate effect

Introduction

Organic compounds with a long hydrocarbon chain and polar group, e.g. organic acids, alcohols or esters, can form monomolecular films at the air-water interface [1]. Such film-forming substances accumulate at interfaces and change the physico-chemical properties of humid aerosol particles, cloud droplets and raindrops. Provided that the surface film has a sufficient concentration and a particular interfacial structure with certain rheological properties, the other phenomenon of importance in hydrometeor physics like a barrier effect on the mass, water vapour or trace gases transport through the water surface [2], the rain-forming process in a number of ways are all surface-film mediated [3]. The predominating and well identifiable components are the n-alkanoic acids (fatty acids) with 12 to 18 carbon atoms as most likely film-forming compounds on rain water [4, 5]. However, a complex

mixture of substances with different physicochemical properties has been found on rain water, which can form monomolecular films at the air-water interface [2, 4-9].

A key problem addressed in this paper is the proper determination of surface film rheological properties occurring at the rain drop surface from Langmuir trough surface pressure – area isotherm studies performed on rain water samples collected at different rain rates. That requires the partitioning effect of the surfactant molecules between the surface and bulk phases to be accounted for [10, 11].

A corrective factor, x_s , relating the area per molecule A_m of the rain drop to Langmuir-trough studied films, for the same surfactant-containing rain water sample, depends on the physicochemical nature of the film-forming material, i.e. the partitioning coefficient $K_p = \Gamma/c$ (surface adsorption/bulk concentration ratio) and a degree of the rain water interfacial system area development = A_r/V_r (total area of rain drops exposed to atmosphere/volume of the rain water sample). The latter parameter

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depends on the form of the rain drop diameter distribution function (widely assumed to be the Marshall-Palmer one) and rain rate I_r . It should be pointed out that a traditional Marshall-Palmer (M-P) drop size distribution (DSD) was derived from limited observation data and for different kinds of rain events. The real DSD could be very different. A general form of DSD could be assumed as exponential and Gamma distribution. The M-P DSD is only a specific case of an exponential DSD. This paper discusses the similarity of DSD shapes between the experimental and M-P distribution that could affect the surfactant partitioning effect evaluation. The main advantage of the Marshall-Palmer parametrization for DSD is that it bears a functional dependence on only one variable, namely the rain rate. Precipitation reference data obtained by others at similar environmental conditions (wind speed, temperature) and collected in corresponding rain event regimes (rain rate and mean raindrop diameter) were adopted in considerations on the similarity of DSD shapes between the experimental and M-P distribution at different rain rates. The hypothesis presented here could provide a basis for systematically comparing characteristics of rain water films taken at different interfacial rain event regimes.

In this report we also determine a few of the rain water surface film parameters (bulk concentration – c , surface adsorption – Γ , mean molecular mass – M_w of surfactants, film pressure – π , lowering of the surface tension of pure water) and estimate the corrective factors where for model considerations the measurements of fatty acids in Bloomington, Indiana, USA [4], and in Bensheim, Germany [5] have been used. Finally, the rain water film structural parameters were evaluated in model Langmuir trough studies and corrected according to partitioning hypotheses using the disdrometer data on a set of rain water events observed in Gdańsk, Poland, in May 2002.

In the future, further compounds can be included into the formalism which was developed for fatty acids here, although their nature and film-forming properties are not well known until now.

In the accompanying paper on rain water film properties a novel concept of the film structure quantification in terms of the rheological parameters – indicators resulting from the scaling procedures applied to the surface pressure – area isotherms and surface pressure – temperature isochors, obtained in Langmuir trough measurements performed on rain water samples, will be presented.

Theoretical Background

Partitioning of Surfactants at the Air-Water Interface

We compare the surface rheological properties of organic films occurring originally at the raindrop surfaces exposed to atmosphere (having a total area = A_r) and these obtained from the Langmuir trough studies (with an area of the trough = A_L) performed on the same rain water sam-

ple of bulk volume V . It requires the partitioning effect of surfactant molecules between the surface and bulk phases to be estimated [10, 11].

Owing to mass conservation, the total amount of lipid, n (mol), must be subject to the relation:

$$n = A\Gamma + Vc \quad (1)$$

involving interfacial area A , surface concentration Γ (mol per unit area), bulk volume V , and subphase concentration c (mol per unit volume), respectively. Provided a thermodynamic equilibrium has been established, the surface pressure π (force per unit length) is functionally determined by the variable Γ alone (other possible external variables such as temperature and pressure being fixed). In addition, there is a functional relationship between Γ and c [1].

Owing to the above reasoning we conclude that calculating an apparent molecular area A_m ($= 1/\Gamma N_A$) at a given π simply as A divided by the total number of lipid molecules may produce variable results depending on the experimental circumstances. With respect to the true molecular area A_m' one obtains:

$$A_m' = (1 - x_s) A_m \quad (2)$$

Therefore, the disagreement of the reported A_m' could easily be due to a somewhat different choice of the ratio A/V .

The fraction having entered the subphase x_s is readily derived by means of Eq. (1), namely:

$$x_s = (V/n)c = (1 + K_p[A/V])^{-1} \quad (3)$$

involving an apparent partition coefficient $K_p = \Gamma/c$ that depends on π . The latter parameter can be computed from the relations between surface pressure and concentration and between the concentration and surface adsorption given by the Szyszkowski and Langmuir isotherm equations, respectively [1]:

$$\pi = RT\Gamma_\infty \ln(1 + c/a) \quad (4)$$

$$\Gamma = \Gamma_\infty [c/(c+a)] \quad (5)$$

with Γ_∞ – the saturation adsorption and a – the Szyszkowski surface activity coefficient.

For long-chain fatty acids, the saturation adsorptions Γ_∞ are almost the same (the corresponding limiting area per molecule is 27-32 Å²), hence the variance of the parameter K_p with the number of hydroxyl groups in the surfactant molecule is attributed to the variation of the activity coefficient a [12, 13].

Equation (4) can be extended to a multicomponent system assuming ideal surface behaviour and equal saturation adsorptions ($\Gamma_\infty = \Gamma_{\infty 1} = \Gamma_{\infty 2}$) of the compounds [14]:

$$\pi = RT\Gamma_\infty \ln(1 + c_1/a_1 + c_2/a_2 + \dots) \quad (6)$$

where c_1 and c_2 are the monomer concentrations of the film-composing surfactants, and a_1 and a_2 are the corresponding Langmuir-Szyszkowski constants, respectively.

Relation between A_r and I_r

Based on Marshall-Palmer (M-P) size distribution [15], we can evaluate an approximate total area A_r of the raindrops exposed to the atmosphere contained in a liter of rain water.

Assuming the (M-P) size distribution, the following dependence between the mean raindrop diameter \bar{D} and rain rate I_r can be obtained [16]:

$$\bar{D} \text{ (M-P)} = 0.895 I_r^{0.21} \text{ (mm)} \quad (7)$$

The total area A_r of raindrops contained in a volume V_r of rain water can be expressed:

$$A_r = n_d 4\pi \left(\frac{\bar{D}}{2} \right)^2 = 6V_r / \bar{D} \quad (8)$$

with the number of drops:

$$n_d = V_r / \frac{4}{3} \pi \left(\frac{\bar{D}}{2} \right)^3 \quad (9)$$

By using the M-P droplet size distribution, it can be estimated that the raindrops by themselves have a surface area of 40,000–120,000 cm² l⁻¹ depending on the rain intensity, whereas in the Langmuir-type film balance used in [7], a liter of rain water had a surface area of ca. 800 cm².

There has been much effort to determine the shape of falling raindrops (see [17]) for a review of the observational data, empirical axis-ratio relations derived from them, and relations based on theoretical considerations. Other studies revealed the importance of vortex shedding, collisions, and turbulence or wind shear [18, 19], which can cause drops in the free atmosphere to have mean shapes that differ from equilibrium.

Experimental Methodology

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

Rainwater was collected using a V-shaped polypropylene collector with a 50 cm diameter (the tray collection area is 1,434 cm²) 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 contact angle $\approx 124^\circ$) having an area of 30×30 cm². 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 using a CCD camera connected to a PC-class 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 (π -A) isotherm measurements of the rain water films, an initial trough area (1,200 cm²) of the conventional rectangular Langmuir trough (30×40×0.8 cm) is compressed, with an average deformation speed $\Delta A/\Delta t$ chosen arbitrarily to be 0.60 cm² s⁻¹, by moving stepwise every 30s two barriers towards each other symmetrically around the film pressure sensor. 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), accurate within 0.1 mN m⁻¹. The obtained 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 [20–22].

The comprehensive literature DSD data, analyzed in the next section, were taken from carefully monitored precipitation measurements performed at the eastern end of Vancouver Island, British Columbia, Canada during the winter of 1984–85 under calm conditions, generally with wind speeds below 1.2 m s⁻¹ [23]. Rainfall rate (corresponding to a low rain rate range of 0.1 to 1.2 mm h⁻¹) was measured continuously with an AES tipping-bucket rain gauge and drop-size distribution was determined with a Joss-Valdovogel RD-69 disdrometer [24]. Another representative data sets on the DSD parameters retrieved for samples of convective and trailing stratiform rain obtained during the 15 February 1999 squall-line event, the Tropical Rainfall Measuring Mission (TRMM) Brazil campaign, are analyzed [25]. The DSD reference data originated from 2D-video and RD-69 disdrometer evaluations at rather low rain rates ($I_r < 5$ mm h⁻¹). Representative samples of DSD measurements were made in convective rain (2-min-averaged registrations). According to the Glossary of Meteorology (1959) [26], we are concerned here with “small” ($0.8 \leq D \leq 1.1$ mm) or “mid-size”

(1.1 ≤ D ≤ 2.2 mm) drops and “light” ($I_r < 2.5 \text{ mm h}^{-1}$) to “moderate” ($2.5 \leq I_r \leq 7.6 \text{ mm h}^{-1}$) rain.

Results and Discussion

Evaluation of A_r

Adopting the relation between \bar{D} and I_r (see Eq. (7)), A_r can be evaluated without the measurement of raindrop diameter spectra. However, at low rain rates ($I_r = 0.4 \text{ mm h}^{-1}$) a histogram of drop diameter distribution may significantly differ from the M-P standard shape, as illustrated in Fig. 1. The distribution exhibits three distinctly separated local maxima and consists of distributions overlapping each other. More details on drop diameter variations are revealed by an analysis of the distribution shape in a wide range of rain rates reported in the literature [23–25]. It should be born in mind that a traditional Marshall-Palmer DSD is applied here. It is well-known that the M-P DSD was determined on limited observation data and for different kinds of rain events. A general form of DSD could be assumed exponential and Gamma distribution. The M-P DSD is only a particular case of an exponential DSD with specific constant values. DSD precipitation literature data, reported by others and derived at similar rain event regimes, were selected for intercomparisons of the similarity of DSD shapes between the experimental and M-P distribution at different rain rates.

A good approximation of the experimental distribution of drop diameter spectra is obtained by expanding the Gaussian function $p_n(D)$ into a Gram–Charlier series, taking into account statistical moments up to the fourth one. The polynomial function has the form [27]:

$$p(D) = p_n(D) \left[1 + \frac{A_1}{6} H_3(z) + \frac{A_2}{24} H_4(z) + \dots \right] \quad (10)$$

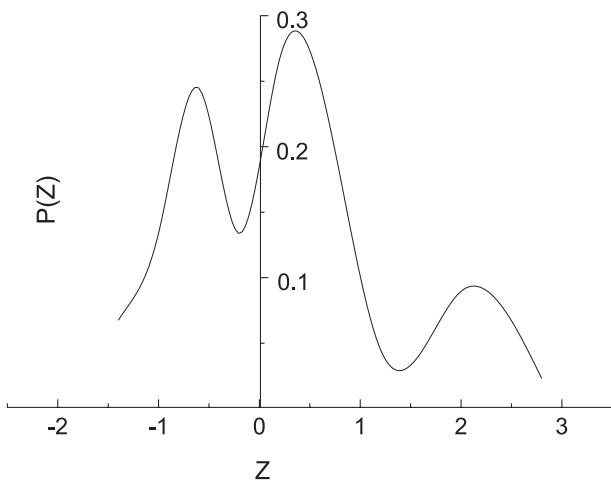


Fig. 1. Exemplary histogram of raindrop diameter distribution for low rain rate ($I_r = 0.4 \text{ mm h}^{-1}$), as a function of normalized random variable $z = (D - \bar{D})/\sigma$; data from [24].

where $p_n(D)$ – the Gaussian distribution, \bar{D} , D – the mean and temporal drop diameters, σ – the standard deviation, $z = [D - \bar{D}]/\sigma$ – the normalized random variable, $H_3(z) = z^3 - 3z$ and $H_4(z) = z^4 - 6z^2 + 3$ – Hermite polynomials, $A_1 = \mu_3/\sigma^3$ – the asymmetry coefficient (skewness), $A_2 = (\mu_4/\sigma^4) - 3$ – the flattening coefficient (kurtosis), μ_3, μ_4 – the third and fourth central statistical moments.

Fig. 2 presents asymmetry coefficient A_1 as a function of rain rate I_r for disdrometer data reported in the literature [23–25]. In the wide range of I_r , the coefficient has a positive value that means the distribution exhibits a strong right-hand asymmetry if compared to the reference normal one. An increase in I_r intensifies a right-hand asymmetry ($|A_1|$ grows; see the solid line in Fig. 2 representing the best-fit approximation to the experimental points).

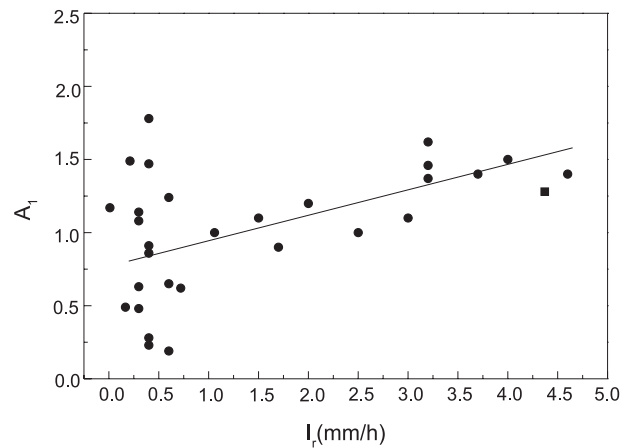


Fig. 2. Asymmetry coefficient A_1 (skewness) of raindrop diameter distribution versus rain rate I_r ; data from [23–25]. The solid line represents the best-fit approximation to the data ($r^2 = 0.63$). ■ – data point for experimental distribution from Fig. 4.

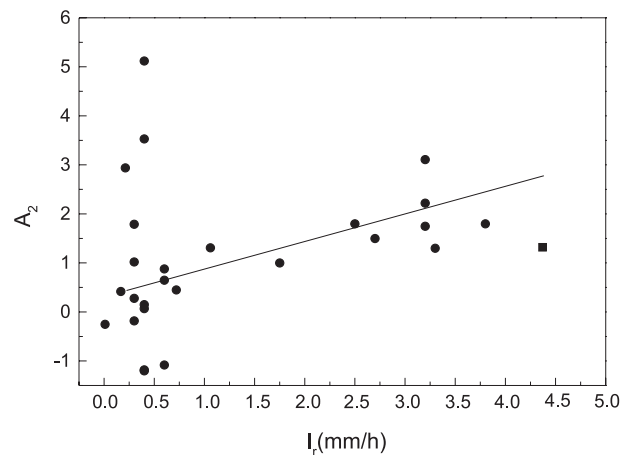


Fig. 3. Flattening coefficient A_2 (kurtosis) of raindrop diameter distribution versus rain rate I_r ; data from [23–25]. The solid line corresponds to the best-fit approximation to the data ($r^2 = 0.67$). ■ – data point for the experimental distribution from Fig. 4.

The peakedness coefficient A_2 versus rain rate I_r is presented in Fig. 3. The values of A_2 are generally positive, which means that the distribution is sharper than the normal one. As I_r increases, continuous sharpening of the distribution is observed (A_2 grows as illustrated by the solid line representing the best-fit approximation to the experimental points in Fig. 3).

Parameters A_1 and A_2 describe in a regular way the deviations of the experimental distribution from the Gaussian one, in which values of \bar{D} and σ – are introduced from the experimental data [27]. A large variability of the parameters A_1 and A_2 could be noticed in the low rain rate range ($I_r < 1 \text{ mm h}^{-1}$); as a result, the rain-drop diameter spectra may vary in shape from the M-P standard function [28].

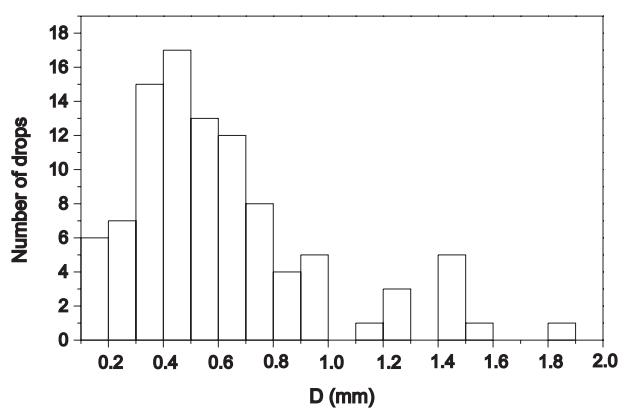


Fig. 4. Histogram of raindrop diameter distribution obtained from disdrometer data on 28.05.2002 at a terrace of the Mathematics, Physics and Informatics Department building (University of Gdańsk, Poland; $I_r = 4.37 \text{ mm h}^{-1}$; $T = 19^\circ\text{C}$).

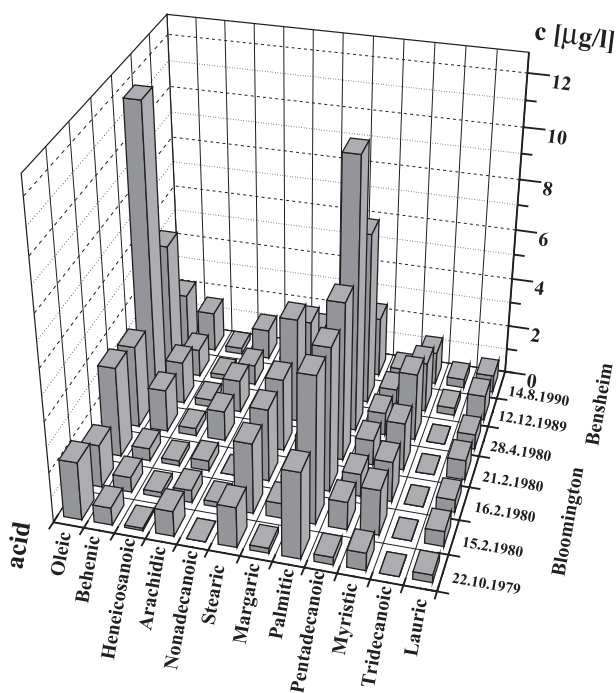


Fig. 5. Bulk concentration distribution of n-alkanoic acids (fatty acids) found in rain water samples, based on data from [4, 5].

A histogram of raindrop diameter distribution obtained in the course of the present study from disdrometer data at $I_r = 4.37 \text{ mm h}^{-1}$ is presented in Fig. 4. The histogram shape exhibits an apparent right-hand asymmetry of the distribution. The deviation parameters of A_1 (skewness) and A_2 (kurtosis) appear to be 1.28 and 1.32, respectively. These data points are also included in Figures 2 and 3 being within the approximation error, close to the best-fit line resulting from disdrometer data reported by others at the same I_r .

The mean drop diameter \bar{D} computed from Eq. (7), for such a value of I_r , is equal to 1.2 mm that leads to $A_r = 49,720 \text{ cm}^2 \text{ liter}^{-1}$. However, directly from the experimental distribution one obtains $\bar{D} = 0.62 \text{ mm}$ and $A_r = 58,125 \text{ cm}^2 \text{ liter}^{-1}$. A self coincidence of both A_r values is within 14%, which points to the similarity of shapes between the experimental and M-P distribution functions. Equation (7) provides a useful basis for the proper evaluation of A_r at higher I_r where the measurement of drop size spectra is avoided.

Structural Signatures of Rain Water Film

Chemical analyses of rain water samples pointed out to a group of long-chain fatty acids as basic surfactants determining the rheology of surface films [5]. As a result of their well-established surface activity, factor K_p should vary in a rather narrow range for a particular rainwater sample, the film structural parameters are mainly determined by the A/V ratio of the interfacial system. For the exemplary rain water sample, such a ratio is $A_r/V_r = 58.13 \text{ cm}^{-1}$ for a surface film at the developed surfaces of rain drops, and is equal only to $A_L/V_L = 0.88 \text{ cm}^{-1}$ when studied in our Langmuir trough system. Equation (2) relating A_m' and A_m provides the basis for a proper comparison of the surface film state taken at different interfacial systems, in particular present at a rain drop surface that is not directly measurable.

The mean values of the parameters c , Γ , K_p , π , M_w entering Eqs.(3-6) are computed from the molar ratios x_i of each fatty acid component in the mixture as follows: the mean $c = \sum x_i c_i$, where c_i is the bulk concentration of i -th component, for instance. This implies that we are concerned with an ideal mixed monolayer formed from completely immiscible compounds. The total area of the film is then obtained by adding the film areas of all the acids. It is surprising that the total film area of a mixed film is not affected by interactions of acids in different states of phase. But the measurements showed only deviations of the total film area by approximately 10% against the sum of the film areas of a single acid [29, 30]. This behavior simplifies the modeling of the mixed film considerably. Data on the rain water fatty acids concentrations distribution, as depicted in Fig. 5, were used as model inputs and taken from Table 6 of [3], whereas the compound specific constants for fatty acids originate from [31]. Palmitic, stearic and oleic acids had the highest concentra-

tions among the fatty acids in rain water collected in rural areas [4, 5].

Values of the rain water film parameters together with the correction coefficients K_p and x_s are collected in Table 1. The predicted surface pressures at rain water drop surfaces evaluated from Eq.(6) are rather low (1.9-5.4 mN m⁻¹) exhibiting a quasi-ideal 2D gas behavior characteristic of a diluted surfactant solution with $c \approx 10^{-3}a$, as can be noticed from Table 1. Films with very small concentrations (corresponding to the area per molecule larger than 50 nm²) can be described as a 2D gas. The partitioning into the aqueous subphase at equilibrium depends on the surface pressure but also on the area/volume ratio of the measuring trough. The partitioning factor K_p ranges from 5.3 to 13.7 cm, and the higher values are noticed for rain water samples collected in a summer-autumn season (see data on 14.08.90 and 22.10.79 at Bensheim and Bloomington, respectively). It can result from a higher relative contribution of more hydrophobic (less soluble) fatty acids in these samples, and reflects a source-specific concentration pattern of a few main sources of rain water surfactants (leaf abrasion, ocean surface, biomass burning). The final corrective factor x_{sr} ranges from 1.3 to 3.3 $\times 10^{-3}$, for the rain drop's developed surface and is 57.6 to 63.2 times lower than x_{sl} found for the Langmuir trough film. The higher values of corrective factor x_{sr} are noticed for winter season. In order to minimize x_s at a given pressure one can only try to make A/V as large as possible, in particular, by reducing the subphase volume. The ratio x_{sl}/x_{sr} is a sensitive function of I_r and the particular Langmuir trough system features with a minor role played by K_p .

A more thorough description of the rain water film structure requires additional mechanisms taking place at the rain drop-film covered surface (evaporation and result-

ing shrinkage of the rain drop controlled by the film compression state [32], and the reaction of gaseous O₃ with a surface layer of surfactants at the air-water interface [33], for instance) to be accounted for in further studies.

Conclusion

Rain drop films exhibited rather low surface pressures characteristic of a quasi-ideal 2D gas behaviour found in a diluted surfactant solution (with $c \approx 10^{-3}a$), and are composed of slightly soluble immiscible components of mean molecular masses within 261-270 Daltons in agreement with chemical analysis findings.

The presented approach allows one to recover the film parameters originally present at the rain drop surface from the Langmuir trough measurements by means of the corrective factor x_s , consisting of the partitioning term K_p and the interfacial area development term A/V . The latter quantity depends on rain rate I_r and the form of the drop size distribution function differing significantly from the Marshall-Palmer one at low I_r (< 1 mm h⁻¹). A traditional Marshall-Palmer drop size distribution is applied here. Since the M-P DSD was determined on limited observation data and for different kinds of rain events, the real DSD could be very different. The M-P DSD is only a specific case of an exponential DSD. The similarity of DSD shapes between the experimental and M-P distribution is discussed that can play a significant rule in the partitioning effect evaluations. The partitioning factor K_p related to the physico-chemical composition of the film-composing material exhibited seasonal and source-specific features and varies in a rather narrow range (5.3-13.7 cm) being of secondary importance in comparison to the interface development term.

Table 1. Raindrop surface film parameters and partitioning correction factors with concentrations of fatty acids in rain water taken from [4, 5].

Measurement site (date)	\bar{c} moles cm ⁻³ ×10 ⁻¹¹	\bar{M}_w Dalton	$\bar{\Gamma}$ moles cm ⁻² ×10 ⁻¹¹	$\bar{\pi}$ mNm ⁻¹	K_p cm	$x_{sr}^a \times 10^{-3}$	x_{sl}^b
Bloomington							
22.10.1979	0.7	270	6.8	2.0	8.8	1.9	0.12
15.02.1980	1.2	261	6.5	1.9	5.3	3.2	0.19
16.02.1980	1.3	263	7.6	2.1	5.7	3.0	0.18
21.02.1980	1.3	266	9.4	3.6	7.1	2.4	0.15
28.04.1980	3.0	269	16.0	5.4	5.2	3.3	0.19
Bensheim							
12.12.1989	1.6	262	9.3	2.9	5.9	2.9	0.17
14.08.1990	0.6	266	7.9	3.6	13.7	1.3	0.08

^a Assuming $A_r = 58,125$ cm²/1 liter of rain water obtained from the experimental disdrometer data; ^b Assuming $A_L = 808.9$ cm²/1 liter of rain water in the Langmuir trough; corresponding to the author's experiment conditions ($I_r = 4.37$ mm h⁻¹, $T=19^\circ\text{C}$); $A_r/V_r = 58.13$ cm⁻¹, $A_L/V_L = 0.81$ cm⁻¹.

Considerations concerning the partitioning effect correction can be also extended to other interfacial systems with highly developed surfactant-covered surfaces (emulsions, foams and aerosol clouds) of significant importance in environmental studies.

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