

# Adsorptive properties of natural water surfactant films. Dead Vistula catchment water studies\*

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## Abstract

The paper contains the results of natural film experiments carried out on inland waters in the Dead Vistula (Martwa Wisła) catchment area during 1999–2002 using the integrated Langmuir trough-Wilhelmy plate system, which ‘cuts out’ an undisturbed film-covered area without any physicochemical sample processing. The static film parameters result from the generalized scaling procedures applied to the surface pressure-area isotherms. They appear to correspond well to observations of the film composition ( $A_{\text{lim}}$ ,  $M_W$ ,  $E_{\text{isoth}}$ ), film solubility and the miscibility of its components (via  $R$ ,  $\Delta S_c$  and  $y$  factors), and surface concentration ( $\pi_{\text{eq}}$ ,  $\Gamma_{\text{eq}}$ ). A novel approach is presented for the adsorption dynamics on the basis of the mixed kinetic-diffusion model and analyses of the dynamic surface pressure plots, which leads to the determination of the effective relative diffusion coefficient  $D_{\text{eff}}/D$  and activation energy barrier  $E_a/RT$ . There is reason to believe that certain classes of film-forming components or ‘end-members’ may dominate the static and dynamic surface properties. Some of these substances can be used as

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source-specific surface-active biomarkers to trace temporal and spatial changes due to environmental factors or the production of biological matter. The concept was tested for the Dead Vistula river and its tributaries. The results demonstrate that natural films are a complex mixture of biopolymeric molecules covering a wide range of solubilities, surface activities and molecular masses with an apparent structural film architecture. Such studies could lead to the development of film structure parameters – indicators of ecosystem quality and the state of the environment.

## 1. Introduction

### 1.1. Marine surfactants – sources and diversity

Organic matter (OM) in the ocean occurs as particulate organic matter (POM), sometimes termed seston, and dissolved organic matter (DOM). Dissolved organic carbon (DOC) is the largest actively exchanging pool of organic carbon in the ocean (Druffel & Bauer 2000). DOM in the sea is a very complex mixture of substances with different physicochemical properties. A large fraction of DOM has surface-active (SA) properties (Hunter & Liss 1981). These SA substances make up a very reactive part of the organic matter in the sea. According to their surface-active properties, such substances accumulate at marine interfaces, thereby influencing mass and energy transfer between the thus modified interfaces. In the northern Adriatic, for example, the maximum and minimum values of DOC vary in a narrow range within a factor of two (Vojvodic & Cosovic 1996), while SA substances demonstrate variations within a factor of 15. Clearly, the latter parameter is much more sensitive to variations in environmental conditions such as changes in chemical and physical parameters and the resulting biological responses. The effect is particularly well reflected in the increased SA substance concentration in the surface layer (Gasparovic & Cosovic 2001). Recently, there has been growing interest in elucidating the part played by organic acids in biogeochemical processes in natural waters (McKnight et al. 1990). The total pool of dissolved organic acids is made up of labile, mostly low molecular weight substances and recalcitrant species. Recalcitrant substances make up the larger fraction of higher molecular weight acids, composed mainly of humic substances (Gasparovic et al. 1998). Polysaccharides with acidic properties can be found in the water column as a result of algal extracellular excretion or autolysis. Besides proteins and lipids, polysaccharides are also labile in sea water and are promptly decomposed. Interactions between the products of decomposition of marine macromolecules lead to the formation of natural gebiopolymers, in which carbohydrate carbonyl units have been found (Romankevich 1984).

Melanoids are polymers similar to natural humic substances obtained by the dehydration and condensation of sugars and amino acids. They are known as kerogen precursors and geochemical lipid sinks (Larter & Douglas 1980).

Some of these compounds are only slowly degraded or are transformed to more stable chemical structures (Volkman et al. 1998), and can thus be used as biomarkers for assessing sources of OM in the marine environment. For instance, Saliot et al. (2001) used lipid markers (sterols, fatty acids and pigments) in POM isolated from Amazon River waters during a high flood period in June 1989 to estimate the relative proportion of the terrigenous and autochthonous fractions. Measurements of SA substance concentrations during a 10-year period in the same region showed that low values are more frequent in winter months, whereas the highest concentrations occur in the period from spring to autumn (Vojvodic & Cosovic 1996).

Sources of surfactants in the marine microlayer include marine organisms, terrestrial sources delivered by runoff or atmospheric transport, and petroleum sources at oil seeps or spills. The single largest source is production by autochthonous marine organisms, principally phytoplankton, which exude natural surfactants as metabolic by-products (Zutic et al. 1981). The generally accepted view is that the ubiquitous oceanic background of degraded biopolymeric and heterogeopolymeric material has the potential to generate measurable surface films even in oligotrophic waters (Williams 1986). Specific inputs of fresh bioexudates and biopolymeric material from local biological events are superimposed on this background signal. The Polish coastal zone of the southern Baltic Sea is a recipient of river waters that collect material from an area greater than the territory of Poland and carry them to the sea. Hence, the entire coastal zone is constantly subjected to severe anthropogenic pressure.

## 1.2. Sea surface films

Natural sea surface films are derived from bulk seawater SA dissolved organic matter (DOM) of biogenic origin. Surfactants are concentrated at the air-sea interface by numerous physical processes, including diffusion, turbulent mixing, bubble and particle transport, and convergent circulations driven by wind, tidal forces, and internal waves. The composition of sea surface films is largely undefined, although significant enrichments of many specific classes of compounds in the surface microlayer have been demonstrated (for a review, see Hunter & Liss 1981). Natural sea films most resemble layers composed of proteins, polysaccharides, humic-type materials and waxes (Van Vleet & Williams 1983). The presence of relatively small amounts of certain lipids (free fatty acids, fatty alcohols or triglycerides) in films composed primarily of proteins and carbohydrates can

strongly affect the resultant film pressure (surface pressure-area isotherm shape) of multicomponent films. The results presented in Bock & Frew (1993) suggest that the multicomponent films typical of the ocean surface exhibit a more complex response to physical forcing than do classical single-component insoluble monolayer films (Adamson 1982). The elastic behavior of seasurface films is controlled not only by surface concentration, but also by pronounced compositional and conformational changes in response to changes in surface pressure. These transitions are a consequence of complex constituent interactions and the dynamic exchange of material with the bulk solution. These mechanisms indicate a need to understand the dynamics of competitive adsorption for natural surfactants with their rates for diffusional and structural transient processes (Gelbart et al. 1994). This concept has been tested for marine surface waters at several stations in offshore regions of the southern Baltic Sea and inland waters: in the catchment area of the Dead Vistula (Martwa Wisła) and its tributaries (Motława, Radunia, Strzyża) and selected streams, lakes and other water bodies during a 12-year period. These waters represent a more or less closed ecological system where confluence and river water inputs are enriched with municipal effluents and mixed in the Dead Vistula estuary.

The principal limitation of previous work was the inability to compare  $\pi$ - $A$  isotherms in terms of specific area or mean molecular area. Frew & Nelson (1992) attempted to normalize the  $\pi$ - $A$  curves by using specific area based on a number of bulk chemical parameters – analytical data for dry weight, UV absorbance, and carbon, nitrogen and lipid content; specifically, for each parameter the raw film area data [ $\text{cm}^2$ ] for the isotherms were normalized or ‘scaled’ by dividing the respective parameter, e.g.  $\text{cm}^2/\text{microgram carbon}$ , by the total film content. In these studies, we fitted the  $\pi$ - $A$  data using a two-dimensional virial equation of state. It is possible to interpret the virial coefficients in terms of the mean number of moles present in the film and the specific limiting area, which we have done following Barger & Means (1985). Since 1990, the first systematic studies of natural films in coastal waters of the Baltic Sea have concerned surface pressure-area isotherms (Pogorzelski 1992, Pogorzelski et al. 1994). The mean molecular mass  $M_W$  ( $= 0.65$ – $9.7$  kDa) and limiting specific area ( $= 2.7$ – $31.6$   $\text{nm}^2/\text{molecule}$ ) of the surfactants composing the film were obtained from isotherm scaling and point to polymer-like biomolecules with an apparent structural organization at the air/water interface (Pogorzelski 2001). The degree of mixing and formation of layered structures of surfactants in a multicomponent natural film can be predicted by means of the 2D polymer scaling theory applied to the isotherms and expressed by the value of the scaling exponent  $\gamma$  demonstrated by the interfacial

system (Pogorzelski 1996). Moreover, stress-surface pressure relaxation measurements revealed a two-step relaxation process at the interface with characteristic times  $\tau_1$  (1.1–2.8) and  $\tau_2$  (5.6–25.6) seconds, suggesting the presence of diffusion-controlled and structural-organization molecular mechanisms (Pogorzelski & Kogut 2001b). Recently, a novel approach proposed for the description of surfactant adsorption kinetics has been based on the mixed kinetic-diffusion model (Eastoe et al. 2001). The effective relative diffusion coefficient  $D_{\text{eff}}/D$  and energy activation barrier  $E_a/RT$  can be obtained from the slope of the dynamic surface pressure  $\pi$ - $t$  plots at short ( $t \rightarrow 0$ ) and long ( $t \rightarrow \infty$ ) adsorption time intervals (Pogorzelski & Kogut 2001a). The advantage of this formalism as well as the scaling procedures applied to the surface pressure-area isotherms is that measurement of the surfactant bulk concentration is avoided. The principal motivation for these studies was to demonstrate that the evolution of an environmental state is followed by corresponding changes in the natural surface film rheology. A set of selected static and dynamic film structure parameters may act as indicators for the novel aquatic-ecosystem quality assessment technique to be developed. The close transfer function – the film parameters versus biological event features – remains to be established on the basis of a comprehensive data set.

## 2. Surface film parameters – theoretical background

### 2.1. Static film properties – scaling procedures

For natural films, the isotherms of which differ significantly from ideal-gas behavior  $\pi A_m = kT$ , the following quadratic equation of state e.g. the 2D virial equation, was proposed and scaled according to specific area (Barger & Means 1985):

$$\pi A = C_0 + C_1 \pi + C_2 \pi^2, \quad (1)$$

where  $k$  is the Boltzmann constant,

$\pi = \gamma_0 - \gamma$  is the surface pressure of the film,

$\gamma_0, \gamma$  – the surface tensions of solvent (water) and surfactant solution, respectively,

$A_m$  – the area per film molecule related to the Gibbs' adsorption  $\Gamma$ ;  
 $A_m = 1/\Gamma N_A$ ,

$T$  – the temperature in Kelvins,

$N_A$  – the Avogadro number,

$C_0, C_1, C_2$  are the virial coefficients,

$A$  is the film-covered area (in  $\text{cm}^2$ ).

It is possible to interpret the virial coefficients, obtained from the best-fit procedure applied to the recorded isotherms, in terms of the mean number

of moles  $n_m$  present in the film, the specific limiting area  $A_{\text{lim}}$ , and the mean molecular mass  $M_W$  of the film-forming surfactant mixture as described in detail elsewhere (Pogorzelski 2001, Pogorzelski & Kogut 2001b).

The description of the 2D film states includes the dilational elasticity modulus (or Gibbs' modulus)  $E_{\text{isoth}}$ , which expresses the static, compressional response of a film to compression or dilation corresponding to the recording of an isotherm in its thermodynamic equilibrium (Adamson 1982):

$$E_{\text{isoth}} = -d\pi/d \ln A. \quad (2)$$

The isotherm hysteresis may be attributed to different arrangements of the molecules in the compression and dilation cycles, and must involve a change in the entropy  $\Delta S_c$  of the film-adjacent water layer system. According to the fundamental laws of thermodynamics applied to the isothermal compression-expansion cycle of the 2D film system (Pogorzelski 2001), the change in entropy between the initial  $A_i$  and final  $A_f$  film areas is

$$\Delta S_c = S_{\text{dil}} - S_{\text{com}} = \Delta W/T, \quad (3)$$

where  $\Delta W = W_{\text{dil}} - W_{\text{com}}$  is the difference in the work done; both terms are defined in a similar way:

$$W_{\text{com}} = - \int_{A_i}^{A_f} \pi \, dA. \quad (4)$$

The work of expansion can be derived in the same manner from the expansion isotherm plot. Since it is the ratio of these two quantities, the isotherm reversibility  $R$  (Hühnerfuss & Alpers 1983),

$$R = 100 (W_{\text{dil}}/W_{\text{com}}) \%, \quad (5)$$

is more a qualitative measure of the entropy effect of surface films of different chemical structure depending on the film's compression or dilation velocity, as already shown for natural seawater samples (Pogorzelski et al. 1994).

The characterization of the miscibility or phase separation of the monolayer-forming components requires a knowledge of the intermolecular interactions and physicochemical parameters governing the segregation or mixing. Recently, the  $\pi$ - $A$  isotherms of natural marine films have been analyzed to derive the scaling exponent  $y$  from the relation  $E_{\text{isoth}} = y\pi$  applicable to the high-frequency limit of the surface modulus according to the 2D polymer film scaling theory (Pogorzelski 1996). It was postulated that the concept of the structural arrangements of molecules in a model 3-component system (insoluble polymer spread on a surfactant solution) closely related to the value of  $y$  (see Fig. 1 in Pogorzelski 1996) can also be extended to natural marine multicomponent systems.

## 2.2. Parameters of adsorption dynamics

The diffusion-controlled adsorption of an aqueous surfactant solution at an air/water interface was first treated quantitatively by Ward & Tordai (1946), although an analytical solution for the surface tension decay  $\gamma(t)$  cannot be obtained. At short and long adsorption times and sufficiently low concentrations, the following approximate expressions for solutions of nonionic surfactants can be given (Eastoe et al. 2001):

$$\text{at zero adsorption time, } B \equiv [d\gamma/d(t^{1/2})]_{t \rightarrow 0} = -2RTc(D/3.14\dots)^{1/2}, \quad (6)$$

$$\begin{aligned} \text{at infinite adsorption time, } A \equiv [d\gamma/d(t^{-1/2})]_{t \rightarrow \infty} = \\ = (RT\Gamma_{\text{eq}}^2/2c)(3.14\dots/D_{\text{eff}})^{1/2}. \end{aligned} \quad (7)$$

The parameters  $c$ ,  $\Gamma_{\text{eq}}$ ,  $D$  and  $D_{\text{eff}}$  represent the bulk concentration, the equilibrium surface adsorption excess ( $\gamma = \gamma_{\text{eq}}$ ), the monomer and effective diffusion coefficients, respectively. Nonetheless, experimental results have shown that diffusion-controlled adsorption deviates considerably from the decay of dynamic surface tension at long adsorption times (Kragel et al. 1995). Eastoe et al. (2001) suggested that if the mechanism was mixed diffusion-activation (kinetic) adsorption, then the effective diffusion coefficient should obey the Arrhenius-type relationship

$$D_{\text{eff}} = D \exp(-E_a/RT), \quad (8)$$

where  $E_a$  is the activation energy barrier. Once the surfactant molecule monomer has diffused to the subsurface, there may be an adsorption barrier present preventing the monomer from adsorbing. This will cause the molecule to back-diffuse into the bulk rather than adsorbing, thereby increasing the time scale of the surface tension decay, consequently  $D_{\text{eff}} \ll D$ . This barrier may be due to increased surface pressure, to a certain configuration the monomer has to adopt at the interface, or result from the availability of an 'empty site' in the interface which may hinder adsorption. The dynamic surface tension  $\gamma(t)$  (or dynamic surface pressure  $\pi(t)$ ;  $d\gamma \equiv d\pi$ ) measured along the whole time scale of the adsorption process allows the slopes  $A$  and  $B$  to be determined. Furthermore, by combining eqs. (6) and (7), the following relation for the effective relative diffusion coefficient can be obtained (Pogorzelski & Kogut 2001a):

$$(D_{\text{eff}}/D)^{1/2} = -(R^2T^2\Gamma_{\text{eq}}^2/AB), \quad (9)$$

where measurement of the bulk concentration is avoided. The determination of  $D_{\text{eff}}$  needs values of  $\Gamma_{\text{eq}}$  which are taken from the isotherm scaled, as shown in Pogorzelski (2001), at  $\pi_{\text{eq}}$  leading to  $A_{\text{eq}} = 1/\Gamma_{\text{eq}} N_A$ , where  $\pi_{\text{eq}} = \pi$  (at  $t \rightarrow \infty$ ).

By applying the Gibbs-Helmholtz equation, the separate entropy  $\Delta S$  and enthalpy  $\Delta H$  contributions to the free energy change for the formation of an activated state (an activated state forms prior to adsorption) of the  $E_a$  barrier can be expressed in the form (Eastoe et al. 2001):

$$\ln(D_{\text{eff}}/D) = -E_a/RT = \Delta S/R - \Delta H/RT. \quad (10)$$

Thus, the apparent enthalpy and entropy changes can be obtained from the Arrhenius plot  $-\ln(D_{\text{eff}}/D)$  vs  $1/T$ .

### 3. Experimental

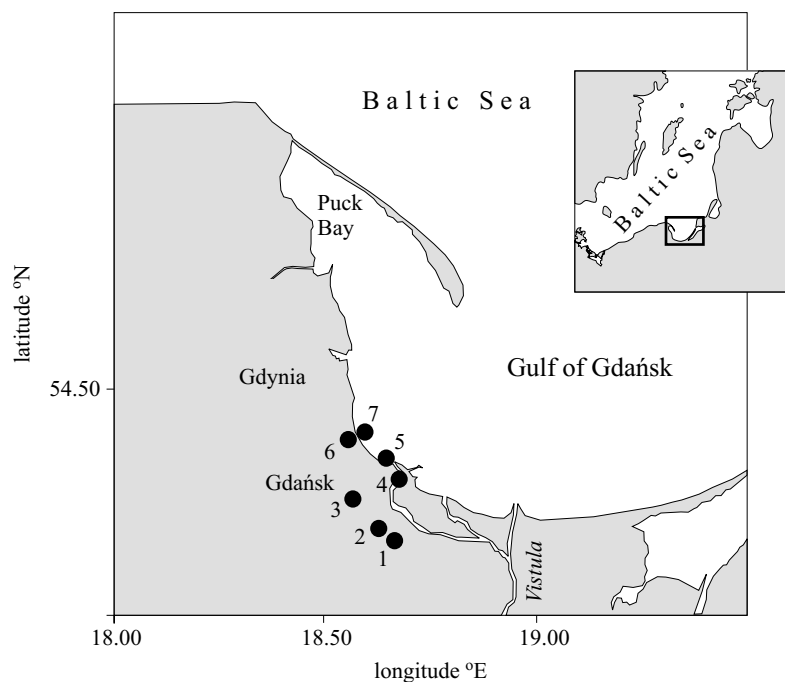
#### 3.1. Sampling locations

Natural marine surfactant adsorption studies in shallow off-shore waters of the Baltic Sea (Gulf of Gdańsk, Poland) as well as in inland waters were carried out over a 2-year period (2000–2002). The locations of the sampling sites in the Baltic Sea and natural inland stations (rivers, a stream, a lake, a pond) were shown in Fig. 1 of Pogorzelski & Kogut (2001b). Additional sampling locations, included in the course of the studies reported here, are situated on the tributaries (the Motława, Radunia and Strzyża rivers) of the Dead Vistula catchment area as depicted in Fig. 1. A diagram of riverine water mixing in the Dead Vistula catchment area is given below.

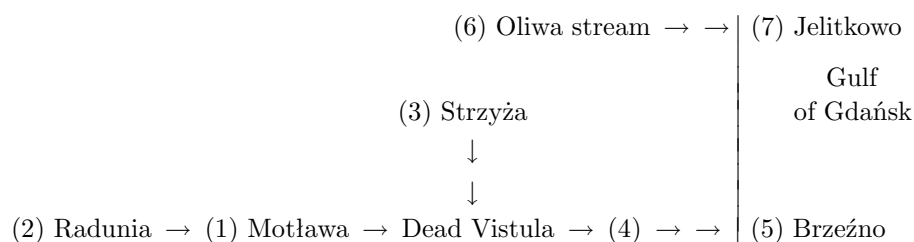
#### 3.2. Methodology

The novel sampler is a submersible rectangular double-walled vessel which ‘cuts out’ an undisturbed volume of sea water. The most valuable property of this device, described in detail elsewhere (Pogorzelski 1992, Pogorzelski et al. 1994), is that the collection and Langmuir trough isotherm analyses are performed without any transfer or chemical processing of the microlayer material. For dynamic surface pressure  $\pi(t)$  measurements, the sampled film was maintained in the trough for 20 min. to allow it to attain the temperature of the experiment (13–22°C), which was measured with a thermocouple placed just below the air/water interface. Next, the surface pressure was recorded just after the surface had been swept with a Teflon barrier to remove the molecules already adsorbed. Surface pressures were measured with the Wilhelmy plate method using a 5-cm-wide piece of filter paper attached to the force sensor (PS4, NIMA, England); they were accurate to within 0.1 mN m<sup>-1</sup>. Paper plates give zero contact angles; this is because the plate is essentially a sheet of water supported by a swollen, hydrated web of cellulose. A rectangular piece of filter paper has a thin waterproof barrier of melted paraffin wax. This significantly reduces not only capillary rise in a thin porous medium but also slow changes in the apparent plate mass, due to swelling and hydration, with





**Fig. 1.** Locations of the sampling stations in the Dead Vistula catchment area and adjacent shallow waters of the Baltic Sea: 1 – Motława river, 2 – Radunia river, 3 – Strzyża river, 4 – Dead Vistula river, 5 – Brzeźno, 6 – Oliwa stream, 7 – Jelitkowo



time. We have found agreement in the pressure range studied between glass- and paper-plate isotherm records. The dynamic surface pressure dependence is complete after 1–2 hours when  $\pi(t) = \pi_{\text{eq}} = \text{const}$ , i.e. when no noticeable surface pressure variations can be detected. After that time, the surface pressure  $\pi$ – $A$  area isotherm measurements are performed on the same film sample in order to derive the saturation adsorption  $\Gamma_{\text{eq}}$  – the quantity entering the adsorption dynamics dependencies. The initial Langmuir trough area  $A_0 = (1200 \text{ cm}^2)$  is compressed with an average deformation speed  $u = \Delta A / \Delta t$  to  $0.6 \text{ cm}^2 \text{ s}^{-1}$  by moving two paraffin wax-coated glass sliders towards each other symmetrically around the

film pressure sensor. The film barriers were moved stepwise in 1-cm increments during a time of 3 s; 30 s were then allowed to elapse after each barrier movement for the surface pressure to become constant, after which the pressure was measured. The establishment of thermodynamic equilibrium in the monolayer during isotherm studies is essential in order to obtain the proper rheological film parameters. Any relaxation processes in the film could affect the shape of the isotherms and consequently the recovered film signatures. The effect depends on the Deborah number ( $De$ ), a dimensionless parameter defined as the ratio of the film relaxation time  $\tau$  to the ‘time of observation’ (a reciprocal of the strain rate of a film:  $t_{\text{obs}} = [(\Delta A/A)/\Delta t]^{-1}$ , as argued in isotherm studies (Kato et al. 1992). The stress-relaxation measurements performed on natural marine films revealed a two-step relaxation process at the interface with characteristic times  $\tau_1$  (1.1–2.8) and  $\tau_2$  (5.6–25.6) seconds (Pogorzelski & Kogut 2001b). In the isotherm studies reported here,  $t_{\text{obs}} = 1500$  s, which leads to  $De = 0.017$  ( $\ll 1$ ), and corresponds to the recording of an isotherm of an interfacial system in its quasi-equilibrium state. The film’s temperature is an important factor determining its thermodynamic state, in particular during compression in a nearly horizontal section of the  $\pi$ – $A$  isotherm typical of a first-order 2D phase transition in a film where very small or no surface pressure gradients occur (Pogorzelski & Kogut 2003). This leads to  $E_{\text{isoth}} \approx 0$  at particular values of  $\pi_c$  and  $T_k$ , affecting the static film parameters recovered from the fitting procedure applied to the isotherms at higher surface pressures (Pogorzelski 2001). Average characteristics of the natural films were obtained on the basis of several water sample replicates (6–10) collected at sites no more than 2–5 meters apart on a single day under calm wind conditions ( $V_{10} < 3 \text{ m s}^{-1}$ ). Wind velocities at a height of 3 m above the water surface were recorded with a cap anemometer (YA-45, MORS, Poland) at the instant of sample collection. These data were converted into the mean horizontal wind speed  $V_{10}$  at a reference height of 10 m. The temperatures of the water samples and the ambient air were also registered simultaneously.

However, during the period of the experiment the surface film may be partially dispersed by air flow, waves, or tidal currents, so the surface under study is only partially coated with the film. In such a case, a fractional filling factor,  $F$ , can be introduced: it is defined as the ratio of the area covered by the film to the total area under consideration (Pogorzelski 1992). Fig. 1 in Pogorzelski (1994) presents  $F$  as a function of  $V_{10}$  for studies of natural films carried out at two different sites in the Baltic Sea. With increasing wind speed the value of  $F$  drops rapidly. The surface can be assumed to be uniformly film-covered ( $F = 1$ ) only in the lowest wind

speed range, up to  $V_{10} < 2.5 \text{ m s}^{-1}$ ; for stronger winds the filling factor is wind-speed dependent. As a first approach, it was found that  $F$  appears to be a linear function of  $V_{10}$  ( $F = -0.14 V_{10} + 1.31$  at  $2.3 < V_{10} < 4.7 \text{ m s}^{-1}$ ). Moreover, the  $E_{\text{isoth}}$  ( $V_{10}$ ) dependence exhibits a steep decrease within the velocity range  $0.5\text{--}4 \text{ m s}^{-1}$  as illustrated in Fig. 6 of Pogorzelski et al. (1994). There is an asymptotic tendency to reach a constant value for  $V_{10} > 7 \text{ m s}^{-1}$ , when wind waves are expected to disrupt the films, which then reform by diffusion from subsurface water. One of the environmental factors affecting the adsorption energy barrier  $E_a$  is the elevated surface pressure of the film exposed to wind shear stress ( $\sim V_{10}^2$ ). Measurements of surface adsorption kinetics at different wind speeds from the range  $0.8\text{--}13.6 \text{ m s}^{-1}$  lead to the relation  $E_a/RT = C V_{10}^D$  with the best-fit parameters  $C = 1.70 \pm 0.04$  and  $D = 0.33 \pm 0.06$  (Pogorzelski & Kogut 2001a). The variability of these film parameters with environmental factors permits correction of their measurements taken under different weather conditions, something that will be essential in future, more detailed studies.

## 4. Results and discussion

### 4.1. Static surface rheology

The static film parameters  $A_{\text{lim}}$ ,  $M_W$ ,  $E_{\text{isoth}}$ ,  $\Delta S_c$ ,  $y$ ,  $R$  derived from force-area studies for inland water and seawater samples (Pogorzelski 2001, Pogorzelski & Kogut 2001b) are set out in Table 1. Values of the structural parameters for films formed from a mixture of natural river water surfactants are rather widely distributed:  $E_{\text{isoth}} = 19.31\text{--}42.69 \text{ mN m}^{-1}$ ,  $A_{\text{lim}} = 3.85\text{--}545.16 \text{ nm}^2/\text{molecule}$ ,  $M_W = 9.45\text{--}166.7 \text{ kDa}$ ,  $R = 58.42\text{--}98.41\%$ ,  $\Delta S_c = (-0.09\text{--}7.04) \times 10^{-7} \text{ J K}^{-1}$ , and  $y = 13.6\text{--}16.2$ . In reference to the Baltic Sea studies, carried out at 6 stations along the southern Baltic coast from Brzeźno to Oksywie at similar temperatures, one can note the following river water samples signatures differences:  $E_{\text{isoth}}$  values exhibit greater variability, molecular areas are several times higher, the value of  $M_W$  is one order of magnitude higher, the isotherm reversibility  $R$  is as much as 50% higher, while the negative entropy change  $\Delta S_c$  (related to  $R$ ) is significantly lower, and finally the miscibility factor  $y$  is apparently higher in comparison to the marine water samples. The values obtained for the inland water films exhibit a mixture of surfactants of higher molecular masses ( $M_W \uparrow$ ) occupying larger molecular areas ( $A_{\text{lim}} \uparrow$ ) at the air/water interface, possessing lower film material solubility ( $\Delta S_c \downarrow$  and  $R \uparrow$ ) in the compression-expansion cycle, and lower miscibility ( $y \uparrow$ ) of surface-active compounds in the film. If we compare values of the film parameters for the Dead Vistula tributaries and those taken from the marine sampling sites close

**Table 1.** Static structural parameters of surfactant films on natural waters derived from ( $\pi$ - $A$ ) isotherm studies

No.	Sampling station (date)	$A_{\text{lim}}$ [nm <sup>2</sup> molec <sup>-1</sup> ]	$M_W$ [kDa]	$E_{\text{isoth}}$ [mN m <sup>-1</sup> ]	$\Delta S_c$ [J mol <sup>-1</sup> K <sup>-1</sup> × 10 <sup>-7</sup> ]	$y$	$R$ [%]
<b>Inland waters</b>							
1	Motława river (07.12.2001)	32.97	9.45	19.31	-6.71	16.0	58.4
2	Radunia river (04.02.2002)	545.16	166.7	42.69	-0.09	14.6	98.4
3	Strzyża river (22.05.2002)	28.87	11.95	20.21	-7.04	13.6	76.8
4	Dead Vistula river (05.02.2002)	62.44	20.52	24.36	-0.62	15.1	88.1
5	Oliwa stream (06.02.2002)	17.07	12.07	20.28	-1.23	12.3	65.8
<b>Baltic Sea</b>							
6	Brzeźno (12.07.1999)	7.79	4.06	29.12	-70.4	13.9	57.5
7	Jelitkowo (09.07.1999)	8.09	4.59	22.94	-73.7	13.8	58.6
8	Orłowo (sampler) (28.06.1990)	8.46	1.75	28.96	-72.2	3.7	51.6
	Orłowo (bottle) (28.06.1990)	31.57	9.71	6.65	-133.5	7.9	35.9

Symbols:  $A_{\text{lim}}$  – limiting molecular area,  $M_W$  – molecular mass,  $E_{\text{isoth}}$  – dilational elasticity modulus,  $\Delta S_c$  – change in the entropy,  $y$  – scaling parameter,  $R$  – isotherm reversibility.

to the area where the Dead Vistula enters the Gulf of Gdańsk, measured in the period of limited biological activity (December–February), we find that the values recorded in the Dead Vistula and its tributaries (Motława and Strzyża) are similar. Surprisingly,  $A_{\text{lim}}(\text{Motława}) + A_{\text{lim}}(\text{Strzyża}) \approx A_{\text{lim}}(\text{Dead Vistula})$ . At the same time, for Radunia water samples, evidence for the presence of surfactants of several times higher molecular masses with very large molecular areas ( $545.16 \text{ nm}^2/\text{molecule}$ ) forming almost insoluble ( $R = 98.4\%$ ) and compact films ( $E_{\text{isoth}} = 42.69 \text{ mN m}^{-1}$ ) was found. The Radunia river seems to be a source of surfactants of high surface activity. The increase in both  $M_W$  and  $A_{\text{lim}}$  can be observed for film subsurface samples (collected in a bottle from 0.5 m deep water) if referred to the surface microlayer values, that is also correlated to the corresponding increase of the scaling parameter  $y$  (from 3.7 to 7.9; see line 8 in Table 1). This is in agreement with observations reported by Barger & Means (1985) (see Table IV in that paper) for Atlantic Ocean waters. This is evidence for the transition of the multicomponent film structure from a homogeneous mixture to segregated, more ordered complex structures with domains or aggregates of surfactant molecules ( $y \uparrow$ ). Such an evolution to the new molecular arrangement with a certain loss of the system's degrees of freedom leads to a larger entropy change than would be expected for a structureless microlayer sample (compare  $\Delta S_c$  with line 8 in Table 1). Isotherm measurements performed on microlayer samples (with  $c_x$  – unknown surfactant concentration) and dilutions of microlayer water in ultrapure distilled water ranging from 10–100% microlayer water by volume showed the following film parameter variability for concentrations  $c_x$  and  $c_x/2$ , respectively (the measurements were performed on water samples collected at Jelitkowo on 10.08.2002):

for  $c_x$        $E_{\text{isoth}} = 27.47 \text{ mN m}^{-1}$ ,  $\Delta S_c = -6.81 \times 10^{-8} \text{ J K}^{-1}$ ,  $y = 10.2$ ,  
                   $R = 77.56\%$ ;

for  $c_x/2$      $E_{\text{isoth}} = 15.73 \text{ mN m}^{-1}$ ,  $\Delta S_c = -5.06 \times 10^{-8} \text{ J K}^{-1}$ ,  $y = 14.6$ ,  
                   $R = 70.56\%$ .

Comparisons of the isotherm-derived parameters obtained at the same marine station (Orłowo) in successive years from 1990 to 2002 points to a continuously rising trend of  $A_{\text{lim}}$ ,  $M_W$ ,  $y$  and  $\Delta S_c$ . It appears that the microlayer film is becoming enriched by a wide variety of heavier and larger surfactants, differentiated in their physicochemical properties and capable of forming ever more complex interfacial structures. The data noted during a one-year period at the same sampling site (Jelitkowo, Baltic Sea) showed a continuous increase in the relative occurrence of more condensed films (with higher  $E_{\text{isoth}}$ ) starting in spring and becoming especially high

in autumn. The data summarized in Table 1 for inland waters sampled in summer (July–August) and winter (December–February) demonstrated a regular tendency:

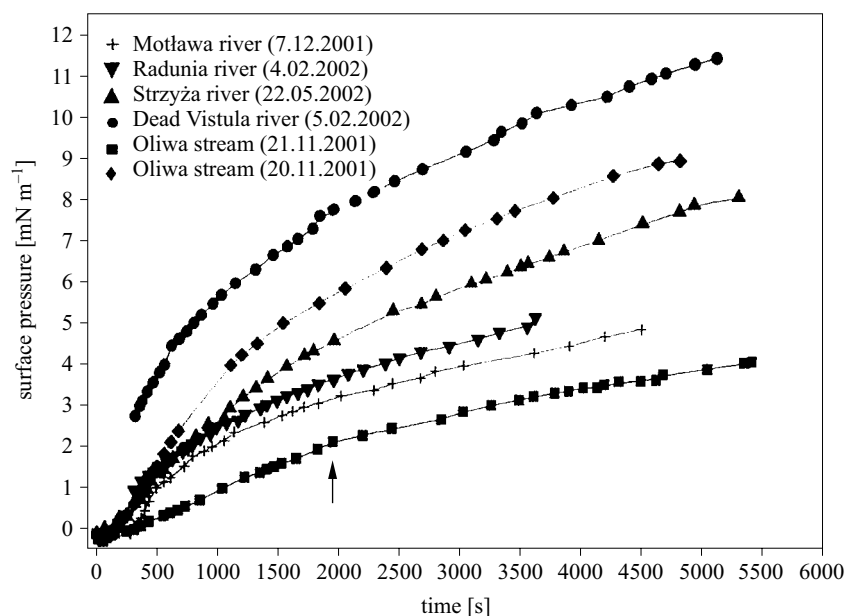
$$\begin{array}{l} \text{winter} \left[ \begin{array}{l} y, A_{\text{lim}}, M_W > y, A_{\text{lim}}, M_W \\ R, E_{\text{isoth}}, \Delta S_c < R, E_{\text{isoth}}, \Delta S_c \end{array} \right] \text{summer} \\ \text{season} \left[ \begin{array}{l} \\ \end{array} \right] \text{season} \end{array}$$

This correlation is in line with seasonal biological productivity and the summer increase in human activity. Measurements of SA substance concentrations during a 10-year period in the same region of the Mediterranean Sea showed that low values are more frequent in winter months, while the highest concentrations occur from spring to autumn (Gasparovic & Cosovic 2001). The mean values of isotherm reversibility are contained within the range 51.6–64.2% for the sampler-collected probes, whereas they reach only 35.9–45.6% for bottle samples (Pogorzelski et al. 1994). In isotherm hysteresis studies of insoluble crude oil product monolayers spread on the original seawater surface, values of  $R$  lay between 62.3 and 94.7%. It appears that  $R$  is closely related to the solubility of the film-forming material, assuming higher values for slightly soluble monolayers. A general trend has been identified, namely, that an increase in  $E_{\text{isoth}}$  is followed by a corresponding increase in  $R$  (Pogorzelski et al. 1994). Histograms of the elasticity modulus  $E_{\text{isoth}}$  distribution obtained in Baltic Sea studies (see for instance Fig. 5 in Pogorzelski et al. 1994) and taken in different seasons (from spring to autumn) are observed to exhibit a bimodal feature, as already reported in Bock & Frew (1993) (see Fig. 4). There it was argued that these bimodal distributions are consistent with the result of a competitive adsorption process at the air/water interface and suggested that certain general classes of components or end-members may dominate the properties of a static film. In particular, a multicomponent film is postulated with the presence of distinct end-member components diluted by variable amounts of compounds which did not strongly influence the  $\pi$ – $A$  curve or which redissolved into the bulk solution. Logically, these end-members would be the most insoluble, hydrophobic compounds in the film. A priori, we would expect soluble polymeric exudates and surface-active metabolic products to yield monolayer films which are relatively more compressible ( $E_{\text{isoth}} \downarrow$ ) than those derived from lipoidal material. The potential role of nitrogen-containing surfactants as end-members in controlling film elasticity is of considerable interest as demonstrated in Bock & Frew (1993). They measured carbon nitrogen  $C/N$  ratios in the film material, reasoning that enhanced contributions to films of relatively soluble biopolymeric materials such as proteins would be reflected in lower  $C/N$  values. In Fig. 3 of Bock & Frew (1993),  $C/N$  weight ratios were

plotted versus maximum  $E_{\text{isoth}}$ . A significant correlation was found between these two parameters, and generally higher  $C/N$  ratios were accompanied by a higher maximum elasticity, indicating that incorporation of nitrogen-rich materials or other biopolymeric materials tends to lower film elasticity. It should be pointed out that no attempt was made to identify the surfactants in the experiments reported here. Nevertheless, the scaling approach illustrated here will be particularly useful in making such correlations when more detailed chemical information on the film material is available.

#### 4.2. Adsorption kinetics parameters

Fig. 2 shows the dynamic surface pressure  $\pi-t$  time plots for inland water samples. A cusp point followed by a pronounced plateau region ( $\pi = \pi_{\text{eq}}$ ;  $\pi_{\text{eq}}$  – is the equilibrium surface pressure at long adsorption times  $t \rightarrow \infty$ ) was observed in almost all of the  $\pi-t$  curves, as indicated by the arrow. The discontinuity demonstrates that a condensed phase is formed



**Fig. 2.** Dynamic surface pressure – time dependencies, for inland water samples collected in the Dead Vistula catchment area at temperatures ranging from 13.4 to 19.1°C: Oliwa stream (21.11.2001), Dead Vistula (05.02.2002), Strzyża river (22.05.2002), Radunia river (04.02.2002), Oliwa stream (20.11.2001), Motława river (07.12.2001). The arrow indicates the cusp point for the phase transition observed at  $T < T_k$

at a certain critical surface pressure  $\pi_c$  and temperature  $T_k$ , as widely discussed for marine water films elsewhere (Pogorzelski & Kogut 2001a). Values of  $\pi_{\text{eq}}$  are proportional to the surface concentration of surfactants  $\Gamma_{\text{eq}}$  which is derived from the  $\pi$ - $A$  isotherm scaled, as shown in Pogorzelski (2001) and Pogorzelski & Kogut (2003), at  $\pi_{\text{eq}}$  leading to  $A_{\text{eq}} = 1/\Gamma_{\text{eq}} N_A$ . However, for measurements carried out at high temperatures ( $T > T_k$ ) and low  $\pi_{\text{eq}}$ , ideal 2D gas behavior can be assumed with  $\Gamma_{\text{eq}} = \pi_{\text{eq}}/RT$ . Dynamic surface pressure dependencies plotted versus  $1/\sqrt{t}$  and  $\sqrt{t}$  at long and short adsorption time intervals, respectively, allow one to derive the adsorption kinetics parameters (Pogorzelski & Kogut 2001a), summarized in Table 2, for inland and marine (for comparison) water samples. Values of  $D_{\text{eff}}/D$  (ranging from 0.01–0.87) and  $E_a/RT$  distributed within the range 0.14–4.54 agree well with the data reported for non-ionic surfactant solutions of pre-cmc (critical micelle concentration) concentrations at comparable temperatures (see Eastoe et al. 2001, where the mean  $E_a/RT = 3$  and  $D_{\text{eff}}/D = 0.038$  at  $T = 20^\circ\text{C}$  are reported). It has been shown (Kragel et al. 1995) for fulvic acid films extracted from seawater sampled off Livorno (Tyrrhenian Sea, Italy) that the majority of biopolymeric molecules ( $M_W \approx 50$  kDa) are probably aggregated as  $D_{\text{eff}} \ll D$ . According to Einstein's classical formula for the diffusion coefficient ( $D = kT/6\pi\eta R_{\text{mon}}$ , where  $\eta$  is the solution viscosity and  $R_{\text{mon}}$  is the surfactant monomer radius; Birdi (1997)), it appears that the radius of surfactant aggregates  $R_{\text{agr}} \gg R_{\text{mon}}$ . It should be pointed out that for salt-free ionic surfactant solutions, electrostatic interactions have been shown to drastically affect the adsorption kinetics (Diamant & Andelman 1996). However, the effect of adding mobile ions, whose concentration usually exceeds that of the surfactant, is to screen the electrostatic interactions. As a result, when salt is added (the situation occurring in seawater), the ionic surfactant adsorption becomes similar to the non-ionic case. With reference to marine water samples, values of  $\pi_{\text{eq}}$  and  $\Gamma_{\text{eq}}$  are significantly higher, especially in summer, which corresponds to the higher surface activity and concentration of the surfactants occurring in inland waters. Similar  $D_{\text{eff}}/D$  ( $= 0.87$  and  $0.84$ ) and  $E_a/RT$  ( $= 0.14$  and  $0.17$ ) values are observed for the Dead Vistula and Radunia water samples, respectively, whereas the same values, though in a different range, are measured for both the Motława and Strzyża rivers as follows:  $D_{\text{eff}}/D = 0.071$  and  $E_a/RT = 2.65$  but studied in different seasons. These results points to the physicochemical similarity of surface-active material and suggests that the Radunia tributary is principally responsible for the enrichment of Dead Vistula waters in SA matter. Measurements of the adsorption kinetics performed on inland water samples in the temperature range  $13.6$ – $35.6^\circ\text{C}$  demonstrated a regular tendency: an

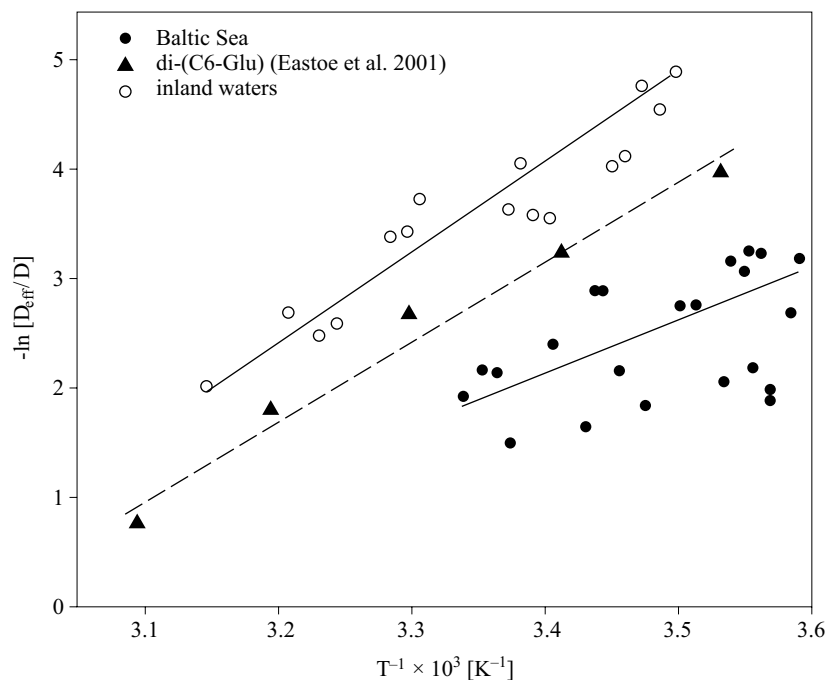


**Table 2.** Parameters of adsorption kinetics of natural surfactants in inland and sea waters

No.	Sampling station (date)	$T$ [°C]	$\pi_{\text{eq}}$ [mN m <sup>-1</sup> ]	$D_{\text{eff}}/D$	$E_a/RT$	$\Gamma_{\text{eq}}$ [mol cm <sup>-2</sup> × 10 <sup>-10</sup> ]
<b>Inland waters</b>						
1	Motława river (02.08.2001)	22.7	5.8	0.001	4.54	6.36
	Motława river (07.12.2001)	13.5	2.1	0.0713	2.65	4.90
2	Radunia river (04.02.2002)	15.3	2.2	0.8412	0.17	5.22
3	Strzyża river (2.05.2002)	18.8	1.7	0.0711	2.65	3.08
4	Dead Vistula river (02.08.2001)	23.1	2.6	0.1175	2.14	5.05
	Dead Vistula river (05.02.2001)	13.4	4.8	0.87	0.14	5.49
5	Oliwa stream (05.04.2001)	17.9	6.1	0.0389	3.25	7.52
<b>Baltic Sea</b>						
6	Brzeźno (01.08.2001)	22.2	7.8	0.0105	4.55	3.18
7	Jelitkowo (24.05.2001)	19.0	12.9	0.0278	3.58	5.31

Symbols:  $T$  – absolute temperature,  $\pi_{\text{eq}}$  – equilibrium surface pressure (at  $t \rightarrow \infty$ ),  
 $D_{\text{eff}}/D$  – effective relative diffusion coefficient,  $E_a/RT$  – activation energy (in  $RT$  units),  $\Gamma_{\text{eq}}$  – saturation surface adsorption.

increase in  $T$  in  $D_{\text{eff}}/D \rightarrow 1$  and  $E_a/RT \rightarrow 0$ . Further information on the dynamic features of the interaction between film-forming molecules and the water subphase can be derived from the Arrhenius-type  $\ln(D_{\text{eff}}/D)$  versus  $T^{-1}$  plots as depicted in Fig. 3, for a non-ionic diluted ( $c \ll \text{cmc}$ - critical micelle concentration) surfactant solution and the natural marine and inland water samples. The model nonionic surfactant is a di-chained glucamide



**Fig. 3.** Arrhenius-type  $\ln(D_{\text{eff}}/D)$  versus  $T^{-1}$  plot, for riverine ( $\circ$  – Dead Vistula station; studied in November–February) and marine waters ( $\bullet$  – Jelitkowo station; obtained in May–September). The dotted line corresponds to the reference data ( $\blacktriangle$ ) for a di-(C6-Glu) solution at  $5 \times 10^{-4} \text{ mol dm}^{-3}$  ( $c \ll \text{cmc}$ ) from (Eastoe et al. 2001). The fitted solid lines give:  $\Delta H = +51.2 \text{ kJ mol}^{-1}$ ;  $\Delta S = +144.0 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $R = 0.91$ ; Baltic Sea), and  $\Delta H = +24.81 \text{ kJ mol}^{-1}$ ;  $\Delta S = +240 \text{ J K}^{-1} \text{ mol}^{-1}$  ( $R = 0.96$ ; Dead Vistula)

with the generic formula  $(\text{C}_6\text{H}_{13})_2 \text{C}[\text{CH}_2\text{NHCO}(\text{CHOH})_4\text{CH}_2\text{OH}]_2$  referred to as (di-(C6-Glu)) in the text. It belongs to a new class of nonionic ‘sugar surfactants’. For the di-(C6-Glu), the reference data yield enthalpy  $\Delta H = +62 \pm 1 \text{ kJ mol}^{-1}$  and entropy  $\Delta S = +180 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  contributions to the free energy change  $E_a$  when the Gibbs-Helmholtz equation is applied. For natural water films, they are equal to  $\Delta H = +51.2 \pm 4 \text{ kJ mol}^{-1}$ ;  $\Delta S = +144.0 \pm 6 \text{ J K}^{-1} \text{ mol}^{-1}$  (marine water) and  $\Delta H = +24.8 \pm 3 \text{ kJ mol}^{-1}$ ;

$\Delta S = +240 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  (inland water). It is interesting to note that the adsorption process is entropy-controlled ( $\Delta ST > \Delta H$ ) for the model surfactant solution and sea water samples, but for inland waters there is evidence for an enthalpy-controlled mechanism ( $\Delta ST < \Delta H$ ) in the temperature range 13–19°C. The positive entropy change for the formation of the activated state is consistent with the hydrophobic effect and a ‘release of ordered water molecules’ as observed in the aggregation phenomenon of solvated surfactant molecules and points to the different surfactant mixture composition in the natural marine and inland waters under study.

## 5. Concluding remarks

In this paper, our emphasis has been on the multicomponent character of natural surfactant films and the consequent complexities involved in any attempt to predict the interfacial elastic properties due to the diverse chemical makeup of such films. One of the possible descriptions of the complex film structure and its evolution with the environmental factors is the application of generalized scaling procedures to the commonly available surface pressure-area and dynamic surface pressure dependencies. The advantage of such formalisms is that measurement of the surfactant bulk concentration (in general unknown) and chemical identification of the film-forming components is avoided. The selected surface parameters reflect several mechanisms and signatures of film structure evolution, like molecular composition (related to  $A_{\text{lim}}$ ,  $M_W$ ,  $E_{\text{isoth}}$ ), film solubility and component miscibility (via  $R$ ,  $\Delta S_c$  and  $y$  factors), surface concentration ( $\Gamma_{\text{eq}}$ ,  $\pi_{\text{eq}}$ ) and competitive adsorption ( $D_{\text{eff}}/D$ ,  $E_a/RT$ ), and the variability of their values is much more dynamic than is the case with bulk surfactant solutions parameters. There is reason to believe that certain general classes of components or ‘end-members’ may dominate the static and dynamic surface properties of natural water films. Some of these compounds are slowly degraded or are transformed to even more stable chemical structures, which enables them to be used as source-specific surface-active biomarkers to trace temporal and spatial changes. The values of the selected parameters of rheological films undergo significant changes following the mixing of natural river waters in the Dead Vistula catchment area and adjacent marine waters in the Gulf of Gdańsk (southern Baltic Sea). A set of selected static and dynamic film structure parameters can be used as indicators for the novel ecosystem quality assessment technique based on surface rheology studies of natural waters. However, the establishment of the transfer function

– the film parameters versus environment event features – remains to be determined on the large comprehensive data collection supplemented with direct observations of film structure evolution.

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