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## Surface rheology parameters of source-specific surfactant films as indicators of organic matter dynamics

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**Key words:** Baltic sea, biosurfactants, Dead Vistula catchment area, scaling procedures, spatial-temporal variability, surface films

### Abstract

The paper contains the results of natural film experiments carried out on inland and coastal waters in the Dead Vistula catchment area and mouth during 2000–2002, using the integrated Langmuir trough–Wilhelmy plate system. The static film parameters result from the generalized scaling procedures applied to the surface pressure–area isotherms. They appear to reflect in a quantitative and sensitive way 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  $\gamma$  factors), and surface concentration ( $\pi_{\text{eq}}$ ,  $\Gamma_{\text{eq}}$ ). The adsorption kinetics parameters: effective diffusion coefficient  $D_{\text{eff}}/D$  and activation energy barrier  $E_a/RT$  are derived from dynamic surface pressure. There is a reason to suggest that certain classes of film-forming components or ‘end-members’ may dominate the static and dynamic surface properties. Variation in the surface rheological parameters of source-specific biosurfactants is postulated to reflect organic matter dynamics in natural waters and were measured for the Dead Vistula river, its tributaries and the adjacent coastal area.

### Introduction

Heterogeneity in the chemical composition of sea surface films due to variation in sources of surfactant materials and in physical dynamics during film formation may lead to spatial and temporal variability in interfacial physical properties (Williams, 1986). The structure of the adsorbed layer and adsorption kinetics depends in a complex way on the interactions between molecules themselves and with the water sub-phase. Hence, it is of interest to get insight into the morphology, structural changes, build-up mechanisms, and involved interactions in and at the microlayer. A complete compositional or structural description of naturally occurring surfactants is not currently feasible. Instead of analyzing the chemical composition, it should be possible to scale microlayer film surface pressure–area isotherms and dynamic

surface pressure–time dependences in terms of the static and dynamic structural parameters, reflecting the natural film morphology, and resulting from the generalized physical formalisms adopted to multicomponent surfactant films (Pogorzelski, 2001; Pogorzelski & Kogut, 2001a, b, 2003).

The goals of this work were to provide a basis for systematically comparing force–area and dynamic surface pressure characteristics for natural surface films collected in different water environment regimes to relate film viscoelastic structural properties to chemical composition and origin of source-specific biosurfactants.

#### *Marine surfactants – origin 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). According to their SA properties, such substances accumulate at marine interfaces influencing mass and energy transfer between the thus modified interfaces. As the maximum and minimum values of DOC in the northern Adriatic vary in a narrow range within a factor of two (Vojvodic & Cosovic, 1996), while SA substances demonstrate variations with a factor of 15, one can conclude that the latter parameter is much more sensitive to changes in environmental conditions such as changes in chemical and physical parameters and resulting biological responses. The effect is particularly reflected in the increased SA substances concentration in the surface layer (Gasparovic & Cosovic, 2001). Measurements of SA substances concentrations during a 10-year period in the same region showed that low values are more frequent in winter months while highest concentrations occur in the period from spring to autumn (Vojvodic & Cosovic, 1996).

Biosurfactants are SA agents produced by certain types of microorganisms during growth on insoluble substrates. Microbial degradation of certain hydrocarbon contaminants has been demonstrated to be facilitated by simultaneous production of biosurfactants. Microbial biosurfactants are comprised of a wide variety of chemical structures including glycolipids, lipopeptides, phospholipids, fatty acids, neutral lipids, and certain polysaccharide-protein complexes. Biological surfactant synthesis is influenced by environmental conditions such as nitrogen availability and divalent cation concentration (Sekelsky & Shreve, 1999). Recently, compounds representing aquatic lipid classes (summarized in Table 1 of Striby et al., 1999) have been separated and quantified using a thin layer chromatography-flame ionization detection (TLC-FID) and used as biogeochemical markers for the comprehensive study of organic matter dynamics in relation to ecosystem functioning in the productive layers of the ocean (Goutx et al., 2003). Interactions between the products of decomposition of marine macromolecules lead to the formation of natural geobiopolymers, in which carbohydrate carbonyl units were found (Romankevich, 1984). In addition, the degradation status of organic matter can be

Table 1. Static structural parameters of surfactant films on natural waters derived from ( $\pi$ -A) isothermal 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> $\times 10^{-7}$ )	$Y$	$R$ (%)
<i>Inland waters</i>							
1	Motlawa river (20.08.1998)	3.78	2.01	23.27	-31.8	16.2	62.3
	Motlawa 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	Strzyza river (22.05.2002)	28.87	11.95	20.21	-7.04	13.6	76.8
4	Dead Vistula river (21.08.1998)	4.58	2.76	23.31	-44.3	14.3	69.2
	Dead Vistula river (16.07.1999)	3.85	1.96	26.15	-34.2	13.9	64.2
	Dead Vistula river (05.02.2002)	62.44	20.52	24.36	-0.62	15.1	88.1
5	Oliwa stream (25.07.1999)	3.81	2.03	25.85	-37.1	14.7	78.3
	Oliwa stream (21.11.2001)	268.12	104.52	38.19	-0.67	19.8	90.7
	Oliwa stream (06.02.2002)	17.07	12.07	20.28	-1.23	12.3	65.8
<i>Baltic Sea</i>							
6	Brzezno (12.07.1999)	7.79	4.06	29.12	-70.4	13.9	57.3
7	Jelitkowo (09.07.1999)	8.09	4.59	22.94	-73.7	13.8	58.6
8	Jelitkowo ( $c_x$ ) (25.05.2001)	60.84	24.82	22.82	-4.04	14.8	55.4
	Jelitkowo ( $c_x/2$ ) (25.05.2001)	65.29	20.53	20.19	-0.67	11.7	87.3
9	Orlowo (sampler) (28.06.1990)	8.46	1.75	28.96	-72.2	3.7	51.6
	Orlowo (bottle) (28.06.1990)	31.57	9.71	6.65	-133.5	7.9	35.9

assessed through the quantification of acyl-lipid degradation products in lipid extracts (Derieux et al., 1998). Lipid transformations result from the activity of extracellular enzymes which reduce the size of biomolecules. Lipolytic enzymes attack the ester bonds of biogenic acyl-lipids and release free lipid components: alcohols (ALC) and free fatty acids (FFA) being released from waxes (WSE), while diglycerides (DG), monoglycerides (MG) and again FFA are released from glycerides. These natural surfactants form surface films for which variability in surface rheological parameters may be useful for tracking organic matter dynamics in marine systems.

Some of these compounds degrade only slowly or are transformed to more stable chemical structures (Volkman et al., 1998). For instance, Salot et al. (2001) used lipid markers (sterols, fatty acids and pigments) in the POM isolated from Amazon River waters during a high flood period in June 1989 to estimate the relative portion of the terrigenous and autochthonous fractions.

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). Additional SA materials are contributed by the breakdown of dead organisms and subsequent chemical and biological transformations. A 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 riverine waters which collect material from the area exceeding the territory of Poland and outlet into the sea. In this regard, the entire coastal zone remains under severe anthropogenic influence. We evaluate the reproducibility of the methodology and provide examples of its application in the Dead Vistula catchment area and adjacent shallow Baltic Sea regions where intensive mixing of waters containing source-specific surfactants that

leads to formation of complex multicomponent films evolving with the environmental spatial, temporal and seasonal changes.

### *Sea surface films*

Natural sea surface films are derived from bulk seawater SA 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 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 affect strongly the resultant film pressure (surface pressure–area isotherm shape) of multicomponent films. Figure 5 in Van Vleet & Williams (1983) shows that relatively small amounts of lipid (by weight) can influence disproportionately the surface isotherm properties of complex films. The results presented in (Bock & Frew, 1993) suggest that the multicomponent films that are typical of the ocean surface exhibit a more complicated 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, interactions of surfactants with the aqueous sub-phase, but also by pronounced compositional and conformational changes in response to changes in surface pressure. The effect of ionic strength and pH of the water sub-phase, on isotherms, should be also emphasized (Simon-Kutscher et al., 1966; LoNostro & Gabrielli, 1993); this is especially important in view of the large salinity difference between the Baltic (6–8 ppt) and Mediterranean (38 ppt) Seas. These factors were not controlled during the course of the study. 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).

A principal limitation of previous work was the inability to compare surface pressure  $\pi$ –area  $A$  isotherms in terms of specific area or mean molecular area because surface concentrations and molecular mass could not be specified as well as the chemical makeup of the films. Frew & Nelson (1992) attempted to normalize the  $\pi$ – $A$  curves using specific area based on the several bulk chemical parameters. In these studies, we fit the  $\pi$ – $A$  data using a two-dimensional virial equation of state. It is possible to interpret the virial coefficients in terms of mean number of moles present in the film and specific limiting area, which we have done following Barger & Means (1985). Since 1990, the first systematic natural film studies in coastal waters of the Baltic Sea have concerned surface pressure–area isotherms obtained with a novel device for sampling water and for measuring the surface isotherms of untreated surface microlayer water samples (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 nm<sup>2</sup>/molecule) of surfactants composing the film point to the 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  $y$  demonstrated by the interfacial system (Pogorzelski, 1996). Recently, the novel approach proposed for the description of surfactant adsorption kinetics is 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, 2001b). The advantage of this formalism as well as the scaling procedures applied to the surface pressure–area isotherms is that the measurement of surfactant bulk concentration is avoided. Furthermore, it seems to provide supplementary information on natural film

morphology apart from the chemical analyses of the film-forming material. The main expectation of these studies is that the surface rheological parameters of biosurfactant films manifested at the air–water interface could be followed to trace SA biomarkers spatial-seasonal-temporal evolutions. This concept has been tested for marine surface waters in several stations offshore regions of the southern Baltic Sea and inland waters: in the catchment area of the Dead Vistula with its tributaries (Motława, Radunia, Strzyża) and selected streams, lakes and other water bodies during a 12-year period. These waters represent a rather closed ecological system where junction and river water inputs are enriched in municipal effluents and mixed in the Dead Vistula estuary. The close transfer function: the film parameters versus biologic event features remains to be established on the large comprehensive dataset.

## Surface film parameters – theoretical background

### *Static film properties – scaling procedures*

For natural films, 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:

- $\pi$ ,  $\gamma_o - \gamma$  is the surface pressure of the film,
- $\gamma_o$ ,  $\gamma$ , the surface tensions of solvent (water) and surfactant solution, respectively,
- $C_0$ ,  $C_1$ ,  $C_2$  are the virial coefficients,
- $A$  is the film-covered area (in cm<sup>2</sup>).

It is possible to interpret the virial coefficients, obtained from the best-fit procedure applied to the registered  $\pi$ – $A$  isotherms, in terms of the mean number of moles  $n_m$  present in the film, specific limiting area  $A_{\text{lim}}$ , and mean molecular mass  $M_w$  of the film-forming surfactant mixture as described in detail elsewhere (Pogorzelski, 2001; Pogorzelski & Kogut, 2001a, 2003).

The description of the 2D film states includes the dilational elasticity modulus (or Gibbs' modulus)  $E_{\text{isoth}}$  expressing the static, compressional response of a film to compression or dilation

corresponding to the isotherm registration in its thermodynamic equilibrium (Adamson, 1982):

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

The isotherm hysteresis may be attributed to different arrangements of the molecules in the compression and dilation cycles, and must be concerned with a change of entropy  $\Delta S_c$  ( $\Delta S_c = \Delta W/T$ , where  $\Delta W = W_{\text{dil}} - W_{\text{com}}$  is the difference in the work derived from integration of the expansion and compression isotherm plots) of the film-adjacent water layer system, and  $T$  is the temperature in Kelvin.

The isotherm reversibility  $R$ :

$$R = 100(W_{\text{dil}}/W_{\text{com}})\% \quad (3)$$

gives rather a qualitative measure of the entropy effect of surface films of different chemical structure depending on the film 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 can be expressed in terms of the 2D polymer film scaling theory via  $\gamma$ -scaling exponent derived from the relation  $E_{\text{isoth}} = \gamma\pi$  as shown in (Pogorzelski, 1996). Low values of  $\gamma$  ( $< 3.5$ ) stand for a homogeneous mixed film ('good' solvent condition), higher  $\gamma \approx 8$  ('theta' solvent case) lead to less film homogeneity observed as patches or domains of film-forming components. The highest  $\gamma$  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.

#### *Parameters of adsorption dynamics*

At short and long adsorption times and sufficiently low concentrations, the following approximate dynamic surface tension  $\gamma(t)$  expressions for non-ionic surfactant solutions can be given (Eastoe et al., 2001):

at zero absorption time,

$$B_a \equiv \left[ d\gamma/d(t^{1/2}) \right]_{t \rightarrow 0} = -2RTc(D/3.14 \dots)^{1/2} \quad (4)$$

at infinity absorption time,

$$A_a \equiv \left[ d\gamma/d(t^{-1/2}) \right]_{t \rightarrow \infty} = (RT\Gamma_{\text{eq}}^2/2c)(3.14 \dots / D_{\text{eff}})^{1/2} \quad (5)$$

The parameters  $c$ ,  $\Gamma_{\text{eq}}$ ,  $D$  and  $D_{\text{eff}}$  represent the bulk concentration, the equilibrium surface adsorption-excess (at  $\gamma = \gamma_{\text{eq}}$ ), the monomer and effective diffusion coefficients, respectively. Eastoe et al. (2001) suggested that if the mechanism was the mixed diffusion-activation (kinetic) adsorption then the effective diffusion coefficient should obey the Arrhenius-type relationship:

$$D_{\text{eff}} = D_{\text{exp}}(-E_a/RT) \quad (6)$$

with  $E_a$  being the activation energy barrier. 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  $A_a$  and  $B_a$  to be determined. Furthermore, putting together Eqs. (4) and (5), the following relation for the effective relative diffusion coefficient can be obtained (Pogorzelski & Kogut, 2001b):

$$(D_{\text{eff}}/D)^{1/2} = -(R^2T^2\Gamma_{\text{eq}}^2/A_aB_a) \quad (7)$$

where the measurement of the bulk concentration is avoided. The  $D_{\text{eff}}$  determination 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  $\pi_{\text{eq}} = \pi(\text{at } t \rightarrow \infty)$ . However, for measurements carried out at high temperatures ( $T > T_k$  – critical temperature of the 2D phase transition in the film; see (Pogorzelski & Kogut, 2002b, 2003)), and low equilibrium surface pressures, the ideal 2D gas behavior can be assumed with  $\Gamma_{\text{eq}} = \pi_{\text{eq}}/RT$ .

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  $E_a$  barrier can be expressed in the form (Eastoe et al., 2001):

$$\ln(D_{\text{eff}}/D) = -E_a/RT = \Delta S/R - \Delta H/RT. \quad (8)$$

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

## Experimental

### *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 in 2000–2002. The locations of the sampling sites in the Baltic Sea and natural inland stations (rivers, a stream, a lake, a water pond) were already shown in Figure 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 Figure 1.

### *Methodology*

The novel film sampler is a submersible rectangular double-walled vessel which ‘cuts out’ an undisturbed sea area region measuring  $45 \times 35$  cm and 8 cm thick. 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 transferring and without any chemical processing of the microlayer material. A detailed description of the measuring procedures

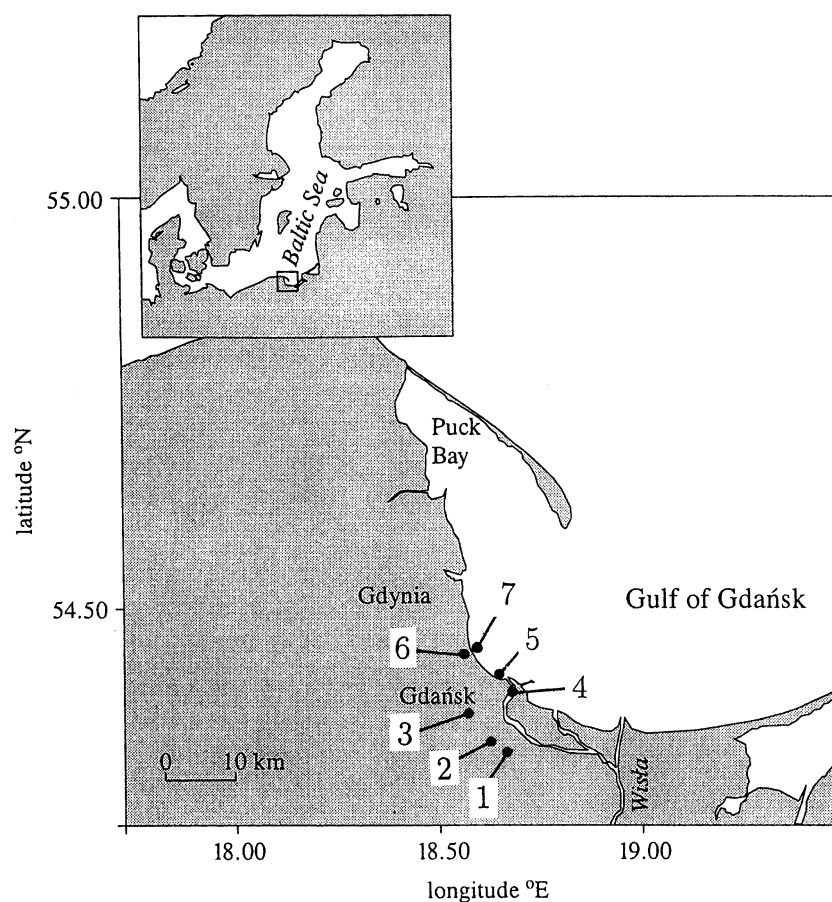


Figure 1. Locations of the sampling stations in the Dead Vistula catchment area and adjacent shallow marine waters of the Baltic Sea: 1 – Motława river; 2 – Radunia river; 3 – Strzyża river; 4 – Dead Vistula river; 5 – Brzeźno; 6 – Oliwa stream; 7 – Jelitkowo.

and physical conditions adopted in surface pressure–area isotherm and dynamic surface pressure registrations can be found in Pogorzelski & Kogut (2001a, b, 2003).

#### *Environmental factors effect on film parameters*

Several different mechanisms of relaxation processes taking place at multicomponent surface film under compression can be distinguished from the dynamic surface pressure relations like: desorption, dissolution, collapse, formation of surface micelles, evaporation, surface chemical reaction, Marangoni effect as summarized in Table 1 of Fuente-Feria & Patino (1994). They all lead to a certain film viscoelasticity, depending on the time scale of the film deformation. 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, 2001a). The film's temperature is an important factor determining the film thermodynamic state in particular during compression in a nearly horizontal section of the  $\pi$ – $A$  isotherm that is typical for a first-order 2D phase transition in the film where no or very small surface pressure gradients occur (Pogorzelski & Kogut, 2003). That leads to  $E_{\text{isoth}} \approx 0$  at particular values of critical  $\pi_c$  and  $T_k$  affecting the static film parameters recovered from the fitting procedure applied to the isotherms at higher surface pressures (Pogorzelski, 2001).

The effects of ionic strength and pH of the aqueous sub-phase on the isotherms should be pointed out; this is important in view of the large salinity difference between the Baltic (6–8 ppt) and Mediterranean (38 ppt) Seas. However, salinity, ionic strength and pH buffering capacity were not parameters simultaneously measured during the course of the study. Nonetheless, all long-chain molecules, fatty acids, lipids, lipoproteins and other partially degraded lipid materials forming seasurface films will concentrate apparently with their negatively charged groups in the surface layer (LoNostro & Gabrielli, 1993). The neutrality required of the film phase is met by cations in the adjacent sublayer. Hence, compression attracts the cations into the microlayer, whilst expansion repels them. This negative entropy effect implies an increased ordering effect on the film-forming

molecules as accepted generally for insoluble and/or sparsely soluble SA compounds (Gelbart et al., 1994). Fairly marked effects of changing the pH of the substrate are frequently observed. As shown for fatty acids, the collapse pressure increases with increasing pH. An obvious case is that of the fatty acid monolayers; these will be ionized on alkaline substrates and, as a result of repulsion between the charged polar groups, the film becomes gaseous and liquid-expanded at much lower temperature than does the acid (Adamson, 1982). A similar situation is found with long chain amines on acid substrates. The effect is caused by more than just the pH. Clearly, the nature of the counter-ion is very important (Simon-Kutscher et al., 1996); this is especially important if there is a tendency to form an insoluble salt, with the film ion. Thus, the presence of quite low concentrations ( $10^{-4}$  M) of divalent ions leads to the formation of the metal soap of a fatty acid film, unless the pH is quite low. Such films are much more condensed than are the fatty acid monolayers themselves. In contrast, the stable microbubble-surfactant monolayers could be formed on aqueous sub-phases containing salt concentrations, from zero up to at least 1 M of having pHs between 1.1 and 12.3 (D'Arrigo, 1984). Judging from the fact that the sub-phases of either distilled water, 0.1 M HCl (pH = 1.1), 0.1 M NaOH (pH = 12.3) or 0.1 M NaF all yielded rather similar  $\pi$ – $A$  curves, it appears clear that electrostatic interactions play a very minor role in the formation of the glycopeptide–acyl lipid complexes contained in the microbubble-surfactant monolayer. This finding agrees well with the results from biochemical work, which indicated that glycopeptide–lipid–oligosaccharide complexes are reversibly held together by hydrogen bonding and non-polar interactions (Van Vleet & Williams, 1983).

During the period of experiment, the surface film may be partially dispersed by air flow, waves, or tidal currents, so the surface under study is coated with the film only in part. In such a case, the fractional filling factor  $F$  represents the ratio of the area covered with a film to the total area considered (Pogorzelski, 1992). Figure 1 in Pogorzelski (1994) presents  $F$  as a function of  $V_{10}$  (= wind speed at a reference height of 10 m), for natural film studies carried out in two different sites in the Baltic Sea. One can observe a rapid



drop of  $F$  with increasing wind. The surface can be assumed uniformly film-covered ( $F = 1$ ) only in the lowest wind speed range to  $V_{10} < 2.5 \text{ ms}^{-1}$ ; for higher 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  $2.3 < V_{10} < 4.7 \text{ ms}^{-1}$ ). Moreover, the  $E_{\text{isoth}}$  ( $V_{10}$ ) dependence exhibits a steep decrease within the velocity range  $0.5\text{--}4 \text{ ms}^{-1}$  as illustrated in Figure 6 of Pogorzelski et al. (1994). There is an asymptotic tendency to reach a constant value for  $V_{10} > 7 \text{ ms}^{-1}$  where wind waves are expected to break disrupting the films which are then reformed by a diffusion process from subsurface water. One of the environmental factors affecting the adsorption energy barrier  $E_a$  is the increased 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  $0.8\text{--}13.6 \text{ ms}^{-1}$  lead to the following relation  $E_a/RT = CV_{10}^N$  with the best-fit parameters  $C = 1.70 \pm 0.04$  and  $N = 0.33 \pm 0.06$  (Pogorzelski & Kogut, 2001b). Its derivative against  $V_{10}$ , i.e.  $dE_a/dV_{10} = 0.56 V_{10}^{-0.67}$ , computed for the middle velocity ( $= 3 \text{ m s}^{-1}$ ) from the range observed in these field measurements (largely ranging from  $1$  to  $7 \text{ m s}^{-1}$ ) indicates an increase in  $E_a/RT = 0.27$  following a  $1 \text{ m s}^{-1}$  wind speed growth. The exhibited film parameters variability with the environmental factors allows one to correct the data taken at different weather conditions required in more detailed future studies.

## Results and discussion

### Static surface rheology

Static film parameters: limiting specific area  $A_{\text{lim}}$ , mean molecular mass  $M_w$ , dilational elasticity modulus  $E_{\text{isoth}}$ , the change in entropy  $\Delta S_c$ , scaling exponent  $\gamma$ , isotherm reversibility  $R$  derived from force–area studies, for inland water samples and seawater ones, for comparison after (Pogorzelski, 2001; Pogorzelski & Kogut, 2001a) are collected in Table 1. Values of the structural parameters for films formed from a mixture of natural riverine water surfactants are rather widely distributed:  $E_{\text{isoth}} = 19.31\text{--}42.69 \text{ mN m}^{-1}$ ,  $A_{\text{lim}} = 3.85\text{--}545.16$

$\text{nm}^2 \text{ molec}^{-1}$ ,  $M_w = 9.45\text{--}166.7 \text{ kDa}$ ,  $R = 58.42\text{--}98.41\%$ ,  $\Delta S_c = (-0.09 \text{ to } -7.04) \times 10^{-7} \text{ J K}^{-1}$ , and  $\gamma = 13.6\text{--}16.2$ . In reference to the Baltic Sea studies, recorded at 6 stations along the southern Baltic coast from Brzeźno to Oksywie and performed at similar temperatures, one can note a larger variability of  $E_{\text{isoth}}$  values, several times higher molecular areas, an order of magnitude higher  $M_w$ , as much as 50% higher isotherm reversibility  $R$ , whereas a negative entropy change  $\Delta S_c$  (related to  $R$ ) is significantly lower, and finally the miscibility factor  $\gamma$  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 a compression–expansion cycle, and lower miscibility ( $\gamma \uparrow$ ) of SA compounds in the film. The increase of 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 with the corresponding increase of the scaling parameter  $\gamma$  (from 3.7 to 7.9; see 8 in Table 1). That remains in agreement with observations reported in (Barger & Means, 1985; Table IV), for the Atlantic Ocean waters. This is an evidence of the multicomponent film structure transition from a homogeneous mixture to segregated, more ordered complex structures with domains or aggregates of surfactant molecules ( $\gamma \uparrow$ ). Such a film evolution to the new molecular arrangement with a certain reduction of the degrees of freedom in the system leads to a larger entropy change than it is supposed for a structureless microlayer sample (compare  $\Delta S_c$  for 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 to 100% microlayer water by volume showed the following film parameters variability, for  $c_x$  and  $c_x/2$  concentrations, respectively (the measurements were performed at Jelitkowo on 10.08.2002):

$$\begin{aligned} \text{For } c_x \quad E_{\text{isoth}} &= 27.47 \text{ mN m}^{-1}; \\ \Delta S_c &= -6.81 \times 10^{-8} \text{ JK}^{-1}; \quad \gamma = 10.2; \\ R &= 77.56\% \end{aligned}$$

For  $c_x/2$   $E_{\text{isoth}} = 15.73 \text{ mN m}^{-1}$ ;  
 $\Delta S_c = -5.06 \times 10^{-8} \text{ JK}^{-1}$ ;  $y = 14.6$ ;  
 $R = 70.56\%$

Comparisons of the isotherm-derived parameters obtained at the same marine station (Orłowo) in the subsequent years starting from 1990 up to 2002 points to a continuous increase trend of  $A_{\text{lim}}$ ,  $M_w$ ,  $y$  and  $\Delta S_c$  with  $R$  decreasing. It appears that the microlayer film is becoming enriched in a wide variety of heavier, larger and differentiated in their physicochemical properties surfactants capable of forming more and more complex interfacial structures. Mean elasticity modulus  $E_{\text{isoth}}$  measured during a one-year period in the subsequent months at the same sampling site (Jelitkowo, Baltic Sea) demonstrated a continuous increase starting in spring and becoming especially high in summer with a steady-value period to the end of autumn as depicted in Figure 2. Data summarized in Table 1, for inland waters sampled in summer (July–August) and winter (December–February) seasons demonstrated a regular tendency:

$$\left( \begin{matrix} \text{winter} \\ \text{season} \end{matrix} \right) y, A_{\text{lim}}, M_w > y, A_{\text{lim}}, M_w \left( \begin{matrix} \text{summer} \\ \text{season} \end{matrix} \right)$$

$$R, E_{\text{isoth}}, \Delta S_c < R, E_{\text{isoth}}, \Delta S_c$$

This correlation goes in line with the seasonal biological productivity and the summer-time development of human activity. Measurements of SA substances concentrations during a 10-year period in the same region of the Mediterranean Sea proved that low values are more frequent in winter months while highest concentrations occur in the period from spring to autumn (Gasparovic & Cosovic, 2001). The isotherm reversibility mean values are contained in the range 51.6–64.2% for the sampler-collected probes, whereas they reach only 35.9–45.6% for those bottle-sampled (Pogorzelski et al., 1994). In isotherm hysteresis studies on insoluble crude oil product monolayers spread at the original seawater surface,  $R$  values lay between 62.3 and 94.7%. It appears that  $R$  is related closely to the solubility of the film-forming material, assuming higher values for slightly soluble monolayers. A general trend has been identified that an increase in  $E_{\text{isoth}}$  is followed by the corresponding increase in  $R$  (Pogorzelski et al., 1994). The natural riverine waters' mixing effect on the surface rheology of the resulting film can be learned from the spatial-sequential diagram presented in Figure 3, where mean values of the film parameters are given at sampling stations in the

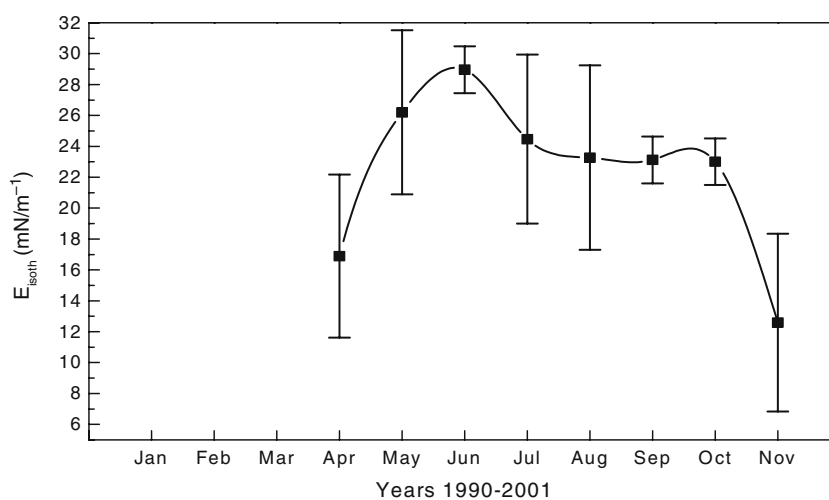


Figure 2. Seasonal variation of mean  $E_{\text{isoth}}$  for natural films collected in Jelitkowo (Baltic Sea), in a one-year cycle registered in the period from 1990 to 2001 (data averaged over each month). Error bar corresponds to the standard deviation from the mean.

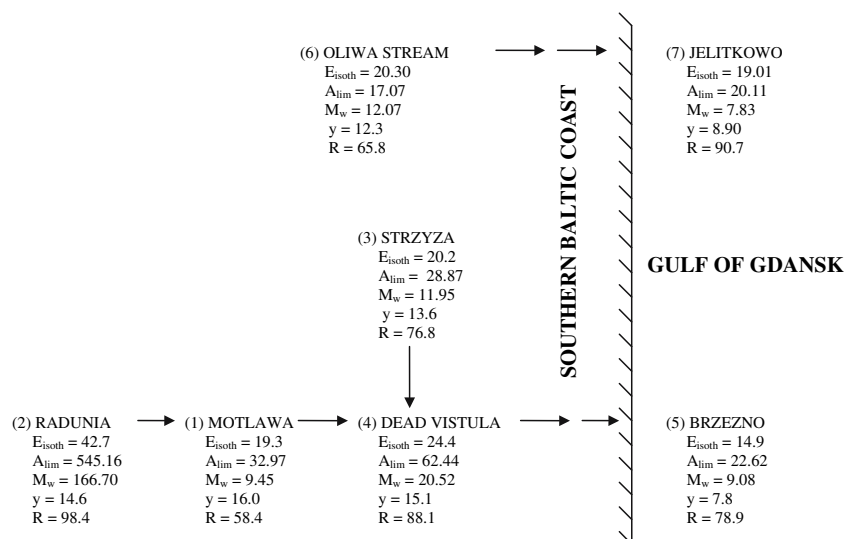
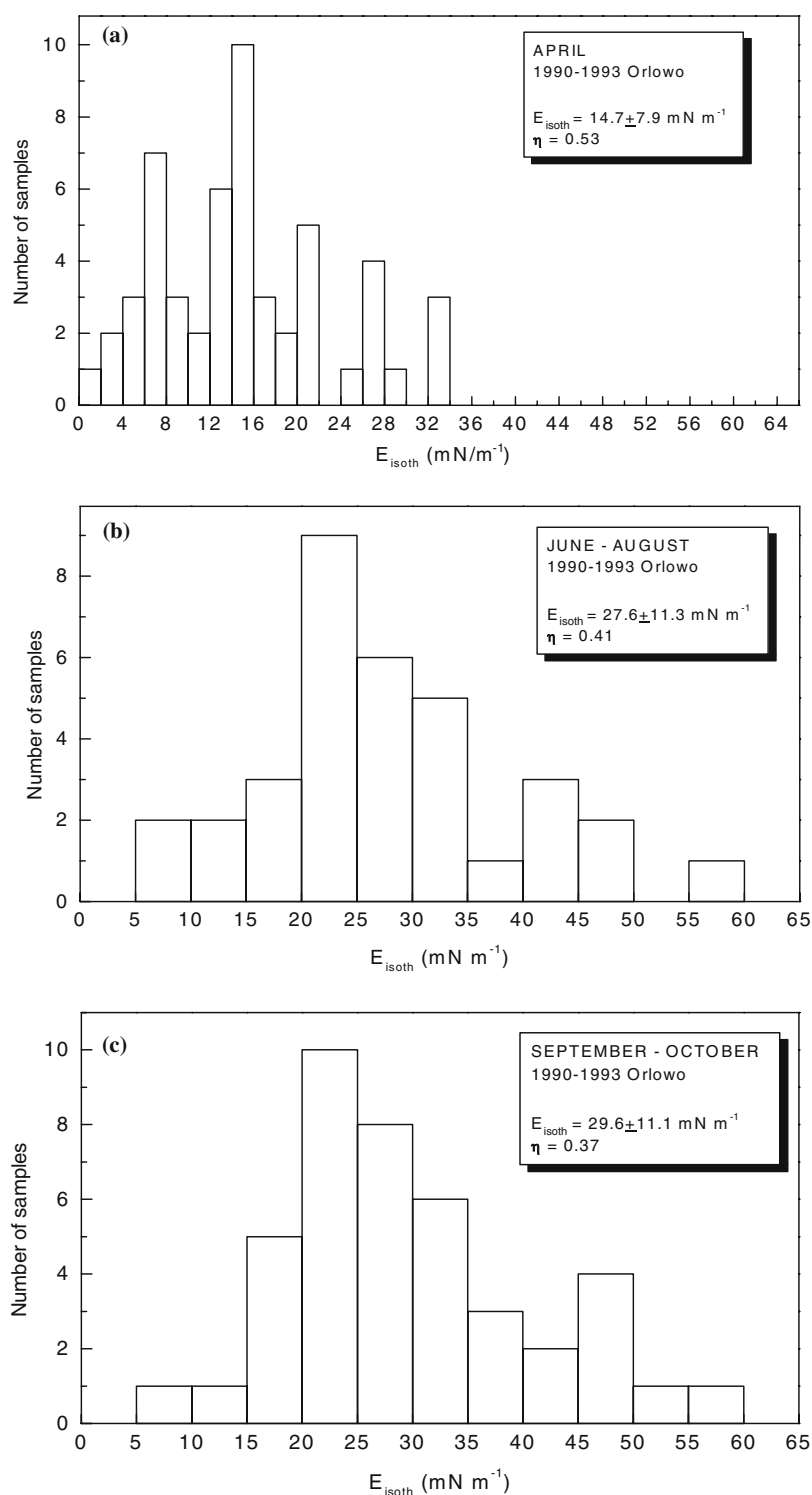


Figure 3. A diagram of riverine water mixing in the Dead Vistula catchment area and mean values of the rheological film parameters taken at selected stations in the Dead Vistula river, and its tributaries adjacent to coastal marine waters in the period November 2001 – February 2002. –Parameters' units:  $E_{\text{isoth}}$  (mN m<sup>-1</sup>),  $A_{\text{lim}}$  (nm<sup>2</sup> molec.<sup>-1</sup>),  $M_w$  (kDa),  $y$  (-),  $R$  (%).

Dead Vistula with its tributaries and from the marine sampling site close to the Dead Vistula estuarine area in the Gulf of Gdańsk. Measurements performed in the period of limited biological activity (December–February) show the similar values recorded in the Dead Vistula and its tributaries (Motława and Strzyża). Surprisingly,  $A_{\text{lim}}(\text{Motława}) + A_{\text{lim}}(\text{Strzyża}) \approx A_{\text{lim}}(\text{Dead Vistula})$ . It points to similar relative contribution of the both water tributaries in the formation of the resulting film on the water formed from common mixing. A certain analogy to the ideal mixtures of non-interacting components can be noticed, where the mean value of the mixture parameter is a simple sum of the component parameter values multiplied by their (molar, mass, volume etc.) ratios in the mixture. In the case of the SA material mixtures the resulting film signatures depend not only on concentrations but on surface activity and properties of the aqueous subphase. 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 nm<sup>2</sup> molec.<sup>-1</sup>) forming almost insoluble ( $R = 98.4\%$ ) and compact films ( $E_{\text{isoth}} = 42.7$  mN m<sup>-1</sup>) was found. The Radunia river seems to be a source of surfactants of high surface activity and of anthropogenic origin. Elasticity modulus  $E_{\text{isoth}}$  of natural marine films

observed at the Baltic Sea station (Orłowo) in the 4-year period (1990–1993) showed a statistical distribution which histograms are presented in Figure 4, for different seasons: (a) spring (April); (b) summer (June–August); and (c) autumn (September–October). Histograms are observed to exhibit a bimodal feature, as already reported in (Bock & Frew, 1993 see Fig. 4). There it was argued therein, these bimodal distributions are consistent with the result of competitive adsorption process at the air–water interface, and suggested that certain general classes of components or “end-members” may dominate the static film properties. Histograms from Figure 4b, c consist of two separate overlapping distributions with maxima in the range of lower ( $E_{\text{isoth}(1)} = 22.5$  mN m<sup>-1</sup>) and higher ( $E_{\text{isoth}(2)} = 45$  mN m<sup>-1</sup>) film elasticities. One can note that the ratio of the maxima peak heights (number of samples at Fig. 4 related to the relative occurrence) between these two distributions at  $E_{\text{isoth}(1)}$  to  $E_{\text{isoth}(2)}$  are similar and equal to 9/3 and 10/4, for relations from Figure 4b, c, respectively. It suggests that the film is built up of at least two classes of natural surfactants of differentiated surface activity capable of forming films of elasticities varying around the maximum distribution values. A relative contribution of the particular component in the film structure (molar ratio) is indirectly related to the



*Figure 4.* Histograms of the elasticity modulus  $E_{\text{isoth}}$  distribution, for natural marine films collected in the Baltic Sea (offshore from Orłowo, Gulf of Gdańsk) in (a) April; (b) June–August; (c) September–October measured during a 4-year period (1990–1993). Denotations:  $E_{\text{isoth}}$  = mean value  $\pm$  SD (standard deviation);  $\eta$  = SD/mean value – is the variability coefficient.

peak heights ratio of the  $E_{\text{isoth}}$  distribution. Such a concept should be confirmed by detailed chemical analyses of the film composition.

In particular, the 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 under near-static measurement conditions 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 exudes 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 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 the films of relatively soluble biopolymeric materials such as proteins would be reflected in lower C/N values. In Figure 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, generally higher C/N ratios were accompanied by 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.

#### Adsorption kinetics parameters

Figure 1 in Pogorzelski & Kogut (2001b) show the exemplary dynamic surface pressure  $\pi$ - $t$  time plots for marine water samples. Dynamic surface pressure dependences plotted versus  $\sqrt{t}$  and  $1/\sqrt{t}$  at short and long adsorption time intervals, allow one to derive the adsorption kinetics parameters (Pogorzelski & Kogut, 2001b), which are 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 the classical Stokes–Einstein formula for the diffusion coefficient

Table 2. Adsorption kinetics parameters of natural surfactants in inland and sea waters

No.	Sampling station (date)	$T$ ( $^\circ\text{C}$ )	$\pi_{\text{eq}}$ (mN m $^{-1}$ )	$D_{\text{eff}}/D$	$E_a/RT$	$\Gamma_{\text{eq}}$ (mol cm $^{-2} \times 10^{-10}$ )
<i>Inland waters</i>						
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
	Oliwa stream (06.02.2002)	15.3	3.2	0.01	4.48	6.05
<i>Baltic Sea</i>						
6	Brzezno (18.04.2001)	16.4	3.0	0.1129	2.18	1.24
	Brzezno (01.08.2001)	22.2	7.8	0.0105	4.55	3.18
7	Jelitkowo 04.04.2001	14.7	5.8	0.1568	1.85	2.42
	Jelitkowo (24.05.2001)	19.0	12.9	0.0278	3.58	5.31

( $D = kT/6\pi\eta R_{\text{mon}}$ , 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  $R_{\text{agr}} \gg R_{\text{mon}}$ . Values of  $D$  for linear molecules are reported to be some 30% greater than that for substances of spherical molecules (Hsu et al., 2000). It should be pointed out that for salt-free ionic surfactant solutions electrostatic interactions are demonstrated 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 (situation found in seawater), the ionic surfactant adsorption becomes similar to the non-ionic case. In reference to marine water samples, values of  $\pi_{\text{eq}}$  and  $\Gamma_{\text{eq}}$  are significantly higher, especially in summer season, 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. It is worth to notice that the same values are measured for both the Motlawa and Strzyza rivers as follows:  $D_{\text{eff}}/D = 0.071$  and  $E_a/RT = 2.65$  but studied in different seasons. These results point to the physicochemical similarity of SA material and suggest that the Radunia tributary is principally responsible for the enrichment of Dead Vistula waters in SA matter. Temperature measurements of the adsorption kinetics performed on inland water samples in the range  $13.6$ – $35.6$  °C demonstrated a regular tendency: an increase of  $T$  results in  $D_{\text{eff}}/D \rightarrow 1$  and  $E_a/RT \rightarrow 0$  corresponding to a transition of the adsorption mechanism from the activated-diffusion to purely diffusion-controlled one (Dukhin et al., 1995). 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  $1/T$  plots, for a non-ionic diluted ( $c \ll \text{cmc}$ ) surfactant solution and the natural marine and inland water samples (data not shown). The model nonionic surfactant is di-chained glucamide referred to as (di-(C6-Glu)) in the text. For the di (C6-Glu), the reference data yield enthalpy  $\Delta H = +62 \pm 1 \text{ kJ mol}^{-1}$  and entropy  $\Delta S = +180 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$  contribu-

tions to the free energy change  $E_a$  by applying the Gibbs'–Helmholtz equation. Whereas 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 marine water samples but for inland waters enthalpy-controlled mechanism is evidenced ( $\Delta ST < \Delta H$ ) at the temperature range  $13$ – $19$  °C (Dukhin et al., 1995). These differences may reflect an energy requirement for molecules of differentiated surface activity to attain sufficient energy to penetrate the film (Eastoe et al., 2001). The physical mechanism of activated state formation and the film structure interaction with the adjacent water subphase are discussed in terms of  $\Delta S$  and  $\Delta H$  in (Eastoe et al., 2001). 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 natural marine and inland waters under study (Defay et al., 1997).

### Concluding remarks

In this paper, our emphasis is on the multicomponent character of natural surfactant films and the consequent complications in attempting to predict interfacial elastic properties due to the diverse chemical makeup of such films. One of the possible descriptions of the complex film structure and its variation in relation to the environmental factors is the application of the generalized scaling procedures to the relatively easily available surface pressure–area and dynamic surface pressure dependences. The advantage of such formalisms is that the 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 the film structure evolution such as: molecular composition (related to  $A_{\text{lim}}$ ,  $M_w$ ,  $E_{\text{isoth}}$ ), film solubility and components miscibility (via  $R$ ,  $\Delta S_c$  and  $\gamma$  factors), surface concentration

( $\Gamma_{eq}$ ,  $\pi_{eq}$ ) and competitive adsorption ( $D_{eff}/D$ ,  $E_a/RT$ ) with a much higher variability of values (dynamics) than bulk surfactant solution parameters have. There is a reason to suggest that certain general classes of SA components appearing at stable relative contributions 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 and thus they can be used as source-specific SA biomarkers to trace temporal and spatial changes. Data presented here demonstrate a significant source-specific parameters variability attributed to natural riverine water circulation in the Dead Vistula catchment area and adjacent marine waters in the Gulf of Gdańsk (southern Baltic Sea). A set of the selected static and dynamic film structure parameters may be used as sensitive indicators for assessment of organic matter dynamics a technique based on surface rheology studies of natural waters. However, the establishments 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, and chemical analyses of natural surfactants.

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