

# Static and dynamic properties of surfactant films on natural waters\*

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## Abstract

The paper contains the results of natural surface film surface pressure – area experiments carried out in inland waters and shallow offshore regions of the Baltic and Mediterranean Seas during 1990–99 under calm water conditions using the Langmuir trough – Wilhelmy filter paper plate system, which ‘cuts out’ an undisturbed film-covered sea area without any initial physico-chemical sample processing. The limiting specific area  $A_{\text{lim}}$  ( $268\text{--}3157 \text{ \AA}^2/\text{molecule}^{-1}$ ) and mean molecular mass ( $0.65\text{--}9.7 \text{ kDa}$ ) of microlayer surfactants were determined from the 2D virial equation of state applied to the isotherms. Film structure signatures were derived from  $\pi - A$  isotherm hysteresis and application of the 2D polymer scaling theory. The stress-relaxation measurements revealed a two-step relaxation process at the interface with characteristic times  $\tau_1$  ( $1.1\text{--}2.8$ ) and  $\tau_2$  ( $5.6\text{--}25.6$ ) seconds suggesting the presence of diffusion-controlled and structural organization

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relaxation phenomena. The results demonstrate that natural films are a complex mixture of biomolecules covering a wide range of solubilities, surface activity and molecular mass with an apparent structural organization exhibiting a spatial and temporal variability.

## 1. Introduction

The physical and chemical properties of sea surface microlayer films have been studied extensively in the past (Hunter & Liss 1981). In particular, considerable effort has been focused on the measurement of surface pressure-area  $\pi - A$  isotherms and the elastic properties of marine films (Jarvis et al. 1967, Barger & Means 1985, Frew & Nelson 1992, Bock & Frew 1993). A serious limitation of previous work was the inability to compare  $\pi - A$  isotherms in terms of specific area or mean molecular area, because neither surface concentrations and molecular mass nor the chemical makeup of the films could be specified. In addition, there is no really satisfactory standard method for collecting a sample for analysis from the sea surface, and the surface pressure-area characteristics depend on the sample treatment (Garrett & Duce 1980). Natural sea surface films are derived from bulk seawater surface-active dissolved organic matter of biogenic origin. Surfactants are concentrated at the air-sea interface by numerous physical processes, including adsorption, diffusion, turbulent mixing, bubble and particle transport, and convergent circulations driven by wind, tidal forces, surface and internal waves. The composition of sea surface films is largely undefined, although significant enrichment of many specific classes of compounds in the surface microlayer have been demonstrated (Hunter et al. 1981). It seems reasonable to expect the chemical composition of natural films to respond dynamically to physical forcing factors (Frew & Nelson 1992), and that this response might be reflected in surface pressure-area isotherms ( $\pi - A$ ).

This paper presents data for  $\pi - A$  isotherms of films from Baltic and Mediterranean coastal waters and from inland waters; the films were collected with a novel device for sampling water and for measuring the surface pressure-area relationships of untreated water microlayer samples (Pogorzelski 1992, Pogorzelski et al. 1994). Further information on the film structure was obtained from the entropy change  $\Delta S_c$  attributed to the isotherm hysteresis found in a compression-expansion cycle. Moreover, the degree of mixing and formation of layered structures of surfactants in a multicomponent film can be predicted by means of the 2D polymer film scaling theory applied to the isotherms, by means of the value of the scaling exponent  $y$  exhibited by interfacial systems (Pogorzelski 1996). Marine film isotherms may be scaled according to specific area,

as shown by Barger & Means (1985), and fitted using a two-dimensional virial equation of state. The virial coefficients are interpreted in terms of the mean number of moles present in the film, the specific limiting area and the mean molecular mass of the surfactants composing the film. The time scale and nature of the relaxation processes taking place in natural films can be determined in stress-relaxation experiments (van Hunsel & Joos 1989). The dynamic surface pressure response of a natural film to a step-rapid ( $< 1$  s) relative film area deformation ( $= \Delta A/A \sim 0.07\text{--}0.23$ ) was approximated using a double exponential decay with two relaxation times. This indicates the complex nature of relaxation film behaviour at different time scales of film deformation (Joos et al. 1992, Serrien et al. 1992). Relaxation processes of the interfacial system lead to the surface viscoelasticity  $E$ . Most real systems are viscoelastic and the dilational modulus is a complex quantity. The present mathematical formulation shows clearly that the surface viscoelasticity, as defined by a periodic procedure and derived with a non-periodic procedure applying various surface area  $\Delta A/A$  perturbation functions such as step functions, square pulses or linear disturbances, can be identified as the same physical quantity (Miller et al. 1991).  $E$  is an intrinsic property of an interfacial phase independent of the type of surface excitation characterizing its dynamic behaviour. Within the framework of the diffusional viscoelasticity model, the natural film viscoelastic modulus can be expressed by means of the rheokinetic parameters of the stress-relaxation experiment (Jayalakshmi et al. 1995). By contrast, in the case of the sinusoidal procedure, relaxation properties are derived from observations of the time-lag (phase angle) between  $\Delta A/A$  excitation and the surface tension response. The aim of the present paper was to evaluate the spatial and temporal variability of the static and dynamic response parameters observed in natural multicomponent surface films to compression and expansion.

## 2. Theory

### 2.1. Force-area isotherm parameters

The simplest equation of state to describe surface films is the well-known 2D analogue of the ideal gas law:

$$\pi A_m = kT, \quad (1)$$

where  $k$  is the Boltzmann constant,

$$\pi = \gamma_0 - \gamma - \text{the surface pressure of the film,}$$

- $\gamma_0, \gamma$  – the surface tension of solvent and surfactant solution respectively,  
 $A_m$  – the area per molecule,  
 $T$  – the temperature in Kelvins.

For natural films, the isotherms differ significantly from ideal-gas behaviour as expressed by eq. (1), and a very good fit for the values of  $\pi - A$  can be obtained with a least-squares best fit parabola through the data. The following quadratic equation of state, e.g. a virial equation of state, was proposed by Barger & Means (1985):

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

where  $C_0, C_1, C_2$  are the virial coefficients, and  $A$  is the film area (in  $\text{cm}^2$ ).

$C_1$  can be interpreted as the limiting specific area occupied by the molecules in the film, and  $C_0$  can be assumed equal to  $XnkT$  in the limiting case when  $\pi$  approaches zero.

$$C_0 = XnkT, \quad (3)$$

where  $n$  is the number of molecules in the unknown film.

$X = 0.5$  is related to the interaction forces in the monolayer, and is determined as the mean value of Langmuir trough isotherm measurements with several model natural film-forming substances (Barger & Means 1985). Comparing eqs. (1) and (2),  $X = 1$  is attributed to the ideal-gas film behaviour not evidenced in natural films.

Then the number of molecules and moles  $n_m$  in a film can be determined:

$$n = 2C_0/kT, \quad (4)$$

$$n_m = n/N_A, \quad (5)$$

where  $N_A$  is the Avogadro number.

The limiting molecular area  $A_{\text{lim}}$  (in  $\text{\AA}^2$ ) can be expressed as (Frew & Nelson 1992)

$$A_{\text{lim}} = C_1 n^{-1} \times 10^{16}. \quad (6)$$

According to the scaling procedure applied to a variety of natural microlayer films (Barger & Means 1985), the area  $A_{20}$  (at  $\pi = 20 \text{ mN m}^{-1}$ ) is first calculated from eq. (2).

The proportional mass (in  $\mu\text{g}$ ) of the average pure compound (chosen as a reference) is

$$m = 24 \times (A_{20}/119.54). \quad (7)$$

The resulting number of micrograms is taken to be equivalent to the number of moles  $n_m$ , and simple division yields the mean molecular mass  $M_W$  (Barger & Means 1985):

$$M_W = m/n_m. \quad (8)$$

This scaling concept was tested for a large number of marine microlayer films (spread and adsorbed) and one-component film-forming substances found in subsurface waters (Barger & Means 1985).

The description of the film states includes the dilational elasticity modulus (or Gibb's modulus), where  $E_{\text{isoth}}$  expresses the static compressional response of a film to the compression or dilation corresponding to isotherm registration in its equilibrium (Adamson 1982):

$$E_{\text{isoth}} = -d\pi/d \ln A. \quad (9)$$

The isotherm hysteresis may be attributed to different arrangements of the molecules in the compression and dilation cycles. Now, since different degrees of organization must be related to entropy  $S$ , the hysteresis of the compression-expansion curves is presumably correlated with a change in the entropy  $\Delta S_c$  of the film-adjacent water layer system (Hühnerfuss & Alpers 1983). The well-known negative entropy effect related to molecular reorientation (Zhou & Pethica 1986), and multilayer build-up has already been encountered with regular organic films under static conditions (Rapp & Gruler 1990).

According to the fundamental laws of thermodynamics applied to the isothermal compression-expansion cycle of a 2D film system ( $T = \text{const}$ ,  $dS = dQ/T$ ;  $dQ = dW$ , where  $Q$  and  $W$  are the heat provided and work done respectively), the change in entropy  $\Delta S_c$  between the initial  $A_i$  and final  $A_f$  film areas is

$$\Delta S_c = S_{\text{dil}} - S_{\text{com}} = \Delta W/T, \quad (10)$$

where  $\Delta W = W_{\text{dil}} - W_{\text{com}}$  is the respective work difference between the dilation and compression cycles, both defined in the same way:

$$W_{\text{com}} = - \int_{A_i}^{A_f} \pi dA. \quad (11)$$

The work of expansion  $W_{\text{dil}}$  can be derived in the same manner from the expansion isotherm plot.

The characterization of the miscibility or phase separation of the monolayer-forming components requires a knowledge of the intermolecular interactions and physicochemical parameters governing segregation or mixing. The components usually tend to separate when they differ greatly in their structure and molecular areas. Recently, the  $\pi - A$  isotherms of natural marine films have been analyzed to derive the scaling parameter  $y$  from the relation  $E_{\text{isoth}} = y\pi$  applicable to the high-frequency limit of the surface modulus (Pogorzelski 1996). It was postulated that the concept of the structural arrangements of molecules in a three-component system (an insoluble polymer spread on a solution of surfactants) closely related

to the value of  $y$  can also be extended to natural marine multicomponent systems (Pogorzelski 1996). It was shown that 2D miscibility depends on the interfacial orientation of the components at the liquid surface. Low values of  $y < 3.5$  indicate a homogeneous mixed film, higher  $y \approx 8$  lead to less film homogeneity observed as patches or domains of film-forming compounds in such a complex film. The highest values of  $y > 10$ –16 indicate that the vertical segregated film structure forms nearly separate layers at the interface with the most insoluble compound on the top of this layered system (see Fig. 1 in Pogorzelski 1996).

## 2.2. Rheokinetic parameters of the surface film adsorption-desorption mechanism

The adsorption process of an aqueous surfactant solution at the air/water interface consists of two steps. One step is the transport of surfactant molecules from the bulk phase to the subsurface along a concentration gradient – the diffusion step; the other is the transport of molecules from the subsurface to the surface – the adsorption step. If the rate of the first step is much slower than that of the second, the whole process is controlled by diffusion (Eastoe & Dalton 2000). Diffusion-controlled adsorption kinetics was first treated quantitatively by Ward & Tordai (1946). However, an analytical solution for the surface tension decay  $\gamma(t)$  cannot be obtained. At short times and sufficiently low concentrations, the surface molecules interact quasi-ideally, and the following approximate expression can be given for the dynamic surface tension (Kragel et al. 1995, Eastoe & Dalton 2000):

$$\gamma(t) = \gamma_0 - 2RT c (Dt/\pi)^{\frac{1}{2}} \quad \text{when} \quad t \rightarrow 0. \quad (12)$$

On the other hand, if the bulk-to-surface transport is always diffusion controlled, a  $\gamma(t) \sim 1 t^{-\frac{1}{2}}$  dependence is found at long times:

$$\gamma(t) = \gamma_{\text{eq}} + (RT\Gamma^2/2c)(\pi/Dt)^{\frac{1}{2}} \quad \text{when} \quad t \rightarrow \infty. \quad (13)$$

In these equations  $\gamma_0$ ,  $\gamma_{\text{eq}}$  are the surface tensions of the pure solvent and the equilibrium surface tension of the solution,  $\Gamma$  is the surface adsorption,  $c$  – the surfactant bulk concentration,  $R$  – the gas constant, and  $D$  – the monomer diffusion coefficient of the surfactant in the bulk. The case of diffusion-driven adsorption followed by molecular reorientation at the interface has been theoretically handled by Joos et al. (1992) and Serrien et al. (1992):

$$\gamma(t) = \gamma_{\text{eq}} + [(\gamma_0 - \gamma_{\text{eq}} - B) \exp(-4t/\pi\tau_D)^{\frac{1}{2}} + B] \exp(-t/\tau_R), \quad (14)$$

where  $B$  and  $\tau_R$  are the amplitude and the characteristic time of the

reorientation process of the adsorbed molecules, and  $\tau_D$  is the diffusion relaxation time given by

$$\tau_D = 1/D (d\Gamma/dc)^2. \quad (15)$$

The surface viscoelasticity  $E$  – the surface dilational modulus – is defined as the infinitesimal change in surface tension due to a relative change in film area  $A$  when a monolayer is compressed or expanded (Lucassen-Reynders 1993, Williams & Prins 1996):

$$E = d\gamma/(dA/A) = -d\pi/d\ln A. \quad (16)$$

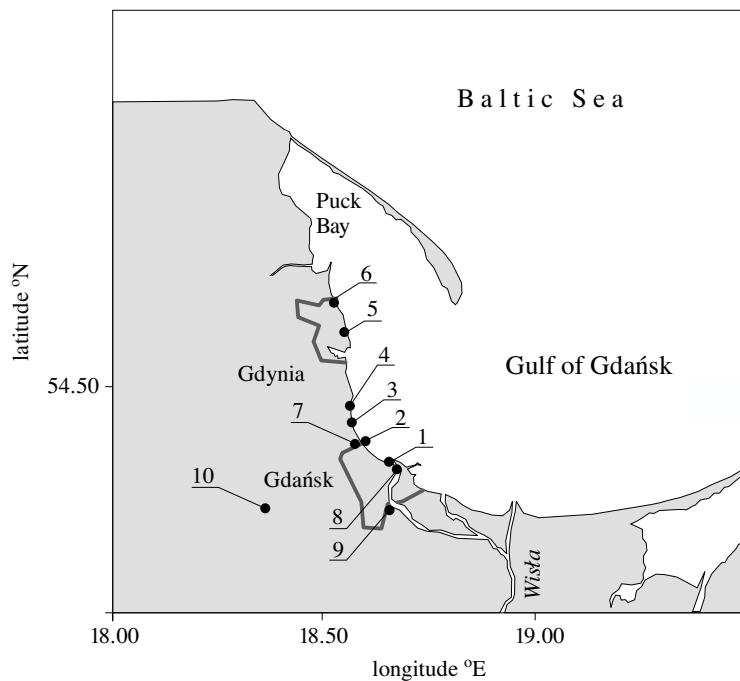
Most real systems are viscoelastic and the dilational modulus is a complex quantity composed of real  $E_d$  (dilational elasticity) and imaginary  $E_i$  ( $= \omega\eta_d$ , loss component) parts:

$$E = E_d + i \omega\eta_d \quad \text{also} \quad = E_0 \cos \theta + iE_0 \sin \theta, \quad (17)$$

where  $\eta_d$  is the surface dilational viscosity,  $\omega$  – the angular frequency of periodic oscillations,  $E_0$  ( $= -\Delta\pi/(\Delta A/A)$ ) represents the amplitude ratio between surface stress and strain, and  $\theta$  is the loss angle of the modulus.

### 3. Experimental

Natural surface film experiments in shallow offshore waters of the Baltic (Gulf of Gdańsk) and Mediterranean (Livorno), as well as in inland waters, were carried out in the period 1990–96 under calm sea conditions as already reported in Pogorzelski et al. (1994). The locations of the sampling sites in the Baltic Sea and natural inland stations (rivers, a stream and a lake) are shown in Fig. 1. The novel film sampler is a submersible rectangular double-walled vessel which ‘cuts out’ an undisturbed portion of sea measuring  $45 \times 35$  cm and 8 cm thick. The most valuable property of this device, described in detail elsewhere (Pogorzelski 1992), is that the collection and Langmuir trough isotherm analyses are performed without the microlayer material having to be transferred or chemically processed. The sampler consists of a rectangular plastic tray 50 cm long, 40 cm wide and 6 cm high with a shallow Langmuir trough ( $30 \times 40 \times 0.7$  cm) in the bottom made of plastic paraffin wax-coated pieces. In order to perform  $\pi - A$  isotherm measurements after an equilibration of 30 minutes, i.e. the standard period chosen for practical purposes, the initial trough area ( $= 1200$  cm<sup>2</sup>) is compressed with an average deformation speed  $u = \Delta A/\Delta t$  taken arbitrarily to be  $0.60$  cm<sup>2</sup> s<sup>-1</sup> in that two barriers are moved towards each other symmetrically around the film pressure sensor every 30 s. Surface pressures were measured with the Wilhelmy plate technique using a 5-cm-wide piece of filter paper attached to the arm of a Cahn electrobalance; they were accurate to within  $0.1$  mN m<sup>-1</sup>.



**Fig. 1.** Locations of natural surface film study sites in the Baltic Sea: 1 – Brzeźno, 2 – Jelitkowo, 3 – Sopot, 4 – Orłowo, 5 – Gdynia, 6 – Oksywie; inland waters: 7 – Potok Oliwski (Oliwa stream), 8 – Martwa Wisła (Dead Vistula) river, 9 – river Motława, 10 – Lake Jasień

The Wilhelmy plate was suspended over the central point of the trough and oriented perpendicular to the barriers. Dynamic film characteristics was evaluated from stress-relaxation studies (van Hunsel & Joos 1989). The surface pressure-time response  $\pi(t)$  of the surface film to a step-rapid ( $\Delta t = 0.19\text{--}1.1\text{ s}$ ) relative surface area deformation  $\Delta A/A$  ( $= 0.07\text{--}0.23$ ) applied to the sample by moving the barriers, was recorded for several minutes. The reported static and dynamic film parameters are the mean value of 6–9 measuring runs performed at a given site.

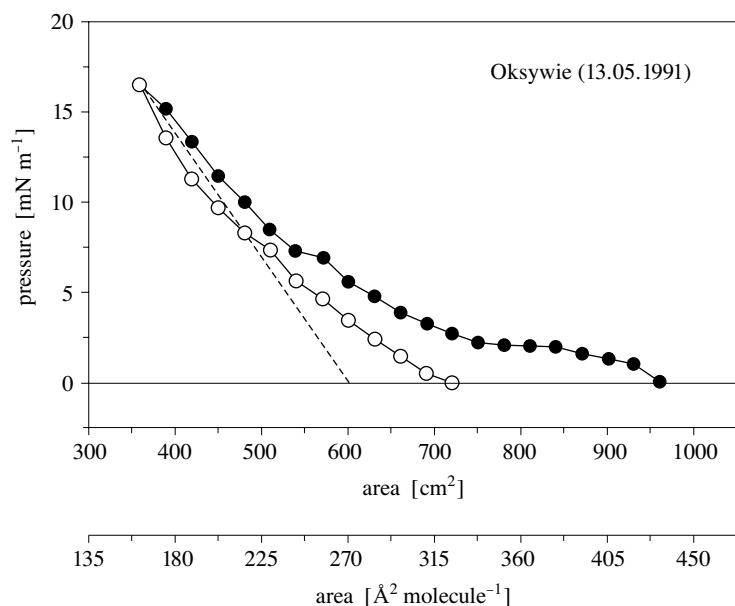
The sampler, the levelling device, and the Cahn electrobalance resting on the measuring table are situated near the sampling site on the shore.

## 4. Results and discussion

### 4.1. Force-area natural film characteristics

The typical  $\pi - A$  isotherm of marine films studied in the shallow offshore waters of the Baltic (Gulf of Gdańsk) is depicted in Fig. 2.





**Fig. 2.** Surface pressure-area isotherm of sea surface sample collected in shallow coastal waters off Oksywie on 13 May 1991. Compression (o-o) and expansion (●-●) curves. The dashed line indicates the limiting specific area  $A_{\text{lim}}$

The lower area per molecule scale was constructed according to the scaling concept. The limiting specific area  $A_{\text{lim}}$  is obtained by extrapolating the linear part of the isotherm plot curve to  $\pi = 0$  (see dashed line in Fig. 2). The isotherms are typical of surfactants forming expanded films: though increasing monotonically, they exhibit several plateaus corresponding to pure phase changes and kinks reflecting phase higher-order transitions. The gentle slope of the plots of the untreated samples at large film areas represents a squeezing out of the less surface-active molecules as the film is compressed. Such behaviour has been noted previously by several investigators for natural oceanic films (Jarvis et al. 1967, van Vleet & Williams 1983, Barger & Means 1985, Frew & Nelson 1992).

In order to look further at possible systematics, the  $\pi - A$  data can be fitted using a two-dimensional virial equation of state (Barger & Means 1985). The virial coefficients are interpreted in terms of the mean number of moles  $n_m$  present in the film and the limiting specific area  $A_{\text{lim}}$  following Barger & Means (1985). Fitted coefficients, limiting areas, mole numbers, and mean molecular mass are set out in Table 1. Values of  $A_{\text{lim}}$  range from 268.8 to 3157.5  $\text{\AA}^2 \text{ molecule}^{-1}$ , for sea-surface samples and are generally lower (377.8 to 779.7) for the inland probes. They are several times higher for subsurface (bottle-collected) samples (compare 1 and 2 in Table 1). The films

**Table 1.** Virial coefficients for the two-dimensional equation of state and surface characteristics of natural-water films

No.	Sampling station	$y$	$\Delta S_c$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	$C_0$ [erg]	$C_1$ [cm <sup>2</sup> ]	$C_2$ [cm <sup>3</sup> dyn <sup>-1</sup> ]	$A_{\text{lim}}$ [Å <sup>2</sup> molecule <sup>-1</sup> ]	$n_m$ [× 10 <sup>-9</sup> ]	$M_W$ [kDa]
<b>Baltic Sea</b>									
1	Orłowo (sampler) 28.06.1990	3.7	-72.2	170.1	700.1	-25.9	846.5	13.74	1.75
	Orłowo 19.08.1998	12.7	-64.6	256.6	742.8	-19.6	586.4	21.03	3.43
	Orłowo 15.07.1999	13.7	-69.3	222.4	758.5	-20.5	685.9	18.36	3.93
2	Orłowo (bottle) 28.06.1990	7.9	-133.5	30.7	471.1	-15.1	3157.5	2.47	9.71
3	Brzeźno 30.07.1992	7.0	-59.3	135.8	641.2	-22.2	712.9	10.97	2.21
	Brzeźno 12.07.1999	13.9	-70.4	202.6	766.0	-23.4	779.7	16.31	4.06
4	Jelitkowo 29.07.1992	4.8	-36.2	383.4	881.4	-24.62	473.1	30.97	0.77
	Jelitkowo 09.07.1999	13.8	-73.7	190.8	766.3	-20.4	809.2	15.72	4.59
5	Sopot 31.07.1992	10.3	-29.5	124.7	500.0	-18.12	823.9	10.07	2.38
	Sopot 23.09.1998	13.4	-46.8	185.8	814.7	-52.5	886.3	15.3	1.84
	Sopot 06.07.1999	13.9	-209.3	125.0	837.3	-25.69	1381.8	10.06	6.58

**Table 1.** (continued)

No.	Sampling station	$y$	$\Delta S_c$ [J mol <sup>-1</sup> K <sup>-1</sup> ]	$C_0$ [erg]	$C_1$ [cm <sup>2</sup> ]	$C_2$ [cm <sup>3</sup> dyn <sup>-1</sup> ]	$A_{\text{lim}}$ [Å <sup>2</sup> molecule <sup>-1</sup> ]	$n_m$ [× 10 <sup>-9</sup> ]	$M_W$ [kDa]
6	Gdynia 07.08.1992	4.7	-33.6	225.9	471.0	-26.78	432.1	18.24	1.33
7	Oksywie 13.05.1991	5.0	-10.7	485.5	599.4	-16.07	268.8	37.04	0.65
<b>Mediterranean Sea</b>									
8	Livorno 27.06.1991	3.3	-56.9	182.9	903.1	-23.89	1014.7	14.77	1.62
<b>Inland Waters</b>									
9	Motława river 20.08.1998	16.2	-31.8	365.8	680.1	-19.55	377.8	29.94	2.01
10	Martwa Wisła river 21.08.1998	14.3	-44.3	320.5	764.8	-21.0	458.8	26.1	2.76
	Martwa Wisła river 16.07.1999	13.9	-34.2	377.6	713.0	-22.7	385.3	30.7	1.96
11	Oliwa (stream) 25.07.1999	14.7	-37.1	367.4	681.2	-20.8	381.4	29.65	2.03
12	Jasień (lake)	20.8	-35.4	344.2	766.0	-22.4	779.7	16.31	4.06

Symbols:  $y$  – scaling parameter,  $\Delta S_c$  – change in the entropy,  $C_0, C_1, C_2$  – virial coefficients,  $A_{\text{lim}}$  – limiting area,  $n_m$  – number of moles,  $M_W$  – molecular mass.

studied at Oksywie – a station situated away from human settlements with their sewage – and samples collected just after strong wind events during which intensive water mixing took place exhibited the lowest values of  $A_{\text{lim}}$  and  $M_W$ . The mean molecular masses of marine surfactants lie in the range 0.65 – 9.71 kDa (one dalton equals one atomic mass unit).  $M_W$  values are many times higher for samples of subsurface water with respect to the microlayer films under calm sea conditions. Such a difference almost disappears for samples taken at higher wind speeds ( $\geq 6 \text{ m s}^{-1}$ ). An increase in both  $M_W$  and  $A_{\text{lim}}$  recorded for subsurface samples, if referred to microlayer values, is also correlated with a corresponding increase in the scaling parameter  $y$  (from 3.7 to 7.9). This is evidence of the multicomponent film structure transition from a homogeneous mixture to segregated, more ordered complex surfactant domains or aggregate structures. During a compression-expansion cycle, such a vertically organized interfacial system should evolve to a new structure with a certain loss of the system's degrees of freedom, which in turn leads to a larger entropy  $\Delta S_c$  change ( $-133.5 \text{ J mol}^{-1} \text{ K}^{-1}$ , see 2 in Table 1) than is expected for a homogeneous structureless microlayer sample ( $= -72.2 \text{ J mol}^{-1} \text{ K}^{-1}$ , see 1 in Table 1). The mean molecular masses of inland samples lie within a rather narrow range 1.96–4.06 kDa. Note the comparable values of  $M_W$ , both measured on the same date, for the Martwa Wisła (Dead Vistula) river and its tributary, the Motława.

The general results reported here agree well with the conclusions of van Vleet & Williams (1983) that natural marine films are not composed primarily of free fatty acids, alcohols or hydrocarbons, although these compounds have all been found in surface film samples. More oxygenated molecules of higher molecular weight are indicated. The glycopeptide-lipid-oligosaccharide complex, such as that described by D'Arrigo et al. (1984), appears to be more consistent with the observations of surface characteristics of marine films found in the Baltic. The same hydrophil-lipophil balance (HLB) observed in the model compounds (Barger & Means 1985) must occur as an average property of the reported natural surface-active material. None of the model compounds widely used in oceanic studies have molecular weights of several thousand, so very large polymer-like materials with comparable film characteristics are suggested as being present. It must be pointed out, however, that no attempt was made to identify the surfactants in the experiments reported here. Intercomparison of the force-area parameters measured at the same marine station in consecutive years from 1990 to 1999 points to a continuously increasing trend in  $A_{\text{lim}}$ ,  $M_W$ ,  $y$  and  $\Delta S_c$ . It seems that the microlayer film is becoming enriched in a wide variety of larger and heavier surfactants, differentiated in their physico-chemical

properties, that are capable of forming more and more complex interfacial structures.

Field samples collected in the Baltic and Mediterranean Seas, as well as inland probes, showed nanomolar amounts of surface-active material which occupied a rather large surface area per molecule and had a high molecular mass, comparable to those reported for a variety of oceanic samples (Frew & Nelson 1992) ( $M_W = 1.5\text{--}5$  kDa,  $A_{\text{lim}} = 400\text{--}800$  Å<sup>2</sup> and  $n_m = 14\text{--}119 \times 10^{-10}$  moles).

As can be seen in Fig. 2, the expansion curve does not overlap the compression curve. If a compression isotherm was completed without pauses and the barrier motion then reversed, the expansion isotherm was steeper but had a similar shape. The final surface pressure for a fully-expanded monolayer tended to be somewhat lower, suggesting some loss of molecules from the interface. The surface concentrations for these films were not measured, therefore it is not possible to determine whether the apparent shift to the left of the dilation isotherm curves was due to an actual loss of film material or to changes in conformational or intermolecular associations. Losses from the film could have occurred via desorption, micelle formation, or collapse to a multilayered solid phase. Conformational mechanisms could include more efficient packing due to nonpolar interactions, coiling of biopolymer chains, and looping of polymer segments into bulk solution. The elasticity modulus  $E_{\text{isoth}}$  is apparently higher for the compression isotherm  $E_{0\text{com}}$  than for the expansion  $E_{0\text{dil}}$  of the same water sample. It is clear that the mechanical compression-expansion cycle leads to a more condensed monolayer structure. During the compression cycle, the molecules squeezed out would then return to the interface with a certain relaxation time during the expansion cycle (Bock & Frew 1993).

This pattern is characteristic of irreversible processes and indicates that the work done by compression  $W_{\text{com}}$  is higher than that recovered at expansion  $W_{\text{dil}}$ , which is accompanied by a negative entropy change  $\Delta S_c$ , as summarized in Table 1. The work difference ranges from  $-3.0$  to  $-39.6$  kJ mol<sup>-1</sup>. The entropy change varies in the range  $-10.7$  and  $-133.5$  J mol<sup>-1</sup> K<sup>-1</sup> or (in natural units of  $R$ ;  $R$  is the gas constant) appears to be  $-1.29$  to  $-16.0$   $R$ . The entropy effect (leading to a more organized monolayer state) is most significant for data sets 1 and 2 in Table 1. Values of  $\Delta S_c$  are lowest for the samples collected in a relatively pure sea area (see 7 in Table 1), and differ from each other by a factor of almost two between microlayer and subsurface water samples taken at the same location. Inland water probes again demonstrated a low  $\Delta S_c$  variability ( $-31.8$  to  $-44.3$  J mol<sup>-1</sup> K<sup>-1</sup>). The Mediterranean microlayer samples showed comparable values of  $\Delta S_c$ .

Similar results have been obtained with many other micro-layer samples collected in both eastern and western United States coastal waters, suggesting that compression hysteresis appears to be a universal phenomenon in multicomponent sea surface films leading to compositional changes (Bock & Frew 1993). In particular, the multicomponent film is postulated with the presence of distinct ‘end-member’ components diluted by variable amounts of components 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 components in the films. Natural films at the air-water interface are almost certainly not pure monolayers but are best characterized as poorly organized, heterogeneous macromolecular films, whose influence may extend several micrometers into the bulk solution. Relatively hydrophobic material diffusing to the interface is effectively irreversibly adsorbed. However, there is probably extensive and continual dynamic exchange of the more water-soluble surfactant species in and out of the bulk solution, with substantial quantities of weakly surface-active polar organics associated via hydrogen bonding and ionic interactions with more hydrophobic film material.

Recently, the  $\pi - A$  isotherms of natural marine surface films have been analyzed to derive the scaling parameter  $y$  (set out in Table 1 for the samples in question) from the relation  $E_{\text{isoth}} = y\pi$  applicable to the high-frequency limit of the surface modulus (Pogorzelski 1996). Values of  $y$  for 1 and 8 in Table 1 clearly indicate a mixed film structure, whereas in other samples, partially organized structures are likely to be present. All the inland waters data of  $y$  values are characteristic of highly organized films ( $y = 13.5 - 20.8$ ). For comparison, values of  $y$  determined by others for natural films in oceanic waters lie in a similar range (Panchenko et al. 1990). At low film pressure  $1 < \pi < 2 \text{ mN m}^{-1}$ , they obtained  $y = (5.5 \pm 2.2)$  for coastal waters in San Diego Bay, and  $y = (6.6 \pm 1.5)$  in shallow waters of the Atlantic Ocean. The  $E_{\text{isoth}}$  vs  $\pi$  plots from Fig. 7 in Bock & Frew (1993) for different times elapsed from the moment of collection, allows the time evolution of adsorbed film structure to be predicted as expressed by a value of  $y$ . The continuous increase in the isotherm slopes starting from  $t = 20 \text{ min}$  to  $5 \text{ h}$   $20 \text{ min}$  after collection corresponds to a  $y$  parameter increase from 4.3 to 6.5, which leads to the formation of more organized film structures with time.

#### 4.2. Dynamic behaviour of natural films

The establishment of thermodynamic equilibrium in a monolayer is not a trivial process, in particular in the case of compression in a nearly

horizontal section of the  $\pi - A$  isotherm (see Fig. 2), which is typical of a first-order phase transition, where very slight or no surface pressure gradients occur in the monolayer. Upon rapid compression of a monolayer across a phase transition, non-equilibrium structures like the dendritic domains of the more condensed phases are formed, as demonstrated in the case of 1-monopalmitoyl-rac-glycerol monolayers with the BAM technique during the relaxation process (Gehlert & Vollhardt 1997).

The velocity of the film compression effect on the isotherms of natural films has already been addressed (see Fig. 3 in Pogorzelski 1996) and discussed on the basis of hydrodynamics in terms of the reduced Reynolds number. The time scale of the relaxation processes taking place in natural films can be evaluated from stress-relaxation studies (van Hunsel & Joos 1989). The surface pressure-time response of a marine surface film to a rapid ( $\Delta t \approx 0.75$  s) relative surface area deformation  $\Delta A/A_0$  ( $= 0.12$ ) for a sample collected at Jelitkowo on 29 November 1997 (Baltic Sea coastal region, Poland) is presented in Fig. 3a. The rate of the relaxation processes can be analyzed by means of the first-order relation (Nino et al. 1998)  $\ln [(\pi_\infty - \pi_t) / (\pi_\infty - \pi_0)] = -\lambda_i t$ , where  $\pi_\infty$ ,  $\pi_0$ , and  $\pi_t$  are the surface pressures at steady-state conditions, at time  $t = 0$ , and at any time  $t$  respectively; and  $\lambda_i$  is the first-order rate constant related to the relaxation time  $\tau_i$  ( $\tau_i = 1/\lambda_i$ ). The equation applied to the decay curve  $\pi(t)$  from Fig. 3a yields two linear regions. The characteristic relaxation times  $\tau_1$  and  $\tau_2$ , together with the applied step deformation time  $\Delta t$ , the relative area change  $\Delta A/A$ , and the amplitude of the dilational modulus  $E_0$  ( $= -\Delta\pi/(\Delta A/A)$ ) for the films in question are given in Table 2.

The transition time  $t_{1-2}$ , equal to 2.8 s corresponding to a change in the relaxation mechanism, was obtained analytically as the point of intersection of the linear fits correlated with each step in the desorption mechanism. The decay of the  $\pi(t)$  curve in Fig. 4a can be approximated using a double exponential relation  $\pi(t) = \pi_1 \exp(-t/\tau_1) + \pi_2 \exp(-t/\tau_2)$  according to a two-step reaction process that apparently takes place at the interface with relaxation times  $\tau_1 = 2.4 \pm 0.2$  and  $\tau_2 = 12.2 \pm 0.3$  seconds. For several marine samples so far evaluated, relaxation times have been in rather narrow ranges:  $\tau_1$  (1.3–2.9 s) and  $\tau_2$  (10.1–25.6 s). It can be seen that for the inland water samples, they are shorter (1.1–2.0 s and 5.6–13.3 s). As a result, when deformation times  $\Delta t \sim \tau_1$  are too long, the faster relaxation mechanism can escape detection using this method. Moreover, it has been found that the shorter time depends on the film surface pressure decreasing with increasing  $\pi$  as follows:  $\tau_1 = 2.0$  ( $\pi = 1.5$  mN m<sup>-1</sup>);  $= 1.6$  ( $\pi = 7.5$  mN m<sup>-1</sup>) and  $= 1.1$  ( $\pi = 17.6$  mN m<sup>-1</sup>) seconds, for

**Table 2.** Rheokinetic parameters obtained in the desorption stress-relaxation experiment on natural organic films on water

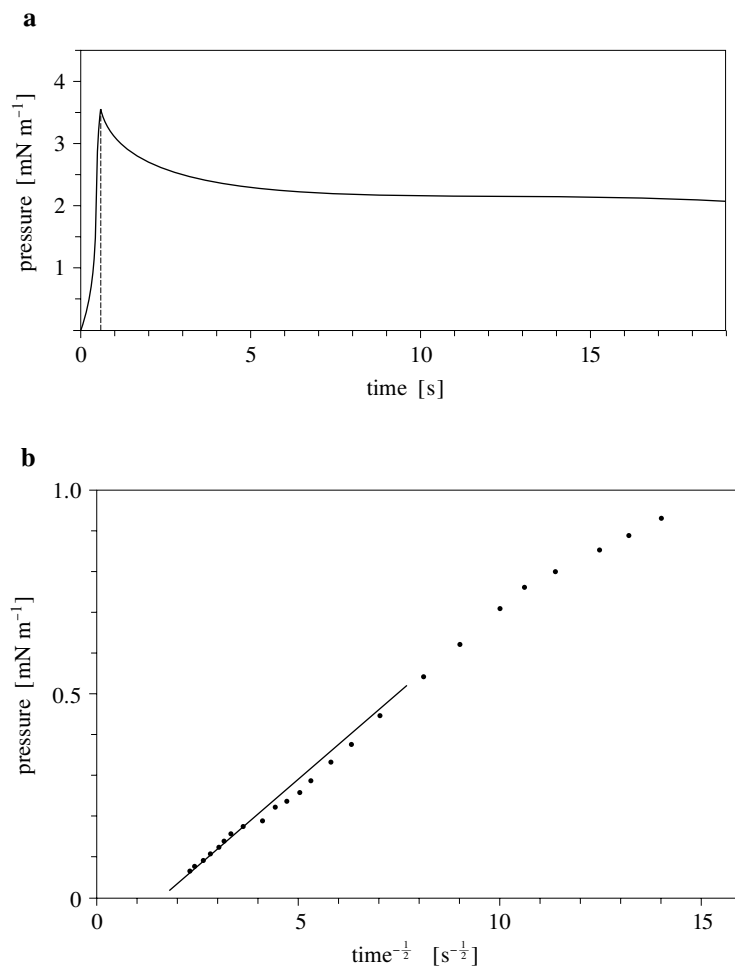
No.	Sampling station	$\Delta A/A$	$\Delta t$ [s]	$\tau_1$ [s]	$\tau_2$ [s]	$E_0$ [mN m <sup>-1</sup> ]	$E_{\text{isoth}}$ [mN m <sup>-1</sup> ]	$E_d$ [mN m <sup>-1</sup> ]	$E_i$ [mN m <sup>-1</sup> ]	$\theta$ [°]
<b>Baltic Sea</b>										
1	Brzeźno 12.07.1999	0.13	0.37	2.0	21.9	19.07	29.12	16.83	1.8	6.1
2	Jelitkowo 29.11.1997	0.12	0.70	2.43	12.16	12.08	25.81	10.32	1.34	7.4
	Jelitkowo 09.07.1999	0.10	0.63	2.8	12.20	29.65	22.94	25.89	3.36	7.4
3	Orłowo 19.08.1998	0.15	0.22	1.3	14.91	21.46	20.35	18.94	2.02	6.1
	Orłowo 15.07.1999	0.08	0.32	1.61	10.14	27.5	24.48	24.14	2.68	6.3
4	Sopot 23.09.1998	0.08	0.37	2.56	10.21	21.49	23.12	19.32	1.84	5.7
	Sopot 06.07.1999	0.21	0.40	2.86	16.60	22.01	29.22	19.72	1.88	5.4
<b>Mediterranean Sea</b>										
5	Livorno 20.11.1997	0.23	1.1	1.97	25.6	3.57	5.72	2.86	0.49	9.8
<b>Inland Waters</b>										
6	Motława river 20.08.1998	0.15	0.32	2.03	13.26	19.55	23.24	17.44	1.73	5.7



**Table 2.** (continued)

No.	Sampling station	$\Delta A/A$	$\Delta t$ [s]	$\tau_1$ [s]	$\tau_2$ [s]	$E_0$ [mN m <sup>-1</sup> ]	$E_{\text{isoth}}$ [mN m <sup>-1</sup> ]	$E_d$ [mN m <sup>-1</sup> ]	$E_i$ [mN m <sup>-1</sup> ]	$\theta$ [°]
7	Motława 13.06.2000	0.13	0.33	1.65	11.8	20.65	24.16	18.48	2.75	5.7
8	Martwa Wisła river 16.07.1999	0.11	0.19	1.14	5.60	28.66	26.15	25.44	2.62	5.9
9	Oliwa (stream) 25.07.1999	0.16	0.33	1.91	12.75	21.87	25.85	19.86	1.95	5.8
10	Jasień (lake) 13.07.1999	0.07	0.35	1.36	8.65	28.66	29.65	24.70	3.08	7.1

Symbols:  $\Delta A/A$  – relative surface area change,  $\Delta t$  – applied step deformation time,  $\tau_1, \tau_2$  – relaxation times,  $E_0, E_{\text{isoth}}, E_d, E_i$  – elasticity modulus,  $\theta$  – loss angle of the modulus.



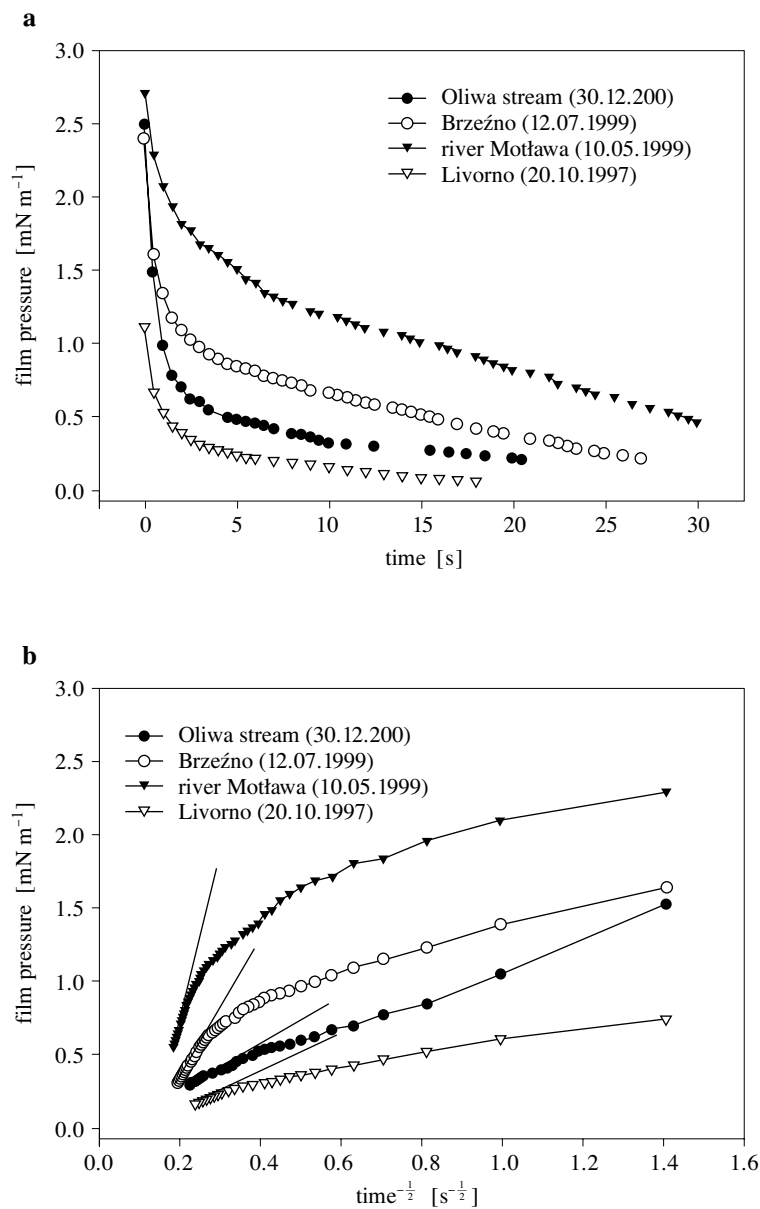
**Fig. 3.** Results of stress-relaxation experiments:  $\pi(t)$  dependence of surface pressure vs time after a rapid ( $\Delta t = 0.75$  s; see dotted line) relative film area ( $\Delta A/A_0 = 0.12$ ) compression for a marine film sample collected at Jelitkowo (Baltic Sea coastal region, Poland) on 29 November 1997 (a); surface pressure  $\pi(t)$  plotted vs  $t^{-\frac{1}{2}}$  (b). Sample state:  $t_W = 19.2^\circ\text{C}$ ,  $A_0 = 780 \text{ cm}^2$ ;  $\text{pH} = 7.6$

the Motława river film collected on 10 May 2000. A similar trend has been already found in the investigation of the dynamic behaviour of stearic acid monolayers at the air-water interface (Cirak et al. 1999). At the beginning of the compression, in a 2D gaseous film phase with a low orientational order, the relaxation process is relatively slow ( $\tau \sim 3$  s). On the other hand, in a 2D solid phase where the molecules are aligned perpendicularly to the interface, the monolayer responds to the external compression stimulation much faster ( $\tau \sim 1$  s).

It would be of interest to consider the rate of relaxation processes of surfactant films at the oil-water and air-water interface, mainly because of the different solubility of the hydrocarbon chains of the surfactant in the oil phase. Protein films have also been subjected to a rapid-step change in area ( $\Delta A/A \simeq 0.1$ ) at both types of interface (Murray 1997). The results of our studies show two dominant relaxation times of the O–W monolayer ( $\tau_1 \sim 2$  and  $\tau_2 \sim 64$  s) and A–W monolayer ( $\tau_1 \sim 2$  and  $\tau_2 \sim 24$  s). The longer of the two relaxation times,  $\tau_2$ , is seen to be approximately  $3\times$  larger for the O–W monolayer compared with the A–W interface. Dynamic surface pressure – time dependences plotted versus  $\sqrt{t}$  and  $1/\sqrt{t}$  at short and long time intervals respectively allow one to calculate the time scale and the nature of relaxation processes on the basis of the rheokinetic mixed diffusion-kinetic adsorption model (Eastoe & Dalton 2000).

In Fig. 3b, the film pressure decay versus  $t^{-\frac{1}{2}}$  exhibits a linear section starting from about  $t = 7.7$  s, which suggests that diffusion-controlled relaxation phenomena are occurring (van Hunsel & Joos 1989). Exemplary  $\pi(t)$  decay curves obtained for film samples collected in the Baltic, Mediterranean Sea and inland waters stations demonstrate a similar behaviour, as depicted in Fig. 4a. All the  $\pi(t)$  dependences plotted as a function of  $t^{-\frac{1}{2}}$  in Fig. 4b exhibit a linear section at ‘long times’, as expected for diffusion-controlled processes. The values of the diffusion coefficient  $D$  can be calculated via the slope of the linear part of the  $\gamma(t^{-1/2})$  plot according to eq. (13) at  $t \rightarrow \infty$ . Such a determination needs values of  $\Gamma$ , which are usually taken from the fitted Langmuir and Frumkin isotherms. At low concentrations, a linear dependence of  $\gamma$  on  $\sqrt{t}$  is expected (see eq. (12), for  $t \rightarrow 0$ .) In this time window, the  $D$  value can be calculated without any knowledge of the absorption isotherm using only the bulk concentration  $c$ . It has been shown (Kragel et al. 1995) for fulvic acid films extracted from seawater sampled in Livorno (Tyrrhenian Sea, Italy) that the majority of biomolecules ( $M_W \approx 50$  kDa) are probably aggregated, and  $D_{\text{long time}} \ll D_{\text{short time}}$ ; at long adsorption times the transport of biopolymers does not control the adsorption process alone. Similar film signatures ( $M_W$  of several kDa) of film-forming material were indicated in the Baltic Sea and inland water samples. The film deformation rate adopted in these isotherm studies (one barrier step every 30 seconds) satisfies the condition of isotherm measurement under equilibrium conditions in the light of the time scale of the relaxation processes exhibited in the dynamic measurements.

An interface can manifest viscoelastic properties due to the resistance of the monolayer to deformations (elastic modulus) and the associated relaxations in the surface region (surface viscosity) (Jayalakshmi et al. 1995).



**Fig. 4.** Results of stress-relaxation experiments:  $\pi(t)$  decay dependence of surface pressure vs time after a rapid relative film area  $\Delta A/A_0$  compression for a marine film sample collected in the Baltic (Brzeźno) and Mediterranean (Livorno) coastal regions, and in inland waters (river Motława, Oliwa stream) (a); surface pressure  $\pi(t)$  (b) plotted vs  $t^{-1/2}$  for plots from (a). Environmental parameters: Brzeźno ( $t_W = 22.4^\circ\text{C}$ , pH 8.8,  $\Delta A/A_0 = 0.13$ ), Livorno ( $t_W = 21^\circ\text{C}$ , pH 9.4,  $\Delta A/A_0 = 0.07$ ), river Motława ( $t_W = 12.9^\circ\text{C}$ , pH 6.8,  $\Delta A/A_0 = 0.15$ ), Oliwa stream ( $t_W = 7^\circ\text{C}$ , pH 7,  $\Delta A/A_0 = 0.1$ )

Most real systems are viscoelastic and have both shear and dilational components. If the shear components are neglected, one may express the surface dilational viscoelastic modulus  $E$  in the case of periodic oscillations as a complex quantity  $E = E_d + i\omega\eta_d$  with real (dilational elasticity  $E_d$ ) and imaginary (surface dilational viscosity  $\eta_d$  term) parts; both are potentially functions of the radial frequency  $\omega$  of periodic deformations. As can be seen in Table 2, the static surface elasticity  $E_{\text{isoth}}$ , which is useful in describing the compressional behaviour of a surface film under very low compression rates, differs from the value of  $E_0$ . The static values are rather higher than the dynamic ones for the given film. In the reported stress-relaxation experiment we consider relatively short (0.1 to 1 s) deformation responses relevant to wave damping in the capillary-short gravity water wave frequency range. Within the framework of the diffusion model for dilational viscoelasticity one obtains (Jayalakshmi et al. 1995)  $E_d = E_0[(1 + \Omega)/(1 + 2\Omega + 2\Omega^2)]$  and  $E_i = E_0[\Omega/(1 + 2\Omega + 2\Omega^2)]$ , where  $\Omega = (\omega_0/\omega)^{1/2}$ ,  $\omega_0 = 1/2\tau_D$ ,  $\tan \theta = \Omega/(1 + \Omega)$ . Here  $\omega$ ,  $\omega_0$  are the angular frequency and characteristic angular frequency of diffusion, and  $\theta$  is the loss angle of the modulus ( $\tan \theta = \omega\eta_d/E_d$ ). However, for a rough evaluation of the viscoelasticity of the film under study, the aforementioned  $E_d$ ,  $E_i$  and  $\theta$  parameters can be obtained by putting quantities derived from the stress experiment, i.e.  $\omega_0 \equiv 1/2\tau_1$  and  $\omega \equiv 2\pi/\Delta t$ . The values of the rheokinetic parameters are presented in Table 2; they demonstrate that we are concerned with elastic films ( $E_d \cong E_0$ ;  $E_d \gg E_i$ ) at angular frequencies  $\omega > \omega_0$  with the loss angle  $\theta$  ranging from 5.4 to 9.8 degrees. For example, a model slick-forming material (OLME – oleic acid methyl ester) used in oceanographic studies exhibited a comparable viscoelasticity ( $E_0 = 10 \text{ mN m}^{-1}$ ,  $\theta = 5 \text{ deg}$ , (Gade et al. 1998)).

## 5. Conclusions

The limiting specific area  $A_{\text{lim}}$  (268–3157  $\text{\AA}^2/\text{molecule}^{-1}$ ) and mean molecular mass  $M_W$  (0.65–9.71 kDa) of marine and inland water microlayer surfactants obtained from film isotherms fitted using a 2D virial equation of state and scaled according to specific area, indicate the presence of a multicomponent system with polymer-like materials comparable to those reported for a variety of oceanic samples (Frew & Nelson 1992). The apparent isotherm hysteresis during a compression-expansion cycle corresponds to a negative entropy change  $\Delta S_c$  (–10.7–133.5  $\text{J mol}^{-1} \text{K}^{-1}$ ) related to a more organized monolayer state.

Application of the 2D polymer film scaling theory to the pressure-area isotherms yielded scaling parameter  $y$ -values (3.33–10.25) for seawater samples corresponding to the vertically segregated multicomponent film

structure. This is dependent on the concentration, surface activity and chemical structure of surface-active components, and is especially apparent in the inland-water samples (13.9–20.8).

The stress-relaxation  $\pi(t)$  measurements revealed a two-step relaxation process at the interface with characteristic times  $\tau_1$  (1.4–2.8 s) and  $\tau_2$  (5.6–25.6 s), suggesting the presence of diffusion-controlled and molecular reorientation relaxation phenomena again leading to a complex film model. The viscoelasticity of natural films derived from the diffusion model was estimated within the deformation frequency range 0.9–5.3 Hz relevant to water wave damping in the capillary-short gravity frequency region. It turned out that the real part of the viscoelasticity modulus is much higher than the imaginary one, with the loss angle ranging from 5.4 to 9.8 degrees; natural films demonstrated a purely elastic behaviour. The static and dynamic film parameters exhibited a spatial and temporal variability. A more thorough interpretation awaits comprehensive natural film data sets and information derived from supplementary techniques for detailed structure studies.

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