Structural and thermodynamic signatures of marine microlayer surfactant films

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Abstract

Natural surface film experiments in inland waters and shallow offshore regions of the Baltic and Mediterranean Seas were carried out in the time period 1990–1999 under calm sea conditions using a novel device for sampling and force-area studies. The sampler-Langmuir trough-Wilhelmy filter paper plate system ‘cuts out’ an undisturbed film-covered sea area to perform π-A studies without any initial physico-chemical sample processing. The limiting specific area \( A_{\text{lim}} \) (2.68–31.57 \text{nm}^2/molecule) and mean molecular mass \( M_w \) (0.65–9.7 kDa) of microlayer surfactants were determined from the 2D virial equation of state applied to the isotherms. Enthalpy \( \Delta H \) and entropy \( \Delta S \) of the 2D first-order phase transitions were evaluated using the Clausius-Clapeyron equation applied to the isotherms. Miscibility of film components and film structure evolution is expressed by the scaling exponent \( y \) adopting the 2D polymer film scaling theory. The stress-relaxation measurements revealed a two-step relaxation process at the interface with characteristic times \( \tau_1 = 1.1–2.8 \) and \( \tau_2 = 5.6–25.6 \) seconds suggesting the presence of diffusion-controlled and structural organisation relaxation phenomena. The obtained results suggest that natural films are a complex mixture of biomolecules covering a wide range of solubilities, surface activity and molecular masses with an apparent structural organisation exhibiting a spatial and temporal variability.

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1. Introduction

The physical and chemical properties of sea surface microlayer films have been studied extensively (Hunter and Liss, 1981). Considerable effort has been focused on measurement of surface pressure-area \( \pi-A \) isotherms and elastic properties of marine films (Jarvis et al., 1967; Barger and Means, 1985; Frew and Nelson, 1992; Bock and Frew, 1993).

A principal limitation of previous work was the inability to compare \( \pi-A \) 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 and Nelson (1992) attempted to normalise the \( \pi-A \) curves using specific area based on the several bulk chemical parameters-analytical data for dry weight, UV absorbance, and carbon, nitrogen and lipid content, specifically, for each parameter the raw area data (\text{cm}^2) for the isotherms were normalised or ‘scaled’ by dividing by total film content of
the respective parameter (i.e., for instance cm\(^2/\mu g\) carbon).

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 and Means (1985).

Natural sea surface films are derived from bulk seawater surface-active dissolved organic matter of biogenic origin. The composition of marine films is largely undefined, although significant enrichment of many specific classes of compounds in the surface microlayer have been demonstrated (Van Vleet and Williams, 1983; D’Arrigo et al., 1984). It seems reasonable to expect the chemical composition of natural films to respond dynamically to physical forcing factors (Frew and Nelson, 1992), and that this response might be reflected in surface pressure-area \(\pi\)-A isotherms and surface pressure–time \(\pi\)-t dependences.

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 pressure-area relationships of untreated water microlayer samples (Pogorzelski, 1992; Pogorzelski et al., 1994). 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 film scaling theory applied to the isotherms and expressed by the value of the scaling exponent \(y\) demonstrated by the interfacial system (Pogorzelski, 1996). The mean molecular mass \(M_w\) (= 0.65–9.7 kDa) and limiting specific area \(A_{lim}\) (= 2.7–31.6 nm\(^2/\)molecule) of surfactants composing the film were obtained from marine isotherms scaled according to Barger and Means (1985), and point to the polymer-like biomolecules with an apparent structural organisation at the air/water interface (Pogorzelski, 2001). Moreover, the stress-surface pressure relaxation measurement revealed a two-step relaxation process at the interface with characteristic times \(\tau_1\) (1.1–2.8) and \(\tau_2\) (5.6–25.6) seconds suggesting the presence of diffusion-controlled and structural organisation molecular mechanisms (Pogorzelski and Kogut, 2001).

Most real systems are visco-elastic and the dilational modulus is a complex quantity. In the frame-work of the diffusional visco-elasticity model, the natural film visco-elastic modulus can be expressed by means of the rheokinetic parameters of the stress-relaxation experiment (Jayalakshmi et al., 1995). The aim of the paper is to evaluate a spatial and temporal variability of the static and dynamic response parameters observed in natural multicomponent surface films to compression and expansion.

2. Theory

The simplest equation of state to describe surface films is the 2D analog of the ideal gas law:

\[ \pi A_m = kT \tag{1} \]

where \(k\) is the Boltzmann constant, \(\pi = \gamma_0 - \gamma\)-the surface pressure of the film, \(\gamma_0\), \(\gamma\)-the surface tension of solvent and surfactant solution, respectively, \(k\) the surface pressure of the film, \(A_m\) the area per molecule and \(T\) is the temperature in Kelvins.

A further refinement was used by Schofield and Rideal (Adamson, 1982):

\[ \pi (A_m - A_o) = XkT \tag{2} \]

where \(X\) factor is related to the interaction forces between molecules in the monolayer, \(A_o\)-the area occupied by the adsorbed hydrophilic head groups of surface-active molecules. \(X = 0.5\) was determined as the mean value of Langmuir trough isotherm measurements with several model natural film-forming substances (Barger and Means, 1985). Comparing Eqs. (1) and (2), one can note \(X = 1\) is attributed to the ideal-gas film behaviour not evidenced in natural films.

The primary difficulty in examining natural films is that very little is known about them except the variation in surface pressure with the area confining the film \(A\) (not area per molecule). The number of molecules \(n\), molecular mass \(M_w\) and mass of the surface-active substance are unknown.

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 (a virial
equation of state) was proposed by Barger and Means (1985):

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

(3)

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

There is a direct relationship between Eqs. (2) and (3) when the film area instead of area per molecule is used in Eq. (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.

$$C_0 = Xn k T,$$

(4)

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

A series of known compounds were studied in the film balance, and data reported in the literature were analysed, which leads to the value of the interaction constant $X=0.5$ (Barger and Means, 1985).

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

$$n = 2C_0/kT,$$

(5)

$$n_m = n/N_A,$$

(6)

where $N_A$ is the Avogadro number.

The limiting specific molecular area $A_{lim}$ (in nm$^2$) can be expressed as (Frew and Nelson, 1992):

$$A_{lim} = C_1 n^{-1} \times 10^{14},$$

(7)

Since the area covered with a film of a pure substance at a constant value of $\pi$ is directly proportional to the mass $m$ on the surface, it is possible to extend this computation to all the natural films (Barger and Means, 1985).

According to the scaling procedure applied to a variety of natural microlayer films first the area $A_{20}$ (at $\pi = 20$ mN m$^{-1}$) is calculated from Eq. (3) using the fitting constants $C_0$, $C_1$, $C_2$.

Because approximately $24 \pm 6.2$ mg of the known compounds (16 model surface-active substances evi-

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<th>No.</th>
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<th>$C_1$ (cm$^2$)</th>
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<th>$A_{lim}$ (A$^2$ molec.$^{-1}$)</th>
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denced by chemical analyses in natural films, as shown in Table 2 of Barger and Means (1985), were required to match the area ($= 119.54 \text{ cm}^2$) of a standard sample at $\pi = 20 \text{ mN m}^{-1}$ in every case regardless of film type, the assumption was made that the natural film sample also had a mass of 24 $\mu\text{g}$.

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

$$m = 24 \times (A_{20}/119.54),$$

(8)

The resulting number of micrograms is taken as equivalent to the number of moles $n_m$, and a simple division yields the mean molecular mass estimate $M_w$ (Barger and Means, 1985):

$$M_w = m/n_m,$$

(9)

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

$$E_{isoth} = -d\pi/d\ln A$$

(10)

Most real systems are visco-elastic and the dilational modulus is a complex quantity composed of real $E_d$ (dilational elasticity) and imaginary $E_i (= \omega\eta_d)$ parts (Williams and Prins, 1996):

$$E = E_d + iE_i \quad \text{also} \quad E = E_o \cos \theta + iE_o \sin \theta$$

(11)

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

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 $\Delta S_c$ of the film-adjacent water layer system (Hühnerfuss and Alpers, 1983). According to the fundamental laws of thermodynamics applied to the isothermal ($T = \text{const.}$, $dS = dQ/T$; $dQ = dW$, where $Q$ and $W$ are the heat provided and work done, respectively) compression-expansion cycle of a 2D film system, the change of entropy $\Delta S_c$ between the initial $A_i$ and final $A_f$ film areas is:

$$\Delta S_c = S_{dil} - S_{com} = \Delta W/T$$

(12)

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

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

(13)

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

The characterisation of the miscibility or phase separation of the monolayer forming components requires knowledge about the intermolecular interactions and physicochemical parameters governing the segregation or mixing. Usually, the components tend to separate when they differ greatly in their structure and molecular areas. Recently, the $\pi$-$A$ isotherms of natural marine films have been analysed to derived the scaling parameter $y$ from the relation $E_{isoth} = y\pi$ 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 (insoluble polymer spread on a surfactants solution) closely related to the value of $y$ can also be extended to natural marine multicomponent systems (Pogorzelski, 1996). It has been shown that the 2D miscibility depends on the interfacial orientation of the components at the liquid surface. Low values of

Fig. 1. Locations of the study sites of natural surface film in the Baltic Sea: 1-Brzezno, 2-Jelitkowo, 3-Sopot, 4-Orlowo, 5-Gdynia, 6-Oksywie; and inland waters: 7-Oliwa stream, 8-Dead Vistula river, 9-Motlawa river, 10-Jasien lake.
y < 3.5 stand for a homogeneous mixed film, higher values of y \approx 8 lead to less film homogeneity observed as patches or domains of film-forming compounds in such a complex film. The highest y values y>10–16 indicate that the vertically segregated film structure forms almost separate layers at the interface with the most insoluble compound on top of this layered system (see Fig. 1 in Pogorzelski, 1996).

3. Experimental

Natural surface film experiments in shallow offshore waters of the Baltic (Gulf of Gdansk) and the Mediterranean (Livorno) Seas as well as in inland waters were carried out in the period 1990–2001 under calm sea conditions as already partially reported in Pogorzelski et al. (1994).

Locations of sampling sites in the Baltic Sea and natural inland stations (rivers, streams and lake) are shown in Fig. 1. The novel film sampler is a submersible rectangular double-walled vessel which ‘cuts out’ an undisturbed sea area. The most valuable property of this device, described in detail in Pogorzelski (1992), is that the collection and Langmuir trough isotherm analyses are performed without any transport or chemical processing of the microlayer material. In order to perform \( \pi-A \) isotherm measurements, the initial trough area (= 1200 cm\(^2\)) is compressed, with an average deformation speed \( u = \Delta A / \Delta t \) chosen arbitrarily to be 0.60 cm\(^2\) s\(^{-1}\), by moving two barriers stepwise towards each other. Surface pressures were measured with a Wilhelmy plate technique using a piece of filter paper (5 cm wide) attached to the arm of a Cahn electrobalance; they were accurate to within 0.1 mN m\(^{-1}\). Dynamic film characteristics were evaluated from stress-relaxation studies (Van Hunschel and Joos, 1989). The surface pressure-time response \( \pi(t) \) of surface film to a rapid (\( \Delta t = 0.19–1.1 \) s) relative surface area deformation \( \Delta A / A (=0.07–0.23) \) applied to the sample by barrier movement was registered for several min. The reported static and dynamic film parameters stand for an average value over 6–9 measuring runs performed at the given site. The sampler, levelling device, and Cahn electrobalance resting on the measuring table were situated near the sampling site on the shore. After equilibrating for 30 min, i.e., the standard period chosen for practical purpose, \( \pi-A \) isotherms were recorded.

4. Results and discussion

The typical \( \pi-A \) isotherm of marine films studied in shallow offshore waters of the Baltic (Gulf of Gdansk) is depicted in Fig. 2. The lower area per molecule scale was constructed according to the scaling concept. The limiting specific area \( A_{lim} \) 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: they increase monotonically but exhibit several plateaus corresponding to pure phase changes and kinks reflecting phase transitions of higher orders. The main feature of the isotherm shown in Fig. 2 is a plateau region (at \( \pi_t = 1.3 \) mN m\(^{-1}\)) representing the first-order phase transition. The latent heat \( \Delta H \) of the 2D phase transition can be calculated from a suitable form of the Clausius-Clapeyron equation applied to the isotherm (Adamson, 1982):

\[
\Delta H = \left( \frac{d\pi}{dT} \right) (A_2 - A_1)T,
\]

where \( A_1, A_2 \) are the molecular areas at the beginning and the end of transition at constant temperature \( T \), and \( \pi_t \) is the transition surface.
pressure at T. For an isothermal reversible process, the consequent change in entropy is \( \Delta S = \Delta H/T \). Values of \( \Delta H \) and \( \Delta S \) are equal to 25.15 kJ mol\(^{-1}\) and 89.83 J K\(^{-1}\) mol\(^{-1}\). This approach required the phase-diagram \((\pi_c, T)\), which was already determined for natural films collected in the Baltic Sea coastal regions from analyses of isotherms taken at different temperatures, as shown in Pogorzelski (2001).

The temperature effect on the marine film isotherms is illustrated in Fig. 3. In the \( \pi-A \) isotherm at \( T = 17.2 \) °C (Fig. 3), a pronounced inflection point in the curve followed by a plateau region was observed. Such a plateau region is typical for a first-order phase transition from a low-density fluid-like to a condensed phase. The dotted line with an apex forms the border of the two-phase coexistence region for the G (gas)-L (liquid) transition characteristic for this type of isotherm. The phase transition starts at the critical surface pressure \( \pi_c \) with the corresponding critical molecular area. The critical surface pressure is temperature-dependent \((\Delta \pi_c/\Delta T = 0.21 \text{ mN m}^{-1} \text{ K}^{-1})\), and the size of the plateau region decreases with increasing temperature. An ideal phase transition between two phases should exhibit a horizontal plateau region and two inflection points in the \( \pi-A \) isotherms. The apex corresponds to the critical temperature above which a condensed phase cannot be formed. For example, they are equal to \( \pi_c = 916 \text{ mN m}^{-1} \) and \( T_k = 313–316 \text{ K} \), for glycolipids and phospholipids with dihexadecyl chains (Schneider et al., 2001). The critical surface pressure \( \pi_c \) necessary for the phase transition increases with increasing temperature, as can be seen from the phase diagram \( \pi_c-T \) created for natural marine films from \( \pi-A \) isotherm studies performed in the temperature range \( T = 6–32 \) °C (compare Fig. 3 in Pogorzelski, 2001). As a first approach, the following linear relationship between \( \pi_c \) and \( T \) (in °C) can be derived: \( \pi_c = 1.0 + 0.21(T-6.7) \), valid in the temperature range \( 6.7 < T < 26 \) of interest in these studies. Non-ideal properties during the formation and the growth of two-dimensional condensed-phase aggregates (Melzer et al., 1998) such as kinetic effects between the molecules or aggregates lead to an increase in the surface pressure during the phase transition in the Langmuir monolayer and hence to a non-horizontal plateau and to a completely smoothed second inflection point. These effects are much weaker in the slow phase-transition process in Gibbs monolayers.

Consequently, the supersaturation of the fluid-like phase and coalescence or deformation of aggregates can cause a non-horizontal plateau feature and a smoothed second inflection point as can be noticed in the exemplary isotherms taken at higher temperatures in Fig. 3.

Moreover, the recent theoretical treatment (Ruckenstei, 2001) demonstrates that the transition from the liquid expanded to the condensed phase can be either horizontal or inclined depending upon the ranges of attractive and repulsive interactions between molecules in the film.

When the attractive interaction has a much longer range than the repulsive one, thermodynamics favours the aggregation of the molecules of the condensed phase in a single large aggregate, and a first-order horizontal transition will occur. When the repulsive interaction has a much longer range, the free energy of the system becomes smaller and the new phase is dispersed as islands in the old one, instead of forming a separate bulk phase, and a non-conventional first-order inclined transition will take place. It is likely that the phospholipid monolayers belong to the latter kind, while the fatty acid monolayers belong to the former when they are little dissociated (sufficiently low pH values), and to the latter when they are dissociated (high pH values).

Pure phase change (e.g., from a liquid-expanded phase to a liquid-condensed phase) is not commonly
observed in the marine microlayer films. It is also likely that collapse effects and non-Newtonian surface rheologies lead to more complex interactions such as gelation or aggregation. Other related mechanisms (e.g., film polymerisation and intermolecular bonding) result in similar film states (Bock and Frew, 1993).

Fit coefficients, limiting areas, mole numbers, and mean molecular weights are collected in Table 1. Values of A_{lim} range from 2.68 to 31.57 nm² molecule⁻¹, for sea surface samples, and are generally lower (3.77 to 7.79) for inland probes. They are several times higher for subsurface (bottle-collected) samples (compare 1 and 2 in Table 1). Lowest values of A_{lim} and M_w were exhibited by films studied at the Oksywie station, which is situated away from human settlements with their municipal effluents, and in samples collected just after strong wind events where intensive water mixing took place.

The mean molecular weights of marine surfactants are 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 in reference to the microlayer films under calm sea conditions. Such a difference almost disappears for samples taken at higher wind speeds (≥ 6 m s⁻¹). An increase of both M_w and A_{lim} values observed for subsurface samples in reference to the microlayer is also correlated with the corresponding increase of scaling parameter y (from 3.7 to 7.9). That is evidence of the multi-component film structure transition from a homogeneous mixture to segregated more ordered complex surfactant domains or aggregate structures. Such a vertically organised interfacial system should, during a compression-expansion cycle, evolve into a new structure with a certain loss of the system degrees of freedom leading to a larger entropy ΔS_c change (−133.5 J mol⁻¹ K⁻¹, see 2 in Table 1) than expected for a homogeneous structureless microlayer sample (−72.2 J mol⁻¹ K⁻¹, see 1 in Table 1). Mean molecular weights of inland samples are in a rather narrow range of 1.96–4.06 kDa. Similar values of M_w were measured for the Dead Vistula river and its tributary the Motlawa on the same date.

The general results reported here agree well with the conclusions of Van Vleet and 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 described in D’Arrigo (1984) and D’Arrigo et al. (1984), appears to be more consistent with observations of surface characteristics of marine films found in the Baltic. None of the model compounds widely used in oceanic studies have molecular weights of several thousands, so very large polymer-like materials with comparable film characteristics are

### Table 2

Rheokinetic parameters obtained in the desorption stress-relaxation experiment on natural organic films on water

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample date</th>
<th>ΔA/A</th>
<th>Δt (s)</th>
<th>τ₁ (s)</th>
<th>τ₂ (s)</th>
<th>E₀ (mN m⁻¹)</th>
<th>E_{swath} (mN m⁻¹)</th>
<th>E_d (mN m⁻¹)</th>
<th>E_i (mN m⁻¹)</th>
<th>✓ (deg)</th>
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<tr>
<td>Baltic Sea:</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Brzezno 12/7/99</td>
<td>0.13</td>
<td>0.37</td>
<td>2.0</td>
<td>21.9</td>
<td>19.07</td>
<td>29.12</td>
<td>16.83</td>
<td>1.8</td>
<td>6.1</td>
</tr>
<tr>
<td>2</td>
<td>Jelitkowo 29/11/97</td>
<td>0.12</td>
<td>0.70</td>
<td>2.43</td>
<td>12.6</td>
<td>12.08</td>
<td>25.81</td>
<td>10.32</td>
<td>1.34</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>Jelitkowo 9/7/99</td>
<td>0.10</td>
<td>0.63</td>
<td>2.8</td>
<td>12.20</td>
<td>29.65</td>
<td>22.94</td>
<td>25.89</td>
<td>3.36</td>
<td>7.4</td>
</tr>
<tr>
<td>3</td>
<td>Orlowo 19/8/98</td>
<td>0.15</td>
<td>0.22</td>
<td>1.3</td>
<td>14.91</td>
<td>21.46</td>
<td>20.35</td>
<td>18.94</td>
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<td>6.1</td>
</tr>
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<td></td>
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<td>0.32</td>
<td>1.61</td>
<td>10.14</td>
<td>27.5</td>
<td>24.48</td>
<td>24.14</td>
<td>2.68</td>
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<td>Sopot 23/9/98</td>
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<td>0.40</td>
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<tr>
<td>5</td>
<td>Livorno 20/10/97</td>
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<td>1.10</td>
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<td>3.57</td>
<td>5.72</td>
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<td>0.49</td>
<td>9.8</td>
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<td></td>
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<tr>
<td>6</td>
<td>Motlawa 20/8/98</td>
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<td>13.26</td>
<td>19.55</td>
<td>23.24</td>
<td>17.44</td>
<td>1.73</td>
<td>5.7</td>
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<tr>
<td>7</td>
<td>Dead Vistula (river) 16/7/99</td>
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<td>0.19</td>
<td>1.14</td>
<td>5.60</td>
<td>28.66</td>
<td>26.15</td>
<td>25.44</td>
<td>2.62</td>
<td>5.9</td>
</tr>
<tr>
<td>8</td>
<td>Jasien (lake) 13/7/99</td>
<td>0.07</td>
<td>0.35</td>
<td>1.36</td>
<td>8.65</td>
<td>28.66</td>
<td>29.65</td>
<td>24.70</td>
<td>3.08</td>
<td>7.1</td>
</tr>
<tr>
<td>9</td>
<td>Oliwa (stream) 25/7/99</td>
<td>0.16</td>
<td>0.33</td>
<td>1.91</td>
<td>12.75</td>
<td>21.87</td>
<td>25.85</td>
<td>19.86</td>
<td>1.95</td>
<td>5.8</td>
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</table>
suggested to be present. It must be pointed out 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 subsequent years from 1990 to 1999, points to a trend of continuous increase 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 heavier and larger surfactants differentiated in their physicochemical properties and 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 weight comparable to those reported for a variety of oceanic samples ($M_w = 1.5–5$ kDa, $A_{\text{lim}} = 4.0–8.0$ nm$^2$/molecule, and $n_m = 14–119 \times 10^{10}$ moles) (Barger and Means, 1985).

As shown in Fig. 2, the expansion curve does not retrace the one representing compression. This pattern is characteristic of irreversible processes and indicates that the work of compression $W_{\text{com}}$ is higher than recovered at expansion $W_{\text{dil}}$, which is accompanied by a negative entropy change $\Delta S_c$, and isotherm reversibility $R$ as summarised in Table 1. The work difference ranges from $-3.0$ to $39.6$ kJ mol$^{-1}$. The entropy change varies in the range $-10.7$ and $-133.5$ J mol$^{-1}$ K$^{-1}$ or (in natural units of $R$, where $R$ is the gas constant) appears to be $-1.29$ to $-16.0$ R. The most significant entropy effect (leading to a more organised monolayer state) can be observed for data most significant entropy effect (leading to a more organised films ($y = 13.5–20.8$)). 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 $1 < \pi < 2$ mN/m, 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 of Bock and Frew (1993), for different times elapsed from the moment of collection, allow 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 $t = 20$ min to 5 h 20 min after collection corresponds to the $y$ parameter increase from 4.3 to 6.5, which leads to formation of more organised film structures with time.

The establishment of thermodynamic equilibrium in the monolayer is not trivial, in particular during compression in a near-horizontal section of the $\pi$-$A$ isotherm (see Fig. 2) that is typical for a first-order phase transition where no or very small surface pressure gradients occur in the monolayer. The relaxation process in monolayers should affect the shape of isotherms and consequently the recovered film parameters. The effect depends on the dimensionless parameter Deborah De number defined as the ratio of the film relaxation time $\tau$ to the ‘time of observation’ (a reciprocal of the strain rate of a film: $t_{\text{obs}} = [(dA/A)/dt]^{-1}$, as argued in Kato et al. (1992). If the De number is much less than unity, the interfacial system is in its quasi-equilibrium thermodynamic state. The time scale of the relaxation processes taking place in natural films can be evaluated from stress-relaxation studies (Vanhunsel and Joos, 1989). The surface pressure-time response of marine surface film to a rapid ($\Delta t = 0.75$ s) relative surface area deformation $\Delta A/A_o$ ($= 0.12$), for a sample collected at Jelitkowo on 29 November 1997 (Baltic Sea coastal region, Poland) is presented in Fig. 4. The rate of the relaxation processes can be analysed by the first-order equation (Nino et al., 1998):

$$\ln \left[\left(\pi_\infty - \pi_t\right) / \left(\pi_\infty - \pi_o\right)\right] = \lambda_i t,$$

where $\pi_\infty$, $\pi_o$, and $\pi_t$ are the surface pressures at steady-state conditions, at time $t = 0$, and at any time $t$ or $\lambda_i$ 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. 4 yields two linear regions. The characteristic relaxation times $\tau_1$ and $\tau_2$, together with the applied step deformation time $\Delta t$, relative area change $\Delta A/A$, and an amplitude of the dilational modulus $E_{\text{iso}} (= \Delta \pi/(\Delta A/A))$, for the studied films are collected in Table 2.
The decay $\pi(t)$ curve in Fig. 4 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 evaluated up to now, relaxation times were in rather narrow ranges: $\tau_1 (1.3-2.9 \text{ s})$ and $\tau_2 (10.1-25.6 \text{ s})$. Note that for the inland waters samples they are shorter (1.1-2.0 \text{ s} and 5.6-13.3 \text{ s}, for details see Pogorzelski and Kogut, 2001). As a result, for too long deformation times $\Delta t \sim \tau_1$, the faster relaxation mechanism can escape detection by the method applied. Moreover, it has been found that the shorter time depends on the film surface pressure decreasing with an increase of $\pi$ as follows: $\tau_1 = 2.0$ ($\pi = 1.5 \text{ mN m}^{-1}$); $\tau_2 = 1.6$ ($\pi = 7.5 \text{ mN m}^{-1}$) and $= 1.1$ ($\pi = 17.6 \text{ mN m}^{-1}$) seconds, for Motlava river film collected on 10 May 2000. The shorter time is related to the mechanism of surfactant separation within the multicomponent film as suggested by Andelman (pers. comm., 2001).

The film deformation rate adopted in these isotherm studies leads to De number values as low as 0.009, and fulfills the condition of isotherm registration in its equilibrium. An interface can manifest visco-elastic 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). As shown in Table 2, static surface elasticity $E_{\text{iso}}$, useful in describing the compressional behaviour of a surface film under very low compression rates differs from the value of $E_o$. Static values are rather higher than the dynamic ones for the given film. In the stress-relaxation experiment here reported we consider relatively short (0.1 to 1 s) deformation responses relevant to wave damping in the capillary-short gravity water wave frequency range. In the framework of the diffusion model for dilational visco-elasticity (Jayalakshmi et al., 1995) one obtains:$E_d = E_o [((1 + \Omega)/(1 + 2\Omega + 2\Omega^2)]$ and $E_i = E_o [(\Omega/(1 + 2\Omega + 2\Omega^2)]$, where $Q = (\omega_0 - \omega)^{1/2}$, $\omega_0 = 1/2\tau_D$, tan$\theta = \Omega/(1 + \Omega)$. Here $\omega, \omega_0$ are the angular frequency and characteristic angular frequency for diffusion, respectively, and $\theta$ is the loss angle of the modulus (tan $\theta = \omega\tau_D/E_o$) for periodic oscillations. However, for a rough evaluation of the studied film visco-elasticity, the $E_d, E_i$ and $\theta$ parameters mentioned above can be obtained by putting quantities derived from the stress experiment, i.e., $\omega_0 = 1/2\tau_2$ and $\omega = 2\pi/\Delta t$. The values of the rheokinetic parameters are collected in Table 2, and demonstrate that we are concerned with elastic films ($E_d, E_i \gg E_o$) at deformation rates $\omega \approx \omega_0$, with the loss angle $\theta$ ranging from 5.4 to 9.8 degrees.

5. Conclusions

The limiting specific area $A_{\text{lim}} (2.68-31.57 \text{ nm}^2/\text{molecule})$ and mean molecular mass $M_w (0.65-9.71 \text{ kDa})$ 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 point to the presence of a multicomponent system with polymer-like materials comparable to those reported for a variety of oceanic samples. The apparent isotherm hysteresis during a compression-expansion cycle corresponds to a negative entropy change $\Delta S_e (10.7-133.5 \text{ J mol}^{-1} \text{ K}^{-1})$ related to a more organised monolayer structure evolution. The 2D polymer film scaling theory, applied to the pressure-area isotherms, exhibited the scaling parameter $y$-values (3.33–10.25) for marine samples corresponding to the vertically segregated multicomponent film structure dependent on the concentration, surface activity and chemical structure of surface-active components, especially apparent in the inland 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 molecule reorientation relaxation phenomena again leading to a complex film model. Visco-elasticity of natural films derived from the diffusion model approximated within the deformation frequency range 0.9–5.3 Hz relevant to water wave damping in the capillary-short gravity frequency region 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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**References**


