

**Kinetics of marine
surfactant adsorption
at an air/water interface.
Baltic Sea studies***

OCEANOLOGIA, 43 (4), 2001.
pp. 389–404.

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KEYWORDS

Marine films
Surface adsorption
Adsorption kinetics
Diffusion coefficient
Adsorption barrier

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Manuscript received 25 October 2001, reviewed 22 November 2001, accepted 30 November 2001.

Abstract

The paper contains the results of studies of natural surface film adsorption kinetics carried out in inland waters and in shallow offshore regions of the Baltic Sea during 2000–01 under calm sea conditions. The novel approach presented here for the adsorption dynamics is based on the mixed kinetic-diffusion model and analyses of the surface pressure-time plots at short ($t \rightarrow 0$) and long ($t \rightarrow \infty$) adsorption time intervals. Values of the effective relative diffusion coefficient D_{eff}/D ($= 0.008 - 0.607$) and energy barrier for adsorption E_a/RT ($= 0.49 - 7.10$) agree well with the data reported for model non-ionic surfactant solutions of pre-cmc concentrations. Wind speed is one of the factors affecting the adsorption barrier via the increased surface pressure of the natural film exposed to wind shear stress ($\sim U_{10}^2$), and enters the relation $E_a/RT = 1.70 U_{10}^{\frac{1}{3}}$.

1. Introduction

The physical and chemical properties of sea surface microlayer films have been studied extensively in the past (Hunter & Liss 1981). In

* The study was supported by grant BW/5200–5–0213–1 from the Polish Council for Scientific Research (KBN), and carried out within the framework of the scientific activity of the University of Gdańsk (supported from DS/5200–4–0024–01).

particular, considerable effort has been focused on the measurement of surface pressure-area π - A isotherms and the elastic properties of marine films (Barger & Means 1985, Frew & Nelson 1992, Bock & Frew 1993). 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 has been demonstrated (van Vleet & 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 & Nelson 1992), and that this response might be reflected in surface pressure-area (π - A) isotherms and surface pressure-time dependences.

Since 1992, 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} ($= 2.7 - 31.6$ nm²/molecule) of surfactants making up the film were obtained from marine isotherms scaled according to Barger & Means (1985), and indicate 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 τ_1 (1.1 - 2.8) and τ_2 (5.6 - 25.6) seconds, suggesting the presence of diffusion-controlled and structural organisation molecular mechanisms (Pogorzelski & Kogut 2001).

The aim of this paper is to evaluate the surface adsorption kinetics of marine water surfactants within the framework of the mixed diffusion-kinetic model (Eastoe et al. 2001). In brief, this model assumes that the rate-determining step is the transport of surfactant monomer from the subsurface to the interface, and that an adsorption barrier (of activation energy E_a related to the effective diffusion coefficient D_{eff} via an Arrhenius-type relationship) hinders adsorption. This barrier may be due to increased surface pressure or attributed to the lower availability of free surface sites. There may also be steric and orientational constraints on the molecule close to the interface that could prevent adsorption. Thus, rather than adsorbing, the molecule will back-diffuse into the bulk, thereby prolonging the time required to

attain equilibrium. E_a and D_{eff} values can be obtained from the slope of the surface pressure $\pi(t)$ -time dependences plotted against $t^{\frac{1}{2}}$ at short time intervals ($t \rightarrow 0$), and versus $t^{-\frac{1}{2}}$ at long time ($t \rightarrow \infty$) intervals respectively. The advantage of the formalism presented here is that the measurement of surfactant bulk concentration is avoided.

Wind shear stress ($\sim U_{10}^2$; U_{10} is the wind velocity at 10 m, Wei & Wu 1992) induces an increase in surface pressure at the film-covered surface, thus affecting the activation energy E_a ; this was confirmed by measurements of the dynamic surface pressure $\pi(t)$ at different wind speeds.

To our knowledge, this is the first paper in which the surface adsorption dynamics of marine surfactant solutions has been quantitatively calculated, although the surface tension-time dependences observed during film formation have already been reported (see for example van Vleet & Williams 1983, Mass & Milgram 1998).

It would be of particular oceanographic value to evaluate the environmental factors affecting the surfactant adsorption dynamics as well as their spatial and temporal variability.

2. Dynamic surface tension – theoretical background

The adsorption process of an aqueous surfactant solution at the air/solution interface consists of two steps. The first is the transport of surfactant molecules from the bulk phase to the subsurface along a concentration gradient, i.e. the diffusion step; the second one is the transport of molecules from the subphase to the surface, i.e. 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 (Liu & Messow 2000).

Diffusion-controlled adsorption kinetics was first treated quantitatively by Ward & Tordai (1946); however, an analytical solution for the surface tension decay $\gamma(t)$ is unobtainable. For short times and sufficiently low concentrations, the following approximate expression can be given for the dynamic surface tension (Eastoe & Dalton 2000)

$$\gamma(t) = \gamma_0 - 2RTc(Dt/3.14\dots)^{\frac{1}{2}} \quad \text{at } t \rightarrow 0. \quad (1)$$

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

$$\gamma(t) = \gamma_{\text{eq}} + (RT\Gamma_{\text{eq}}^2/2c)(3.14\dots/D_{\text{eff}}t)^{\frac{1}{2}} \quad \text{at } t \rightarrow \infty. \quad (2)$$

In these equations γ_0 and γ_{eq} are the surface tensions of the pure solvent (water) and the equilibrium surface tension of the solution, c is the surfactant bulk concentration, Γ_{eq} the saturation surface adsorption (at $\gamma(t) = \gamma_{\text{eq}}$), D the monomer diffusion coefficient of the surfactant in the bulk, R the gas constant, and T the absolute temperature.

If pure Fickian diffusion is the only mechanism for mass transport to the interface, one should find that $D = D_{\text{eff}}$. However, for dilute solutions ($c < \text{CMC}$ – critical micellar concentration) of non-ionic surfactants, experimental evidence for a mixed diffusion-kinetic adsorption mechanism has been established (Kragel et al. 1995).

Once the monomer has diffused to the subsurface, there may be an adsorption barrier (E_a – activation energy) present preventing the monomer from adsorbing. This will cause the molecule to back-diffuse into the bulk rather than adsorbing there, thus the time scale of the surface tension decay will be increased; consequently $D_{\text{eff}} < D$. This barrier may be due to increased surface pressure, attributed to a certain configuration that the monomer has to adopt at the interface, or result from the availability of an ‘empty site’ in the interface or the presence of micelles (above CMC) that may hinder adsorption.

The adsorption barrier can be quantified by an Arrhenius-type relationship in terms of D_{eff} (Eastoe & Dalton 2000)

$$D_{\text{eff}} = D \exp(-E_a/RT), \quad (3)$$

with E_a being the activation energy.

The effective diffusion coefficient D_{eff} can be obtained from the linear part of the $\gamma(t^{-\frac{1}{2}})$ plot at long times $t \rightarrow \infty$ according to eq. (2). The slope of these lines is given by the approximate equation

$$A \equiv [d\gamma/d(t^{-\frac{1}{2}})]_{t \rightarrow \infty} = (RT \Gamma_{\text{eq}}^2/2c)(3.14\dots/D_{\text{eff}})^{\frac{1}{2}}, \quad (4)$$

from which the diffusion coefficient can be derived.

The determination of D_{eff} needs values of Γ_{eq} , which are taken from the fitted Langmuir and Frumkin isotherms. As a first approach, the 2D ideal gas equation of state can also be used to obtain $\Gamma_{\text{eq}} = (\gamma_0 - \gamma_{\text{eq}})/RT$. To obtain information about the mechanism at the beginning of the adsorption process, the slope of the curves $\gamma(t^{\frac{1}{2}})$ at short times $t \rightarrow 0$ (see eq. (1)) can be used to determine D

$$B \equiv [d\gamma/d(t^{\frac{1}{2}})]_{t \rightarrow \infty} = -2RT c (D_{\text{eff}}/3.14\dots)^{\frac{1}{2}}. \quad (5)$$

In this time window, the diffusion coefficient D is related only to the bulk concentration c .

The dynamic surface tension $\gamma(t)$ measured along the whole time scale of the adsorption process allows the slopes A and B to be determined. Furthermore, by combining eqs. (4) and (5), the following relations for the activation energy of adsorption and relative effective diffusion can be obtained

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

and

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

where the measurement of the bulk concentration is avoided.

3. Experimental

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 the period 2000–01 under calm sea conditions. The locations of the sampling sites in the Baltic Sea and natural inland stations (rivers, a stream and a lake) were shown in Fig. 1 of Pogorzelski & Kogut (2001).

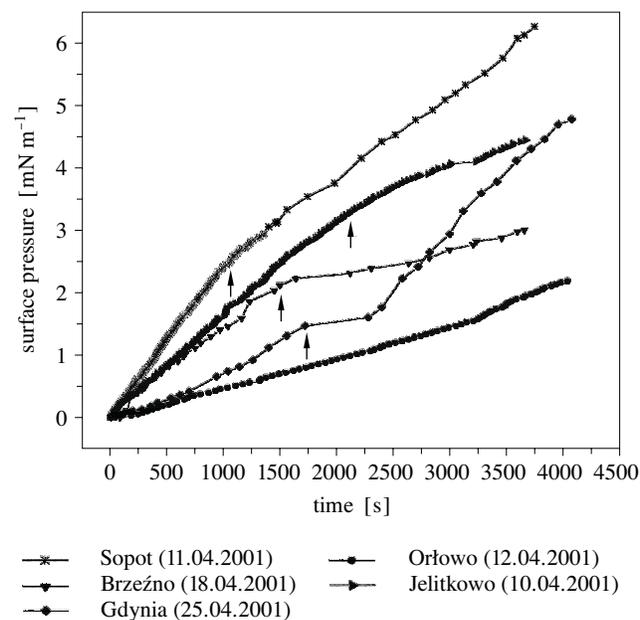


Fig. 1. Dynamic surface pressure-time dependences for seawater samples collected in coastal waters of the Baltic Sea. The arrows indicate the cusp points for the phase transition

The novel film sampler is a submersible rectangular double-walled vessel which ‘cuts out’ an undisturbed volume of sea measuring 45×35 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 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 paraffin wax-coated plastic pieces.

For measuring the surface pressure $\pi (= \gamma_0 - \gamma(t))$ -time (t) dependence, the collected film was maintained for 20 min in the trough to reach the experimental temperature ($16 - 22^\circ\text{C}$), which was measured with a thermocouple placed just below the air/water interface. Then the surface pressure was registered just after the surface had been swept with a teflon barrier to remove the molecules already adsorbed. Surface pressures were measured with the Wilhelmy plate method using a piece of filter paper (5 cm wide) attached to the arm of the force sensor (GM2 transducer + UL5 microbalance accessory, Scaime, France); they were accurate to within 0.1 mN m^{-1} .

The dynamic surface pressure $\pi(t)$ dependence is completed after 1–2 hours when ($\pi(t) = \pi_{\text{eq}} = \text{const}$), i.e. no noticeable surface pressure variations can be detected. After that time, the surface pressure π – A area isotherm measurements are performed on the same film sample so that the surface adsorption Γ_{eq} entering the adsorption dynamics dependences can be derived. The initial Langmuir trough area A_0 (1200 cm^2) is compressed with an average deformation speed $u = \Delta A / \Delta t$ to be $0.6 \text{ cm}^2 \text{ s}^{-1}$ by moving stepwise every 30 s two paraffin wax-covered glass sliders towards each other symmetrically around the film pressure sensor.

The establishment of thermodynamic equilibrium in the monolayer during isotherm studies is essential in order to obtain the proper rheological film parameters. Any relaxation processes in the films could affect the shape of the isotherms and consequently the recovered film signatures. The effect depends on the dimensionless parameter – the Deborah De number, defined as the ratio of the film relaxation time τ to the ‘time of observation’ (the reciprocal of the strain rate of a film $t_{\text{obs}} = [(\Delta A / A) / \Delta t]^{-1}$, as argued in (Kato et al. 1992)). The stress-relaxation measurements performed on natural marine films revealed a two-step relaxation process at the interface with characteristic times τ_1 (1.1 – 2.8) and τ_2 (5.6 – 25.6) seconds (Pogorzelski & Kogut 2001). In the isotherm studies reported here, $t_{\text{obs}} = 1500 \text{ s}$, which leads to $\text{De} = 0.017 (\ll 1)$, and corresponds to the isotherm registration of the interfacial system in its quasi-equilibrium state.

The sampler, levelling device and surface pressure unit resting on the measuring table are situated near the sampling site on the shore.

4. Results and discussion

Fig. 1 shows the dynamic surface pressure π – t time plots for seawater samples collected in coastal waters of the Baltic Sea. A cusp point followed by a pronounced plateau region was observed in almost all of the π – t curves,

as indicated by the arrow in Fig. 1. Surface pressure-area isotherms of several soluble and insoluble amphiphiles at the air/water interface also have similar types of cusp points followed by plateau regions; this is widely assumed for a first-order phase transition (Melzer & Volhardt 1997, Fainerman et al. 1997). It has been found that both thermodynamic properties such as critical surface pressure π_c and temperature T_k for the phase transition, and major morphological features of the condensed phase domains such as shapes and crystal structures, are similar for both Gibbs and Langmuir monolayers (Melzer et al. 1998).

The discontinuity in the reported $\pi-t$ curves indicates that a condensed phase is formed. However, above a certain temperature, a continuous rise leading to the equilibrium surface pressure after a long time is observed (see the data for Orłowo (12 April 2001) in Fig. 1). The temperature effect on the marine film isotherms is illustrated in Fig. 2. The dotted line with the

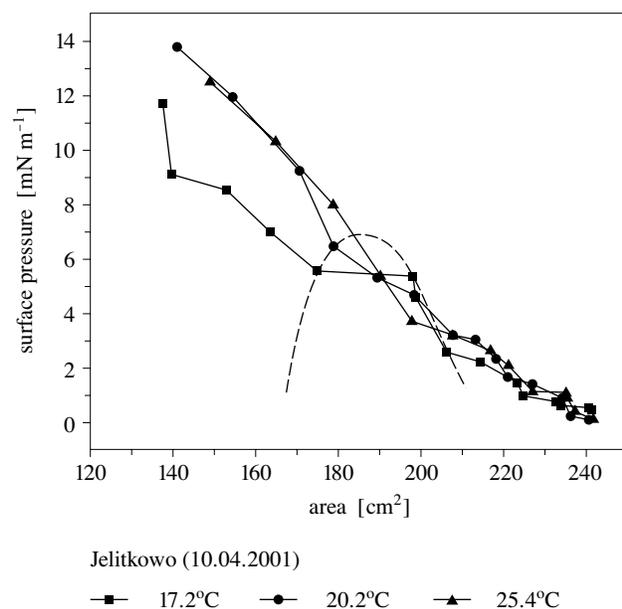


Fig. 2. Surface pressure-area $\pi-A$ isotherms of a seawater film collected at Jelitkowo on 10 April 2001 at different temperatures. The 2D phase gas-liquid coexistence dotted line was fitted by a 4th-order polynomial

peak forms the border of the two-phase coexistence region for the G (gas)-L (liquid) transition characteristic of this type of isotherm. An increase in temperature leads to a rise in the transition pressure and a decrease in the coexistence region. The peak corresponds to the critical temperature above which a condensed phase cannot be formed. For example, the transition

pressure and critical temperature are equal to $\pi_c = 9 - 16 \text{ mN m}^{-1}$ and $T_k = 313 - 316 \text{ K}$ respectively, for glycolipids and phospholipids with dihexadecyl chains (Schneider et al. 2001).

The critical surface pressure π_c necessary for the phase transition increases with rising temperature, as can be seen from the phase diagram $\pi_c - T$ drawn for natural marine films from $\pi - A$ isotherm studies performed in the temperature range $T = 6 - 32^\circ\text{C}$ (compare Fig. 3. in Pogorzelski 2001). As a first approach, the following linear relationship between π_c and T (in $^\circ\text{C}$) 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. Above the critical temperature, the monolayers could not display the cusp point in the $\pi - T$ curves. In particular, for the natural film from Orłowo (12 April 2001) studied at $T = 17.9^\circ\text{C}$, the value of π_c predicted from the relation $\pi_c - T$ is equal to 3.4 mN m^{-1} , whereas $\pi_{\text{eq}} = 2.2 \text{ mN m}^{-1}$ is significantly lower.

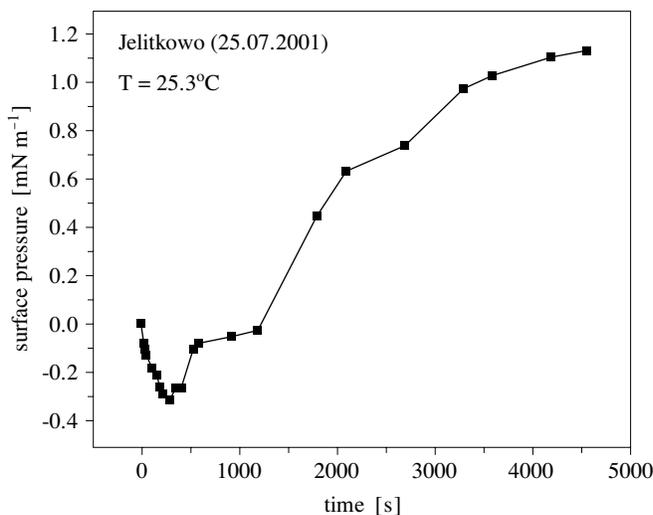


Fig. 3. Dynamic surface pressure $\pi - t$ dependence for a seawater sample collected at Jelitkowo on 25 July 2001 at $T = 25.3^\circ\text{C}$. An example of unconventional adsorption behaviour

The establishment of thermodynamic equilibrium in the monolayer is not trivial, in particular during compression in a nearly horizontal section of the $\pi - A$ isotherms. This is typical of a first-order phase transition at π_c , where very small or no surface pressure gradients occur and the Gibbs elasticity $E_{\text{isoth}} = -d\pi/d \ln A$ is close to zero. As a result, several dynamic processes in systems with adsorbed organic films, like wind-driven surface wave damping, foam stability, and gas bubble oscillations, are likely to be significantly modified around a particular value of π_c .

Fig. 3 shows the surface pressure versus time for a water sample collected at Jelitkowo on 25 July 2001. For this particular sample, the normal surface pressure adsorption behaviour ceased and changed after about 20 minutes. This unconventional behaviour was occasionally observed on very old films by Mass & Milgram (1998). The reason for it is not known, although possibilities include a chemical reaction, such as oxidation, with the possible sinking of dense reaction products, a slow change in the molecular arrangement within the film, and evaporation of some of the chemical species in the film. Recently, the adsorption kinetics of *n*-hexadecyl phosphate monolayers adsorbed at the air/water interface were studied by Brewster angle microscopy (Hossain et al. 2000). The surface pressure-time plot, reported there in Fig. 1a, shows a plateau region at about $\pi = 0$ up to $t = 400$ seconds, and after completion of the first-order transition, the surface pressure increases abruptly from zero to the final equilibrium value. The phase transition is attributed to the gradual change of morphology of the uniform monolayers to form a mosaic texture. Moreover, the actual adsorption kinetics model involving diffusion and a surface exchange barrier could lead to a different equation for π versus time, which is unknown in the chemical mixtures that make up seawater surfactants.

Dynamic surface pressure (DSP) $\pi-t$ time dependences plotted versus \sqrt{t} and $1/\sqrt{t}$ at short and long time intervals respectively allow one to derive the adsorption dynamics parameters according to eqs. (4) and (5), finally leading to eqs. (6) and (7).

Fig. 4a shows the dynamic surface pressure (DSP) $\pi-t$ time dependence, for a seawater sample collected at Jelitkowo (Gulf of Gdańsk, Baltic Sea) on 24 May 2001 at $T = 19.0^\circ\text{C}$. In Fig. 4b, DSP is plotted against $t^{\frac{1}{2}}$ in accordance with eq. (1) as $t \rightarrow 0$, and Fig. 4c presents DSP plotted versus $t^{-\frac{1}{2}}$ in accordance with eq. (2) as $t \rightarrow \infty$. The straight lines are least square fits to the data as $t \rightarrow 0$ and $t \rightarrow \infty$ respectively. They are required to determine the slopes A and B entering the adsorption kinetic equations. The equilibrium adsorption Γ_{eq} is derived from $\pi-A$ isotherms scaled, as shown in Pogorzelski & Kogut (2001), at π_{eq} leading to $A_{\text{eq}} = 1/\Gamma_{\text{eq}} N_a$ where N_a is the Avogadro number. However, for measurements carried out at high temperatures ($T > T_k$) and low equilibrium surface pressures, ideal 2D gas behaviour can be assumed with $\Gamma_{\text{eq}} = \pi_{\text{eq}}/RT$.

The wind speed effect on the adsorption kinetics is demonstrated in Fig. 5. DSP plots at different wind speeds are presented, for a seawater sample collected at Oksywie (a site distant from human settlements with their municipal effluents just after period of strong wind events at low water temperature $T = 7.2^\circ\text{C}$) on 26 April 1991.

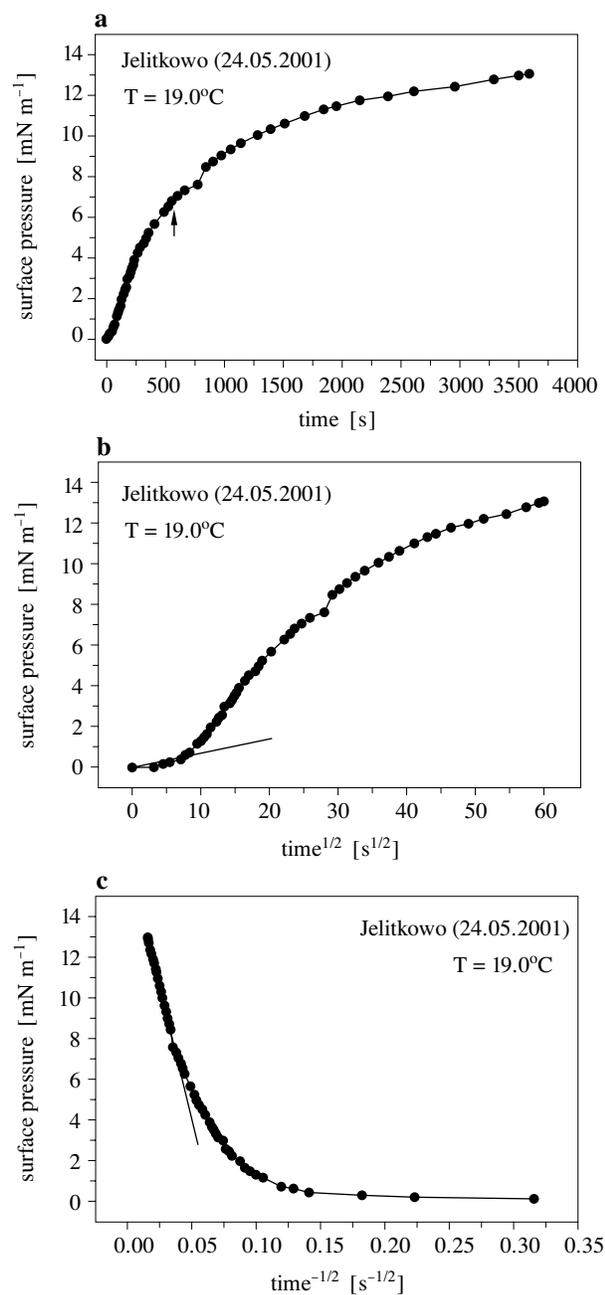


Fig. 4. Dynamic surface pressure-time $\pi-t$ dependence for a seawater sample collected at Jelitkowo on 24 May 2001 at $T = 19.0^\circ\text{C}$ (a); DSP plotted against $t^{1/2}$ in accordance with eq. (1). The line is the least squares fit to the data as $t \rightarrow 0$ (b); DSP plotted against $t^{-1/2}$ in accordance with eq. (2). The line is the least squares fit to the data as $t \rightarrow \infty$ with the intercept fixed at π_{eq} (c)

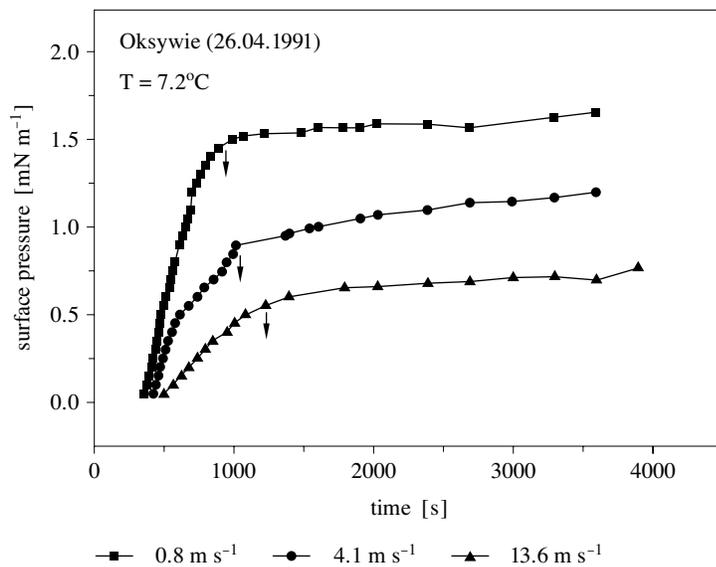


Fig. 5. Dynamic surface pressure-time $\pi-t$ dependence for a seawater sample collected at Oksywie on 26 April 1991, at different wind speeds $U_{10} = 0.8, 4.1$ and 13.6 m s^{-1}

With increasing wind speeds, the cusp point is shifted to longer times $t_{cs} = 13 \text{ min}$ (0.8 m s^{-1}); 14.8 min (4.1 m s^{-1}) and 19.6 min (13.6 m s^{-1}), and the equilibrium surface pressure is lowered systematically from 1.5 to 0.9 and 0.6 mN m^{-1} respectively.

The parameters of the adsorption kinetics derived from the dynamic surface pressure-time dependences for several seawater samples collected in the Baltic Sea coastal waters and in inland waters are summarized in Table 1. Values of D_{eff}/D (ranging from 0.008 to 0.058) and E_a (in RT units) distributed within the range $2.18 - 7.10$ agree well with the data reported for non-ionic surfactant solutions of pre-cmc concentrations at comparable temperatures (see Eastoe & Dalton 2000, Eastoe et al. 2001, where the mean $E_a = 3$ and $D_{\text{eff}}/D \approx 0.038$ at $T = 20^\circ\text{C}$ are reported).

For salt-free ionic surfactant solutions, electrostatic interactions are shown to have a drastic effect on the adsorption kinetics (Diamant & Andelman 1996). However, the effect of adding mobile ions, whose concentration usually exceeds that of the surfactant, is to screen the electrostatic interactions. As a result, when salt is added (the situation in seawater), the ionic surfactant adsorption becomes similar to the non-ionic case (Diamant & Andelman 1996). One of the factors determining the adsorption barrier E_a is the increased surface pressure of the film-covered surface resulting from the wind shear stress $\tau_s = \rho_a c_f U_{10}^2$, where

Table 1. Relative effective diffusion coefficients and energy barriers from the adsorption kinetics of natural surfactants in sea and inland waters

No.	Sampling station	T [°C]	A [mN m ⁻¹ s ^{1/2}]	B [mN m ⁻¹ s ^{-1/2}] × 10 ⁻²	π_{eq} [mN m ⁻¹]	Γ_{eq} [mol cm ⁻²] × 10 ⁻¹⁰	D_{eff}/D	E_a/RT	U_{10} [m s ⁻¹]
Baltic Sea									
1	Jelitkowo 14.11.2000	18.5	328.12	6.36	6.9	2.85	0.1911	1.65	3.0
2	Jelitkowo 04.04.2001	14.7	110.6	12.00	5.8	2.42	0.1568	1.85	2.0
3	Jelitkowo 24.05.2001	19.0	256.6	10.81	12.9	5.31	0.0278	3.58	3.7
4	Jelitkowo 25.07.2001	23.3	363.2	16.31	11.2	4.55	0.2223	1.50	9.7
5	Orłowo 12.04.2001	17.9	150.68	0.80	2.2	0.93	0.0532	2.84	5.0
6	Sopot 14.04.2001	17.4	247.48	3.50	6.6	2.54	0.0532	2.93	3.5
7	Brzeźno 18.04.2001	16.4	68.02	4.40	3.0	1.24	0.1129	2.18	4.0
8	Brzeźno 01.08.2001	22.2	298.35	2.10	7.8	3.18	0.0105	4.55	3.2
9	Gdynia 25.04.2001	19.5	84.46	0.60	4.8	1.99	0.0008	7.10	2.2
10	Oknywie 26.04.1991	7.2	59.68	13.80	1.5	1.99	0.1468	1.91	0.8

Table 1. (continued)

No.	Sampling station	T [°C]	A [mN m ⁻¹ s ^½]	B [mN m ⁻¹ s ^{-½}] × 10 ⁻²	π_{eq} [mN M ⁻¹]	Γ_{eq} [mol cm ⁻²] × 10 ⁻¹⁰	D_{eff}/D	E_a/RT	U_{10} [m s ⁻¹]
11	Oksywie 26.04.1991	7.2	62.66	12.50	0.9	1.99	0.1327	2.02	4.1
12	Oksywie 26.04.1991	7.2	35.08	4.80	0.6	1.99	0.0061	5.09	13.6
Inland Waters									
13	Oliwa (stream) 05.04.2001	17.9	261.76	2.80	6.1	2.52	0.0389	3.25	1.0
14	Martwa Wisła river 02.08.2001	23.1	169.66	1.35	2.6	1.05	0.1175	2.14	2.4
15	Motława river 02.08.2001	22.7	144.0	2.41	5.8	2.36	0.0106	4.54	2.1
16	Jasień (lake) 05.09.2001	20.0	247.97	0.78	6.7	2.75	0.0018	6.32	0.0
Mediterranean Sea									
17	Livorno* 24.06.1993	23.0	–	–	11.0	4.47	0.0080	4.32	?
18	Livorno 27.06.1991	24.0	46.78	16.41	6.7	2.55	0.0375	3.28	7.0

* Data from Kragel et al. 1995. Symbols: T – absolute temperature; A , B – slopes of the DSP plots at $t \rightarrow \infty$ and $t \rightarrow 0$ time intervals, according to eq. (4) and (5); π_{eq} – equilibrium surface pressure; Γ_{eq} – saturation surface adsorption; D_{eff}/D – relative diffusion coefficient; E_a/RT – activation energy in RT units.

$\rho_a = 1.29 \times 10^{-3} \text{ g cm}^{-3}$ is the air density, $c_f = 2.3 \times 10^{-3}$ the friction coefficient and U_{10} the wind speed at the reference height $h = 10 \text{ m}$ (Wei & Wu 1992).

An increase in U_{10} leads to decreasing E_a and D_{eff}/D , as shown in Table 1 (see 10–12). In order to quantify the effect, the relation $E_a/RT = C U_{10}^D$ can be postulated with the best-fit parameters $C = (1.70 \pm 0.04)$ and $D = (0.33 \pm 0.06)$. The $E_a(U_{10})$ dependence is of a steady-value asymptotic character at high wind speeds. Its derivative against U_{10} , i.e. $dE_a/dU_{10} = 0.56 U_{10}^{-0.67}$, computed for the middle velocity ($\sim 3 \text{ m s}^{-1}$) from the range observed in our field measurements (largely ranging from 0 to 7 m s^{-1}), indicates an increase in $E_a (= 0.27)$ following a 1 m s^{-1} wind speed growth.

The kinetic diffusion parameters obtained for inland water samples $D_{\text{eff}}/D = 0.0018 - 0.5711$ and $E_a = 0.56 - 6.32$ do not differ systematically from those recorded, for instance, at two stations located in the Mediterranean in 1991 and 1993, despite the large salinity difference. It has been shown (Kragel et al. 1995) for films of fulvic acids extracted from seawater sampled in Livorno (Tyrrhenian Sea, Italy) that the majority of biomolecules (molecular mass – $M_W \approx 50 \text{ kDa}$) are probably aggregated. Similar film material signatures (M_W of several kDa) were also indicated in the Baltic Sea and inland water samples (Pogorzelski 2001, Pogorzelski & Kogut 2001).

The large variability in the parameters reported at the same station along a spring-summer time period (see 2–4 in Table 1) points to further factors affecting the adsorption kinetics that have to be included in subsequent considerations. However, a more thorough interpretation requires a larger set of comprehensive natural film data and information from supplementary techniques for direct film structure studies.

5. Conclusions

For the first time, the effective relative diffusion coefficient D_{eff}/D ($= 0.008 - 0.6069$) and energy barrier for adsorption $E_a (= 0.49 - 7.10$ in RT units) of natural surfactants were determined for sea (Gulf of Gdańsk, Baltic Sea, Poland and Livorno, Mediterranean Sea, Italy) and inland water samples from dynamic surface pressure measurements.

The novel approach proposed here for the description of the adsorption kinetics is based on the mixed kinetic-diffusion model and analyses of the surface pressure-time plots at short ($t \rightarrow 0$) and long ($t \rightarrow \infty$) adsorption time intervals. This procedure has the advantage that measurement of the surface concentration of natural surfactants is avoided.

Values of D_{eff}/D and E_a agree well with the data reported for model non-ionic surfactant solutions of pre-cmc concentrations at comparable temperatures.

One of the environmental factors affecting the adsorption energy barrier is the increased surface pressure of the natural film exposed to wind shear stress ($\sim U_{10}^2$). Measurements of surface kinetics at different wind speeds from 0.8 to 13.6 m s⁻¹ lead to the following relation $E_a/RT = C U_{10}^D$ with the best-fit parameters C ($= 1.70 \pm 0.04$) and D ($= 0.33 \pm 0.06$).

Significant variability in the adsorption kinetics parameters requires additional environmental and physicochemical factors to be included for a more thorough description of the system.

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