Aspects of the physical properties and the visco-elastic features of the sea water – oil system*

S. Saeid Khalifa, Stanisław Pogorzelski,
Bogumił Linde, Antoni Śliwiński
Institute of Experimental Physics,
University of Gdańsk,
Gdańsk

Abstract

The influence of the physical properties of commonly-used oils entering the marine environment from various sources on the visco-elastic features of sea-water samples was examined under laboratory conditions. The physical properties of the sea water samples collected from the Baltic sea were determined as well. The visco-elastic features of sea water samples in the presence of oil films, the surface pressure – area $(\pi - A)$ isotherm during, compression and dilation and the surface pressure – time $(\pi - t)$ dependence were examined by means of the Langmuir trough system. The elasticity modulus ε, the reversibility values R and the observed relaxation time τ were computed from the above dependences.

1. Introduction

The physical properties of five oil substances (Gasoline 94, Gasoline 86, Diesel oil, Selectol plus engine oil and extra 15 oil) were determined in the laboratory (Pogorzelski, 1991). The oil-sea water interfacial tension $\gamma_{o/w}$ with insoluble oil substances floating on sea water was measured as well. Insoluble oil substances spread over bulk sea water as a monolayer, the excess oil (particularly heavy oils) remaining as lenses. The equilibrium thickness δ^2 of these floating lenses (Adam, 1941; Adamson, 1960; Pogorzelski et al., 1986) may be expressed as

$$\delta^2 = -\frac{2S_{o/w}\rho_w}{g\rho_o\rho},$$
(1)

where

$S_{o/w}$ – spreading coefficient,

g – acceleration due to gravity,

ρ_w – density of solvent (sea water),

ρ_o – density of solute (oil substance).

The spreading coefficient $S_{o/w}$ of oil films is given by (Adamson, 1960; Hoult, 1969; Pogorzelski *et al.*, 1986)

$$S_{o/w} = \varepsilon_w - \varepsilon_o - \varepsilon_{o/w},$$
(2)

where

$\varepsilon_w, \varepsilon_o$ – are the free surface energies of water and oil respectively,

$\varepsilon_{o/w}$ – is the interfacial free energy at the oil-water interface.

Substances forming monolayers will usually spread until the available surface is covered, the excess material remaining at the surface as lenses or solid particles. The pressure of the spread monolayer film (Harknis and Boyed, 1941) is given by

$$\pi = \gamma_w - \gamma_{o/w},$$
(3)

where

γ_w – the surface tension of water,

$\gamma_{o/w}$ – the surface tension in the presence of monolayer oil films.

In a Langmuir film balance a known amount of material can be spread on a water surface area per adsorbed molecule; following this, the surface pressure is measured. Such a curve for constant temperature is called an isotherm. The compressional and dilational conditions have a significant influence (at the pressure-area (π A) isotherm) on the conformation of the head-group (group of oil molecules) on a water surface (Griesser *et al.*, 1987). The transition occurring at a lower pressure corresponds to the change into two dimensions from the liquid to the vapour (L/V) state, and it is well-known that this transition is a first-order one. At higher pressures and densities a second transition is usually described as representing the change from a 'liquid-expanded' to a 'liquid-condensed' state (Le/Lc). This transition is regarded as a 'higher order' one (Adam, 1941; Harknis, 1952).

The susceptibility of the monolayer to surface deformation is expressed in its visco-elastic features, *i.e.* the surface elasticity modulus and surface viscosity modulus. The elasticity modulus of a spreading monolayer film is time-dependent only if relaxation within the monolayer has taken place. Elasticity only occurs as a result of adsorption (at the interface with the film), and arises from the non-uniformity of the surface system; it is given by the surface stress and strain relationships at the compression-dilation

surface area. It may be computed by graphical derivation of the adsorption isotherm curve and expressed by (Beckmann, 1958; Lucassen and Lucassen, 1969; Gilbert, 1971; Alpers and Garret, 1983)

$$E_o = -A(d\pi/dA). \tag{4}$$

In a complex system, the most important property of the surface phase is the surface free energy. During recompression, the surface phase passes through the same equilibrium states through which it went during expansion, releasing precisely the same amount of heat at each stage. The work of compression/mol of adsorbed surface (Hühnerfuss and Alpers, 1983) is given by

$$W = \pi(dA)N_A, \tag{4a}$$

where
dA – the change in area/molecule,
π – the surface pressure,
N_A – the Avogadro number.

This work done can be determined for the compression – dilation surface area relationship and described as the reversibility R:

$$R = (E_{\text{dil}}/E_{\text{com}})100\%. \tag{4b}$$

The relaxation time of the physico-chemical processes in monolayers observed during compression/dilation deformations is defined as the time after which the surface pressure has dropped to $1/e \cdot (37\%)$ of the difference between the initial and equilibrium surface pressures, (where e is the Euler constant) recorded after a sufficiently long period (Hühnerfuss and Alpers, 1983; Hühnerfuss and Walter, 1984). The time dependence of the surface pressure decrease allows the relaxation time to be determined from the expression (Hühnerfuss and Alpers, 1983; Hühnerfuss and Walter, 1984)

$$\pi(t) = \pi(t_o) \cdot e^{\alpha t}, \tag{5}$$

where
$\alpha = 1/\tau$,
τ – the relaxation time.

2. Experimental conditions

The physical properties of the five crude oils investigated and the collected sea water samples were determined in the laboratory at a room temperature of 293.0 K and an atmospheric pressure of 101.325 Pa (Pogorzelski, in press a). The oil/sea water surface and interfacial tensions were measured by the Wilhelmy detachment plate method (Brown, 1969; Barger *et al.*, 1974; Chattoraj and Birij, 1984; Brian *et al.*, 1986). The viscosity was measured using a UNIPAN 504 A ultrasonic viscometer. The weight of the

oil substances was measured in a density bottle of known volume in order to determine the densities of the selected oils (Nelkon, 1978).

The Langmuir trough system (James and Prichard, 1974) was used to measure the pressure vs. area isotherm and the surface pressure-time relationship of the films (Pogorzelski, in press a, b). The surface pressure π is measured as a function of the trough area occupied by the oil films spread over the sea water samples. In practice, any change in surface pressure following area compression was read off the deflection angle on the torsion-wire balance scale. Glass barriers were placed at both ends of the trough when the sea water samples and the resting point of the torsion wire balance scale were being calibrated. The oil derivatives were dissolved in hexane to make volatile solutions and were allowed to evaporate for at least 10 minutes. This time interval appeared to be sufficient for the oils to form a monolayer with a stable film pressure. The solution was pipetted carefully onto the sea water sample surface using an 8 mm ϕ capillary tube. The monolayer oil films were compressed by the glass barriers: they were moved towards the centre of the glass trough; the monolayer surface area was calculated for each stage and the surface pressure measured simultaneously. The trough was cleaned several times with a methanol – distilled water solvent. The pressures of the various oil film areas in both compression and dilation were measured directly by means of barriers moved towards and away from the centre of the trough. The reversibility R and the elasticity modulus E_0 were most often measured during $(\pi - A)$ isotherm variation for each oil substance (Lucassen and Hansen, 1967). A similar procedure was used to measure the decrease in surface pressure as a function of time after steep, rapid compression of the film using the barriers. The relaxation time was computed on the basis of the time dependence of the compressed monolayer surface pressure decrease on the $(\pi - t)$ variation (Lucassen and Lucassen, 1969).

3. Results and discussion

The physical properties of the crude oil substances and sea water samples were determined. The oils are commercially available and are common pollutants of coastal zones. The laboratory results are presented in Table 1 (see also Pogorzelski, 1991).

The surface tension of the sea water samples is very low at $34.54 \ \mathrm{mN \cdot m^{-1}}$. This indicates that the concentration of the surface-active molecules existing naturally in the sea is too high to reduce the surface tension. The surface pressure of Selectol plus oil films with fairly long carbon chains of negative spreading coefficient gives rise to a 0.39 cm thick layer. The positive spreading coefficients of the other oil films suggest that monolayer films

Table 1. Physical properties and spreading coefficient of the substances used in the experiment at 293 K and 101.325 Pa

Oil substances	(ρ) Density [kg·m^{-3}]	(η) Viscosity [$mP_a s$]	(γ) Surface tension [mN·m^{-1}]	$(\gamma_{o/w})$ Interfacial tension [mN·m^{-1}]	$(S_{o/w})$ Spreading coefficient [mN·m^{-1}]	(δ) Equilibrium thickness [cm]
Gasoline 94	760.02	0.67	23.65	4.25 (3.178)**	6.64	monolayer
Gasoline 86	761.31	0.59	20.59	2.66 (3.934)**	11.29	monolayer
Diesel oil	847.30	3.54	28.154	8.234	24.70	monolayer
Engine oil (used oil)	877.38	10.504	30.82	11.96 (2.921)**	-8.24	0.39
Extra 15	854.4	11.938	31.076	2.1248	27.89	monolayer
Seawater*	997.87	1.004	34.54	-	-	-
Seawater**	997.87	1.004	61.082	-	-	-

Note:

The values in brackets are computed from the seawater** samples collected from Gdynia beach where the surface tension was 61.082 [mN·m^{-1}]. The seawater* samples were collected from Navy Port in Gdynia.

of these oils can form on the sea water surface. The surface pressure – area isotherms during compression and dilation measured in the laboratory are summarized in Figure 1 (Pogorzelski, in press a).

The $(\pi - A)$ isotherm relationships presented exhibited similar hysteresis behaviour. The elasticity modulus was determined from $(\pi - A)$ curves. The surface pressure as a function of the elasticity modulus of the crude oils is presented in Figure 2.

The low surface pressures of 3–$10 \cdot 10^{-3}$ mN · m^{-1} are oceanographically relevant to the surface pressures at the sea surface.

The pressure of monolayer oil films gives rise to intens hydrophobic and hydrophilic interactions with the adjacent sea water layer. These interactions are related to losses of surface energy as heat during expansion and compression and were evaluated from reversibility values. These show that energy losses are much smaller for light oils than for heavy oils. The filmforming oil substances can be classified on the basis of reversibility in the order: Extra 15 oil (62.23%), Diesel oil (71.37%), Selectol plus oil (81.81%), Gasoline 86 (85.09%) and Gasoline 94 (95.57%). The relaxation time (τ), can be determined from the surface pressure vs. time dependence (Fig. 3 (Pogorzelski, in press b)).
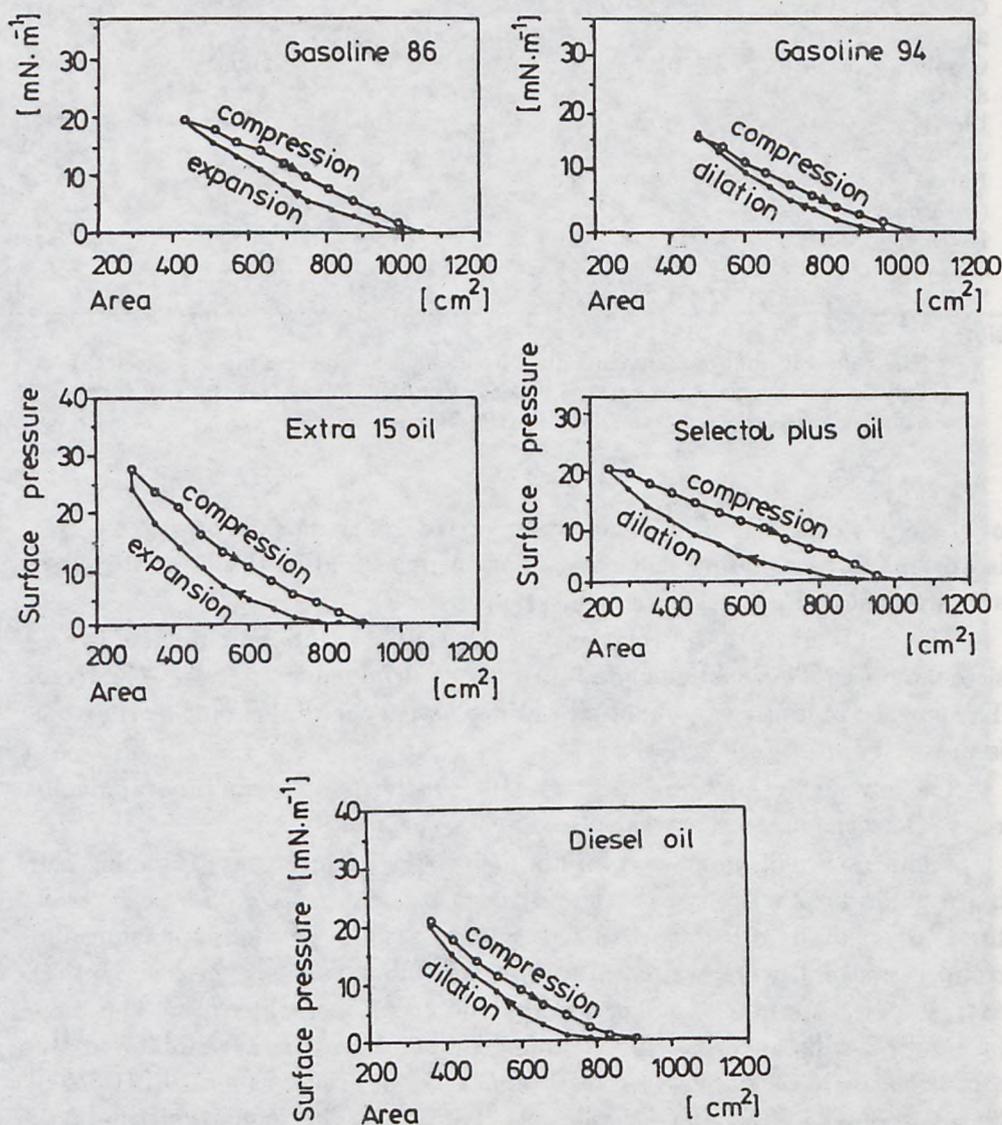
Fig. 1. Surface pressure – area isotherms for oil substances spread onto the surface of sea water samples (reproduced by permission of Deep-Sea Research)
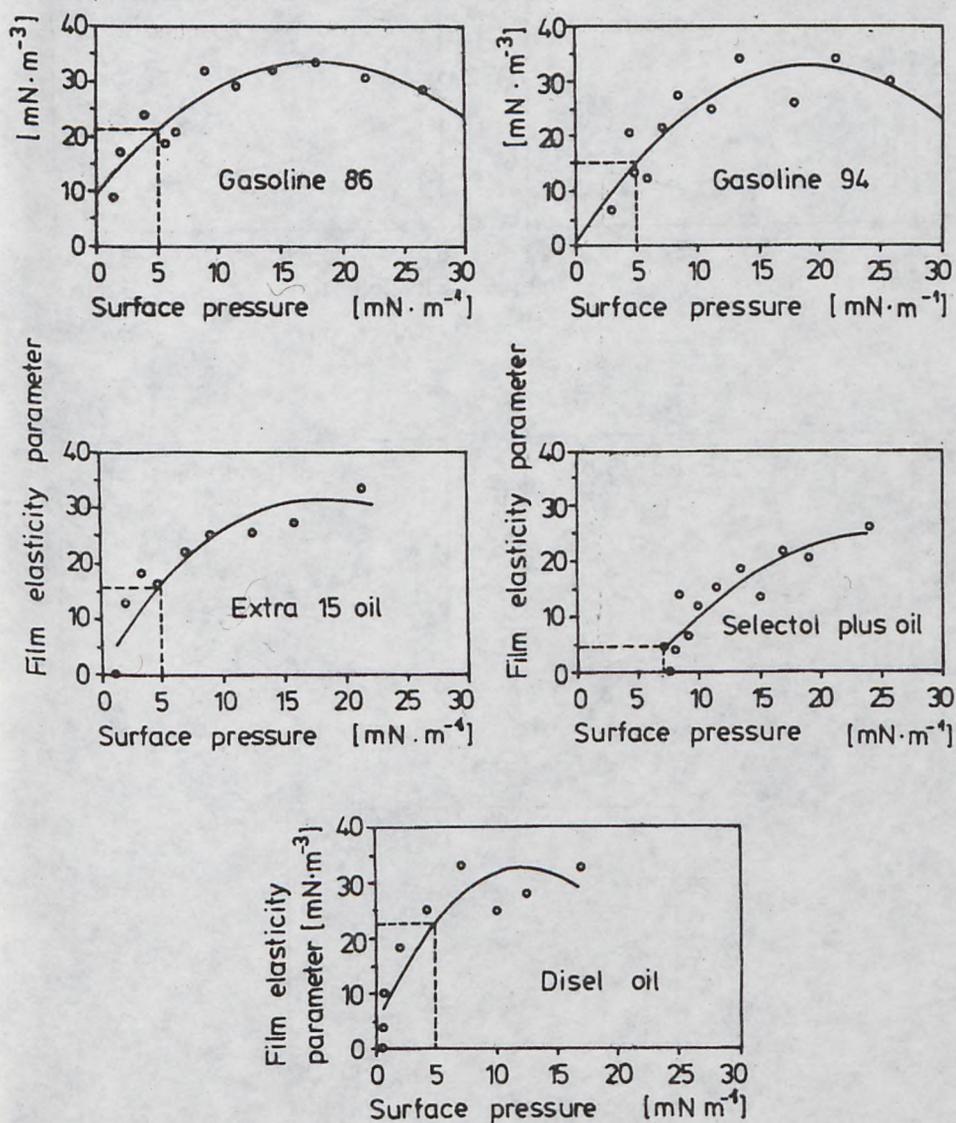
Fig. 2. Dilational elasticity modulus of the spread oil substance films versus surface pressure. The solid line corresponds to the best-fit polynomial approximation
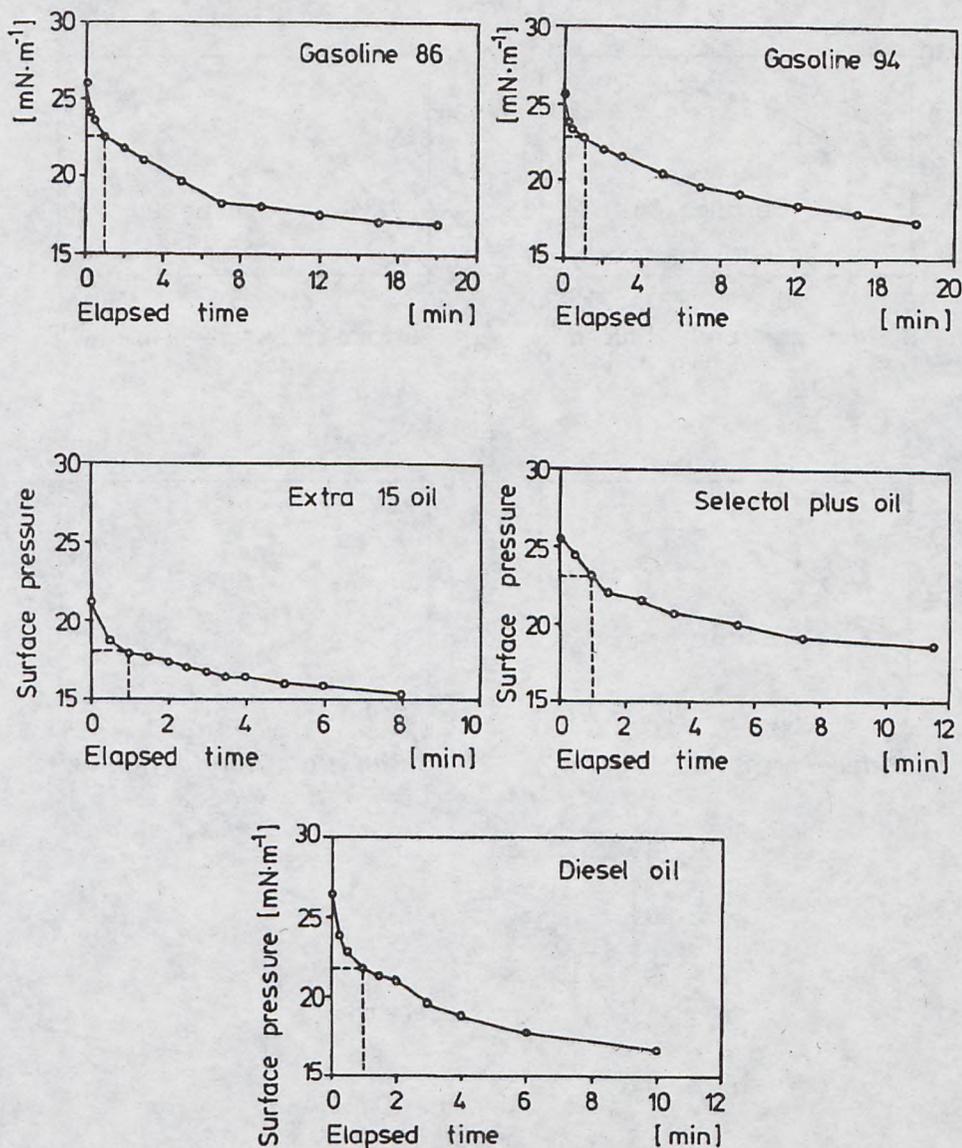
Fig. 3. Surface pressure – time dependence of the spread monomolecular oil substance films (reproduced by permission of Continental Shelf Research)

The relaxation time, which was in the 2–10 min range, may have been due to the presence of unknown chemical compounds in the oil substances.

References

Adam N. K., 1941, *Physics and chemistry of surfaces*, The Uni. Exp. Oxford.

Adamson A. W., 1960, *Physical chemistry of surfaces*, Dep. of Chemistry, University of California, L. A.

Alpers W., Garret W., 1983, *The damping of ocean surface waves by a monomolecular film measured by wavestaff and microwave scatterometers*, J. Geophys. Res., 88, 439–447.

Barger W. R., Danial W. H., Garret W., 1974, *Surface chemical properties of banded sea slicks*, Deep-Sea Res., 21, 83–89.

Beckmann J. T., 1958, *Surface chemistry*, Academic Exp., New York.

Brian M., Charles M. K., Danial B., Francis R., 1986, *Cappilary ripple investigation on monolayers at intermediate elasticities*, J. Chem. Soc., 2, 1723–1761.

Brown B., 1969, *General properties of matter*, Butter worth & Co. Ltd.

Chattoraj D. K., Birij K. S., 1984, *Adsorption and gibbs surface excess*, Plenum Press, New York.

Gilbert W. C., 1971, *Physical chemistry*, Addison–Wesley Publishing Company Inc.

Griesser D., Thistlethwaite P., Urquhart R., Patterson L. H., 1987, *Photophysical behavior in spread monolayers. Dansyl fluorescence as a probe for polarity at the air-water interface*, J. Phys. Chem., 91, 20, 5286–5291.

Harknis W. D., 1952, *The physical chemistry of surface films*, Reinhold Publishers Corp., New York.

Harknis W. D., Boyed E. T., 1941, *The physical chemistry of surface films*, Reinhold Publishers Corp., New York.

Hoult D., 1969, *Oil on the sea*, Plenum Press, New York.

Hühnerfuss H., Alpers W., 1983, *Molecular aspects of the system water/monomolecular surface film and the accurrence of a new anomalous dispersion regime at 1.43 GHz*, J. Phys. Chem., 87, 25, 5251–5258.

Hühnerfuss H., Walter W., 1984, *The termal anomaly of relaxation effects in monomolecular surface films*, J. Coll. Int. Sci., 97, 2, 476–480.

James A. M., Prichard F. E., 1974, *Practical physical chemistry*, Longman Group Ltd.

Lucassen J., Hansen R. S., 1967, *Effects of surfactant aggregation in soluble monolayers on dynamic surface properties*, J. Coll. Int. Sci., 23, 319–332.

Lucassen J., Lucassen E. H., 1969, *Properties of cappilary waves*, Adv. Coll. Int. Sci., 2, 347–395.

Nelkon N., 1978, *Mechanics and properties of water*, Heinemann Educational Book Ltd.

Pogorzelski S., Linde B., Śliwiński A., 1986, *Interrelationship between the process of surface wave generation caused by air stream and wave attenuation process on water covered with a monolayer of crude oil derivative*, Oceanologia, 24, 29–39.

Pogorzelski S., *Monolayer studies of crude oil derivatives at the air-seawater interface*, Deep-Sea Res., (in press a).

Pogorzelski S., *Relaxation studies in, and the Marangoni damping of monolayers of crude oil derivatives on seawater*, Cont. Shelf Res., (in press b).

Pogorzelski S., 1991, *The influence of crude oil spills on the sea surface on ultrasound scattering*, Oceanologia, 31, 107–118.