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

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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 \( \varepsilon \), the reversibility values \( R \) and the observed relaxation time \( \tau \) 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 \( B \) of these floating lenses (Adam, 1941; Adamson, 1960; Pogorzelski et al., 1986) may be expressed as

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\[ \delta^2 = -\frac{2S_{o/w} \rho_w}{g \rho_o}, \]  

where
\[ S_{o/w} \] is the spreading coefficient,
\[ g \] is the acceleration due to gravity,
\[ \rho_w \] is the density of solvent (sea water),
\[ \rho_o \] is the 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)

\[ S_{o/w} = \varepsilon_w - \varepsilon_o - \varepsilon_{o/w}, \]  

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

\[ \pi = \gamma_w - \gamma_{o/w}, \]  

where
\[ \gamma_w \] is the surface tension of water,
\[ \gamma_{o/w} \] is 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 (\( \pi \) \( A \)) 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)

$$E_0 = -A(d\pi/dA).$$  \hspace{1cm} (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

$$W = \pi(dA)N_A,$$  \hspace{1cm} (4a)

where

- $dA$ – the change in area/molecule,
- $\pi$ – 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 $R$:

$$R = (E_{dil}/E_{com})100\%.$$  \hspace{1cm} (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)

$$\pi(t) = \pi(t_0) \cdot e^{\alpha t},$$  \hspace{1cm} (5)

where

- $\alpha = 1/\tau$,
- $\tau$ – 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 rela­
tionship of the films (Pogorzelski, in press a, b). The surface pressure \( \pi \) 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 follo­
wing 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 \( \phi \) 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 mN \cdot m^{-1}. This indicates that the concentration of the surface-active molecules exi­
sting 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 posi­
tive 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

<table>
<thead>
<tr>
<th>Oil substances</th>
<th>Density ($\rho$) [kg·m$^{-3}$]</th>
<th>Viscosity ($\eta$) [mPa·s]</th>
<th>Surface tension ($\gamma$) [mN·m$^{-1}$]</th>
<th>Interfacial tension ($\gamma_{o/w}$) [mN·m$^{-1}$]</th>
<th>Spreading coefficient ($S_{o/w}$) [mN·m$^{-1}$]</th>
<th>Equilibrium thickness ($\delta$) [cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline 94</td>
<td>760.02</td>
<td>0.67</td>
<td>23.65</td>
<td>4.25</td>
<td>6.64</td>
<td>monolayer</td>
</tr>
<tr>
<td>Gasoline 86</td>
<td>761.31</td>
<td>0.59</td>
<td>20.59</td>
<td>2.66</td>
<td>11.29</td>
<td>monolayer</td>
</tr>
<tr>
<td>Diesel oil</td>
<td>847.30</td>
<td>3.54</td>
<td>28.154</td>
<td>8.234</td>
<td>24.70</td>
<td>monolayer</td>
</tr>
<tr>
<td>Engine oil</td>
<td>877.38</td>
<td>10.504</td>
<td>30.82</td>
<td>11.96</td>
<td>-8.24</td>
<td>0.39</td>
</tr>
<tr>
<td>15 (used oil)</td>
<td>854.4</td>
<td>11.938</td>
<td>31.076</td>
<td>2.1248</td>
<td>27.89</td>
<td>monolayer</td>
</tr>
<tr>
<td>Seawater*</td>
<td>997.87</td>
<td>1.004</td>
<td>34.54</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Seawater**</td>
<td>997.87</td>
<td>1.004</td>
<td>61.082</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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.

Aspects of the physical properties and the visco-elastic features...

developed films 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 intense 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 film-forming 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 ($\tau$), 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


