

Selected physical properties of Baltic crude oil

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KEYWORDS

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Abstract

Selected physical properties of Baltic crude oil describing its behaviour during spills on water surfaces have been investigated. The temperature relationships of the density and dynamic viscosity coefficient of fresh crude oil in the 0–35°C range are presented. The linear decrease in crude oil density and exponential decrease in its dynamic viscosity coefficient with increasing temperature were confirmed. Using these data, the mean activation energy of crude oil particles was determined (0.27 eV). The results of investigations into mass and viscosity variations during crude oil evaporation are given. The variations in mass, density and dynamic viscosity coefficient are described using power functions. The dependence of crude oil layer thickness on the rate of oil evaporation was examined: the results indicate that the greatest changes occur during the first 20 hrs of evaporation.

1. Introduction

When they occur in the marine environment in non-natural concentrations, hydrocarbons give rise to significant changes (MTC, 1984; GESAMP, 1993; Zieliński, 1993). The decrease of gas transfer across the seawater surface (Kaniewski, 1975, 1976), attenuation and variations in the spectral light parameters in the water column (Dera and Pawlak, 1988; Kaniewski and Otremba, 1990, 1993; Otremba, 1993), changes to the subsurface seawater layer (Karbowniczek-Gratkowska and Zieliński, 1992) are some of the physical consequences of the presence of

crude oil in seawater. Notwithstanding the toxic properties of hydrocarbons, these changes adversely affect the marine environment (Kaniewski, 1977; Clark, 1982; Lange, 1984; NRC, 1985; Boesch and Rabalais, 1987; GESAMP, 1993).

The pumping of crude oil from the sea bed, the transport of crude oil and its products as well as the operation of ships are all potential threats to the marine environment, so every means of eliminating crude oil pollution there will reduce this threat. In the case of oil spills, only fast and effective cleaning can minimise the damage. Information about the magnitude of the slick, the rate at which the slick is spreading, the physicochemical properties of the oil determining this rate (Elliott *et al.*, 1986; Tyler *et al.*, 1993) and the proper method of slick removal (Hupka and Mydlarczyk, 1976) are of fundamental importance for effective action. A further question is the need for rapid and objective identification of the type of oil involved.

Over one thousand types of crude oil are known, varying in their composition and physical properties (Kajdas, 1979; Petrov, 1984). Additionally, there is a wide range of fuels and types of grease, both synthetic and derived from crude oil. As the density of most of these substances is lower than that of water, they spread over its surface. There are three phases of spreading:

- gravitational,
- inertia-viscosity,
- spread of surface tension,

after which the oil disperses in the water (Hoult, 1972; Gurgul, 1986). In the first phase, the velocity of the oil spill edge on the water surface U is described by the formula

$$U = \sqrt{\lambda g h \frac{\rho_w - \rho}{\rho_w}}, \quad (1)$$

where h denotes the oil layer thickness, g the acceleration due to gravity and λ is a parameter characteristic of the given type of oil (Hoult, 1972). The oil spill radius in this phase is given by

$$R = \left(g V \frac{\rho_w - \rho}{\rho_w} t^2 \right)^{1/4}, \quad (2)$$

where t is time, and V is the volume of spilt oil. These equations hold true whenever the oil density and volume are constant. The composition, and hence the physical properties of crude oil change owing to evaporation, especially of light hydrocarbons. Time-dependent changes in the mass, volume, density and viscosity of crude oil are described by the following equations (Gurgul, 1995):

$$m = m_o \exp(1 - k_1 t), \quad (3)$$

$$V = V_o \exp(1 - k_2 t), \quad (4)$$

$$\rho = \rho_o \exp(1 + k_3 t), \quad (5)$$

$$\eta = \eta_o \exp(1 + k_4 t), \quad (6)$$

where k_1 , k_2 , k_3 and k_4 are coefficients characteristic of a particular type of oil. Eqs. (1) and (2) can therefore be written as

$$U = \sqrt{\lambda g h \left[1 - \frac{\rho_o}{\rho_w} \exp(1 + k_3 t) \right]}, \quad (7)$$

and

$$R = \left\{ V_o g t^2 \exp(1 - k_2 t) \left[1 - \frac{\rho_o}{\rho_w} \exp(1 + k_3 t) \right] \right\}^{1/4}. \quad (8)$$

In the second, inertia – viscosity phase of oil spill, the slick radius is given by

$$R = \left(\frac{g \chi V^2 t^{3/2}}{\sqrt{\nu}} \right)^{1/6}. \quad (9)$$

In the final phase, when the dimensions of the slick are determined by the surface tension of the spilled oil, the radius is

$$R = \sqrt{\frac{\sigma}{\rho} \sqrt{\frac{t^3}{\nu}}}. \quad (10)$$

In both cases, σ denotes surface tension and ν is the coefficient of kinematic viscosity. χ is a factor depending on the respective densities of oil and water ρ and ρ_w , as follows:

$$\chi = \frac{\rho_w - \rho}{\rho_w} = 1 - \frac{\rho_o}{\rho_w} \exp(1 + k_3 t). \quad (11)$$

In all phases, the rate of spread and the radius of the oil slick depend directly on the size of the spill and on the density, viscosity and surface tension of the spilled substance.

The above relationships do not include all the conditions to which a spill is subject to, wave motion in particular. Loss of mass and changes in density, viscosity and surface tension also depend on the conditions under which the oil has been spilt, especially the temperature of evaporation. The dependence of viscosity on temperature is described approximately by the Walther equation (Kajdas, 1979):

$$\log \log(\nu + C) = A - B \log T, \quad (12)$$

where A , B and C are constants, characteristic of the type of oil in question. In the 0–15°C temperature range, the viscosity has been described using

the following temperature function (Gařowski and Kopeć, 1986; Gařowski *et al.*, 1992):

$$\eta = (AT^2 + BT + C)^{-1}. \quad (13)$$

Viscosity, density, surface tension and mass loss during evaporation unequivocally describe physical properties of oil, necessary for forecasting the extent to which the spill will spread. The most important of these parameters are the density and viscosity, since they determine the speed at which the oil slick spreads in the two initial phases, when a properly organised mopping-up operation can be successful.

Oil drilling from the sea bed is a potential source of oil pollution in the Baltic Sea. There is therefore a need to recognise the types of crude oil involved. This paper characterises the physical parameters of Baltic crude oil. It presents the results of investigations into loss of mass during evaporation, and the variations in density and viscosity of freshly evaporating oil with time and temperature.

2. Method

The decrease in oil mass during evaporation was determined by weighing the oil samples on an analytical balance accurate to 0.5 mg. They were evaporated in cylinders of diameter determined to within 0.1 mm. Measurement of mass was started 1 minute after each sample of fresh oil had been poured into the cylinder. Evaporation was carried out at a stable temperature measured to within 0.5°C. The initial thickness of the oil layer was calculated from the initial mass of the sample, the density of the fresh oil and the cylinder diameter.

The density of the oil was determined by means of a hydrostatic torsion scale with a range of mass measurement from 0 to 4 g and accurate to 1 mg. Distilled water was the standard liquid. During the measurement crude oil was placed in a thermostatted glass container. The temperature was stabilised to within 0.5°C, while the density was determined to within 2 kg m⁻³

The dynamic viscosity coefficient was determined by means of a Höppler viscometer using a glass sphere 15.630 mm in diameter with a density of 2.223 kg m⁻³. Water was the standard liquid. The temperature was stabilised to within 0.2°C. This coefficient was determined from the following equation:

$$\eta = \frac{(\rho_k - \rho)t}{(\rho_k - \rho_o)t_o} \eta_o, \quad (14)$$

where

ρ , ρ_o , ρ_k – the respective densities of the substances investigated, water and sphere,

t and t_o – respective sphere sedimentation times in the investigated liquid and in water,

η_o – the dynamic viscosity coefficient of water.

Assuming that the density and viscosity of water are constant, the uncertainty of viscosity determination can be described with good accuracy as follows:

$$\Delta\eta = \frac{\eta_o}{\rho_k - \rho_o} \left[\frac{\rho_k - \rho}{t_o} \left(\Delta t + \frac{t}{t_o} \Delta t_o \right) + \frac{t}{t_o} \left(\Delta\rho + \left| \frac{\rho - \rho_o}{\rho_k - \rho_o} \right| \Delta\rho_k \right) \right]. \quad (15)$$

In each case, the sphere sedimentation time was measured at least ten times using a stop watch accurate to within 0.01 s and the average value used in the calculations. The accuracy of the time measurements was taken to be the difference between the maximum and minimum values divided by the number of readings. Bearing in mind the accuracy of density measurements mentioned earlier, the viscosity was determined with an uncertainty of no more than 2%.

3. Results

3.1. Mass decrease

The mass of Baltic crude oil samples was measured during evaporation, the aim of this being to determine the dependence of mass loss on evaporation time and the initial thickness of the oil layer.

Eight samples of fresh crude oil of various initial masses, from 2 to 12.6 g were evaporated under the same conditions in glass containers with a cross-section of 8.5 cm². These masses corresponded to initial layer thicknesses from 2.94 to 18.4 mm. During the whole process, the temperature varied from 22.4 to 23.2°C, though during the first 200 hours it was 22.6 ± 0.2°C. The graph in Fig. 1 shows the relative mass decrease as a function of evaporation time in three samples with initial thicknesses of 2.94, 9.28 and 18.4 mm. The mass of Baltic crude oil samples was measured during evaporation, the aim of this being to determine the dependence of mass decrease on evaporation time and the initial thickness of the oil layer.

This figure shows that the greatest changes occur in the initial phase of evaporation. However, the dependence described by eq. (3) does not describe the observed changes in crude oil mass during evaporation sufficiently well. The square of the correlation coefficient for this function is < 0.8 right across

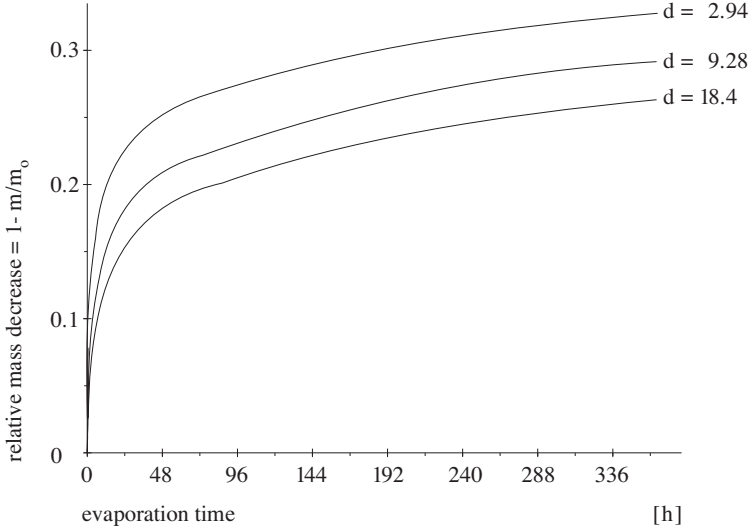


Fig. 1. Relative mass decrease of Baltic crude oil as a function of evaporation time (samples with initial layer thicknesses of 2.94, 9.28 and 18.4 mm)

the variability interval. Much better results can be obtained by using the power function

$$m = m_o[\theta(t + t_o)]^n, \quad (16)$$

where m_o is initial mass, θ , and n are parameters dependent on the layer thickness and t_o is a constant. This function describes mass changes well, both across the entire time range (over 360 hours) and within all smaller time ranges. The square of the correlation coefficient was > 0.98 . Graphs of this function for three selected samples are shown in Fig. 2a. Every plot represents the square of the correlation coefficient (R^2) between experimental results and the values derived using the function in question. The Pearson function was used to derive the correlation coefficients R . Independent measurements of fresh oil mass changes made at a frequency of one minute confirm this dependence (Fig. 2b). The constant $t_o = 200$ s in eq. (16) is only important as far as the description of the initial phase of evaporation (first hour) is concerned. It can be neglected in long-term experiments, so eq. (16) becomes

$$m = m_o(\theta t)^n. \quad (17)$$

The influence of layer thickness on the decrease in relative mass is especially obvious in the initial phase of evaporation. In order to determine this, the

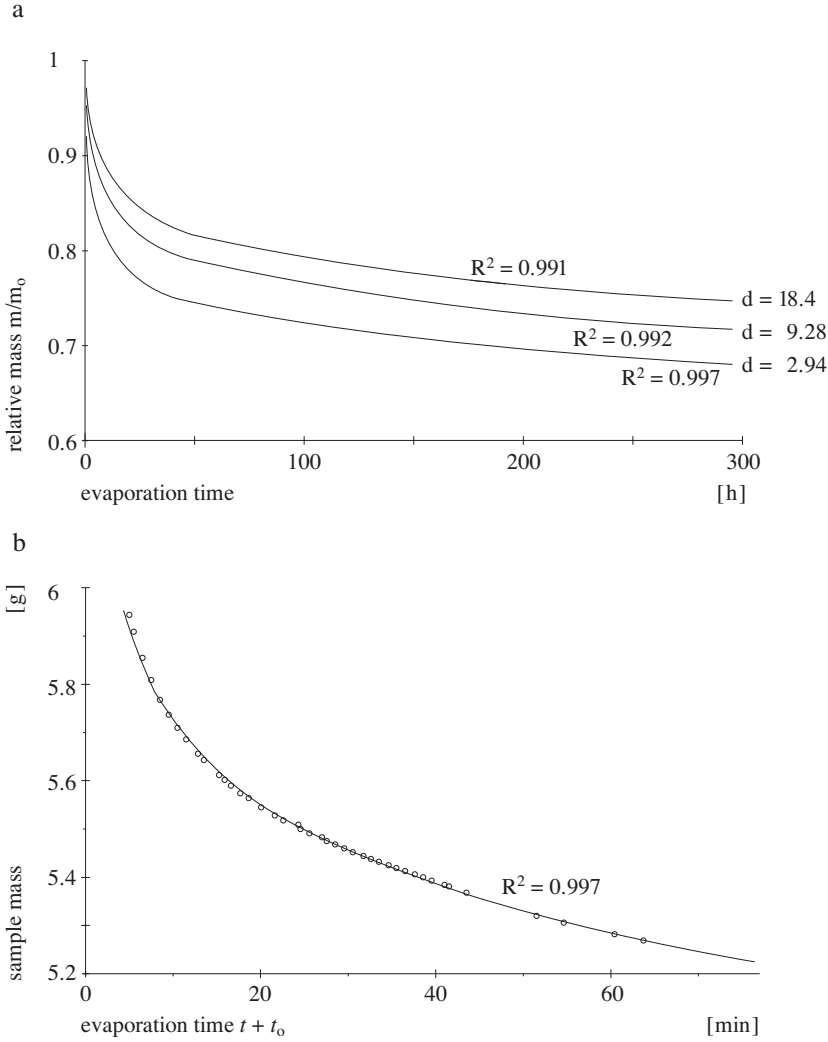


Fig. 2. Mass of Baltic crude oil as a function of evaporation time (eq. (16) with constant t_o)

rate of relative mass decrease v for particular samples was determined. This is defined as the ratio of the time-dependent derivative and mass

$$v = \frac{1}{m} \frac{dm}{dt}. \quad (18)$$

Because of the limited number of results, the average rate was determined over a time interval from the following formula:

$$v = \frac{2(m_1 - m_2)}{(m_1 + m_2)(t_2 - t_1)}, \quad (19)$$

where m_1 and m_2 are sample masses at times t_1 and t_2 . The dependence of mass decrease, derived in this way, on the layer thickness h is best described by

$$v = a(1 - b \ln kh), \quad (20)$$

where a , b and k are constants ($k = 1 \text{ mm}^{-1}$, depends only on the assumed measure of thickness). During the first hour, when the mass decrease in the samples varied from 4.6% to over 10%, this dependence was the most obvious (Fig. 3a). Constant $a = 3.8 \times 10^{-5} \text{ s}^{-1}$, $b = 0.24$. In the fifth hour the rate of mass decrease was much lower (Fig. 3b) and constant $a = 3.2 \times 10^{-6} \text{ s}^{-1}$ and $b = 0.12$. Later, the dependence described by eq. (18) became less obvious and after 20 hours of evaporation, the influence of layer thickness on the rate of evaporation became negligible (Fig. 3c).

The layer thickness h influences the relationship between mass decrease and time described by eq. (16). Both θ and n depend on the layer thickness (Fig. 4a). θ can be described as a function of h as follows:

$$\theta = \alpha [1 + \beta \exp(\kappa h)], \quad (21)$$

where $\alpha = 0.0042 \text{ s}^{-1}$, $\beta = 0.0036$, and $\kappa = 251 \text{ m}^{-1}$. In the range investigated, the dependence of the exponent on layer thickness is not close; however, assuming it to be linear (Fig. 4b), it can be written as

$$n = ch + d, \quad (22)$$

where constants $c = -0.23 \text{ m}^{-1}$ and $d = -0.046$. Using these relationships, the mass of crude oil during evaporation can be written as a function of time and layer thickness thus:

$$m(t, h) = m_o \{ \alpha [1 + \beta \exp(\kappa h)] (t + t_o) \}^{ch+d}. \quad (23)$$

Since the dependence of the exponent on layer thickness within the measured range is negligible and limited to the initial phase influence of t_o , this function can be written as

$$m = m_o \{ \alpha [1 + \beta \exp(\kappa h)] t \}^{0.046}. \quad (24)$$

The rate of relative mass decrease, as defined by eq. (18), can be written as the following function of time t and layer thickness h

$$v = \frac{ch + d}{t + t_o}, \quad (25)$$

where constants c and d are the same as in eq. (22). During longer periods of evaporation this function becomes independent of layer thickness

$$v = -0.046 t^{-1}, \quad (26)$$

and converges to zero.

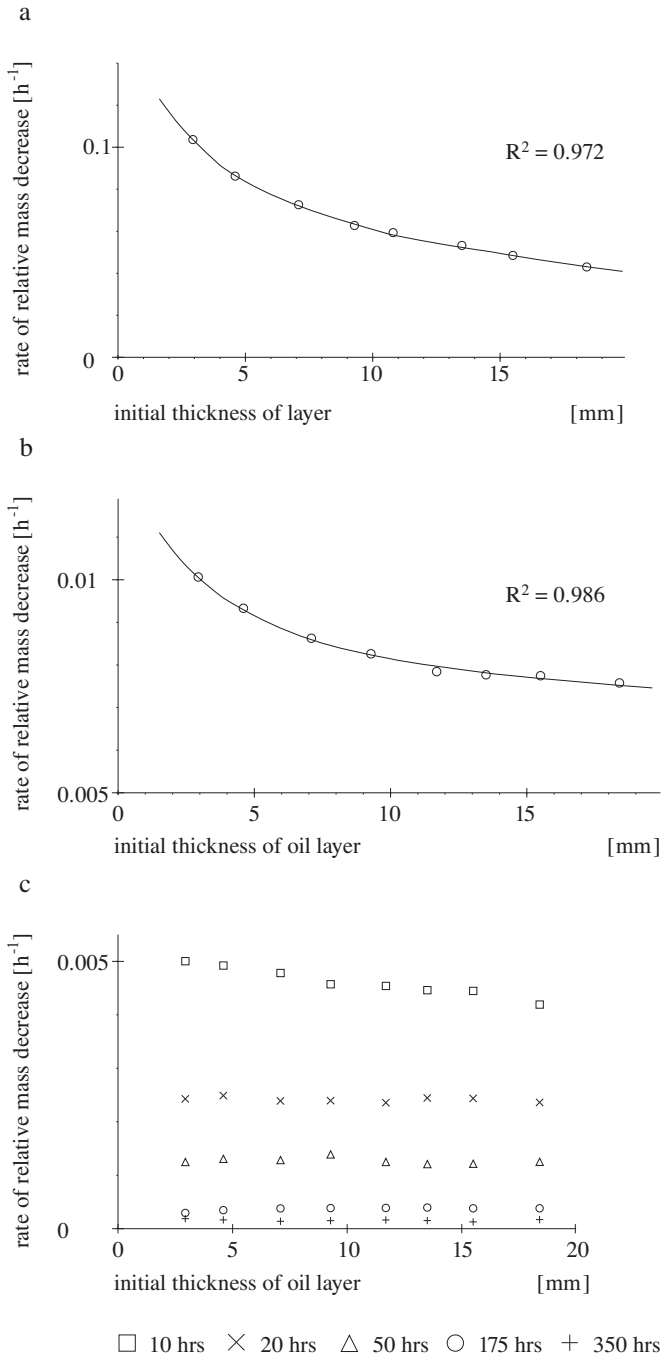


Fig. 3. Dependence of average rate of relative mass decrease of Baltic crude oil on layer thickness in the first hour (a), in the fifth hour (b), later during evaporation (c)

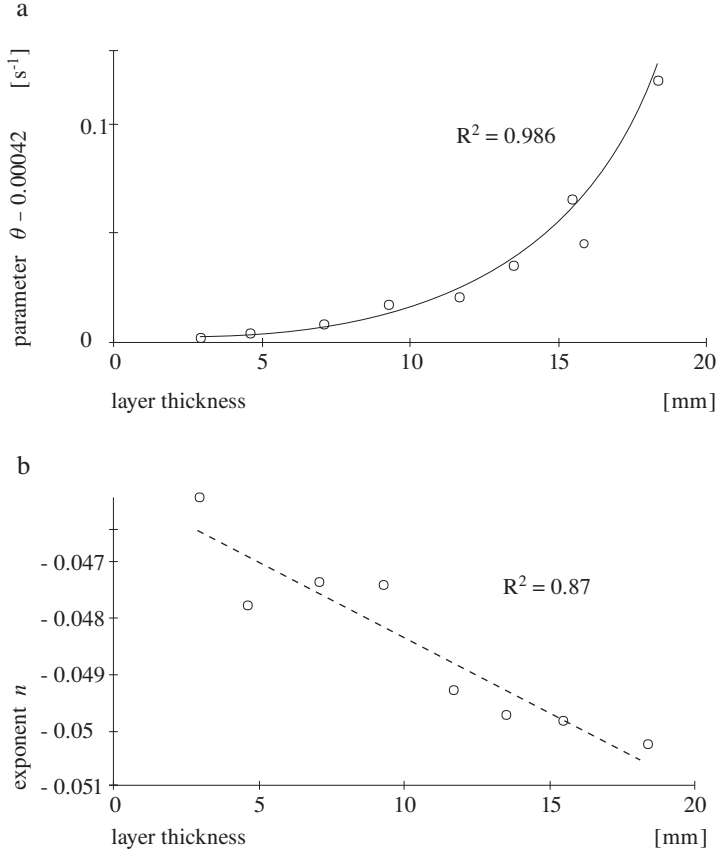


Fig. 4. Dependence of parameter θ (a) and exponent n (b) on crude oil layer thickness

3.2. Density and viscosity

The density ρ and dynamic viscosity coefficient η of fresh Baltic crude oil measured in the temperature range from 0 to 35°C are shown in the Tab. 1. All the results were obtained with the accuracy described in the previous section. Derivations and graphs were made from experimental data (no rounding off).

In the range investigated, the density of fresh crude oil decreases linearly with temperature increase. This dependence is given by

$$\rho = AT + B, \quad (27)$$

where

$$A = -0.846 \text{ kg m}^{-3}\text{K}^{-1},$$

$$B = 1.060 \text{ kg m}^{-3}.$$

The results are shown in Fig. 5.

Table 1. Results of measurements of fresh Baltic crude oil density and viscosity

T [°C]	ρ [kg m ⁻³]	$\eta \times 10^{-3}$ [Ns m ⁻²]	T [°C]	ρ [kg m ⁻³]	$\eta \times 10^{-3}$ [Ns m ⁻²]	T [°C]	ρ [kg m ⁻³]	$\eta \times 10^{-3}$ [Ns m ⁻²]
0	830	10.2	9	821	5.8	18	814	4.4
2	828	8.7	10	821	5.8	20	812	4.1
3	828	8.6	12	819	5.4	25	808	3.44
5	825	7.4	15	817	4.9	30	804	2.88
7	822	6.6	16.2	816	4.7	35	800	2.39

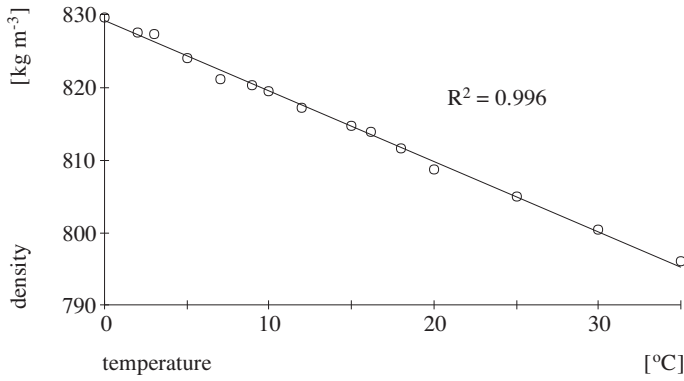


Fig. 5. Density of fresh Baltic crude oil as a function of temperature

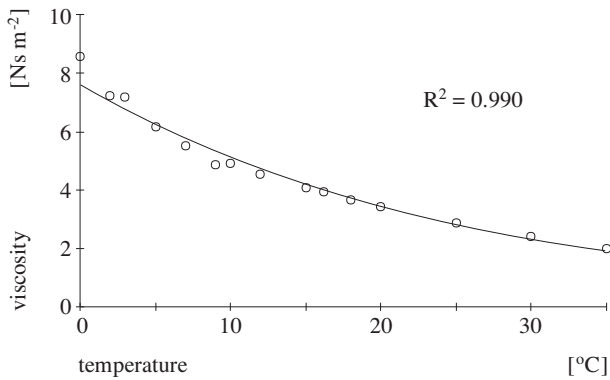


Fig. 6. Viscosity of fresh Baltic crude oil as a function of temperature

The viscosity measurements are shown in Fig. 6. In the investigated range of temperatures, the dynamic viscosity coefficient for fresh oil can be written as the function

$$\eta \propto \exp\left(-\frac{\beta}{T}\right). \quad (28)$$

By substituting E/k for β , where k is the Boltzmann constant, the activation energy E of oil particles can be described as

$$E = \frac{T_1 T_2}{T_1 - T_2} k \ln \frac{\eta_1}{\eta_2}, \quad (29)$$

where η_1 and η_2 are viscosity coefficients at temperatures T_1 and T_2 . Obtained in this way, the mean activation energy of particles of fresh Baltic crude oil is equal to 0.27 eV (4.33×10^{-20} J).

The density and viscosity measurements carried out during evaporation did not confirm the exponential character of their dependence on time as described by eqs. (5) and (6). Both density and viscosity are much more accurately described by a power function. Knowing the initial values ρ_o and η_o , the density ρ and dynamic viscosity coefficient η can be described at any time $t > 0$ using the following equations:

$$\rho = \rho_o(\tau_1 t)^n, \quad (30)$$

$$\eta = \eta_o(\tau_2 t)^m, \quad (31)$$

where $\tau_1 = 0.00104 \text{ s}^{-1}$, $\tau_2 = 0.00055 \text{ s}^{-1}$, $n = 0.259$, and $m = 0.0073$ (at 10°C).

The results are shown in Figs. 7 and 8.

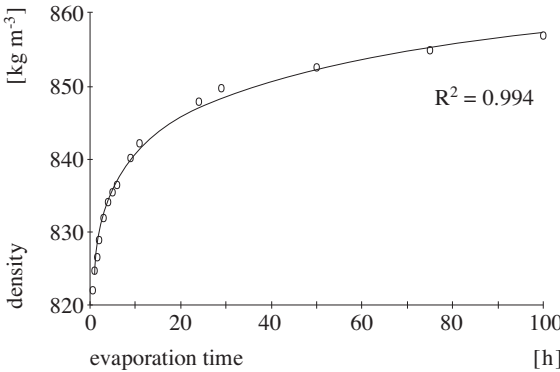


Fig. 7. Time-dependent variations in Baltic crude oil density during evaporation at 10°C

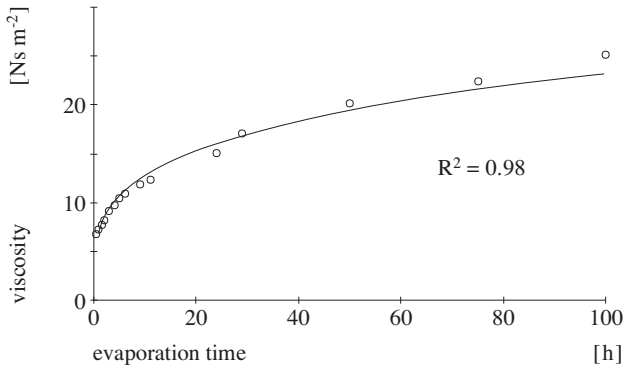


Fig. 8. Time-dependent variations in Baltic crude oil viscosity during evaporation at 10°C

4. Conclusions

Baltic crude oil (density 812 kg m^{-3} at 20°C), belongs to the group of light oils. Its relatively low viscosity enables it to spread rapidly the sea surface even at a temperature of 0°C (fluidity $8.1 \times 10^4 \text{ s m}^{-2}$).

The mass, density and viscosity changes measured during evaporation reveal that these are greatest during the initial evaporation phase up to about 20 hours. They were described using power functions (16), (27) and (28).

The influence of the slick thickness on the rate of evaporation is limited to the initial phase and disappears after 20 hours. During this time the dependence is more obvious when the layer is thinner.

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