Variability in the optical properties of a crude oil – seawater emulsion

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Abstract

The paper analyses the optical properties of a crude oil – seawater emulsion, which is a form of petroleum pollution of the sea. These properties depend on the spillage concentration, the optical characteristics of the seawater and oil in question, and on the size distribution of the oil droplets. They may be described by the attenuation specific cross-sections and absorption specific cross-sections. Specific cross-sections and other optical parameters for droplets of a Baltic crude oil – Baltic seawater emulsion were calculated using Mie's solution. These characteristics were computed for fresh and weathered petroleum.

1. Introduction

Numerous investigations have confirmed the harmful influence of petroleum on the marine environment. The GESAMP (1993) report presents a variety of papers describing the results of this work. Petroleum pollutants turn up in various forms in the marine environment: as aerosols and free molecules in the atmosphere, as oil layers and emulsions on the water surface, as emulsions, suspensions and dissolved phases in the water column and on the bottom sediments.

The complete text of the paper is available at http://www.iopan.gda.pl/oceanologia/

Among their many impacts, oil pollutants modify light fields above and below the water surface. These modifications are manifested by the attenuation of the light passing through an oiled water surface (Otremba 2000), by changes in light absorption in the seawater column due to the formation of an emulsion, and by the scattering of light by particles of such an emulsion. The optical properties of an emulsion can be described by the attenuation specific cross-section and the absorption specific cross-section, which depend on the optical characteristics of the oil and the seawater, on the size distribution of oil droplets and on their concentration.

In the case of pollution with fresh crude, the oil undergoes weathering, which alters its properties. The present paper analyses the changes in the optical properties of a crude oil – seawater emulsion due to oil weathering. The study was carried out with Baltic crude oil and Baltic seawater.

2. Method

Testing the Baltic crude oil[1] was the first step of the study. About 200 cm^3 of fresh petroleum was poured into an open glass container standing in a well-ventilated, dark place, where it was stored for over a year at room temperature (c. 293 K$=$20°C). A small quantity of oil at a time was sampled for the measurements. The refractive index of light ($\lambda = 450 - 650$ nm) was measured at a constant temperature of 293 K using an Abbe refractometer. Then the function representing the spectral relationship of the refractive index n was determined.

The light transmission T of a petroleum sample in hexane solution (relative concentration C) was measured with a *Fluorat–02 Panorama* spectrofluorimeter. The absorption coefficient a characterising the oil was determined from the following relationship:

$$a = \frac{1}{lC} \ln \frac{T_o}{T}, \tag{1}$$

where l – cuvette length and T_o – transmission of the radiation through the pure solvent. It had been demonstrated earlier that hexane solutions of Baltic crude satisfied the Lambert–Beer rule in the investigated wavelength range ($\lambda =>$ 400 to 700 nm) (Stelmaszewski 2001). Then the imaginary part k of the complex refractive index was calculated as

$$k = \frac{a\lambda}{4\pi}. \tag{2}$$

These results were the background against which the light attenuation for the emulsion and its absorption specific cross-sections were computed. The refractive index characterising Baltic seawater was taken from Popov

[1]The *Petrobaltic* company provided a sample of the petroleum in March 1999.

et al. (1979), and the distribution of droplet sizes was assumed after Staroń (1999).

Elements of the scattering matrix characterising the emulsion were calculated according to the Mie theory. Two complex amplitude functions S_1 and S_2 allow two elements (P_{11} and P_{12}) of the matrix to be determined (Król 1998):

$$P_{11} = k^2[(\mathrm{ReS}_1)^2 + (\mathrm{ImS}_1)^2 + (\mathrm{ReS}_2)^2 + (\mathrm{ImS}_2)^2], \tag{3a}$$

$$P_{12} = k^2[(\mathrm{ReS}_1)^2 + (\mathrm{ImS}_1)^2 - (\mathrm{ReS}_2)^2 - (\mathrm{ImS}_2)^2]. \tag{3b}$$

The first element P_{11}, in the form of an angular dependence, defines the angular distribution of the total intensity of the scattered light. The second one P_{12} describes the depolarisation of linearly polarised light parallel and perpendicular to the scattering plane. The elements of the scattering matrix are presented in a convenient normalised form. The scattering function was normalised to its value for the scattering angle $\theta = 0$:

$$I_p = \frac{P_{11}(\theta)}{P_{11}(0)}. \tag{4}$$

The function P_{12} was normalised to appropriate values of element P_{11}:

$$I_m = \frac{P_{12}(\theta)}{P_{11}(\theta)}. \tag{5}$$

The light absorption and attenuation cross-sections describe the interaction of light with oil droplets. Being spherical objects, emulsion droplets scatter light in accordance with Mie's solution for spherical absorbent particles (Król 1985); the light absorption and attenuation cross-sections were thus calculated from this solution.

3. Results

Fig. 1 illustrates the spectral relationships of the refractive index and the light absorption coefficient characterising fresh and weathered Baltic petroleum; the values of these parameters increase during the course of oil weathering. Fig. 2 presents the dynamics of their growth.

The changes in the optical properties of petroleum are a consequence of the modified parameters characterising the emulsion obtained. Fig. 3 shows the angular dependence of the normalised elements I_p and I_m of the scattering matrix for droplets of fresh and weathered oil. These parameters were determined for particles 1 μm in diameter, a dimension covering the most probable range of sizes. Taking the size distribution of the emulsion particles into consideration makes the angular relationships of the elements I_p and I_m clearer. Fig. 4 presents these elements. The assumption

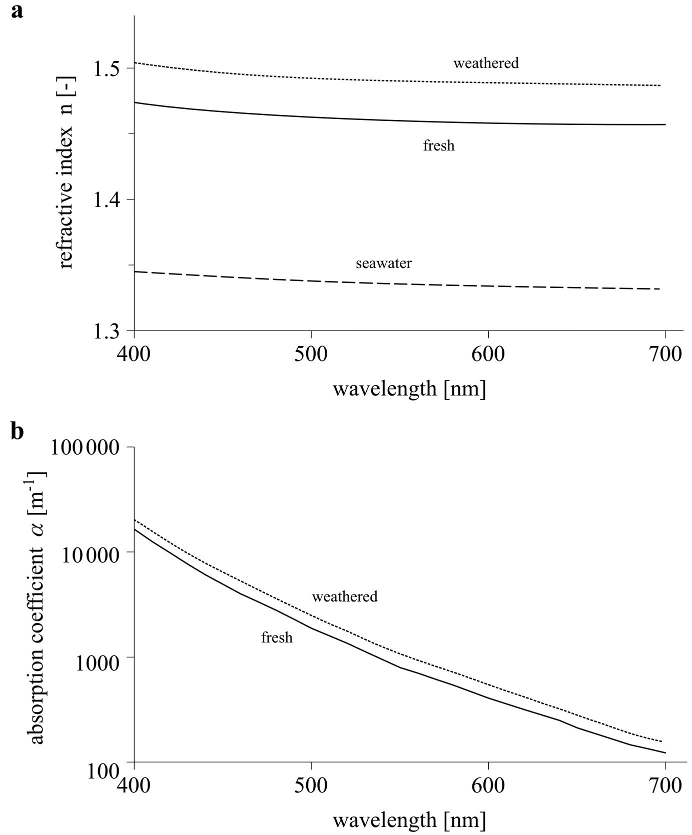

Fig. 1. Spectral relationships of the refractive index (a) and absorption coefficient (b) characterising fresh and weathered Baltic crude oil

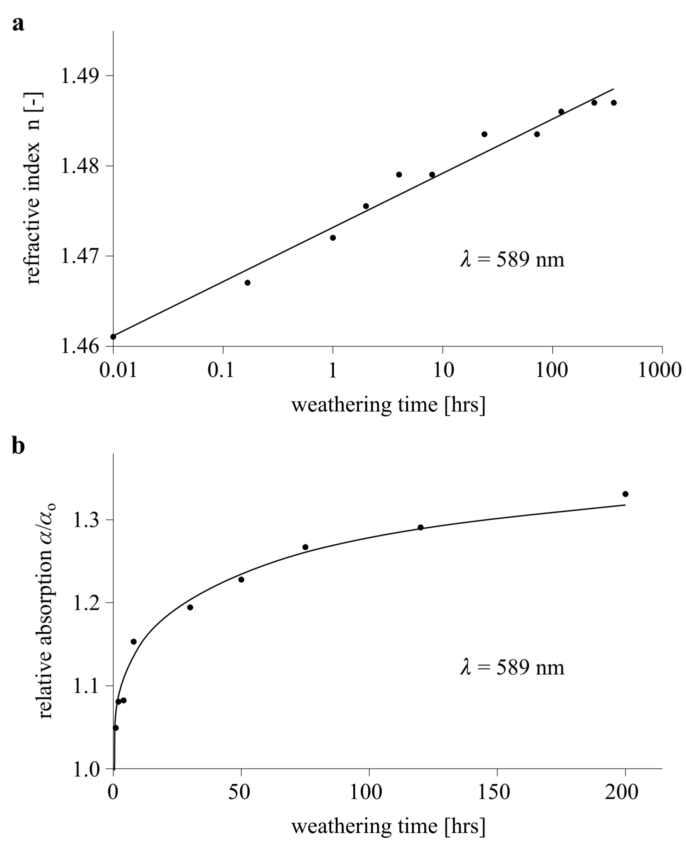

Fig. 2. Changes in the refractive index (a) and and relative absorption coefficient (b) of Baltic crude oil during the course of its weathering

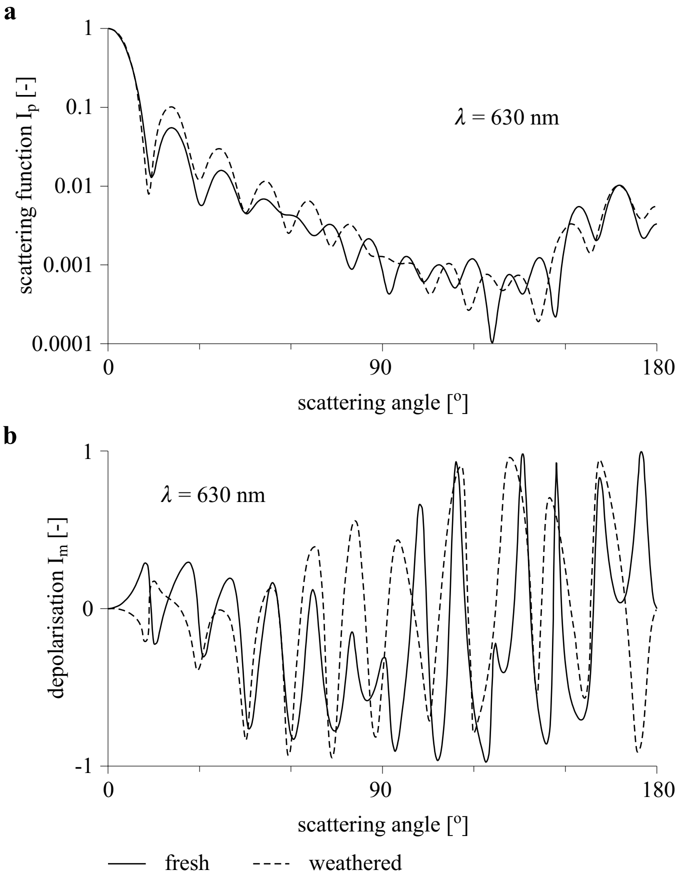

Fig. 3. Normalised scattering function I_p (a) and depolarisation of polarised light of wavelength 630 nm I_m in Baltic seawater (b) describing light scattering on a particle of emulsion calculated for 1 μm-radius droplets of fresh and weathered Baltic crude oil

underlying the calculations was that a log-normal size distribution of the emulsion droplets most suitably characterised the experimental results.

The light absorption and attenuation efficiencies of particles are given by the specific cross-sections obtained by dividing the relative cross-sections by the droplet volume. Specific cross-section spectra of light absorption and attenuation were calculated for droplets of fresh and weathered Baltic petroleum up to 12 μm in diameter; Figs 5 and 6 present spectra of the fresh oil emulsion. The absorption cross-section increases strongly with decreasing light wavelength. This parameter depends on the properties of the oil, but the size of the oil particles does not cause it to vary significantly. In contrast, the light attenuation cross-section depends on both wavelength and droplet size: it reaches a maximum value for particles about 3 μm

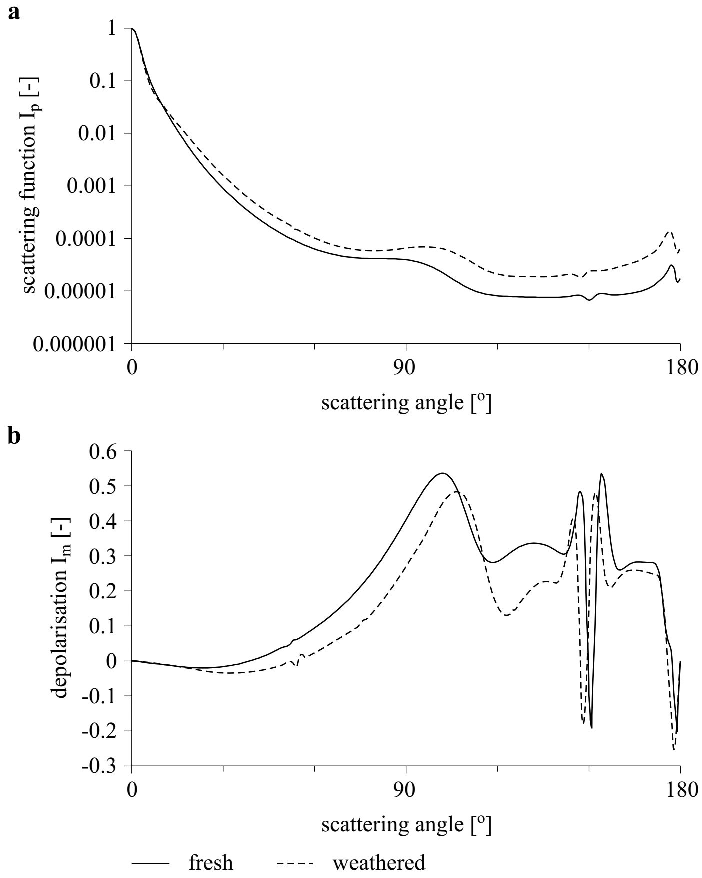

Fig. 4. Normalised scattering function I_p (a) and depolarisation of linearly polarised light of wavelength 630 nm I_m (b) characterising the seawater-Baltic petroleum emulsion

in diameter for light of any wavelength and decreases with the increasing radius. For droplets larger than 5 μm in diameter both the spectral and the size dependencies of the light attenuation cross-section fluctuate.

Taking into consideration the size distribution of the droplets enables the optical properties of the emulsion to be determined. Averaging the specific cross-section spectra of particles over their size distribution yields absorption and attenuation spectra of the emulsion. Fig. 7 shows such spectra for emulsions of fresh and weathered oil. The spectral dependencies of the light absorption cross-section of emulsions are similar to the dependencies of the linear absorption coefficient of oils in the case of both fresh and weathered crude oil. Emulsions of aged oil absorb light to a greater extent than emulsions of fresh oil. The light attenuation cross-section characterising

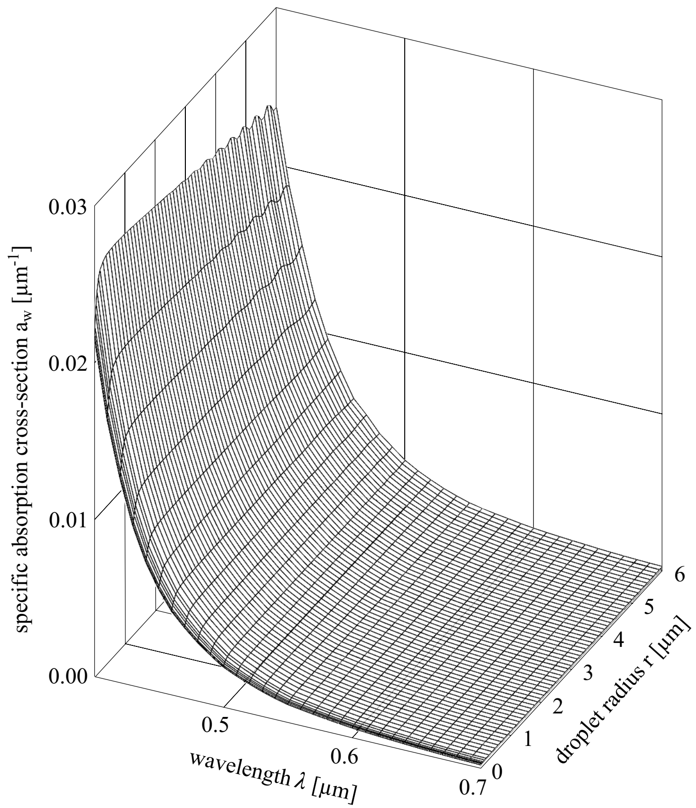

Fig. 5. Light absorption specific cross-section spectrum of fresh Baltic crude oil

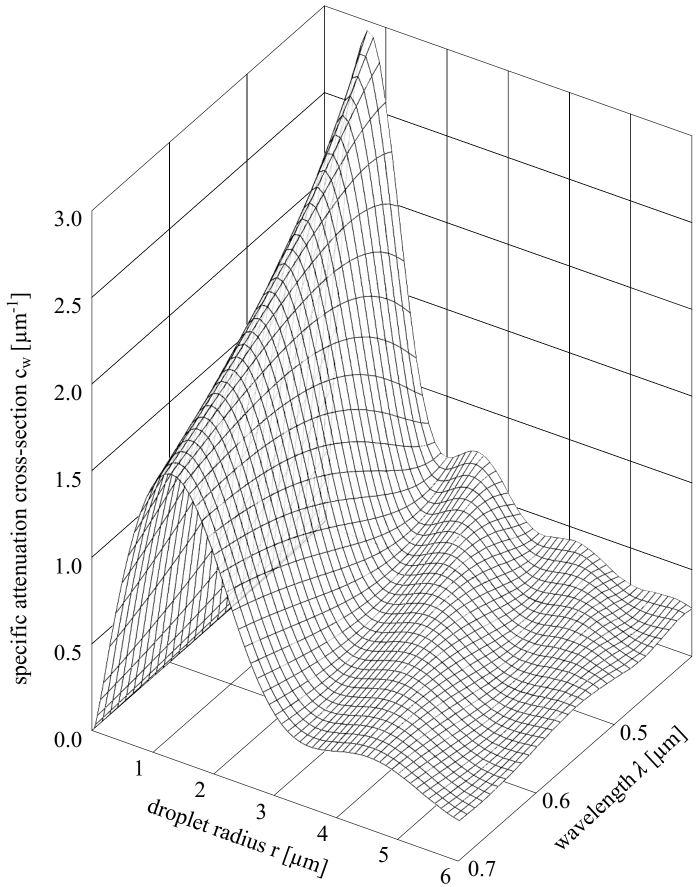

Fig. 6. Light attenuation specific cross-section spectrum of fresh Baltic crude oil

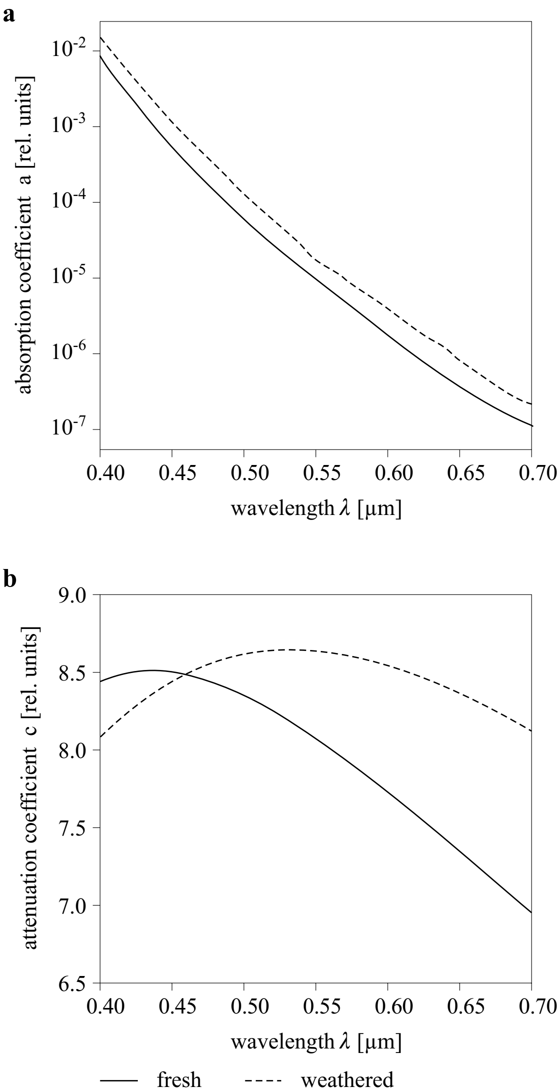

Fig. 7. Light absorption (a) and attenuation spectra (b) characterising oil – water emulsions of fresh and weathered Baltic crude oil

the weathered oil emulsion reaches a maximum for light of $\lambda = \text{c.}\,540$ nm and is higher than in the case of fresh crude.

4. Summary

Weathering is a process causing changes in crude oil, which is reflected in the modification of its optical properties. The increase in the refractive index and the light absorption coefficient of crude oil during its presence in the natural environment is the reason for the increase in light scattering, especially in the case of large angles. Depolarisation of linearly polarised light is greater for fresh crude oil in the case of most scattering angles. The weathering of petroleum has only weak polarisational effects: an emulsion of weathered oil absorbs more light and attenuates the light in the water column to a greater extent than an emulsion of fresh oil. The considerable variability in these modifications at the onset of the weathering process indicates the appropriateness of taking the optical parameters characterising aged petroleum into consideration.

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