Light scattering in Baltic crude oil – seawater emulsion

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Abstract

The paper discusses the scattering of radiation by a Baltic crude oil – seawater emulsion. The scattering spectrum calculated using the Mie solution in the spectral range from 380 nm to 730 nm is compared with the measured spectrum of light scattered through a right angle. Spectra in the wavelength range from 210 nm to 730 nm were measured using a spectrofluorimeter for fresh and stored samples of the Baltic crude oil emulsion. Scattering increases with wavelength in the UV range and then decreases slightly with the wavelength of visible light. The result of the calculation is similar to the measured spectra. Both the calculated and measured spectra display numerous relative extremes throughout the spectral area. Light scattering in the emulsion decreases during storage as the oil concentration in the medium diminishes. The results also demonstrate that the single scattering model describes the phenomenon correctly.

1. Introduction

Petroleum is a very common pollutant of the marine environment and occurs in various forms. Each of these forms exerts its own individual influence on the environment, thereby changing the latter's physical and chemical properties. One of these forms is an oil-water emulsion. Apart from increasing light attenuation, scattering is the optical phenomenon through which such an emulsion makes its presence felt in deep water.

An emulsion – a suspension of oil droplets in water – is a turbid medium. The droplets are spherical particles with a radius of several micrometers, so the Mie solution is suitable for describing the scattering of light by them (van de Hulst 1957). The scattering function characterising an emulsion is an averaged function that takes into consideration the size distribution of the droplets and their concentration. The aim of this work was to corroborate the scattering model. The research questions were two: 1) Can the single scattering model be used to describe the phenomenon? 2) Does the scattering function obtained from calculations correspond to the real scattering spectrum? This paper reports on preliminary studies of this subject carried out for a Baltic crude oil – seawater emulsion.

2. Material and methods

The object of study was Baltic crude oil emulsified in seawater. The seawater was prepared by dissolving the principal sea salts in demineralised water to achieve an ionic composition similar to that of natural water of salinity 7.5 PSU. The emulsion was prepared as follows. Portions of Baltic crude oil dissolved in n-hexane (3 cm^3 of oil and 2 cm^3 of solvent) were poured into a stainless steel vessel containing 10 dm^3 of water. After being stirred with a propeller at 600 rpm (10 s^{-1}) for 3 hours the emulsion was allowed to stabilise for half an hour. Then, a small amount of the emulsion was sampled for the test. The vessel was equipped with a drain valve in the sidewall so that samples could be drawn from the middle of the emulsion bulk. During preparation and storage the emulsion remained in darkness and at constant temperature (20°C).

The intensity of the scattered radiation was measured in the spectral range from 210 nm to 730 nm using a 'Fluorat-02 Panorama' spectrofluorimeter. In this set, the monochromatic illuminating beam passes through the centre of a square, 1 cm long quartz-glass cuvette. The beam is about 1 mm in diameter and has a half-intensity width of 4 nm. The radiation scattered by the emulsion filling the cell was restricted by a diaphragm with a circular hole 0.8 mm in diameter. The measured radiation came from the centre of the cuvette at right angles to the illuminating flux. The solid angle of the scattered beam did not exceed 0.02 sr and was much less than the dilation angle of the receiver. The fluorimeter measures two non-dimensional values: F and T. F is the intensity of the radiation J^{r}

reaching the receiver (fluorescence channel) in relation to the intensity of the illuminating flux J_o:

$$F = \frac{J^r}{J_o}.$$

T (transmission[1]) is the intensity of the light after having passed through the sample J^{ex} in relation to the intensity of radiation reaching the cell J_o:

$$T = \frac{J^{ex}}{J_o}.$$

The parameter S is given by the following equation:

$$S = F\frac{T_o}{T} - F_o \qquad (1)$$

and describes the scattering at the point where this occurs. F and T denote the results of measurements carried out on the tested emulsion, while F_o and T_o are the background parameters (results of measurements performed on the pure medium). S is proportional to the volume scattering function β_{90} characterising the emulsion. Equation (1) allows for molecular scattering in the medium F_o and light attenuation by the emulsion. Equation (1) is derived from the Lambert-Beer law; its correctness is governed by the correctness of the single scattering model used to describe the phenomenon. This has been confirmed by measurements of emulsions diluted to different degrees.

Light scattering can be expressed as follows:

$$\frac{J(\lambda)}{J_o(\lambda)} = \frac{1}{k^2R^2}\int g(r)I(\lambda, r)\mathrm{d}r, \qquad (2)$$

where J and J_o respectively denote the intensities of scattered and illuminating radiation, k (the imaginary part of the complex refractive index) depends on the absorption coefficient a and the light wavelength λ: $k = a\lambda/4\pi$, R denotes distance from the scattering centre and r is the droplet radius (van de Hulst 1957, Bohren & Huffman 1983). The intensity of scattered radiation was calculated using the Mie solution (Król 1984, 1985). The intensity function $I(\lambda, r)$ for the perpendicular direction was calculated for an emulsion droplet of any radius r from 0.5 μm up to 10 μm with a 0.5 μm step. The intensity functions were then averaged with the size distribution g according to the expression

$$\frac{J(\lambda)}{J_o(\lambda)} \propto \lambda^2 \sum_i g(r_i)I(\lambda, r_i)\,. \qquad (3)$$

[1]Sometimes this quantity is called the 'transmittance', whereas the term 'transmission' refers to the physical process of light passing through a sample.

The light refractivity and the absorption coefficient characterising both oil and water and the size distribution of the droplets are the background parameters for the calculations. The size distribution of the emulsion droplets was determined from microscopic measurements using a Burker plate. The optical properties of the oil are known (Kaniewski et al. 2003). Table 1 lists parameters n and k (the real and imaginary parts of the complex refractive index) characterising the petroleum, which were used in the calculations. The water was assumed to be a fully transparent medium. Its refractivity was measured using an Abbe refractometer in the wavelength range 440–660 nm, which enabled the refraction coefficient n to be expressed as the following dependence on the radiation wavelength λ (in μm)

Table 1. Optical parameters n and k (the real and imaginary parts of the complex refractive index) characterising fresh Baltic crude oil with respect to radiation of wavelength λ

λ [nm]	n	k [$\times 10^{-5}$]	λ [nm]	n	k [$\times 10^{-5}$]
380	1.478301	79.7	560	1.459600	3.14
390	1.475902	64.1	570	1.459278	2.80
400	1.473785	52.5	580	1.458983	2.49
410	1.471938	41.1	590	1.458715	2.20
420	1.470310	33.0	600	1.458470	1.94
430	1.468871	26.3	610	1.458247	1.74
440	1.467595	21.3	620	1.458042	1.56
450	1.466462	17.6	630	1.457854	1.41
460	1.465452	14.6	640	1.457682	1.27
470	1.464550	12.5	650	1.457524	1.10
480	1.463743	10.6	660	1.457379	0.99
490	1.463019	8.97	670	1.457245	0.88
500	1.462369	7.46	680	1.457122	0.79
510	1.461784	6.47	690	1.457008	0.73
520	1.461256	5.61	700	1.456903	0.68
530	1.460779	4.78	710	1.456808	0.60
540	1.460347	4.07	720	1.456718	0.53
550	1.459956	3.47	730	1.456635	0.47

$$n = A\frac{1}{\lambda^2} + B, \tag{4}$$

where $A = 3.15 \times 10^{-3}$ μm^2 and $B = 1.32529$. [2]

[2] Relation (4) tallies very well with the standard relationship (Quan & Fry 1995, IAPWS 1997) throughout the range from 300 nm to 750 nm.

3. Results

The majority of Baltic crude oil droplets emulsified in water had a diameter ≤ 2.5 μm. At the same time only a few droplets were > 5 μm in radius. The emulsion particle radii form a size distribution that appears to be best described by a log-normal function. Figure 1 presents the distribution function g and the results of the microscopic measurement. The number of particles of diameter ≤ 2.5 μm ranged from 37 to 48 in a cell of volume 0.004 mm^3. Taking into consideration the size distribution, the relative volume concentration of oil in the emulsion was estimated to be 1.2×10^{-4}. The oil concentration and fragmentation of the particles reach a certain level during emulsification. Prolonging the stirring time or increasing of the speed of propeller rotation do not cause meaningful changes (Mikłaszewicz 2006). Thus, the oil concentration in a fresh emulsion can be considered to be close to the maximum.

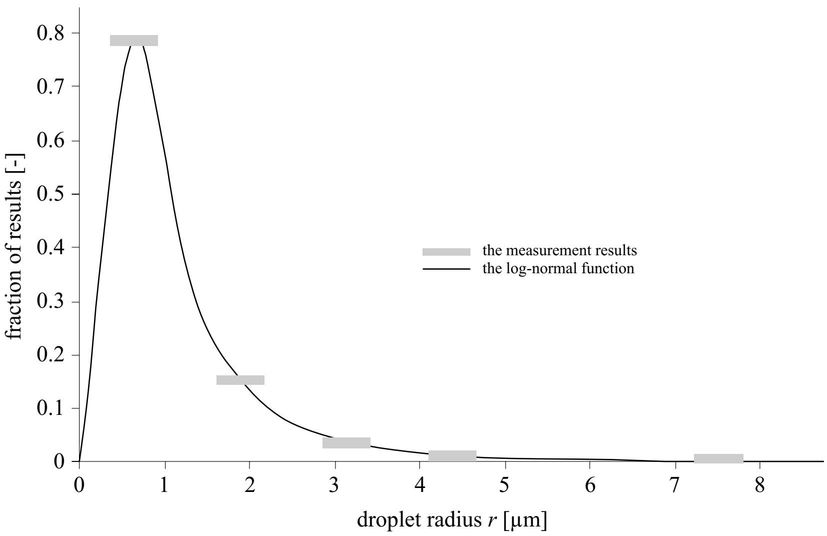

Figure 1. Size distribution of particles in a Baltic crude oil – seawater emulsion

The possible application of the single scattering model is a precondition for the correct calculation of the scattering function as well as of the suitability of equation (1). This was confirmed by the following test. The emulsion was diluted with water, the diluted samples being emulsions with the same composition but different concentrations. Then, scattering and light attenuation were measured for these samples. In the case of the single scattering model, the intensity of scattered radiation S should be proportional to the oil concentration C, while transmission T through a cell filled with emulsion should satisfy the following relation:

$$T = T_o \exp(-\gamma C)\,. \tag{5}$$

T_o denotes the transmission through pure water and γ is a constant (proportional to the light attenuation coefficient). Figures 2 and 3 present

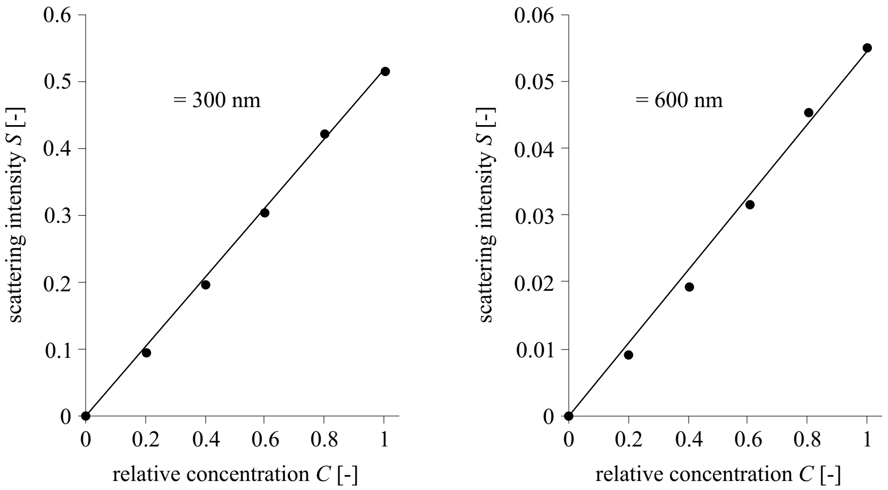

Figure 2. Scattering intensity of Baltic crude oil in a seawater emulsion relative to the oil concentration C for radiation of wavelength $\lambda = 300$ nm (a) and $\lambda = 600$ nm (b)

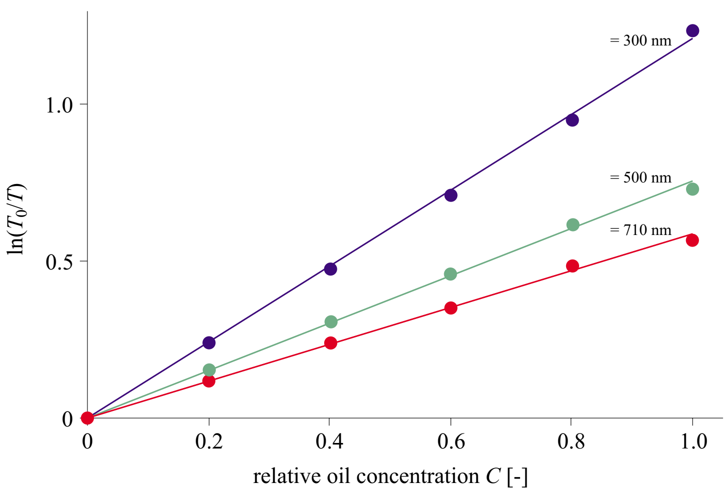

Figure 3. Logarithm of the reciprocal of the relative transmission $\ln(T_o/T)$ with respect to the relative oil concentration C in the Baltic crude oil – seawater emulsion for radiation of a number of wavelengths

the results of the test. Both the scattering intensity S and the expression $\ln(T_o/T)$ are almost linearly dependent on the concentration. Thus, it can be assumed that the single scattering model describes this phenomenon satisfactorily even when the concentration of the emulsion is relatively high.

3.1. Results of scattering measurements

Figure 4 presents a number of the scattering spectra measured on fresh and stored emulsions. The scattering in any sample increases with the radiation wavelength in the UV range and each spectrum has numerous relative extremes in the whole spectral area. The turbidity of the emulsion decreases during its storage. The scattering intensity decreases but the spectrum itself retains its shape. This indicates that the oil concentration falls in an emulsion although its composition is stable.

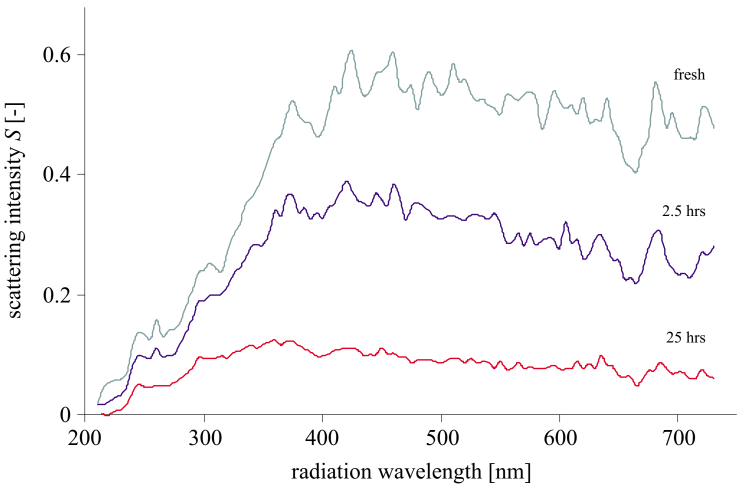

Figure 4. Measured scattering spectra S of Baltic crude oil – water emulsions: fresh (black line), after storage for 2.5 hrs (blue line) and after storage for 25 hrs (red line)

3.2. Results of calculations

The intensity function is a parameter describing scattering at individual particles. The function depends on droplet size, radiation wavelength and the scattering angle. Figure 5 presents spectra of the intensity function of scattering at right angles for wavelengths from 380 nm to 730 nm calculated for Baltic crude oil particles of different radii r.

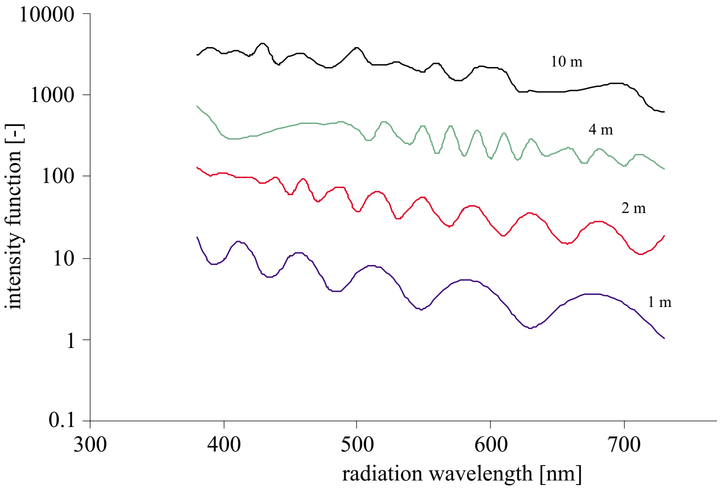

Figure 5. Spectra of the intensity function of scattering at right angles calculated for Baltic crude oil particles of various radii

Taking into consideration the distribution of the particles and the oil concentration one can obtain the volume scattering function β, which describes scattering by an emulsion. The spectrum of the function $\beta_{90}=\beta_{90}(\lambda)$ was compared with the measured spectrum of the fresh emulsion (see Figure 6). It is essential to compare the course of function β with the shape of the

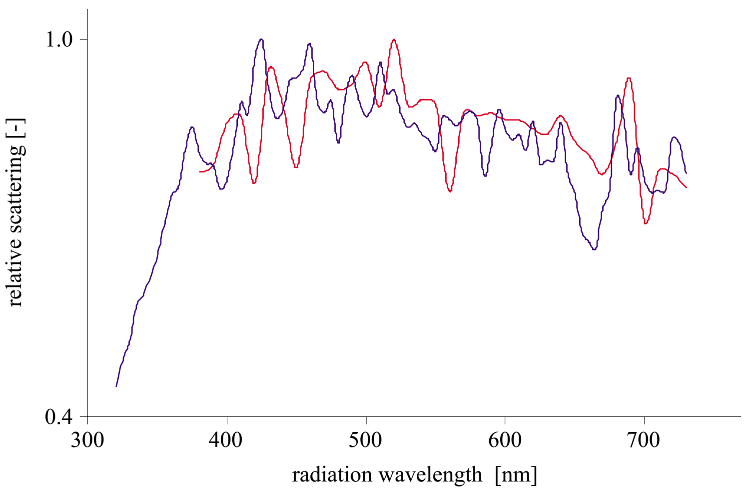

Figure 6. Calculated scattering function of the Baltic crude oil – seawater emulsion (red line) in comparison with the measured spectrum (blue line). The function and spectrum have been normalised to their maximum values

measured spectrum. As a result, the calculated function and the measured spectrum were normalised to their maximum values. The similarity between the spectra is apparent, although they do not coincide. The various maxima of the theoretical function are shifted by several nanometers in relation to the corresponding extremes of the measured spectrum. The following reasons may explain this difference: fresh crude oil is not a stable substance and its properties change during emulsification (Kaniewski et al. 2003, Król et al. 2006), and the optical properties of emulsion droplets are not exactly the same as the properties of the original oil (Stelmaszewski & Toczek 2007).

4. Summary

A Baltic crude oil – seawater emulsion scatters visible light more effectively than UV radiation – the scattering increases with UV wavelength up to about 400 nm. The scattering spectrum has many local extremes throughout the spectral area. The similarities between the scattering spectra of the stored emulsion and the fresh one indicate that the emulsion retains its optical properties.

This test has shown that the volume scattering function based on the Mie solution corresponds with experimental results and that the single scattering model provides an adequate description of the phenomenon.

The above conclusions have been drawn from preliminary experimental studies of only one crude oil emulsion. They will require confirmation by tests carried out on other species, especially oils with stable properties.

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