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Light attenuation parameters of polydisperse oil-in-water emulsion

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This paper presents the method and the results of modelling the light attenuation and absorption spectra in sea water polluted with dispersed oil. The Mie solution has been employed in modelling to derive the cross-sections of light attenuation and its components, absorption and scattering of oil-water emulsion droplets. After the averaging for typical distributions of dispersing particles, these cross-sections allow determination of the optical properties of water polluted with oil substances. It was revealed that oil concentration of about 1 ppm in water causes light attenuation comparable with attenuation in natural water typical for bays of the Baltic Sea (Case 2 water). The method presented facilitates obtaining the information necessary for the modelling of above water upward radiation field in the cases of basins polluted with dispersed oil.

1. Introduction

Oil substances in aquatic environment can be detected by a number of remote sensing techniques which involve light interaction with the medium under investigation. The applicability and efficacy of individual techniques depend on weather conditions, time (night or day), quantity and kind of oil, as well as form of oil in the water (film, suspension) [1]. Earlier, the presence of oil pollutions in the sea could be confirmed only through visual observations. As a result of several hundred observations of oil spills, which had been carried out since 1930 [2], the most likely dependencies between the colour of the sea surface and thickness of oil film were determined [3]. Also other phenomena are investigated, such as dependencies between motion of a ship which discharges waters polluted with oil and the possibility of detecting of this pollution using the observation methods in VIS range of spectrum [4]. The phenomena concerning formation of the upward radiation field over the water surface covered with oil can be investigated using mathematical modelling. Examples of such investigations involve analysis of the impact of film thickness, wavelength and angle of light incidence on light reflectance coefficient on the sea surface [5], and the analysis of the impact of wind speed on visibility of oil film [6].

When modelling the radiation field above the surface of the basin with forms of oil pollution in the water column, it is necessary to know values of the parameters which describe light attenuation in the water column. Light attenuation in natural waters is characterized by the light attenuation coefficient, which is a sum of absorption and scattering coefficients [7]. The impact of oil pollution on the values of these coefficients may be determined from the calculated specific cross-sections of scattering and absorption. It is a function of light wavelength and radii of oil particles in the suspension. If the size distribution of emulsion particles in water is known, spectra of the specific attenuation, scattering and absorption coefficients can be determined.

Such a procedure was applied in this paper for determination of optical properties of oil suspension in the sea water. Section 2 presents the application of the Mie light scattering theory [8] for determination of the specific light attenuation and absorption cross-sections of spherical oil droplets in emulsion. Section 3 describes the methodology of obtaining oil suspension in water and the laboratory derivation of the complex light refraction index in oil. Section 4 presents results from particular stages of calculations and their final result, expressed in the form of spectra of light absorption, scattering and attenuation coefficients in emulsion made of two selected types of crude oil in sea water.

2. Computation of the optical properties of crude oil emulsion in sea water

The Mie theory [8] facilitates computations of the values of cross-sections of light attenuation C_e and light absorption C_a coefficients for arbitrary spherical droplets [9]. The following parameters are included in the theory:

- particle radius r,
- complex light refraction index m for the material the particles are made of,
- light refraction index of the medium in which the light scattering particles are suspended.

The Mie theory is based on the solution of wave equations for electro-magnetic fields derived from the Maxwell equations, with appropriate boundary conditions, on surfaces of light scattering particles. The solution of the light scattering on spherical particles yields the formulae for light scattering, absorption and attenuation cross-sections. These formulae are in the form of complex series and have been described in details [8], [9]. The methodology of these calculations is described in [10].

The specific attenuation cross-section c_s determines the effectiveness of light attenuation, due to scattering and absorption, in an emulsion containing many particles of the same radius r. It is expressed as the ratio of attenuation cross-section and particle volume:

$$c_s = \frac{C_e(r,m)}{v}, \tag{1}$$

which is the sum of a similarly defined specific scattering cross-section

$$c_{ss} = \frac{C_e(r,m)}{v}, \tag{2}$$

and specific absorption cross-section

$$c_{sa} = \frac{C_a(r,m)}{v}. \tag{3}$$

Emulsion which consists of particles of various sizes (polydispersed solution) is characterized by the size distribution function $f(r)$ in the solution unit volume. Then, the emulsion light attenuation coefficient c results from the averaging and can be expressed as follows:

$$c = w \int_{r_{\min}}^{r_{\max}} f(r)\, v(r) c_s(r,m) \mathrm{d}r \tag{4}$$

where w is the volume concentration of oil suspension in emulsion.

The light attenuation coefficient c (4) is a sum of light absorption coefficient a and light scattering b:

$$a = w \int_{r_{\min}}^{r_{\max}} f(r) v(r) c_{sa}(r,m) \mathrm{d}r, \tag{5}$$

$$b = w \int_{r_{\min}}^{r_{\max}} f(r) v(r) c_{ss}(r,m) \mathrm{d}r. \tag{6}$$

In water basins light attenuation coefficient is a sum of light attenuation coefficients of various substances suspended in the water column, including particles of dispersed oil. The component of light attenuation in water, which reflects the presence of oil suspension, may be derived from the multiplication of the specific light attenuation coefficient and the oil volume concentration in water. Therefore, knowledge regarding optical properties of oil, size distribution of spherical suspension droplets and oil concentration in water, allows evaluation of the impact of oil in water on the light attenuation coefficient.

3. Experimental part

3.1. Materials

For investigation of the optical properties of oil suspension in sea water two types of crude oil were used, Romashkino and Petrobaltic, both characterized by different optical properties. The Romashkino type has strong light absorbing and refracting properties, while Petrobaltic belongs to a group of oils which are relatively transparent and do not significantly refract light [5]. As a model of sea water, the NaCl solution in distilled water of specific conductivity as in the case of natural sea water of salinity 7.5 PSU was used. In comparative tests the artificial sea water of the same salinity was used [11]. The salt solutions were sterilized at a temperature of about 90 °C for a period of time of 1 h.

3.2. Size distribution of crude oil suspension droplets in sea water

The water-oil emulsion was prepared using the method of mechanical dispersion of crude oil (50 cm^3) in water (8 dm^3) using the rotating mixer (about 600 rpm) for 1 h. After 24 hours of undisturbed emulsion storage, 5 dm^3 of the emulsion was collected and placed in a thermostatic chamber (10 °C) for one week. Then, 3 dm^3 of oil-water suspension was collected and used in investigations. Such emulsion is a model of stabilized oil suspension in sea water.

The size distribution of the suspension particles was determined using the microscope with micrometric eyepiece. The suspension was placed in the Bürker plate, which allowed the counting of the droplets of sizes exceeding 0.5 μm, in radii ranges every 0.5 μm. The measurement was repeated after one week. The experimental oil particle size distributions obtained can be well described by the log-normal distribution $f(r)$

$$f(r) = C\exp\left(-\frac{\ln^2(r/r_0)}{2\sigma^2}\right) \tag{7}$$

where: r_0 – mean droplet geometric cross-section, σ – constant which characterizes distribution width, C – normalizing constant (depends on crude oil concentration).

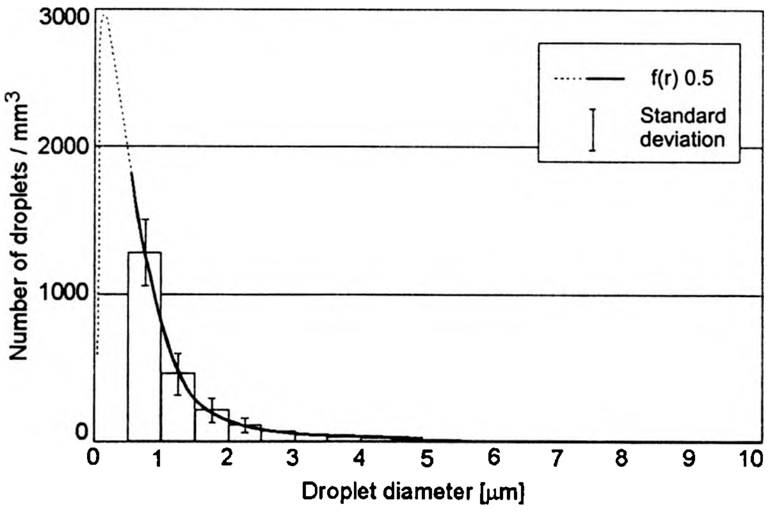

Fig. 1. Example of size distribution of oil droplets in water.

The results of calculated numbers of particles and in particular size ranges per 1 mm^3 of emulsion are presented in Fig. 1, along with the curve of a log-normal distribution (7), which approximates the measurement results. This curve is also used for extrapolation of the size distribution to the range of radii sizes below 0.5 μm (below the limit of particle differentiation). The parameters of distribution function $f(r)$ for one week old emulsion are as follows: $r_0 = 0.11$, $\sigma = 1.08$. In the case of a two week old emulsion, its concentration is several dozen percent lower than in the case of a one week old emulsion, while the distribution parameters do not vary significantly, $r_0 = 0.10$, $\sigma = 1.00$.

3.3. Determination of spectral variations of the complex light refraction index

In order to determine the components of the complex light refraction index of the dispersed emulsion substance remaining after the water centrifuging from the investigated emulsion was used.

Measurements of the real part of the refractive index were taken with an Abbe type refractometer which allows temperature stabilization using an external thermostat. The measurements were taken in a temperature range from 0 °C to 20 °C. The refractometer was illuminated with monochromatic light applied in the 400 nm to 700 nm wavelength range. This monochromatic light was supplied by a 100 W halogen lamp and a Specol 10 spectrophotometer used as a monochromator.

The results of measurements of the real part of the light refraction index in crude oil and sea water of salinity 8 PSU are presented in the form of plots of spectra of the relative light refraction index at the oil-water boundary (Fig. 2**a**).

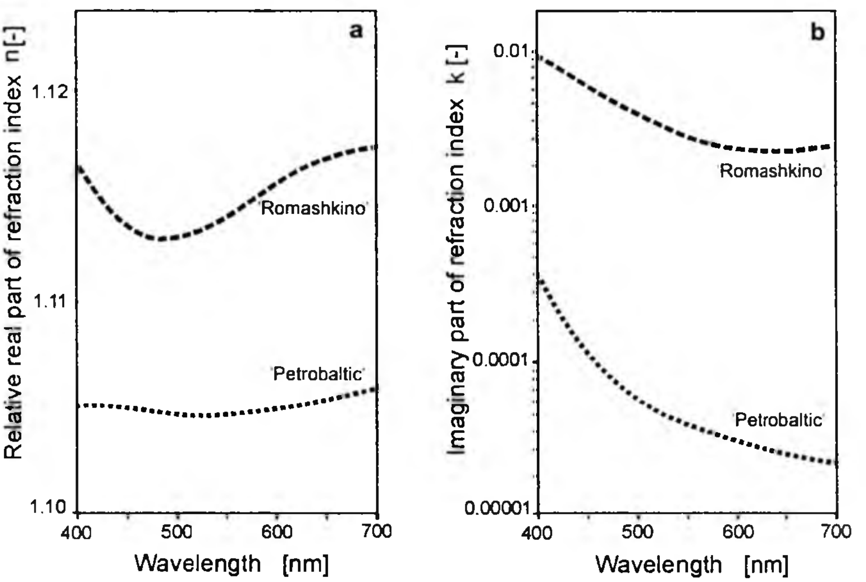

Fig. 2. Components of the complex light refraction index in oil: real part (**a**) in relation to the surrounding medium (sea water), and imaginary part (**b**).

Measurements of the imaginary part of the light refractive index k were taken after the spectral changes of light absorption index α had been made and calculated to fit the parameter $k = 0.25\alpha\lambda\pi^{-1}$. The light absorption index α $[m^{-1}]$

was measured with a Specord M40 spectrophotometer for ranges from 350 nm to 750 nm.

The results of measurements of the dependence of the imaginary part of the refractive index k on wavelength are presented graphically in Fig. 2**b**. The imaginary part k of the refractive index in the Petrobaltic oil at a temperature of 10 °C varies from $2 \cdot 10^{-5}$ ($\lambda = 700$ nm) to $4 \cdot 10^{-3}$ ($\lambda = 400$ nm), while in the case of Romashkino oil the parameter varies from $3 \cdot 10^{-3}$ to $9 \cdot 10^{-3}$, respectively.

4. Calculations and results

Using computer programs based on the Mie solution the calculations of the specific light attenuation and absorption cross-sections were carried out for wavelengths in the range from 400 nm to 700 nm (every 10 nm), and for droplet radii from 0.05 µm to 20 µm (every 0.05 µm). The calculated spectra of cross-sections are in the form of rectangle tables, which consist of 400 × 31 values of these functions. They are presented in Fig. 3.

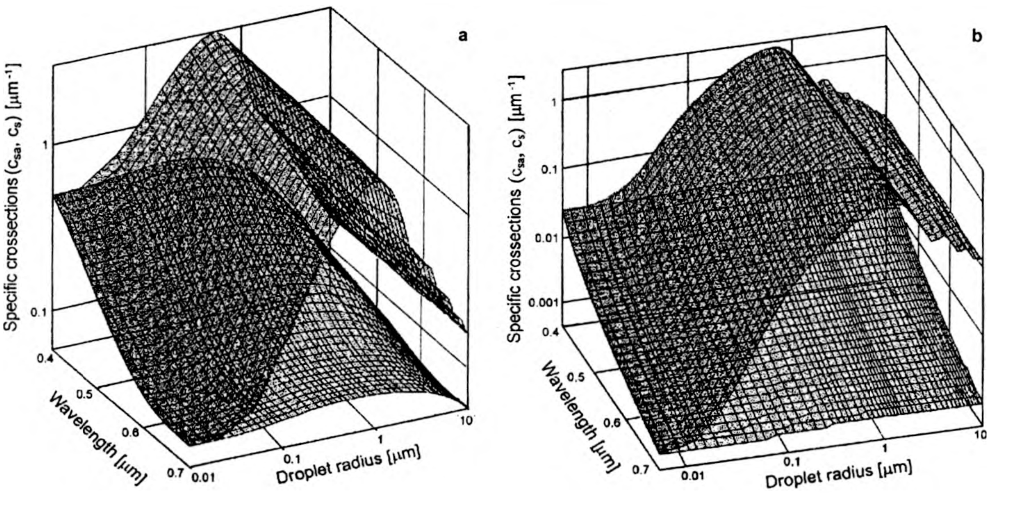

Fig. 3. Specific light attenuation cross-sections c_s (left surfaces) and absorption c_{sa} (right surfaces) for suspension of crude oil types Romashkino (**a**) and Petrobaltic (**b**).

4.1. Spectra of specific attenuation and absorption cross-sections for suspension particles

Figure 3**a** presents the dependence of specific attenuation and absorption cross -sections on sizes of particles of suspension made of crude oil Romashkino type in sea water. This is an example of the situation when crude oil strongly absorbs light. Figure 3**b** presents the same dependence for particles of suspension made of crude oil Petrobaltic type, *i.e.*, weakly absorbing light. The comparison of these plots reveals that in the case of very small oil particles (below 0.1 µm), absorption plays an important role in light attenuation by the suspension. However, absorption contribution is smaller in the case of weakly absorbing crude oil and it is dominant in the case of strongly absorbing crude oil. For particles of diameters comparable with light wavelengths (0.2 μm – 2 μm), scattering dominates in the light attenuation. For particles much larger than light wavelengths (above 3 μm) – in the case of crude oil absorbing light – contribution of scattering and absorption in the light attenuation is comparable, while for particles of crude oil weakly absorbing light, scattering dominates.

The degree of emulsion dispersion has strong influence on specific absorption and attenuation cross-sections and thus on spectra of absorption and attenuation by suspension. The proportions of absorption and scattering in light attenuation depend on the size of suspension particles and on the type of oil (especially on light absorption coefficient).

4.2. Spectra of attenuation and absorption cross-sections for polydispersed suspension

The type of oil, its concentration and dispersion structure decide about the impact of oil suspension on optical properties of polluted water. The impact of the dispersion structure on light attenuation, in accordance with the dependence (4), is derived through the multiplication of the specific attenuation cross-section for the given particle radius by the volume of the particle of this size and by a value of size distribution function. The product yields the distribution of the attenuation cross-section versus radius of particles for the suspension of structure described by the selected size distribution. The calculations of spectra of light attenuation cross -sections and one of its components, absorption cross-sections were made for emulsions of both types of crude oil.

The results of calculations are presented in Figs. 4 and 5. The distributions presented have clear maxima for particles of radii 1 – 2 μm, while the maximum of particle radii distribution is at 0.1 μm (Fig. 1). The shapes of distributions of attenuation cross-sections for suspensions are similar for all light wavelengths. Their values significantly decrease when particle radii exceed 10 μm. However, in the cases of older suspensions, *i.e.*, suspensions with particles of fewer large particles, the interference effects, which are manifested by the function value oscillations, disappear. The attenuation in older suspensions is significantly lower, despite a small change in the shape of the spectrum size.

4.3. Spectra of light attenuation coefficient

As described in Section 2, coefficients of light attenuation c, scattering b and absorption a in the oil suspension in water can be described by integrals (4), (5) and (6). The integrating functions are distributions of attenuation, scattering and absorption cross-sections, respectively. Then the values of the specific attenuation coefficients for particular light wavelengths have been obtained.

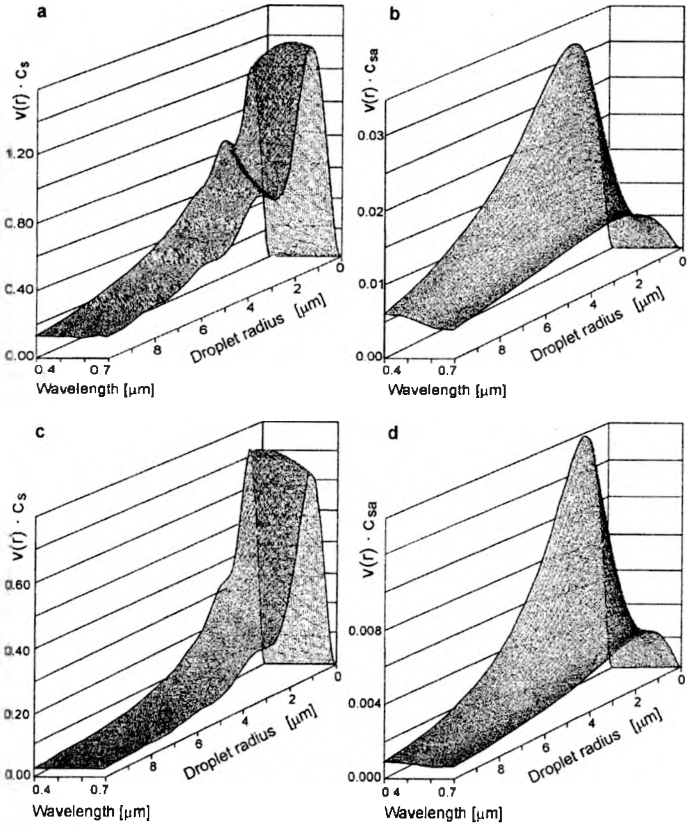

Fig. 4. Distributions of attenuation cross-sections (a) and (c) and absorption cross-sections (b) and (c) versus radius of suspension of crude oil type Romashkino after one weak of aging (a) and (b), after two weaks of aging (c) and (d).

The spectra of the specific attenuation coefficient obtained for both types of crude oil are presented in Fig. 6. These spectra are flat and are located on the same level. However, components of spectra of attenuation coefficients, thus spectra of specific absorption and scattering coefficients strongly depend on light wavelength. In the range of short waves light scattering coefficient increases with light wavelength, while the absorption coefficient decreases. The specific absorption coefficients of the suspension of crude oil Romashkino type are much higher than in the case of the crude oil Petrobaltic suspension.

The values of specific coefficients, expressed in μm^{-1} relate to their values in m^{-1} in the cases where the oil volume concentration is about 10^{-6} (1 ppm). At such oil concentrations in water (in the form of suspension of the size structure similar to the presented example size distributions) the values of specific coefficients are comparable with the values of light attenuation coefficients in natural waters typical for bays of the Baltic Sea (Case 2 water) [12].

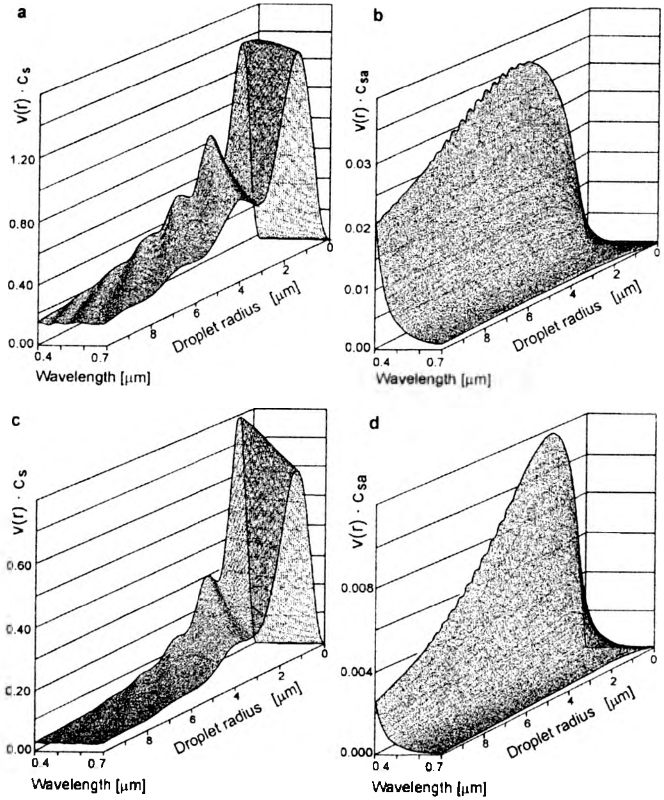

Fig. 5. Distributions of attenuation cross-sections (**a**) and (**c**), and absorption cross-sections (**b**) and (**c**) versus radius of suspension of crude oil type Petrobaltic after one weak of aging (**a**) and (**b**), after two weaks of aging (**c**) and (**d**).

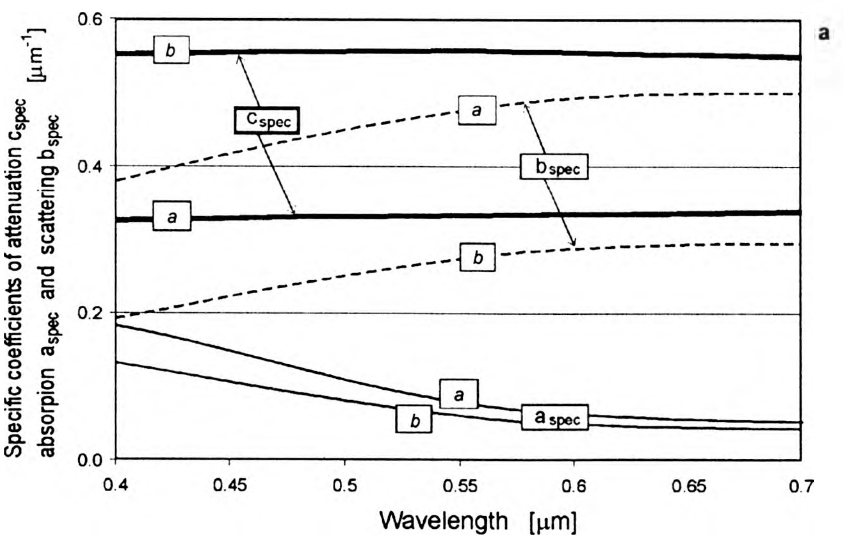

Fig. 6a

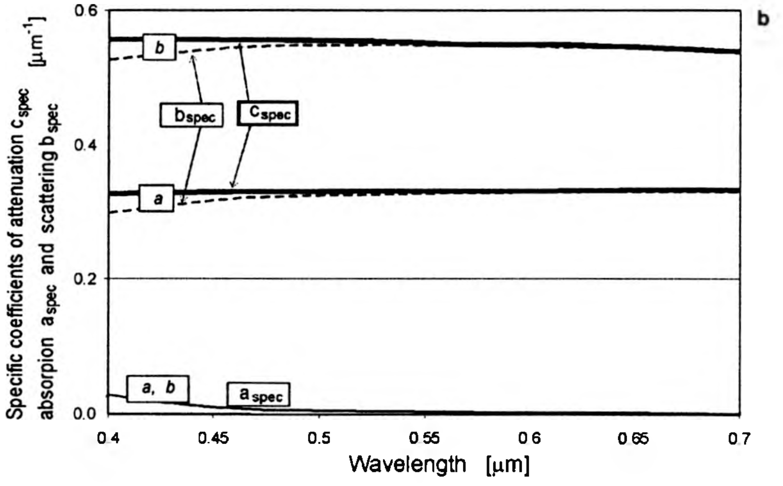

Fig. 6. Spectra of specific coefficients of light attenuation c_{spec}, absorption a_{spec} and scattering b_{spec} of emulsions of crude oil types Romashkino (**a**) and Petrobaltic (**b**) in one weak old emulsion *a* and two weak old emulsion *b*.

5. Conclusions

Knowledge of oil optical parameters and the structure of its emulsion (particle size distribution for the oil suspension in water) facilitates the application of the Mie solution and thus the determination of the suspension optical properties, *i.e.*, the spectra of the suspension absorption, scattering and attenuation coefficients.

Spectra of light attenuation in suspensions of various types of oil in water are basically flat and they are located at the same level. However, absorption and scattering coefficients depend on the light wavelength.

Light attenuation in oil suspensions is mainly caused by light scattering. The most effective scattering occurs for oil particles of radii of about 1 μm.

If the oil suspension concentration in water is about 1 ppm, then light attenuation by such emulsion is comparable with attenuation by natural seawaters typical for bays of the Baltic Sea (Case 2 water).

The spectral distributions of absorption and scattering coefficients obtained from the Mie solution facilitate modeling of radiation fields in waters, in which, beside the natural suspension, the oil emulsion is also present.

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