Determination of the structure of an oil-seawater emulsion from measurements of light attenuation

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Light attenuation
Oil-water emulsions
Structure of
polydispersive systems

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Abstract

The effect of the statistical distribution parameters of nonabsorbing particles on the transparency of polydispersive systems is described. A method of inverting the transmission spectra into the size distribution of scattering particles is presented. It was tested on an emulsion of Baltic crude oil in artificial Baltic seawater and was found to provide useful information on the structure of emulsions containing particles < 1 μm in size.

1. Introduction

In the marine environment crude oil and its products occur mostly as surface films or emulsions, containing droplets of various sizes. The fluorescence method (Measures, 1987) and measurement of the intensity of the light reflected from a polluted water surface (Shifrin and Gurevich, 1979) have been successfully used to determine the quantity of oil forming the films. However, workable methods for establishing the concentrations of oil forming the emulsion or colloidal solutions are not yet available. Observation of oil droplets under the microscope (Gurgul, 1986) provides information only about large ones. Likewise, the methods based on the measurement of the light scattered by small droplets have yielded no definite results (Hulst, 1957). Thus, there is a need for new methods permitting information on the structure of emulsions containing particles < 1 μm in size to be obtained fairly rapidly.

It follows from the Mie theory that in monodispersive systems the final form of the transmission spectrum depends on the radii of the scattering particles (Fig. 1). Furthermore, transparency measurements of oil-seawater

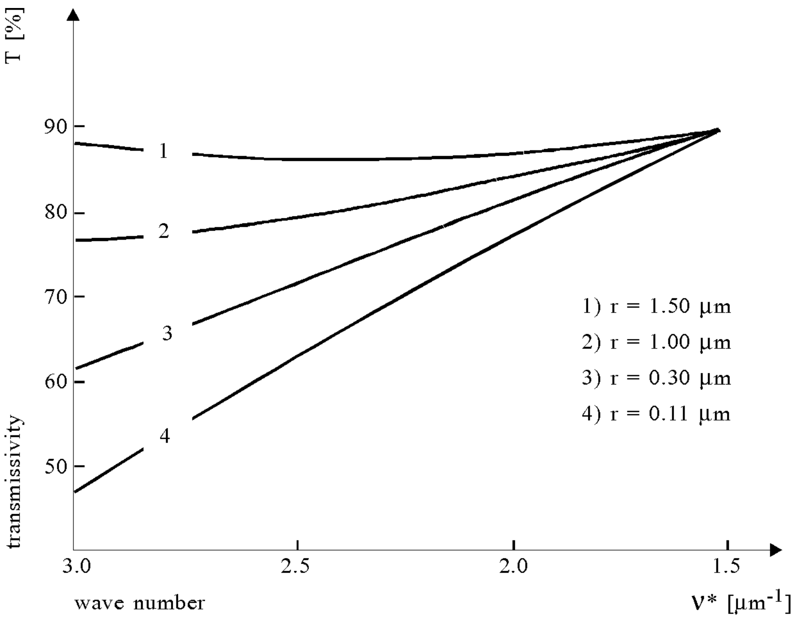

Fig. 1. Transmission spectra for the monodispersive size droplets of Baltic oil calculated according to the Mie scattering theory

emulsions (Dera and Pawlak, 1988; Stoń, 1990) have revealed the spectral dependence of the light attenuation coefficients (LAC) $b(\vartheta^*)$

$$I = I_o \exp[-b(\vartheta^*)\, l], \tag{1}$$

where

$\vartheta^* = 1/\lambda$ – wave number,

l – thickness of the layer,

$I_o(I)$ – intensities of the incoming (attenuated) light.

This paper will consider the problem of light attenuation by polydispersive crude oil – seawater emulsions and the determination of their structure by means of experimentally measured attenuation spectra.

2. Light attenuation in polydispersive emulsions

2.1. The main assumptions

The expression describing the spectral dependence of the LAC in polydispersive media (Stoń and Shifrin, 1990) is

$$b(\vartheta^*) = 2\pi N \int_o^\infty Q\left(r, m(\vartheta^*), \vartheta^*\right) f(r) r^2 dr, \tag{2}$$

where

N – particle concentration,

Q – dimensionless LAC for a particle of radius r and relative refractive index m,
$f(r)$ – distribution function of the radii.

In calculating expression (2) it has been assumed that

1) an oil-water emulsion consists of spherical particles of various radii (Gurgul, 1986)
2) the size distribution takes the form of a gamma-type function

$$f(r) = (\mu/r_o)^{\mu+1} r^{\mu} \exp(-\mu r/r_o)/\Gamma(\mu+1), \quad \mu > 0 \tag{3}$$

where

r_o – modal radius,
μ – width parameter; in monodispersive systems $\mu \to \infty$,
$\Delta r = 2.48/\sqrt{\mu}$ – the half width.

3) the dimensionless LAC for one particle is taken to be (Granovskiy and Stoń, 1994)

$$\begin{aligned} Q &= Q\left(r, m(\vartheta^*), \vartheta^*\right) = f(m)\left[1 - \frac{\sin 2\delta}{\delta} + \frac{1-\cos 2\delta}{2\delta^2}\right], \\ \delta &= 2\pi r \vartheta^* (m-1), \\ f(m) &= (m+1)^2[2m(m^2+1) - (m^2-1)^2]/8m^2. \end{aligned} \tag{4}$$

The choice of droplet distribution function must be related to the mechanism of particle formation. Under natural conditions emulsions are formed as a result of long-term wave-motion of the sea surface. Kolmogorov (1941) showed that the particle-size spectrum in such a process is described by the log-normal distribution. As this is similar to the gamma-distribution (Shifrin, 1983), it will be taken to be the mathematically simpler one. On the basis of measurements of the angular distribution of the scattered radiation, Oshchepkov *et al.* (1988) showed that function (3) is sufficient to describe the structure of an oil-water emulsion.

2.2. The theoretical basis

The following dimensionless quantities are used:

$$\begin{aligned} a &= r/r_o, \qquad \vartheta = \vartheta^* r_o, \\ \beta &= 2\pi(m-1), \qquad \delta = \beta\vartheta a, \qquad b(\vartheta) = r_o\, b(\vartheta^*). \end{aligned} \tag{5}$$

Then

$$Q = f(m)\left[1 - \frac{\sin 2\beta a\vartheta}{\beta a\vartheta} + \frac{1-\cos 2\beta a\vartheta}{2(\beta a\vartheta)^2}\right], \tag{6}$$

and

$$f(r)dr = \mu^{\mu+1} a^{\mu} \exp(-\mu\, a) da/\Gamma(\mu+1). \tag{7}$$

The dimensionless LAC takes the form

$$b(\vartheta,\beta)=\frac{2\pi N r_o^3\mu^{\mu+1}}{\Gamma(\mu+1)}f(m)\int_o^\infty\left(1\;-\;\frac{\sin 2\beta\,a\vartheta}{\beta\,a\vartheta}+\frac{1-\cos 2\beta\,a\vartheta}{2(\beta\,a\vartheta)^2}\right)\times$$
$$\times\;a^{\mu+2}e^{-\mu\,a}da. \tag{8}$$

After the integrals have been calculated and some transformations made, the final form of the LAC is obtained

$$b(\vartheta^*)=2\pi N r_o^2(\mu+2)(\mu+1)\mu^{-2}f(m)\Theta_\mu(x), \tag{9}$$

where the transparency function $\Theta_\mu(x)$ is defined as

$$\Theta_\mu(x)=1-\frac{2A}{x(\mu+2)}+\frac{2(1-B)}{x^2(\mu+2)(\mu+1)}, \tag{10}$$

and

$$A=(\cos\phi)^{\mu+2}\sin[\phi(\mu+2)],\quad B=(\cos\phi)^{\mu+1}\sin[\phi(\mu+1)], \tag{11}$$

$$\phi=\arctan(x),\qquad x=4\pi(m-1)r_o\,\vartheta^*\,\mu^{-1}. \tag{12}$$

From (9) it is seen that as a function of ϑ^*, LAC $b(\vartheta^*)$ depends on the parameters μ, r_o of the distribution. They are contained in $\Theta_\mu(x)$ or, more precisely, in parameter x.

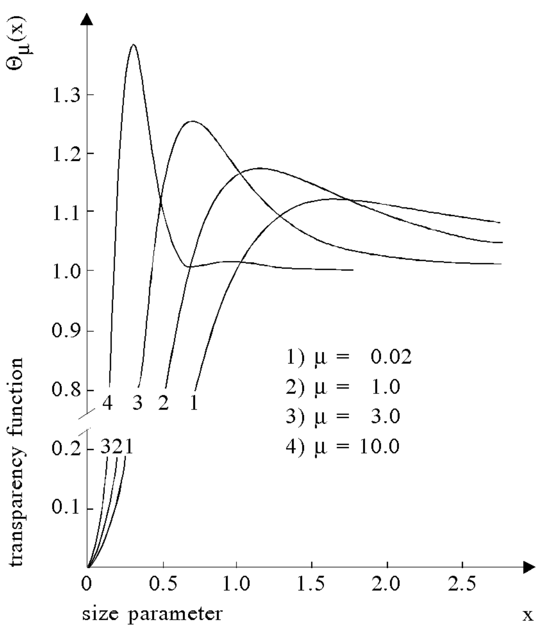

Fig. 2. Dependence of the transparency function $\Theta_\mu(x)$ on the distribution width μ

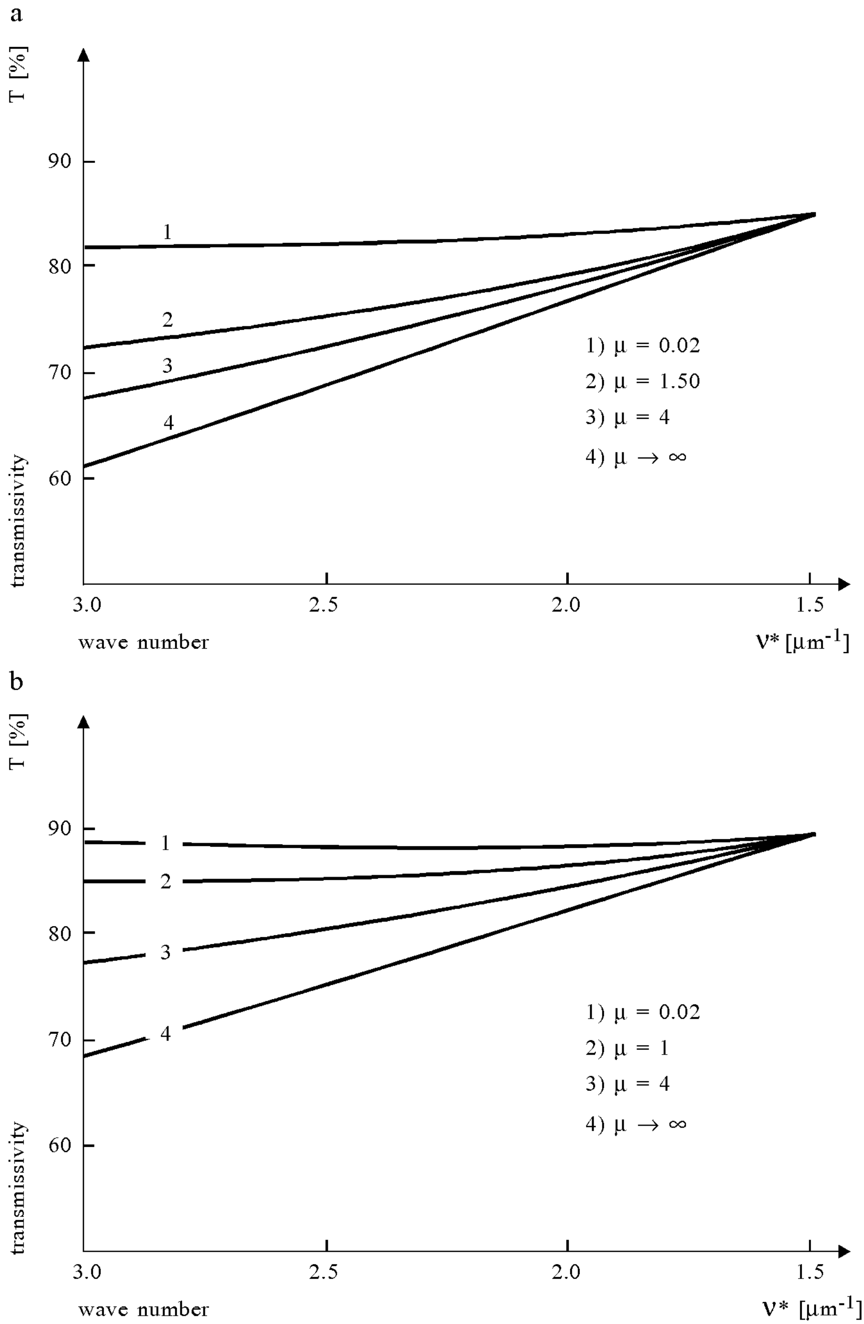

Fig. 3. Dependence of the transmission spectra in the visible light region for polydispersive Baltic oil-seawater emulsions on the parameter μ; $\bar{r} = 0.3\,\mu$m (a), $\bar{r} = 0.6\,\mu$m (b)

Fig. 2 illustrates the influence of the distribution width on the transparency function. For very broad distributions $\Theta_\mu(x)$ has a poorly visible maximum. As the width decreases within the same interval of values of x, additional, distinct maxima appear with concurrently steepening slopes $d\Theta_\mu(x)/dx$. It follows that the transparency spectrum of an emulsion made up of large particles need not depend on the wavelength of the incoming light for every degree of polydispersion. On the contrary, the pronounced spectral dependence of the LAC indicates that the emulsion contains small particles and may serve as an information source about their statistical distribution parameters.

Fig. 3 represents the influence of the degree of polydispersion μ on the shapes of the transparency spectra. Emulsions consisting of Baltic oil with droplets of different mean radii r were sampled. For clarity, all the spectra have been normalised to 90% transparency at $\vartheta^* = 1.5\,\mu$m. It is seen that an increase in μ (for the same radius) makes the spectrum more neutral. The smaller the value of r, the more pronounced the spectral dependence of the LAC becomes (for the same width).

2.3. Experimental details

The emulsions of Baltic crude oil (density 0.791 g cm^{-3}, relative refraction index 1.089 (Stoń and Wrembel, 1990)) in artificial Baltic water were produced by means of ultrasonic dispersing agent UD 20. Although the dispersion frequency was much higher than the frequency of comminution of the surface film by the moving sea, it did enable a stable emulsion to be obtained rapidly as a result of the long-term action of wind-generated waves. At the same time, short-term changes in the optical properties of the oil itself were eliminated. In the course of dispersion, part of the oil was observed to precipitate in the form of clots. The method of preparing the emulsion is described in detail in Stoń (1990).

The transmission spectra were measured on a SPECORD UV–VIS spectrophotometer. Tab. 1 shows the data obtained for the spectrum of a freshly-made emulsion containing 73 mg of crude Baltic oil in 1 dm^3 of Baltic sea water. This spectrum will be used later to determine the polydispersive structure of that emulsion.

3. Selection of the distribution parameters

For any emulsion the parameters r_o and μ of its size distribution, together with its concentration N are assumed constant. Therefore, the ratio of two values of LACs with different ϑ^* is equal to that of the transparency functions (Stoń and Shifrin, 1990)

$$b(\vartheta_i{}^*)/b(\vartheta_1{}^*) = \Theta_\mu(x_i)/\Theta_\mu(x_1) \equiv \Theta_i/\Theta_1. \tag{13}$$

Table 1. Quantities characterising the emulsion investigated

Wave number	Wave length	Transmissivity	Normalised transparency function
$\vartheta^*[\mu^{-1}]$	λ [nm]	$T(\vartheta^*)$ [%]	Θ_i/Θ_1
1.5	666.7	57.0	1.000
1.6	625.0	53.0	1.129
1.7	588.2	49.0	1.269
1.8	555.6	46.0	1.381
1.9	526.3	43.0	1.501
2.0	500.0	40.0	1.630
2.1	476.2	37.0	1.769
2.2	454.5	34.0	1.919
2.3	434.8	31.5	2.055
2.4	416.7	29.5	2.172
2.5	400.0	27.0	2.329
2.6	384.6	25.0	2.466
2.7	370.4	23.0	2.615
2.8	357.1	21.0	2.776
2.9	344.8	19.0	2.954
3.0	333.3	17.5	3.101

Bearing in mind the constancy of the relative refraction index m over the whole visible-light range, the ratios of the wave numbers can be replaced by the ratios of the corresponding parameters x

$$\vartheta_i{}^*/\vartheta_1{}^* = x_i/x_1. \tag{14}$$

The information on the emulsion structure, *i.e.* on the values of r_o and μ, is obtained by comparing two relationships – the measured value of $b(\vartheta_i{}^*)/b(\vartheta_1{}^*)$, and the theoretical one Θ_i/Θ_1 taken from (10). This comparison is optimised by the choice of parameter μ in the probability function

$$F(\mu) = \sum_n (Y_{T_n} - Y_{E_n})^2, \tag{15}$$

where the summation includes all the measured wave-number data (T_n and E_n denote the theoretical and experimental values respectively). Such a model is selected in which $F(\mu)$ has the sharpest minimum and which at the same time does not exceed the value of δF resulting from the measurement accuracy

$$\delta F(\mu) = 2\sum_n (Y_{T_n} - Y_{E_n})\delta Y_{E_n}. \tag{16}$$

When $Y_{E_n} = b_i/b_1$,

$$\delta Y_{E_1} = Y_{E_1}\left(\frac{\delta b_i}{b_i} + \frac{\delta b_1}{b_1}\right). \tag{17}$$

The values of $\delta b_i = \delta b_1$ are determined by the precision of the transparency measurements δT.

4. Determination of the emulsion structure

The method of determining the emulsion structure outlined above was applied to suspensions of Baltic oil in Baltic seawater. The transmission spectrum $T(\vartheta^*)$ of the stable emulsion is given in Tab. 1. According to the demands of the method, $T(\vartheta^*)$ is transformed into the spectrum of the relative transparencies $Y_{E_n} = b_i/b_1$ and compared with the theoretical relationship $Y_{T_n} = \Theta_i/\Theta_1$. Analysis of the behaviour of $F(\mu)$ (15) shows that, within the bounds of error δY and with the measurement accuracy $\delta T = 0.5\%$, an emulsion can have several values of μ for which $F(\mu)$ is a minimum (Fig. 4). The value of δF illustrates the measurement errors. Fig. 4 also shows the relationship of $\Delta x(\mu)$, where Δx indicates the range of possible values of x_1 at the level of measurement error δF.

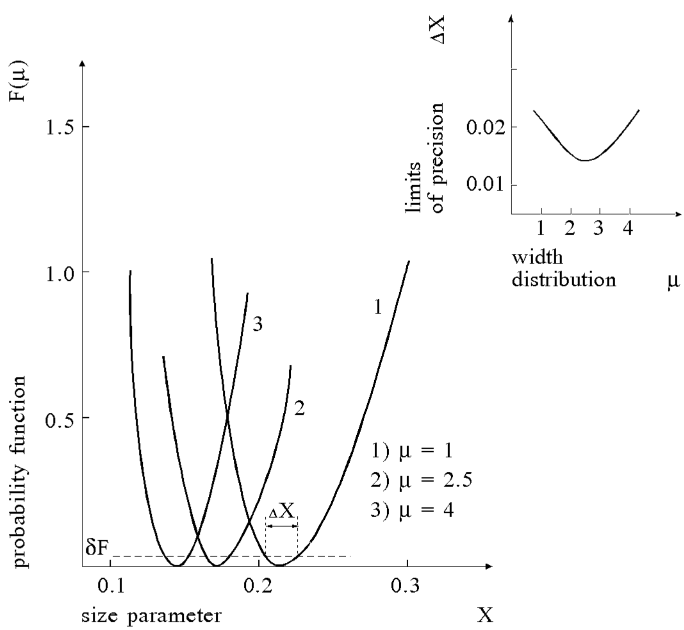

Fig. 4. Dependence of the probability function $F(\mu)$ on the size parameter x for various values of the statistical distribution width μ

On the basis of Fig. 4 the following conclusion can be drawn: for the emulsion under consideration, the most probable parameters are $\mu = 2.5$ and $x_1 = 0.17$. Taking $\vartheta_1{}^* = 1.5\,\mu$m, the modal radius $r_o = \mu x_1/4\pi(m-1)\vartheta_1{}^* = 0.253\,\mu$m is obtained. These dimensions are in good agreement with the data of other workers (Lapshin *et al.*, 1990). In the present study it was shown that after the oil was stirred magnetically in water (volume ratio 1:1000) for 1 hour, droplets 0.1 mm in radius were found to be in the top water layers, while the 1 μm droplets remained in the bottom layers.

The number of oil droplets with a mean radius $r = (\mu + 1)r_o/\mu$ in unit volume is $N = b(\vartheta_1{}^*)\mu^2/2\pi r_o^2(\mu+2)(\mu+1)f(m)\Theta_1$. The droplet distribution according to size is shown in Fig. 5 by the solid line (the optimum solution); the area between the broken lines contains all the distribution functions lying within the limits of uncertainty of selection of the properties of parameter x_1.

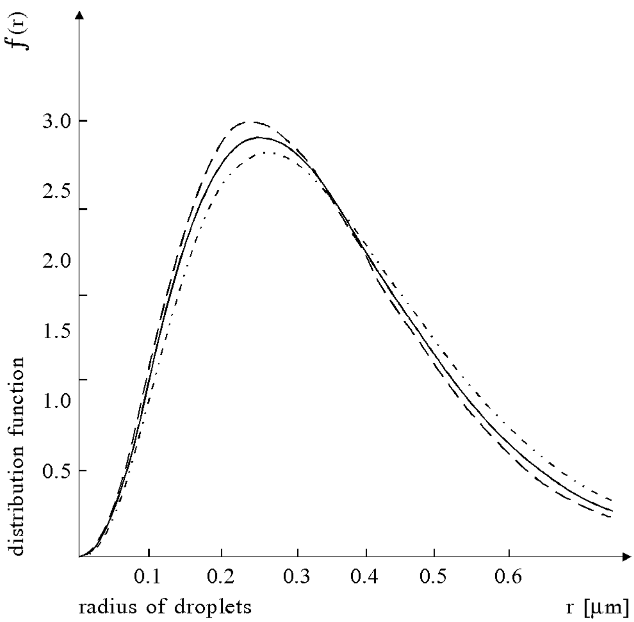

Fig. 5. Droplet size distribution in the Baltic oil emulsion investigated

The calculated mass concentration for the emulsion in question

$$C = \frac{4}{3}Nd\int_o^\infty f(r)r^3dr, \tag{18}$$

d (density of the oil) is equal to 67.1 mg dm^{-3} and is in good agreement with the concentration applied (73 mg dm^{-3}).

5. Summary and conclusions

This paper describes a method for determining the structure of polydispersive oil-seawater emulsions by measuring transmission spectra in the visible-light region. The choice of this spectral range is justified by the fact that light absorption is small there, the minimum being at $\lambda = 480$ nm.

It has been shown that the shape of the spectrum $T(\vartheta^*)$ is influenced not only by the sizes of the scatttering particles but also by the widths of their statistical distribution.

Matching $T(\vartheta^*)$ by means of the least squares method with the theoretical transparency function allows several pairs of distribution parameters μ, x to be defined. However, the choice of optimum pair, applied to the transformation of the transmission spectrum into a scattering-particle spectrum, enables an additional narrowest minimum criterion (minimal χ^2 criterion) to be found.

It should be noted that expression (10) was derived on the assumption that μ can take any positive value. However, in Shifrin and Perelman (1963) the transparency function of the polydispersive system was described by two different relationships only for whole, odd and for whole, even values of μ.

The spectral dependence of $\Theta_\mu(x)$ can be used for further investigations of solutions containing particles < 1 μm in size, which are not visible under the optical microscope. For larger particle sizes the transmission spectrum does not depend on the wavelength. The structure of sets containing particles the dimensions of which are of the order of micrometers or more must be determined by investigations of light scattered at small angles (Shifrin, 1983) and possibly by microscopic methods (Gurgul, 1986).

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