Light scattering in crude oil—sea water colloidal systems*

JADWIGA MROZEK-LEJMAN
Pedagogical College
Szczecin

ANDRZEJ ZIELIŃSKI, TADEUSZ KRÓL
Polish Academy of Sciences, Institute of Oceanology
Sopot

KONRAD WITKOWSKI
University of Gdańsk, Institute of Physics
Gdańsk

Manuscript received April 17, 1984, in final form December 21, 1984.

Abstract

A method of determination of time-dependent changes in structure of solutions of crude oil in artificial sea water as a function of selected physical parameters is presented in the paper. The changes can indirectly reflect some of the processes of self-purification of the sea environment polluted with soluble and emulsified crude oil derivatives. The method, which has been laboratory-tested for colloidal solutions of crude oil in artificial sea water, utilizes the light scattering phenomenon for the determination of concentration and average size of oils droplets.

1. Introduction

Increasing amounts of pollutants of crude oil origin introduced to the marine environment can result in unpredictable changes leading to total degradation of this environment. This concerns mainly those petroleum components which undergo dispersion under the influence of meteorological and hydrological factors, forming emulsions and colloidal systems in the marine environment. These fractions remain in sea water for a long time, filling water depths down to 400 m [13]. The components of these fractions have toxic and carcinogenic properties [1,6] and constitute a direct or indirect threat to biosphere.

The indirect factors degrading the marine environment include:
— disturbance of the balance of gases exchange, water vapour and solar energy at the sea-atmosphere interface,

— formation of toxic compounds as a result of chemical reactions,

— disturbance of the hydrosphere composition through chemical bonding of essential nutrients.

These factors also have a decisive effect on the dynamics of self-purification processes of the marine environment. However, these processes are little recognized and, particularly for crude oil-sea water colloidal systems, the mechanisms of the influence of physical and chemical factors on their dynamics are unknown.

One of the methods of investigation of the structure and dynamics of changes of such a system can be a method utilizing the light scattering phenomenon. The method permits to determine time-dependent changes in the average size of small droplets and the concentration of crude oil in a colloidal solution. The changes are due to various external factors, the effect of which is revealed in the shape and absolute values of the light scattering function $\beta(\theta)$ volume.

The knowledge of scattering properties of these systems is also primary importance for modelling the light field over and below the surface of the sea polluted with crude oil. The determination of light field forms the basis for selection of suitable passive remote methods of monitoring of sea pollution of this type.

2. Preparation of solutions

The experiments were carried out with colloidal solutions of crude oil in artificial sea water. B-type sea water of the salinity $S = 35^o/_{oo}$ and pH = 8.2 was prepared according to the PN-66/C-065502 standard [8].

Crude oil was introduced into artificial sea water in the 1 : 80 volumetric ratio and emulsified using an electric stirrer and an ultrasonic vibratoı operating at the frequency $f = 22$ kHz. After defined stirring time, the emulsion formed was filtered through a sintered glass filter R4 ($d = 5 - 15 \cdot 10^{-6}$ m) and placed in closed glass bottles of capacity $v = 2.8 \cdot 10^{-4}$ m³. Filtering process aimed at separation of dissolved and colloidal phases. The solutions prepared in this manner were stored in a thermostated compartment at $T = 291$ K. Some of the samples were exposed to light of the intensity $I = 31$ Wm^{-2}. The light source were Polam Double Light fluorescent tubes placed in a manner ensuring uniform illumination of all samples [7]. The remaining samples were stored in darkness.

3. Apparatus

The measurements of intensity of scattered light were carried out by means of the apparatus designed at the Division of Technical Physics of the Gdańsk University and described in detail elsewhere [11, 12]. A schematic diagram of the apparatus is shown in Figure 1. The light source Z is a He-Ne laser of power $P = 10$ mW, generating a light beam of minimum divergence. After passing through a system of

lenses L and diaphragms D_1 the beam is directed to a measuring dark chamber by means of fibre optics. Fibre optics is used in order to depolarize and collimate the beam to the desired dimensions optical filter F, polarizing prism P and diaphragm system D_2) and to eliminate light scattering on dust particles contained in the air. The beam formed in this manner enters a quartz cell containing the investigated solution. The cell is ideally flat-parallel for the incident beam and cylindrical for scattered light. A system of thermostats $A_1 - A_3$ provides temperature stabilization in order to maintain identical conditions of measurements.
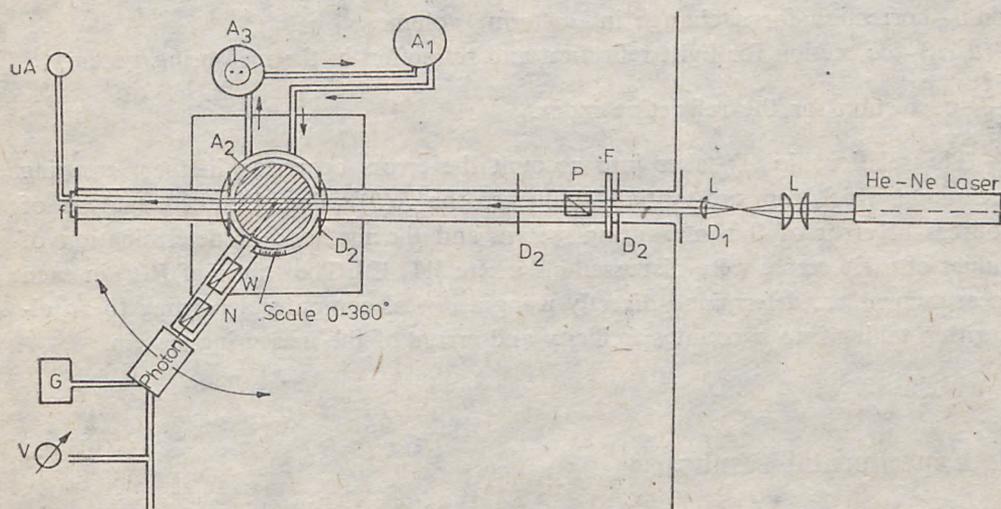

Fig. 1. Schematic diagram of the apparatus for the measurment of scattered light intensity

The incident beam passing through the measuring cell leaves the chamber through a collecting fibre optics containing in its circuit a photomultiplier for the measurement of the initial beam intensity. Scattered light passes through a Wollastone prism W or, alternatively, through a Glan prism N and is recorded by a photomultiplier.

A system recording scattered light is placed on a rotational optical bench, which can rotate around a vertical axis passing through the center of the measuring cell. During rotation of the bench the cell remains motionless. This design allows the measurement of intensity of light scattered in various directions ($\theta = 1 - 155$ deg). The knowledge of reduced scattered intensity light for the angle $\theta = \pi/2$ is essential in these measurements. It can be determined from the ratio of the intensity of light scattered at the right angle by the investigated sample to the intensity of light scattered by a standard of known absolute value of $I(\lambda, \pi/2)$. Carbon tetrachloride CCl_4, for which the absolute value of scattering cross-section for $\lambda = 632.8$ nm is equal to $R_{CCl_4} \pi/2 = 2.95 \cdot 10^{-4}$ m^{-1}, was used as a standard in the present investigations.

The absolute values of cross-section $R(\theta)$ for the investigated solution were determined from the relationship:

$$R(\theta) = \frac{I(\theta)}{I_s(\pi/2)} R_s \sin \theta f(\theta, n_0) \frac{\tilde{n}_0^2}{\tilde{n}_s^2}, \tag{1}$$

where:

$I(\theta)$ — intensity of light scattered by the investigated solution at the angle θ,

$I_s(\pi/2)$ — intensity of light scattered at the angle $\theta = \pi/2$ by the standard,

R_w — absolute value of cross-section for the standard ($\theta = \pi/2$),

$\sin \theta$ — correction for a change in scattering volume,

$f(\theta, n_0)$ — correction for light reflection and refraction in the measuring system,

$\dfrac{\tilde{n}_0^2}{\tilde{n}_s^2}$ — correction for the refractive index.

The relationship (1) takes into account the errors occurring in the measuring technique which can substantially influence the $R(\theta)$ value. Detailed analysis of sources of error of this measuring system and the methods of determination of values of these errors were discussed elsewhere [11, 12]. The values of $R(\theta)$ in each measurement are determined directly using a digital computer according to an algorithm taking into account specificity and errors of the measuring system.

4. Experimental results

Three series of colloidal solutions differing in emulsification time t_m, which was equal to $t_m = 900$, 1800, and 3600 s, respectively, were prepared for the experiments. Each solution was divided into two portions, one of which was stored in darkness whereas the other one was exposed to light. The observation time for all the samples was $t_e = 7$, 14, 21, and 28 days.

The measurements of values of the light scattering function β at the angle ranging from $\theta = 20°$ to $155°$ were carried out for each series directly after preparation of the samples and after various observation time.

Exemplary results of the determination of this function for the colloidal solution of $t_m = 900$ s and varying time t_e are depicted in Figure 2. Figure 2b illustrates the results of measurements for the samples of the same solution stored in darkness. Figure 3a shows the measured values of the function β for the colloidal solutions of $t_m = 3600$ s and various time t_e. The values of the β function for the samples of the same t_m stored in darkness are presented in Figure 3b. The experimental values of the $\beta_n(\theta)$ function shown in Figures 2 and 3 are given in the form reduced to the value of the $\beta_n(\pi/2) = 1$ function. The course of the $\beta_n(\theta)$ function for the remaining samples is of identical character. The observed differences consist mainly in the change of the absolute values of the $\beta_n = \beta_n(\theta)$ functions and, to a smaller extent, in the change of shape of this function.
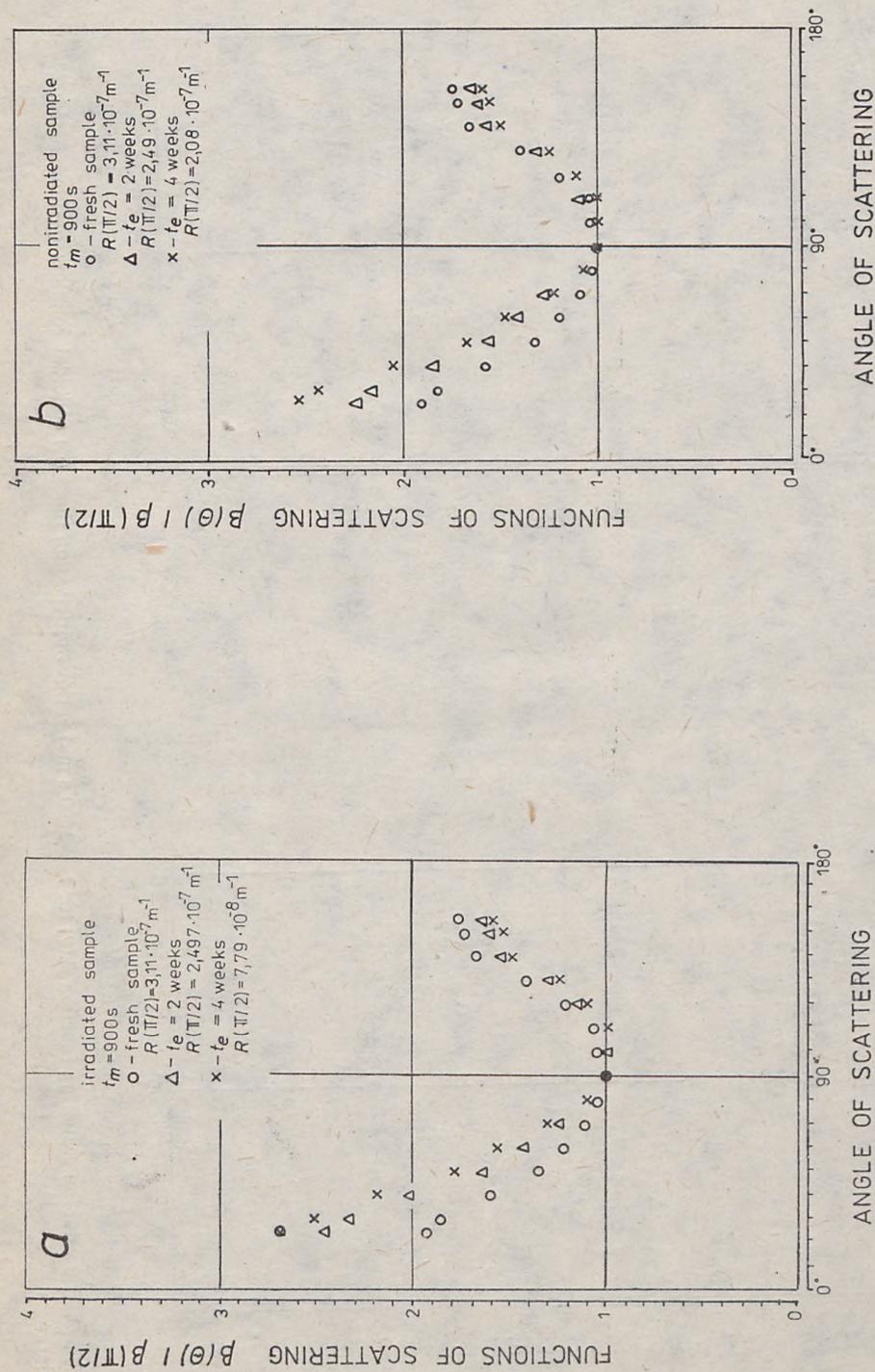
Fig. 2. The values of scattering function $\beta_n(\theta)$ for $t_m = 900$ s and various observation times (t_e) colloidal solution: a—illuminated; b—stored in the darkness
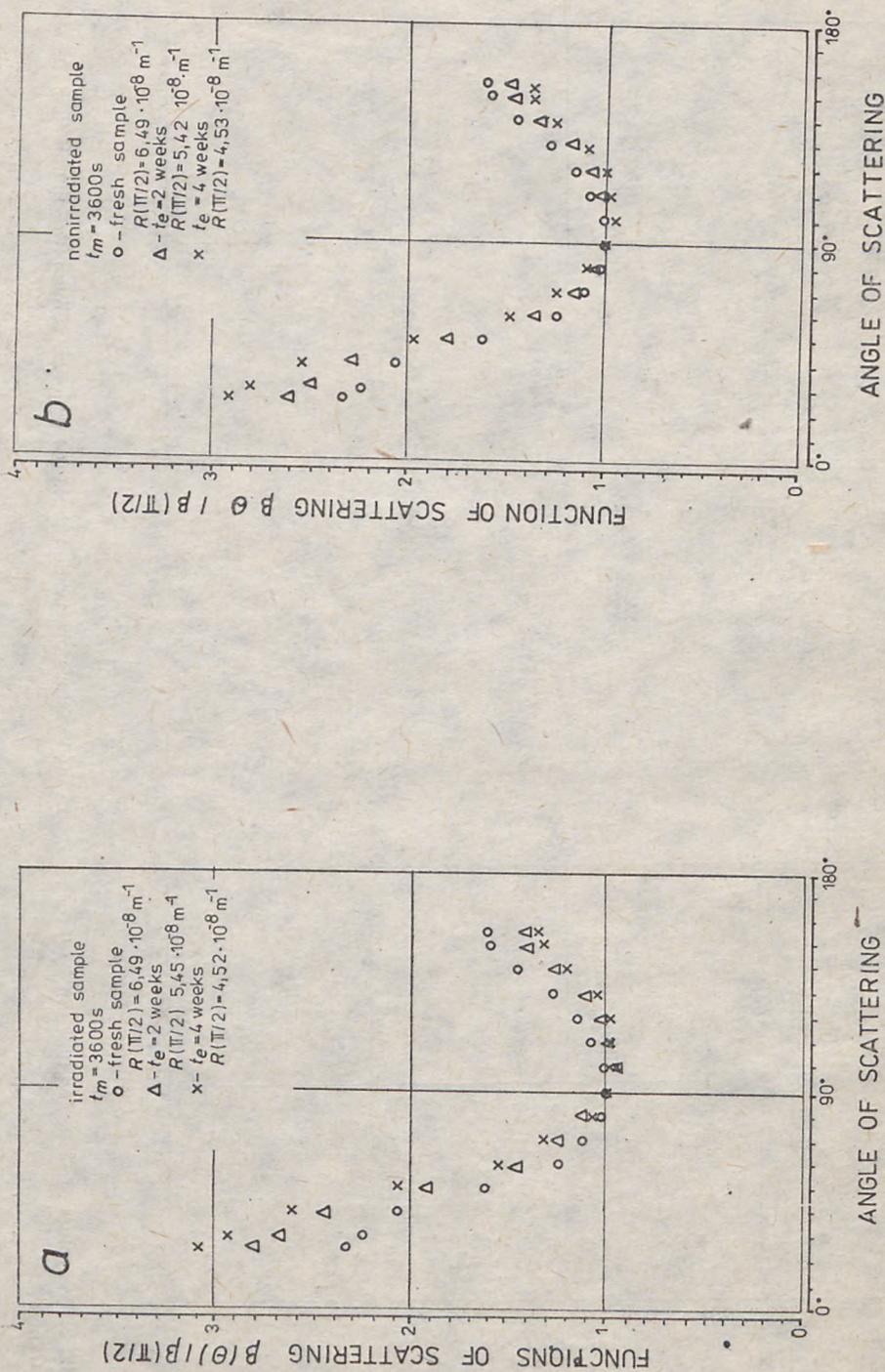
Fig. 3. The values of scattering function $\beta_n(\theta)$ for $t_m = 3600$ s and various observation times (t_e) colloidal solution: a — illuminated; b — stored in the darkness

5. Discussion

The method of preparation of crude oil colloidal solutions in artificial sea water presented in section 2 determines the size distribution of crude oil particles.

Treating in further considerations crude oil particles as spherical, the maximum size of these particles can be calculated. For the investigated solutions this maximum size was estimated as $r_m \simeq 2 \cdot 10^{-6}$ m. However, the number of oil particles of this size in the solution is very small, because during filtration the effective size of pores of the sintered glass filter R4 decreases rapidly due to sedimentation of oil droplets. Hence, the average particle size is considerably smaller than r_m and can be determined to a good approximation by comparison of the experimental distribution of the $\beta_n(\theta)$ function with theoretical variability of this function. Theoretical values of the normalized function $\beta_n(\theta)$ can be determined on the basis of Mie solution or, less accurately but much easier, by means of the Rayleigh-Gans model for the so-called 'soft particles'.

According to this model, the β function for light scattered at an arbitrary angle with respect to the direction of unpolarized monochromatic incident beam is described by the relationship:

$$\beta(\theta) = K(1 + \cos^2 \theta)\left[\frac{3}{u^3}(\sin u - u\cos u)\right]^2, \tag{2}$$

where: K — proportionality factor; $u = \frac{2\pi r}{\lambda}\sin(\theta/2)$. The value of the proportionality

constant K depends on the intensity of incident light I_0, sizes and concentration of scattering particles and their refractive index.

For the function $\beta(\theta)$ normalized to $\beta_n(\theta)$ and determined experimentally according to equation (2), the following dependence is valid:

$$\beta_n(\theta) = \frac{\beta(\theta)}{\beta(\pi/2)} = \frac{(1 + \cos^2\theta)\left[\frac{3}{u^3}(\sin u - u\cos u)\right]^2}{\left[\frac{3}{u_{\pi/2}^3}(\sin u_{\pi/2} - u_{\pi/2}\cos u_{\pi/2})\right]^2}, \tag{3}$$

where: $u_{\pi/2} = \sqrt{2}\dfrac{\pi r}{\lambda}$.

The function $\beta_n(\theta)$ defined in this manner eliminates unknown proportionality constant K and describes the investigated cases for which the relative refractive index of crude oil in water (n_r) is close to $n_r \simeq 1.1$. The values of the $\beta_n(\theta)$ function calculated from equation (3) and normalized to unity for $\theta = \pi/2$ are presented as a function of the crude oil particle size r in the form of a set of curves in Figure 4.

The approximate values of the average radius of crude oil droplets in the solution can be determined by comparing the experimental and theoretical $\beta_n(\theta)$ functions. The comparison of these functions consists in assigning to a set of experimental
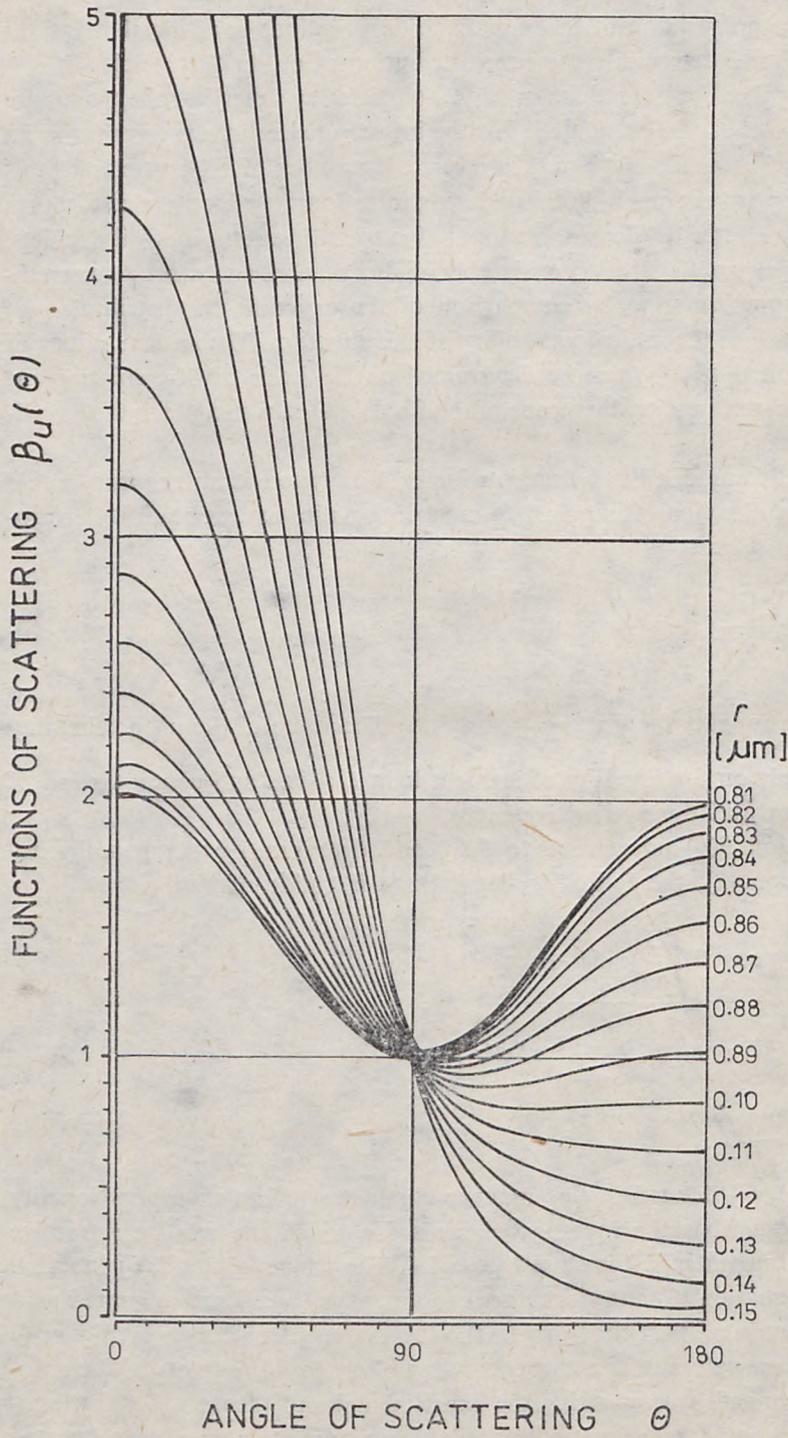
Fig. 4. The results of theoretical calculations of reduced light scattering function for various radii *r* of crude oil droplets in artificial sea water of $s = 35^0/_{00}$, $\lambda = 632.8$ nm
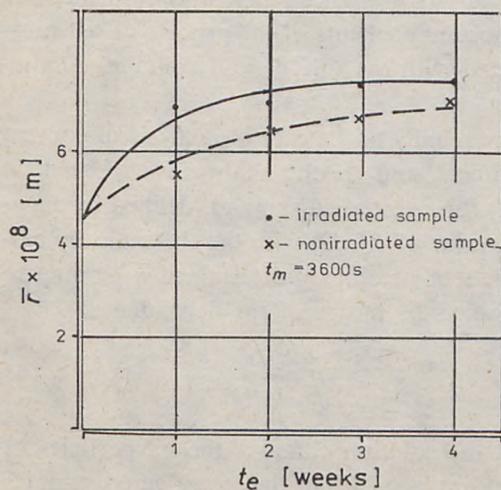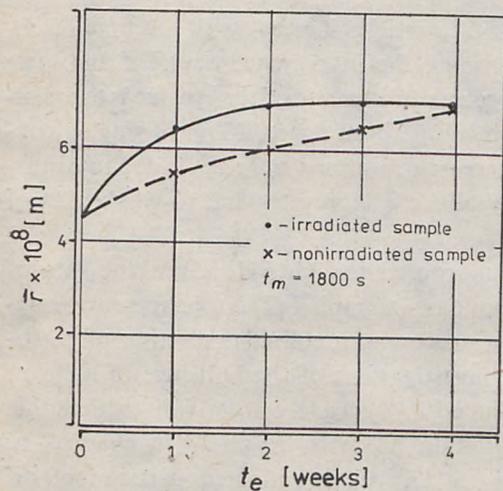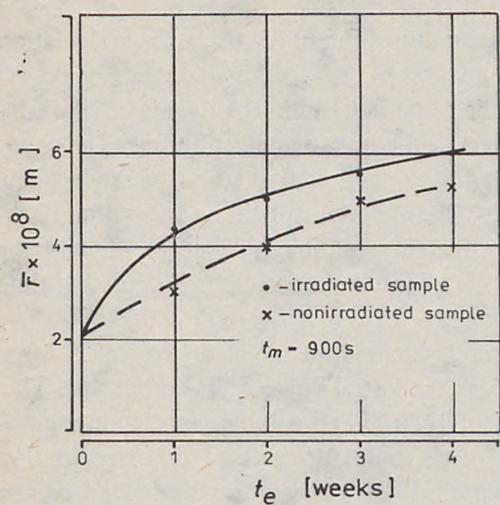
Fig. 5. The change in average radius $\bar{r}$ of crude oil droplets in colloidal solution of various t_m as a function of observation time (t_e) for samples illuminated and stored in the darkness

points a theoretical curve (Fig. 4) of a given radius r, for which the average deviation between the experimental values is the smallest.

Application of such a procedure permitted to determine the dynamics of variation of the average size of crude oil droplets in the investigated solutions. The changes of an average radius $\bar{r}$ of oil droplets for the colloidal solution of crude oil in artificial sea water of $t_m = 900$, 1800, and 3600 s, exposed to light and stored in darkness, are depicted in Figure 5. In all investigated solutions the average value of the radius $\bar{r}$ is the smallest for samples immediately after preparation. The mixing time t_m influences the initial value of $\bar{r}$.

As follows from comparison of Figures 5 sections the effect of time t_m is large for times $t_m < 1800$ s. For times $t_m > 1800$ s, the initial value of $\bar{r}$ is constant. This effect can be associated with evaporation of volatile and soluble petroleum components during the process of mixing. Thus, it should be expected that the limiting value of time t_m influencing the process of crude oil dispersion will depend on the kind of the investigated oil.

For illuminated samples the $\bar{r}$ value of oil particles increses with the time of observation t_e. The increase is monotonic for all the investigated samples and after $t_e = 7$ days $\bar{r}$ reaches a steady value. The process of increase of the $\bar{r}$ value is associated mainly with the cohesion forces, which bring about aggregatilon of single droplets into larger clusters. Inhibition of the increase of $\bar{r}$ after $t_e > 7$ days is due to disturbance of the condition of floating stability of these aggregates and to weakening of the cohesion forces interaction.

Identical processes occur in samples unexposed to light. However, the rate of these processes is lower than for the illuminated samples. This phenomenon suggests the effect of light on the coagulation process of a colloidal solution of petroleum. It has been demonstrated in earlier investigations of the influence of light on physical properties of sea water contaminated with crude oil derivatives that this phenomenon is associated with photooxidation processes resulting in changes of physical and chemical structure of crude oil [7, 10]. Illuminated particles of oil tend to aggregate more rapidly, forming clusters of higher sedimentation or floating rate. This constitutes one of the most important elements of the process of self-purification in the marine environment polluted with the soluble and colloidal components of petroleum.

These tendencies can be observed more readily in the case of analysis of content of these contaminants as a function of time t_e and t_m. the analysis was based on knowledge of the absolute value of $R(\pi/2)$ for the studied samples, defined by equation (1). Comparison of the experimental value of $R(\pi/2)$ with the theoretically calculated scattering functions for the droplets of previously determined $\bar{r}$ permits to estimate the concentration N of these droplets by means of the dependence:

$$N = \frac{\pi R_{CCl_4}(\pi/2)}{\lambda^2} \frac{R(\pi/2)}{\beta(\bar{r}, \pi/2)}. \tag{4}$$

Knowing the N value and assuming that the solution contains the oil particles of the radius $\bar{r}$, the volume concentration of crude oil C_v in the investigated samples
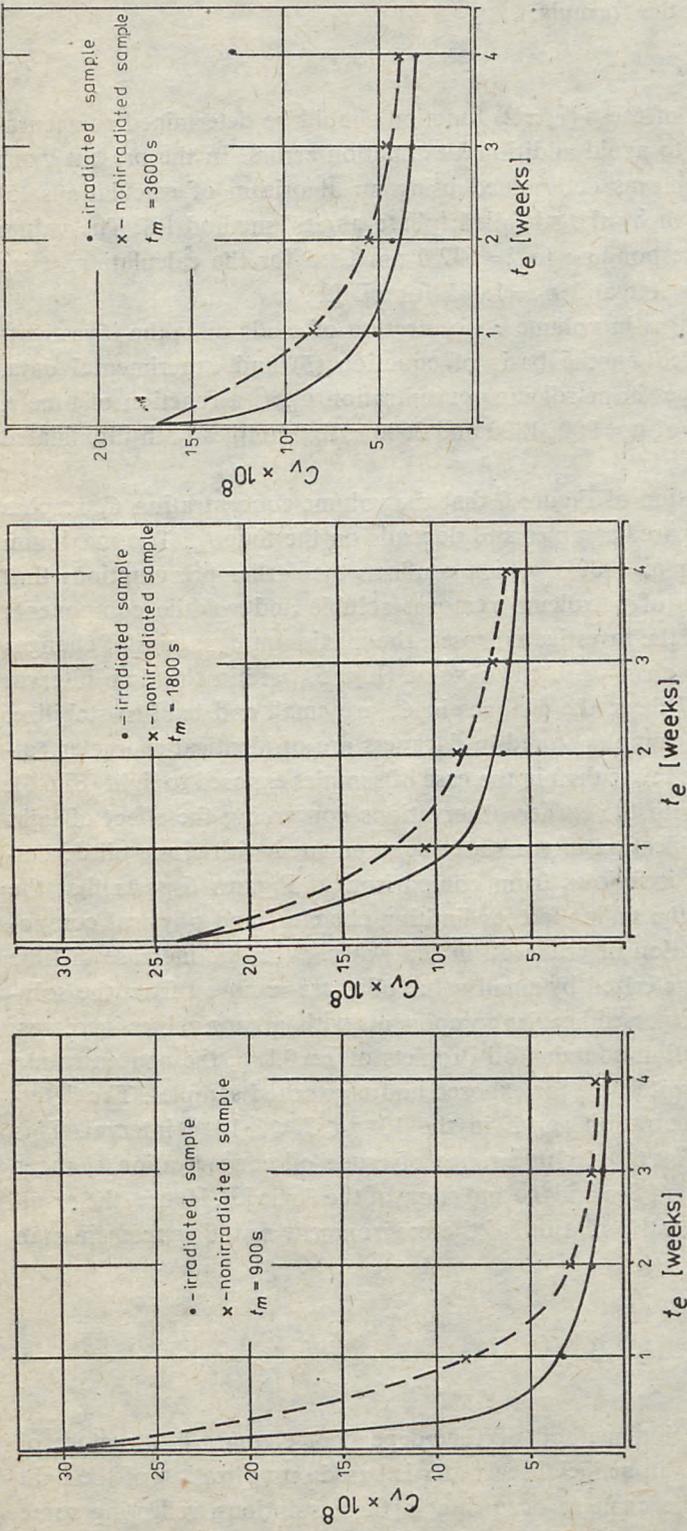
Fig. 6. The effect of observation time (t_e) on the volume concentration of crude oil in colloidal solution of various t_m for samples illuminated and stored in the darkness

can be calculated from the formula:

$$C_v = \frac{4}{3}\pi N \bar{r}^{-3}. \tag{5}$$

The theoretical value of the $\beta(\bar{r}, \pi/2)$ function should be determined as accurately as possible in order to avoid additional estimation errors. In the present work the value of the function was determined using an algorithm of calculations (5) based on full Mie solution by the so-called 'phase angles' method [4]. The values of refractive indices corresponding to $\lambda = 632.8$ nm used for the calculations were equal to $n_w = 1.338$ for water and $n_0 = 1.485$ for oil [9].

The dynamics of changes in volume concentration of crude oil in the investigated samples was calculated on the basis of equation (5) and experimental data. Figure 6 shows the changes in petroleum concentration C_v as a function of time t_e for the colloidal solution of $t_m = 900$, 1800 and 3600 s, for samples both illuminated and stored in darkness.

It follows from inspection of Figure 6 that the volume concentration C_v reaches maximum for freshly prepared samples and depends on the time t_m. The maximum C_v value was achieved for $t_m = 900$ s, which confirms the earlier presumptions that the emulsification process of petroleum removes soluble and volatile components from the solution. For all the investigated cases, the maximum dynamics of changes in C_v occurs, similarly to changes in the $\bar{r}$ value (Fig. 5), within the time interval $t_e \in [0,7 \text{ days}]$. After $t_e > 7$ days, the changes in C_v are small and tend to stabilize.

The changes in C_v for samples stored in darkness are of identical character, although the rate of change is lower than in the case of samples exposed to light (Fig. 6). This result is consistent with the earlier observations concerning the effect of light on the process of self-purification of sea water contaminated with crude oil derivatives [7, 10]. In addition, it follows from comparison of Figures 6 parts that the mixing process is one of the major factors limiting chemical and physical composition of the colloidal solution of crude oil in sea water. With the increase in time t_m light components, characterized by small value of r, are removed from the solution while the content of dispersed heavier components with larger r values increases. After $t_e > 21$ days the solution contains oil droplets of $\bar{r} \simeq 0.8 r_K$, the concentration of which does not change with time for exposed and unexposed samples. The determined value of this concentration varies in the $10^{-8} \leqslant C_v \leqslant 6 \cdot 10^{-8}$ interval. This result falls within the $10^{-9} < C_v < 2 \cdot 10^{-7}$ range of crude oil concentration changes determined for the clean Kara Sea and ice and snow of the Artic [3]. Hence, the result can be consisdered as natural pollution of the environment resulting from human technological activity.

6. Final remarks

The proposed investigation method of time-dependent changes in structure of colloidal crude oil solutions in artificial sea water is based on utilization of the light scattering phenomenon. The changes occurring in these solutions, reflecting some

of self-purification processes of the marine environment, are manifested in the absolute values and the shape of volume scattering function $\beta(\theta)$. For this reason, the method permits to study the dynamics of these processes in terms of various external physical parameters. Thus, the presented version of the method provides in a relatively simple manner numerous new informations required for a complete mathematico-physical model describing the process of self-purification of the marine environment contaminated with soluble and emulsified crude oil derivatives.

The obtained values of the average oil droplets size $\bar{r}$ and the volume concentration C_v are accompanied by some errors resulting from the proposed method of calculating the results. These errors can be partially eliminated if the average value of the oil droplets radius r is calculated on the basis of knowledge of the function of radii distribution $f(r)$, which should be determined experimentally or theoretically. In both cases the problem is very difficult and requires very tedious investigations. The authors undertook preliminary studies aiming at theoretical determination of this function using a method of successive approximations based on the experimental results presented in this paper. The knowledge of this function will permit to determine the volume concentration C_v of fractions of various radii r_i and to monitor in time t_e the dynamics of removal of these fractions from colloidal solutions of crude oil in sea water.

References

1. Anderson I. W., Neff I. M., Cox B. A., Teteni H. E., Hightower G. M., 1974, *Characteristics of Dispersion and Water Soluble Extracts of Crude and Refined Oils and their Toxicity to Estuarine Crustaceans*, Fish. Mar. Bio., 27, p. 75—88.
2. Cwiełkow W. N., Eskin W. J., Frenkel S. J., 1970, *Struktura makrocząsteczek*, PWN, Warszawa.
3. Dmitriev F. A., Pivovarov S. W., 1983, *Uglievodorody v sniezno-liedieannom pokrovie i vodie v seviernoj chasti Karskovo Moria*, Meteorologija i Gidrologija, 5.
4. Hulst H. C., 1961, *Rassiejanije svieta malymi chasticami*, Izd. Inostrannoj Litieratury, Moskva.
5. Król T., *Prosty model obliczeniowy funkcji rozpraszania na kulistych cząsteczkach rozpraszających*, Stud. i Mater. Oceanolog., 45.
6. Larson R. A., Hunt L. L., Blankenship D. W., 1977, *Formation of Toxic Products from Fuel Oil by Photooxidation*, Environ. Sci. Technol., 11, p. 492—496.
7. Otremba Z., 1983, *Wpływ oświetlenia na zużycie tlenu przez oleje zemulgowane w wodzie morskiej*, Doctor's Thesis, WSM Gdynia.
8. Polska Norma PN-66/C-065502, 1966, *Zastępcza woda morska*, Pol. Komit. Normalizacyjny.
9. Popov I. N., Fiedorov K. N., Orłov W. M., 1979, *Morskaja voda*, Izd. Nauka, Moskva.
10. Tjessem K., Palmork K. H., 1984, *An overview of auto/photooxidation of petroleum in the marine environment*, Marine Chem. Working Group Meeting—Rostock.
11. Woliński L. M., 1968, *Bemerkungen zur Schwankungstheorie der Lichtstonung in Flüssigkeiten*, Optik, 27, p. 558—569.
12. Woliński L. M., 1972, *Rozpraszanie światła i związane z nim badania właściwości fizyko-chemicznych cząsteczek*, Wyd. Uniw. Gdań.
13. Zhurbas W. M., 1978, *Osnovnyje mechanizmy rasprostranienija nefti v morie*, Mech. Zhidkosti i Gaza, 12.