

NANOPARTICLE MIXTURES OF ANTHRACENE AND β -CYCLODEXTRIN TESTING BY OPTICAL SPECTROSCOPY

Alexandra Bezrukova¹, Monika Lubomska² and Marek Rogalski²

¹ Faculty of Medical Physics and Bioengineering, St. Petersburg State Polytechnical University, Polytekhnicheskaya 29, St. Petersburg 195251, Russia

² Laboratory of Thermodynamic and Chemical Analysis, University of Metz, 57045 Metz Cedex, France

Received: February 03, 2008

Abstract. This contribution reported the inverse optical problem solution for characterization of interactions between anthracene and different concentrations of β -cyclodextrin in water dispersions by optical spectroscopy: absorption spectra, integral static (time average) light scattering spectra, and intensity of differential static light scattering at 90 degrees. These measurements are compatible, nondestructive, and can provide information about the processes in "ill-defined" three-dimensional disperse systems (3D DS) with nanoparticle mixtures: aggregation and inclusion of anthracene in β -cyclodextrin.

1. INTRODUCTION

Interactions between anthracene [1-3] and β -cyclodextrin [4,5] are till now of great interest [6-10]. Mixtures of these molecules in water can be considered as nanoparticle three-dimensional disperse systems (3D DS). The 3D DS with nanoparticles as disperse phase are so called "ill defined" systems [11]. Light scattering is sensitive to the parameters and size distributions of the scattering particles. There are several modifications of light scattering method such as integral static (time average) light scattering, differential static light scattering, differential dynamic light scattering, etc. The solution of inverse optical problem for light scattering is "ill-conditioned" (i.e. there are many particle size distributions that correspond to similar scattering signal) [11,12]. That is why no one method of characterization by light scattering is absolute, but as sensitive tool it can be used for "ill defined" 3D DS control [13-17].

2. MATERIALS AND METHODS

Water mixtures of 3D DS with particles of anthracene (one concentration at all experiments, 0.025 g/l) with different concentrations of β -cyclodextrin particles were studied. The β -cyclodextrin concentrations in Moles per litre were the following: 1) $1.75 \cdot 10^{-6}$; 2) $8.75 \cdot 10^{-6}$; 3) $1.75 \cdot 10^{-5}$; 4) $8.75 \cdot 10^{-5}$; 5) $1.75 \cdot 10^{-4}$; 6) $8.75 \cdot 10^{-4}$; 7) $1.75 \cdot 10^{-3}$; 8) $8.75 \cdot 10^{-3}$ M/l. The mixtures of anthracene with different β -cyclodextrin concentrations were stabilised at room temperature with magnetic stirring for 48 hours. Extinction of light due to absorption and integral static light scattering was measured at Shimadzu UV 1205 spectrophotometer at wavelengths from 200 nm up to 700 nm. Aperture angle of photo receiver is 4 degrees. For solution of inverse optical problem for integral light scattering the "turbidity spectrum method [11] was used. Differential (at detector angle 90 degrees) laser (wavelength 633 nm) static light scattering was

Corresponding author: Alexandra Bezrukova, e-mail: bezr@PB1097.spb.edu

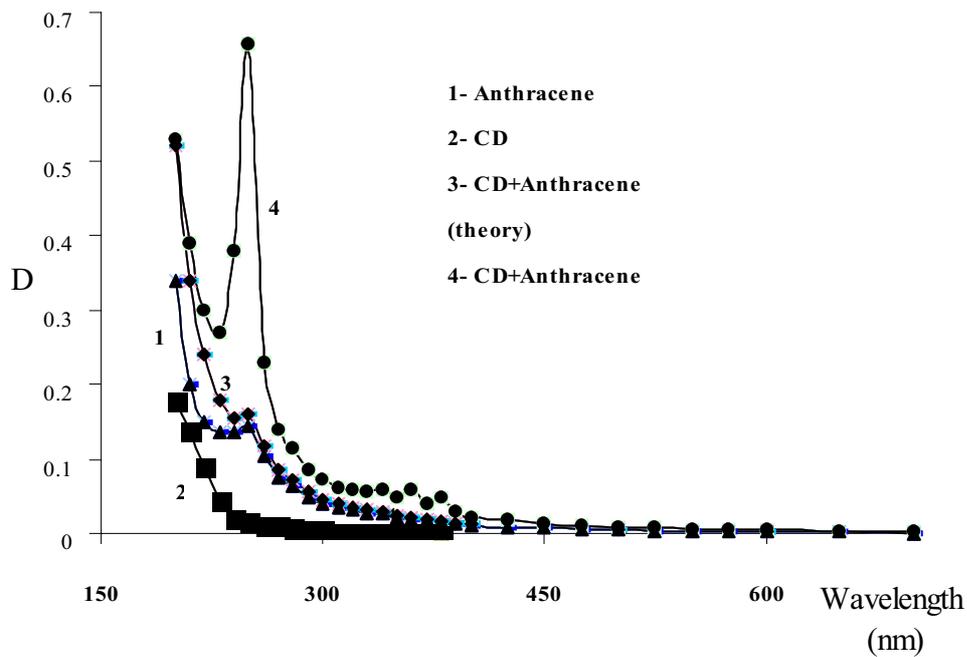


Fig. 1. Optical density dependence from wavelength (from 200 to 700 nm) for water 3D DS with nanoparticles of anthracene, β -cyclodextrin, and their mixture (at the same concentrations) measured at Shimadzu recording spectrophotometer (points are drawn for presentation). 1 - Anthracene; 2 - β -cyclodextrin at concentration – $8.75 \cdot 10^{-3}$ M/l; 3 - Mixture of anthracene and β -cyclodextrin at the same concentrations (theory - at the absence of interactions between particles of anthracene and β -cyclodextrin); 4 - Mixture of anthracene and β -cyclodextrin at the same concentrations (experiment).

measured at Malvern Autosizer 4700 with diaphragm 150 and temperature 25.0 °C.

3. RESULTS AND DISCUSSION

Optical density (D) spectra are presented in Fig. 1. The dependence $D(\lambda)$ is shown in the range of wavelengths λ (from 200 nm up to 700 nm) for water 3D DS with nanoparticles of anthracene (curve 1), β -cyclodextrin (at the highest concentration used in experiments - $8.75 \cdot 10^{-3}$ M/l - curve 2) and their mixture at the same concentrations (curves 3-4).

In general, it is possible to measure transmittance of light T at spectrophotometer

$$T = (I_1 / I_0) 100\%, \quad (1)$$

where I_1 and I_0 are the intensities of transmitted (outgoing through a cuvette) and incident light correspondingly. Optical density D (another names: absorbency A , extinction of light E) and turbidity τ are connected with T by formulas:

$$D = -\lg T = \lg(I_0 / I_1), \quad (2)$$

$$\tau = -\ln T / l = 2.3D / l, \quad (3)$$

where l is the length of optical way (length of a cuvette in cm).

Integral static (time average) light scattering is extinction of light due to scattering at all angles (except aperture angle of photo receiver). At the interval of wavelength λ , where there is no absorption of light, D is the measure of integral light scattering. For absorbing nanoparticles with effective diameter d comparable with λ at first approximation:

$$D(\lambda) = D_{sc}(\lambda) + D_{abs}(\lambda), \quad (4)$$

where $D_{sc}(\lambda)$ and $D_{abs}(\lambda)$ are the densities connected with scattering and absorption, correspondingly.

Fig. 2 presents in bilogarithmical scale optical density dependence from wavelength of 200 nm up to 700 nm for water 3D DS with studied nanoparticles. The slope of linear parts of spectra (there is no absorption of light from 400 to 700 nm) is so called wavelength exponent $n(\lambda)$ [11]:

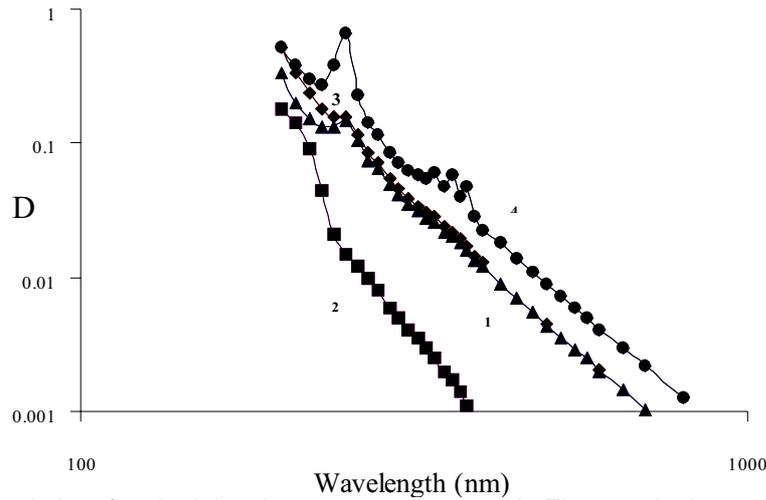


Fig. 2. Bilogarithmical plot of optical density spectra presented in Fig.1. 1- Anthracene; 2- β -cyclodextrin at the highest concentration used in experiments – $8.75 \cdot 10^{-3}$ M/l; 3- mixture of anthracene and β -cyclodextrin at concentration – $8.75 \cdot 10^{-3}$ M/l (theory - at the absence of interactions between particles of anthracene and β -cyclodextrin); 4 - Mixture of anthracene and β -cyclodextrin at concentration – $8.75 \cdot 10^{-3}$ M/l (experiment).

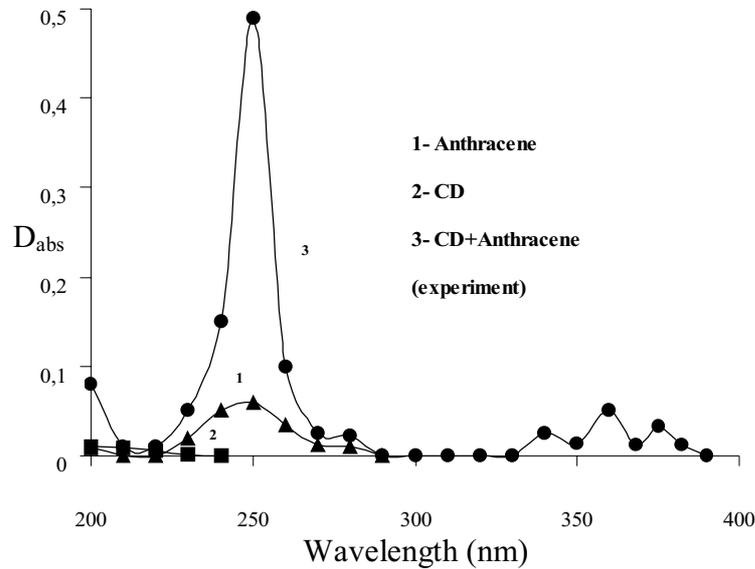


Fig. 3. $D_{\text{abs}}(\lambda)$ - absorption optical density spectra (from 200 to 400 nm) for water 3D DS with nanoparticles of anthracene, β -cyclodextrin and their mixture at the same concentrations. 1- anthracene; 2- β -cyclodextrin at the highest concentration used in experiments – $8.75 \cdot 10^{-3}$ M/l; 3- Mixture of anthracene and β -cyclodextrin at concentration – $8.75 \cdot 10^{-3}$ M/l (experiment).

$$n(\lambda) = -\partial \lg D(\lambda) / \partial \lg \lambda, \quad (5)$$

$n(\lambda)$ is a characteristic function of relative size of particles α , and relative refractive index of particles m :

$$\alpha = \pi a \mu_0 / \lambda, \quad (6)$$

$$m = \mu_p / \mu_0, \quad (7)$$

where λ is the wavelength in the middle of interval; μ_0 and μ_p are the refractive indexes of dispersive medium and disperse phase (particles), correspondingly. For particles in water as dispersive medium $\mu_0 = 1.33$ and the effective diameter:

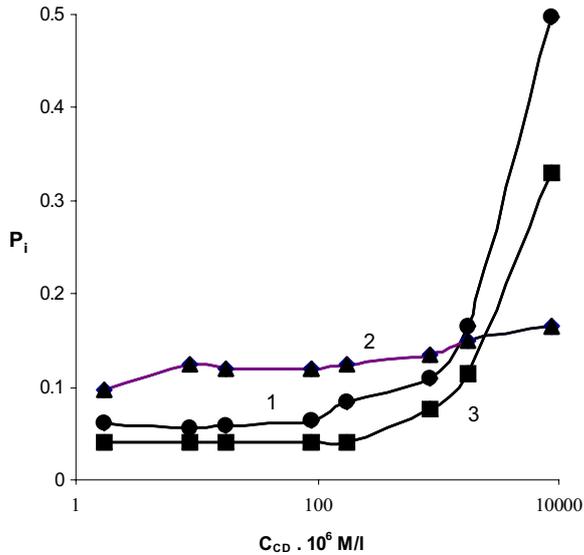


Fig. 4. Semi-logarithmic plot of anthracene and β -cyclodextrin nanoparticle mixture optical parameters (P_i) dependencies from β -cyclodextrin concentration in mixtures. 1 - $P_1 = D_{abs}(250)$; 2 - $P_2 = D_{sc}(250)$; 3 - $P_3 = I(633,90)$ - intensity of differential static light scattering at 633 nm and 90 degree angle of scattering, in arbitrary units. Concentrations of β -cyclodextrin in M/l: 1) $1.75 \cdot 10^{-6}$; 2) $8.75 \cdot 10^{-6}$; 3) $1.75 \cdot 10^{-5}$; 4) $8.75 \cdot 10^{-5}$; 5) $1.75 \cdot 10^{-4}$; 6) $8.75 \cdot 10^{-4}$; 7) $1.75 \cdot 10^{-3}$; 8) $8.75 \cdot 10^{-3}$ M/l.

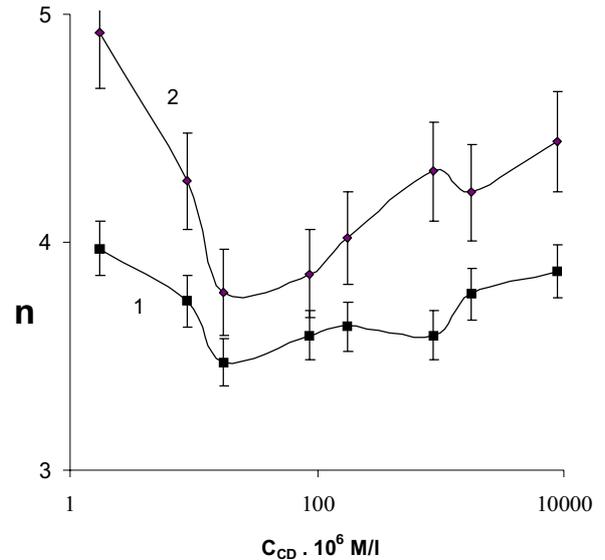


Fig. 5. Semi-logarithmic plot of wave length exponent - $n(\lambda)$, at $\lambda = 250$ nm and $\lambda = 500$ nm, dependencies from β -cyclodextrin concentration for mixtures of anthracene and β -cyclodextrin nanoparticles. 1 - $n(250)$. 2 - $n(500)$. β -cyclodextrin concentrations in M/l: 1) $1.75 \cdot 10^{-6}$; 2) $8.75 \cdot 10^{-6}$; 3) $1.75 \cdot 10^{-5}$; 4) $8.75 \cdot 10^{-5}$; 5) $1.75 \cdot 10^{-4}$; 6) $8.75 \cdot 10^{-4}$; 7) $1.75 \cdot 10^{-3}$; 8) $8.75 \cdot 10^{-3}$ M/l.

$$d = 0.24\alpha\lambda. \quad (8)$$

From calculations of characteristic function $n(\alpha, m)$ [11] it is possible to determine α and d . In the interval $2 < n < 4$ $n(\alpha, m)$ does not depend on m (the result of Mie's theory in this range). If μ_p is known, from $D_{sc}(\lambda)$ one can calculate N , the mean number of particles, and M , the mean disperse phase mass [11]. Numerical calculations by Mie's theory for model gamma-distribution of particles and experiments with bimodal latex suspensions have shown that the mean effective particle size determined by the turbidity spectrum method from $n(r)$ calibrations (r is the radius of particles) for monodisperse spherical particles corresponds with the minimal error [11] to the relationship:

$$\bar{r}_n = \left[\frac{\overline{r^{n+4}}}{\overline{r^{n+2}}} \right]^{1/2}. \quad (9)$$

Analysis of spectra $D(\lambda)$ in bilogarithmic plot in Fig. 2 gives the absorption spectra $D_{abs}(\lambda)$, which are presented in Fig. 3. It is supposed that at the

absence of interactions between particles the spectrum of mixture will be the sum of constituent spectra of mixture components. It is seen in Fig. 2 (curve 4) and in Fig. 3 (curve 3) that in mixture there is enhancement of anthracene main absorption band at 250 nm, absorption shoulder at 280 nm and appearance of absorption band (340 - 390 nm) with three peaks: 340, 360, and 375 nm. One can suppose that due to interactions between particles the number of absorbing particles increased. Selforganized inclusion of anthracene molecules in hydrophobic cavity of β -cyclodextrin can cause such changes.

Fig. 4 and Fig. 5 present $D_{abs}(250)$, $D_{sc}(250)$, $n(250)$, and $n(500)$ dependencies from the β -cyclodextrin concentrations in mixtures. It can be seen that at low concentrations of β -cyclodextrin $D_{sc}(250)$ increases (Fig. 4, curve 2), but $n(250)$ and $n(500)$ decrease (Fig. 5). These changes can be connected with the formation of aggregates in mixtures. At the middle β -cyclodextrin concentrations

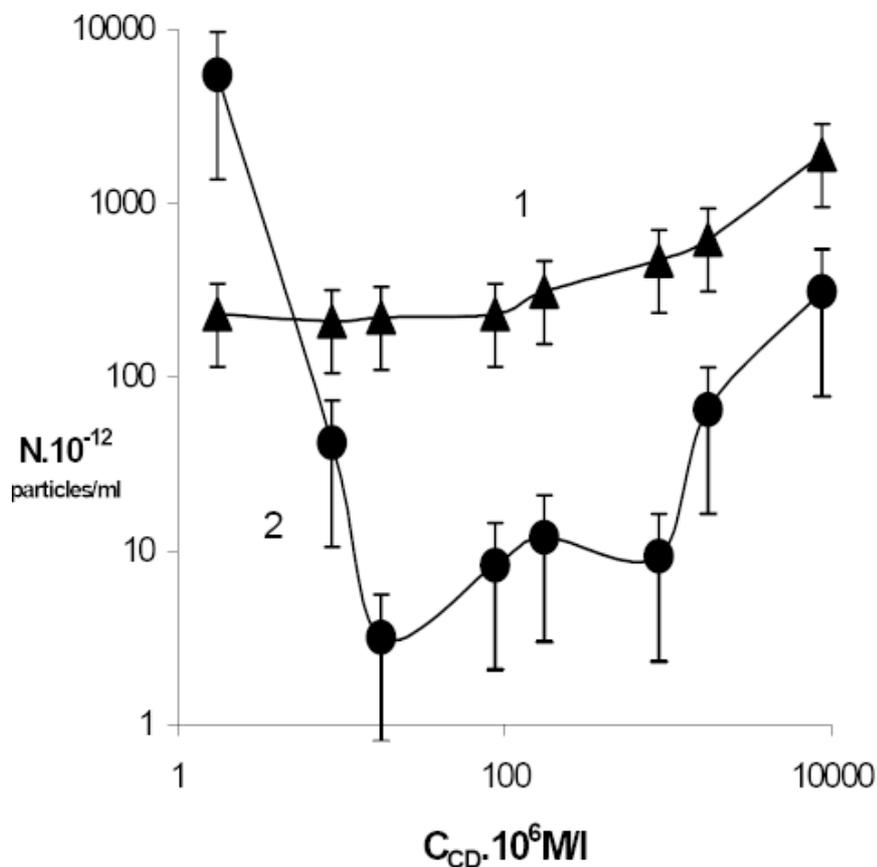


Fig. 6. Bilogarithmical plot of N (number of nanoparticles in ml) dependencies from β -cyclodextrin concentration for mixtures of anthracene and β -cyclodextrin. 1- N_{abs} - the number of absorbing particles, 2 - N_{sc} - the effective mean number of scattering particles. β -cyclodextrin concentrations in M/l: 1) $1.75 \cdot 10^{-6}$; 2) $8.75 \cdot 10^{-6}$; 3) $1.75 \cdot 10^{-5}$; 4) $8.75 \cdot 10^{-5}$; 5) $1.75 \cdot 10^{-4}$; 6) $8.75 \cdot 10^{-4}$; 7) $1.75 \cdot 10^{-3}$; 8) $8.75 \cdot 10^{-3}$ M/l.

the increase of $D_{sc}(250)$ begins which can be connected with the increase of anthracene molecules included in β -cyclodextrin cavity with the formation of nanoparticles with refractive index μ_p , higher than refractive indexes of β -cyclodextrin μ_{CD} and anthracene nanoparticles μ_A . The evidence for the increase of such nanoparticles is the dependence of $I(633,90)$, intensity of differential static light scattering at 633 nm and 90 degree angle of scattering (Fig. 4, curve 3). $D_{sc}(250)$ dependence (Fig. 4, curve 2) and $n(250)$ dependence (Fig. 5, curve 1) are less sensitive to the process of anthracene inclusion in β -cyclodextrin than D_{abs} dependence (Fig. 4, curve 1) and $I(633,90)$ dependence (Fig. 4, curve 3).

Analysis of spectra $D_{sc}(\lambda)$ in bilogarithmical plot in Fig. 2 gives the information about average size

of particles. Using linear approximation it is possible to calculate $n(250)$ in the interval of wavelengths from 200 to 300 nm, and $n(500)$ in the interval from 400 nm to 600 nm. It was shown that the slope of spectra for anthracene dispersion $n(250) = 3.91$ is less than for β -cyclodextrin at the highest concentration used in experiments, $8.75 \cdot 10^{-3}$ M/l, $n(250) = 6.50$; and is slightly more than $n(250)$ for the most of mixtures (Fig. 5). The lowest limit of spectroturbidimetry method corresponds to $\alpha = 0.2$ or according formula (8) for $\lambda = 250$ nm to effective $d = 12$ nm and for $\lambda = 500$ nm to $d = 24$ nm. The more is the value of $n(\lambda)$, the less is effective d (d values vary in mixtures from 12 to 60 nm).

For mixtures (Fig. 5) both $n(250)$ and $n(500)$ decrease at low β -cyclodextrin concentrations, which is connected with the formation of aggre-

gates, and increase from the middle concentrations simultaneously with the slight increase of $D_{sc}(250)$ (Fig. 4, curve 2) and increase of $D_{abs}(250)$ (Fig. 4, curve 1) and $l(633,90)$ (Fig. 4, curve 3), which is connected with the process of anthracene inclusion in β -cyclodextrin.

At spherical approximation the diameter of anthracene molecule [3] is about 0.4 nm. It is possible to conclude from $n(250)$, $\alpha = 0.3$ and effective $d = 18$ nm, that in anthracene 3D DS there are aggregates of molecules. At the approximation of β -cyclodextrin molecule as cylinder [4] with diameter 1.5 nm, height 0.8 nm, and cavity diameter about 0.6 nm, it is possible to suggest from $n(250) = 6.51$ that in β -cyclodextrin 3D DS there are no aggregates, but mainly molecules (nanoparticles). So, in β -cyclodextrin 3D DS with concentration $8.75 \cdot 10^{-3}$ M/l the number of β -cyclodextrin molecules is $N_{CD} = 5 \cdot 10^{21}$ particles/ml.

Mixtures of anthracene and β -cyclodextrin in water are bicomponent polymodal 3D DS, which particle size distribution consists of at least from the following 5 modes:

- anthracene molecules;
- β -cyclodextrin molecules;
- β -cyclodextrin molecules included anthracene molecules;
- aggregates of anthracene molecules;
- aggregates of β -cyclodextrin with anthracene.

Optical parameters can reflect most changes in the state of such complex systems. At the solution of optical problem by spectroturbidimetry method it is possible to obtain the effective mean number of scattering particles (in particles per cm^3):

$$N_{sc} = 2 \cdot 10^{10} \frac{D_{sc}(250)}{d^3 g(\alpha, m) l} \quad (10)$$

where d in micrometers, $g(\alpha, m)$ is the specific turbidity [11] in cm^{-1} , $m = \mu_p / \mu_0$ is the relative particle refractive index, and l is the optical length in cm. For example, in mixture of anthracene and β -cyclodextrin at concentration $8.75 \cdot 10^{-3}$ M/l: $D_{sc}(250) = 0.165$, $n(250) = 3.78$, $\alpha = 0.37$, $d = 22$ nm, $g = 1.0 \text{ cm}^{-1}$ (if to suppose that $m = 1.10$) and $N_{sc} = 3 \cdot 10^{14}$ particles per cm^3 (or per ml). If to assume that anthracene molecular absorption coefficient [3] $\epsilon(253) = 160000 \text{ mole}^{-1} \text{ cm}^{-1}$, it is possible to estimate the number of absorbing particles N_{abs} according to the equation:

$$D = \epsilon(\lambda) Cl \quad (11)$$

where C in M/l and l in cm. At the highest studied β -cyclodextrin concentration optical density connected with absorption (Fig. 3, curve 3) is $D_{abs} = 0.497$, $C_{abs} = 3.1 \cdot 10^{-6}$ M/l and $N_{abs} = 1.9 \cdot 10^{15}$ particles/ml.

The number of nanoparticles dependencies from β -cyclodextrin concentration for mixtures of anthracene and β -cyclodextrin are presented in Fig. 6 in bilogarithmical scale. It can be seen that N_{sc} and N_{abs} in mixture with the highest studied β -cyclodextrin concentration $8.75 \cdot 10^{-3}$ M/l are approximately of the same order.

4. CONCLUSIONS

The following information can be obtained from the analysis of experimental optical density spectra: 1) anthracene and β -cyclodextrin nanoparticles in water dispersive medium can interact with changes of anthracene absorption spectra most probably due to inclusion in the hydrophobic cavity of β -cyclodextrin; 2) size distribution of nanoparticles in mixtures is not the sum of size distributions of constituents; 3) the mean effective size of particles in mixture is larger than the size of initial anthracene and β -cyclodextrin particles. In these mixtures there are such processes as aggregation and inclusion of anthracene molecules in β -cyclodextrin.

The inverse optical problem solution by the turbidity spectrum method for integral static light scattering data measured at spectrophotometer can present complex information about state of 3D DS with nanoparticles. All modifications of light scattering method are nondestructive and compatible. Such measurements can be organized as simultaneous for on-line control and can provide useful information about the state of "ill-defined" 3D DS with nano- and micro-particles [13-17].

ACKNOWLEDGEMENTS

Alexandra G. Bezrukova is acknowledged the Academy Nancy-Metz, France for the support of research.

REFERENCES

- [1] A.N. Terenin, *Photonics of Dye molecules and Related Compounds* (Moscow, Nauka, 1967), In Russian.
- [2] C.A. Parker, *Photoluminescence of Solutions with Applications to Photochemistry and Analytical Chemistry* (Elsevier Publishing Company, 1968.)

- [3] J.R. Lakowicz, *Principles of Fluorescence Spectroscopy* (Plenum Press, 1983).
- [4] J. Szejtli // *Chem. Rev.* **98** (1998) 1743.
- [5] L. Milgrom // *Chemistry in Britain* **2** (2002) 21.
- [6] T. Nakatsubo, S.I. Nagasaka, T. Yoshinari, Y. Takahashi, A. Yamamoto, T. Goto and A. Kasuya // *Journal of the Physical Society of Japan* **73** (2004) 3015.
- [7] Y. Liu, Y.-L. Zhao, E.-C. Yang and H.-Y. Zhang // *Journal of Inclusion Phenomena* **50** (2004) 3.
- [8] W. Zheng and M.A. Tarr // *Journal of Physical Chemistry B* **108** (2004) 10172.
- [9] M. Lubomska, P. Gierycz and M. Rogalski // *Fluid Phase Equilibria* **238** (2005) 39.
- [10] L. Chunmao, M. Junze and Y. Zhang // *Luminescence* **20** (2005) 261.
- [11] V.J. Klenin, *Thermodynamics of Systems Containing Flexible Chain Polymers* (Elsevier, 1999).
- [12] K.S. Shifrin and G. Tonna, In: *Advances in Geophysics*, ed. by Renata Dmowska and Barry Saltzman (Academic Press, **34**, 1993), p. 175.
- [13] A.G. Bezrukova, In: *Proceedings of SPIE*, Vol. **3107**, ed. by Giovanna Cecchi, Torsten Lamp, Rainer Reuter and Konradin Weber (1997) 298.
- [14] A.G. Bezrukova, In: *Proceedings of Material Research Society* Vol. **711**, ed. by Steven C. Moss (2002) FF7.9.
- [15] A.G. Bezrukova, In: *Proceedings of SPIE* Vol. **5400**, ed. by Alexander I. Melker (2004) 189.
- [16] A.G. Bezrukova // CD: *2006 Spring National Meeting Conference Proceedings* (New York: AIChE, 2006).
- [17] A.G. Bezrukova // In: *Proceedings of SPIE* Vol. **6253**, ed. by Alexander I. Melker (2006) 62530C-1.