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Mixtures of 3D disperse systems with nano- and micro-particles: Optical characterization

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Abstract

Multiparameter analysis of simultaneous optical data for systems of nano- and/or micro-particles (3D disperse systems, dispersions, colloids, ensembles) by presentation of system characteristics as *N*-dimensional vectors of optical parameters (*N*D-vectors) can help to elucidate changes in the state of the particles in systems. In this paper, the application of the *N*D-vector approach is shown on the examples of dispersion mixtures: a mixture of influenza virus particles with albumin proteins (as a model of dispersions at the process of vaccine production); a mixture of coli bacillus and clay dispersions (as natural water model). This approach can serve as an on-line control platform for the management of technological processes with mixtures.

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Keywords: Absorption; Bacteria; Clay; 3D disperse systems; Light scattering; Micro-particles; Nano-particles; Mixtures of particles; *N*D-vectors; Viruses.

1. Introduction

Ensembles of nano- and/or micro-particles can be considered as three-dimensional disperse systems (3DDS) with particles as a disperse phase in the dispersive medium [1]. Multiparametric analysis of optical data for 3DDS can provide further progress in detailed characterization of 3DDS with particles of different nature (biological, mineral, metallic, organic, inorganic and their mixtures). This analysis includes the following:

(1) simultaneous measurements of 3DDS by different compatible nondestructive optical methods such as refractometry, absorbance, fluorescence, light scattering (integral and differential, static and dynamic, unpolarized and polarized);
(2) solution of inverse optical problem by different methods and technologies of data interpretation. Taking into account the optical theory [1–8] and some experimental results [9–22] served as the basis for elaboration of so-called *N*D-vector approach [15] as the platform for on-line control of 3DDS state.

2. Materials and methods

Our studies [9–22] have been focused on different 3DDS with nano- and/or micro-particles (with

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Table 1
Examples of the kernel s (x, a) and S (x) in Eq. (2) based on the discussion in Ref. [4].

N	x	$s(x, a)$	$S(x)$
1	λ	$\pi a^2 K_e$	$\sigma_e(\lambda) = \int_0^\infty \pi a^2 K_e(\lambda, a) f(a) da$
2	Θ	$(\lambda^2/4\pi^2) i_1$	$I_1 = \int_0^\infty (\lambda^2/4\pi^2) i_1(\Theta, a) f(a) da$
3	Θ	$(\lambda^2/4\pi^2) i_2$	$I_2 = \int_0^\infty (\lambda^2/4\pi^2) i_2(\Theta, a) f(a) da$
4	Θ	$(\lambda^2/4\pi^2)[(i_1+i_2)/2]$	$I(\Theta) = \int_0^\infty (\lambda^2/4\pi^2)\{[i_1(\Theta, a) + i_2(\Theta, a)]/2\} f(a) da$
5	λ	$\Theta = \pi(\lambda^2/4\pi^2)\{[i_1(\pi, a)+i_2(\pi, a)]/2\}$	$\beta(\lambda) = \int_0^\infty (\lambda^2/4\pi^2)\{[i_1(\pi, a) + i_2(\pi, a)]/2\} f(a) da$

Notes: 1. K_e is the extinction coefficient of the individual particle with radius a; σ_e (λ) is the cross-section of light extinction by 3DDS.
2. $s(x,a)$ is the intensity of light scattered at angle Θ by individual particle at the incident light polarized perpendicular to the surface of scattered light measurements; $S(x)$ is the intensity of light scattered by 3DDS at the incident light polarized perpendicular to the surface of scattered light measurements.
3. $s(x,a)$ is the intensity of light scattered at angle Θ by individual particle at the incident light polarized parallel to the surface of scattered light measurements; $S(x)$ is the intensity of the light scattered by 3DDS at the incident light polarized parallel to the surface of scattered light measurements.
4. $s(x,a)$ is the intensity of unpolarized light scattered at angle Θ by individual particle or so- called indicatrix of the individual particle, i.e., the S_{11} element of light scattering matrix; $S(x)$ is $S_{11}(\Theta)$, i.e., the indicatrix of 3DDS.
5. $S(x)$ is $\beta(\lambda)$, the wavelength dependence of indicatrix for $\Theta=\pi$, the so-called volume coefficient of back scattering.

diameter less than 10 µm) and their mixtures: proteins and nucleic acids; proteins and polymers; liposomes and viruses; liposomes carrying various substances (X-ray contrast agents, metallic particles, enzymes, viruses, antibiotics, etc.); liquid crystals with surfactants; mixtures of *Coli bacillus* with kaolin; mixtures of anthracene with cyclodextrin [16–18]; samples of natural and water-supply waters; air sediments in water, etc. In this paper, the application of the *N*D vector approach is shown through examples of 3DDS mixtures such as:

(1) a mixture of biological nanoparticles of influenza viruses (strain A1-H1N1) and of albumin proteins;
(2) a mixture of mineral bimodal kaolin dispersions (consisting of nano- and micro-particles) with biological *Coli bacillus* micro-particles (strains K-802 and AB 1157 [22]).

In our previous articles [18–22], we described the main optical methods used in our studies for 3DDS characterization: spectroturbidimetry, refractometry, fluorescence, absorbency, integral light scattering, differential static and dynamic light scattering, measurements of light scattering matrix elements. The measurements of dispersions were made under the same conditions. The uncertainty was about 5–10%.

Optical particle characterization in the range of nanometers up to about ten micrometers requires sophisticated data inversion techniques. The inverse problem can be formulated as a solution of the linear first-kind Fredholm integral equation of the finite domain (1) [4], where the measured (experimental) optical characteristic $S(x)$ is related to $f(a)$ that is the unknown particle size distribution [4]:

$$S(x) = \int_{a_{\min}}^{a_{\max}} s(x, a) f(a) da, \quad (1)$$

where a is the radius of an individual particle; $a_{\min}$, $a_{\max}$ are the limiting radii of particle size distribution, $s(x, a)$ is the kernel of the equation known from experiment or from the theory of light scattering for the individual particle with radius a.

In Eq. (1), x can be a scattering angle Θ or a wavelength λ, or a frequency ν. At $a_{min}=0$ and $a_{max}=\infty$ Eq. (1) converts into the linear first-kind Fredholm integral equation of infinite domain [4]:

$$S(x) = \int_0^\infty s(x, a) f(a) da, \quad (2)$$

The examples of the kernel $s(x, a)$ and $S(x)$ in Eq. (2) are presented in Table 1 (based on the discussion in Ref. [4]).

In addition to Notes to Table 1, it is necessary to remark that the complex refractive index of the particle substance is entered as a parameter in all kernels [4]. For homogeneous spherical particles, the kernel $s(x,a)$ can be calculated according to Mie theory [1–4]. In our previous papers, we discussed the 3DDS problem of polydispersity and polymodality [21] and the possibility of measuring polarization [22] for 3DDS characterization. For polymodal polydisperse 3DDS, the regularization technique is often used for

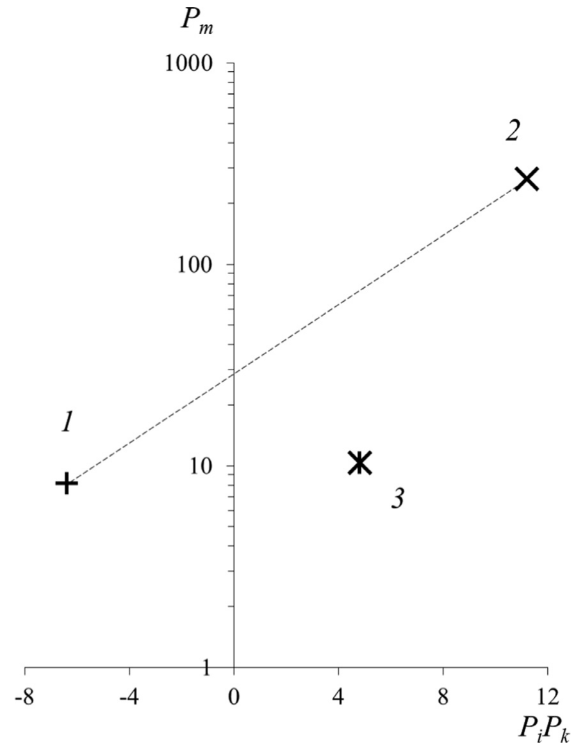

Fig. 1. Example of optical data presentation as 3D-vectors **P** {P_i, P_k, P_m} for dispersions of biological nanoparticles: (1) – influenza virus dispersion (strain A1-H1N1), (2) – albumin dispersion, (3) – the mixture of influenza virus and albumin dispersions in ratio 1:1.

solving the inverse light scattering problem [1–8]. The information-statistical methodology [23,24] also can be used for characterization of complex 3DDS.

3. Results and discussion

Experience suggests that the set of optical parameters of the so-called "second class" [15] (obtained by processing the measured values and independent on the concentration of particles) is unique for each 3DDS [15]. In other words, each 3DDS can be characterized by an N-dimensional vector in an N-dimensional space of the "second-class" optical parameters (ND-vector) [15]. In our previous paper [18], mixtures of anthracene with cyclodextrin were characterized by four-dimensional (4D) vectors. It was supposed in Ref. [18] that the position of mixture ND-vector on the line connecting the separate component ND-vector points could be the justification that there is no interaction between particles in the mixture.

The mixture of pure nanoparticles of the influenza virus (strain A1-H1N1) and albumin proteins (as an example of impurity) can be considered as a model of dispersions in the technological process of vaccine production. The influenza virus particle was approximated as a homogeneous sphere with the mean diameter $d = 100$ nm. To determine the virus concentration, the bilayer sphere approximation [1] was used.

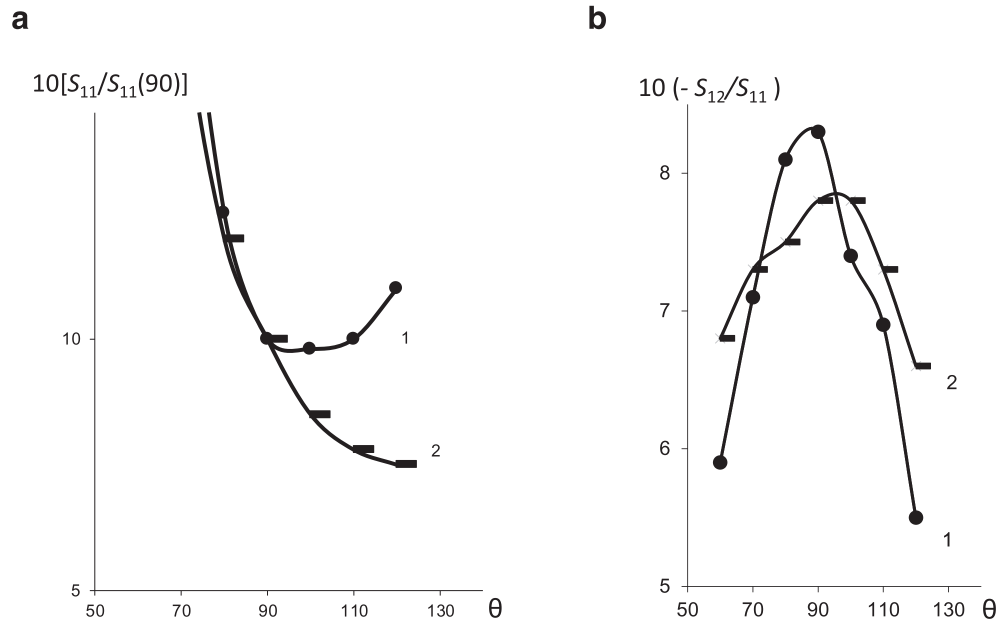

Fig. 2. Plots of 90°-normalized S_{11} (a) and -S_{12}/S_{11} (b) versus scattering angle Θ in degrees (S_{11} is the first element of the light scattering matrix, -S_{12}/S_{11} is the polarization of scattered light [3]) for two modes (1, 2) of bimodal kaolin dispersion; n (500) = 1.5 (the 1st mode); n (500) = 0.2 (the 2nd mode).

In order to design the optimal scheme for dispersions' on-line control, the 3D-vector (based on light extinction parameters [21]) was suggested for differentiation of influenza virus dispersion, albumin dispersion and their mixture (Fig. 1). In the vaccine production process, it is important to know the degree of virus dispersion purification from protein impurities. It can be concluded from Fig. 1 that the positions of 3D-vectors **P** $\{P_i, P_k, P_m\}$ for the constituent dispersions of the mixture (points 1 and 2) are suitable for differentiation of these dispersions not only by value but also by sign. The preparation of vaccine will be better if the position of 3D-vector for mixture (Fig. 1, point 3) will be closer to the 3D-vector position of the influenza virus (Fig. 1, point 1). It is also possible to suppose from the mixture 3D-vector position (Fig. 1, point 3) apart of the line-connected constituent dispersions vectors, that there are interactions between virus particles and protein molecules in mixtures.

The mixture of biological *coli bacillus* micro-particles with mineral bimodal kaolin dispersions (consisting of nano- and micro-particles) could be considered as the natural water model. Mineral bimodal kaolin dispersions were characterized by different methods [21]. The justifications of mainly different forms of particles in different modes of size distribution for kaolin *3*DDS were obtained at polarization measurements at angles θ about 90 degrees (Fig. 2). The shifts of the positions of the $S_{11}(\theta)$ minimum in Fig. 2a and of the maximum of scattered light polarization ($-S_{12}/S_{11}$) in Fig. 2b for fraction of "coarse" particles (curves *2*) to $\theta > 90$ are the evidence that there are aspheric particles [3,5,6] in kaolin dispersions. The kaolin nanoparticles (the first mode [21]) can be approximated as homogeneous spheres and the kaolin micro-particles (the second mode and "tail" of particle mass distributions [21]) as homogeneous oblate (based on electronic microscopy data) ellipsoids of rotation [11].

Coli bacillus bacterial cells (*Escherichia coli*, *E. coli*, *coli bacillus* rods) were approximated as homogeneous prolate ellipsoids of rotation and as volume-equivalent spheres with the mean diameter of cells $d = 1.0$ µm for strain K-802 and $d = 1.3$ µm for strain AB 1157 (Figs. 3–6).

According to Ref. [18], both situations can be observed for the mixtures of *coli bacillus* and mineral bimodal kaolin dispersions with nano- and micro-particles (Fig. 3, based on the integral and differential static light scattering parameters [21]), i.e., the supposed interaction between the constituent dispersions for the mixture with n (500) = 1.2 and the absence of that for the mixture with n (500) = 1.6. The detailed analysis of the data for the mixture of kaolin with *E.coli* strain AB 1157 (Fig. 4 and 5) showed that there is interaction between the particles in this dis-

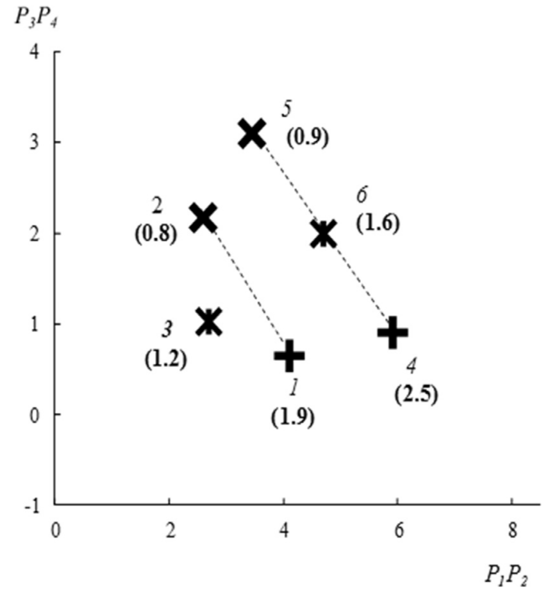

Fig. 3. Examples of optical characterization of two 3DDS mixtures (in ratio 1:1) and their constituents as 4D-vectors **P** $\{P_1, P_2, P_3, P_4\}$: (1) – dispersion of *E. coli* strain AB 1157, (2) kaolin dispersion with n (500) = 0.8 and their mixture (3); dispersion of *E. coli* strain K-802 (4), kaolin dispersion with n (500) = 0.9 (5) and their mixture (6); numbers in brackets are the n (500) values for the corresponding dispersions.

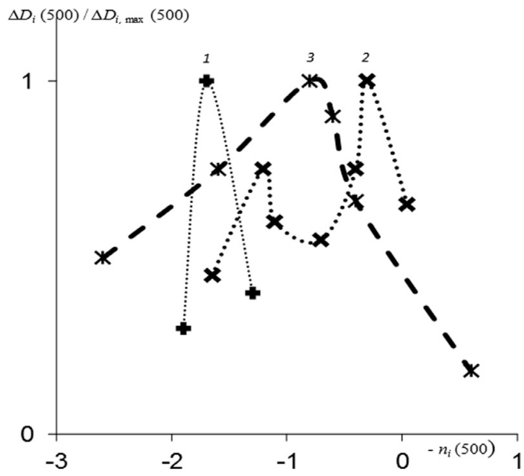

Fig. 4. Plots of ΔD_i (500)/$\Delta D_{i,\max}$ (500) versus ($-n_i$ (500)) value registered at dispersion sedimentation (somewhat equivalent to particle size distribution); the data presented: *E. coli* strain AB 1157 (1) (n (500) = 1.9); kaolin dispersions (2) (n (500) = 0.8); their mixture (3) in ratio 1: 1 (n (500) = 1.2).

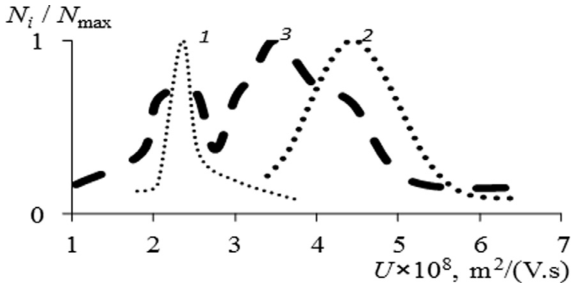

Fig. 5. Particle number distributions from particle electrophoretic mobility (U) for the same dispersions relative to those in Fig. 4. The form of mixture distribution is the evidence in favor of kaolin and bacteria heteroaggregation.

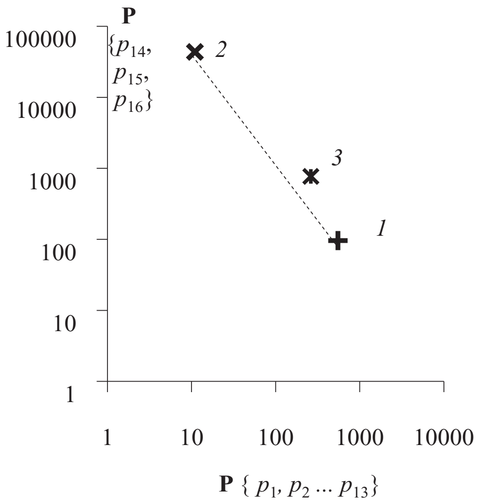

Fig. 6. The optical characteristics as 16D-vectors **P** {p_1, p_2, …, p_{16}} for dispersions with "non-supposed interaction of particles in mixture" (according to 4D-vectors approach in Fig. 3): dispersion of *E. coli* (1) strain K-802 (n (500) = 2.5); kaolin dispersion, (2) (n (500) = 0.9) and their mixture (3) in ratio 1:1 (n (500) = 1.6).

persion: the form of mixture distributions is evidence in favor of kaolin and bacteria heteroaggregation.

In Fig. 6, the 16D-vectors (based on the light scattering matrix parameters [22]) of kaolin dispersion, *E. coli* K-802 dispersion and of their mixture are presented. It can be seen that the differentiation of dispersion vector positions in 16D parameter space is about several orders and that the "non-supposed" (according to 4D-vector approach in Fig. 3) interaction between bacterial and kaolin particles can also occur. The data of polarization measurements for kaolin *3*DDS (Fig. 2) allows to predict that the (prolate bacterial – kaolin "small" spherical) and the (prolate bacterial – "coarse" oblate) particle interactions can be different. In addition to the discussion in Ref. [21] about natural 3DDS polymodality, taking into account the shape of the particles makes the model for solving inverse problem of mixtures more complex.

4. Summary

The information about the integral state of the 3DDS and about the changes of its state at any influence can be sufficient for controlling many technological processes. *N*D-vectors can reflect the changes in the state of the mixtures. In this case, the polymodality of particle size distributions [21] and the difference of particle forms are no obstacle. Combination of the *N*D-vector's approach with other methods of inverse problem solution can help to investigate the processes in 3DDS such as aggregation, disaggregation, coalescence, heteroaggregation, sedimentation, etc. The proposed approach allows the study of any 3DDS as an intact non-destroyable unity, with minimal interference. It can demonstrate the unique potentials of solving problems of polymer science, bio- and nanotechnology, medicine and of environmental protection.

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