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GEOCHEMISTRY

Liophilization of the Surface of Monodisperse Spherical Silica Particles and Synthesis of Opal Photon-Crystalline Structures from Liophile Suspensions

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In natural conditions, some minerals (e.g., hydrophile colloidal clay minerals) form liophile colloidal suspensions, which are characterized by a low interphase surface energy σ ($\sigma < \beta kT/4\pi r^2$, where $\beta = 20$ is the coefficient depending on the concentration of particles in suspension and r is the size of particles), a great affinity to disperse media, and the ability of spontaneous transition to the free disperse state. In contrast to liophobe colloidal systems, where $\sigma \gg \beta kT/4\pi r^2$, these minerals are thermodynamically stable. Amorphous silica has hydrophile properties when particles are 5–10 nm in size. However, the silica particles >50 nm in size behave as liophobe ones [1]. Monodisperse spherical silica particles, MSSP (200–300 nm in size), which make up opal structures, are not dispersed spontaneously, and MSSP suspensions obtained by synthesis of opal with technique [2] are liophobe materials. Their relative kinetic stability and some liophile-type properties are caused by the presence of a stabilizing electrolyte in the system and occurrence of the double diffusion layer of counterions around the negatively charged MSSPs. However, the direct relation of suspension stability to the concentration and type of electrolyte, a low threshold of coagulation, and special sensitivity to the presence of alien electrolytes strongly restrict modification of MSSP surface and expansion of possible synthesis of various opal structures as photon crystals.

However, it is known [3, 4] that adsorption of organic matter of weathered rocks, soils, and bottom sediments in water basins at the surface of mineral particles hampers their adhesion and enhances hydrophile properties of dispersed sediments. This phenomenon suggested the idea of liophilization of the MSSP surface under experimental conditions, transfer of the system into the region of thermodynamic stability, and solution of the aforementioned problems.

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Thus far, liophile MSSP suspensions have never been obtained or described. In this communication, we give the characteristics of these suspensions and transitional liophile–liophobe suspensions for the first time. Liophilization of the surface is possible on the basis of surface active agents (SAA). We have chosen the known solvent dimethylsulfoxide $(CH_3)_2SO$ (hereafter, DMSO), which is mixed with water and alcohol in different proportions. The replacement of alcohol or aqueous disperse medium (in the context of technique [2]) of the liophobe MSSP with the DMSO yields thermodynamically stable suspensions that have principally different properties typical of liophile colloidal systems. The liophile character of the suspensions is proved, first of all, by spontaneous dispersion of opal nanocrystals from the MSSP into the DMSO and transfer of some amount of silica into the colloidal solution as microparticles, which make up the MSSP [5], and primary colloidal particles.

The polar DMSO molecules (dipole moment 4.3 D) behave with respect to MSSP as a surface active agent and form a dense layer of molecules oriented vertically to the surface similarly to other SAAs [6]. Precisely this DMSO layer firmly connected with the particle surface imparts liophile properties to the MSSP in a disperse medium of the DMSO. As in the case of other SAAs, when 100% of the disperse medium consists of the DMSO, the adsorbed layer can be not unique. The multilayer coating of the MSSP surface with the polar DMSO molecules is more likely.

Liophile MSSP suspensions are transparent owing to the close refractive indexes of MSSP and DMSO (1.46 and 1.47, respectively). The spectrophotometric examination of fresh MSSP suspensions (diameter = 260 nm, volumetric concentration of particles in suspension = 10%) within a wavelength range of 300–800 nm shows only insignificant absorbance at 300–450 nm. Suspensions with a mixed disperse medium, which contains 10, 30, and 50% alcohol or water, are not transparent and become milky white (this is typical of liophobe suspensions). Despite a gradual linear variation of the refractive index of the disperse medium in

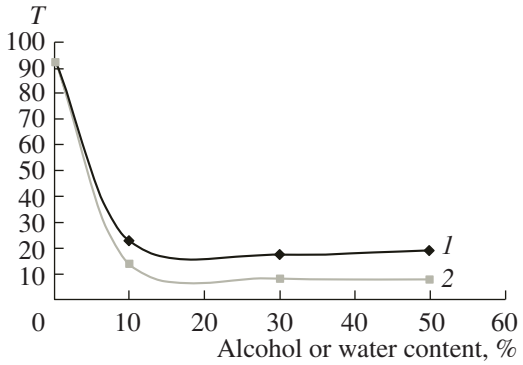

Fig. 1. Light transmittance at a wavelength of 500 nm versus (*1*) alcohol or (*2*) water content in the MSSP suspension with the dispersion medium DMSO.

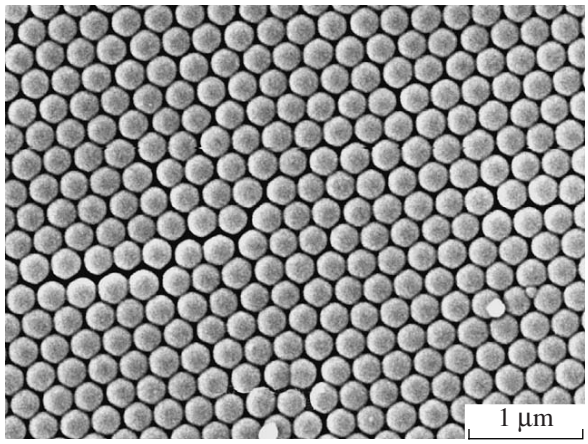

Fig. 2. SEM image of the surface of a monocrystalline opal film obtained from liophile suspension with the DMSO.

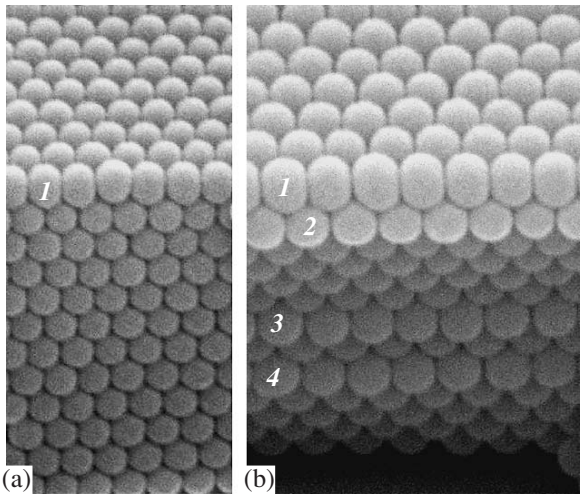

Fig. 3. (a) Homogeneous structure of vertical fracture of monocrystalline opal film. Particles of the upper layer (*1*) are elongated in the vertical direction as a result of additional growth. Image (b) demonstrates layers (*3, 4*) consisting of particles similar to (*1*) within the structure. Fracture steps are formed at these layers.

the mixtures, the transmittance for medium wavelengths in the visible part of the spectrum abruptly changes only within a range of the first 10% (Fig. 1). Hence, the refractive index in the DMSO shell (n_1) remains virtually unchanged up to 10% content of water or alcohol (i.e., the DMSO shell is retained), whereas the difference in refractive indexes n_1 and n_2 (disperse medium) increases. However, the transmittance remains later at approximately the same level. This implies that the difference between n_1 and n_2 after 10%-admixture also remains constant, likely owing to a decrease in n_1 parallel to the variation of n_2. This phenomenon can only be explained by desorption of the polar DMSO molecules from the DMSO-modified MSSP surface. However, for suspensions with an age of one month or more, the relationship between transmittance and the concentration of water or alcohol becomes close to linear, thus indicating the complex dynamics of liophilization of the MSSP surface before reaching equilibrium.

In liophile MSSP suspensions, it is impossible to obtain a condensed solid-type ordered MSSP structure by sedimentation of particles on the vessel bottom as in the case of synthesis of opal [7]. Dimethylsulfoxide shells around MSSP particles prevent their contacts and formation of nanocrystals with balanced counteracting forces—molecular attraction of MSSPs and electrostatic repulsion of their counterion atmospheres.

However, the MSSP concentration on the vessel bottom increases as a result of sedimentation with the formation of "liquid sediment" (coacervate), in which the particles are separated by liquid interlayers. Judging from weak diffraction effects, some ordering in localization of particles is achieved in the coacervate. We obtained photon-crystalline (PHC) films from such concentrated films in restricted zones (under confined conditions due to decrease in the total volume of liquid by evaporation) and the meniscus zone. In terms of quality (reflectance >95%), these films surpass the PHC films prepared from liophobe alcohol suspensions [8–12]. The mechanism of nanocrystallization in this case is different and should be considered elsewhere. Here, it is important to note that SEM examination confirms the monocrystalline character of the film and the complete absence of domains and twins in the film consisting of 25–30 MSSP layers (this is the 3D opal structure) over an area of 1–2 cm^2 (Figs. 2, 3).

The character of fractures, the only defect responsible for 4% light dispersion, is different in this case. The fractures are not typical tension cracks related to drying and crosscutting MSSP rows. Instead, they extend along these rows and represent insignificant local divergence of particle rows, emphasizing eventually their hexagonal packing. The dense packing of MSSP particles and their partial deformation typical of the films produced in liophobe suspensions is not observed here.

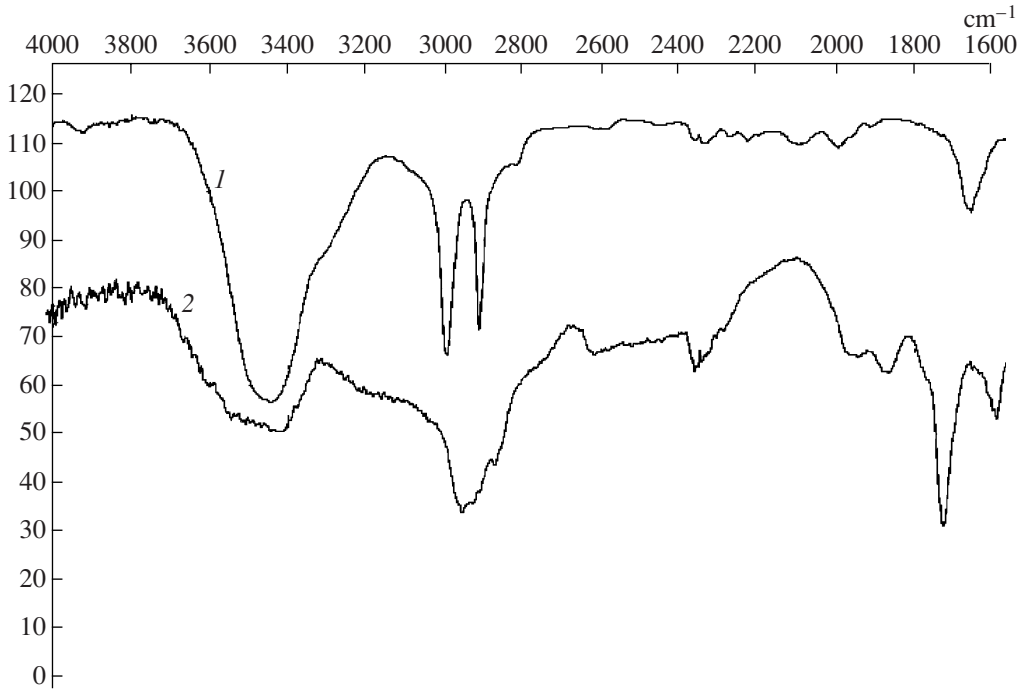

Fig. 4. (*1*) IR transmission spectra of the MSSP film from suspension with the DMSO; (*2*) IR transmission spectra of the DMSO.

The particles show a slight contact. The drying of films at normal temperature in air does not provide for the complete removal of the DMSO, which is firmly connected with the particle surface and serves as a barrier for the immediate and wide contact of particles. This is indicated by IR transmission spectra with minimums at 2800–3000 cm^{-1} and 3300–3800 cm^{-1} that are characteristic of the DMSO (Fig. 4). Despite a more loose structure, the mechanical strength of PHC films obtained in liophile suspensions with the DMSO turns out to be much higher than in films grown from liophobe alcohol suspensions. This effect may be accounted for by the agglutinative action of silica in primary colloidal particles bound with the DMSO (bridges connecting the particles are formed during the drying of silica). The interaction between the DMSO and silica, which is produced during the partial fine dispersion of MSSP, is yet to be studied. This silica not only makes up bridges, which connect the particles, but also participates in the spreading of MSSPs in the upper layer of the film. Owing to this effect, the upper layer consists of oblong particles (Fig. 3a). Judging from the photomicrograph (Fig. 3b), this effect is manifested repeatedly in some cases as a result of rhythmic deposition of silica on some MSSP layers. In the photomicrograph, these oblong particles are largely concealed within the structure. They form steps in the case of film rupture. Such a mechanism of periodic release of silica from colloidal solution may explain the appearance of layers of large MSSP particles in the structure of smaller particles during the natural process of noble opal formation in Brazil [13, 14] as an alternative to the version of joint nanocrystallization of particles of different sizes [15].

Thus, the experimental data presented above show that liophilization of the surface of liophobe dispersed minerals not only substantially changes the formation mechanism of colloidal mineral species, but also leads to qualitatively new (previously unattainable) results. In this connection, we can affirm that issues of the production of high-quality PHC films from the MSSPs and the production of photon heterostructures with alternating layers of particles of different dimensions can only be solved on the basis of liophile suspensions.

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