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Transfer of nanodiamonds from the aqueous phase to the organic phase in the presence of oleylamine

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ABSTRACT

A radiotracer technique with tritium-labeled nanodiamonds (NDs) has been used to study the distribution of NDs in water/octane system. The surface of NDs has been modified by heat treatment (oxidation) in air and functionalization using oleylamine (OLA) as surfactant. It has been shown that oxidized NDs are concentrated in the aqueous phase, the distribution ratio ($D = C_O/C_W$) being 0.016 (C_O and C_W are the concentrations of the NDs in octane and water, respectively). The addition of OLA to the NDs hydrosol/octane system leads to increase in the distribution ratio and the concentration of NDs near the water/octane interface by a factor of three. The dispersion of NDs directly in a solution of OLA in octane followed by addition of water leads to more pronounced increase in the distribution ratio (by two orders of magnitude), and the major fraction of the nanoparticles (about 70%) is concentrated near the water/octane interface. Adsorption isotherm of OLA on NDs has been obtained; it has been found that the adsorption is irreversible due to the formation of ion pairs between surface carboxylic groups of NDs and amino groups of OLA. The nanoparticles and their dispersions have been investigated by Fourier transform infrared spectroscopy, dynamic light scattering, Boehm titration, interfacial tensiometry, optical microscopy, ζ-potential and pH measurements.

1. Introduction

Detonation nanodiamonds (NDs) are widely used due to their mechanical strength, chemical resistance, biocompatibility, and high adsorption activity [1–6]. The successful application of NDs in drug delivery systems and polymer-based composites requires information on the localization of the nanoparticles in complex systems containing regions of different polarity and interfaces. Therefore, elucidation of the details of the methods to control the transfer of NDs from an aqueous phase to an organic one and the concentration of NDs at these interfaces is of definite practical importance.

Energy of particle separation from a water/oil interface (E) is related to the particle radius r, the surface tension σ between water and the oil, and the contact angle θ in the particle/water/oil system via the following equation [7–9]:

$$E = \pi r^2 \sigma (1 \pm cos\theta)^2 \quad (1)$$

Hence, the particles preferentially wetted by water ($\theta < 30°$) or oil ($\theta > 150°$) exhibit low energies of “adhesion” to the interface and are predominantly concentrated in the corresponding phase. In contrast, the particles with contact angle close to 90° exhibit the highest energy of separation from the interface and transfer to the bulk phase; this energy exceeds that of heat motion, thus favoring the particles location at the interface. This is used to stabilize the emulsions using particles (the so-called Pickering emulsions [7–10]). Consequently, changing the wetting conditions by surface modification is a possible way to control the distribution of nanoparticles in a biphasic water/oil system. It is known that surfactants can efficiently adjust preferential wetting [11,12]. However, studies on diamond surface wetting have been scarce to date [13–15]; moreover, the known reports have been devoted to the wetting of diamond coatings prepared via chemical vapor deposition (CVD). For example, it has been demonstrated [13] that the contact angle value is strongly affected by the procedure of the surface treatment and the ratio of sp^3/sp^2 carbon atoms at the surface; an oxidized diamond surface is perfectly wetted by water (contact angle of water droplet in air $\theta = 23°$), whereas a graphitized surface is poorly wetted by water ($\theta > 85°$). In general, the oxidation of a nanodiamond surface should favor its wetting with water since such treatment

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eliminates residual sp^2 carbon atoms and leads to the formation of oxygen-containing hydrophilic groups. Hydrophobization of the nanodiamond surface can be achieved via the covalent grafting of hydrocarbon or fluorocarbon moieties at the functional groups of the NDs surface [16–20] or via surfactant adsorption [19,21–23]. For example, it has been reported [22] that oleylamine is adsorbed on oxidized NDs with the formation of charge-transfer complexes with acidic groups at the surface of the particles; thus, such surface hydrophobization allows the preparation of stable NDs dispersions in a series of organic solvents. The study of NDs modification with a mixture of oleic acid and octadecylamine [23] has shown that the formation of hydrogen bonds between the components of the surfactant mixture as well as between the surfactants and the NDs gives rise to a strongly bound ordered adsorption layer which hydrophobizes the surface.

Our earlier studies [14,24] have demonstrated that a radiotracer method using tritium-labeled nanodiamonds is a reliable approach to determine the location of NDs in biphasic water/organic liquid systems. This procedure is highly sensitive and selective, thus allowing the determination of tiny amounts of the substance in the contacting phases and the calculation of the NDs content at the interface from the material balance equation. Moreover, a procedure to introduce the tritium label in NDs and prepare the specimen with acceptable radioactivity has been elaborated [25].

This work aimed to quantify the distribution of NDs in a water/octane system and to elucidate the influence of adsorption layers of a surfactant (oleylamine, OLA) on the tendency of the phases to come in contact with the distribution of NDs and the tendency for the NDs to concentrate at the interface. The obtained data demonstrated the possibility for NDs to transfer from the aqueous phase to the interface and to the organic phase facilitated by the presence of a surfactant hydrophobizing the surface of the nanoparticles.

2. Experimental

Detonation nanodiamonds (SKTB Tekhnolog, St. Petersburg, Russia) were oxidized in air at 420°C for 2 h [22,26]. The oxidized NDs were used in all the reported experiments.

Other materials used in this work included oleylamine (OLA, Sigma-Aldrich, 70%), *n*-octane (*pure* grade, IREA 2000, Russia), scintillation cocktail (Ultima Gold^{TM}, PerkinElmer Inc., USA), and distilled water.

The tritium-labeled nanodiamonds ([^{3}H]NDs) were prepared via a tritium thermal activation method according to the procedure described in Ref. [25]. The developed technique allows obtaining radiolabeled materials with tritium stabilized in chemically inert sp^3 C—H bonds on the surface of NDs. An aqueous suspension of the oxidized NDs (0.8 mL) with a solid content of 0.3 mg was distributed on the walls of a glass reaction vessel and lyophilized. The reaction was carried out with a protium-tritium mixture with a tritium content of 10%. Tritium atoms were generated by the atomization of gaseous tritium on a W wire at 2000 K of a device designed for labeling with gaseous tritium. The reaction was performed for 10 s and then repeated after exchange of the gaseous phase with its fresh portion. The tritium-labeled nanodiamonds were suspended in 4 mL of water with the help of sonication. To remove labile tritium, the suspension was dried on a rotary evaporator and resuspended in water. The specific radioactivity of the specimen was equal to 0.1 TBq/g.

The distribution of NDs in a biphasic water/octane system was studied as follows. An aqueous dispersion of the [^{3}H]NDs (1 mL, concentration of 0.20 g/L, specific radioactivity $a = 0.3$ GBq/g) was brought in contact with 1 mL of octane, vigorously shaken, and equilibrated. Aliquots of the aqueous and organic phases (volume V_{al}) were sampled, and their radioactivity I_{al} was measured using a RackBeta 1215 liquid scintillation spectrometer (LKB, Finland). The ND concentration in each phase was calculated as follows:

$$C = \frac{I_{al}}{\varepsilon a V_{al}} \tag{2}$$

In Eq. (2), ε is the efficiency of tritium detection, determined for each experiment (30–40%). The radioactivity value of the organic phase was measured 20 min after the beginning the experiment and was close to that measured one day later, thus evidencing the equilibration of the system.

From the concentrations of [^{3}H]NDs in the aqueous C_{aq} and the organic C_{org} phases, we determined the distribution ratio D:

$$D = \frac{C_{org}}{C_{aq}} \tag{3}$$

Using the material balance equation, we then calculated the fraction of [^{3}H]NDs at the water/octane interfacial layer X:

$$X = \frac{m_{ND} - (C_{org}V_{org} + C_{aq}V_{aq})}{m_{ND}}$$

with m_{ND} being the mass of NDs in the analyzed system, V_{org} and V_{aq} being the volumes of the organic and aqueous phases, respectively. The validity of the obtained data was confirmed by the absence of significant precipitation of the NDs during the system equilibration.

OLA was labeled with tritium by tritium thermal activation method (the method similar to that discribed in [26,27]). OLA was modified for 10 s at the temperature of tritium activation 1850 K. [^{3}H]OLA was purified by extraction in a water/octane system. The extraction was repeated six times. The specific radioactivity of the [^{3}H]OLA was equal to 47.4 GBq/g.

For determination of the distribution ratio of OLA in a water/octane system, solution of the [^{3}H]OLA in octane (1 mL, concentration of 0.3 wt%) was brought in contact with 5 mL of water, vigorously shaken, and equilibrated. Aliquots of the aqueous and organic phases (volume V_{al}) were sampled, and their radioactivity I_{al} was measured. Surfactant concentration in the aqueous and octane phases and distribution ratio were calculated using Eqs. (2) and (3).

The adsorption of OLA on NDs from octane was determined by measuring the decrease in the [^{3}H]OLA concentration in a solution. NDs was added to OLA solutions of different concentrations that contained certain quantities of [^{3}H]OLA. This dispersion was preliminary treated in an ultrasonic bath for 20 min. After 1 h, the dispersions were centrifuged using an Eppendorf MiniSpin centrifuge for 30 min (rotation rate 12,000 rpm) to separate the NDs. An aliquot (V_{al}) of supernatant fluid was then sampled, and the count rate of tritium radiation (I_{al}) was measured. Adsorption (Γ) on NDs was calculated using the equation:

$$\Gamma = \frac{(C_0 - C_{eq})V}{m}$$

where V is the volume of the solution, m is the mass of the NDs sample, C_0 and C_{eq} are the initial and equilibrium concentrations of [^{3}H]OLA, calculated using Eq. (2).

Then the supernatant fluid was sampled, and 1 mL of octane was added to measure the quantity of irrebersibly bound OLA. The system was shaken and centrifuged, octane was sampled, and a liquid scintillation cocktail was then added to the residue. The system was mixed, and the count rate I was measured. The value of [^{3}H]OLA irreversible adsorption on NDs was measured using equation:

$$\Gamma = \frac{I}{\varepsilon m a}$$

To elucidate the effect of OLA on the distribution of NDs, OLA was added to the organic phase of the aqueous dispersion of the [^{3}H]ND/octane system; the concentration of OLA was 0.3 wt% with respect to octane. The distribution coefficient and the fraction of NDs in the surface layer were determined as described above.

Alternatively, another method to bring the phases in contact was