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Colloidal behavior of detonation nanodiamonds in the aqueous-organic liquid systems in the presence of pluronic P123

Ivan Yu. Myasnikov, Oxana A. Soboleva, Maria G. Chernysheva and Gennadii A. Badun*

Department of Chemistry, M.V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.
Fax: +7 495 932 8846; e-mail: badunga@yandex.ru

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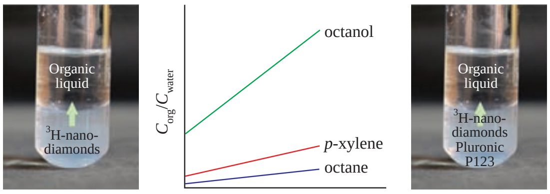
Polymeric nonionic surfactant pluronic P123 significantly increases the distribution ratio of nanodiamonds in the aqueous-organic liquid systems.



Nanoparticles are of considerable importance for the development of modern technology.[1–3] Physicochemical properties and low toxicity of the nanodiamonds (NDs) provide for their potential use in the biomedical applications.[4–12] To prepare stable suspensions of the nanoparticles either in aqueous or organic media a surface modification by the surfactants is usually applied.[13–17] To estimate the penetration ability of the NDs through the cellular membrane it is essential to study systematically whether NDs could transfer into the organic phase from the aqueous suspension. In this context, the distribution ratio of nanoparticles in the octanol–water system is the most commonly used parameter.[18] However, the determination of NDs concentration in both organic and aqueous phases is rather difficult task. Therefore, we suggested an application of the tritium labeled NDs.[19] The surface modification and fractionation of NDs significantly improve their colloidal stability.[20] Any surface modification of NDs, in particular in the presence of the surfactants in NDs aqueous suspension, can strongly change their octanol–water distribution ratio. The goal of this research was to reveal the influence of polymeric nonionic surfactant pluronic P123 on the colloidal behavior of NDs in the aqueous suspensions and in the aqueous-organic liquid systems.

Tritium labeled NDs[†] of the specific radioactivity of 58 TBq g^{-1} were suspended in the water with final concentration of 0.2 g dm^{-3}. The aqueous suspension was characterized by dynamic light scattering and laser micro-electrophoresis using Zetatrac (Microtrac, USA). NDs exhibited the average diameter of aggregates of *ca.* 100 nm and zeta potential of +34 mV, illustrating that the species are highly aggregated. Relative stability of the sample is determined by the electrostatic repulsion and hydration of surface groups.

The suspension (1 cm^3) has been shaked with 1 cm^3 of octane, *p*-xylene or octanol for 24 h, followed by the incubation at room temperature for 48 h. Then the aliquots of organic and water phases were transferred into a vial containing Ultima Gold scintillator (PerkinElmer), and the counting rate was measured using the liquid scintillation spectrometer RackBeta 1215 (LKB, Finland). The concentrations of NDs in each phase (c_x) and the distribution ratio (D) were calculated as:

$$c_x = \frac{I_x}{\varepsilon V a_{sp}}, \qquad (1)$$

$$D = \frac{c_{org}}{c_{water}}. \qquad (2)$$

Here I_x is the counting rate of tritium β-radiation; V is the volume of the aliquot; ε is the registration efficiency of tritium β-radiation in the Ultima Gold scintillation cocktail; a_{sp} is the specific radioactivity of the NDs.

To reveal the effect of pluronic P123 on the NDs distribution in the water-organic liquid system, pluronic P123 with the final concentration varied from 1×10^{-7} to 1×10^{-3} mol dm^{-3} was added to the aqueous suspension. Then the experiment was performed according to the same procedure.

The values of D for free NDs were 0.009±0.002, 0.026±0.002, and 0.13±0.01 in water–octane, water–*p*-xylene, and water–octanol systems, respectively. Compared with carbon nanotubes, the NDs are able to transfer into organic phase even in the absence of electrolytes and surfactants in the aqueous phase.[21] It was found that the addition of pluronic resulted in the increase of D by a factor of 5, 4, and 3 for octane, *p*-xylene, and octanol, respectively. Pluronics exhibit high affinity to nonpolar liquids, and are used along with low molecular weight nonionic surfactants[22] for the stabilization of water–oil nanoemulsions.[23] It has to be emphasized that pluronic P123 itself exhibits high distribution ratio in the organic liquids, namely 0.5±0.1, 0.8±0.2, and 1.5±0.5[24] for octane, *p*-xylene, and octanol, respectively. Moreover, it was found that the surface tension of pluronic solution at the air–water interface increased when it was measured in the upper solution of NDs–pluronic mixture after the precipitation of solids (Figure 1).

There are two possible explanations of such a phenomenon. On the one hand, at the air–water interface polypropylene oxide (PPO) groups of pluronic are located in the air resulting in the decrease in the surface tension. In the presence of NDs particles PPO groups are attracted to the graphitized regions of the NDs surface that leads to the reduction of the surface tension.[25] The

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[†] Detonation NDs (Sinta, Belarus) and Pluronic P123 (Sigma–Aldrich) were used as received. Tritium label was introduced into NDs by means of tritium thermal activation technique as described previously.[19]

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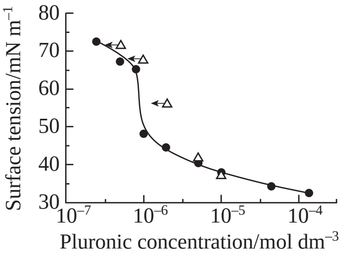

Figure 1 Surface tension isotherm of pluronic P123 at the air–water interface (black symbols), and the same after NDs addition and precipitation (open symbols).

fact is confirmed by a small reduction of ζ-potential from +34 to + 22 mV.

On the other hand, the changes in the distribution ratio and in the surface tension can be explained by the diamond surface modification with the molecules of P123 diminishing pluronic concentration in the aqueous phase (shown by arrows in Figure 1).[26–28] At the same time, the presence of pluronic does not affect the particles size when pluronic concentration is less than 10^{-3} mol dm^{-3}. At the concentration of P123 close to 10^{-3} mol dm^{-3} NDs form aggregates of about 150 nm in diameter. At this high concentration pluronic P123 exists in the aqueous phase in the form of micelles.[29]

In conclusion, the technique for the NDs determination in the organic phase has been developed. The addition of pluronic P123 into the NDs suspension significantly increases the affinity of the NDs to the organic phase, and results in the formation of stable NDs suspension in both aqueous and organic phases. The work is underway to determine the amount of pluronic that can be bound to the NDs surface.

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