The formation of nanoparticles in the process of ultrasonication of the pure water

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Abstract. Ultrasonication is a very convenient method for the preparation of various dispersions. However, it is often not clear what influence the ultrasonication procedure is on the purity of the prepared dispersion. In this paper, we show that the prolonged ultrasonication of the pure water results in dispersion formation. We characterized the nanoparticles in the resulted dispersion by the TEM, DLS, conductivity, and zeta potential measurements. This work points to the possible source of contamination of the sonicated dispersions.

1. Introduction

Ultrasonic equipment is widely used in various applications, for example, for dispersing particles of various nature in a liquid, homogenizing, and emulsions preparation, for cleaning surfaces (ultrasonic baths for cleaning), for welding and therapeutic applications.

In the ultrasonic treatment technique, sound waves with frequency range equal or more than 20 kHz are used. Rapid changes of pressure in liquid formed by a vibrated activator (horn) lead to the formation of small vapor-filled cavities in places where the pressure is relatively low. When subjected to higher pressure, these cavities, called "bubbles" or "voids," collapse and can generate a shock wave that is strong very close to the bubble, but rapidly weakens as it propagates away from the bubble.

Ultrasonic equipment is used for fine grinding of solids or liquids, for transferring substances into a dispersed state (dispersion) with the formation of a sol under the action of ultrasonic vibrations. Particles, drops, or aggregates are destroyed as a result of repeated exposure to their surface of pulsed loads accompanying the closure of cavitation bubbles [1]. Besides, it is also possible grinding due to the collision of the powder particles resulting from their random movement under the influence of ultrasound.

In [2-4], the authors obtained stable aqueous dispersions of n-alkanes without the addition of surfactants using ultrasonication (22 kHz, 75 W). The dispersion particles had an average size (radius) of about 100 nm and a zeta potential of up to -50 mV. In this paper, we study the effect of ultrasonic radiation on pure water when a submersible titanium activator (horn) is used. The observed dispersion formation may explain the high stability of ultrasonicated n-alkane dispersions without the
addition of surfactants. This kind of information can be interesting in applications related to the production of various types of dispersions.

2. Experimental

Samples for studies were prepared from deionized water produced by the Simplicity UV (Millipore, Bedford, MA, USA). The volume of each sample was 10 mL. For sample preparation, we used an ultrasonicator UZDN-A (22 kHz, 75 W, Russia) with a titanium submersible activator. Three samples were prepared. For two samples (sample G1 and sample G2), the sonication was carried out in glass vials. One sample was prepared in a plastic cuvette (sample P1). Sample P1 in a plastic cuvette and sample G1 in one of the glass vials were prepared by successively sonicating ten times for 30 seconds. Moreover, before each of the ten sonications, the scattered light intensity, particle size utilizing dynamic light scattering (DLS), conductivity, and particle zeta potential were measured.

For the second sample G2 in a glass vial, the preparation was performed by single sonication for 300 seconds, and the same measurements were performed as for the two samples described above. Thus, we could study both the effect of the vessel's material in which the sonication took place and the effect of the sonication procedure. For all three samples, a change in time of such properties as scattered light intensity, particle size (DLS), conductivity, and zeta potential of the particles was studied. Before each measurement, the samples were intensively mixed so that the particles settled between measurements were redispersed. Sample G1 was also examined by transmission electron microscopy 40 days after preparation.

For analysis by transmission electron microscope (TEM), 5 µL of dispersion was dropped on a formvar TEM grid (Ted Pella, Redding, CA, USA) and dried at room temperature. TEM micrographs were obtained using a JEM-2100 electron microscope (JEOL, Japan) at an accelerating voltage of 200 kV and additionally using a LEO912 AB OMEGA (Carl Zeiss, Germany). Energy-dispersive X-ray spectroscopy analysis (EDX) was performed with JED-2300 (JEOL, Japan) analysis station.

Scattered light intensity, conductivity, particle size, and zeta potential were measured using Photocor Compact-Z equipment (Russia). With a scattering angle of 90 degrees for measurements of scattered light intensity and particle size and a scattering angle of 20 degrees for zeta potential measurements. The laser wavelength was 654 nm; the laser power was 30 mW. Each measurement was carried out at least three times and the average value of the obtained results was found.

3. Results and discussion

Figure 1 shows the results of measurements of scattered light intensity, conductivity, particle size, and zeta potential for samples G1 and P1 before each of the ten sonications. Figure 1 shows that with an increase in the sonications of samples G1 and P1, an increase in the scattering intensity in both samples is observed. In the sample G1, the scattering intensity grows linearly with each sonication treatment, and in the sample P1, the dependence has the form of a growing exponential. The intensity of the scattered light in sample G1 after ten sonications is 2.5 times greater than in sample P1. The conductivity of sample G1 increases with each sonication and, after ten treatments, is approximately 2.5 times higher than the initial value. For sample P1, the conductivity remains the same within the accuracy of the measurements. No particles were observed by the DLS method in pure water. After 1-2 sonications in samples G1 and P1, 80-90 nm particles were detected by DLS. Within the limits of measurement accuracy, the particle size does not change after repeated sonications. However, the reproducibility of size measurements is low, which may be due to the low concentration of such particles and the broad size distribution of such particles in the samples. The zeta potential of these particles does not vary with the number of sonications. For particles in sample G1, the zeta potential is about -40 mV, for particles in sample P1 about -20 mV. One can say that the sonicating vessel material affects the change in the physicochemical properties of the sample.
Figure 1. The dependence of the intensity of the scattered light, conductivity, radius and zeta potential of particles on the number of sonications. A, B, C, D and E, F, G, H for samples G1 and P1, respectively.

After ten sonications over one day, samples G1 and P1 were used to measure the scattered light intensity, conductivity, particle radius, and zeta potential over several weeks. The results of these measurements are presented in Figure 2.

It can be seen from Figure 2 that, 2-3 days after dispersion, the scattering intensity in samples G1 and P1 decreases 2-3 times and subsequently does not change significantly. This decrease may be because, after sonication, the samples are not in equilibrium, and in the first 2-3 days, they come to an equilibrium state. Such equilibrium establishment times are close to equilibrium establishment times in a system containing nanobubbles and are associated with the lifetime of such nanobubbles [5-8]. In water, nanobubbles can be visualized using Cryo-EM [9], and their size and concentration can be measured using various experimental techniques (DLS, NTA) [10]. At the same time, the particle radius measured by the DLS method during the observation period increased from 100-130 nm to 250-300 nm in both samples.

Samples G1 and P1 are characterized by an increase in conductivity after several days and stabilization at the level of 0.05 mS/cm and 0.03 mS/cm, respectively. The zeta potential in the studied samples decreases monotonously, and the observation time changes approximately twofold over time. An increase in the average particle size and a decrease in the zeta potential modulus indicates low stability of this dispersion.

Figure 3 shows the results of measurements of scattered light intensity, conductivity, particle radius, and zeta potential for sample G2 within 28 days after sample preparation. Samples G1 and G2 were prepared in the same glass vials. The sonication time is the same for 5 minutes, but sample G1 was sonicated ten times for 30 seconds, and sample G2 was sonicated once for 300 seconds. Comparing the results of studies of samples G1 and G2 (Figs. 1, 2, and 3), it can be seen that the properties of these samples differ slightly in the first days after preparation, but subsequently, after establishing equilibrium values, they become close in their values. The intensity of the scattered light is notably different in these samples immediately after preparation, but after the observation time, it stabilizes at around 1.5×10^6 counts per second (cps). The samples' conductivity increases by about three times; the particle radius increases from 90-100 nm to 200-250 nm, and the zeta potential decreases by about two times in absolute value.
Figure 2. Dependence of scattered light intensity, conductivity, particle radius and zeta potential on the time elapsed after sonication. A, B, C, D and E, F, G, H — for samples G1 and P1, respectively.

Figure 3. The time dependence of the scattered light intensity, conductivity, particle radius and zeta potential for sample G2.
Figure 4 shows microphotographs obtained using TEM for sample G1 40 days after preparation. Microphotographs clearly show that particles with sharp edges, not spherical, are present in the studied sample. This form is typical for particles obtained by mechanical grinding of a large piece of material. EDX analysis of the detected nanoparticles showed that the nanoparticles have titanium in their composition. The Kα line of titanium (4.508 keV) was present in all the obtained EDX spectra. Also present were Cu lines (TEM grid material). Lines of other metals were not uniquely identified. These titanium-containing particles appeared in the sample, breaking off from the surface of the titanium horn of the sonicator. From the analysis of microphotographs, one can conclude that the sizes (diameter) of these particles lie in the range of 50–300 nm, which is consistent with the results obtained for these particles by the DLS method. With an increase in the sonication time, the formation of these particles can explain the increase in light scattering intensity.

In Figure 4A, in addition to the particles described above with a size of 50–300 nm, one can notice that there are light and dark areas on microphotographs. TEM microphotographs of these regions with maximum magnification did not allow for reliable identification of individual particles. The dark areas in this figure indicate the presence in the sample of some substance forming a film upon drying. In this work, we were not able to determine what kind of substance it is. It likely provides an increase in the conductivity of the samples.

4. Conclusions
The formation of the nanoparticles in pure water after sonication with a titanium submersible activator (horn) was studied.

It was shown that the treatment of pure water by ultrasonication leads to the formation of titanium-containing nanoparticles in it with a size of 50–300 nm with a zeta potential of around -30 mV and an increase in the conductivity of water. Most likely, this process is due to the erosion of the submersible horn surface. It should be noted that the sonicated dispersions can be contaminated by the eroded horn material, which could affect particle size, conductivity, and zeta potential of the particles in the prepared dispersion.

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