

## NEW EXPERIMENTAL DATA ON THE BUBSTON CLUSTERS IN AQUEOUS SALT SOLUTIONS

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Using independent methods of interference phase microscopy (IPM), dynamic light scattering (DLS) and polarization scatterometry (PS), we provide a direct experimental evidence for the spontaneous formation of clusters composed of ion-stabilized bubbles (bubstons) in the volume of pre-filtered aqueous ionic solutions. Here we have not studied nanobubbles adhered to solid hydrophobic interface. Experimental routine is described in detail [1, 2], while a theoretical interpretation of the results is given in [3]. In the IPM experiment we measured the spatial distribution of refractive index across a bubston cluster in aqueous NaCl solutions at different concentrations; for a cluster with a mean radius of 1  $\mu\text{m}$  we obtained a value  $n = 1.26$ , i.e. refractive index is slightly higher than that of the gas phase, but less than the refractive index of aqueous salt solution. Thus the particles spontaneously arisen in the liquid sample may be bubston clusters; indeed, excess in the refractive index compared to the water can be attributed to the contribution of liquid interlayers between the gas cores. Furthermore, in the DLS experiment with filtered salt solutions at various concentrations we found that the addition of ions results in appearance of scatterers with a non-symmetric size distribution function; this function can be approximated by an exponential curve. The minimum size of the scatterers (which corresponds to the peak of the function) belongs to tens of nanometers, and the exponential tail extends to the micron scale. The scatterer minimum size slightly increases with growing the content of ions. In accordance with a kinetic model, the minimum size of the scatterers corresponds to individual bubstons with a fixed radius, the higher radii are related to dimers, trimers and other clustered particles arisen as a result of the ballistic (driven by an attractive force) aggregation of bubstons [4]. To prove the cluster nature of the scatterers we carried out the PS experiments with the wavelength  $\lambda = 532$  nm, in these experiments, we measured the angular dependencies of the scattering matrix elements. It was found that the angular dependence of the first element of the matrix  $F_{11}$  (the scattering indicatrix) can be approximated by a theoretical curve, describing the scattering by particles greater than or about the wavelength. At the same time, the angular dependences for the rest of elements of the matrix are similar to the functions, corresponding to the Rayleigh scattering; we note that these elements give an idea of the internal structure of the scatterers. Such a behavior of matrix elements is typical for nanoparticle clusters. The monomers in the clusters can be associated with nanobubbles (bubstons), which are also revealed as nanometer-scale particles in the DLS experiment. Clusters can reach a size of about micron as it was observed in both DLS and IPM experiments. We have solved the inverse scattering problem: we have theoretically determined certain characteristics of the ensembles of bubston clusters (the average number of monomers in a cluster, the mean bubston radius, the fractal dimension of clusters) that fit best the experimental data for all 16 elements of the scattering matrix. For these clustered particles we modeled their effective refractive index as a function of the gyration radius of the cluster. For a radius of 0.5  $\mu\text{m}$  we arrive at  $n = 1.28$ , which is very close to the value measured in the IPM experiment ( $n = 1.26$ ). It follows from here that the solid nanoparticles, which were not filtered and always present in the aqueous salt solution (the refractive index of these nanoparticles, by our assumption, must be greater than that of water) is not likely to contribute significantly to the formation of the bubston clusters. We have also measured the characteristic lifetime of bubston clusters for the samples of ionic solutions, which were settled for several months in hermetically sealed polypropylene flasks. Thus we found that after settling within 5 - 6 months micron-sized particles completely disappear. As was detected in the DLS experiment, the size distribution function in the settled samples becomes narrower, compared to the non-settled samples. The minimum size (the size of a separate bubston) retains its value, while the exponential tail decays at about 200 nm. Thereby, Rayleigh-like scattering in the settled samples is dominant. The disappearance of micron-sized particles after a long-term settling cannot be associated with simple floating-up of bubston clusters due to the Archimedes force; by our estimations, in the samples that we used the floating-up is completely terminated in just a few hours. From our viewpoint, the clusters float to the liquid surface and break down there, and the released gas molecules re-enter into the liquid volume, where the spontaneous

generation of new bubstons with their subsequent aggregation with the formation of clusters occurs. However, the rate constant of floating-up for micron-sized clusters and their destroying is evidently higher than the rate constant of new-cluster formation, which eventually leads to the disappearance of large clusters. It is worth noticing that the contribution of the bubston clusters to the mean intensity of the light scattering is distinguished provided that the ionic concentration  $C > 10^{-3}$  M. At lower concentrations the level of the scattering intensity does not exceed the natural background attributed to the scattering by the refractive index fluctuations. To get information about the bubston clusters at very low concentrations of ions, we have developed a technique for measuring the concentration of such clusters in the sporadic (probabilistic) regime of an optical (laser-induced) breakdown of liquid. The optical breakdown experiments showed what properties of dissolved gas molecules are necessary for an effective nucleation of bubstons. It appeared that the gas molecules must be capable of interaction with the dipolar water environment. It follows from here that the nucleation of bubstons becomes impossible if the dissolved molecular gases are replaced with helium. Indeed, helium is atomic gas, which has the lowest electron polarizability. In addition, helium is chemically inert, and has minimal size, so can freely diffuse between the water molecules without distorting the hydrogen bond network. We developed a technique of the helium washing of liquid samples, which effectively removes all the dissolved molecular gases and replacing them with helium. Such processing allows us to remove completely the dissolved molecular gases from a liquid sample, replacing these gases with helium. As a result of such processing, water samples acquires new properties: optical breakdown threshold increases by 2 - 3 orders of magnitude, and their boiling arises at 170 - 180 C under 1 Atm of He. Since the helium-washed water does not contain dissolved gases, for such water pH = 7 and the redox - potential  $E_h = 0$  (these parameters for deionized water samples, which were subsequently processed by the helium-washing routine, were pH = 5.5 and  $E_h = 300 - 400$  mV respectively). Therefore, the oxidation processes are essentially suppressed in the helium-washed water: we kept a steel plate in such water within 24 hrs, and this plate was not covered by corrosion spots, while the same steel plates kept in the control samples of deionized (but non-processed) water became rusty very soon. We also studied emulsions of dodecane and perfluorohexane, prepared in the control samples of the non-processed water and in the helium-washed water without addition of surfactants. It turned out that the emulsions with the helium-washed water maintain stability within much longer time compared to the emulsions prepared in the non-processed water.

## References.

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