Shedding light on the formation of nanodroplets in aqueous solutions of polar organics

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A team of researchers in Russia worked together to shed new light on the heterogeneous nature of a polar organic liquid mixed with water. They used laser light as a tool in two ways, dynamic light scattering and phase microscopy, that allowed them to demonstrate the existence of stable nanodroplets of tetrahydrofuran (THF) in the bulk of aqueous electrolyte solutions and to develop a new theory that explains the spontaneous generation of heterogeneous nanoparticles in aqueous solutions of polar organic solutes in terms of nanodroplet formation due to "twinkling" hydrogen bonds.

Until recently it was thought that heterogeneous particles in binary mixtures of polar organic compounds could either be gas nanobubbles or giant stable molecular complexes, formed by the molecules of the solute or solvent. In an article appearing this week in the *Journal of Chemical Physics*, a research team that included scientists from four different Moscow institutions used THF, which has infinite solubility in water and which, in aqueous solutions of low THF concentrations, allows observation of abnormally high scattering of light due to the spontaneous formation of some heterogeneous centers. Combining dynamic light scattering with a novel experimental technique called laser phase microscopy that can measure the refractive index of nanometer-scale objects in liquids in addition to their sizes, allowed them to determine that the nanodroplets being observed in aqueous mixtures of THF at low concentrations basically consist of pure THF.

"We began by repeating previous laser light scattering experiments using dynamic light scattering, which actually confirmed the abnormally high level of scattering in this concentration range; demonstrating that the scattering centers are nanometer-scale particles," said N.F. Bunkin, a professor from Bauman Moscow State Technical University. Since the two pure liquids are mixed in a fixed ratio, these particles should consist of THF and water in a certain ratio. The problem, however, is that the light scattering experiments cannot be used to determine the percentage of these components in the scattering particles. "We managed to solve this problem by using a unique phase microscope that we developed in collaboration with other scientists from Russia; one that can measure not only the size of the nanoparticles in a liquid, but also determine their refractive index," Bunkin explained. "We found that the refractive index of the scattering objects in THF-water mixtures practically coincides with the refractive index of pure THF though, in accordance with the reference data, such THF nanodroplets just cannot exist in the solution of such concentration."

However, for the research team the biggest challenge was not the experiment, or even the development of the new microscope, but the development of a theory that incorporated and explained their results. Intuition suggests that the spontaneous formation of pure THF droplets in dilute aqueous solutions should be somehow controlled by the parameters of the interaction of water and THF molecules via hydrogen bonding. Roughly speaking, the THF molecule can either form a hydrogen bond with a neighboring water molecule, or not. If quite a large amount of THF molecules, localized in a nanometer-scaled area of the liquid solution, simultaneously rupture the hydrogen bonds with the neighboring water molecules, a nanodroplet of pure THF is created in this area, a fact was observed in this experiment.

The team is already looking ahead to the next steps in this research. The kinetics of nanodroplet nucleation is still beyond the scope of their

proposed model. They are planning to carry out similar experiments with aqueous solutions of organic liquids from the furan group which has different polarizability and dipole moments, and with solutions of water isotopes (H20, D20 and deuterium depleted water) that have different energies of intermolecular hydrogen bond and to explore the role of dissolved gas.

More information: N. F. Bunkin et al, Droplet-like heterogeneity of aqueous tetrahydrofuran solutions at the submicrometer scale, *The Journal of Chemical Physics* (2016). DOI: 10.1063/1.4966187

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