

STUDY OF THE CHARACTERISTICS OF THE HYDRATION OF CARBON NANOPARTICLES IN AQUEOUS DISPERSIONS USING THE SPIN PROBE ESR METHOD

Rozhkov S.P., ²Rozhkova N.N.

Institute of Biology Karelian Research Center RAS, 185910 Petrozavodsk, Russia

² Institute of Geology Karelian Research Center RAS, 185910 Petrozavodsk, Russia

* Fax: 7(8142)769810, E-mail: rozhkov@krc.karelia.ru

Introduction

The biomedical direction being the most perspective application of carbon nanomaterials proposes an interaction of these materials with water. Furthermore, from environmental point of view it would be helpful to use water as a medium in spite of the carbon apparent hydrophobicity, for the development of the carbon material science technologies. Methods of aqueous dispersions of nanocarbons preparation without using SAS are worked out [1]. But the question of their stabilization under aggregation process arises [2]. A diluted fullerene solution looks like transparent brown dispersion containing both separate hydrated fullerenes and their hydrated fractal clusters of different dimensions. The smallest one keeps 13 hydrated molecules of C_{60} and has radius of 3-4 nm, otherwise the largest cluster has radius of 60 nm.[3]. The fullerene hydration and stabilization in colloids are rather complicated problem. The most prevailing and proved hydration model is based on donor-acceptor complexes of water molecules with fullerenes including several layers of solvents [3]. Actually the formation of specific hydrated shells around nanoparticles preventing on coagulation is one of the main factors of their stability. Therefore, to study the properties of these shells has to be of a primary importance.

The behavior of pure water is still unclear although there are rather many ways of water investigations. To study water modified with the surface of nanoparticles is particularly complex. First of all because the ratio of this water is small or properties differ slightly in comparison with the bulk water.

Methods and objectives

In the spin probe ESR method, the bulk water problem was solved methodically by freezing nanocarbon dispersions with predominant freezing-out of a bulk water fraction in comparison to the water fraction modified by the surface of nanoparticles. The latter is frozen out at lower temperatures, and the spin probe retains recorded mobility in this water phase for a longer time. The phases localized near polar and non-polar groups

are freezing consequently [4]. This method can be employed to make measurements at any concentrations of disperse phase particles. A 4-Oxo- TEMPO (Sigma) hydrophilous spin probe was introduced at a concentration of 0.1 mM into colloid shungite carbon ShC (ShC is a natural carbon composite) solutions of varying concentrations (0,1, 1,0 и 10 mg/ml), and for control purpose into fullerene (C_{60}/C_{70} FWS) and aerosil solutions. ShC solutions were prepared similar to C_{60} FWS [1]. At such a probe concentration their exchange interaction in EPR spectra is not apparent. EPR probe spectra were taken in the temperature range of 287K – 230 K at a step of 1-2 K.

The effective correlation times of spin probe rotation τ^{sp} and inverse rotation frequencies $1/\tau^{\text{sp}}$ were estimated from the EPR spectra; this provided a basis for calculating the effective thermodynamic parameters of probe rotation activation (energy ΔE , enthalpy ΔH and entropy ΔS) in different micromedia in the Arrhenius coordinates. Variations in the isotropic constant of the superfine structure (SFS) of the spectrum A_0 , which characterizes an interaction between a nitroxyl fragment of the probe and surrounding water molecules, were also studied.

Results and discussion

It appeared that no valid difference in probe mobility in different solutions is observed in the range of the liquid state of solutions ($\Delta E = 5.1 \pm 0.4 \text{ kJ/M}$, $\Delta H = 9.0 \pm 0.2 \text{ kJ/M}$, $\Delta S = 14 \pm 1 \text{ J/M K}$) because probe concentration in the solution volume predominates. Upon freezing of the solution (at – 13 °C because of water supercooling in a narrow capillars), the ambient microviscosity of the probe rises considerably with an increase in distribution with respect to correlation times, and signals from the probes located in the unfrozen water layer near the surface of nanoparticles persist as the most mobile.

The most substantial changes in the thermodynamic parameters of rotation activation are observed for all samples over the temperature range of 250 K – 230 K. In this case, probe rotation

frequency for both ShC and C₆₀FWS samples containing diluted concentrations of carbon nanoparticles (0.1 mg/ml), remains practically unchanged in a relatively wide temperature range 255-245 K and only after that begins to decrease.

Available data show that in low-concentration carbon nanoparticle solutions the isotropic constant SFS of the spin probe A₀ decreases rapidly immediately after freezing, which suggests that the probe is located in a medium, where water does not form a hydrogen bond with a nitroxyl fragment. This could be structured water in a hydrophobic cavity; it has low dissolving ability and a distinctive cluster structure with undistorted hydrogen bonds. These cavities between hydrophobic surfaces presumably have optimum sizes [4] because in large cavities (50 nm cavities in the aerosol in our experiment) effects are not observed.

Based on SAXS and SANS data the cavities dimensions that are acceptable for water in the clusters of fullerenes and ShC are estimated to be in the range of nanometers – tens nanometers.

This water phase in the cavity can be destroyed by osmotic forces: either by adding an electrolyte or by increasing the concentration of the disperse phase (nanoparticles).

It was observed in the experiment with presence of NaCl and increasing of the dispersion phase when the constant SFS A₀ noticeably increase.

When the water in the hydrophobic cavities is already frozen, the water, which is presumably bound to polar groups on the surface of nanoparticles and which allows the spin probe to show dynamic behaviour, has remained. As freezing continues to 230 K and lower, this water fraction also loses mobility, but in different manners, depending on the composition of the solution and its stability to aggregation, which is reflected in rotation activation parameters.

In colloid solutions with a low concentration of carbon nanoparticles (resistant to aggregation) there exist both hydrophobic cavities filled with water clusters (microphases) showing a distinctive structure and the polar sites of the surface that coordinate water molecules and form a separate microphase. Water in the nonpolar cavities is the

first to be destroyed under the influence of an electrolyte or high carbon nanoparticle concentrations (the stability of solutions decreases substantially). We assume that it is water in these cavities that prevent direct interaction between nanoparticles in a cluster and their coagulation, and polar parts are exposed on the external surface of a carbon cluster. As solutions of any carbon nanoparticle concentrations coagulate rapidly after thawing, the original structure of water in the cavities is not restored.

Conclusions

The separated phases of near-surface water that are coordinating by hydrophobic surface areas and by the cavities of non-polar structures, and the phases that are forming near polar groups, were observed in aqueous dispersions of fullerenes and nanoparticles of ShC applying the spin probe ESR method in freezing dispersions.

Dynamic and structural properties of these phases correlate with stability of nanoparticles to aggregation.

References

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