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# Stabilization of nanodiamond dispersions with nonionic surfactant Igepal CA-630 in water and dimethyl sulfoxide

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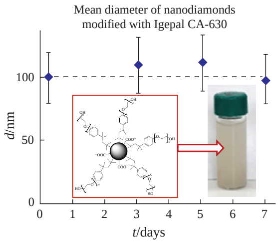
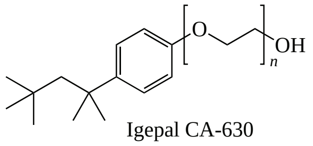
**Nanodiamond dispersions in water and DMSO were stabilized with adsorbed layers of nonionic surfactant Igepal CA-630. Adsorption isotherms of Igepal CA-630 onto nanodiamonds from water and DMSO reveal the structure of the adsorbed layers. The stabilized aqueous dispersions retain their resistance to aggregation for at least 7 days, while the dispersions in DMSO are stable for 3 days.**



*Keywords*: detonation nanodiamonds, adsorption, nonionic surfactant, Igepal CA-630, spectrophotometry, IR spectroscopy, dynamic light scattering, dispersion stabilization.

Stabilization of dispersions of detonation nanodiamonds (NDs) in various media is required for employment of NDs as fillers in composite polymeric materials to promote their hardening,[1–3] as well as for their use as carriers for biologically active substances, biosensors,[4] optical filters[5] and abrasive materials. In composite polymeric materials, NDs are employed to promote hardening. The effectiveness of NDs largely depends on their resistance to aggregation in the polymeric matrix, especially during the fabrication process[1–3] from aqueous suspensions for polyvinyl alcohol (PVA) films[1,2] and from dispersions in DMSO for the polyacrylonitrile ones.[3] The distribution of NDs in the polymer matrix also affects the surface[6] and optical[7] properties of the composites. Thus, the search for effective ways of stabilizing NDs in different media is relevant for the preparation of polymer composite films with a uniform distribution of particles. Surfactants are known as effective stabilizers of ND dispersions in various media.[8–12] The purpose of this work was to explore the adsorption of a nonionic surfactant onto NDs from aqueous medium and DMSO as well as to evaluate the effect of adsorption layers of the surfactant on stability of the ND dispersions. The nonionic surfactant Igepal CA-630 represents an ethoxylated branched octylphenol with an average degree of polymerization $n = 9$ and HLB value of 13.0. It is highly soluble in water or DMSO and is used as an effective stabilizer for ND dispersions.[8]



Igepal CA-630

Pristine NDs (see Online Supplementary Materials) were oxidized with air in a tube furnace at 420 °C for 2 h to eliminate non-diamond forms of carbon and increase the amount of acidic groups on the surface.[12–14] Aqueous dispersions of NDs were obtained by ultrasonic treatment and contained particles with an average diameter of 100 nm and ζ-potential of –37 mV at pH 5.3. Acording to our data,[15] the isoelectric point value of these NDs was 3. The dispersions were stable for 2 days. In DMSO the average particle size for the dispersion was 150 nm, the dispersion had been stable for less than 1 day, after that the particles aggregated, settled and formed a precipitate.

Surface tension isotherms of Igepal CA-630 in water and DMSO reveal that the surfactant behaves as a conventional micelle-forming one in aqueous solution and as a surface-inactive substance in DMSO (Figure 1). The latter result means that the hydrocarbon chains of Igepal CA-630 are located in the liquid DMSO phase, while polyoxyethylene fragments are disposed at the air–liquid surface. For an opposite layout, the surface tension would decrease with the concentration elevation. Thus, hydrocarbon chains of the surfactant are considered to have more affinity to DMSO compared with the polyoxyethylene ones.

Adsorption of Igepal CA-630 onto NDs was calculated from a decrease in the surfactant concentration in the solution using spectrophotometric measurements[†] according to the equation:

$$\Gamma = \frac{(C_0 - C_\mathrm{s})V}{m},$$

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[†] UV-VIS spectra were recorded using a Helios Zeta double-beam spectrophotometer (Thermo Fisher Scientific, USA). Igepal-630 solutions exhibited pronounced maxima at 275 nm in water and 289 nm in DMSO. From the dependence of optical density at $\lambda_\mathrm{max}$ ($A_\mathrm{max}$) *vs.* the surfactant concentration, extinction coefficients $\varepsilon$ were determined as equal to 1377 and 1689 $\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$ for water and DMSO, respectively. For the adsorption measurement, 2.5 mg $\mathrm{ml^{-1}}$ dispersion of NDs was prepared by ultrasonication, then aliquots of the dispersion were added to the surfactant solutions. After the adsorption equilibrium had been established for 1 d, number-average particle size distribution and ζ-potential of the particles (in aqueous media) were measured using a Zetatrack laser particle size analyzer (Microtrack, USA). Then the ND dispersions in the surfactant solutions were precipitated in a MiniSpin microcentrifuge (Eppendorf, Germany) at 12400 rpm for 5 h. After that, the absorption spectra of supernatants were recorded and the surfactant concentration $C_\mathrm{s}$ was determined from absorption intensity of the supernatant as $C_\mathrm{s} = A_\mathrm{max}/\varepsilon$.

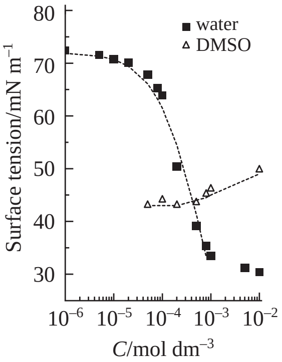

**Figure 1** Surface tension isotherms of Igepal CA-630 in water and DMSO.

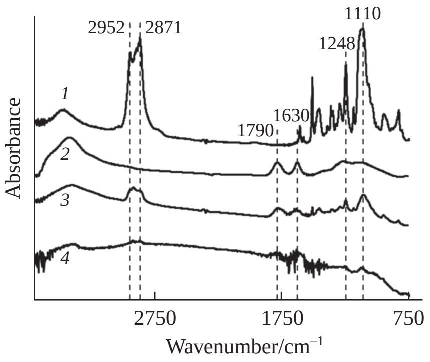

**Figure 3** IR spectra of (*1*) Igepal CA-630 and (*2*) NDs as well as NDs modified with Igepal CA-630 from (*3*) water and (*4*) DMSO.

where $C_0$ and $C_s$ were initial and equilibrium concentrations of the surfactant, respectively, in mol dm$^{-3}$, $V$ represented solution volume in dm$^{-3}$ and $m$ was the weight of NDs in g.

It was found that adsorption of the surfactant onto NDs from aqueous solutions significantly exceeded that from DMSO (Figure 2). It is known that organic amphiphilic molecules, *e.g.*, various types of surfactants,[12,16,17,18] proteins,[19] polymers[20] and drugs[21] can interact with surface either by polar groups or due to hydrophobic interactions. We have shown that the hydrophobic interactions play a decisive role in the adsorption of surfactants onto NDs from aqueous solutions.[15] Therefore, the low values of Igepal CA-630 adsorption from DMSO can be attributed to the absence of hydrophobic interactions with the surface of NDs. NDs modified with Igepal CA-630 adsorption layers originated from water are thermally stable up to 260 °C. When the modification occurs in DMSO, the system is thermally stable up to 290 °C (Figure S1, See Online Supplementary Materials).

IR spectra were recorded for the oxidized NDs, Igepal CA-630 and the NDs modified with Igepal CA-630 layers adsorbed from aqueous media and DMSO (Figure 3).[‡] The spectrum of unmodified oxidized NDs reveal clear peaks at 1790 and 1630 cm$^{-1}$ corresponding to vibrations of C=O and O–H groups as well as a broad peak at ~3500 cm$^{-1}$ most often associated with a presence of adsorbed water on the surface of NDs. In the spectrum of Igepal CA-630, the peaks at 2952 and 2871 cm$^{-1}$ correspond to the vibrations of $CH_2$ groups in hydrocarbon chains, while the peaks at 1248 and 1110 cm$^{-1}$ can be assigned to C–O stretching vibration in the ethoxylated chain.[12,16,22–24] For NDs with Igepal CA-630 adsorbed from aqueous solutions, peaks at 2952 and 2871 cm$^{-1}$ are attributed to the adsorbed surfactant molecules, the spectra of this dispersion exhibit almost all the peaks present of unmodified NDs and the pure surfactant. It can be concluded that the adsorption proceeds through hydrophobic interactions.

By the contrast, the spectrum of NDs modified with Igepal-630 from DMSO contains almost no peaks of polar groups on the ND surface as well as no peaks of Igepal CA-630 due to low adsorption value as well as possible interactions between polar groups of NDs and the surfactant. The suggested structures of the surfactant layers on the ND surface in water and DMSO are shown in Figure 4.

Dispersions of NDs obtained after ultrasonic treatment contained particles with an average diameter of 100 and 150 nm in water and DMSO, respectively. After modifying by Igepal CA-630 from an aqueous solution, the average particle diameter remained almost unchanged. The ζ-potential of the particles varied from –17 mV in the $5\times10^{-5}$ mol dm$^{-3}$ surfactant solution to –23 mV in the $1\times10^{-3}$ mol dm$^{-3}$ one. The negative value of ζ-potential is explained by the presence of ionized carboxyl groups on the ND surface. The particle size measured in aqueous solutions of Igepal CA-630 after 3, 5 and 7 days after preparation of the dispersion remained almost unchanged, confirming aggregation stability of the system [Figure 5(*a*)].

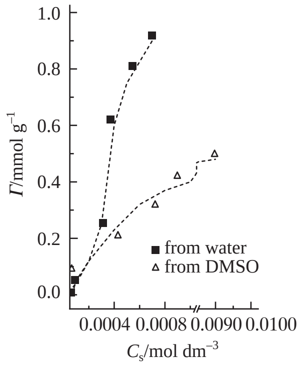

**Figure 2** Isotherms of Igepal CA-630 adsorption onto NDs from water and DMSO.

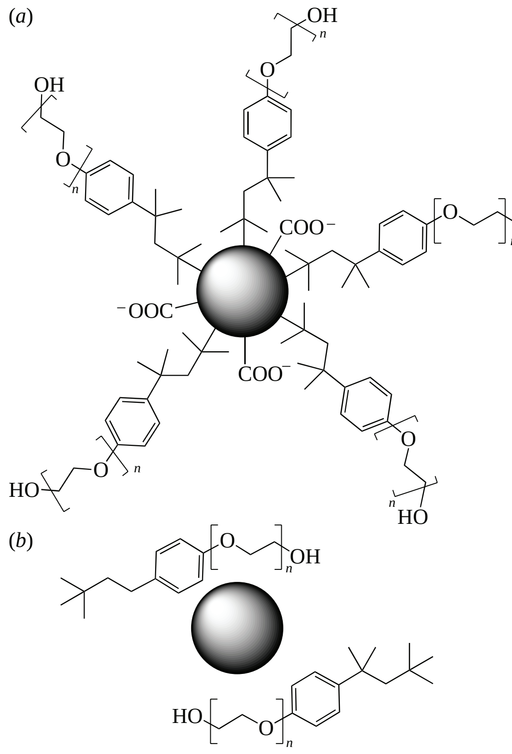

**Figure 4** Suggested structure of Igepal CA-630 adsorption layers onto NDs in (*a*) water and (*b*) DMSO.

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[‡] IR spectra were recorded in KBr pellets using a Nicolet IR spectrometer (Thermo Fisher Scientific, USA).

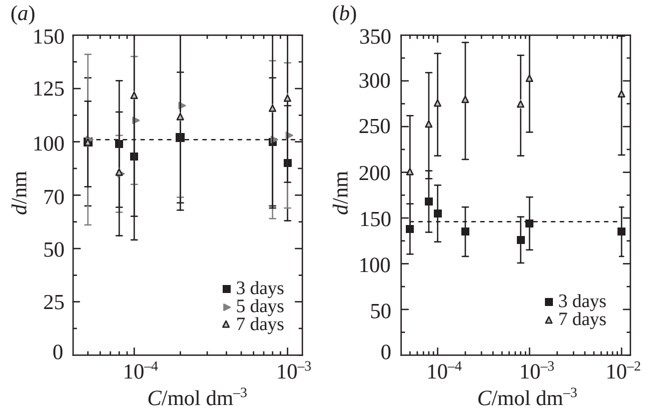

**Figure 5** Average diameter of NDs in the presence of Igepal CA-630 in (*a*) water and (*b*) DMSO. Dashed lines correspond to average NDs diameter in solutions without surfactant.

The particle size for Igepal CA-630 solutions in DMSO obtained immediately after preparation was close to that of unmodified NDs and did not change within 3 days. On a longer time scale the particle size increased, which indicated a loss of aggregation stability. The higher the surfactant concentration, the larger the size of the formed aggregates [Figure 5(*b*)].

The stability of ND dispersions in water and DMSO increases markedly in the presence of Igepal CA-630 adsorption layers. Aggregative stability of the hydrosol is ensured both by electrostatic repulsion provided from ionized groups on the surface of NDs and by steric repulsion of the Igepal CA-630 layers. Dispersions of NDs in DMSO are less stable due to lower adsorption of the surfactant and the resulting weaker steric stabilization.

In summary, aggregation-resistant ND dispersions in different media were prepared. These systems can be employed to create polymeric composites with a uniform distribution of nanoparticles.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.05.041.

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