SUPPORTING INFORMATION to the paper

Toward the better understanding of C$_{60}$ organosols

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Some examples of the re-charging of C$_{60}$ colloidal species in CH$_3$CN

It should be noted that, the re-charging begins even in extremely diluted solutions of acids and calcium perchlorate and the coagulation. The systems with the re-charged colloidal species are shown in Figures 1–3. In entire acetonitrile, the pK$_a$ values for HClO$_4$ and CF$_3$SO$_3$H are 1.57 and 2.60, respectively.$^1$

![Figure 1](image1.png)

**Figure 1.** Acetonitrile with 1 vol. % toluene, C$_{60}$: $4 \times 10^{-6}$ M, 0.01 mM Ca(ClO$_4$)$_2$.

![Figure 2](image2.png)

**Figure 2.** Acetonitrile with 1 vol. % toluene, C$_{60}$: $4 \times 10^{-6}$ M, 0.01 mM HClO$_4$. 

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Figure 3. Acetonitrile with 1 vol. % toluene, $C_{60}: 4 \times 10^{-6}$ M, 0.01 mM CF$_3$SO$_3$H.

Figures 4 and 5 demonstrate the rise in the size of fullerene colloidal species, which are re-charged in 0.15 mM CF$_3$SO$_3$H; $\zeta = +29 \pm 7$ mV.

Figure 4. Acetonitrile with 1 vol. % toluene, $C_{60}: 4 \times 10^{-6}$ M, 0.15 mM CF$_3$SO$_3$H (starting conditions).

Figure 5. Size increase in time: the same organosol (Figure 4) after 20 minutes.

Normally, the $C_{60}$ colloids re-charged by acids are unstable in time, exhibiting growth of the particles.
Experiments with the C\textsubscript{60} sol prepared using Deguchi’s hand-grinding technique

Some experiments have been made with the C\textsubscript{60} colloid in acetonitrile prepared following the Deguchi’s procedure of hand-grinding in an agate mortar, with further sonication\textsuperscript{2}. The latter was carried out with 15–30 min time intervals. The particle size was determined by DLS technique: 273 ± 5 nm (by number), 296 ± 8 nm (by volume), and 280 ± 5 nm (by intensity); PDI = 0.264 ± 0.009; ζ = –31.0 ± 1.2 mV. If the ultrasound treatment was permanent, somewhat smaller species were obtained. The TEM data are exemplified below (Figure 6). The species are as a rule more monolithic as compared with the sol obtained via the dilution of toluene solution by acetonitrile.

![Figure 6. The TEM images of the colloidal particles, which were obtained by hand-grinding.](image)

If the organosol has been prepared with acetonitrile which contained ionol, the zeta-potential was substantially less negative, ζ ≈ –7 mV.

The primary electrospray data for the C\textsubscript{60} sol in acetonitrile–benzene (1 : 1 by volume) are given below; fullerene concentration 4.0 × 10\textsuperscript{-5} M.
The electrospray data

**Figure 7.** The $C_{60}$ sol in acetonitrile–benzene (1 : 1 by volume) are given below; fullerene concentration $4.0 \times 10^{-5}$ M.
Other solvent systems

The C$_{60}$ organosols in other solvents exhibit as a rule a higher polydispersity and a less negative zeta-potential as compared with the colloid systems in acetonitrile and acetonitrile – benzene mixed solvent.

\[ \zeta = -16.5 \pm 2.5 \text{ mV} \]

**Figure 8.** The C$_{60}$ sol in toluene + DMSO mixed solvent, 1:1 by volume; fullerene concentration $3.4 \times 10^{-5}$ M.

\[ \zeta = -21.0 \pm 1.3 \text{ mV} \]

**Figure 9.** The C$_{60}$ sol in methanol with 1 vol. % toluene; fullerene concentration $4 \times 10^{-6}$ M.
Figure 10. The same sol (Figure 9), but with 0.01 M 2,6-di-tert-butyl-4-methylphenol; 1 h 18 min after preparation: rise in size without changes in the zeta-potential.

Figure 11. UV-visible absorption of $4 \times 10^{-6}$ M C$_{60}$ sol in methanol with 1 vol. % toluene; optical path 1.00 cm.

Calculations of the surface charge density

The interfacial electrostatic potential, $\Psi$, of the colloidal species is determined by the surface charge density and the ionic strength of the bulk. Though $|\Psi| > |\zeta|$, for the relatively low-charged species the experimentally available zeta-potential may be used as the interfacial one in order to estimate the value of the surface charge density, $q_s$. For such calculations, the Ohshima – Healy – White equations for spherical and cylindrical particles$^3$ may be used:
\[ q_s(\text{sphere}) = \frac{2\varepsilon \kappa RT}{F} \sinh(Y/2) \left( 1 + \frac{2}{\kappa r \cosh(Y/4)} + \frac{8 \ln[\cosh(Y/4)]}{(\kappa r)^2 \sinh^2(Y/2)} \right)^{\frac{1}{2}}; \]

\[ q_s(\text{cylinder}) = \frac{2\varepsilon \kappa RT}{F} \sinh(Y/2) \left( 1 + \frac{K_0^2(\kappa r)}{K_2(\kappa r)} \right)^{\frac{1}{2}}. \]

Here, \( Y = \Psi F / RT \), \( F \) is the Faraday constant, \( \kappa \) is the reciprocal Debye length, \( r \) – radius of the particle, \( \varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1} \), and \( K_n(\kappa) \) is the modified Bessel function of the second kind of order \( n \). For acetonitrile at \( T = 298 \text{ K} \), \( \varepsilon = 36. \)

For species with diameter of AE 200 nm, even the equation for the flat double electrical layer may be used. For example, the estimates of the surface charge \( q_s \) in 1:1 electrolyte solution of concentration \( c \), M in acetonitrile have been processed using the following equation:

\[ q_s = 0.49 \sqrt{c} \sinh \frac{\zeta}{51.38} \]

Here \( \Psi \) stands for the interfacial electrical potential, mV, \( q_s \) is expressed as charge per nm². If the \( \zeta \) values are used for the NaClO₄ concentrations well below the CCC (which is around 0.1 mM), the mean value is \( |q_s| = 7.85 \times 10^{-4} \) elementary charges per nm², i.e., \( 1.27 \times 10^3 \) nm² per one charge.

In the Ca(ClO₄)₂ solutions around 0.15 mM, the \( |\zeta| \) value of re-charged colloidal species of the fullerene are even higher than in extremely diluted NaClO₄ solutions. This gives evidence for a higher \( q_s \) value and is in line with the high CCC value, necessary for the lowering of the potential barrier in terms of the DLVO theory.

**References**