SUPPORTING INFORMATION to the paper

# Toward the better understanding of C_{60} organosols

Nikolay O. Mchedlov-Petrossyan, Nika N. Kamneva, Younis T. M. Al-Shuuchi, Andriy I. Marynin, Olexiy S. Zozulia, Alexander P. Kryshtal, Vladimir K. Klochkov, Sergey V. Shekhovtsov

## Some examples of the re-charging of C_{60} colloidal species in CH_3CN

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_3SO_3H are 1.57 and 2.60, respectively.[1]
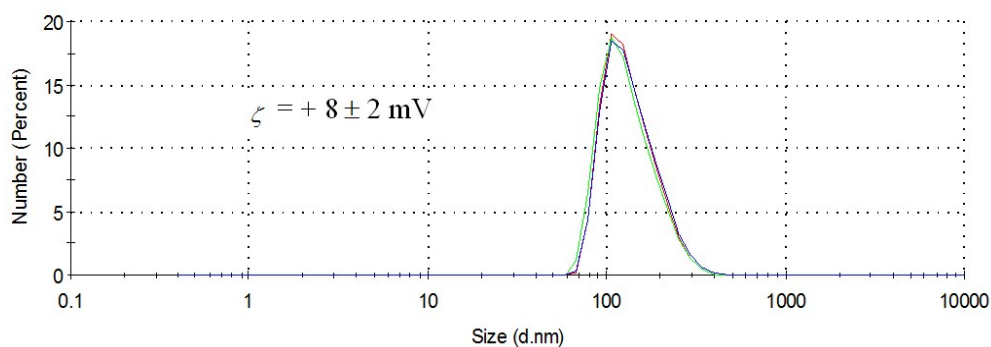
Figure 1. Acetonitrile with 1 vol. % toluene, C_{60}: 4×10^{-6} M, 0.01 mM $Ca(ClO_4)_2$.
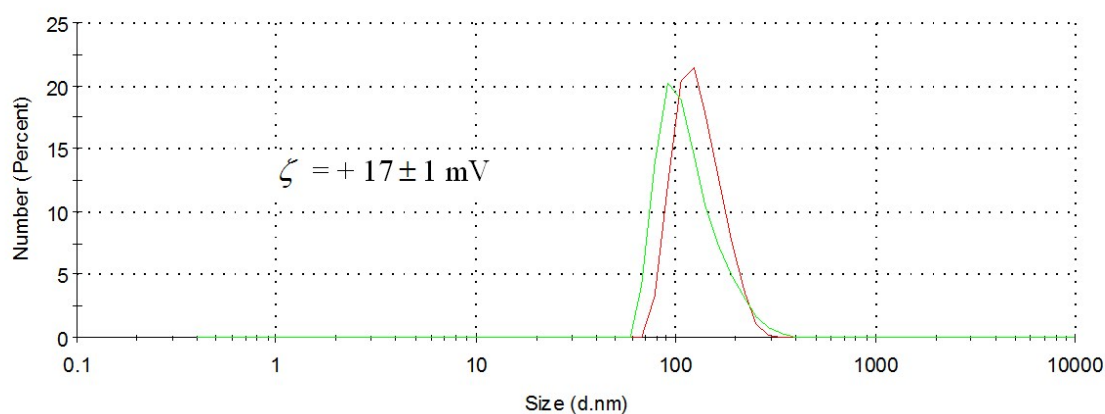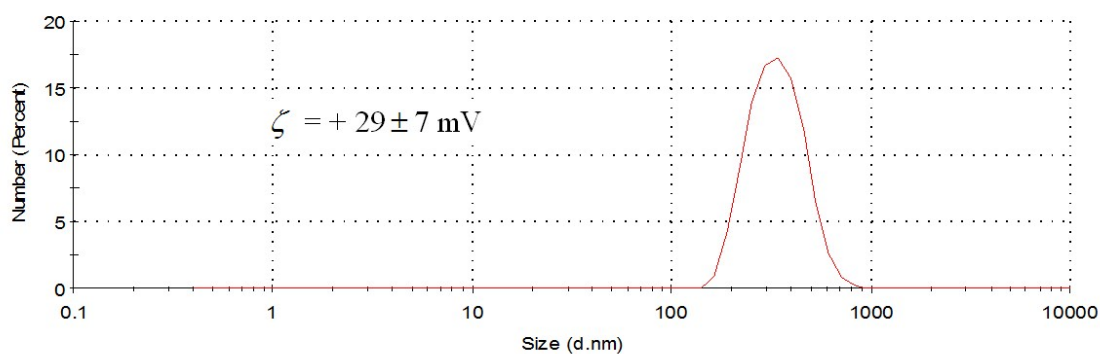

Figure 2. Acetonitrile with 1 vol. % toluene, C_{60}: 4×10^{-6} M, 0.01 mM $HClO_4$.
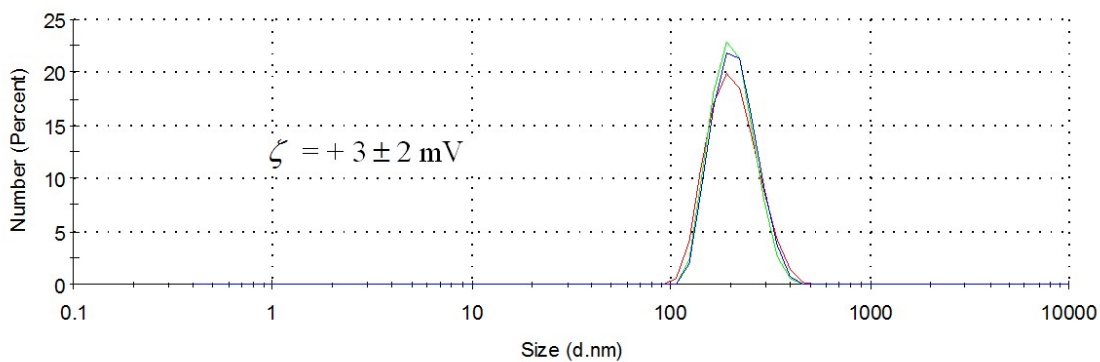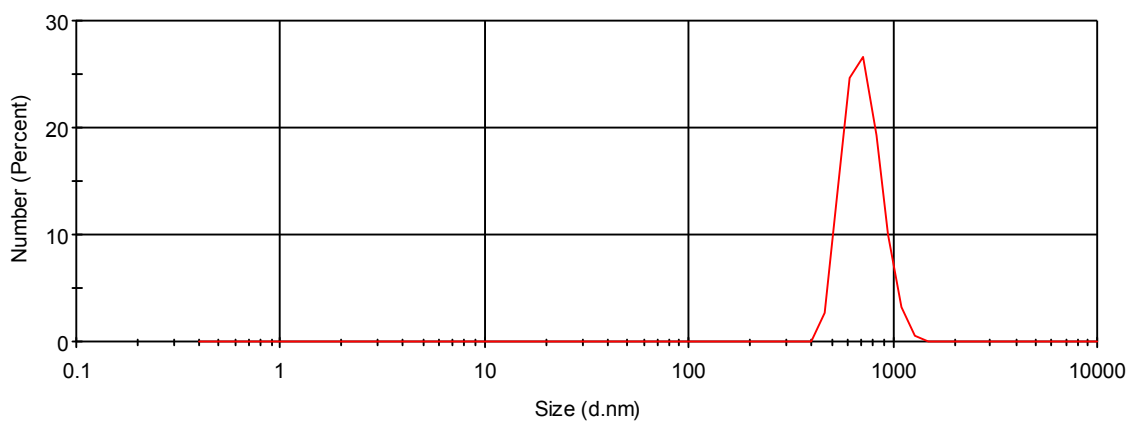
Figure 3. Acetonitrile with 1 vol. % toluene, C_{60}: 4×10^{-6} M, 0.01 mM CF_3SO_3H.

Figures 4 and 5 demonstrate the rise in the size of fullerene colloidal species, which are re-charged in 0.15 mM CF_3SO_3H; $\zeta = +29 \pm 7$ mV.

Figure 4. Acetonitrile with 1 vol. % toluene, C_{60}: 4×10^{-6} M, 0.15 mM CF_3SO_3H (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_{60} sol prepared using Deguchi's hand-grinding technique

Some experiments have been made with the C_{60} colloid in acetonitrile prepared following the Deguchi's procedure of hand-grinding in an agate mortar, with further sonication.[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 $= 0.264 \pm 0.009$; $\zeta = -31.0 \pm 1.2$ 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.
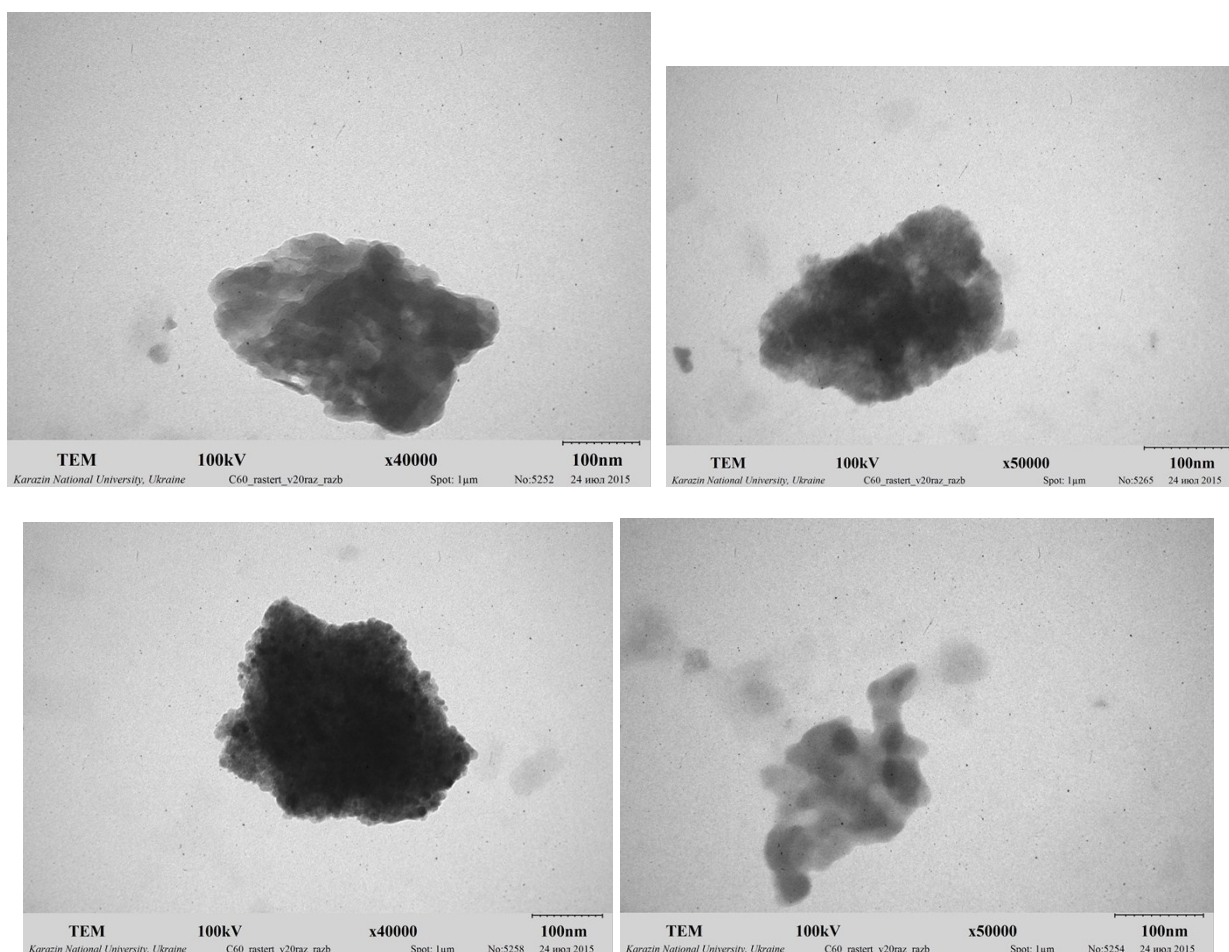

Figure 6. The TEM images of the colloidal particles, which were obtained by hand-grinding.

If the organosol has been prepared with acetonitrile which contained ionol, the zeta-potential was substantially less negative, $\zeta \approx -7$ mV.

The primary electrospray data for the C_{60} sol in acetonitrile–benzene (1 : 1 by volume) are given below; fullerene concentration 4.0×10^{-5} M.
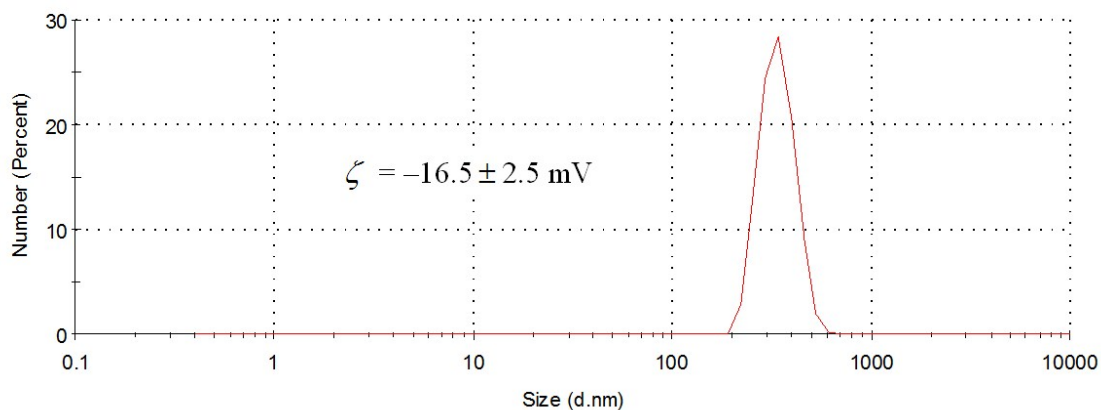
The electrospray data
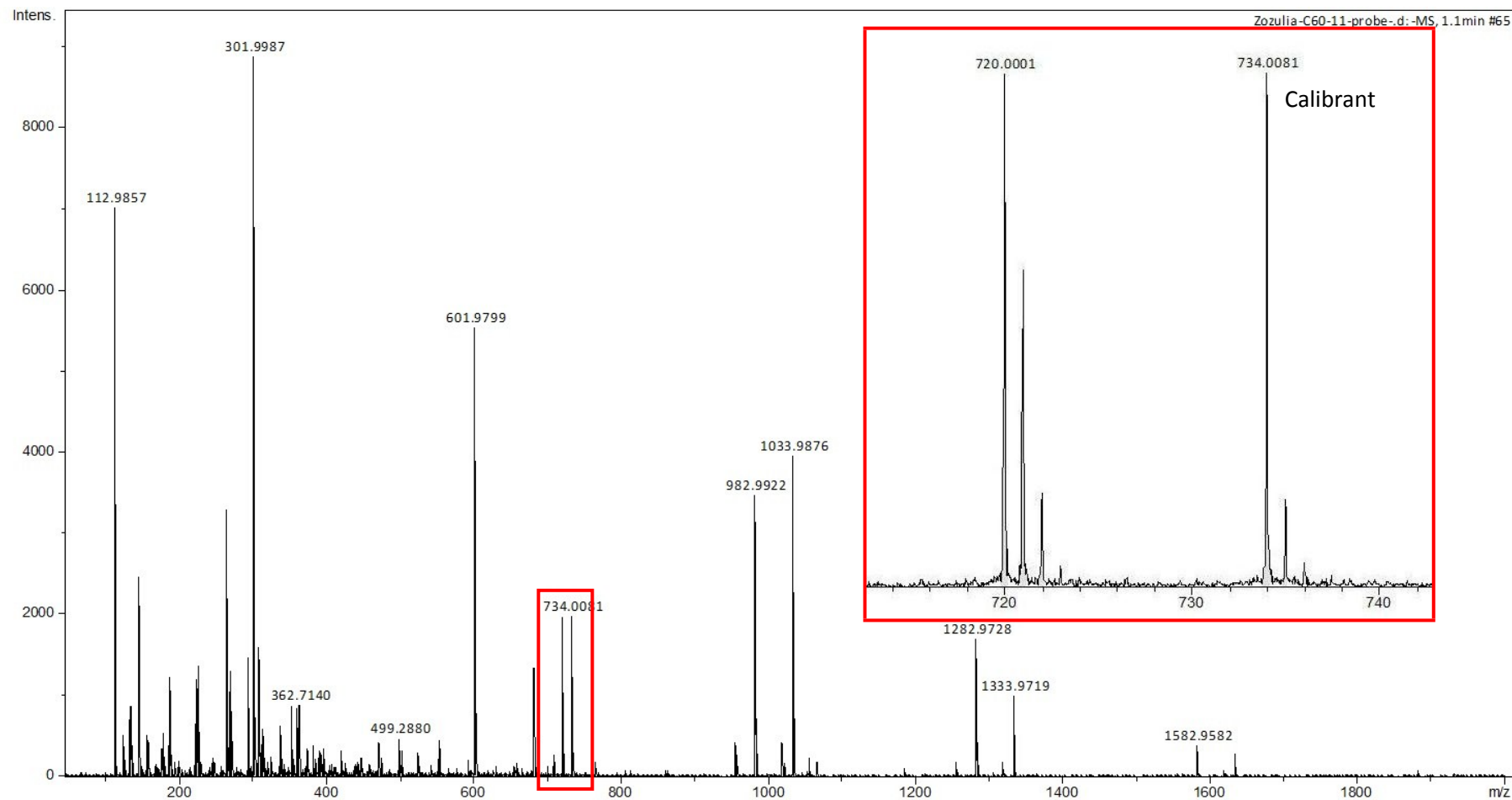
Figure 7. The C_{60} sol in acetonitrile–benzene (1 : 1 by volume) are given below; fullerene concentration 4.0×10^{-5} M.

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.
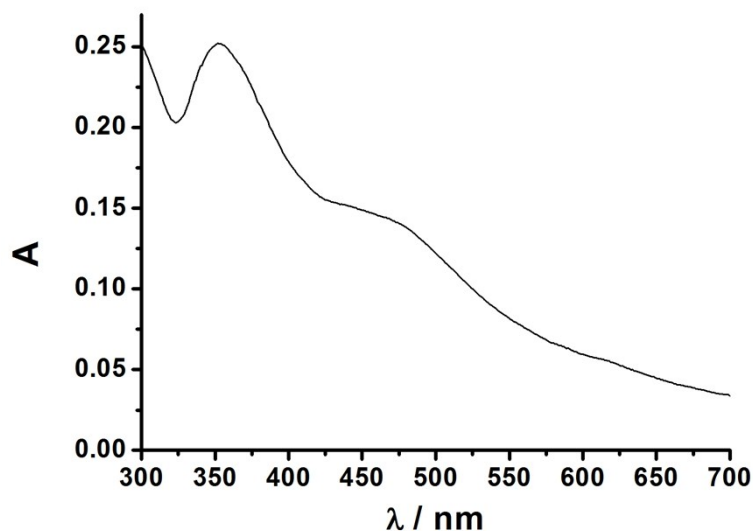

Figure 8. The C_{60} sol in toluene + DMSO mixed solvent, 1:1 by volume; fullerene concentration 3.4×10^{-5} M.
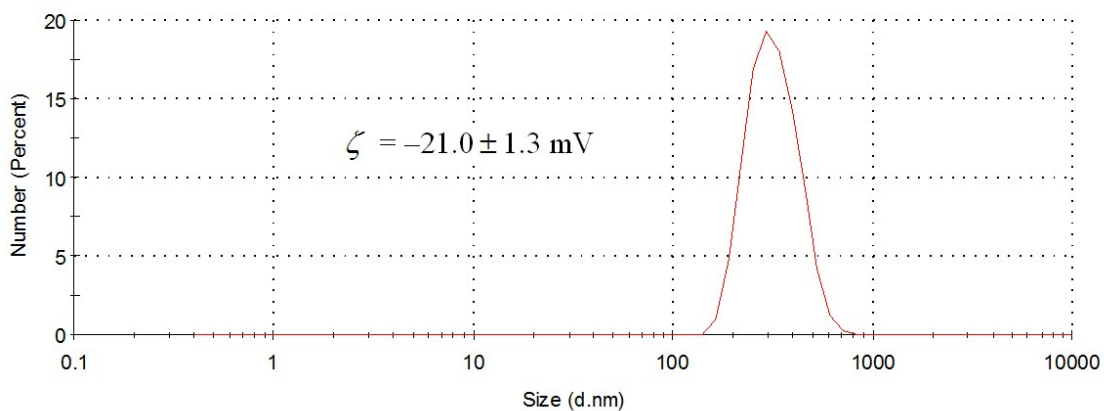
Figure 9. The C_{60} sol in methanol with 1 vol. % toluene; fullerene concentration 4×10^{-6} M.
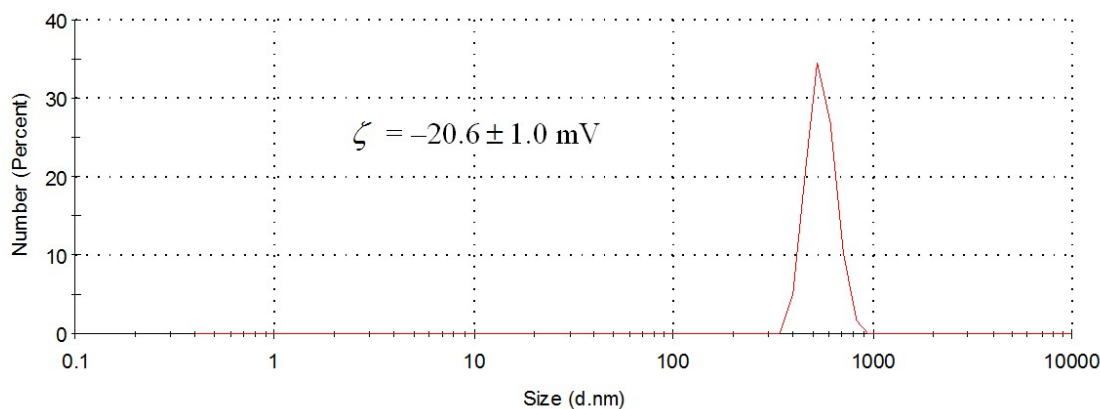
Figure 10. The same sol (Figure 9), but with 0.01 M 2,6-di-tert-butyl-4-methylphenol; 1 h 18 min after preparation: rise in size without changes in the zeta-potential.

Figure 11. UV-visible absorption of 4×10^{-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, Ψ, 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:

$$q_s(\text{sphere}) = \frac{2\varepsilon\varepsilon_o \kappa RT}{F} \sinh(Y/2) \left(1 + \frac{2}{\kappa r \cosh^2(Y/4)} + \frac{8\ln\left[\cosh(Y/4)\right]}{(\kappa r)^2 \sinh^2(Y/2)} \right)^{\frac{1}{2}};$$

$$q_s(\text{cylinder}) = \frac{2\varepsilon\varepsilon_o \kappa RT}{F} \sinh(Y/2) \left(1 + (\frac{K_1^2(\kappa r)}{K_0^2(\kappa r)} - 1)\frac{1}{\cosh^2(Y/4)} \right)^{\frac{1}{2}}.$$

Here, $Y = \Psi F / RT$, F is the Faraday constant, κ is the reciprocal Debye length, r – radius of the particle, $\varepsilon_o = 8.854 \times 10^{-12}$ F m^{-1}, and $K_n(x)$ is the modified Bessel function of the second kind of order n. For acetonitrile at $T = 298$ 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 Ψ stands for the interfacial electrical potential, mV, q_s is expressed as charge per nm^2. If the ζ values are used for the NaClO$_4$ 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 nm^2, i.e., 1.27×10^3 nm^2 per one charge.

In the Ca(ClO$_4$)$_2$ solutions around 0.15 mM, the $|\zeta|$ value of re-charged colloidal species of the fullerene are even higher than in extremely diluted NaClO$_4$ solutions. This gives evidence for a higher q_s value and is in line with the high CCC$_2$ value, necessary for the lowering of the potential barrier in terms of the DLVO theory.

References

1. T. Fujinaga and I. Sakamoto, *Pure Appl. Chem.*, 1980, **52**, 1387–1396.
2. S. Deguchi and S.-a. Mukai, *Chem. Lett.* 2006, **35**, 396–397.
3. H. Ohshima, T. W. Healy and L. R. White, *J. Colloid Int. Sci.* 1982, **90**, 17–26.