

CARBON NANOTUBES IN LIQUID MEDIA: INFLUENCE OF SOLVATION ON THE COLLOIDAL STABILITY

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This article presents the results of a study of the colloidal properties of multiwalled carbon nanotubes (MWCNTs) in water and two organic solvents. This work continues the systematic study of the aggregation stability and coagulation of carbon nanoparticles in various solvents with the aim of identifying the contribution of solvation to the colloidal properties of these widely used systems. The samples were characterized by EDS and XPS methods. The suspension was prepared using ultrasonic treatment in N-methyl-pyrrolidin-2-one and diluted 100-fold with water, acetonitrile, or dimethyl sulfoxide. The working concentration of MWCNTs carbon nanotubes was $5 \times 10^{-4} \text{ g L}^{-1}$. The size of negatively charged particles in water, 95 vol% aqueous CH_3CN , and 95 vol% DMSO was determined by dynamic light scattering: the Z_{aver} values are 249 ± 15 , 265 ± 42 and 146 ± 8 nm, respectively, which corresponds to the diameter of the equivalent sphere. TEM images show that the CNT diameter in aqueous suspension is approximately 9–11 nm and the length is approximately 40–170 nm. Critical coagulation concentrations (CCC) of NaCl were determined using the Fuchs function. These values differ significantly in water and 95% acetonitrile: CCC = 230 and 1.0 mM, respectively. In 95% DMSO, coagulation is less pronounced. The effects were discussed in terms of Gutmann's Donor Numbers for organic solvents and the specificity of hydration of non-polar materials in water. The CCC of HCl in water is 1.5 mM, which suggests the role of acid-base properties in the formation of the negative charge of the MWCNT colloidal particles.

Keywords: carbon nanotubes, suspensions in water, acetonitrile, dimethyl sulfoxide, critical coagulation concentration, solvation.

Introduction

Carbon nanotubes, CNT, belong to the widely used and studied carbon nanomaterials [1-4]. The dispersion and properties of the CNT in water and in some organic solvents was explored by many authors. The colloid properties of CNT in water have been examined in detail [5, 6]; a collection of the critical coagulation concentrations (CCC), determined by fourteen research groups, was presented and analyzed in our previous publication [6]. However, studies of colloidal stability have been conducted almost exclusively for aqueous systems; data concerning organic solvents are scarce [7-9]. We recently published two papers devoted to the coagulation of carboxylated single-walled nanotubes by electrolytes in aqueous-organic solvents with a high, up to 95 vol%, content of the second component [10, 11]. Here we present some results of a study on the coagulation of other CNT suspensions in water, 95 vol% acetonitrile aqueous solution, and 95 vol% dimethyl sulfoxide (DMSO). Acetonitrile is a proto- and cationophobic solvent, whereas DMSO is a well-known proto- and cationophilic solvent with pronounced electron-donating properties. The Gutmann's donor numbers, DN, are 14.1 and 29.8, respectively [12]. Both of them are polar, with relative permittivity values ϵ_{r25} of 35.9 and 46.4, respectively [12]; for water, $\epsilon_{r25} = 78.4$. Consequently, the electrolytes dissociate quite strongly in all the solvents studied.

The aim of this work was to test the generality of observations on the effect of solvation on the colloidal stability of nanotube suspensions obtained in previous studies [10, 11].

Experimental

The sample of CNT was provided to us by the late Dr. A. V. Kravchenko. The solid sample was dispersed in N-methyl-pyrrolidone-2-one [13] under sonication for 2 h at 42 kHz, 70 W, and decanted. Thus obtained solution was diluted 100-fold with water, acetonitrile, or DMSO. In the last two cases, 5 vol% of water was added, either with or without electrolytes. The concentration of the suspensions was about 5×10^{-4} g L⁻¹. For the characterization of the colloidal particles and determining the CCC values, the dynamic light scattering method was used with a Zetasizer Nano ZS Malvern Instrument apparatus (UK) at 25°C, at a scattering angle of 173°. For size determination, all measurements were made 10 times for a working solution; each determination was based on 12–16 runs. The values of the electrokinetic potential (ζ -potential) were averages of three determinations; for each determination, 12–20 runs were made. For the determination of the coagulation rate, 10 size measurements were made, with automatically performed 12–16 runs. The size of particles was expressed as Z-average (Zaver) values. Zaver is the intensity-weighted mean hydrodynamic size of the ensemble collection of particles. The time period from mixing the solutions to the first measurement was no more than 3 min. The calculations of the ζ -potential values were made using the Henry–Ohshima equation [14]. The transmission electron microscopy (TEM) studies were carried out using FEI Titan G2 Cubed 60–300 TEM operated at 200 kV.

The composition analysis of the solid samples was carried out using an energy-dispersive spectrometry (EDS) system, Bruker XFlash 5010, installed on a scanning electron microscope Tescan Vega 3 LMH. Energy-dispersive spectra were acquired from areas of 100×100 μm . Quantification of the spectra was performed using the self-calibrating detector mode.

The X-ray photoelectron spectra (XPS) of the core levels of the sample elements were obtained using JEOL XPS 2400 X-ray spectrometer (Japan). The working vacuum during the experiment was 10^{-7} Pa. The radiation of a magnesium anode with an energy of the Mg K $_{\alpha}$ line of 1253.6 eV was used. The energy resolution was 0.1 eV. The calibration of spectra was performed taking into account the Au 4f line energy ($E = 83.8$ eV). For every studied line the number of scans was at least 200. Analysis of surface element composition was carried out by taking into account the receiving spectra at the same modes and scattering cross sections

Results and Discussion

The EDS measurements indicate following content of main components (in atomic %): C 90.28, O 3.34, Yb 1.43, and Ni 2.27. The results of XPS study are presented in Fig. 1

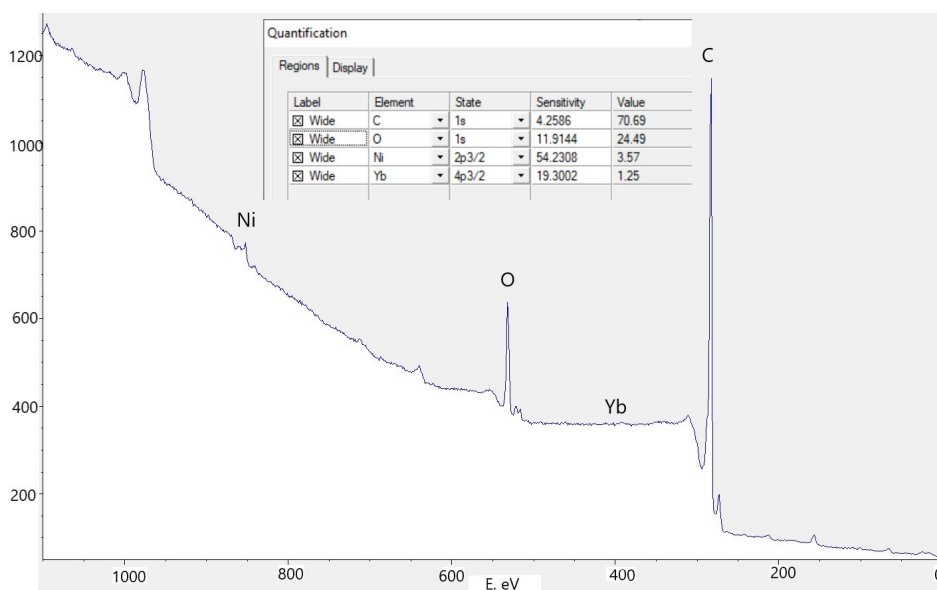


Fig. 1. Wide X-ray photoelectron spectrum of the sample.

Intense peaks are observed for carbon and oxygen. The presence of Ni is detected by several characteristic lines, whilst the Yb peak in the spectrum appears slightly above the background noise. The

XPS measurements indicate the following content of main components (in atomic %): C 70.69, O 24.49, Yb 1.25, and Ni 3.57 (Fig. 1). The difference in the ratios of chemical elements between the two methods can be explained by the different depth of photoelectron emission in the XPS method and the depth of electron interaction in the EDX method.

The full width at half maximum (FWHM) of the C 1s spectrum is 1.31 eV, which is slightly greater than that of pyrolytic graphite (1.20 eV, Fig. 2). It should be noted that an increase in the FWHM of the C 1s spectra is characteristic of all carbon nanostructures.

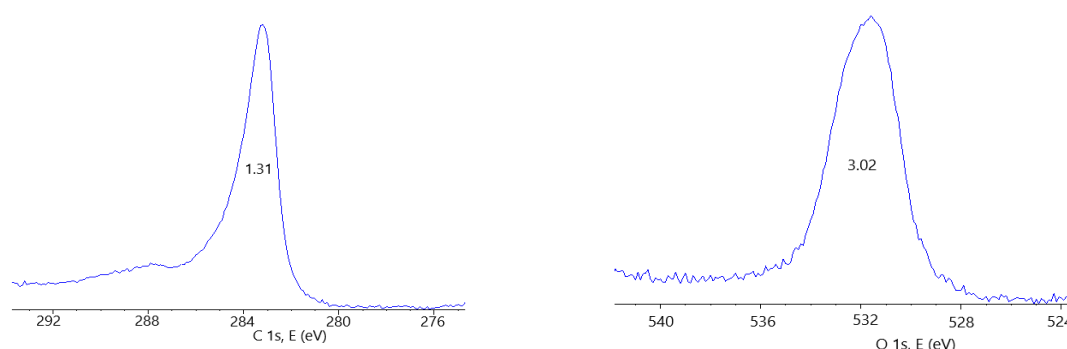


Fig. 2. XPS spectra of the C and O.

The FWHM of the O 1s lines for oxides of light elements is ~ 1.5 eV. In this sample, we observed a rather significant FWHM for the oxygen line: 3.02 eV (Fig. 2). A blurred main peak is also observed. This indicates that oxygen is present in various oxygen-containing components. Based on the widths of the oxygen lines, it can be concluded that oxygen is present in 3–4 different chemical positions.

The particle size distribution of the suspension in three solvents is shown in Fig. 3. The DLS measurements give the hydrodynamic diameter of the equivalent sphere. In water, 95 vol% acetonitrile, and 95 vol% DMSO, the Zaver values are 249 ± 15 , 265 ± 42 , and 146 ± 8 nm, respectively. The PDI values are 0.300, 0.149, and 0.311, respectively. The particles are negatively charged; $\zeta = -19.1 \pm 2.5$, -5.0 ± 2.2 , and -26.8 ± 3.7 mV in water, 95 vol% acetonitrile, and 95 vol% DMSO, respectively.

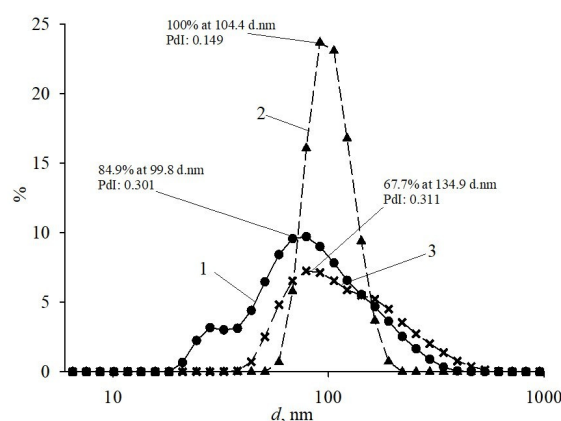


Fig. 3. Particle size distribution by volume in the CNT suspension in water (1), 95 vol% acetonitrile (2), and 95 vol% DMSO (3).

The TEM image of the CNTs obtained from a dried aqueous suspension on a substrate is exemplified in Fig. 4.

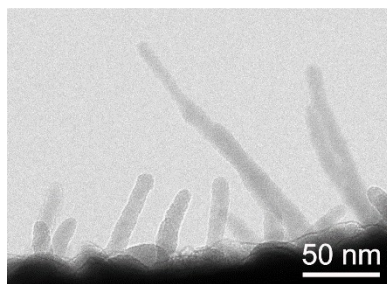


Fig. 4. TEM image of the dried aqueous suspension of the CNTs on a substrate.

Judging by the estimation of the average diameter 9–11 nm, the CNT are rather multi-walled than single-walled. The length of the tubes varies from 40 to 170 nm; the upper limit can be even higher since the ends are somewhat hidden in the substrate. In Fig. 5, the aggregates are presented together with the HRTEM image. The structure of the material looks amorphous.

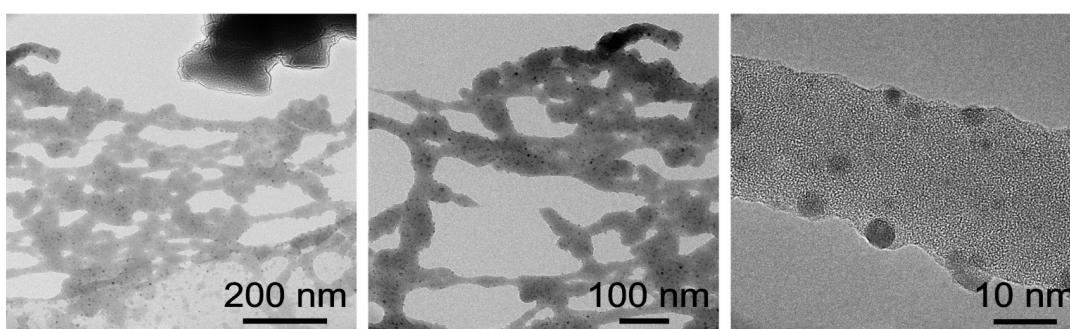


Fig. 5. TEM and HRTEM images of the dried aqueous suspension of the CNT.

Coagulation was studied using the rate of particle size increase, using the Fuchs function, Eq. (1).

$$W = \frac{k_{\text{rapid}}}{k} = \frac{[(\partial r / \partial t)_{t \rightarrow 0}]_{\text{rapid}}}{(\partial r / \partial t)_{t \rightarrow 0}} \quad (1)$$

Here k and k_{rapid} are the rate constants of slow and rapid coagulation, respectively. The time dependences are exemplified in Fig. 6.

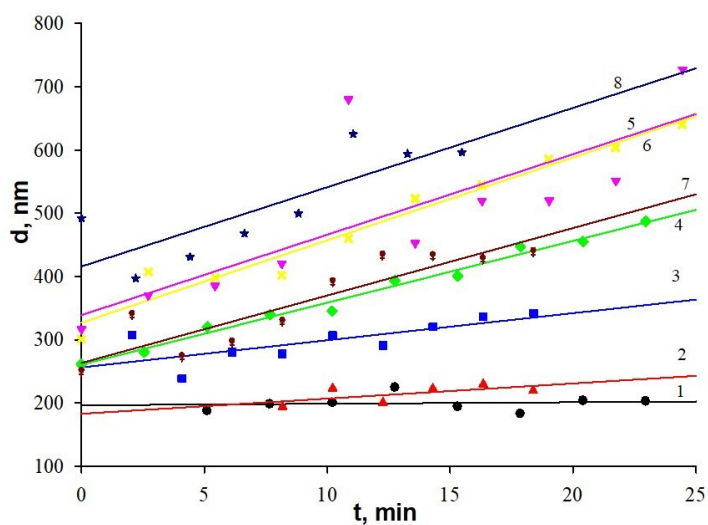


Fig. 6. Growth of the particle size with time. CNT dispersion in 95 % acetonitrile; NaCl concentration, mM: 0.1 (1), 0.25 (2), 0.5 (3), 0.75 (4), 1.0 (5), 1.25 (6), 2.5 (7), and 3.5 (8).

The dependence of the reciprocal Fuchs function on the logarithm of the electrolyte concentration (in mM) is shown in Fig. 7. The CCCs ($\pm 15\text{--}20\%$) correspond either to the plateau or apparent decrease in the rate of particle growth.

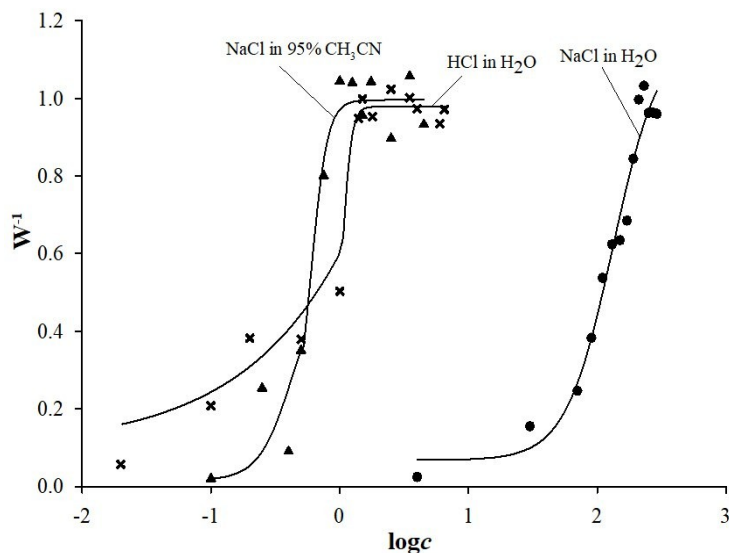


Fig. 7. The dependence of reciprocal Fuchs function on the logarithm of the electrolyte concentration, mM: NaCl in water (circles), NaCl in 95 vol% acetonitrile (triangles), and HCl in water (crosses)

In water and 95 vol. % acetonitrile, $\text{CCC}(\text{NaCl})$ are 230 and 1.03 mM, respectively. In 95 vol% DMSO, no distinct signs of particle size increase were observed within the range of NaCl concentration from 8 to 200 mM NaCl, although the ζ value turns from -26.8 ± 3.7 mV in the salt-free solution to -8.4 ± 4.2 mV in 100 mM NaCl solution, due to the screening of the surface charge.

It should be noted that the CCC value for HCl in water is 1.52 mM. The ζ value turns from -19.5 ± 2.5 mV in water to -10.0 ± 0.8 mV in 0.2 mM HCl. However, at the acid concentration of 5 mM, i.e., above the CCC, overcharging takes place: $\zeta = +8.3 \pm 0.7$ mV. Such effects allow assuming that the negative interfacial charge of the colloidal particles is caused by the ionization of the oxygen-containing groups or/and adsorption of the HO^- ions. The last mechanism for graphene [15] or orientation of the HO^- ions near the paraffin surfaces [16] is proved in the literature [15, 16]. Other reason is the suppression of the acid dissociation of the oxygen-containing functional groups by the hydrochloric acid.

The study of coagulation carried out in this work allows us to draw some conclusions. In a 95% acetonitrile solution, the suspension is much less stable than in water. In contrast, DMSO stabilizes the colloidal dispersion of interest. The ratio of CCC values for NaCl in water and 95% acetonitrile is 223. In our previous work [11], the CCC values in water and 95 vol% acetonitrile were found to be 150 mM and 0.89 mM, respectively. Hence, the above ratio is 168 for another sample of CNT. In 95% DMSO, the $\text{CCC}(\text{NaCl})$ value was 96 mM [11]. Therefore, the COOH-decorated SWCNT suspension is also much more stable in water than in 95% acetonitrile. The difference in the surface charge (see the above ζ values) alone is unlikely to explain such a significant effect. As it was assumed previously [11], the huge difference between the CCCs in water and acetonitrile (with 5% water) is caused by the poor solvation of the electrophilic CNT, which is a kind of a Lewis acid, like their relatives' fullerenes [17, 18] and graphene [19], by the cationophobic acetonitrile. On the other hand, it can be concluded that there is a stabilizing factor in the aqueous colloidal system under study, in addition to the molecular attraction and electrostatic repulsion, assumed by the DLVO theory in the original version. Therefore, it deals about a third contribution to the energy of the inter-particle interaction, which is called "structural", or solvation contribution [11]. The cationophilic solvent DMSO strongly solvates the CNT, which stabilize the colloidal system. The difference between CH_3CN and DMSO is from this viewpoint explained by the DN values of 14.1 and 29.8, respectively. Analogous conclusions were made basing on the CCCs of fullerenes C_{60} and C_{70} in water, acetonitrile, and DMSO [20].

Conclusions

The results presented in this article confirm our previously made conclusions concerning the pronounced role of the solvation of carbon nanomaterials. The value of critical coagulation concentration of NaCl in water is two orders of magnitude higher than that in 95 vol% aqueous acetonitrile. The same observation was made by us earlier basing on results with COOH-decorated SWCNT. It convincingly indicates that the solvation factor, which can be considered as a third contribution to the energy of inter-particle interaction, besides the molecular attraction and electrostatic repulsion, can be in some cases substantial. In the case of water, it is the hydration of CNT, which is a kind of a Lewis acid, analogous to fullerenes and graphene. The key role of solvation is emphasized by the powerful stabilization of the electrophilic CNT dispersion by DMSO, which is a typical cationophilic solvent; in 95 vol% DMSO, the CNT suspension is even more stable than in water.

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Conflict of Interest: The authors declare no conflict of interest

Authors Contributions: V. I. Haidar: Investigation, Visualization, Data curation, Formal analysis, Writing – original draft. K. D. Skliarova: Investigation, Visualization. V. L. Karbivskii: Investigation, Visualization, Data curation, Writing – original draft, Resources. A. P. Kryshtal: Investigation, Visualization, Formal analysis, Resources. S. I. Bogatyrenko: Validation, Visualization, Formal analysis, Resources. N. O. Mchedlov-Petrosyan: Conceptualization, Supervision, Writing – review & editing.

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У цій статті представлено результати дослідження колоїдних властивостей багат шарових вуглецевих нанотрубок (MWCNT) у воді та двох органічних розчинниках. Дана робота є продовженням систематичного вивчення агрегативної стійкості та коагуляції вуглецевих наночастинок у різних розчинниках з метою виявлення внеску сольватаційної складової в колоїдні властивості цих широко використовуваних систем. Зразки були охарактеризовані методами EDS та XPS. Суспензію готували з використанням ультразвукової обробки в N-метилпіролідін-2-оні та розбавляли у 100 разів водою, ацетонітрилом або диметилсульфоксидом. Робоча концентрація вуглецевих нанотрубок становила 0,05 мас./об.%. Розмір негативно заряджених частинок у воді, 95 об.% водному ацетонітрилі та 95 об.% ДМСО визначали за допомогою динамічного розсіювання світла: значення Z_{aver} становлять 249 ± 15 , 265 ± 42 та 146 ± 8 нм відповідно, що відповідає діаметру еквівалентної сфери. TEM-зображення показують, що діаметр частинок у водній суспензії становить приблизно 9–11 нм, а довжина – при-

близно 40–170 нм. Критичні концентрації коагуляції (ККК) NaCl визначали за допомогою функції Фукса. Ці значення суттєво відрізняються у воді та 95 об.% ацетонітрилі: ККК = 230 і 1.03 мМ відповідно. У 95 об.% ДМСО коагуляція менш виражена. Оцінка результатів проведена з урахуванням донорних чисел Гутмана для органічних розчинників та специфіки гідратації неполярних матеріалів у водному середовищі. ККК HCl у воді становить 1.5 мМ, що свідчить про роль іонів HO⁻ у формуванні негативно-го заряду колоїдних частинок MWCNT.

Ключові слова: вуглецеві нанотрубки, суспензії у воді, ацетонітрил, диметилсульфоксид, критична концентрація коагуляції, сольватація.

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