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Spectroscopic study of suspensions of single-wall carbon nanotubes in polyaniline solutions in *N*-methylpyrrolidone in UV—Vis—NIR regions

A. G. Ryabenko,* L. S. Fokeeva, and T. V. Dorofeeva

Institute of Problems of Chemical Physics, Russian Academy of Sciences,
1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588. E-mail: aryabenk@icp.ac.ru

Stable suspensions of carbon nanoparticles in polyaniline solutions in *N*-methylpyrrolidone were compared with the suspensions in aqueous solutions of cetyltrimethylammonium bromide using spectrophotometry in UV—Vis—NIR regions. Polyaniline in low concentrations in *N*-methylpyrrolidone was found to be a more efficient surfactant than cetyltrimethylammonium bromide in water. Analysis of the optical spectra of suspensions of carbon soots in solutions of the polymer made it possible to reveal a noticeable change in the spectra of the starting polyaniline and nanotubes, indicating the chemical interaction of polyaniline with the carbon nanotubes.

Key words: single-wall carbon nanotubes, polyaniline, UV spectroscopy, IR spectroscopy.

Single-wall carbon nanotubes are promising field emitters of electrons and extremely strong reinforcing materials due to their uniquely small thickness and high mechanical strength.[1—3] However, their potentialities were not realized until presently, because they undergo self-assembling during preparation to form thick (diameter from 50 to 200 nm) bundles due to the strong van der Waals interaction. They are insoluble because of the same interaction. Nevertheless, repeated attempts were made to prepare composites by mechanical mixing[4,5] when only external nanotubes in the bundles interact with a polymeric matrix.

The use of various surfactants in aqueous media makes it possible to obtain stable suspensions of the nanotubes in water. However, in these suspensions the bundles are desintegrated only partially, and the fraction of isolated nanotubes does not exceed 5%.[6] In this case, the weight of a surfactant dissolved in water exceeds the weight of suspended nanotubes several times, which, however, does not influence the optical properties of the nanotubes.[6] It is known[7,8] that conducting polymers can act as surfactants in organic solvents. Experimental and theoretical studies show that a polymer should contain a conjugated "skeleton" to "dissolve" nanotubes efficiently. This skeleton should embrace carbon nanotubes and should contain substituents favoring the dissolution of a polymer in a solvent.[9] Polyconjugated polymers were used in several works.[10—12] Polyaniline (PA) is a conducting polymer possessing a unique stability. Composites of carbon nanotubes (CNT) with PA were obtained on the basis of multiwall nanotubes[7] or single-wall carbon nanotubes (SWNT), which were introduced into the monomer before polymerization. In this case, the composite was obtained *in situ* during the synthesis of the polymer,[13] and the bundles of the nanotubes were not desintegrated. In our opinion, it is more promising to introduce single-wall nanotubes into a solution of the already prepared polymer followed by ultrasonic treatment, which partially desintegrates the bundles.[14] However, presently the mechanism of interaction of PA with SWNT remains unclear. It was shown[15] by Raman spectroscopy that charge-transfer interactions are observed along with the van der Waals interaction of a multiwall nanotube with a polymeric matrix. This conclusion was drawn on the basis of a substantial distinction in the spectra of the composite and its components. In particular, a remarkable decrease in the intensity of the band at 1485 cm^{-1} (corresponding to plane C—C vibrations in the quinoid groups of doped PA) as compared with the band at 1161 cm^{-1} was observed. It is likely that particular regions (namely, quinoid units) of the polymeric chain interact with the nanotube to decrease the total number of quinoid units.[15] This fact can be explained[15] by the charge transfer resulting in the transformation of the quinoid rings of PA into benzoid rings.

The doping influence of nanotubes in PA was shown[16] by IR spectroscopy. However, based on the IR spectra, the authors concluded[17] that PA and the carbon nanotubes do not interact.

Optical spectroscopy is a direct method of studying electronic states of both polymers and nanotubes. How-

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ever, the optical properties of stable suspensions of SWNT in PA solutions were not studied in detail. The characteristic absorption spectrum of SWNT is determined by two factors[18]: π-plasmon absorption providing a continuous absorbance with the band edge at 272 nm, which decreases slowly toward longer waves (this type of absorbance is typical of any carbon particle) and additional absorption caused by the 1D van Hove singularities (only single-wall nanotubes are characterized by this absorption). The position of absorption bands of the van Hove singularities is determined by the type of a nanotube and its diameter. In this work, we used nanotubes obtained in an arc reactor in the presence of the Ni/Y catalyst. Samples represented a mixture of nanotubes with different diameters (in a range of 1.3—1.6 nm) and of different type (metallic or semiconducting, depending on the angle at which the carbon sheets were rolled up during the synthesis). A smaller number of the produced SWNT has a conductivity of the metallic type (their content in the mixture is usually assumed to be 33%), and the array of these tubes gives an absorption band at 610—820 nm with a maximum at ~700 nm. Other nanotubes are characterized by the semiconductive conductivity and give an absorption band with a maximum at 1020 nm. The composition of SWNT by types and diameters is the same in all samples used in the present work.

Thus, the absorption spectra of PA and nanotubes overlap only partially. The absorbance of the metallic nanotubes is imposed on the absorption band of the quinoid groups of PA (maximum at 620 nm), and the absorbance of the semiconducting nanotubes is beyond the absorbance of PA. Since band intensities of the semiconducting and metallic nanotubes in these samples were known from the spectra of aqueous suspensions, we could analyze independently the changes in the electronic structures of PA and nanotubes.

The applied purpose of this work is to develop a method for preparing suspensions of SWNT in organic solvents with a maximum degree of desintegration of SWNT bundles. At the first stage of the complex investigation, we studied PA. As already mentioned, the latter, first, is the most stable polyconjugated polymer and, second, PA has been studied in detail by spectroscopy. It should be noted that the role of the state of the polyconjugated polymer (conducting or non-conducting) in suspensions of SWNT was not considered to date. We were interested in the possibility to use the main (not doped) form of PA for the preparation of suspensions of SWNT. Therefore, we chose *N*-methylpyrrolidone (NMP) as a solvent. A similar study in *m*-cresol solutions, where PA exists in a partially doped conducting form, is in progress.

In this work, in studying the mechanism of interaction of PA with SWNT, we used spectrophotometry in UV—Vis—NIR regions to study suspensions of SWNT in solutions of PA in NMP. The spectra of SWNT suspensions in an organic solvent were compared with those of suspensions of the nanotubes in aqueous solutions of cetyltrimethylammonium bromide (CTAB). Aqueous suspensions were chosen as reference samples, because the dispersion properties of CTAB have been studied well earlier.[6] In addition, among surfactants used presently for the preparation of aqueous suspensions of SWNT, this surfactant is efficient at its lowest concentration in water. We determined its minimum concentration in water to prepare stable suspensions and showed that CTAB exerted no effect on the spectral properties of SWNT.

As follows from a comparison of the dispersion properties of PA and CTAB, PA makes it possible to obtain stable suspensions of SWNT at substantially lower concentrations of PA in a solution and to prepare suspensions in which the weight of SWNT is 2.3-fold greater than the weight of PA. A comparative analysis of the spectra of the suspensions showed that the spectra of the SWNT suspensions in solutions of PA in NMP are not the sum of the spectra of the components. The addition of SWNT to a solution of PA substantially changes the spectrum of PA. In addition, the spectrum of SWNT in these suspensions differs remarkably from their spectra in aqueous suspensions. Thus, the interaction of PA molecules with SWNT was shown to result in a noticeable mutual perturbation of their electronic structures.

Experimental

Polyaniline was synthesized by the oxidative polymerization of aniline at −5 °C, as described previously.[19]

Single-wall nanotubes were obtained by the electric arc evaporation of graphite in the presence of the Ni/Y catalyst.[20] Purification was carried out by oxidation and centrifugation.[6] The purity of nanotubes was determined spectrophotometrically.[6]

UV—Vis-NIR spectra were recorded at room temperature in a quartz cell with a thickness of 0.3, 1.0, 2.0, and 10 mm using a Perkin—Elmer Lambda EZ 210 spectrophotometer. Spectra of SWNT suspensions in aqueous solutions were compared with those of SWNT suspensions in PA solutions in NMP at different amounts of SWNT relatively to the unit volume of the solution and weight of dissolved PA. Suspensions were prepared by the ultrasonic treatment of mixtures of the solutions with an SWNT powder using a mushroom-type top. The amount of the introduced energy was monitored by heating the solution.

Results and Discussion

In aqueous solutions of CTAB, the minimum content of the surfactant necessary for the preparation of stable suspensions depends on the amount of nanotubes in the carbon soot.[6] The 0.05% content of CTAB is enough for the carbon soot containing 15—20% SWNT, and the weight of suspended SWNT is 0.33—0.7 of the weight of dissolved CTAB. For carbon soots with an SWNT content higher than 80%, a 0.2% solution should be used, and the weight of dissolved CTAB, in this case, is 12-fold greater than the weight of suspended nanotubes. This is related to the fact that fine carbon particles preventing the close contact of SWNT exist between particular nanotubes in bundles at a low SWNT content. As a result, the van der Waals interaction between the tubes is weakened. Fine particles are burnt out during purification by gas-phase oxidation, particular nanotubes in bundles come in contact, the van der Waals interaction enhances, and a greater amount of a surfactant is needed for the preparation of a suspension.

The typical absorption spectrum of a suspension of the pure nanotubes in a 0.2% aqueous solution of CTAB is presented in Fig. 1. The absorbance increasing with a change in λ from 450 nm to 250 nm is related to the surface π-plasmon absorption, whose "tail" is extended to the very end of the detected range at 1100 nm. The band of the additional absorbance at 610—820 nm is related to the first 1D van Hove singular band of metallic tubes, and the band at 850—1100 nm is caused by the second 1D van Hove singularity of semiconducting tubes. As has been shown[6] by the comparison of the spectrum of an aqueous suspension and dry SWNT film, no remarkable influence of the surfactant and water on the optical spectrum of SWNT is observed in aqueous suspensions. This indicates that the interaction of the nanotube with water molecules and a surfactant exerts no effect on its electronic structure and 1D van Hove singular bands. The surface area of the van Hove bands is proportional to the amount of the nanotubes in a solution. In addition, the spectra of fine particles of amorphous carbon that are present as admixtures and the spectra of SWNT are additive.[6] This allows one to determine the content of SWNT in the samples by spectrophotometry.

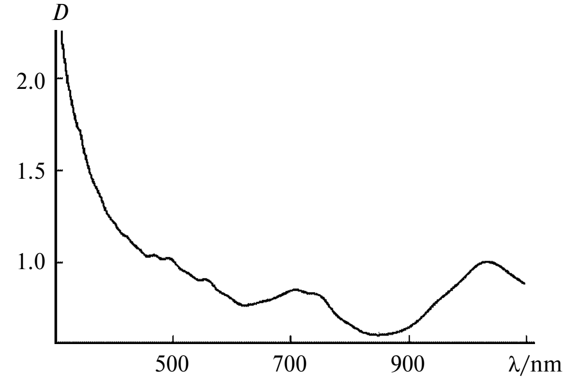

Fig. 1. Absorption spectrum of a suspension of the pure nanotubes in a 0.2% aqueous solution of CTAB.

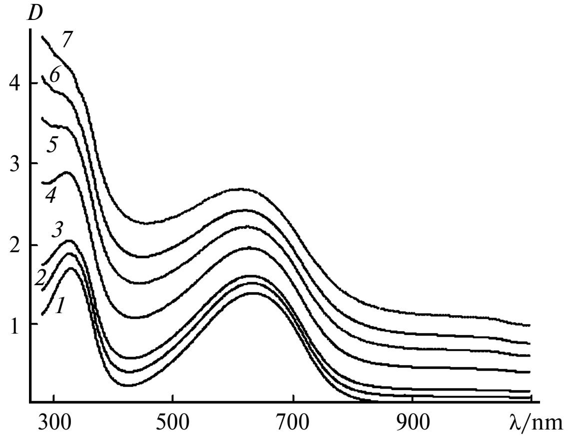

Fig. 2. Transformation of the spectra of solutions of PA in NMP with an increase in the carbon soot content for the nanotubes relatively to the PA weight: starting 0.013% solution of PA in NMP (*1*); 13 (*2*), 31 (*3*), 75 (*4*), 121 (*5*), 155 (*6*), and 232% carbon soot of the PA weight (*7*). Spectra *1—3* were recorded in a 2-mm cell, spectra *4—7* were recorded in a 1-mm cell but they are presented in the figure as multiplied by 2 for comparison. The reference cell is filled with NMP.

A quite different situation is observed in suspensions of SWNT with PA (Fig. 2). The spectra of suspensions of the carbon soot containing 15% SWNT in a solution of PA in NMP are presented in Fig. 2. The content of PA in a solution was 0.013%, and the SWNT content changed from 13 to 232% of the PA weight. Certain weighed samples of the carbon soot were successively added to a solution of PA in NMP, and then the mixture was ultrasonicated. Thus, the concentration of PA in NMP is almost fourfold lower than that of CTAB in water, and the maximum overall weight of suspended particles in this solution is 2.3 times greater than the weight of dissolved PA. In this case, the weight of the carbon soot suspended in 1 mL of NMP is comparable with the weight of the carbon soot suspended in water. Thus, PA in low concentrations in NMP is a more efficient surfactant than CTAB in water.

As can be seen from the data in Fig. 2, the addition of a black powder to a solution increases the absorbance at all wavelengths.

The spectra of the starting solution of PA (curve *1*) and suspension in an aqueous solution with CTAB of approximately the same amount of the carbon soot as in the PA solution with the maximum content of the carbon soot (curve *2*) are presented in Fig. 3. The differential spectra should correspond to the absorption spectrum of the carbon soot in an aqueous solution, if the spectra of the mixture are the sum of the spectra of individual components. A comparison of curve *2* and curves *3* and *4* (see Fig. 3) shows that this is not true: the shapes of the curves are similar only in the region of absorption of the semiconducting tubes (820—1100 nm), and another part of the spectral range exhibits remarkable differences in the shape of these spectra. The superposition of the spectra (Fig. 4) shows distinctly that the shape of the spectra

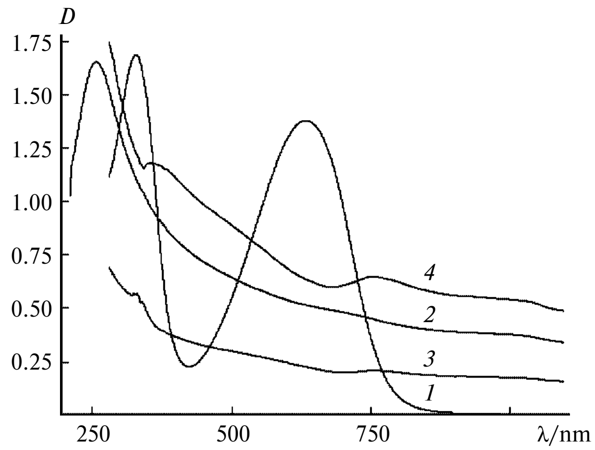

Fig. 3. Comparison of the spectra of a solution of PA in NMP (*1*), suspension of the carbon soot in an aqueous solution with CTAB (*2*), and suspensions of the carbon soot in a solution of PA (*3*, *4*). Curve *3* corresponds to curve *3* in Fig. 2, and curve *4* corresponds to curve *7* in Fig. 2 but, unlike Fig. 2, both spectra were recorded when the reference cell was filled with the starting solution of PA in NMP.

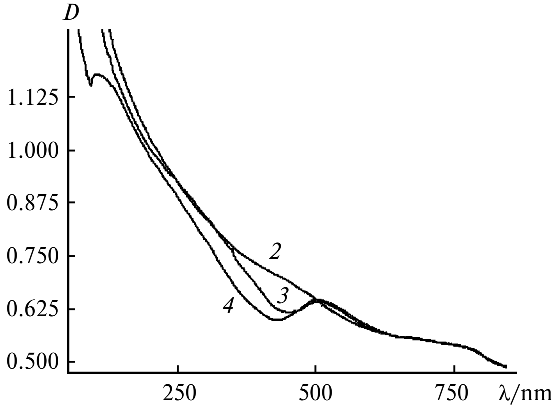

Fig. 4. Comparison of the absorption spectra of suspensions of the carbon soot in water and in NMP: spectra *2—4* and spectra *2—4* (see Fig. 3), which reduced by multiplication to the same absorbance at a wavelength of 1100 nm.

coincides perfectly in a region of 820—1100 nm, the spectra are close at 500—350 nm but exhibit noticeable distinctions near 650 nm, and this discrepancy increases with an increase in the amount of the carbon soot. The coincidence of the shapes of the spectra of the carbon soot SWNT in an aqueous suspension and in an organic solvent with PA in an interval of 820—1100 nm indicates that molecules of these solutions exert no effect on the absorption spectrum of the semiconducting nanotubes. The decrease in the absorbance of a suspension of the nanotubes in an organic solvent near 650 nm compared to the absorbance in an aqueous medium can be explained by a decrease in the absorbance of both PA and metallic nanotubes. The latter assumption seems less probable, because the absorption band of the metallic nanotubes is the sum of the bands of the metallic tubes of different diameters of which the most part belongs to the nanotubes of two diameters, and these nanotubes are characterized by bands with maxima at 700 and 750 nm. When assuming that the spectra are not additive because of the transformation of the spectra of the nanotubes, we can conclude that only the spectrum of the nanotubes with a short diameter changes, whereas the spectrum of the nanotubes with a longer diameter containing the absorption band at 750 nm remains unchanged. This seems improbable.

The assumption that the absorbance of PA weakens agrees well with the conclusions of the earlier published works,[15,16] because the absorption band of PA with a maximum at 620 nm corresponds precisely to the absorbance of the quinoid groups.

To confirm this assumption, we prepared suspensions of the pure nanotubes in solutions of NMP with a high content of PA. The spectra of these solutions are presented in Fig. 5. Solutions were prepared by the successive addition of a necessary amount of the nanotubes followed by ultrasonication: upon the first addition the solution was twice ultrasonicated, and then, after the addition of the second portion of the nanotubes to the same solution, ultrasonication was carried out two times more. The limiting content of the pure nanotubes was 0.09 mg in 1 mL of a solution. The subsequent addition of the pure nanotubes to the prepared solution of a mixture induced the formation of flakes. Thus, a suspension of the pure nanotubes with the content >0.1 mg in 1 mL of a solution cannot be obtained at a high concentration of PA. Note

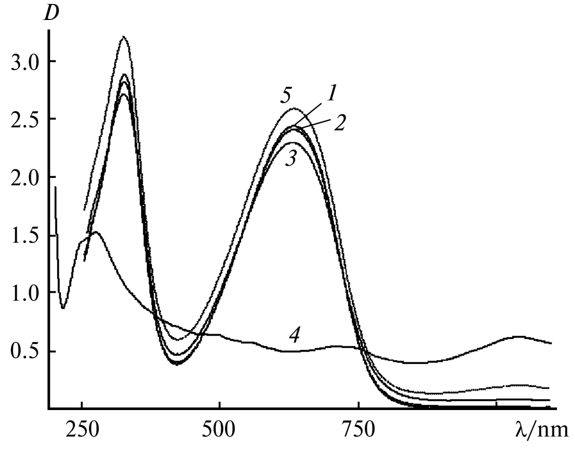

Fig. 5. Spectra of a 0.13% solution of PA in NMP and suspensions of the nanotubes in the same solution: pure PA (*1*); solution with addition of 0.03 (*2*) and 0.09% nanotubes (*3*); aqueous suspension of the nanotubes with a nanotube content of 0.09% (*4*); theoretical spectrum of a mixture of PA and SWNT obtained by the summation of the spectra for the 0.3-mm cell (*5*). The spectra were recorded in cells with a thickness of 0.3 (*1—3*) and 1 mm (*4*).

that a suspension of 0.3 mg of the carbon soot in 1 mL was prepared at a low PA concentration. However, it is not surprising, because, as mentioned above, the carbon soot with a low content of the nanotubes forms suspensions much more easily than the pure nanotubes do.

The theoretical spectrum of the mixture is presented in Fig. 5 (curve *5*) for comparison. The spectrum was obtained by the summation of the spectra of the nanotubes and the starting solution of PA. It is seen that the experimental spectrum of the mixture with a maximum content of SWNT (curve *3*) is much less intense than the theoretical spectrum. The maximum discrepancy is observed at 620 and 320 nm. Moreover, it is seen that, unlike Fig. 2, according to which the addition of the black powder increases the absorbance of a suspension, in this case, this addition decreases the absorbance in the maxima at 620 and 320 nm. Note that the solution with the maximum content of nanotubes accepted a larger amount of the ultrasonic energy than the solution with a smaller amount of nanotubes. A prolongation of the ultrasonic treatment decreases the size of particles suspended in a solution and, correspondingly, increases the overall absorbance of the suspension.**[6]** In our case, an opposite tendency is observed at wavelengths of 620 and 320 nm. It is clear that this is precisely the absorbance of PA which decreases at these wavelengths. It should be noted that additives of finely dispersed graphite exert the same effect on the spectrum of PA (decrease in the absorbance at 320 and 620 nm and an increase in the absorbance in a minimum at 425 nm). This transformation of the PA spectrum occurs upon weak doping of PA. This effect is related, most likely, to the complete conjugation of π-electrons on the surface of the carbon nanotube and graphite.

In addition, it is seen that at wavelengths of 800—1100 nm, where PA does not absorb, an increase in the absorbance caused by the absorption of the nanotubes is lower than it could be expected. It should be taken into account that the spectrum of the nanotubes in an aqueous solution presented in the figure was recorded in a 1-mm cell, while the spectrum of a suspension of the nanotubes in a PA solution was obtained in a cell 0.3 mm thick. Taking this into account, we can deduce that the increase in the absorbance at 820 nm is 1.3-fold lower than the expected value, and the relative intensity of the van Hove band with a maximum at 1020 nm is lower than the expected value by 13 times. In other words, the relative intensity of the van Hove band of semiconducting nanotubes decreased tenfold compared to the background π-plasmon absorption of these tubes. Therefore, the interaction of these nanotubes with PA molecules disturbs the one-dimensional character of their structure. This indicates a possibility of local charge transfer from particular units of a polyaniline molecule to a nanotube.

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