

Dispersion of Nitric Acid-Treated SWNTs in Organic Solvents and Solvent Mixtures

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The dispersion of pristine and nitric acid-treated single-wall carbon nanotubes (SWNTs) has been studied in organic solvents and solvent mixtures using optical absorption, as a function of settling time. The extinction coefficients of both the pristine and acid-treated tubes at 500-nm wavelength was measured to be 25.5 (mg/L)⁻¹ cm⁻¹ in various solvents. The dispersibility of nitric acid-treated tubes increased with the solvent's hydrogen-bonding ability and reached 27 mg/L in ethanol and 35 mg/L in water. Nitric acid-treated tubes could also be dispersed in butanol/toluene and xylene/ethanol mixtures, which are known to be poor solvents for the pristine SWNTs.

Introduction

Single-wall carbon nanotubes' (SWNTs) property^{1–3} translation into composites depends on their dispersibility in common solvents and polymer matrices.^{4–7} SWNTs typically exist in the form of quasicrystalline bundles containing hundreds of individual nanotubes.^{8,9} As-synthesized HiPco SWNTs typically contain 35 wt % catalytic impurity.¹⁰ Individual pristine SWNTs can be isolated in micelles using surfactants.^{11,12} Pristine SWNT dispersion in various solvents has been studied using optical spectra.^{13,14} SWNT solvents have been characterized by high values for electron pair donicity (β), negligible values for the hydrogen-bond donating parameter (α), and high values for the solvatochromic parameter (π^*).^{15,16} *N*-methylpyrrolidone (NMP) and *N,N*-dimethylformamide (DMF)^{13,17} are examples of good SWNT solvents, whereas solvents such as xylene, toluene, and alcohols exhibit poor solubility for the pristine SWNTs (Table 1).¹⁴ To disperse SWNTs in common polymers¹⁸, it is desirable for one to enhance their solubility in common organic solvents and solvent mixtures. SWNT solubility can be enhanced by sidewall^{19–21} or end-cap²² functionalization.^{23,24}

Nitric acid treatment functionalizes^{22,25–27} nanotubes and, depending on the severity of the reaction conditions (temperature and nitric acid concentration), can also result in the degradation of the small-diameter tubes.^{28,29} The infrared spectra of the acid-treated SWNTs have been measured by different research groups.^{22,29,30} Here we report the dispersion behavior of nitric acid-treated single-wall carbon nanotubes (f-SWNTs) in organic solvents and solvent mixtures, and the dispersibility has been correlated to the solvent solubility parameter.¹⁸

Experimental Section

For oxidation with nitric acid, 400 mg of unpurified HiPCO SWNTs (containing about 35 wt % catalyst, from CNI Inc., Houston, TX) were sonicated in 200 mL of 7 M nitric acid for 2 h using a Fisher Scientific water bath sonicator (42 kHz, 70 W) maintained at 25–30 °C. The sonicated dispersion was refluxed at 100 °C for 2 h. The resulting suspension was diluted with 2 L of distilled water, the nanotubes were allowed to precipitate, and most of the water was removed by decanting.

TABLE 1: Solvent Solubility Parameters¹⁸ and Dispersibility of Functionalized (f-) and As-Purified (AP-) Single-Wall Carbon Nanotubes (SWNTs) in Various Solvents

solvents	δ_d	δ_p	δ_h	δ_t^a	solubility(mg/L) ^b	
					f-SWNTs	AP-SWNTs
toluene	18.0	1.4	2.0	18.2	<1	<1
xylene	17.8	1	3.1	18	<1	<1
nitromethane	15.8	18.8	5.1	25.1	7	
acrylonitrile	16.5	17.4	6.8	24.8	13	
DMF	17.4	13.7	11.3	24.8	18	20
1-butanol	16	5.7	15.8	23.1	25	<1
ethanol	15.8	8.8	19.4	26.6	27	<1
ethyleneglycol	17	11	26	32.9	32	
H ₂ O	15.5	16	42.4	47.9	35	<1

^a Total solubility parameter (MPa^{0.5}), which is defined as $\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, where δ_d is the dispersive contribution, δ_p is the polar contribution, δ_h is the hydrogen-bonding contribution. ^b The sonication time was over 96 h, and the settling time was 12 h.

To eliminate the residual acid, we repeated this process several times. Finally, the dispersion was filtered through filter paper (Fisher Scientific, no. 1), washed repeatedly with distilled water on the filter paper, and dried at room temperature for a day. The resulting bulky SWNT mat contained 80–85 wt % water as determined by thermogravimetric analysis. This suspension was not dried completely because drying results in insoluble SWNTs. For the solubility study, all of the solvents were used as received and were obtained from Aldrich or Fisher Scientific. We additionally used as-purified (AP-) HiPCO SWNTs (containing about 2 wt % catalyst, from CNI Inc.) for solubility comparison with functionalized (f-) SWNTs.

Scanning electron microscopy was done on a LEO 1530 thermally assisted FEG SEM (at 15 kV) on the gold-coated samples. Raman spectroscopy was performed on a Holoprobe Research 785 Raman Microscope using 785-nm incident laser wavelength. The infrared (IR) spectra were recorded on an Equinox 55 (Bruker Optics) in KBr tablets. UV–vis–NIR spectra were recorded on a Cary 5G (Varian) spectrometer using a 10-mm glass cell (Fisher Scientific).

Results and Discussion

The SEM images of both the pristine unpurified and acid-treated SWNTs show SWNT bundles (Figure 1). The raman

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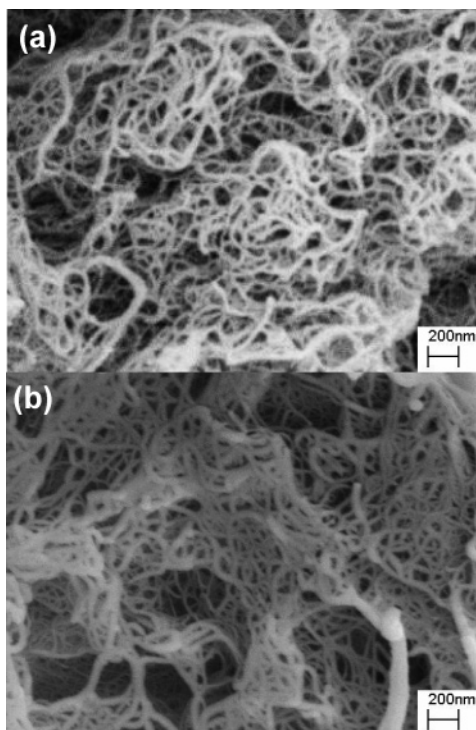


Figure 1. Scanning electron micrographs of (a) unpurified SWNTs and (b) f-SWNTs.

spectra^{31–33} of the two types of tubes have been compared in Figure 2. The radial breathing mode (150–300 wavenumber) as well as the relatively low intensity of the disorder band ($\sim 1300\text{ cm}^{-1}$) suggests that nanotubes have not been significantly damaged under the moderate nitric acid treatment conditions used in this work. However, the peak at 1625 cm^{-1} in the FTIR spectra (Figure 3) does suggest functionalization with carboxylate groups ($-\text{COO}^-$) under these nitric acid treatment conditions, whereas infrared absorption at $1600\text{--}1580\text{ cm}^{-1}$, assigned to nanotube phonon modes, is observed in unpurified pristine SWNTs.³⁴ By comparison, in our previous study²⁹ when purified HiPCO nanotubes (with 2% metal catalyst) were refluxed in 6 M nitric acid, it resulted in

significant degradation of the smaller diameter tubes, which were converted to amorphous carbon as was observed by scanning electron microscopy and radial Raman breathing mode spectra (Figures 3b and 4 in ref 29). On the surface, it appears that the current work utilizes harsher nitric acid treatment conditions (7 M nitric acid refluxed for 2 h) than the previous study²⁹ (6 M nitric acid refluxed for 2 h). However, nanotube degradation is much more significant in the previous study than in the current work. We think that this is due to the difference in the amount of catalyst present in the two studies. In the previous work, purified nanotubes with only 2 wt % metal catalyst were used, whereas in the current work, as-produced nanotubes with 35 wt % catalyst were used. The net effect of this difference in the catalyst impurity would be that more nitric acid would be used for reaction with the catalyst in the current study than in the previous study. This explains why nanotube degradation is significantly less in the current study, than that reported previously, even though a higher concentration of nitric acid has been used in this study. In addition, the nanotube concentration in aqueous nitric acid and the reflux temperatures are also different in the two studies, affecting degradation.

For determining dispersibility, we sonicated unpurified, as-purified, and acid-treated nanotubes in the desired solvent for various times using a Fisher Scientific water bath sonicator (42 kHz, 70 W) maintained at $25\text{--}30^\circ\text{C}$. With increasing sonication time, SWNTs debundle into smaller diameter ropes or as individuals and they partially reaggregate into larger diameter ropes when sonication stops, unless they are surrounded by surfactant molecules. In the current study, no surfactant has been used. The dispersion can depend on the type of nanotubes, their length, sonication time, temperature, power, and frequency. The optical absorption of as-purified (AP-) SWNTs in *N,N*-dimethylformamide (DMF), a good SWNT solvent,¹³ and that of the f-SWNTs in 1-butanol as a function of sonication time are shown in Figure 4.

SWNT van Hove transitions^{35–39} can be observed in both the pristine and the functionalized tubes (Figure 4a–c). The presence of van Hove transitions in the functionalized tubes further suggests that the electronic structure is mostly preserved, indicating limited side-wall damage and hence limited func-

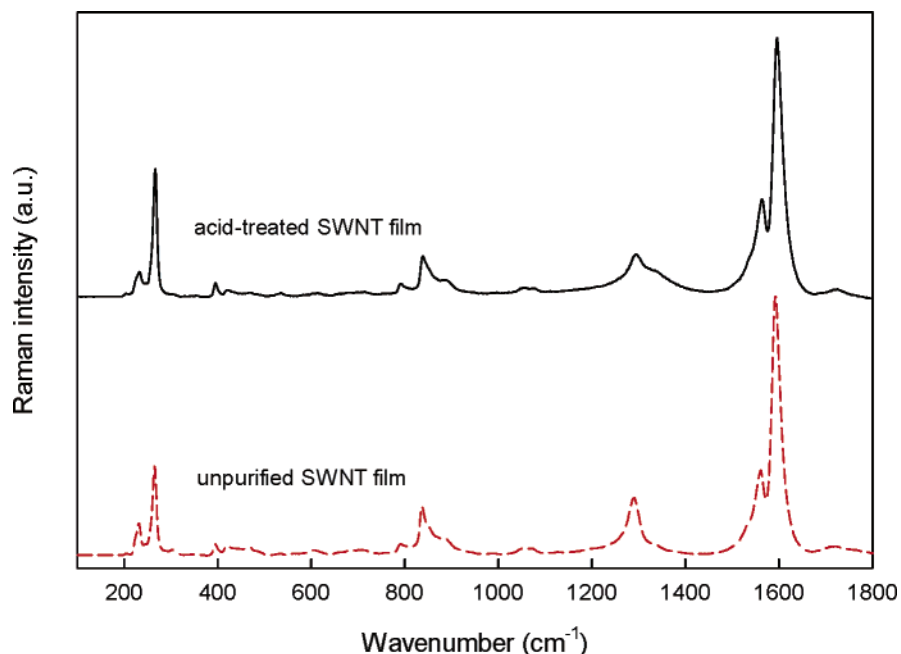


Figure 2. Raman spectra of the pristine unpurified and acid-treated SWNTs.

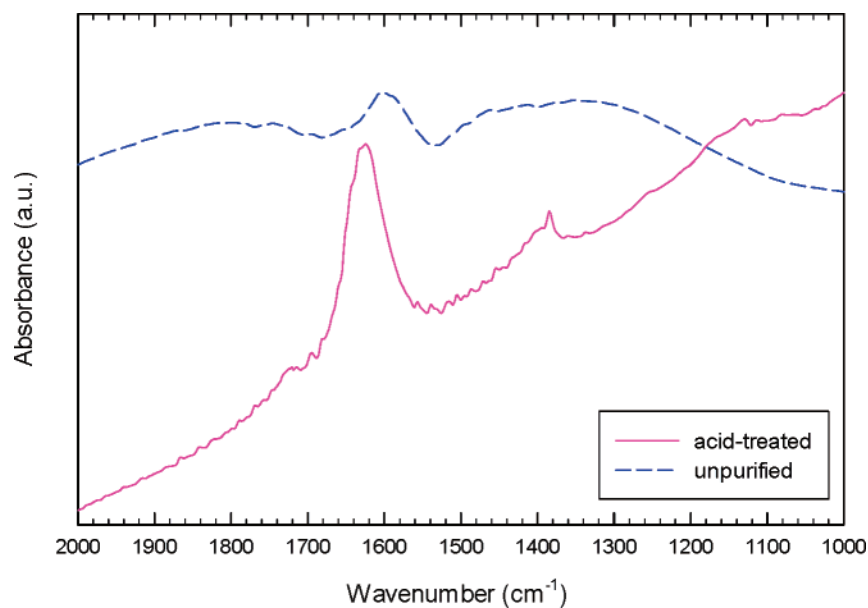


Figure 3. FTIR spectra of unpurified and acid-treated SWNTs.

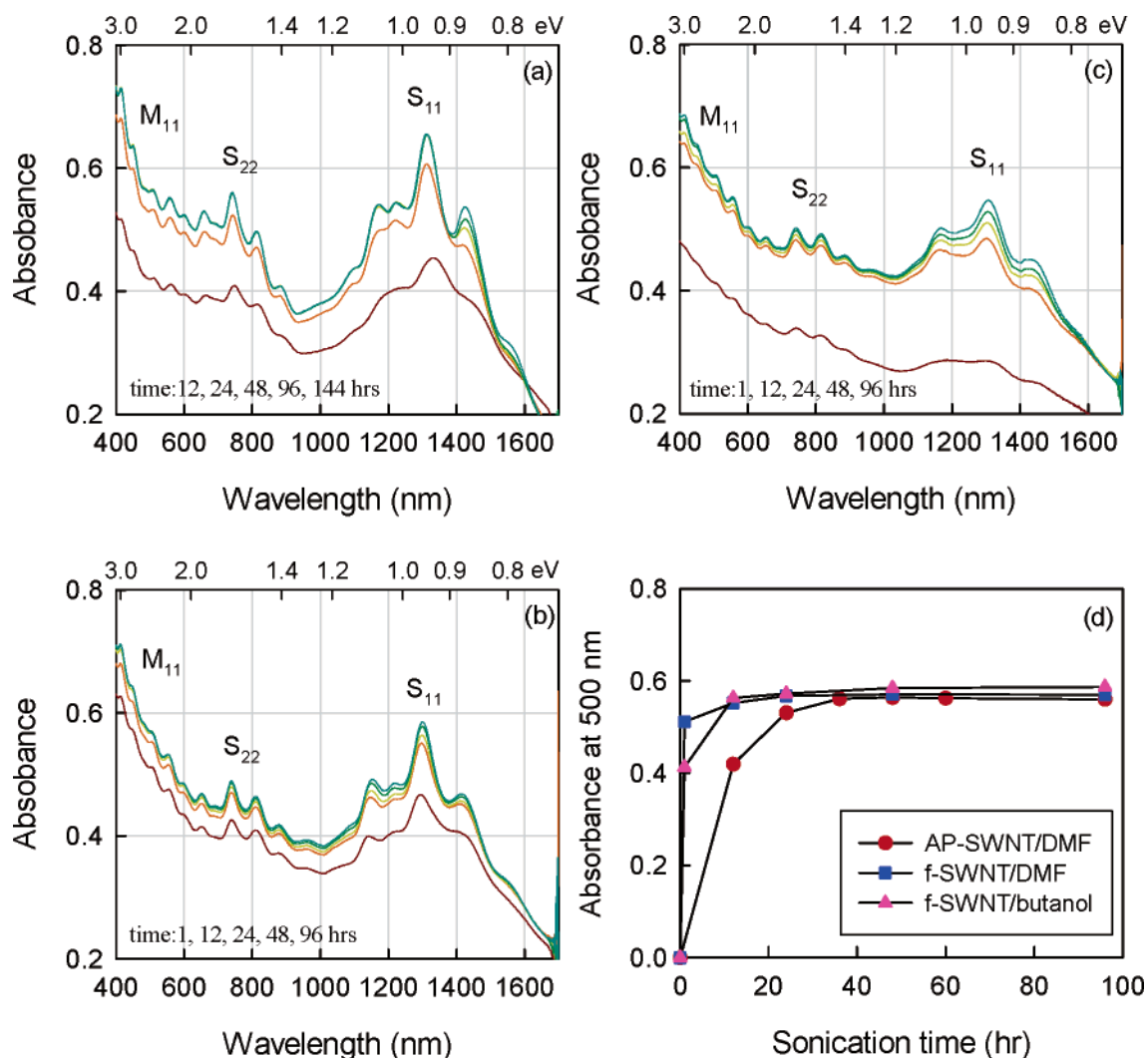


Figure 4. Optical absorption spectra of (a) AP-SWNTs/DMF, (b) f-SWNTs/DMF, and (c) f-SWNTs/butanol at nanotube concentration of (20 mg/L). (d) Absorbance at 500 nm at various sonication times for the three systems.

tionalization in this study. In Figure 4, the first set (0.7–1.4 eV), the second set (1.4–2.3 eV), and the slightly overlapping third set (2.0–3.1 eV) of transitions correspond to the first band gap (S_{11}) and the second band gap (S_{22}) of semiconducting tubes

and the first band gap (M_{11}) of metallic tubes, respectively.¹¹ For AP-SWNT/DMF, the optical absorption increased up to 36 h of sonication in the entire spectral range, whereas the peak resolution increased noticeably in the S_{11} region. In the f-SWNT/

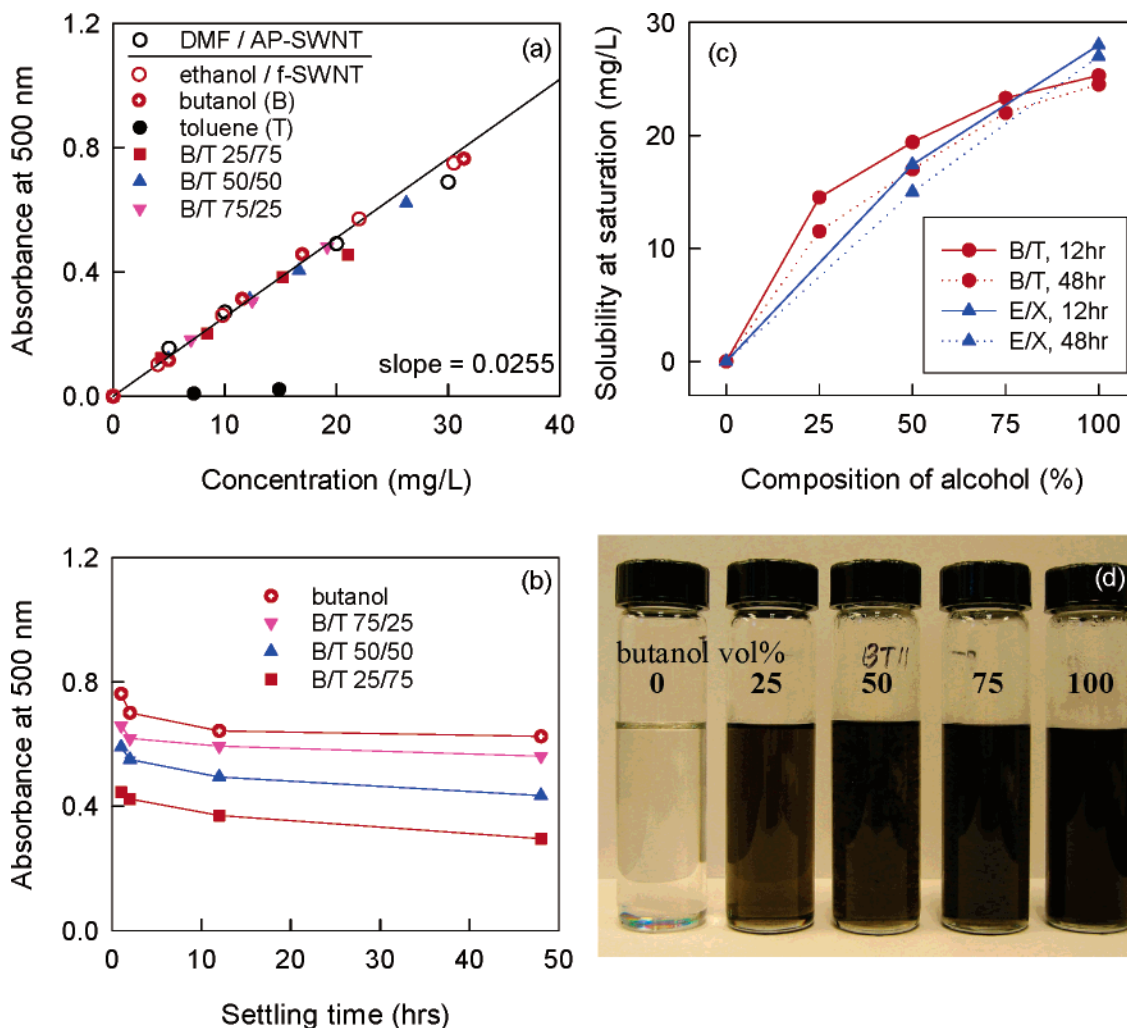


Figure 5. (a) Optical absorbance (at 500 nm) of f-SWNTs in pure ethanol, butanol, toluene, butanol–toluene mixtures, and as-purified (AP-) SWNTs in DMF at various SWNT concentrations. (b) Optical absorbance of f-SWNT in butanol and butanol(B)/toluene(T) mixtures as a function of settling time. (c) Saturation solubility of acid-treated (f-) SWNTs as a function of composition of alcohol in butanol–toluene and ethanol–xylene mixtures after 12 and 48 h of settling time. (d) f-SWNTs dispersibility at saturation concentration for various butanol/toluene compositions.

butanol, there was little change in the absorption or peak resolution with sonication time after 12 h. Absorbance at the M_{11} band gap (500 nm) as a function of sonication time (Figure 4d) shows that pristine AP-SWNTs take much longer to reach saturation, whereas the f-SWNTs reach the saturation state in a shorter period of time than the pristine nanotubes.

To quantify dispersibility, we prepared initial nanotube dispersions at <5 mg/L in a given solvent or a solvent mixture (e.g., butanol/toluene) by sonication, and the optical spectra were collected. Subsequently, small amounts of precisely weighed nanotubes were added to these vials followed by sonication. Each time, optical spectra were collected immediately after the vials were removed from the sonication bath. On the basis of solubility, unfunctionalized SWNTs have been characterized for electron donating and poor hydrogen-bonding ability.¹³ Nitric acid treatment functionalizes SWNTs with carboxylic groups, which enhances their hydrogen-bonding ability, thus allowing for broader solvent selection. For example, f-SWNTs can be dispersed in alcohols such as ethanol and 1-butanol, whereas pristine nanotubes cannot be dispersed in these solvents.

The optical absorption at 500 nm for AP-SWNTs in DMF, and f-SWNTs in pure alcohols, toluene, and in toluene/butanol mixtures plotted as a function of nanotube concentration yields

a straight line with a slope of 0.0255 (Figure 5a). The extinction coefficient⁴⁰ value for this data is 25.5 (mg/mL)⁻¹ cm⁻¹. The extinction coefficient value of 28.6 (mg/mL)⁻¹ cm⁻¹ has been reported for pristine HiPco SWNTs,¹⁴ whereas a much lower value of 9.7 (mg/mL)⁻¹ cm⁻¹ was reported for arc-discharge-functionalized SWNTs⁴¹ at the same energy of 2.48 eV (500 nm), and a higher value of 97 (mg/mL)⁻¹ cm⁻¹ was reported for SWNTs functionalized with lipophilic and hydrophilic dendra.⁴² The different values of extinction coefficients at a given energy, at least in part, may be due to the different diameter and chirality distribution in different types of tubes.

The linear-least-squares fit in Figure 5a can be used as a calibration curve to determine HiPCO-SWNT saturation dispersion. For determining maximum SWNT solubility in a given solvent, we added an excessive amount of nanotubes (higher than the expected saturation concentration) to 20 mL of solvent followed by prolonged sonication (longer than 96 h). The excess nanotubes showed reaggregation initially, but the reaggregation rate dropped subsequently (12 h to several days, Figure 5b). Samples were extracted from the clear solution in the upper portion of the vial using a pipet, and the optical spectra were recorded after 1, 2, 12, and 48 h of settling time. The absorbance of the stable solution (at which the reaggregation rate begins to

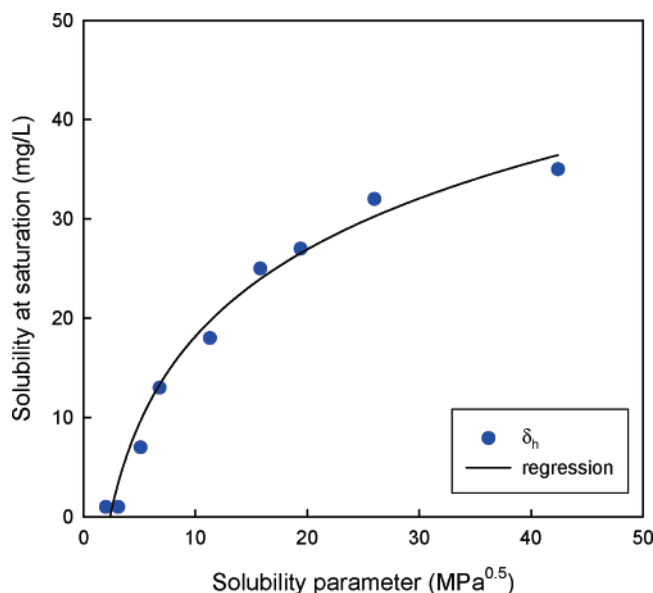


Figure 6. Saturation solubility of the f-SWNTs in various solvents as a function of the hydrogen-bonding component of the three-dimensional solubility parameter.

level off) and the linear relationship in Figure 5a were used to determine the nanotube saturation concentration in a given solvent.

The solubility values in butanol/toluene and ethylene/xylene mixtures after 12 and 48 h of settling time (following 96 h of sonication) are also plotted in Figure 5c. The SWNT solubility on nitric acid functionalization increased to 27 mg/L and 25 mg/L in ethanol and butanol, respectively. Nitric acid-treated SWNTs could not be dispersed in toluene and xylene but exhibit good dispersibility when an alcohol such as butanol or ethanol is added (Figure 5d). However, the pristine tubes are not dispersed even in such solvent mixtures.

The dispersibility of pristine and acid-treated SWNTs as well as the solvent solubility parameters are listed in Table 1. The solubility of the acid-treated SWNTs increases with increasing hydrogen-bonding component in the solubility parameter (Figure 6), whereas the polar component as well as the total solubility parameter do not appear to play a significant role. The nitric acid functionalizes SWNTs with carboxyl groups at ends and at defect sites (Figure 3), enhancing their solubility in hydrogen-bondable solvents. However, for the pristine SWNTs, the polar component of the solubility parameter was critical in governing SWNT dispersion in organic solvents¹³ and in poly(methyl methacrylate) PMMA.⁴³

Conclusions

The unpurified single-wall carbon nanotubes were treated in 7 M nitric acid at 100 °C. Under these acid treatment conditions, nanotubes were functionalized but did not result in significant degradation. The dispersion behavior of pristine and nitric acid-treated nanotubes was characterized using optical absorption in various organic solvents and solvent mixtures. Dispersion of nitric acid-treated tubes was enhanced significantly in hydrogen-bondable solvents such as ethanol and butanol as well as their mixtures with toluene and xylene. However, pristine tubes exhibited rather poor dispersion in these solvents and solvent mixtures. The dispersion of the acid-treated SWNTs in solvent mixtures such as ethanol/xylene provides a route for SWNT dispersion/exfoliation in polymers such as polypropylene.

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