Isotropic−Nematic Phase Transition of Single-Walled Carbon Nanotubes in Strong Acids

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Abstract: We present the first quantitative assessment of the maximum amount of nanotubes that can exist in the isotropic phase (ϕ_{max}^{iso}) of single-walled carbon nanotubes (SWNTs) in Brønsted−Lowry acids. We employ a centrifugation technique in conjunction with UV−vis−nIR spectroscopy to quantify ϕ_{max}^{iso}, which is also the critical concentration of the isotropic−nematic transition of SWNTs in strong acids. Centrifugation of biphasic dispersions of SWNTs, that is, acid dispersions consisting of an isotropic phase in equilibrium with an ordered nematic liquid crystalline phase, results in a clear phase separation, where the isotropic phase is supernatant. Dilution of the isotropic phase with a known amount of acid followed by UV−vis−nIR absorbance measurements yields ϕ_{max}^{iso}, that is, the maximum concentration of SWNTs that can exist in the isotropic phase in a given acid for a given SWNTs' length distribution. At low SWNT concentration (below 200 ppm) in superacids, light absorbance in the range from 400 to 1400 nm scales linearly with concentration. This Beer's law behavior yields calibration curves for measuring SWNTs' concentration in acids. We find that the critical concentration of the isotropic−nematic transition increases with acid strength in accordance with the previously proposed sidewall protonation mechanism for dispersing SWNTs in acids.

Carbon nanotubes are seamless cylinders composed of carbon atoms in a regular hexagonal arrangement, closed on both ends by hemispherical caps. They occur as both single-walled (SWNTs) and multi-walled (MWNTs) nanotubes. SWNTs combine low density with superb mechanical, electrical, and thermal properties; thus, they could be used in many potential applications.[1] Strong van der Waals forces (0.5 eV/nm) cause as-produced SWNTs to pack into thin (tens of nanometers) ropes,[2] which form disordered entangled networks with poorer mechanical, electrical, and thermal properties than macroscopically aligned systems of SWNTs.[3] Liquid-phase processing techniques for producing aligned macroscopic SWNT materials require dispersing SWNTs by overcoming the van der Waals forces and then aligning them in the liquid phase. Several routes for dispersing SWNTs in liquids have been attempted, including dispersion of pristine tubes in various solvents[4,5] and function-alization of SWNTs to disperse them in organic solvents.[6−8] All of these methods have failed to achieve significant concentration of SWNTs in the liquid. With the aid of surfactants[9] or DNA,[10−12] SWNTs have been dispersed at low concentrations (tens of parts per million as individuals[13] and up to ~1 vol % as thin bundles[14,15]). Surfactant-stabilized dispersions, however, require expensive chemicals and must be achieved through sonication, which may shorten SWNTs.[16] Covalently function-alized SWNTs dissolve without sonication,[17,18] but their elec-

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(1) Baughman, R. H.; Zakhidov, A. A.; de Heer, W. A. *Science* **2002**, *297*, 787.
(2) Bronikowski, M. J.; Willis, P. A.; Colbert, D. T.; Smith, K. A.; Smalley, R. E. *J. Vac. Sci. Technol. A: Vac. Surf. Films* **2001**, *19*, 1800.
(3) Vigolo, B.; Penicaud, A.; Coulon, C.; Sauder, C.; Pailler, R.; Journet, C.; Bernier, P.; Poulin, P. *Science* **2000**, *290*, 1331.
(4) Ausman, K. D.; Piner, R.; Lourie, O.; Ruoff, R. S.; Korobov, M. *J. Phys. Chem. B* **2000**, *104*, 8911.
(5) Sun, Y.; Wilson, S. R.; Schuster, D. I. *J. Am. Chem. Soc.* **2001**, *123*, 5348.
(6) Riggs, J. E.; Guo, Z.; Carroll, D. L.; Sun, Y.-P. *J. Am. Chem. Soc.* **2000**, *122*, 5879.
(7) Chen, J.; Rao, A. M.; Lyuksyutov, S.; Itkis, M. E.; Hamon, M. A.; Hu, H.; Cohn, R. W.; Eklund, P. C.; Colbert, D. T.; Smalley, R. E.; Haddon, R. C. *J. Phys. Chem. B* **2001**, *105*, 2525.
(8) Bandyopadhyaya, R.; Nativ-Roth, E.; Regev, O.; Yerushalmi-Rozen, R. *Nano Lett.* **2002**, *2*, 25.
(9) Wang, H.; Zhou, W.; Ho, D. L.; Winey, K. I.; Fischer, J. E.; Glinka, C. J.; Hobbie, E. K. *Nano Lett.* **2004**, *4*, 1789.
(10) Zheng, M.; Jagota, A.; Semke, E. D.; Diner, B. A.; Mclean, R. S.; Lustig, S. R.; Richardson, R. E.; Tassi, N. G. *Nat. Mater.* **2003**, *2*, 338.
(11) Zheng, M.; Jagota, A.; Strano, M. S.; Santos, A. P.; Barone, P.; Chou, S. G.; Diner, B. A.; Dresselhaus, M. S.; Mclean, R. S.; Onoa, G. B.; Samsonidze, G. G.; Semke, E. D.; Usrey, M.; Walls, D. J. *Science* **2003**, *302*, 1545.
(12) Strano, M. S.; Zheng, M.; Jagota, A.; Onoa, G. B.; Heller, D. A.; Barone, P. W.; Usrey, M. L. *Nano Lett.* **2004**, *4*, 543.
(13) Moore, V. C.; Strano, M. S.; Haroz, E. H.; Hauge, R. H.; Smalley, R. E.; Schmidt, H. K.; Talmon, Y. *Nano Lett.* **2003**, *3*, 1379.
(14) Islam, M. F.; Rojas, E.; Bergey, D. M.; Johnson, A. T.; Yodh, A. G. *Nano Lett.* **2003**, *3*, 269.
(15) Badaire, S.; Zakri, C.; Maugey, M.; Derre, A.; Barisci, J. N.; Wallace, G.; Poulin, P. *Adv. Mater.* **2005**, *17*, 1673.
(16) Shelimov, K. B.; Esenaliev, R. O.; Rinzler, A. G.; Huffman, C. B.; Smalley, R. E. *Chem. Phys. Lett.* **1998**, *282*, 429.
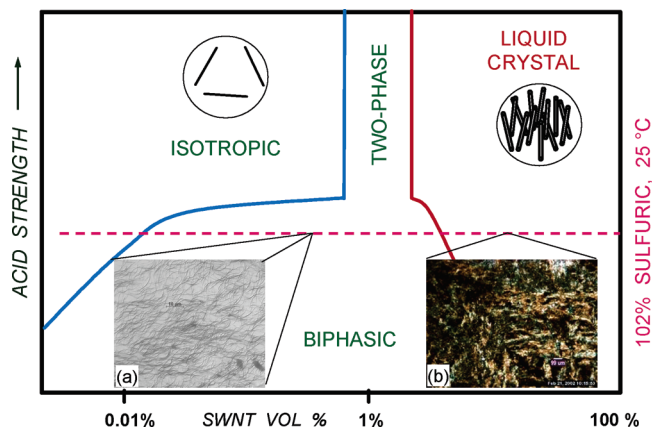
Figure 1. Postulated phase diagram of SWNTs in acids. In 102% sulfuric acid, the biphasic region extends from a concentration of ∼100 ppm to ∼8%. These critical concentrations are expected to vary with the strength of the acid used.

tronic properties are altered, although frequently these properties can be restored by removing the functional groups after processing by controlled heating. Recently, superacids (e.g., fuming sulfuric and chlorosulfonic acids) have been shown to be promising solvents for SWNTs.[19,20] Strong acids protonate the sidewalls of SWNTs,[20,21] resulting in a delocalized fractional positive charge on the carbon atoms; this charge induces tube−tube repulsion and promotes dispersion by counteracting the van der Waals attraction.

Rheology and microscopy[19] have shown that the phase behavior of SWNTs in acids parallels the phase behavior of rod-like macromolecule dispersions.[22] Figure 1 shows the postulated phase diagram of SWNTs in 102% H_2SO_4. With increasing concentration, SWNT−superacid dispersions transition from an isotropic solution, where individual SWNTs are randomly oriented, to a biphasic system, where an ordered liquid phase (liquid crystal) is in equilibrium with the isotropic phase. Raising the concentration increases the proportion of ordered phase until the system becomes a fully liquid crystalline dope that can be solution spun into highly aligned fibers.[19,23] Inset (a) of Figure 1 shows the seemingly endless strands of SWNTs (ordered liquid phase) in biphasic region, and inset (b) shows the birefringent nature of the fully liquid crystalline dispersion of SWNTs. The critical concentrations at which the ordered phase first appears and at which the fully liquid crystalline single phase is achieved depend on the solvent quality and aspect ratio distribution of rods. Solvent quality is a measure of energetic interactions between rods and solvent; such interactions are typically considered in terms of Flory's theory[24] and subsequent refinements.[25] Flory's theory[24] is based on nearest-neighbor

interactions and does not account for possible short-range repulsion between SWNTs in superacid accompanied to the long-range attraction. Quantitative theory of orientational behavior of rod-like polyelectrolytes in dilute solution has been developed.[26,27] Conceptually, however, SWNTs in strong acids are different from a rod-like polyelectrolyte because the acid is expected to screen electrostatic interactions much more strongly than a dilute electrolyte solution, and because tube−tube van der Waals attractive forces are expected to play an important role—they are negligible in rod-like polymers. To date, theories for rod-like macromolecules do not account for possible long-range attractive interactions that are typical of many colloidal systems.[28] The effect of long-range attractive forces on the phase behavior of SWNT/superacid dispersions is yet not understood. Potemkin and Khokhlov[27] and Maeda[26] assume the potential to be a sum of the hard-rod term and electrostatic term, but they do not consider the strong van der Waals interaction between SWNTs. As remarked by Dogic and co-workers,[29] much remains to be done to understand and predict the behavior of rods whose interactions are more complex than simple Onsager-like[25] hard rods.

Until now, attempts to quantify the maximum amount of nanotubes that can exist in the isotropic phase (ϕ_{max}^{iso}) of SWNTs in acids (the critical concentration at which the system becomes biphasic) have not been successful. In lyotropic polymeric liquid crystals, optical microscopy is often used to measure this critical concentration based on the detection of birefringent droplets of aligned phase. In SWNT−acid dispersions, however, optical microscopy provides only qualitative information because these dispersions are extremely sensitive to humidity and slide preparation techniques, and because the aligned phase is thread-like and difficult to detect.[19] Similarly, rheology, neutron scattering, and X-ray scattering provide only qualitative estimates of the isotropic−nematic phase transition.

Here we report a simple and accurate technique for quantifying the isotropic−nematic phase transition concentration of SWNTs in strong acids; it relies on centrifugation in conjunction with a method for measuring the concentration of dispersions of SWNTs in strong acids by UV−vis−nIR spectroscopy. The SWNTs used in this study were produced from the high-pressure carbon monoxide (HiPco, batch HPR 126.2) process[2] at Rice University and were purified according to literature methods.[30] Purified SWNTs contained less than 5 wt % iron and amorphous carbon impurities. ACS-certified oleum (∼20 wt % excess SO_3, density = 1925 kg/m^3) and chlorosulfonic acid (density = 1753 kg/m^3) were used as received from Sigma Aldrich; 102% sulfuric acid (2 wt % excess SO_3) was prepared by mixing the oleum with 96% sulfuric acid in the ratio of 1.1 mL of oleum/mL of H_2SO_4. The measured viscosity and density of the 102% sulfuric acid were 25 mPa·s and 1880 kg/m^3, respectively, at 25 °C. In 102% sulfuric acid, the excess SO_3 ensures that the isotropic−nematic phase transition of the SWNTs would not be affected by the uptake of trace amounts of moisture from the environment. The SO_3 content of the nominal 102% sulfuric

(17) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257.
(18) Dyke, C. A.; Tour, J. M. *J. Phys. Chem. A* **2004**, *108*, 11151.
(19) Davis, V. A.; Ericson, L. M.; Parra-Vasquez, A. N. G.; Fan, H.; Wang, Y.; Prieto, V.; Longoria, J. A.; Ramesh, S.; Saini, R. K.; Kittrell, C.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E.; Pasquali, M. *Macromolecules* **2004**, *37*, 154.
(20) Ramesh, S.; Ericson, L. M.; Davis, V. A.; Saini, R. K.; Kittrell, C.; Pasquali, M.; Billups, W. E.; Adams, W. W.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2004**, *108*, 8794.
(21) Zhou, W.; Heiney, P. A.; Fan, H.; Smalley, R. E.; Fischer, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 1640.
(22) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gulrich, L. W. *Macromolecules* **1977**, *10*, 1390.
(23) Ericson, L. M.; et al. *Science* **2004**, *305*, 1447.
(24) Flory, P. J. *Proc. R. Soc. London A* **1956**, *234*, 73.
(25) Donald, A.; Windle, A. *Liquid Crystalline Polymers*, 2nd ed.; Cambridge University Press: New York, 2005.

(26) Maeda, T. *Macromolecules* **1991**, *24*, 2740.
(27) Potemkin, I. I.; Khokhlov, A. R. *J. Chem. Phys.* **2004**, *120*, 10848.
(28) Israelachvili, J. N. *Intermolecular and Surface Forces*, 2nd ed.; Academic Press: New York, 1992.
(29) Dogic, Z.; Purdy, K. R.; Grelet, E.; Adams, M.; Fraden, S. *Phys. Rev. E* **2004**, *69*, 051702.
(30) Chiang, I. W.; Brinson, B. E.; Huang, A. Y.; Willis, P. A.; Bronikowski, M. J.; Margrave, J. L.; Smalley, R. E.; Hauge, R. H. *J. Phys. Chem. B* **2001**, *105*, 8297.
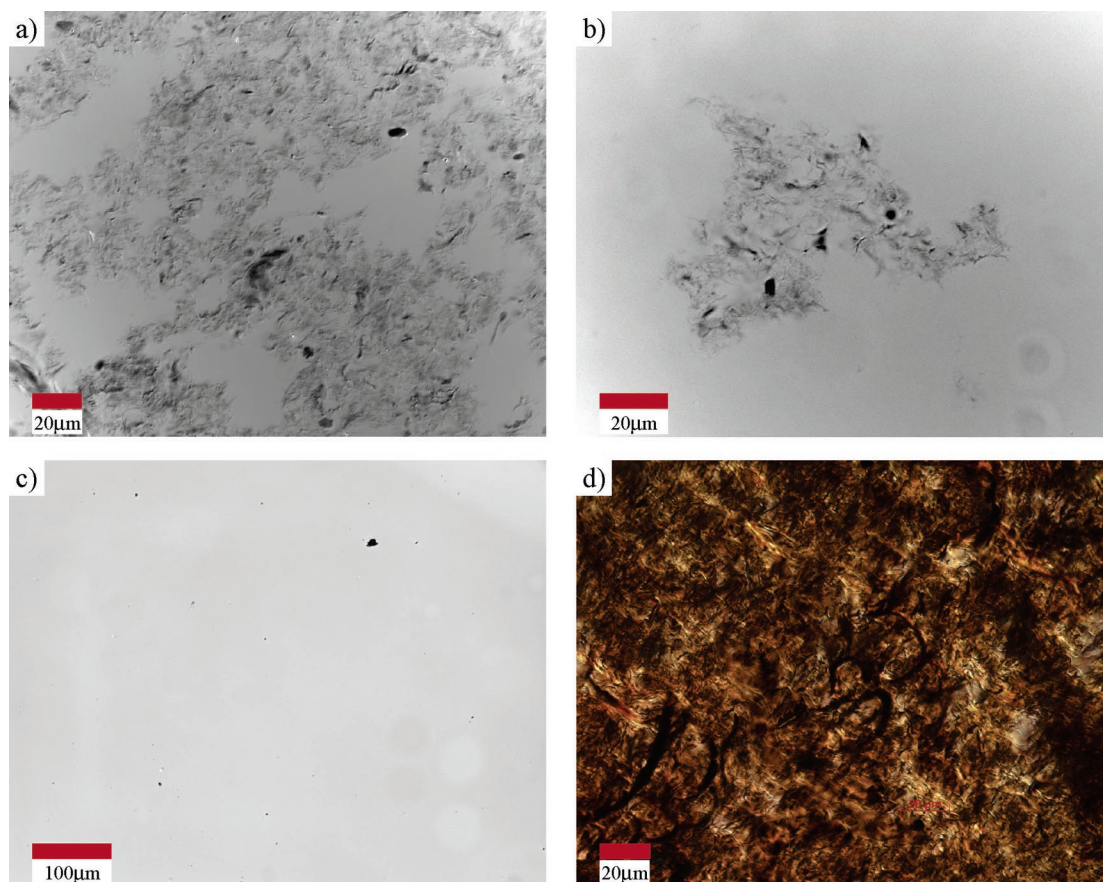
Figure 2. Microscopic appearance of the SWNTs dispersed in 123% sulfuric acid. (a) The initial dispersion (1500 ppm) is biphasic and shows the characteristic spaghetti structure. (b) The top phase of the centrifuged sample after 4 h of centrifugation is predominantly structureless with occasional small spaghetti regions. (c) The top phase of the centrifuged sample after 52 h of centrifugation is optically uniform and structureless. (d) The bottom phase of the centrifuged sample after 52 h of centrifugation viewed between crossed-polars shows birefringent polydomain structure.

acid and oleum was checked with a standard titration procedure;[31] the measured SO_3 content was found to be within 1% of the nominal value. SWNT dispersions were prepared by gentle mixing with a magnetic stir bar (no sonication) for a minimum of 72 h at room temperature in an anhydrous environment (a glovebox with a dewpoint of $-50\,°C$) to prevent moisture ingress. After mixing, the samples were centrifuged on a Fisher Centrific Model 225 Benchtop centrifuge at 5100 rpm. UV−vis−nIR absorbance spectra were measured on a Shimadzu UV-3101PC spectrometer in 1 mm path length Starna cells with Teflon closures. Optical microscopy was performed on a Zeiss Axioplan optical microscope using flame-dried glass slides and coverslips assembled in the above glovebox and sealed with foil tape.

Flory predicted that biphasic dispersions of rods could be separated into isotropic and ordered phases by application of external forces, such as ionic or centrifugal forces.[24] Such predictions have been confirmed experimentally and used for scalable length fractionation of rod-like polymers.[32,33] Aharoni and Walsh[32] reported that the biphasic dispersions of rigid backbone polymers, poly(hexyl isocyanate) and poly(50% butyl + 50% *p*-anisole- 3-propylisocyanate), partition into more concentrated anisotropic and more dilute isotropic phases by

gravity over a 1 week period. Conio and co-workers[33] centrifuged the biphasic mixtures of poly(*n*-hexyl isocyanate), covering the molecular weight range from 24 000 to 524 000 in dichloromethane and toluene at 3000−6000 rpm for times ranging from 4 to 24 h to effect a clean separation of the two phases. Analogously, it should be possible to separate the biphasic dispersions of SWNTs in acids into isotropic and aligned phased by centrifugation.

Centrifugation of biphasic SWNT−acid dispersions for an extended period of time indeed results in separation of the isotropic and ordered phases. Figure 2a shows the microscope image of a biphasic dispersion of SWNTs (0.15 wt %) in 123% H_2SO_4. When this dispersion is centrifuged for as little as 2 h, the opacity of the top phase drastically drops. During the continuous process of centrifugation, the liquid at the top is gradually depleted of the aligned phase (Figure 2b). At the end of the centrifugation, the isotropic phase at the top is optically uniform (Figure 2c), whereas the anisotropic phase at the bottom of the vial is birefringent and displays polydomain structure (Figure 2d).

The SWNT concentration in the isotropic phase was quantified using light absorption. We found that the UV−vis−nIR absorbance of dilute dispersions of SWNTs in superacids follows Beer's law at concentrations up to hundreds of parts per million in the wavelength range between $\sim$400 and 1400 nm. When a monochromatic light passes through a solution, Beer's law[34] states that $\log_{10}(I(x)/I_0) = -kcx$ where I_0 and $I(x)$ are the

(31) Sulfuric Acid, Fuming. In *Reagent Chemicals*, 9th ed.; American Chemical Society: Washington, DC, 2002; pp 645−646.
(32) Aharoni, S. M.; Walsh, E. K. *Macromolecules* **1979**, *12*, 271.
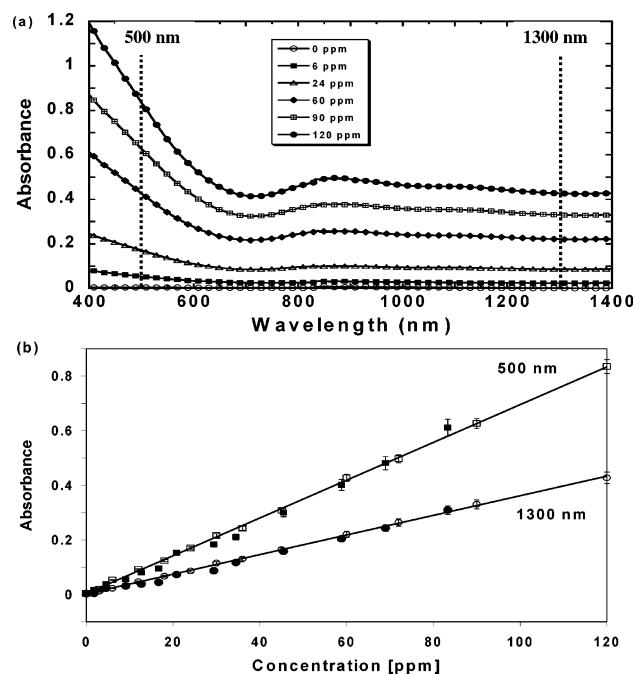(33) Conio, G.; Bianchi, E.; Ciferri, A.; Krigbaum, W. R. *Macromolecules* **1984**, *17*, 856.

Figure 3. (a) UV−vis−nIR absorbance spectra of SWNTs in 102% H_2SO_4 at different concentrations and corresponding (b) calibration line at 500 and 1300 nm. The open and closed symbols in (b) are from two different data sets.

Table 1. The Maximum Amount of SWNTs (HiPco, batch HPR 126.2) in the Isotropic Phase (ϕ_{max}^{iso}) in Different Acids[a]

acid	Hammett acidity [−]	ϕ_{max}^{iso} [ppm]	proportionality constant, k, at 500 nm [ppm^{-1} mm^{-1}]
96% H_2SO_4	−9.8	80	0.008
98% H_2SO_4	−10.44	110	0.008
102% H_2SO_4	−12.48	130	0.007
123% H_2SO_4	−13.48	260	0.006
ClSO$_3$H	−13.8	4100[b]	0.009

[a] The ϕ_{max}^{iso} of SWNTs grows with the strength of the acid. The slope of the calibration line varies slightly with the strength of the acid. No birefringent phase was observed in the 96 and 98% H_2SO_4 samples; thus, below (roughly) 100% H_2SO_4, the nematic phase does not form, and the dilute isotropic phase is in equilibrium with a solid phase (likely a crystal solvate[19]). [b] The starting concentration of SWNTs for this experiment was 5000 ppm.

light intensity entering and exiting the test cuvette, x is the path length of 1 mm, c is the SWNT concentration, and k is an experimentally determined proportionality constant known as the absorptivity or extinction coefficient. Figure 3 shows the absorption spectrum of SWNTs in 102% H_2SO_4 at different concentrations (these six spectra are representative of data at more then 20 concentrations) and the corresponding calibration lines at 500 and 1300 nm (two independent measurements fall on the calibration curve within 5%). The proportionality constant k depends slightly on acid strength; its value at 500 nm in different acids is tabulated in Table 1. The UV−vis−nIR spectra of SWNTs in 102% H_2SO_4 and other superacids do not exhibit absorption peaks for specific chirality vectors of SWNTs, which is dominant in water-based dispersions of SWNTs.[10] The first van Hove features arising from transitions involving the $\nu_1 \rightarrow c_1$ transitions of the SWNTs are sensitive to adsorption of any species on the surface of the nanotubes. Since ν_1 valence
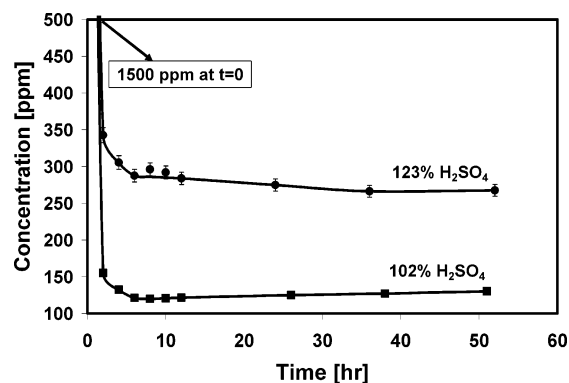

Figure 4. Concentration of SWNTs in the supernatant phase versus centrifugation time in 102 and 123% H_2SO_4. The maximum concentration of SWNTs in the isotropic phase grows with the amount of free SO$_3$.

electrons become largely depleted in the protonation process with strong acids,[20] they do not contribute to UV−vis−nIR absorption peaks for specific chirality vectors of SWNTs.

Figure 4 shows the concentration of SWNTs, as measured by light absorption, in the top layer of the centrifuge tube as a function of centrifugation time. The concentration of SWNTs in the top phase drops drastically for the first 6−8 h of centrifugation. Further centrifugation (up to 50 h) does not affect the concentration of SWNTs in the isotropic phase; thus, the isotropic phase is stable. Figure 4 also shows that, if the process is carried on identical SWNTs by using higher amount of free SO$_3$, a higher concentration of SWNTs is found in the isotropic phase (130 ppm in 102% and 260 ppm in 123% H_2SO_4). This shows conclusively and quantitatively that the maximum amount of nanotubes in the isotropic phase of SWNTs in oleum depends on SO$_3$ concentration.

Table 1 shows that, for SWNTs from the same batch, higher amounts of free SO$_3$ result in higher amounts of SWNTs in the isotropic phase. The strength of an acid can be quantified in terms of Hammett acidity.[35−37] Increasing SO$_3$ content increases the Hammett acidity of the acid. With increasing SO$_3$ content from 96 to 123% H_2SO_4, the amount of SWNTs in the isotropic phase increases from 80 to 260 ppm. In pure ClSO$_3$H, an even stronger acid, the maximum concentration of SWNTs in the isotropic phase is more than an order of magnitude higher than that in 123% H_2SO_4. These findings are consistent with the proposed protonation mechanism for SWNT dispersal in acid:[19,20] stronger acids have greater protonating power, thus they result in increased charge stabilization and the overall amount of SWNTs in the isotropic phase.

A centrifugation technique has been developed to separate the isotropic phase from the anisotropic phase present in the biphasic SWNTs/superacid dispersions. The UV−vis−nIR absorption spectra have been successfully calibrated to measure the concentration of dilute dispersions of SWNTs in strong acids. Centrifugation in different superacids revealed that the amount of SWNTs in the isotropic phase grows with Hammett acidity of the solvent. This work opens the way to the quantitative

(34) Zhao, B.; Itkis, M. E.; Niyogi, S.; Hu, H.; Zhang, J.; Haddon, R. C. *J. Phys. Chem. B* **2004**, *108*, 8136.

(35) Gillespie, R. J.; Peel, T. E.; Robinson, E. A. *J. Am. Chem. Soc.* **1971**, *93*, 5083.

(36) Hammett acidity function is not a unique property of the solvent alone, but depends on the base with respect to which it is measured.[37] Hammett acidity function values in Table 1 were an average of measurements using seven aromatic nitro compounds as base indicators. Similar measurements should be carried out using SWNTs as the conjugate base.

(37) McNaught, A. D.; Wilkinson, A. *IUPAC Compendium of Chemical Technology*, 2nd ed.; Blackwell Science: Oxford, UK, 1997; p 6.

determination of phase diagrams of SWNTs in strong acids and other solvents and to further understanding the mechanism of SWNT stabilization in such dispersions.

Supporting Information Available: Complete ref 23. This material is available free of charge via the Internet at http://pubs.acs.org.

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