Rheological investigation of single-walled carbon nanotubes – induced structural ordering in CTAB solutions†

Ofra Ben-David,[a] Einat Nativ-Roth,[ab] Rachel Yerushalmi-Rozen*[ab] and Moshe Gottlieb*[ab]

Received 14th November 2008, Accepted 12th February 2009
First published as an Advance Article on the web 17th March 2009
DOI: 10.1039/b820404g

The rheological behavior of aqueous dispersions of single-walled carbon nanotubes (SWNTs) in solutions of the cationic surfactant cetyl trimethyl ammonium bromide (CTAB) was investigated. The steady shear viscosity as a function of the applied shear rate was monitored in different concentrations of surfactant which correspond to different mesophases. We found that the presence of SWNTs had a dramatic effect on the behavior of the combined system not observed with other additives: a significant increase in the low shear-rate viscosity of SWNT dispersions, and shear thinning replacing Newtonian behavior were observed for CTAB concentrations below the onset of the surfactant hexagonal phase. As CTAB concentration increases the rheological behavior of the SWNT-CTAB system and the native CTAB solutions become more alike. We suggest that the origin of the observed phenomena is the good size-match between SWNTs and elongated CTAB micelles. Thus dispersed SWNTs may induce the formation of size-matched elongated CTAB micelles that further orient under the action of external shear. A similar effect was not observed in dispersions of multi-walled carbon nanotubes or carbon black particles, suggesting that the cooperative behavior is not invoked when significant size-mismatch exists between the surfactant micelles and the dispersed additives.

1. Introduction

Single-walled carbon nanotubes (SWNTs) are tubular structures with a diameter of ~1 nanometer and a length of few tens of microns. SWNTs may be dispersed in aqueous solutions of different ionic surfactants at low surfactant concentrations.[1–3] As was shown in a variety of cases, a stable dispersion of individual tubes readily forms following sonication of a powder of pristine SWNTs in the solution.[4] In the absence of SWNTs, at surfactant concentrations well above the critical micellar concentration (cmc), a rich phase behavior of the surfactant molecules results in self-assembly on a hierarchy of length scales: micelles merge into elongated structures known as worm-like micelles that further pack and orient into lyotropic liquid crystalline (LC) phases. This hierarchical structure buildup is observed for example, in the phase diagram of the cationic surfactant cetyltrimethylammonium bromide (CTAB) depicted in Fig. 1. CTAB solutions at 30 °C are isotropic at concentrations below 23 wt% (*cf.* Fig. 1), with mostly spherical micelles at low concentrations.[5] As the CTAB concentration approaches the isotropic-to-nematic (I–N) transition, elongated cylindrical micelles become dominant. At $C_{CTAB} > 23$ wt% LC phases are formed.

Recently we reported that the presence of dispersed nanostructures may modify the phase behavior of self-assembled CTAB structures.[6,7] At CTAB concentrations above 5 wt% dispersions of carbonaceous particles (carbon black, CB; carbon nanotubes, CNTs) de-mix and phase-separate into two coexisting phases of similar CTAB concentrations: a clear upper phase that is depleted of the carbonaceous structures and a lower phase that is enriched by the additives. At higher CTAB concentrations (above 22 wt%), under conditions leading to the formation of lyotropic liquid crystalline phase in the native CTAB solutions, a re-entrant single-phase was observed. In this phase SWNTs were incorporated into the liquid crystalline phase while preserving the *d*-spacing of the native system.[7]

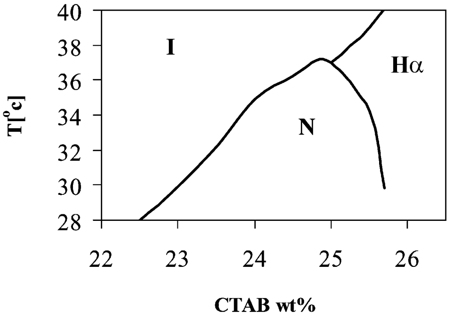

Fig. 1 Phase diagram for the water–CTAB system (from optical measurements). **I** – isotropic, **N** – nematic, **Hα** – hexagonal.[1]

Cryo-TEM imaging of thin films prepared from the additive-rich lower phase revealed that the presence of individual SWNTs resulted in the formation of an ordered cylindrical phase, as depicted in Fig. 2, at CTAB concentrations as low as 9 wt%, well below the concentrations leading to LC formation in the native surfactant solutions. The effect was found to be exclusive to SWNTs, and similar behavior was not detected in dispersions of MWNTs or CB.

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[a] *Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel. E-mail: rachely@bgu.ac.il; mosheg@cs.bgu.ac.il*
[b] *Ilze Kats Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, Beer-Sheva, 84105, Israel*

† Electronic supplementary information (ESI) available: Additional experimental information. See DOI: 10.1039/b820404g

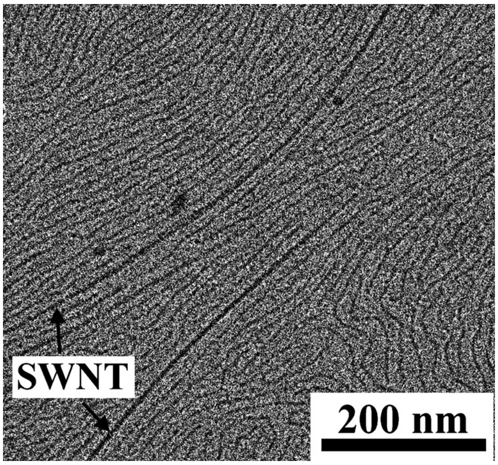

Fig. 2 Cryo-TEM image taken from dispersions of SWNTs in CTAB $C_{CTAB} = 12$ wt%, $C_{SWNT} = 0.1$ wt%.[6,7] The arrows point to SWNTs.

Cryo-TEM images such as the one depicted in Fig. 2 are obtained by blotting down a droplet of the bulk dispersion into an ultra-thin film. Hence, the observed morphologies have been formed under strong *confinement* and after exposure to poorly controlled *high shear rates* in the range of 10^3–10^6 s^{-1} during blotting.[8,9] The ability to induce the formation of ordered phases by the addition of a specific nano-additive is quite compelling. Thus, it is of interest to elucidate the role of shear and confinement on the self-organization of the combined system. Here we focus on the rheological behavior of the bulk dispersions, and investigate the dynamic phase behavior under controlled shear conditions.

The rheological behavior of native CTAB solutions has been thoroughly investigated.[10–14] Concentrated CTAB solutions were shown to exhibit a non-linear viscoelastic response,[14] flow-induced phase transitions,[12,13] shear-thinning and shear thickening.[10] These phenomena are indicative of morphological deformations[15] and self-organization of CTAB micelles known as shear-induced structuring (SIS).

The rheology of carbon nanotubes (CNT) dispersions is a relatively young field of research.[16–19] Previous studies have focused on correlating the rheological behavior of CNT suspensions with the dispersion quality,[16,19] CNT concentration,[16–19] aspect ratio[16] and degree of orientation.[16,17] The results span a variety of new phenomena not observed before in colloidal or macroscopic systems.

In this work we present a systematic investigation of the rheological behavior of SWNT–CTAB dispersions, at concentrations well above the cmc of the surfactant. Rheology is used to characterize the behavior of the combined system, and probe the microstructural transitions that take place under shear in this multi-component system.

2. Materials and methods

Materials

Raw SWNTs synthesized by arc discharge were purchased from Carbolex, Inc. USA[20] and used as received (AP grade, Carbolex, University of Kentucky, Lexington, Kentucky, USA). According to the manufacturer specifications, the as-prepared AP grade consists of 50–70 vol% SWNTs. The samples also contain graphite, carbon impurities and catalyst (cobalt and nickel, *ca.* 20 nm in diameter). The specific surface area is in the range of 1200–1400 m^2/g.

MWNTs produced by Catalytic Chemical Vapor Deposition were purchased from INP (Toulouse, France). The powder contains 95 vol% MWNTs, with specific surface area of 700–1000 m^2/g. A dry powder of CB, Vulcan P grade, was purchased from Cabot, USA, and used as received. Typical values of specific surface area are 700–1000 m^2/g. Cetyltrimethylammonium bromide (CTAB) (Sigma, Israel H5882, 99% purity) was used as received. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), Pluronic® triblock copolymers P123: PEO_{20}–PPO_{70}–PEO_{20} and F127: PEO_{100}–PPO_{65}–PEO_{100}, were received as a gift from BASF AG Germany and used as received.

Sample preparation

Aqueous solutions of CTAB in concentrations of 5–26 wt% (CTAB in water) were prepared by dissolving the surfactant in water (Millipore water, resistance of 18.2 MΩ cm) at room temperature (25 °C). The solutions were incubated for at least two days before being used.

Liquid dispersions of SWNTs, MWNTs and CB were prepared by sonicating the powder of the raw material (typical concentration of 0.1%) under very mild conditions[21,22] (mini supersonic cleaner, Delta DG-1, 50W, 43 kHz) for 30–40 minutes in 1 wt% CTAB solution. The dispersions were centrifuged (at 4500 rpm for 30 min) and the supernatant was decanted from above the precipitate. As was shown before,[22] the dispersion process is selective towards CNT, and the precipitate mainly contains other colloidal moieties. Yet, we estimate that some of the CNTs precipitate, so that the actual weight percent of the dispersed CNTs is lower than the nominal concentration, designated throughout the text.

Dispersions in higher CTAB concentrations were prepared by adding CTAB to the 1 wt% mother dispersion. The dispersions were allowed to equilibrate over weeks at 30 °C. Dispersions at concentrations above 5 wt% and below 22 wt% spontaneously phase-separated into two coexisting phases of similar CTAB concentration: a clear upper phase and a lower phase enriched by the carbonaceous additive[7] (see also item 1 in ESI†).

Rheological measurements

Rheological measurements were performed using a TA ARES (200 FRTN1) strain-controlled rheometer. Measurements were carried out in a parallel-plate geometry of either 25 or 50 mm diameter and a separation between the plates of 0.5–1.0 mm. To prevent evaporation, the rim of the plates was coated with a thin layer of silicone oil. The temperature was controlled by a Peltier device (±0.1 °C). In most cases the experimental uncertainty in viscosity values was below 20%. For the lowest-viscosity samples the experimental uncertainty was considerably higher at low shear rates due to the extremely low torque values, at the limit of the 200 FRTN1 transducer detection capabilities.

Two types of experiments were performed: steady shear and oscillatory shear. In the case of steady shear the accessible shear rate within the range of 0.1 to 2000 s^{-1} (depending on the sample properties) was scanned using 5 points per decade. At each point measurement were carried out in two directions (clockwise and counter-clockwise) allowing 10 seconds per measurement, and 10 seconds of pre-shear before actual data collection. The total measurement time was 1000–1200 seconds, depending on the sample. Oscillatory measurements were carried out at low strains in the linear viscoelastic regime.

Unless otherwise noted, the lower CNT-enriched phase of the different dispersions was measured. As previously reported, CTAB solutions show aging effects[11,14] and tend to crystallize under shear, especially at lower temperatures and higher CTAB concentrations.[11,14] We therefore used a fresh sample for each experiment, and the reproducibility of the results was tested by repeated measurements for a given batch with a new sample loaded for each measurement. In addition, different batches of the same composition were prepared and the measurements repeated under identical experimental conditions. At the end of each experiment the solutions were examined visually for signs of crystallization, evaporation, shrinkage or deterioration. All the results reported in this paper correspond to experiments at the end of which the solution appeared free from foam and air bubbles, and with no apparent signs of crystallization or evaporation.

3. Results and discussion

The rheological behavior of the ternary SWNT–CTAB–water system was investigated. The importance of the size and morphology of the carbonaceous additive (SWNTs, MWNTs and CB) were also examined. Dispersions of SWNTs in different polymeric dispersing agents (Pluronic® P123 and F127) were measured for comparison.

Rheological behavior of SWNT–CTAB dispersions as a function of CTAB concentration

The steady shear viscosity as a function of the applied shear rate at 30 °C was measured in dispersions of SWNTs (0.1 wt%) at different CTAB concentrations.

In Fig. 3(a,b) we present the steady shear viscosity of the lower phase of SWNT dispersions at $C_{\mathrm{CTAB}} \leq 22$ wt%. The data for the single-phase regime are presented in Fig. 3(c,d). For comparison, the viscosity of the native CTAB solutions at the relevant concentrations is included.

The impact of the presence of SWNTs on the rheological behavior of the system is most pronounced for $C_{\mathrm{CTAB}} = 12$ wt% as clearly seen in Fig. 3(a): the Newtonian behavior observed in the native solution over four decades of shear is transformed into a pronounced shear-thinning behavior (power law exponent $n = 0.4$)[23] by the presence of the SWNTs (Note that here the shear viscosity η is described by a power law in the form of $\eta = m\dot{\gamma}^{n-1}$ where m is the consistency coefficient, $\dot{\gamma}$ the shear rate, and n the power law exponent, for a Newtonian liquid $n = 1$). The low shear-rate viscosity of the SWNT dispersion is more than an order of magnitude higher than that of the CTAB solution. At shear rates above 100 s^{-1} a secondary Newtonian plateau is observed for the SWNT dispersion and its viscosity approaches that of the native CTAB solution.

A similar yet less pronounced effect is observed in Fig. 3(b) with $C_{\mathrm{CTAB}} = 18$ wt%. The low shear viscosity is four times higher in the presence of SWNTs; the practically Newtonian behavior with negligible shear-thinning at very high shear rates (>500 s^{-1}) for the native solution is transformed into a moderate

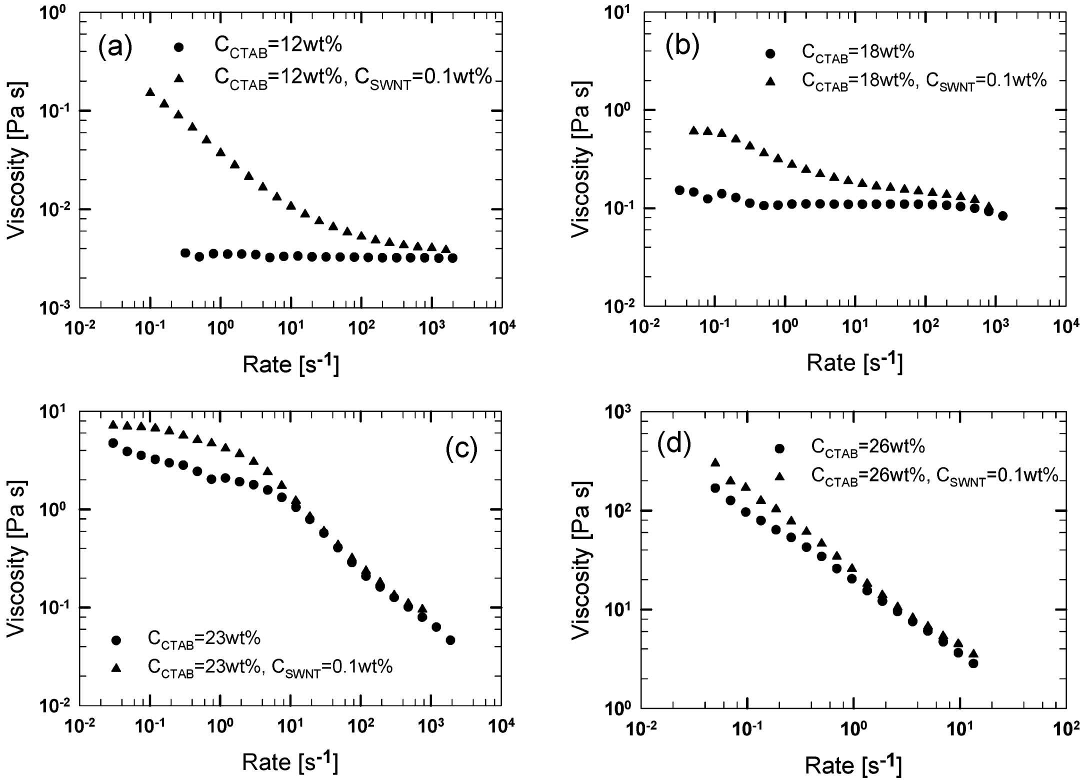

Fig. 3 Steady shear viscosity as a function of the applied shear rate for SWNT dispersions $C_{\mathrm{SWNT}} = 0.1$ wt% (▲) and native solutions of CTAB (●) at 30 °C for different CTAB concentrations: (a) $C_{\mathrm{CTAB}} = 12$ wt%, (b) $C_{\mathrm{CTAB}} = 18$ wt%, (c) $C_{\mathrm{CTAB}} = 23$ wt% and (d) $C_{\mathrm{CTAB}} = 26$ wt%.

shear-thinning (power law exponent $n = 0.7$) at shear rates above 0.1 s^{-1} for SWNT dispersions. Finally the curves of the native solution and the dispersion merge at a shear rate $\dot{\gamma}_{merge} = 800\ s^{-1}$.

Native CTAB solutions of higher concentrations $C_{CTAB} = 23$ and 26 wt% (Fig. 3(c,d) respectively) exhibit a shear-thinning behavior, in agreement with previous studies.[10]

In Fig. 3(c) we present the behavior of SWNT dispersions at $C_{CTAB} = 23$ wt%. Here only a slight increase in viscosity is observed at low shear rates (factor of 2), and the curves of the two systems merge already at $\dot{\gamma}_{merge} \sim 10\ s^{-1}$. It should be noted that the slopes for the two distinct shear-thinning regimes ($n =$ 0.8 and 0.4 respectively) and the transition point between the two ($\sim 5\ s^{-1}$) are almost identical for both systems. With $C_{CTAB} = 26$ wt% (Fig. 3(d)) the dispersion is almost indistinguishable in its rheological behavior from the native solution ($\dot{\gamma}_{merge} \sim 1\ s^{-1}$), exhibiting very high shear-thinning over the entire range of shear rates with a single power law exponent of 0.2.

Table 1 Dimensions of additives

Additive	*D* [nm]	*L* [nm]	Aspect ratio
SWNTs	1–2	$>10^3$	1000
MWNTs	20–50	$>10^3$	50
CB	50–70	50–70	1

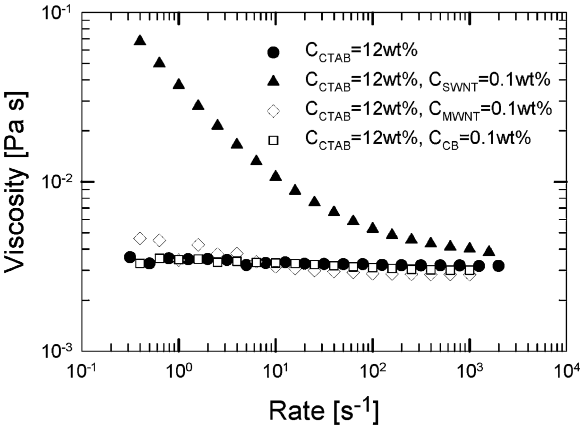

Fig. 4 Steady shear viscosity as a function of the applied shear rate in CTAB ($C_{CTAB} = 12$ wt%) dispersions of 0.1 wt% of additive at 30 °C. Native CTAB solution (●), MWNTs (◇), CB (□), SWNTs (▲).

The results presented in Fig. 3 suggest that the effect of SWNTs on the rheological behavior depends strongly on the concentration of the surfactant: as the concentration of CTAB increases, the difference between the dispersions and the native solutions diminishes. The largest effect is observed in the isotropic regime of the native solutions (Fig. 3(a,b)), while the effect becomes insignificant in the liquid-crystalline regime (Fig. 3(d)). In all cases, at high shear rates the apparent viscosity approaches the asymptotic value of the binary CTAB–water solution. In addition, $\dot{\gamma}_{merge}$ is shifted to lower shear rates as the CTAB concentration increases.

For all four systems described above the primary normal stress difference measured over more than three decades of shear is negligible.

Different carbonaceous additives

The effect of MWNTs and CB was examined for comparison. Dispersions of 0.1 wt% MWNTs or CB in CTAB were prepared. The two additives are similar to SWNTs in composition, surface chemistry and specific surface area, but differ in diameter (MWNTs) and geometry (CB). The characteristic dimensions of the different additives are presented in Table 1.

In Fig. 4 the steady shear viscosity of the lower phase in CTAB dispersions ($C_{CTAB} = 12$ wt%) of the different carbonaceous particles is presented. We clearly observe that the addition of MWNTs or CB does not affect significantly the magnitude of the viscosity or the rheological nature of the dispersions, as it preserves the Newtonian character of the native solutions.

Different dispersing agents

To examine the role of the dispersing agent, we studied the rheological behavior of dispersions of SWNTs in solutions of Pluronic block copolymers, P123 and F127.[24] In Fig. 5 we present the behavior of SWNTs ($C_{SWNT} = 0.1$ wt%) dispersed in P123 solutions with either $C_{P123} = 10$ wt% or 15 wt%. It is clear that the addition of SWNTs to P123 solutions does not modify the rheological characteristics of the copolymer solution, and both the value of the viscosity and the dependence on the shear rate are almost identical to that of the native solution. Similar results were obtained for 0.1 wt% SWNT dispersion in 10 or 15 wt% F127 (not shown).

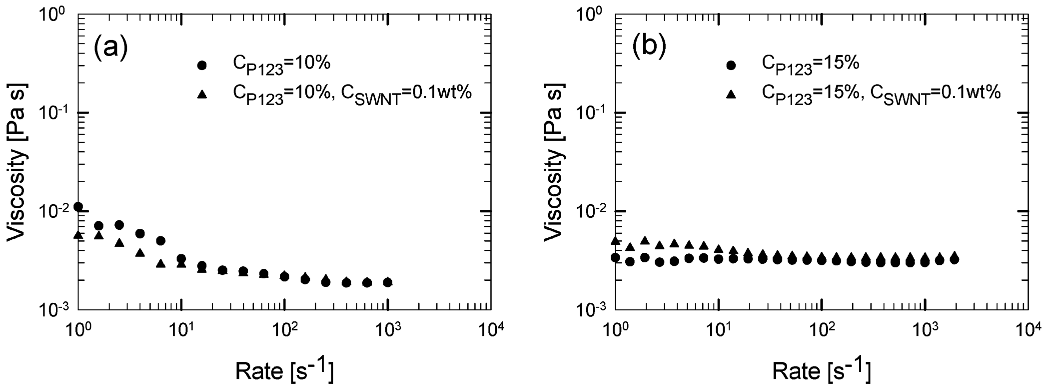

Fig. 5 Steady shear viscosity for dispersion of $C_{SWNT} = 0.1$ wt% (▲) in P123 and the native solution of P123 (●) at concentrations of (a) $C_{P123} = 10$ wt%, (b) $C_{P123} = 15$ wt%, at 30 °C.

Discussion

The rheological behavior of a solution reflects its microstructure as it originates from the inter-particle interactions in the system. In this study we investigated the rheological behavior of aqueous SWNT–CTAB dispersions at CTAB concentrations well above the cmc. The steady shear viscosity as a function of the applied shear rate was monitored in concentrations of the surfactant that correspond to different mesophases. We found that the presence of relatively small concentrations of SWNTs had a dramatic effect on the behavior of the combined system not observed with the other additives examined.

When rigid objects are dispersed in a homogeneous solution the rheological behavior of the resulting dispersion depends strongly on the geometry of the suspended particles. In the case of spherical particles at these extremely low concentrations (volume fraction $\phi \sim 5 \times 10^{-4}$) the viscosity is expected to increase by an insignificant amount (the relative viscosity $\eta_r = \eta_{dispersion}/\eta_{solution} \cong 1 + 2.5\phi$) and the rheological behavior is not expected to be altered. In the case of large aspect ratio rigid cylindrical objects, a 5–10% increase in the viscosity is predicted.[25,26] Indeed, as shown in Fig. 4 and 5, MWNTs or CB dispersed in CTAB solutions and SWNTs in Pluronic solutions follow the expected behavior. Yet, SWNTs dispersed in CTAB solutions (C_{CTAB} <23 wt%) show an order-of-magnitude increase in viscosity and complete modification of the rheological character of the dispersion (Fig. 3). Table 2 and Fig. 6 summarize the observations: A significant increase in the low shear-rate viscosity of the dispersions, and shear-thinning replacing Newtonian behavior are observed for CTAB concentrations below the onset of the hexagonal phase. Clearly as CTAB concentration increases the rheological behavior of SWNT–CTAB system and the native CTAB solution become more alike, the differences in the low shear viscosity diminish and the value of $\dot{\gamma}_{merge}$ decreases. The effect of SWNTs is hardly noticeable in the regime of the CTAB hexagonal phase.

Table 2 Summary of the observations

Sample	$(\eta_r)_{max}$	$\dot{\gamma}_{merge}$ [s^{-1}]	Power law exponent	
			First region	Second region
CTAB12%	25	>10^3	1	—
CTAB12% + SWNTs			0.4	—
CTAB18%	4	800	1	0.8
CTAB18% + SWNTs			0.7	0.6
CTAB23%	2	12	0.8	0.4
CTAB23% + SWNTs			0.8	0.4
CTAB26%	1.8	2	0.2	—
CTAB26% + SWNTs			0.2	—

The observations summarized above raise several questions:

1. What is the source of the unexpected large increase in the viscosity and the onset of non-Newtonian shear-thinning behavior in the presence of SWNTs?

2. Why is this behavior unique to SWNTs (and not MWNTs or CB – see ESI Fig. 1†) dispersions in CTAB solutions (and not in Pluronic® solutions)?

3. Why does the difference between the dispersion and the native solution diminish with increasing CTAB concentration?

We suggest that the issues raised above are related to SWNT-induced structural ordering of CTAB assemblies. As clearly observed in Fig. 2 the presence of SWNTs induces formation of elongated CTAB micelles at concentrations well below the native transition. It has been suggested before that SWNTs are dispersed in aqueous media by anionic surfactants *via* the formation of a dense monolayer[27,28] of surfactant molecules at the nanotube surface. While the hydrocarbon tails adsorb to the graphitic surface, the hydrated polar heads extend into the solution. The resulting hybrid SWNT–surfactant structures may be described as cylindrical micelles, formed around a SWNT embedded in the center with a typical diameter of about ~5 nanometers, similar to that of CTAB elongated micelles.[6,7] Furthermore, the entire CTAB solution undergoes a transition from mostly spherical to mostly elongated micelles. The observed viscosity increase can now be explained by the presence of these elongated structures. As observed, the presence of CB and MWNTs does not induce a similar morphological transition (ESI Fig. 1) and consequentially the viscosity of the dispersion is hardly altered. It is the dimensional matching between the diameter of an individual SWNT and CTAB elongated micelles that induces this transition.

This size matching also allows for the seamless incorporation of the SWNTs into the hexagonal phase of CTAB. As was previously observed,[7] the SWNTs are incorporated without modifying the symmetry, *d*-spacing and domain size of the native CTAB phase. Indeed, as shown above, the rheological behavior

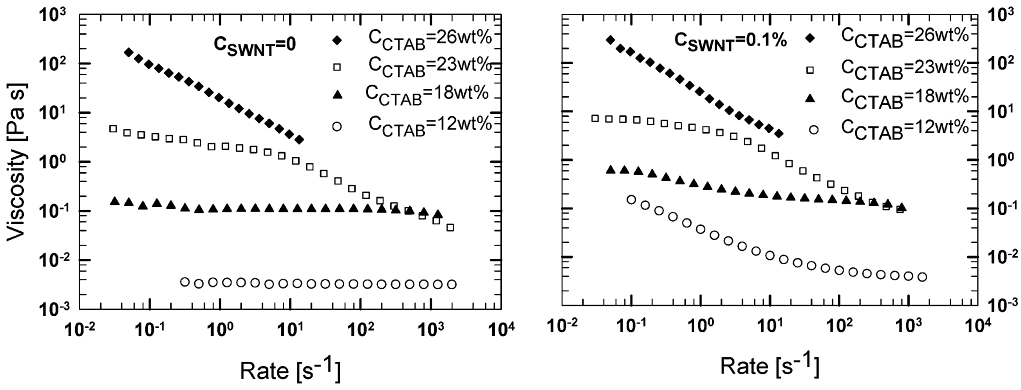

Fig. 6 Summary of rheological observations. Comparison between shear viscosity of native CTAB solutions (left) and the same with 0.1% SWNTs (right).

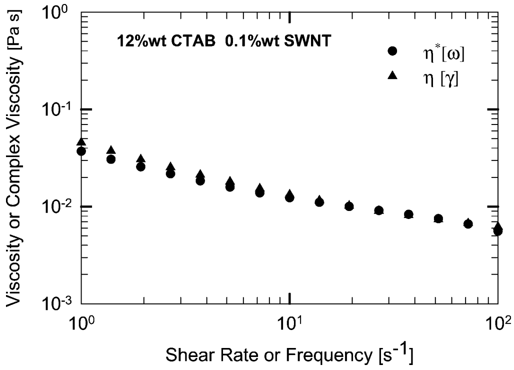

Fig. 7 A plot presenting the Cox–Merz rule for 0.1 wt% dispersion of SWNTs in 12 wt% CTAB solution ($\eta(\dot{\gamma})$ is the shear viscosity and $|\eta^*(\omega)|$ is the magnitude of the complex viscosity).

of CTAB solutions at concentrations above the I–N transition are hardly altered by the presence of SWNTs.

In this scenario shear-thinning results from ordering of the elongated structures by the shearing flow. Thus, in Fig. 3(a) the elongated structures formed due to the presence of dispersed SWNTs in the CTAB solutions are shear-thinning while the mostly spherical micelles of the native solution are clearly Newtonian. At higher concentrations elongated structures are found in both the dispersion and the solution, and as result they similarly exhibit shear-thinning behavior. The identical power law exponents (*cf.* Table 2) indicate that the rheological behavior results from orientational ordering of the CTAB micelles rather than from that of the additives.

Shear-thinning may also result from structure breakup. The cryo-TEM images Fig. 2 (and ESI Fig. 1(c)), obtained after being exposed to the shearing action of blotting,[8,9] tend to support the orientation rather than breakup mechanism. Independently, the coincidence between the steady shear viscosity and dynamic complex viscosity obtained by small-amplitude oscillatory measurements in agreement with the Cox–Merz rule[29] provides further support to the ordering mechanism (Fig. 7).

According to the Cox–Merz rule, the shear viscosity $\eta(\dot{\gamma})$ and the magnitude of the complex viscosity $|\eta^*(\omega)|$ are equal at identical shear rate and the frequency of oscillation values[30,31] as long as the sample is identically structured under the imposed deformation. In complex fluids prone to breakup by steady high shear (*e.g.* surfactant mesophases, physical gels) the system integrity may still be maintained in oscillatory shear due to the small shear amplitude exercised. Hence, departure from the Cox–Merz rule would indicate shear induced break-up, while the graph presented in Fig. 7 presents excellent agreement with the Cox–Merz rule.

5. Conclusions

We have demonstrated that the presence of SWNTs has a dramatic effect on the rheological behavior of CTAB solutions not observed with other additives: A significant increase in the low shear-rate viscosity of SWNT dispersions, and shear-thinning replacing Newtonian behavior were observed for CTAB concentrations below the onset of the surfactant hexagonal phase. We suggest that good dimensional matching between nano-structures and self-assembling molecules are the origin of the observed synergetic behavior leading to modification of the surfactant morphology in the combined system. This behavior is unique to the nanometric regime and differs from the behavior of colloidal particles where significant size-mismatch between the colloidal moieties and the surfactant micelles results in decoupling between the components.

6. Acknowledgements

RYR thanks the Israel Science Foundation (Grant No. 512/06). RYR and MG thank the BSF – United States–Israel Binational Science Foundation. We thank Prof. H. Diamant for enlightening discussions.

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