

Thermodynamically Stable, Size Selective Solubilization of Carbon Nanotubes in Aqueous Media by Self-Assembly with Amphiphilic Block Copolymers

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ABSTRACT

Two molecular modes of amphiphilic block copolymer-carbon nanotube interactions have been suggested in the literature, involving the adsorption of either individual block copolymer molecules or of multimolecular, spherical block copolymer micelles on the carbon nanotube. In both cases, the nature of stability imparted to the dispersion of nanotubes is kinetic, controlled by the steric barrier imposed by the adsorbed individual molecules or micelles. In this study we propose an alternate mode of molecular interaction, wherein the block copolymer molecules self-assemble around the nanotube to generate a thermodynamically stable aqueous nanocolloidal solution. The possibility of such micellar solubilization of nanotubes is examined by constructing a phenomenological theory of nanotube solubilization. Illustrative calculations performed for polyethylene oxide- polypropylene oxide – polyethylene oxide (PEO-PPO-PEO) triblock copolymers show that they are capable of solubilizing carbon nanotubes in aqueous solutions. While the block copolymer molecules that spontaneously form cylindrical micelles are most likely to solubilize the nanotubes, other copolymers whose natural curvature is spherical or lamellar also are capable of forming cylindrical micelles around the nanotubes. Most interestingly, the solubilization is found to be size (diameter) specific suggesting that this can be developed into a practical method to fractionate carbon nanotubes by size or chirality. These general conclusions can be applied to other diblock and triblock amphiphilic copolymers and also to both single wall and multiwall carbon nanotubes.

INTRODUCTION

Extensive research in the last decade has focused on dispersing carbon nanotubes [1-8] in the aqueous medium with the aid of surfactants and/or polymers. Essentially, electrostatic or steric stabilization of dispersions is achieved by physical adsorption of surfactants or polymers onto the nanotube surface. One can visualize the interaction of the amphiphilic copolymers with the nanotubes in terms of the three structural models shown on figure 1.

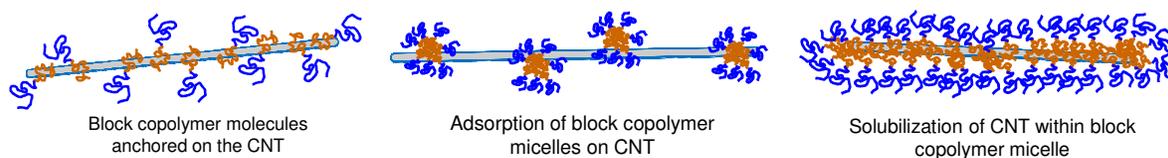


Figure 1. Molecular visualization of different modes of block copolymer-nanotube interactions.

In the first model, the hydrophobic block of the individual block copolymer adsorbs strongly on the nanotube surface, serving as the anchor, while the hydrophilic block extends and swells in the aqueous domain, imparting steric stabilization to the nanotube dispersion. In the second model, spherical micelles of block copolymers adsorb on the nanotube surface and steric stabilization of the dispersion is provided by the interactions involving these micellar aggregates. In contrast, we propose the third structural model where the block copolymer molecules self-assemble around the carbon nanotubes to generate micelles solubilizing the nanotubes. In this case, the nature of stability imparted to the system is thermodynamic. Indeed, the system should be viewed not as a dispersion, but as a thermodynamically stable nanocolloidal solution.

In this paper, we develop a simple phenomenological theory for the molecular assembly of carbon nanotube-block copolymer system in aqueous solution, to examine whether our proposed structural model is thermodynamically favored to occur or not. We consider the solubilization of single nanotube as well as cluster of nanotubes, the cluster being treated simply as a nanotube of larger diameter. The approach and the computational results are applicable to both single wall and multi-wall carbon nanotubes.

THEORY

We consider a system consisting of water, amphiphilic block copolymer and carbon nanotubes. The amphiphilic block copolymer can exist as singly dispersed molecules and also as aggregates in the aqueous solution. These aggregates may be cylindrical micelles solubilizing a single carbon nanotube or a cluster of carbon nanotubes; or alternatively, the aggregates may be free of nanotubes and have spherical, cylindrical or lamellar shape. The aqueous solution coexists with a phase of carbon nanotubes, represented by bundles of nanotubes, which are merely suspended in the aqueous medium. The question we seek to answer is whether the carbon nanotubes will prefer to remain in their own phase because of the strong cohesive nanotube-nanotube interactions or will they be solubilized by the block copolymer micelles to generate a thermodynamically stable, truly nanocolloidal solution. We answer this question by combining a general thermodynamic treatment of self-assembly [9] with a phenomenological free energy model for the solubilization of nanotubes within block copolymer aggregates.

Thermodynamics of aggregation

The equilibrium condition of equality of chemical potentials of block copolymer molecules in all states of existence (singly dispersed molecules, aggregates free of nanotubes, and aggregates with solubilized nanotubes), leads to the following expression for the aggregate size distribution [9]:

$$X_g = X_1^g \exp\left(-\frac{\{\mu_g^0 - g \mu_1^0\}}{kT}\right) = X_1^g \exp\left(-\frac{g \Delta\mu_g^0}{kT}\right) \quad (1)$$

where $\Delta\mu_g^0$ is the difference in the standard state chemical potentials between a block copolymer

molecule present in an aggregate of size g (namely, there are g block copolymer molecules in the aggregate) and a singly dispersed block copolymer in water. Hereafter, this is referred to as the standard state free energy change. X_g is the mole fraction of the aggregate of size g in the solution, X_1 is the mole fraction of the singly dispersed block copolymer, k is the Boltzmann constant and T is the absolute temperature. The standard states for all the aggregates and the singly dispersed copolymer molecule are taken to be infinitely dilute solution conditions. The solvent water and the phase of nanotubes are represented by pure component reference states.

We compare the standard state free energy change on the formation of cylindrical block copolymer aggregates solubilizing carbon nanotubes against the standard state free energy change on the formation of nanotube-free aggregates of different shapes (sphere, cylinder or lamella) and based on minimum free energy criterion, determine whether the block copolymer would form a nanotube-free aggregate or a cylindrical micelle solubilizing a single nanotube or a cluster of nanotubes.

Geometrical variables defining aggregate shapes

The standard state free energy change depends on the size and shape of the aggregate and hence the geometrical variables characterizing the different aggregates should be first defined. We consider AB diblock and symmetric BAB triblock copolymers, where block A is hydrophobic and block B is hydrophilic. The hydrophobic domain of the aggregate consists only of block A and we use the variable R to denote the dimension of this domain. Thus, R is the core radius for sphere or cylinder and the half bilayer thickness for lamella, in the case of nanotube-free aggregates; and R is the thickness of the cylindrical shell of block A surrounding the nanotube, in the case of aggregates with solubilized nanotube. The hydrophilic domain consists of block B and solvent water and we use the variable D to denote the dimension of this domain. Thus, D is the thickness of the shell containing B blocks and solvent water in nanotube-free aggregates as well as nanotubes solubilized aggregates. The variable a denotes the area per block copolymer molecule at the interface between the hydrophobic A and hydrophilic B domains while the variable a_T denotes the area per block copolymer molecule at the interface between the hydrophobic A domain and the nanotube. For convenience, we choose R and D as the two independent variables to perform free energy optimization.

Contributions to the standard state free energy change on aggregation

The expression for the standard state free energy change on aggregation is formulated by identifying all physicochemical changes accompanying micelle formation around a single nanotube or a cluster of nanotubes. A number of contributions to the standard state free energy change arise due to changes in the dilution and deformation states of A and B blocks, the formation of domain A – domain B interface, the localization of the copolymer, the loop formation in the case of the triblock copolymer and the transfer of the nanotube (CNT) from a pure nanotube phase to the interior of the micelle. Thus,

$$\begin{aligned} \Delta\mu_g^0 = & (\Delta\mu_g^0)_{A,dil} + (\Delta\mu_g^0)_{A,def} + (\Delta\mu_g^0)_{int} + (\Delta\mu_g^0)_{B,dil} + (\Delta\mu_g^0)_{B,def} \\ & + (\Delta\mu_g^0)_{loc} + (\Delta\mu_g^0)_{loop} + (\Delta\mu_g^0)_{CNT} \end{aligned} \quad (2)$$

Expressions for each of these contributions, in the absence of nanotubes, have been developed in detail in our previous treatments [10-12] of aggregation in amphiphilic block copolymer solutions. All of these free energy contributions are only indirectly influenced by the solubilization of the nanotube through modified geometrical relations for the aggregates and therefore, are not discussed here. Only the last term accounting for the transfer of nanotube from the nanotube bundle to the micelle is discussed below. Explicit expressions for all of the free energy contributions represented in eq.(2) can be found in ref.[13].

Transfer of nanotube from bulk nanotube phase to the micelle in water

The last free energy contribution in eq.(2) representing the transfer of the nanotube from the bulk nanotube phase (nanotube bundle suspended in the solvent medium) to the micelle interior is critical to controlling the solubilization behavior of the nanotubes in block copolymer micelles. When the nanotubes are transferred from the bulk nanotube phase to the interior of the micelle, the cohesive nanotube-nanotube and A block-A block interactions are replaced by adhesive nanotube-A block interactions. This interchange free energy is represented by the classical Flory interaction parameter χ_{AT} (subscript T denoting the nanotube or nanotube cluster), which can be used to calculate the free energy change corresponding to this transfer process.

Alternately, the transfer process can be viewed as one involving changes in the interfacial states for the nanotubes. In the initial state, the interface of the nanotube or the nanotube cluster is characterized by the interfacial tension $\sigma_{TT} = 0$, since each tube is interacting with other identical tubes, that is, the interface is that between identical surfaces. In the aggregate, the nanotubes (or the nanotubes cluster) has an interface in contact with the hydrophobic block A, characterized by the interfacial tension σ_{AT} . Correspondingly, the free energy change for this transfer process can be written as,

$$\frac{(\Delta\mu_g^0)_{CNT}}{kT} = \frac{(\sigma_{AT} - \sigma_{TT})}{kT} a_T = \frac{\sigma_{AT}}{kT} a_T \quad (3)$$

The interfacial tension σ_{AT} is directly related to the Flory interaction parameter χ_{AT} [13]. Therefore, the calculation of this free energy contribution based on interfacial energy changes as in eq.(3) is exactly equivalent to the calculation based on cohesive/adhesive energy changes.

The interaction parameter χ_{AT} and the interfacial tension σ_{AT} are not dependent on the molecular size of the A block, within the framework of the classical Flory theory. Therefore, once the chemistries of A and B blocks are specified, the nanotube solubilizing ability of diblock or triblock copolymer of any composition and molecular weight (as in figure 2) and size polydispersity (intrinsic to most polymers) can be compared at a given value of χ_{AT} or σ_{AT} .

Model parameters and computational approach

For illustrative purposes, we select PEO-PPO-PEO ($E_X P_Y E_X$) symmetric triblock copolymers which are commercially available in a range of molecular weights and compositions and widely used as polymeric surfactants. The estimation of various molecular constants describing this block copolymer has been described in detail in ref.[12]. The only new parameter needed for the present theory is the interfacial tension σ_{AT} between the carbon nanotube and the

hydrophobic A domain. The condition of $\sigma_{AT} < 0$ mN/m can occur if specific attractive interactions are present between the nanotube surface and the A domain. In the most general case, the polymer-nanotube interactions are non-specific and we expect $\sigma_{AT} > 0$ mN/m. The magnitude of the Flory parameter χ_{AT} can be expected to be of the order of 0 to 1, depending on the compatibility between the hydrophobic A block and the nanotubes. This would roughly translate to interfacial tension σ_{AT} of 0 to 10 mN/m [13]. Clearly, variations in the values for χ_{AT} or σ_{AT} are achieved by selecting different hydrophobic blocks for the copolymer. In this work, although the A block is fixed as polypropylene oxide (and therefore there should be only one σ_{AT} corresponding to this hydrophobe), the numerical calculations have been performed taking different values for σ_{AT} in order to study the influence of this parameter. This is virtually equivalent to comparing block copolymers with different hydrophobic blocks.

The free energy minimizations are carried out using the FORTRAN IMSL (International Mathematical and Statistical Library) Subroutine ZXMW. The minimization is done with respect to the two independent variables R and D. In nanotube-free solutions, the aggregate shape that yields the lowest standard state free energy change on aggregation is taken to be the equilibrium shape. If the standard state free energy change on the formation of the cylindrical aggregate solubilizing the nanotube is lower than that for the formation of the nanotube-free aggregate (sphere, cylinder or lamella), then the solubilization of the nanotubes is considered favorable.

DISCUSSION

Predicted aggregation behavior in nanotube-free block copolymer solutions

The predicted equilibrium aggregate morphologies in the absence of nanotubes are summarized in figure 2 for 21 commercially available PEO-PPO-PEO triblock copolymers of various block compositions and molecular weights. The entries in this figure are arranged such that the weight fraction of PEO in the block copolymer increases from left to right and the molecular weight of the block copolymer increases from top to bottom.

L62-E ₆ P ₃₅ E ₆ Lamella	L63-E ₉ P ₃₂ E ₉ Lamella	L64-E ₁₃ P ₃₀ E ₁₃ Sphere	P65-E ₁₉ P ₂₉ E ₁₉ Sphere		F68-E ₇₇ P ₂₉ E ₇₇ Sphere
L72-E ₆ P ₃₈ E ₆ Lamella			P75-E ₂₄ P ₃₅ E ₂₄ Sphere	F77-E ₅₂ P ₃₅ E ₅₂ Sphere	
		P84-E ₁₉ P ₄₃ E ₁₉ Sphere	P85-E ₂₆ P ₄₀ E ₂₆ Sphere	F87-E ₆₁ P ₄₀ E ₆₁ Sphere	F88-E ₁₀₄ P ₃₉ E ₁₀₄ Sphere
L92-E ₉ P ₅₀ E ₉ Lamella					F98-E ₁₁₈ P ₄₅ E ₁₁₈ Sphere
	P103-E ₁₇ P ₆₀ E ₁₇ Cylinder	P104-E ₂₇ P ₆₁ E ₂₇ Sphere	P105-E ₃₇ P ₅₆ E ₃₇ Sphere		F108-E ₁₃₃ P ₅₀ E ₁₃₃ Sphere
L122-E ₁₁ P ₆₉ E ₁₁ Lamella	P123-E ₂₀ P ₇₀ E ₂₀ Cylinder			F127-E ₁₀₀ P ₆₄ E ₁₀₀ Sphere	

Figure 2. Representation of equilibrium aggregate shapes of PEO-PPO-PEO triblock copolymers in nanotube-free aqueous solutions. For each block copolymer, the entries include the trade name, block composition (the number of ethylene oxide units, E, and propylene oxide units, P), and the equilibrium aggregate shape in dilute aqueous solution.

The theory predicts that lamellar aggregates are favored when the PEO to PPO ratio is small whereas spherical micelles are favored when the PEO to PPO ratio is large. For intermediate PEO to PPO ratios, cylindrical aggregates are favored. These predictions agree with available experimental data on aggregate shapes for the Pluronic block copolymers [12]. Further, the predicted aggregation pattern follows the well-known molecular packing concept obeyed by classical surfactants [14]. According to the molecular packing concept, when the head group repulsions are weak, the equilibrium aggregate-water interfacial area per molecule is small and lamellar aggregates are favored. For strong head group repulsions, the equilibrium area per molecule is large and spherical aggregates are formed. Cylindrical aggregates result for intermediate values of head group repulsions. In the case of block copolymers, the free energy contributions associated with the hydrophilic B domain are analogous to the head group repulsions in classical surfactant micelles. Therefore the pattern of aggregation observed for increasing head group repulsions in surfactants is reproduced in the case of block copolymers with increasing size of the hydrophilic block. One can also combine block copolymers of differing natural curvature (sphere, cylinder or lamella formers in figure 2) to tune the shape of the equilibrium aggregate in mixtures, as is commonly done with the classical surfactant molecules [9].

Predicted size-selective solubilization of nanotubes

For each of the 21 triblock copolymers shown on figure 2, the standard state free energy change on the formation of a cylindrical aggregate solubilizing the nanotube has been computed and compared against the standard state free energy change on the formation of a nanotube-free aggregate. The difference between these two computed free energy changes on aggregation is plotted in figure 3 as a function of the diameter of the nanotube or nanotube cluster, for the model parameters $\sigma_{AT} = 0$ mN/m and 5 mN/m. If the difference between the two standard state free energy changes is negative, then it would imply the preferential formation of cylindrical aggregate solubilizing nanotubes compared to the formation of a nanotube-free aggregate. Note that the standard state free energy change on aggregation is expressed per molecule of the block copolymer in an aggregate. Since the aggregation numbers are typically large, the free energy difference between different aggregates, expressed per aggregate rather than per molecule, is very large implying that the aggregate with lower energy is substantially more stable than all other aggregates.

For $\sigma_{AT} = 0$ mN/m, of the 21 triblock copolymer molecules listed on figure 2, nine molecules (seven of which are shown on figure 3 - left) are found capable of solubilizing the carbon nanotubes or nanotube clusters. Of these, P103 and P123 are block copolymers whose natural curvature is a cylinder (as can be seen from figure 2), while L62, L72, L92, L122, and L63 have lamella as the natural curvature and L64 and P84 have sphere as the natural curvature. All these molecules occur contiguously in figure 2. We can conclude that the molecules with cylinder as the natural curvature are the obvious choices to solubilize the nanotube or nanotube cluster while the molecules whose properties are close to the cylinder formers (as can be seen from their location on figure 2) are also capable of solubilizing the nanotubes or clusters, in spite of their natural curvature being spherical or lamellar.

For $\sigma_{AT} = 5$ mN/m, predicted results show that of the 21 triblock copolymer molecules, only four molecules are capable of solubilizing the nanotubes or nanotube clusters (figure 3 – right). These include the lamella former L63, the cylinder formers P103 and P123 and the sphere former

L64. For $\sigma_{AT} = 10$ mN/m, only the lamella former L63 and the two cylinder formers P103 and P123 are found to solubilize the nanotubes. For $\sigma_{AT} > 14$ mN/m, none of the PEO-PPO-PEO triblocks solubilize any nanotubes. In all cases, as σ_{AT} increases from 0, the block copolymers showing a natural preference for cylinders and other block copolymers whose properties are closest to the cylinder formers are the molecules most likely to solubilize the nanotubes.

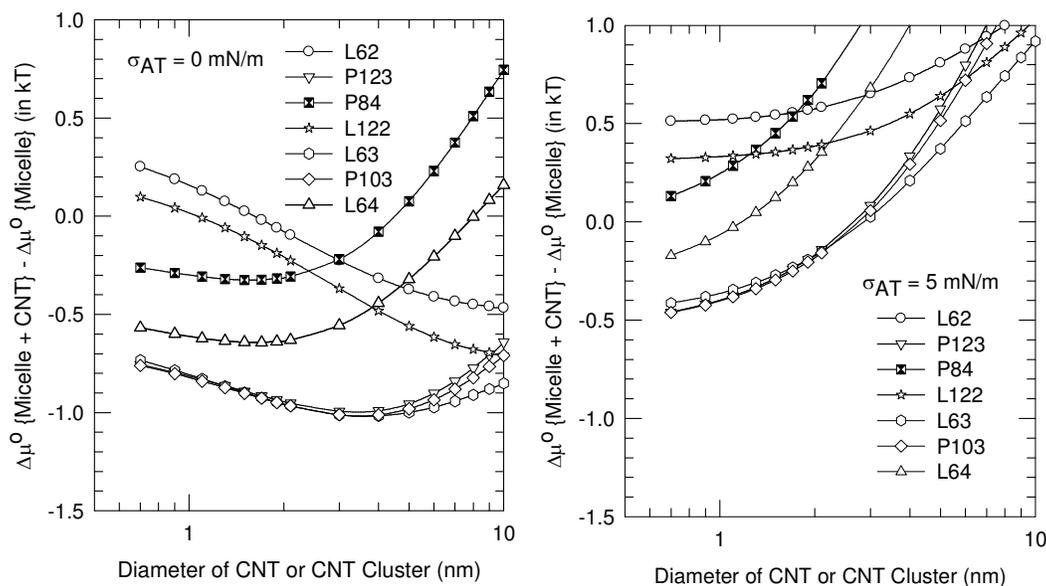


Figure 3. The difference between the standard state free energy change on forming a cylindrical aggregate with solubilized nanotube and the standard state free energy change on forming a nanotube-free aggregate as a function of the diameter of the nanotube or nanotube cluster for the parameter $\sigma_{AT} = 0$ mN/m and 5 mN/m. Negative values correspond to preference for nanotube solubilized aggregates over nanotube-free aggregates.

For all block copolymers, the plotted difference in the free energy changes on aggregation shows a dependence on the size of the nanotube solubilized. This implies that the solubilization process is highly size selective (noting that the free energies are expressed per molecule in figure 3 and the free energy differences expressed per aggregate will be very much larger in magnitude). The results imply that when the block copolymer solution is contacted with the nanotubes, first, the nanotubes for which the free energy change on solubilization is the lowest will be preferentially solubilized. Once all of these nanotubes are solubilized and if free block copolymer micelles are still available, then nanotubes with a higher free energy change on solubilization will be taken up by the micelles. There is a cutoff value for the diameter of the nanotube or nanotube cluster that can be solubilized by a given block copolymer. In this manner a size dependent micellar extraction process for the uptake of nanotubes can be developed.

CONCLUSIONS

We have developed a simple molecular scale theory to describe the solubilization of carbon nanotubes or nanotube clusters by amphiphilic block copolymers in aqueous solutions. The

theory is applicable to both single wall and multi-wall nanotubes since the physics of the tubes is represented by a single interfacial tension parameter, σ_{AT} . We predict that it is possible to solubilize nanotubes or nanotube clusters to generate a thermodynamically stable aqueous nanocolloidal solution, in contrast to the aqueous dispersions of limited kinetic stability generated by simple adsorption of surfactants and/or polymers on the nanotube. The calculated results show that the block copolymer molecules with cylinder as the natural curvature are the obvious choices to solubilize the nanotube or nanotube cluster while the molecules whose properties are close to the cylinder formers are also capable of solubilizing the nanotubes, in spite of their natural curvature being spherical or lamellar. The interfacial tension parameter σ_{AT} (characterizing the difference between the adhesive energy between the nanotube and the A block and the cohesive energy among the nanotubes) can be potentially manipulated by the choice of the hydrophobic block of the block copolymer, thus allowing a variety of diblock and triblock copolymers to solubilize nanotubes and creating a thermodynamically stable nanocolloidal solution. Most interestingly, we predict that the micellar solubilization process is size selective and can be exploited for a potential nanotube size fractionation process.

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