



CHAPTER I

INTRODUCTION

The unique structure and superior properties of single-walled carbon nanotubes (SWNTs) (Dai, 2002) make them promising materials for a number of applications, including probes, bio-sensors, catalyst supports, hydrogen storage, gas separation, composites and multifunctional materials, and so on (Bhushan, 2006). Unfortunately, because SWNTs tend to agglomerate into bundles when dispersed in either water or organic solvents due to strong van der Waals interactions (Girifalco *et al.*, 2000), the realization of their potential has been limited.

One possibility for preventing the SWNT agglomeration is to disperse SWNTs using superacids as solvent (Davis *et al.*, 2009; Parra-Vasquez *et al.*, 2010; Ramesh *et al.*, 2004). Parra-Vasquez *et al.* (2010) demonstrated that the protonation of SWNTs in chlorosulfonic acid enables their dispersion at high concentration (5000 ppm by mass) without damaging the SWNTs. A relatively concentration of individual SWNTs, as high as 3.5 mg/mL, can be dispersed in cyclohexyl pyrrolidone (Bergin *et al.*, 2009). Modification of the SWNT surface, covalently and noncovalently, has been an alternative strategy to stabilize SWNT dispersions. Covalent modification usually causes the SWNTs to lose their exceptional electronic properties because of the severe disruption of the π system (Zhao *et al.*, 2004). Dispersing SWNTs by noncovalent functionalization is particularly attractive, as it preserves the intrinsic properties of SWNTs (Grossiord *et al.*, 2007). In this latter approach, dispersing agents such as surfactants, polymers, or biomolecules adsorb onto the nanotubes via noncovalent interactions.

Surfactants are extensively used to disperse SWNTs in water. Although they are expected to adsorb on the SWNT surface with their hydrophobic tails, while the hydrophilic heads orient towards the solution (Wang, 2009), an ongoing debate attempts to clarify the structure of self-assembled surfactant aggregates on nanotubes. A large number of amphiphilic molecules, including sodium dodecyl sulfate (SDS) (Blanch *et al.*, 2010; Clark *et al.*, 2011; Haggemueller *et al.*, 2008; McDonald *et al.*, 2006; Tan and Resasco, 2005; Yurekli *et al.*, 2004), sodium dodecylbenzene sulfonate (SDBS) (Blanch *et al.*, 2010; Clark *et al.*, 2011;

Haggenmueller *et al.*, 2008; Islam *et al.*, 2003; Matarredona *et al.*, 2003; Okazaki *et al.*, 2005; Tan and Resasco, 2005; Utsumi *et al.*, 2007), hexadecyl-trimethyl ammonium bromide (CTAB), octyl phenol ethoxylate (Triton X-100) (Clark *et al.*, 2011; Tan and Resasco, 2005), sodium cholate (SC), and sodium deoxycholate (DOC) (Blanch *et al.*, 2010; Haggenmueller *et al.*, 2008), have been shown to stabilize SWNT dispersions, with varying effectiveness. Haggenmueller *et al.* (2008) used optical absorption and fluorescence spectroscopy to evaluate the amount of individual SWNTs suspended by various surfactants and reported that bile salt DOC provides better suspension quality compared to other surfactants.

Among various surfactants, SDBS is commonly used for stabilizing SWNT dispersions in aqueous solution without showing strong diameter dependence (Okazaki *et al.*, 2005). It was reported that SDBS can disperse up to 20 mg/mL of individual SWNTs (Islam *et al.*, 2003). The benzene ring in the SDBS molecule is believed to provide superior dispersive ability due to π - π interactions with the SWNTs, despite being located near the hydrophilic end of the molecule (Clark *et al.*, 2011; Islam *et al.*, 2003; Tan and Resasco, 2005). Matarredona *et al.* (2003) analyzing their experimental data suggested that hydrophobic interactions dictate for the most part the agglomeration of SDBS on SWNTs.

Several experimental studies available for SDBS-aided SWNT dispersion in water are supported by very few, molecular simulation studies. Molecular dynamics (MD) simulations have been performed in order to understand the dispersion characteristics with detailed atomic-level information regarding surfactant-SWNT interactions and surfactant packing, and hence provide a valuable complement to experiments. Tummala and Striolo (2009) used extensive all-atom MD simulations and observed that the morphology of SDS surfactant aggregates strongly depends on the nanotube diameter as well as on the surface coverage. Along with Xu *et al.* (2010), they attempted to clarify how the aggregate SDS structures on SWNTs determine effective SWNT-SWNT interactions. Aqueous dispersions of SWNTs stabilized using the bile salt surfactant SC were investigated via MD simulations by Lin and Blankschtein (2010). The results showed that the cholate ions wrap around the tubes with a small tendency to orient perpendicularly to the tube axis. Tummala *et al.* (2010) used MD simulations to describe the self-assembly of flavin

mononucleotide (FMN) adsorbed on SWNTs. They found that the aggregation morphology of aqueous FMN on SWNTs depends on nanotube diameter.

Despite their technological importance, alkylbenzene sulfonates have rarely been considered in MD simulations. Jang *et al.* (2004) simulated sodium hexadecane benzenesulfonate at the water-decane interface. As well as He *et al.* (2010), they simulated monolayers of a series of linear and branched alkylbenzene sulfonates at the water-air interface and observed that the length of alkyl chain and the position of attachment of the benzene ring on the alkyl chain affect the aggregate morphology and the surface tension of alkylbenzene sulfonates at water/air interface. These results are important because they point at the effect of surfactant morphology on practical quantities, specifically the surface tension.

In this study, the adsorption and the self-assembly of SDBS on (6,6), (12,12) and (20,20) SWNTs are investigated via all-atom MD simulations. The effects of SDBS surface coverage and molecular architecture on the aggregate morphology are discussed. Because of computational limitations, all simulations are limited to relatively dilute systems.