



Interactive Forces between SDS-Suspended Single-Wall Carbon Nanotubes and Agarose Gels

Justin G. Clar[†], Carlos A. Silvera-Batista[‡], Sejin Youn[†], Jean-Claude J. Bonzongo[†], Kirk J. Ziegler[‡]
 Departments of Environmental Engineering Sciences[†] and Chemical Engineering[‡]

University of Florida, Gainesville, Florida 32611, USA



1: Motivation & Objectives

➤ Inclusion of SWCNTs in a variety of applications and novel electronic devices has been challenging due to the presence of both Metallic (*m*-) and Semiconducting (*s*-) SWCNTs in as produced batches.

➤ A method commonly used to produce large scale separations of the two fractions is column-based using an agarose gel stationary phase.^{1,2} (Figure 1)

➤ Prior studies have correctly attributed the mechanism of separation as the selective retention of *s*-SWCNTs to the agarose gels, however, few details of the forces driving this selective adsorption are understood.^{3,4}

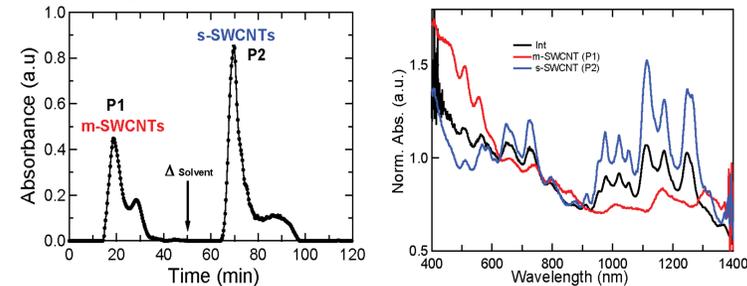


Figure 1: (left) Elution curves of SWCNTs suspended in 1 wt% SDS, using Dextran as medium. Absorbance data points are at $\lambda = 626$ nm. (right) VIS-NIR absorbance spectra from the initial sample and the effluent at the first (P1) and second (P2) peaks.

OBJECTIVES & GOALS

- Achieve a mechanistic understanding of the selective retention of SDS-SWCNTs in agarose gel
- Specifically, to understand the dominant force(s) that drive the selective retention of *s*-SWCNTs during separation.
- This understanding will allow for process optimization that maximizes separation quality, and throughput.

2: Methodology

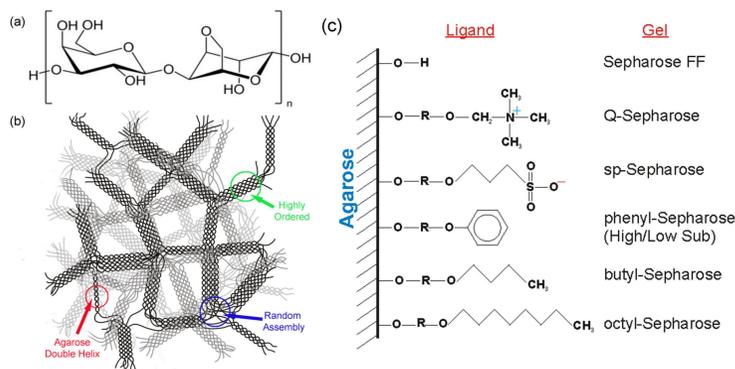


Figure 2: Physical and chemical structure of agarose. (a) Monomeric unit of agarose chains. (b) Polymers organize into double helices and are further stabilized by bundling to form aggregates various structure and size. (c) Ligands added to agarose backbone after functionalization. The R group represents $\text{CH}_2\text{CH}(\text{OH})\text{CH}_2$ chains added during a glycidyl ether coupling reaction. All gels were purchased from GE.

➤ SDS-SWCNTs and agarose gels are complex system with many potential interactive forces between them.

➤ Relative importance of each force can be evaluated by either inhibiting or promoting its significance during adsorption through gel functionalization and solution chemistry modification.

➤ Forces investigated in both equilibrium (batch) and non-equilibrium (column) studies include: **van der Waals (vdW), Ionic (ion exchange), hydrophobic, π - π , and Ion-Dipole**

3: Selected Results

3.1 Hydrophobic Interactions

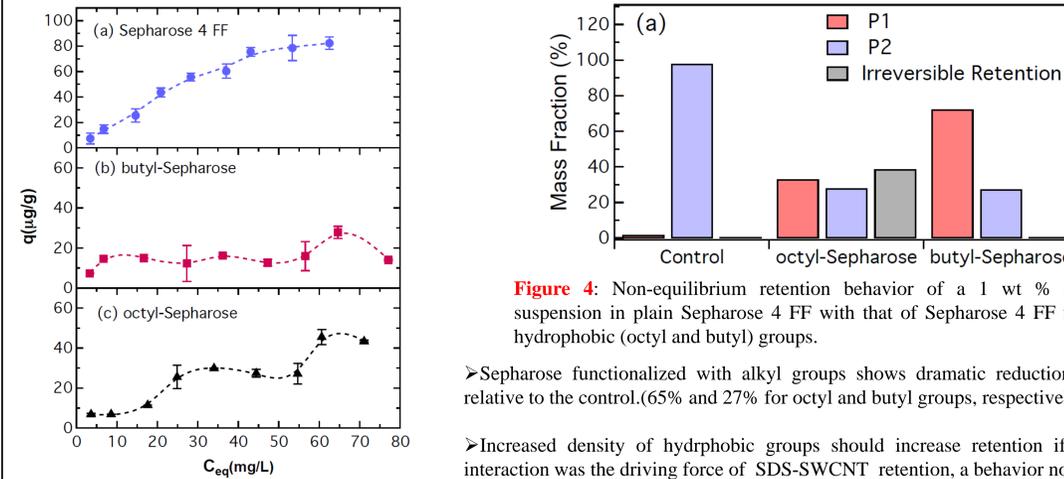


Figure 3: Equilibrium adsorption isotherms for SWCNTs in 1 wt% SDS. Media are (a) plain Sepharose 4 FF (●), (b) butyl-Sepharose (■) and (c) octyl-Sepharose (▲).

Figure 4: Non-equilibrium retention behavior of a 1 wt % SDS-SWCNT suspension in plain Sepharose 4 FF with that of Sepharose 4 FF functionalized hydrophobic (octyl and butyl) groups.

➤ Sepharose functionalized with alkyl groups shows dramatic reduction in retention relative to the control. (65% and 27% for octyl and butyl groups, respectively.)

➤ Increased density of hydrophobic groups should increase retention if hydrophobic interaction was the driving force of SDS-SWCNT retention, a behavior not seen here.

➤ Figure 3 demonstrates that the Langmuir model is not an adequate for these systems, although widely assumed in the literature.^{5,6}

➤ Reduced retention in both batch and columns studies suggest that purely hydrophobic interactions are not the dominant retention mechanism during separation

3.2 π - π Interactions

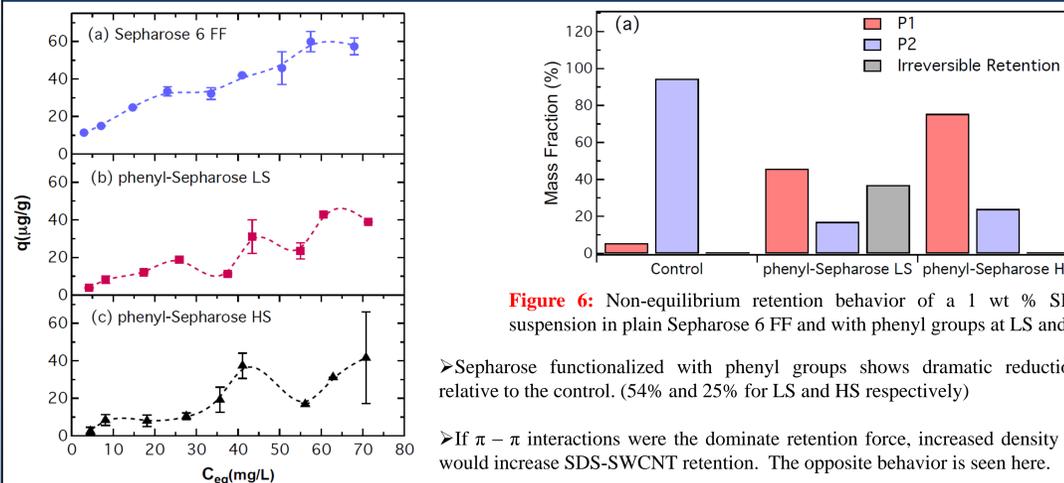


Figure 5: Equilibrium adsorption isotherms for SWCNTs in 1 wt% SDS. The media are (a) plain Sepharose 6 FF (●), (b) phenyl-Sepharose LS (■) and (c) phenyl-Sepharose HS (▲).

Figure 6: Non-equilibrium retention behavior of a 1 wt % SDS-SWCNT suspension in plain Sepharose 6 FF and with phenyl groups at LS and HS

➤ Sepharose functionalized with phenyl groups shows dramatic reduction in retention relative to the control. (54% and 25% for LS and HS respectively)

➤ If π - π interactions were the dominant retention force, increased density of these groups would increase SDS-SWCNT retention. The opposite behavior is seen here.

➤ Again, Langmuir behavior is not seen in phenyl substituted systems. (Figure 5)

➤ Reduced retention in both batch and column studies suggest that π - π interactions are not the dominant retention mechanism during separation.

3.3 Ligand Density & Adsorption Sites

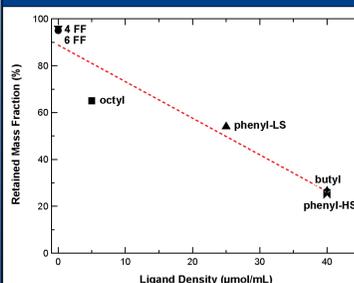


Figure 7: Relationship between ligand density and SWCNT retention (P2) in non-equilibrium experiments

➤ Inverse relationship between retention and ligand density. (Figure 7)

➤ Adsorption sites must be a key piece of agarose backbone found in different locations/confirmations on the surface given by isotherm shape.

➤ Mechanism must account for:
 a) Importance of charged groups (SDS)

b) OH group alteration decreases retention

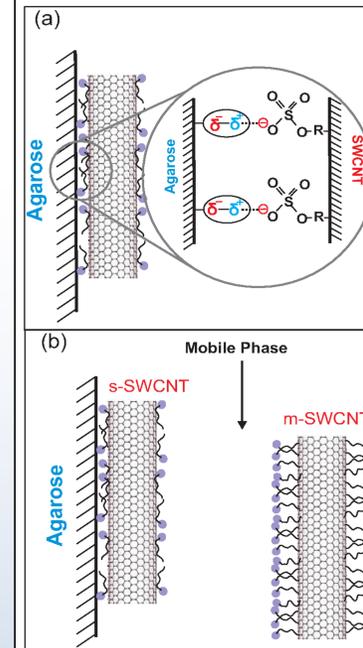
➤ Ion-dipole interactions account these observations:

a) Permanent dipoles of different magnitude measured for agarose

b) SDS-SWCNTs are macro-ions

4: Discussion

4.1 Mechanism & Selectivity



➤ During functionalization, hydroxyl groups are moved/masked from the pristine surface. (See Figure 2) We propose that OH groups are the active adsorption sites.

➤ Dipoles on hydroxyl groups create the potential for an attractive interaction between the dipoles ($\text{H}^{\delta+}$) and the negative charges on the SDS-SWCNTs, *i.e.* ion-dipole interactions

➤ Selectivity driven by inherent differences between *m*- and *s*-SWCNTs.

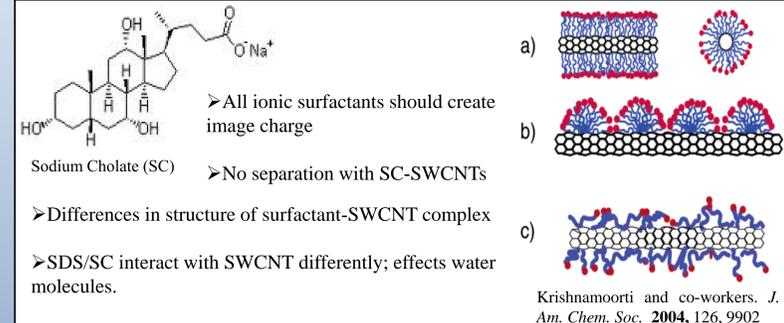
➤ Polarizability of *m*-SWCNTs at least $3x >$ *s*-SWCNTs, creating increased magnitude image charge on *m*-SWCNTs

➤ Larger charge has dual effects

a) Direct repulsion from agarose surface by $\text{H}^{\delta+}$

b) Increase in local charge screening increases ability of SDS to pack on *m*-SWCNT surface increasing surfactant aggregation and limiting interactions with agarose surface.

4.2 Role of SDS



➤ All ionic surfactants should create image charge

➤ No separation with SC-SWCNTs

➤ Differences in structure of surfactant-SWCNT complex

➤ SDS/SC interact with SWCNT differently; effects water molecules.

➤ Enthalpic and entropic effects important for separation

Krishnamoorti and co-workers. *J. Am. Chem. Soc.* 2004, 126, 9902

5: Conclusions

➤ The proposed mechanism of selective retention for SDS-SWCNTs on agarose gels is **Ion-dipole** between ions of SDS head groups and known dipoles of agarose

➤ Selectivity is driven by the increased polarizability of the *m*-SWCNTs species.

➤ Confirmation of hydroxyl groups on the agarose surface are an integral factor during the adsorption process.

➤ Traditional Langmuir isotherms may not be adequate to describe the sorption process during SDS-SWCNT separations on agarose gels in all systems.

6: Acknowledgements



❖ National Science Foundation (CBET-0853347) for support of this research
 ❖ Prof. Yiider Tseng for access to the ultracentrifuge,
 ❖ The Richard Smalley Institute at Rice University for supplying SWCNTs
 ❖ GE for providing Sepharose 6 and 4 FF used in this study.

7: Selected References

- Hirano, A.; et al. *J. Phys. Chem. C* 2011, 115, 21723–21729.
- Tanaka, T.; et al. *Appl. Phys. Express* 2009, 2, 125002–1.
- Liu, H.; et al. *J. Phys. Chem. C* 2010, 114, 9270–9276
- Silvera-Batista, C. A.; et al. *J. Phys. Chem. C* 2011, 115, 9361–9369.
- Hirano, A.; et al. *J. Phys. Chem. C* 2012, 116, 9816–9823
- Hirano, A.; et al. *ACS Nano* 2012, 6, 10195–10205
- Kozinsky, B.; et al. *Phys. Rev. Lett.* 2006, 96, 166801
- Lu, W.; et al. *Nano Lett.* 2009, 9, 1668–1672.