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

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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 (r) 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. (Figure 1)
- Prior studies have correctly attributed the mechanism of separation as the selective retention of m-SWCNTs in the agarose gels; however, few details of the forces driving this selective adsorption are understood. ¹,²

- 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 m-SWCNTs during separation.
- This understanding will allow for process optimization that maximizes separation quality and throughput.

2: Methodology

- Polymeric organo-functionalization of SWCNTs using several methods. The m-SWCNTs are dispersed in an aqueous SDS solution and loaded onto agarose gels. SDS 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 included: van der Waals (vdW), ionic (ion exchange), hydrophobic, π-π, and London-Dipole.

3: Selected Results

3.1 Hydrophobic Interactions

- Figure 3: Equilibrium adsorption isotherms for SWCNTs in 1 wt% SDS. The media are (a) plain Sepharose 4 FF (r), (b) butyl-Sepharose (m) and (c) octyl-Sepharose (m).
- Figure 4: Non-equilibrium retention behavior of a 3 wt % SDS-SWCNT suspension in plain Sepharose 4 FF with that of Sepharose 4 FF functionalized with hydrophilic (octyl) and butyl groups.

3.2 π-π Interactions

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

- If π-π interactions were the dominate retention force, increased density of these groups would increase SDS-SWCNT retention. The opposite behavior is seen here.
- Agam, 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 dominate retention mechanism during separation.

3.3 Ligand Density & Adsorption Sites

- Increase 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:
  - Importance of charged groups (SDS)
  - OH group alteration decreases retention

- Non-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 removed/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 dipole (DH) and the negative charges on the SDS-SWCNTs, (π-π dipole interactions)
- Selectivity driven by inherent differences between m- and r-SWCNTs.
- Polarizability of m-SWCNTs at least 3x > r-SWCNTs, creating increased magnitude image charge on m-SWCNTs.

- Larger charge has dual effects
  a) Direct repulsion from agarose surface by 10^6
  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/Cyt excitant with SWCNT differently effects water molecules.
- Enthalpic and entropic effects important for separation

5: Conclusions

- The proposed mechanism of selective retention for SDS-SWCNTs on agarose gels is based on interactions between 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 is 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 gel in all systems.

6: Acknowledgements

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7: Selected References


- Figure 1: (left) Elution curves of SWCNTs suspended in 1 wt % SDS, using Dextran as medium. Absorbance data points at λ = 620 nm (right) VSWIR absorbance spectra from the initial sample and the eluant at the first (P1) and second (P2) peaks.

- 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 CH, CH3OH, CH3, chains added during a glycosyl ether coupling reaction. All gels were purchased from GE.

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

- Figure 4: Non-equilibrium retention behavior of a 3 wt % SDS-SWCNT suspension in plain Sepharose 4 FF with that of Sepharose 4 FF functionalized with hydrophilic (octyl) and butyl groups.

- Figure 5: Equilibrium adsorption isotherms for SWCNTs in 1 wt% SDS. The media are [a] plain Sepharose 6 FF (r), [b] phenyl-Sepharose LS (m) and, (c) HSA (m).

- 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.

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

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