KINETIC AND PHOTON INDUCED EFFECTS IN SINGLE WALLED CARBON NANOTUBE SOLUTIONS

IISER PUNE

A thesis submitted towards partial fulfilment of

BS-MS Dual Degree Programme

by

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under the guidance of

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INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

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Certificate

This is to certify that this dissertation entitled "**Kinetic and Photon Induced Effects in Single Walled Carbon Nanotube Solutions**" towards the partial fulfilment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by **Paritosh Kumar** at **Indian Institute of Science Education and Research, Pune** under the supervision of **Dr. Harsh Chaturvedi** during the academic year 2012-2013.

Student   Supervisor

PARITOSH KUMAR   HARSH CHATURVEDI

Declaration

I hereby declare that the matter embodied in the thesis entitled "**Kinetic and Photon Induced Effects in Single Walled Carbon Nanotube Solutions**" are the results of the investigations carried out by me at the Department of Physics, IISER Pune under the supervision of **Dr. Harsh Chaturvedi** and the same has not been submitted elsewhere for any other degree.

Student   Supervisor

PARITOSH KUMAR   HARSH CHATURVEDI

To The Almighty . . . . .

Acknowledgements

Abstract

Single walled carbon nanotubes (SWNTs) have potential application in fabrication of nanodevices and sensors. SWNTs are mostly studied as dispersed colloidal solution in non-aqueous solvents like DMF, due to ease in chemical modification and transferability required in the fabrication of such devices. These kinetically stable dispersions help us to understand intermolecular interactions, their solubility and rate of aggregation. These rates depend upon electrical double layer and surface charges of SWNTs. The present work is to determine the stability of SWNTs dispersions in the presence of various coagulants. The stability is discussed keeping in mind the Schulze-Hardy rule and DLVO theory, which has been traditionally used to understand colloidal solutions. While stability of SWNT dispersion is typically desired, aggregation of SWNTs with coagulants and interaction of SWNTs among themselves are affected by size, shape and ionic strength of coagulants; which leads to changes in electrodynamic repulsive and van der Walls attractive forces acting between SWNTs. The study ascertains the relation between Critical Coagulation Concentration (CCC) of SWNT solutions with various inorganic coagulants (like NaBr, $CuCl_2$, $FeCl_3$) and that of traditionally considered spherical ions in colloidal solutions. CCC is the concentration above which onset of rapid aggregation occurs. Along with experimental results of Schulze-Hardy law for nanotubes, novel photon enhanced aggregation in these solutions is also observed. We observed dependence of aggregation rate on optical excitation and band gap energy of individual nanotubes. Photon enhanced aggregation of SWNTs is observed and characterized using spectroscopic techniques. This, dependence of stability of dispersion [CCC] on optical excitation and dielectric property of SWNTs (metallic and semiconducting) is experimentally demonstrated.

[*Keywords*: SWNT, aggregation kinetics, Critical Coagulation Concentration, photon enhanced aggregation]

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List of Symbols and Abbreviations

|	
CNTs	Carbon Nanotubes
SWNTs	Single-Walled Carbon Nanotubes
DLVO theory	Derjaguin-Landau-Verwey-Overbeek theory
M SWNTs	Metallic Single-Walled Carbon Nanotubes
SC SWNTs	Semi-conducting Single-Walled Carbon Nanotubes
P SWNTs	Mixed / Pure Single-Walled Carbon Nanotubes
vdW force	van der Waals force
EDL Repulsion	Electrical Double Layer Repulsion
CCC	Critical Coagulation Concentration
SH Rule	Schulze-Hardy Rule
z	valency of the colloidal counterions
OPV molecule	Oligo-Phenylenevinylene molecule
Ruthenium complex	$[Ru(phenanthroline)_3]^{2+}[PF_6^-]_2$
DMF	N,N-Dimethylformamide
rpm	revolutions per minute
vHs	van Hove singularities
UV-Vis-NIR spectra	Ultraviolet-Visible-Near Infrared spectra
QTH lamp	Quartz-Tungsten-Halogen lamp

CHAPTER 1

Introduction

Single Walled Carbon Nanotubes (SWNTs) are one of the allotropes of carbon that have one dimensional structure and high aspect ratio. SWNTs consist of rolled-up sheets of graphene and have cage-like architecture similar to the hexagonal buckyballs. These functionalized cylindrical carbon molecules with exceptional physicochemical, optical, electrical and mechanical properties[1,2,3,4] have numerous potential applications, as field-effect transistors[5], light-emitting diodes[6] and molecular sensors and devices[7]. Experimentally grown pristine SWNTs (referred as *mixed* or ***Pure*** or ***P SWNTs*** in the remaining document) consists of nanotubes exhibiting metallic and semiconducting electron transporting properties. They are, thus, referred to as *metallic (**M**)* and *semi-conducting (**SC**) SWNTs* respectively.

Our research interest is focused on understanding dispersion and stability of single-walled carbon nanotubes (SWNTs)[8] in solvents and studying their aggregation with each other. Dispersing SWNTs in solutions and understanding their stability and aggregation kinetics is highly desirable to perform efficient chemical modifications so as to functionalize SWNTs to fabricate nanodevices[9-10]. The theory given by Derjaguin & Landau (1941) and Verwey & Overbeek (1948) is commonly known as DLVO theory.[11-12] This theory considers the interaction of colloidal spherical particles. Hence due to inherent approximations and assumptions in theory, it fails to account for behaviour of nanotubes. Thus, modifications in DLVO theory is needed to describe intermolecular interactions in one dimensional nanotubes with different dielectric properties. The present research work has the ability to serve as a model for studying SWNT aggregation kinetics using modified DLVO theory.

Also, novel optical enhanced aggregation of metallic, semiconducting and mixed SWNTs is observed. This results because of induction of forces similar to van der Walls attractive forces between the nanotubes. The aggregation rate is shown to be dependent on the band gap energy and dielectric properties of individual nanotubes. The difference in the aggregation rate of different types of SWNTs has a promising potential to be a novel process to separate out metallic and semi-conducting SWNTs from as produced mixed SWNTs. Also, photon enhanced aggregation of SWNTs,

functionalized with electron donating polymers and optically active molecules molecules are observed because of excitation of surface plasmons. This provides us a strong experimental evidence to believe that efficiency of photo-conversion processes, across the solar spectrum in SWNT based devices would also increases substantially. A clear understanding of these kinetic and optically induced properties of SWNT solutions can give fillip to a novel class of nanomaterials and devices in Opto-electronic, pharmaceutical, and solar energy industries.

1.1 Motivation
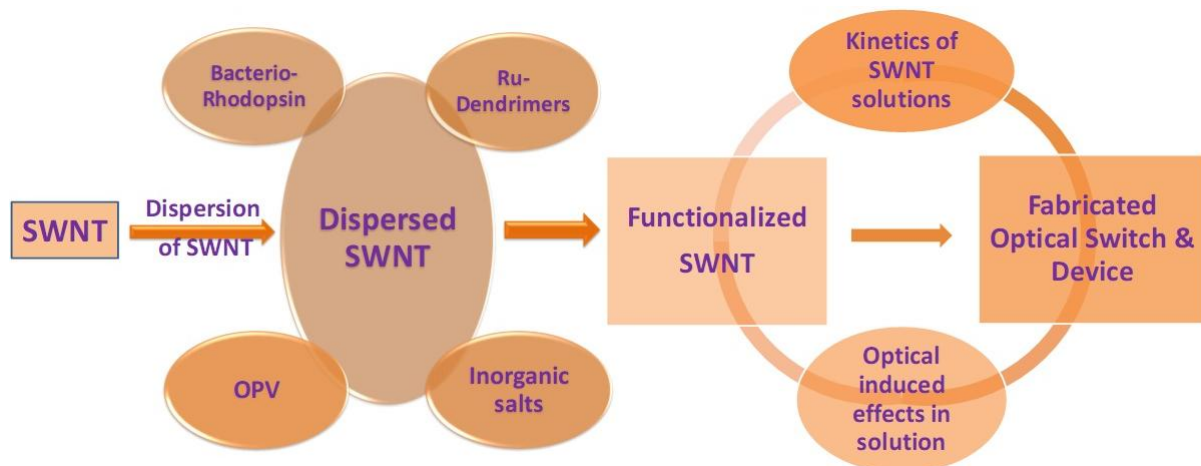
Hamaker[13] gave a general theory of the stability of lyophobic colloids, giving the potential energy of two particles with respect to each other as a function of their mutual distance (1938). He considered the potential curve as a superposition of an attractive potential due to London-van der Waals forces between the particles and a repulsive potential due to the interaction of the double layers surrounding the particles. He gave expressions for the London-van der Waals potential for various cases (two spherical particles, two parallel plates, etc.).

Hamaker gave only a rough estimate of the double-layer interaction potential but assumed it to be repulsive for all distances between the particles. Hamaker's conclusions have been challenged by Langmuir, who argued that a system of charged colloidal particles and oppositely charged counter ions will show an attraction between the particles for certain distances.

The study of the aggregation of colloidal systems was further improvised by Derjaguin-Landau-Verwey-Overbeek (DLVO) theory of lyophobic colloids which states that colloidal dispersions remain stable due to interplay between van der Waals (vdW) attraction and electric double-layer (EDL) repulsion. This EDL repulsion can be reduced by adding ionic coagulants. The minimum concentration of ionic coagulants necessary to cause rapid coagulation of colloids, known as the Critical Coagulation Concentration (*CCC*); which is estimated by following Schulze-Hardy[14-15] rule: $\textbf{\textit{CCC α z}}^{\textbf{\textit{-6}}}$, where z is the valency of the colloidal counter-ions. Analysis of rapid coagulation of CNTs in aqueous media as a function of valence of electrolytic

ions have shown good agreement with SH rules.[16] Although the limitations in approximating the physical and chemical constraints of a SWNT dispersion is appreciated, DLVO theory and Schulze-Hardy rule provide motivation to understand the interactions between SWNTs and give a insight into their aggregation kinetics.

An interesting phenomenon regarding coagulation of colloids in general and CNTs in particular, is its photon enhanced aggregation. Colloidal dispersions are found to aggregate rapidly upon optical excitation in case of metal clusters[17], small metallic particles[18] like gold nanocolloids[19] and other metal colloidal systems[20,21]. Studies have also shown that interaction of SWNTs with electron donating dyes[22] and polymers[23] enhance the photo-conversion processes in solar energy based devices[24]. With an aim to attach large molecular systems to SWNTs, it was shown that specific and strong binding of ruthenium metallodendrimer to the ends of mixed SWNTs rendered the nanotubes to coagulate at a much faster rate than usually observed[25]. Such specific binding of electron donating molecules to metallic and semi-conducting SWNTs has not been studied until now. A detailed study of phenomenon of photon enhanced aggregation of SWNTs, varying in their dielectric properties and band gap energies, would help us to fabricate devices specific to our research objectives. This provides motivation to further study photon enhanced aggregation of pure as produced metallic, semi-conducting and mixed SWNT as well as SWNTs functionalized with other electron donating molecules and ionic coagulants. The limited theoretical and experimental knowledge still leaves much to be explored in the research field. It is both fundamentally challenging and practically useful to understand this novel phenomenon of photon enhanced aggregation and use it for fabrication of molecular devices and sensors.

In the present research work, the focus is on answering the following four questions:

Ques. 1	How dielectric property of nanotubes influence their aggregation rate?
Ques. 2	How cationic charge of the coagulant influence SWNT aggregation rate?
Ques. 3	How optical excitation enhances aggregation rates in unbound pristine SWNTs?
Ques. 4	How optical excitation enhances aggregation rates in SWNTs functionalized with coagulants?

CHAPTER 2

THEORY

2.1   Kinetic studies of SWNTs

To date, DLVO theory is the only one that can give approximate solution for colloid aggregation. Although criticisms have been raised concerning its completeness and rigorousness, DLVO is the most accepted theory in colloidal and nanosciences and is widely adopted to interpret the interactions taking place between particles in micro and nano levels.

DLVO theory predicts the interactions of plates and spheres in colloidal solutions theoretically.
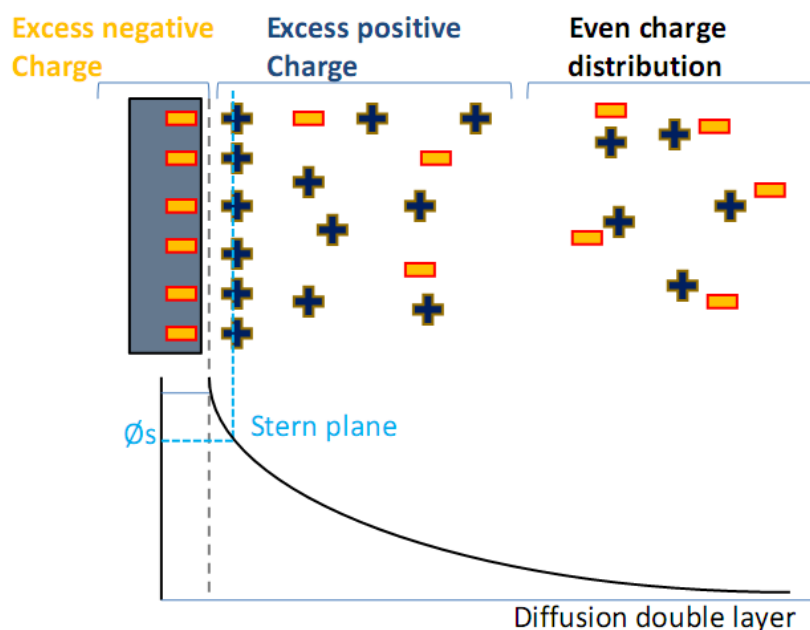
Fig 2.1: Behaviour of ions in solution and formation of electrical double layer (EDL). The diffusion layer is also known as Gouy-Chapman layer.

It considers electrostatic interactions between two charged particles. The two types of interactions considered in the theoretical model are electrical-double-layer (EDL) of repulsion and van der Waals (vdW) forces of attraction. Particles approaching each other in dispersed solution are repelled by overlapping of diffused ionic

atmosphere that surround each of them. This results in increase of the free energy which gives rise to repulsive potential and depends upon Stern potential and thickness of the EDL. This potential is combined with the London-van der Waals attractive potential calculated by Hamaker to obtain curves of potential vs. Distance [Fig 2.2 (a) and (b)].
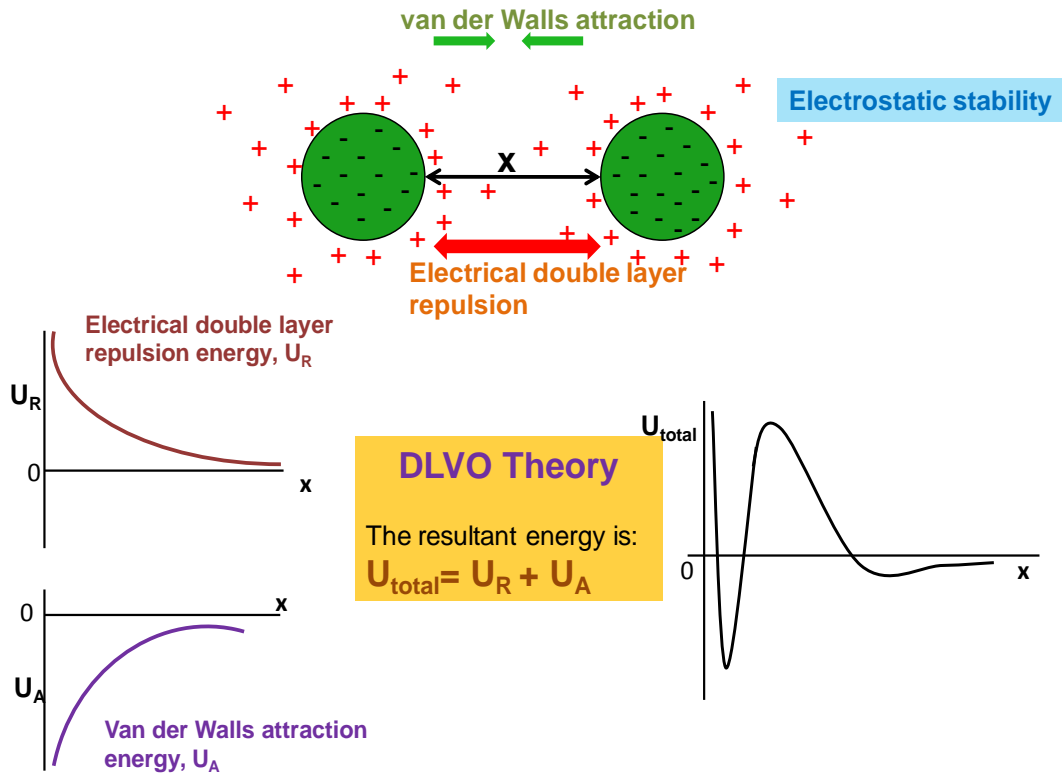
Fig 2.2 (a): DLVO theory describes the stability of colloids with two contributions to the total energy, repulsion between the electrical double layers, U_R and attraction between the colloidal particles, U_A
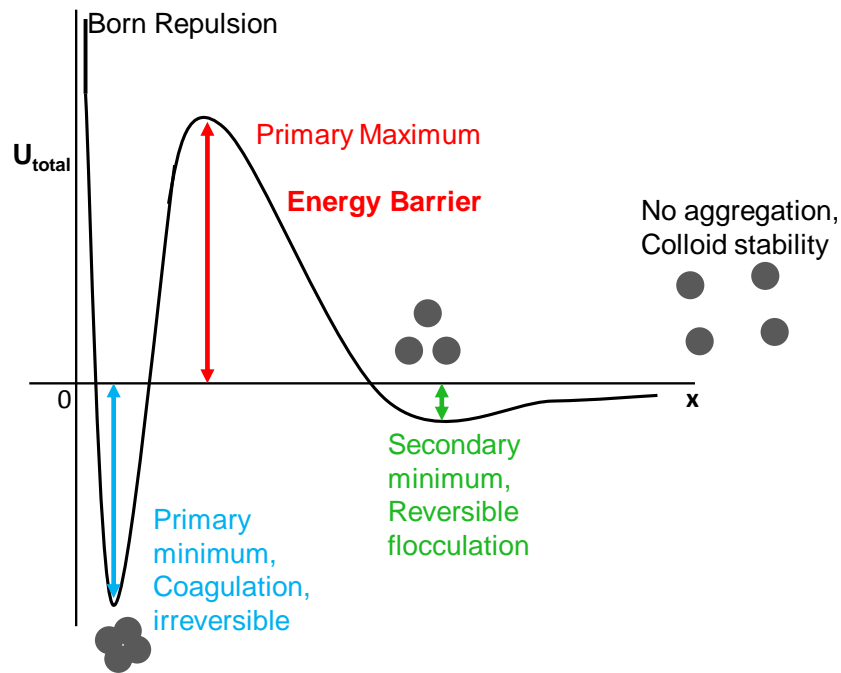
Fig 2.2 (b): Typical energy diagram for colloidal particles in a solution.
(a)The primary minimum indicates that the aggregated state is of the lowest energy condition and this is where we would expect the particles to reside. (b)The primary maximum acts as an activation barrier that must be exceeded for aggregation to occur. As two particles come closer, they must collide with sufficient energy to overcome the barrier provided by primary maximum. (c)The secondary minimum could be seen as a flocculated state but the particles still have to cross the energy barrier to come into close contact at the minimum energy state.

Predictions based on these curves agree for SWNT dispersion and aggregation as well, keeping in mind some assumptions and approximation regarding the geometry and surface properties of cylindrical shaped SWNTs. Lennard-Jones[26] model is used to describe the interactions taking place between two SWNTs by summing up attractive vdW and repulsive EDL forces acting between the SWNTs. The total potential energy of SWNTs interacting with ionic coagulants is

$$\varepsilon(x) = \frac{64 N_0 k_B T}{\kappa} \gamma^2 e^{-2\kappa x} - \frac{H_{121} L}{12\sqrt{2}\, x^{3/2}}$$ **[equ. 2.1]**

where,

γ is the resultant of various approximations done in Poisson-Boltzmann equation (describing electrostatic interactions between molecules in ionic solutions) and

depends on the zeta potential of the SWNT particles and valence charge z of the ions in dispersion;

$1 / \kappa$ is the Debye length, which depends on the number density of ions in the solution, N_0 and the dielectric strength of the solvent; and

H is the Hamaker constant for the system, describing the attractive interaction between the particles.

In solution, SWNTs surface form a layer of counter ions. SWNTs-solvent interactions give rise to a repulsive potential and an electrical double layer forms. The repulsive potential depends upon the thickness of the EDL and the Stern potential. The SWNTs dispersed in solution remain stable due to this electrical double layer repulsion (Fig 2.3).
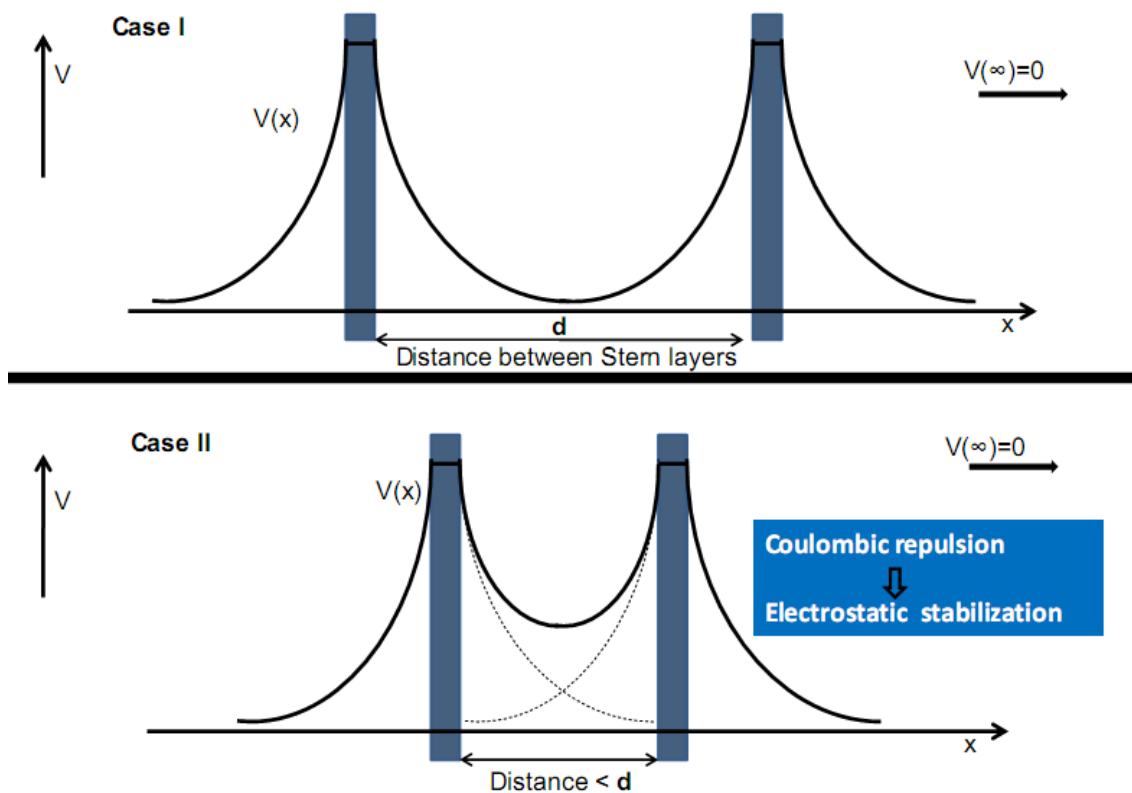
Fig 2.3: Model showing electrical double layer interaction between two SWNT molecules. As the distance between the SWNTs decrease, electrostatic stabilization occurs due to decrease in their repulsion potential. In case II, the dotted lines and solid lines represent potential due to each plate and total potential respectively.

Addition of ionic coagulant causes the repulsive energy barrier to decrease. This leads to enhanced attraction between SWNTs. On increasing the coagulant concentration, the repulsive energy barrier decreases accordingly and ceases to exist at a particular concentration and the effective attractive energy comes into play as explained by DLVO theory and rapid coagulation of SWNTs occurs. The minimum concentration of ionic coagulant needed to cause rapid coagulation of SWNTs, known as Critical Coagulation Concentration (*CCC*), follows the empirical Schulze Hardy Law which states that *CCC* varies with (*1/z*)[6], where *z* is the cationic charge on the coagulant (Fig 2.4)[27].

The condition for rapid aggregation is:

<div align="center">Concentration of added coagulant = CCC</div>

This happens when

$$\varepsilon(x) = 0 \; ; \qquad \left. \frac{\mathrm{d}\,\varepsilon\,(x)}{\mathrm{d}x} \right|_{x=1/\kappa} = 0 \qquad \textbf{[equ. 2.2]}$$

in the DLVO theory [equ. 2.1].
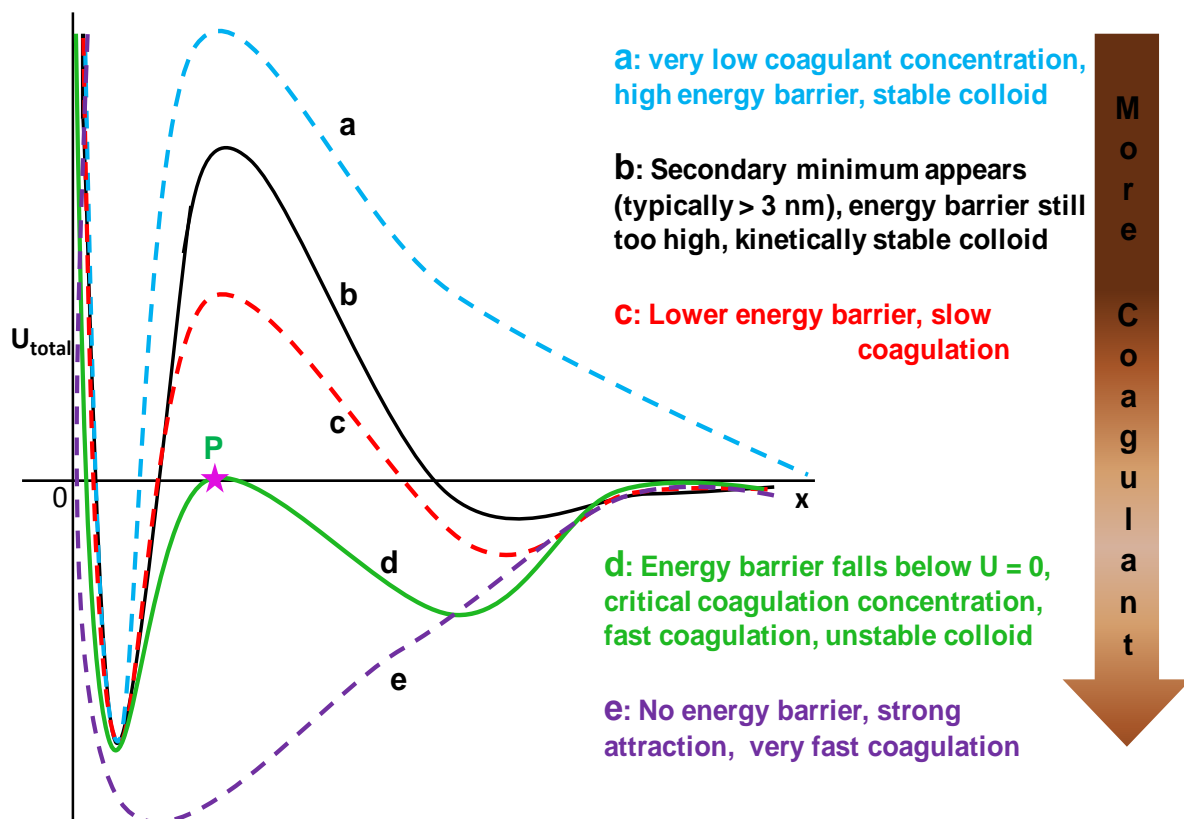
Fig 2.4: DLVO Theory and Variation of Energy with increase in coagulant concentration is shown in the figure. In the above figure, the concentration increases from curve *a* to *e.*

a: Highly charged surfaces in dilute solution with very low coagulant concentration. The Repulsion term dominates and the overall interaction energy becomes positive. The energy barrier is very high and hence the colloid remains stable.

b: The secondary minimum starts appearing but the Energy barrier is still very high, so the colloid is kinetically stable i.e. there may be a little flocculation but true coagulation is difficult.

c: The Energy barrier is lowered further and the coagulation may increase. If the barrier is sufficiently low then the particles may even be able to cross it due to their Thermal energy.

d: Energy barrier has become zero at point *P*, and fast coagulation is possible. The concentration at this point is called 'Critical Coagulation Concentration' (*CCC*) at which coagulation can occur spontaneously. Hence, the colloid becomes unstable. At this point, electrical double layer repulsion potential equals the van der Walls attraction potential.

e: As the concentration of ions has become very large, there is a large attractive van der Waals force, due to which there is no barrier and very fast coagulation takes place).

However, DLVO theory assumes that particles are spherical in shape and interactions between them takes place at the condition that the surfaces are at constant potential[28-29]. It takes into account that the ions and counter ions of ionic coagulant are similar in size with equal charges on them which is rarely true for real colloidal solutions. Schulze-Hardy law also assumes the same and needs to be modified to account for both cations and anions. Also, the particles are considered to be point charges and the effect of particle curvature is neglected for such systems make the evaluation of interaction energy simple. In addition, DLVO theory does not take into account the pH dependent stability of SWNT dispersions and does not account for ionisable surface groups. Surface charges in solution also play an important role in particle interaction and can lead them to form supramolecular assemblies. In typical colloidal dispersions the distance of separation between particles and particles sizes are often larger than the range of these interactions. Another point to be kept in mind is that DLVO theory and Schulze Hardy predict the CCC of counter ions from a static point of view because it focuses on studying the equilibrium properties of colloids. But since coagulation is a rate phenomenon, calculation of CCC should be from a kinetic point of view.

As a result, the classical DLVO theory is found to be far from what is observed for real colloidal systems in general, and SWNT dispersion in particular.

So, to modify the theory for SWNT aggregation, we assume that CCC of counter-ions dependence on pH and type of anion has no effect on SWNT aggregation. Also, the role of Stern layer adsorption needs to be fully understood before including it in our study and is not generally applicable to every system.

SWNTs produced by arc-discharge, chemical vapour deposition and other methods have co-existence of metallic and semiconducting SWNT. The electronic transport properties of metallic or semiconducting SWNTs depend upon their diameter and chirality denoted by the structural indices (n, m)[30]. Each (n, m) nanotube can be considered to be a distinct molecule with a unique structure, because the indices n and m specify the unique manner in which the single layer of graphite is rolled up seamlessly to form the carbon nanotube[31]. About one-third of SWNTs exhibit metallic properties (if n-m =3a, where a is an integer) while the remaining two-thirds act as semiconductor (n-m=3a ±1)[32]. Realization of desired electronic type SWNT based

nanodevices require controlled aggregation studies of each type of nanotube. A small change (less than 1%) in nanotube diameter can result in a dramatic change from a nanotube that is metallic (and could serve as interconnect in an electronic circuit) to one that is semiconducting (and could become the active component of a field-effect transistor).

Keeping in mind these approximations and different electronic properties of metallic and semiconducting SWNTs, we study SWNT aggregation in solutions.

2.2   Photon Enhanced studies of SWNTs

Photon enhanced aggregation of colloidal dispersions has potential to be an exciting and important research area addressing concern across diverse disciplines such as Biotechnology, pharmaceutical nanomaterials optoelectronic devices and emerging technologies. Aggregation rate of slowly aggregating metal colloids have been found to accelerate when irradiated by light. This light induced aggregation is specifically found to accelerate when the colloidal dispersions are irradiated at the Plasmon frequency of the metal clusters and colloids. Photons of particular frequency tend to change the charge on their EDLs[21]. This leads to changing of Columbic forces acting among metallic colloids[19] and clusters[20], thus inducing attractive forces among colloids. This explanation assumes that diffusion region of the EDL experiences light-induced compression and the DLVO forces are altered in presence of light. Irradiation of photons causes the negative charge on the particles to decrease which leads to smaller surface potential. This reduction in repulsive potential barrier between colloids in stable dispersions causes enhanced rapid aggregation.

Another possible reason is the generation of photon enhanced aggregation forces similar to van der Walls forces upon optical excitation of metallic clusters[17] and particles[18]. Photo stimulated aggregation phenomenon of metal sols[21] also follows the same explanation. Excitation of the surface plasmons by irradiation of light induces electromagnetic interactions. Thus, attraction between particles increases and therefore, leads to enhanced aggregation rate.

These explanations can as well be accounted for photon induced aggregation of SWNTs.[33] Reduction in EDL repulsive potential caused by optical excitation causes the SWNTs to aggregate at faster rate. Already electron donating dyes[22] and polymers[23] have been shown to enhance the photo-conversion processes in solar energy based devices[24] and photovoltaic technology.

In the present research work, novel photon induced aggregation of un-functionalized pristine metallic, semi-conducting and mixed SWNTs is introduced. Since electronic conducting properties of metallic, semi-conducting and as produced mixed SWNTs vary because of the difference in their band gap energies and dielectric properties, difference is also observed in the photon enhanced aggregation phenomenon they exhibit. This differential rate of aggregation opens up a novel potential method to separate out metallic nanotubes from semi-conducting nanotubes in mixed SWNT dispersion. If realized to its full potential and practical efficiency, this would be the cheapest, defect free way of separation of metallic and semi-conducting SWNT without use of any surfactants or chemical modifications.

Apart from observing photon enhanced aggregation phenomenon in different types of pristine, un-functionalized SWNTs, it is also observed in nanotubes functionalized with optically active molecules such as (Oligo-Phenylenevinylene (OPV) and Ruthenium complex ($[Ru(phenanthroline)_3]^{2+}[PF_6^-]_2$)) . We observe enhanced rate of aggregation of SWNTs functionalized with optically active molecules, when irradiated with light. Reduction of EDL repulsion potential barrier due to optical excitation causes enhanced rate of aggregation. In novel photon enhanced aggregation of un-functionalized pristine metallic, semi-conducting and mixed SWNTs, Plasmon frequency resonance upon optical excitation causes aggregation. On the other hand, in nanotubes functionalized with optically active molecules, the charges are donated from the optically active molecules onto the bound nanotubes upon optical excitation. This causes enhanced rate of aggregation. It is to be noted that even though the end result of the two processes taking place is enhanced rate of aggregation yet entirely different mechanism regulates the same outcome.

CHAPTER 3

Kinetic studies of SWNTs: Interaction of SWNTs with ionic coagulants

3.1 Preparation of stable dispersed solution of SWNT

'Metallic' (M), 'Semi-conducting' (SC) and 'Mixed' SWNTs were purchased (Nano Integris®-IsoNanotubes, 95% purity) and, well dispersed stable SWNT solutions are prepared for Metallic, Semiconducting and Mixed SWNTs by dispersing 0.7 mg of SWNT in 100 mL N,N-Dimethylformamide (DMF) (Sigma Aldrich®). Kinetic stability of nanotube dispersion which depends upon solvent-SWNT entropic and intermolecular interactions decides the choice of DMF as a potential good solvent. A kinetically stable SWNT dispersion in DMF ensures the integrity of SWNTs and leaves the ends and sidewalls of nanotubes without defects. To disperse the SWNTs in DMF, each solution was ultrasonicated (Branson® Bath Sonicator) for 3-4 cycles of 60 minute each. The prepared dispersed solutions were stable for weeks to few months. Since it is already known that water absorbs readily into DMF, the solutions were kept in air-tight bottles. Apart from moisture content in the DMF, light is also found to affect the dispersion stability of SWNTs. So, all the SWNTs solutions were kept in dark throughout the experiments.

3.2 Methods and Experiments

Following the reported experimental protocol for studying interaction of SWNTs with ionic coagulants and determining the optimum time for coagulation[34], 0.1 M solution of $FeCl_3$ (Sigma Aldrich®)(molecular weight 162.2 g/mol) was prepared (162.2×10^{-3} g in 10 mL) in DMF. Mixtures of various concentrations of $FeCl_3$ salt solution and dispersed semi-conducting SWNT were made and the samples were kept overnight. Concentration solutions (in moles/litre) were made from 10^{-4} - 10^{-11} moles/litre in the following ratios:

[1: 10: 100: 1000: 2000: 10^4: 2 x 10^4: 10^5: 2 x 10^5:10^6: 10^7]

As theoretically predicted, semi-conducting SWNTs tend to coagulate when they interact with ionic coagulant (here $FeCl_3$). After keeping the samples overnight for 12 hours, the samples were centrifuged @ 5000 rpm (Eppendorf® Mini Spin Centrifuge Machine) for 10 minutes to carefully separate the supernatant from the solution. 100 µL of supernatant was collected from centrifuged solution for all samples in the study. The supernatant was analyzed by absorption spectroscopy. Care was also taken to discard and repeat the experiment whenever a floc was aspirated with supernatant.

Absorption is plotted for supernatant of semi-conducting (SC) SWNT coagulated with Fe^{+3} ions at different concentrations (Fig 3.1).
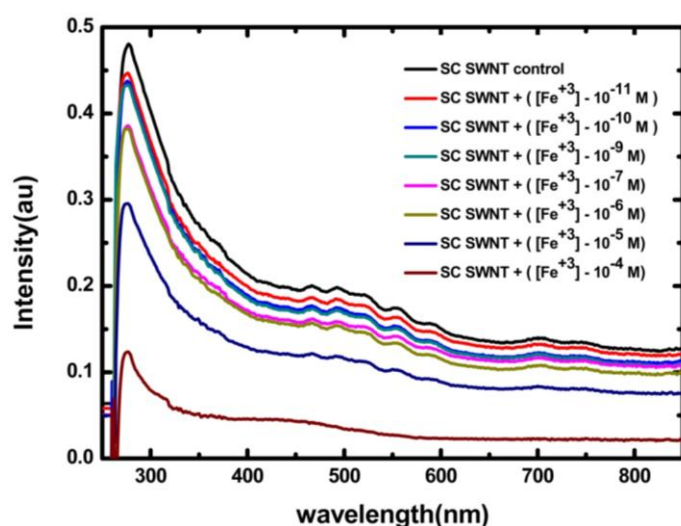
Fig 3.1: Absorption spectra showing semi-conducting SWNT coagulated with Fe^{+3} ions at different concentrations of $FeCl_3$ indicating minimum absorption at higher concentrations of ionic coagulant in SC SWNT dispersion.

Critical coagulation concentration [CCC] is determined by analyzing the absorption spectroscopy of semi-conducting SWNT remained in the supernatant at 800 nm. The absorption was measured at 800 nm to determine the [CCC] because our coordination compounds do not absorb at this frequency and the spectra are relatively flat and free of van Hove singularities. Normalized [SC SWNT] is plotted versus [$FeCl_3$] (Fig 3.2). [$FeCl_3$] is taken on log scale so as to accurately determine the coagulation onset. Normalized semi-conducting SWNT concentration i.e. [SC SWNT] / [SC SWNT]$_0$ is used for calculation of CCC so that the concentration of sample of [SC SWNT] is normalized with respect to original well dispersed solution of semi-conducting SWNT as they remain stable for weeks without significant coagulation.

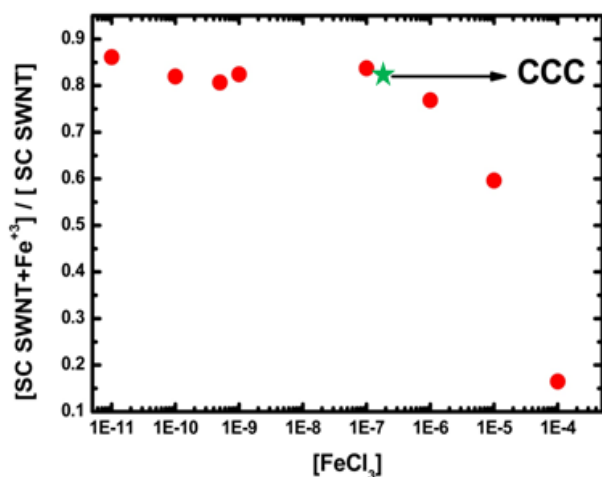**Fig 3.2**: Coagulation curve showing relative [SC SWNT] in DMF as a function of added $FeCl_3$ coagulant. SWNT dispersions are stable when the [$FeCl_3$] is less than CCC. After CCC, the SWNT dispersions tend to coagulate rapidly. Intersection of the linear fits of the data of normalized [SC SWNT], before and after the rapid aggregation of semi-conducting SWNT takes place, gives the CCC (marked as green star). The concentrations in the X-axis are in moles/litre.

The concentration of nanotubes in the supernatant was found to be fairly constant until it abruptly started to decrease with a further increase in concentration of $FeCl_3$. The point, where a small change in concentration of coagulant can render the SWNT dispersion to be unstable and causes it to coagulate, is termed as CCC. This point is effectively found by the intersection of linear fits of data of normalized [SC SWNT] in DMF, before and after the onset of rapid aggregation.

Same procedure was repeated with mixed and metallic SWNT dispersions and CCCs were calculated. It is to be noted that the absorption of aspirated supernatant was measured at 1000 nm for mixed SWNT, at 800 nm for semi-conducting SWNT and at 500 nm for metallic SWNT to determine the [CCC] because our coordination compounds do not absorb at this frequency and the spectra are relatively flat and free of van Hove singularities for respective SWNT dispersions.

To observe the variation of Schulze-Hardy rule for SWNTs, we also found the CCCs with ionic coagulants of +1 and +2 cationic charges of NaBr and $CuCl_2$ respectively, with mixed, metallic and semi-conducting SWNTs.

3.3   Results and Discussion

The concentration of SWNT in the supernatant was determined by UV-Vis-NIR spectroscopy (Perkin Elmer® Lambda 950 UV-Vis spectrometer). Coagulation curves for NaBr, $CuCl_2$ and $FeCl_3$ coagulated with metallic (M), semi-conducting (SC) and mixed (Pure) SWNTs are shown in Fig 3.3.

(a)

(b)

(c)
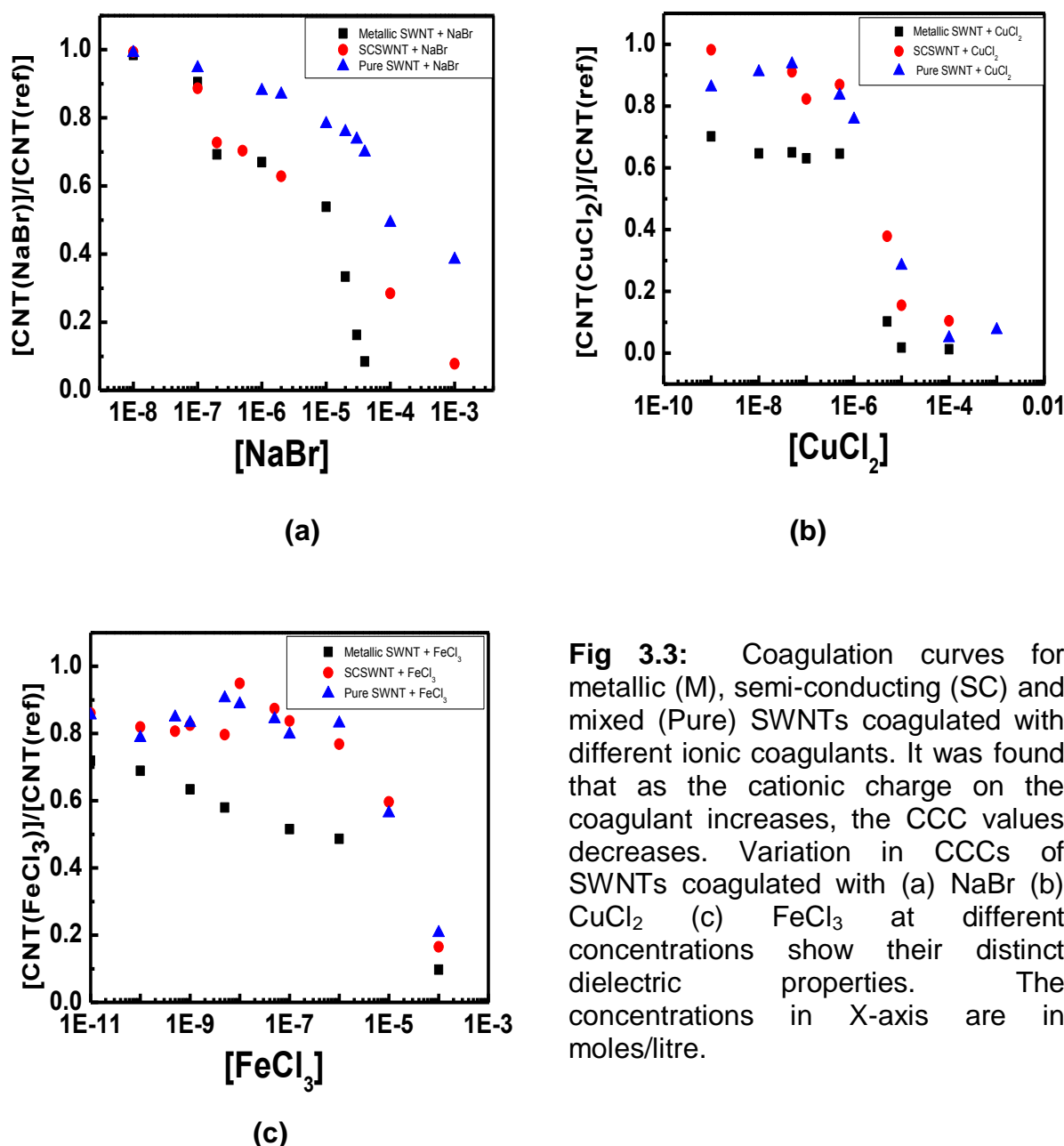
Fig 3.3: Coagulation curves for metallic (M), semi-conducting (SC) and mixed (Pure) SWNTs coagulated with different ionic coagulants. It was found that as the cationic charge on the coagulant increases, the CCC values decreases. Variation in CCCs of SWNTs coagulated with (a) NaBr (b) $CuCl_2$ (c) $FeCl_3$ at different concentrations show their distinct dielectric properties. The concentrations in X-axis are in moles/litre.

The CCC for SWNT coagulated with $FeCl_3$ is found to be lower than the CCC for both SWNT coagulated with NaBr and $CuCl_2$ (Table 1). This is in accordance with Schulze-Hardy rule and DLVO theory. The CCCs for SWNT coagulated with ionic

coagulants of different cationic charge follow the order: $CCC_{NaBr} > CCC_{CuCl_2} > CCC_{FeCl_3}$. Also, variation in the CCC values is observed for three different types of SWNTs indicating that this variation is because of different dielectric properties of metallic (M), semi-conducting (SC) and mixed (Pure or P) SWNTs. We have not taken into account the dependence of type of the anion on values of CCC. All the ionic coagulants used for the study have an anion valency of $(z_-) = -1$ (Br^- and Cl^-). Attempts to study interaction of SWNTs with more coagulants of +3 and +4 charges were unfruitful because of poor solubility of coagulant with DMF.

	M SWNT	SC SWNT	P SWNT	spherical particle
Na^{+1}	8.05E-06	5.32E-06	6.34E-06	1.00E-06
Cu^{+2}	3.06E-06	1.55E-06	1.04E-06	1.56E-08
Fe^{+3}	4.49E-07	2.35E-07	1.45E-07	1.37E-09

Table 1: CCCs for different types of SWNTs and ionic coagulants showing the variation of CCC with cationic charge of coagulant and dielectric properties of SWNTs as compared to that of ideal colloidal system consisting of spherical particles. The concentrations are in moles/litre.
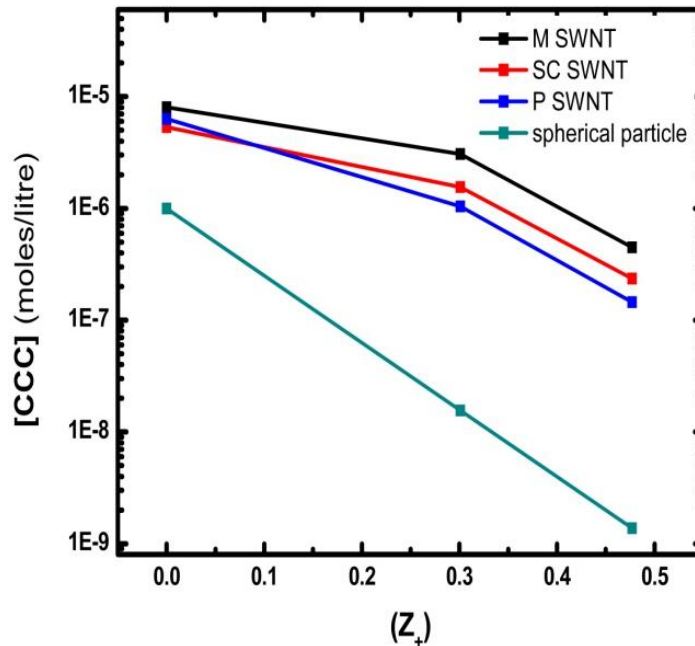
Schulze Hardy plot

Fig 3.4: Schulze Hardy plot showing variation of CCCs with coagulants of different cationic charge as compared to that of ideal spherical particle system as explained by DLVO theory and SH rule. The CCC values in Y-axis are in moles/litre. The values are plotted on log-log scale.

All of the CCC data for ionic coagulants and spherical particle is plotted as a function of (z_+) in log-log scale. The stability of colloidal systems is characterised by Schulze-Hardy (SH) rule, where the critical coagulation concentration (CCC) is related to the valence of the charged coagulant: (CCC) α (z_+)$^{-6}$ i.e. greater the valence of the oppositely charged ion of the electrolyte being added, the faster is the coagulation. The graph describes the variation of CCC of spherical particle colloidal system according to Schulze Hardy rule, but fails to account for relation between other systems where different types of cylindrically shaped SWNTs interact with different ionic coagulants. Classical DLVO theory assumes that the ionic coagulants are symmetric where (z_+) = (z_-). So, as expected, except for NaBr, our study does not follow the results of DLVO theory of lyophobic colloids as the other coagulants (like $FeCl_3$ and $CuCl_2$) are asymmetric where (z_+) ≠ (z_-). This theory needs to be extended to further explain the cases of such asymmetric ionic coagulants.

3.4 Conclusions

It is verified that for SWNTs interacting with inorganic coagulant, CCC values vary with the cationic charges. It can be concluded that as the cationic charge on the coagulant increases, the CCC values decreases. This is in accordance with the SH rule. It was also observed that CCC values vary with the type of the SWNTs depending upon their dielectric properties and therefore Metallic, Semi-conducting and Mixed SWNTs show different CCC values for different set of coagulants. Thus, binding of Metallic, Semi-conducting and Mixed SWNTs with coagulants and interaction of SWNTs among themselves are affected by size, shape and ionic strength of coagulants as well as electrodynamic repulsive forces and van der Walls attractive forces between SWNTs.

Also, CCC values for semi-conducting SWNTs are closer to CCC values for mixed SWNTs as compared to CCC values for metallic SWNTs. This may be attributed to the fact that in mixed SWNTs, semi-conducting SWNTs are more than metallic SWNTs.

SH plot show the variation of CCCs with coagulants of different cationic charge as compared to that of ideal spherical particle system as explained by DLVO theory and SH rule. As expected, it is observed that as the cationic charge on the coagulant increases, the difference of CCC of ideal spherical particle system varies with the systems under study increases. This difference is more evident for ionic coagulant of $z_+ = (+3)$. Thus, it verifies the need of a theoretical description for accurately describing dispersion and aggregation of different types of SWNTs. This would further lead to fabrication of nanotube based devices.

CHAPTER 4

Photon enhanced studies of SWNTs: Interaction of SWNTs with light

4.1   Methods and Experiments

Fundamental studies to find the photon enhanced aggregation rate of SWNTs in solution

Fresh and well dispersed stable solutions of metallic, semiconducting and mixed SWNTs were prepared as described earlier. The stable samples of SWNTs are exposed to UV lamp (250 W) and Quartz-Tungsten-Halogen (QTH) lamp (200 W) of visible-IR frequency for time periods in ratios of [1: 2: 3: 4: 6: 8] starting with 30 minutes. Samples are also kept in dark for the same time periods so as to find the normalized aggregation rate of SWNT in presence of light.

The samples were centrifuged @ 5000 rpm (Eppendorf® Mini Spin Centrifuge Machine) for 10 minutes to carefully separate the supernatant from the solution. As before, care was taken to withdraw the same part of the centrifuged solution (100 µL) for all samples in the study and to avoid aspirating floc along with supernatant. The supernatant was analyzed by UV-Vis-NIR spectrophotometer (Perkin Elmer® Lambda 950 UV-Vis spectrometer). To have minimum Van Hove singularities in the spectra, the absorbance values are taken at 500 nm for metallic SWNT, at 800 nm for semi-conducting SWNT and at 1000 nm for mixed SWNT dispersions.

Normalized SWNT concentration i.e. ($[SWNT]_{light}$ / $[SWNT]_{dark}$) is calculated to observe photon enhanced aggregation phenomenon. This ensures that the [SWNT] exposed to light is normalized with respect to original well dispersed solution of SWNT kept in dark as they remain stable for weeks without significant coagulation.

Photon enhanced aggregation of M and SC SWNTs functionalized with coagulants

For this purpose, well dispersed solution of SWNTs was mixed with coagulant of a fixed concentration. The concentration of coagulant was kept close to and just below the CCC. It is known that when the coagulant concentration is above CCC, the enhancement in photon induced aggregation is not much as most of SWNT has already coagulated and [SWNT] is low to measure[25]. The samples were then exposed to QTH (visible-IR frequency) lamp for time periods in ratios of 1: 2: 3: 4: 6: 8 starting with 30 minutes. Corresponding to each of the samples kept in light exposure, control samples of the same concentrations were kept completely in dark for respective duration of time.

As described above, after exposure of light the samples are centrifuged (@ 5000 rpm, 10 minutes) and the supernatant was analyzed by UV-vis-NIR spectroscopy technique. Absorbance values are taken at 500 nm and 800 nm respectively for metallic SWNT and semiconducting SWNT dispersions. Normalized SWNT concentration i.e. ([SWNT-coagulant] $_{light}$ / [SWNT-coagulant] $_{dark}$) is calculated to find the photon enhanced aggregation rate. All the results were analyzed and graphs were plotted for normalized [SWNT] on Y-axis Vs light exposure time interval on X-axis.

This experimental procedure is used to study photon enhanced aggregation of metallic and semi-conducting SWNTs functionalized with three coagulants: a simple ionic coagulant, NaBr; optically active Oligo-Phenylenevinylene (OPV) molecule (synthesized and donated by Dr. Jayakannan and co-workers[35], IISER Pune) and a Ruthenium complex ($[Ru(phenanthroline)_3]^{2+}[PF_6^-]_2$) (donated by Dr. J.C. Poler, UNCC).

Using NaBr as a coagulant, solutions of a fixed concentration were made i.e. 2.5×10^{-6} M (CCC values for metallic SWNT dispersion = 8.05×10^{-6} moles/ litre and for semi-conducting SWNT dispersion = 5.32×10^{-6} moles/ litre). Similarly, using OPV as a coagulant, fixed concentration was chosen as 10^{-4} moles/ litre (CCC for metallic SWNT dispersion = 7.8×10^{-6} moles/ litre and for semi-conducting SWNT dispersion = 1.7×10^{-4} moles/ litre); and for using Ruthenium complex as coagulant, fixed concentration was chosen as 10^{-8} moles/ litre (CCC for metallic SWNT dispersion = 3.6×10^{-7} moles/ litre and for semi-conducting SWNT dispersion = 1.1×10^{-7} moles/

litre). The CCC data for OPV molecule and Ruthenium complex were taken from Mr. Neeraj Maheshwari.

4.2   Results and Discussion

Finding the photon enhanced aggregation rate of SWNT dispersions

Following data are obtained by exposing metallic, semi-conducting and mixed SWNTs to visible-IR frequency (source: QTH lamp) and UV frequency lamp (Fig 4.1 (a) and (b)).
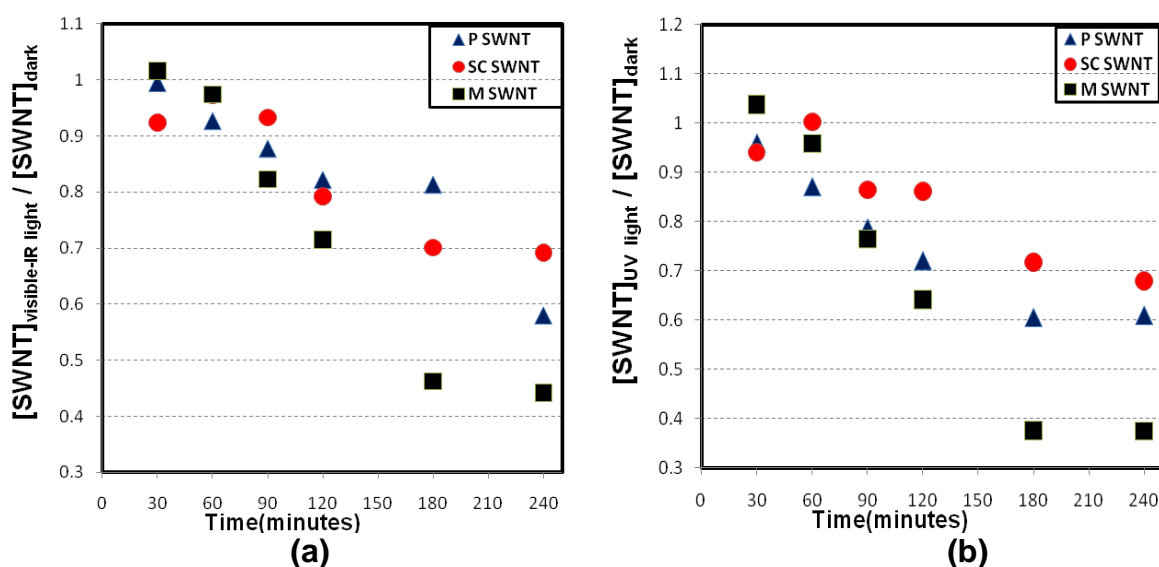
Fig 4.1: Enhanced aggregation of SWNTs as time progresses is seen when exposed to (a) visible-IR frequency QTH lamp and (b) UV frequency lamp. Both the graphs are normalized to ascertain enhanced aggregation rate.

It is proposed that the irradiated photons reduce the repulsive potential barrier between the SWNTs in stable dispersion causing enhanced coagulation rate. At the maximum exposure time interval i.e. 240 minutes, following % of SWNT aggregation takes place:

type of SWNT/ lamp used	UV lamp	QTH lamp
Mixed SWNT	~ 60%	~ 60%
Metallic SWNT	~ 37%	~ 45%
Semiconducting SWNT	~ 68%	~ 70%

Table 2: Percentage of metallic, semiconducting and mixed SWNTs aggregated when exposed to UV and QTH lamps for 4 hours is tabulated. Metallic SWNTs showed maximum photon enhanced aggregation.

Results show that metallic SWNTs aggregate at a faster rate than semiconducting and mixed SWNTs. This may be attributed to the fact that metallic SWNTs are in plasmon resonance with the frequency of irradiated light. However the rates of aggregation are similar for mixed and semi-conducting SWNTs when they are exposed to UV and QTH lamps; whereas it shows little variation for metallic SWNTs. This novel and interesting property of light induced aggregation of metallic SWNTs at faster rate can be utilized to separate metallic SWNTs from semi-conducting SWNTs in mixed SWNTs dispersions.

Longer exposure duration of high energy light was avoided as it is known to create defects and cross-links in CNTs.[36]
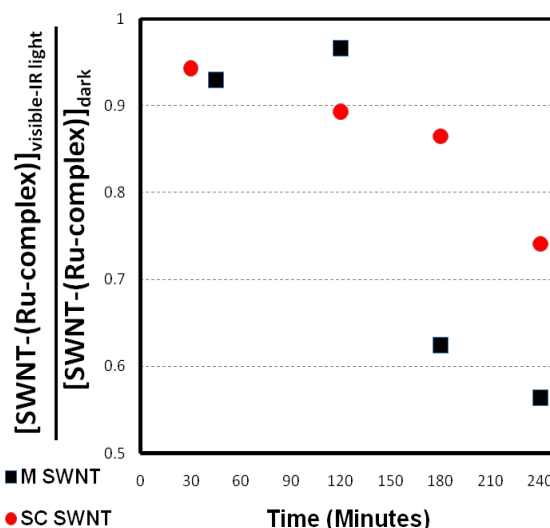
Photon enhanced aggregation of SWNTs functionalized with different coagulants

Studies of photon enhanced aggregation of SWNTs functionalized with different coagulants lead to following results. To observe the enhanced aggregation, solutions of metallic and semi-conducting SWNTs mixed with NaBr, OPV and Ruthenium-complex were exposed to visible-IR frequency light (source: QTH lamp).

Graphs are plotted to compare the difference in rates of aggregation for different types of SWNTs functionalized with two optically active molecules (Fig 4.2 (a) and (b)) and for different types of coagulants used with metallic SWNT (Fig 4.2 (c)).
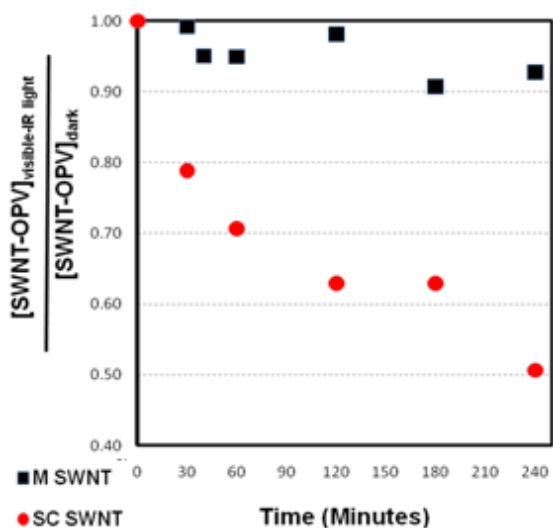
(a)

(b)
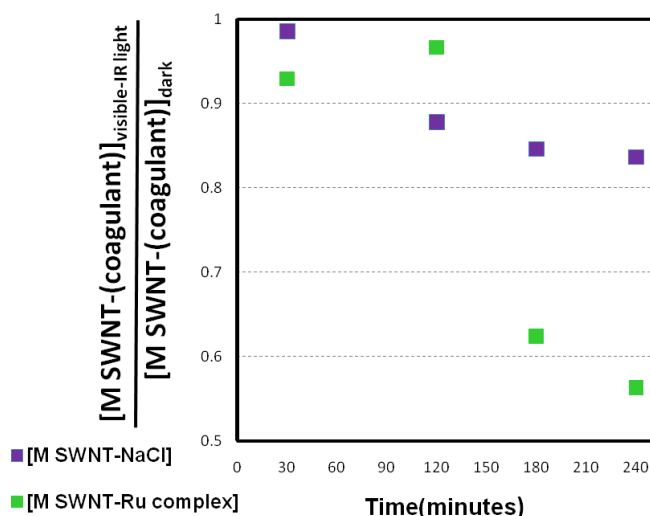
(c)

Fig 4.2: Enhanced photon induced aggregation of (a) metallic and semiconducting SWNTs functionalized with OPV (b) metallic and semiconducting SWNTs functionalized with Ru-complex (c) metallic SWNTs functionalized with different coagulants i.e. NaBr and Ru-complex**.**

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In fig 4.2 (a), the concentration of OPV was 10^{-4} moles/ litre which is well above the CCC for metallic SWNT dispersion ($\sim 10^{-6}$ moles/ litre) and almost equal to CCC for semi-conducting SWNT dispersion ($\sim 10^{-4}$ moles/ litre). Thus, very little change is observed for metallic SWNT aggregation (> 10% enhancement) as most of the SWNTs have already coagulated with OPV and there is very less [SWNT] left in the sample. As for semi-conducting SWNT, huge change in aggregation rate is observed due to light irradiation ($\sim$ 50% enhancement).

In fig 4.2 (b), Ruthenium complex concentration is fixed at 10^{-8} moles/ litre which is below the CCC for metallic and semi-conducting SWNT ($\sim 10^{-7}$ moles/ litre). Nearly 26% and 44% enhancement in aggregation rate is observed for semiconducting and metallic SWNTs respectively. Metallic SWNTs are found to have more enhancements in aggregation rate when samples are exposed to visible-IR frequency light as metallic SWNTs absorbing strongly in visible range are in plasmon resonance with frequency of irradiated photons.

On the other hand, inorganic coagulant used (NaBr) does not possess photoactive property and thus does not show much variation due to photon irradiation. As expected, only $\sim$ 16% enhancement in aggregation of metallic SWNT takes place even when it was exposed to light for 4 hours (Fig 4.2 (c)).

Optically active molecules (OPV and Ruthenium-complex) are understood to absorb light and donate charges to SWNTs. This donation of charges through its π-π electron transfer mechanism from optically active molecules to SWNTs, changes the counter ion concentration interacting with SWNT surface, thereby changing the surface potential. Since the double layer repulsion potential depends upon counter ion concentration and Debye length, decrease in counter ion concentration causes the repulsive potential barrier between SWNTs in stable dispersions to decrease. This leads to enhanced coagulation of SWNTs.

Along with concentration of coagulants, Debye length depends upon their charge too[37]. NaBr has +1 cationic charge; Ruthenium-complex has a charge of +2 cationic whereas the organic molecule OPV has an overall neutral charge. Therefore, different coagulants are found to have varying effect on aggregation rates of SWNTs. Also, since metallic and semi-conducting SWNTs vary in their dielectric properties,

which depend upon its EDL repulsive, vdW attractive and other dispersion forces, the difference in rates for different types of SWNTs is evident.

4.3   Conclusions

Novel phenomenon of photons enhanced aggregation rates of SWNTs is observed. These aggregation rates vary depending upon the charge, concentration and type of coagulant used (photoactive or non photoactive); and type of SWNT used (metallic and semiconducting SWNT). Hence, dependence of dispersion stability [CCC] on optical excitation and dielectric property of SWNTs (metallic and semiconducting) is experimentally demonstrated. The specific enhancement in aggregation rate can be employed for practical purposes in photovoltaic and solar energy based technologies.

Interesting light enhanced separation phenomenon of SWNTs can be an easy and cheap method to separate metallic and semiconducting SWNTs in mixed SWNT dispersions. But, more research work need to be done in this direction to improve the separation percentage. The scientifically challenging and technologically enabling research field of optical enhanced aggregation of SWNTs needs to be extensively studied both theoretically and experimentally.

As photons are known to enhance aggregation rates of colloids, care must be taken while studying using optical instruments to study aggregation kinetics.

Chapter 5

Future Research Direction

We started with an aim to answer the questions regarding the aggregation kinetics and photon enhanced aggregation of SWNT. Our research work gives an important direction in understanding the aggregation of SWNTs by answering these questions.

1	How dielectric properties of nanotubes influence their aggregation rate?	Dielectric properties determine the EDL interactions between SWNTs and type of nanotube present (mixed, metallic or semi-conducting). Therefore, difference in aggregation rates of mixed, metallic or semi-conducting SWNTs is observed for different coagulants used.
2	How cationic charge of the coagulant influence SWNT aggregation rate?	As the cationic charge on the coagulant increases, the aggregation rate varies. The aggregation rate is found to vary in accordance with Schulze-Hardy rule for coagulant with cationic charge +1. The rule shows deviations for higher cationic charged coagulants.
3	How optical excitation enhances aggregation rates in unbound pristine SWNTs?	In photon enhanced aggregation of un-functionalized pristine SWNTs, Plasmon frequency resonance upon optical excitation causes aggregation.
4	How optical excitation enhances aggregation rates in SWNTs functionalized with coagulants?	In nanotubes functionalized with optically active molecules, the charges are donated from the optically active molecules onto the bound nanotubes upon optical excitation. This causes enhanced rate of aggregation.

Future research directions are aimed to focus on extending DLVO theory for one dimensional materials like SWNTs. Also, In aggregation kinetics, DLVO theory assumes that the particles are spherical, and the interaction among particles takes place under the condition that the surfaces are at a constant potential and pH. The type of anion and the finite size of counter-ions are also not account by DLVO theory. Our next research work will focus on varying these parameters and observing the changes in aggregation of SWNTs.

In optical enhanced aggregation studies, we need to find systems (SWNT and optically active molecule) which can give maximum enhancement in aggregation rates. This would enable us to design and fabricate photovoltaic nanodevices.

Many commercial applications based on SWNTs can be developed, from photovoltaic to molecular electronics to sensing. If these real-world applications of SWNTs are to succeed, we must find ways to develop the technology to fabricate SWNTs of a particular type, length and diameter in a controlled fashion – and to incorporate the tubes into lithographic circuits at particular places with practical efficiencies.

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