Chapter 1

NANOPARTICLES, MACROMOLECULES AND THEIR INTERACTIONS

1.1. Introduction

The field of nanoscience and nanotechnology describes the creation and exploitation of materials with structural features having at least one dimension in the nanometer range (1-100 nm). Nanostructures (synthetic or natural) are known to exhibit fascinating physical properties such as surface plasmon resonance, superparamagnetism, extremely high electron mobility, giant magnetoresistance etc. that are significantly different from that of the compositional atoms as well as corresponding bulk materials [1-5]. A nanoparticle, with all the three dimensions in nanoscale is the most fundamental nanostructure which represents the most widespread current form of nanomaterials. The striking features of nanoparticles have been widely used for various multidisciplinary applications in electronics, medicine, energy, catalysis etc. [1-10].

The macromolecules are large molecules having sizes corresponding to that of nanostructured materials and possess novel physico-chemical properties such as self-assembly, viscoelasticity, wide range of biological functions etc [16-19]. Depending upon the nature of interaction of macromolecules with aqueous medium, they are classified as hydrophilic, hydrophobic or amphiphilic. Polar and ionic macromolecules are said to be hydrophilic because of their interaction with water. Non-polar macromolecules are hydrophobic and they do not dissolve in water. On the other hand, amphiphilic molecules are made up of both hydrophilic and
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hydrophobic components [16]. Polymers can be hydrophilic or hydrophobic based on the nature of functional group [19]. Polyethylene glycol is an example of hydrophilic polymer whereas polystyrene is a hydrophobic polymer. Other examples of hydrophobic macromolecules include alkanes, oils, fats etc. Protein, surfactant and some block copolymers are common examples of amphiphilic macromolecules.

The interaction of nanoparticles with macromolecules opens routes for the tuning of rich phase behavior of these systems as well as formation of new hybrid functional materials, which are being employed in wide range of applications. The interaction of nanoparticles with surfactants is utilized extensively for many technical applications associated with enhanced dispersion stability, emulsification, corrosion, enhanced oil recovery, chemical mechanical polishing etc [20]. Nanoparticle-protein complexes have shown their paramount importance in nanobiotechnology (enzymatic behavior, targeted drug delivery and diagnostics) [21]. Figure 1.1 shows the schematic of nanoparticle-biomolecule conjugate utilized to carry the protein drug for the targeted drug delivery. Nanoparticles-polymer composites display enhanced thermal and mechanical properties which are shown to be very useful for developing synthetic materials of high strength [13]. In order to accomplish the control over the performance of the fundamental building block of these hybrid structures, the understanding of nanoparticle-macromolecule interactions is essentially required. The interaction between the constituents participating, nanoparticle and macromolecule, is governed by cooperative effect of many forces such as van der Waals force, electrostatic interaction, hydrogen bonding etc. The resultant behavior of the complex system strongly depends on the characteristics of both the nanoparticles and macromolecules used [20-24]. For example, the adsorption of oppositely charged protein on
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anionic nanoparticles has been found to be dramatically suppressed by manipulating charge at the nanoparticle surface through cationic coating on nanoparticles [24]. However, the

Figure 1.1. Schematic of nanoparticle-biomolecule conjugate for targeted drug delivery.

non-adsorbing nature of macromolecules can give rise to attractive depletion force in these systems. The size difference between nanoparticle and macromolecule can be utilized to observe entropy driven depletion forces and corresponding structural changes in the system [25, 26]. When two components are oppositely charged, nanoparticles may destabilize and undergo macromolecule mediated aggregation. This phenomenon has been observed in number of oppositely charged nanoparticle and macromolecule systems, where the tuning of their electrostatic interaction can result in aggregates of different shapes, patterns and functionalities. If one or both components are nonionic they interact through moderate interactions such as hydrogen bonding or hydrophobic forces or depletion interaction, if the macromolecule remains free in the solution [20, 23, 27]. The characteristics of nanoparticle and macromolecule as well as other solution conditions may be used to tune the degree of their interactions in order to
achieve the desirable system properties. The present thesis provides understanding of the interaction of model silica nanoparticles with different macromolecules. This chapter describes the characteristics of the nanoparticles and macromolecules used, their possible interactions and applications. The layout of the thesis is also given in the end of the chapter.

1.2. Characteristics of nanoparticles

The extraordinary properties of the nanoparticles emerge largely because of two effects, quantum effect and scalable effect [1, 2, 28-32]. Quantum effects like spatial confinement can be observed in the nano size range, when the particle dimension is of the order of the de Broglie wavelength of the particle. A particle behaves as if it is confined in some potential well which otherwise feels free if the confining dimension is larger compared to its wavelength. In confined state, electronic wave function is delocalized over the entire particle and the particle may be regarded as individual atoms. In such situation, the electronic energy levels become discrete instead of continuous band (figure 1.2). Evolution of properties therefore becomes analogous to that happened with increasing atomic number in periodic table [2]. On the other hand, scalable effects are observed due to increased surface area per unit volume with decrease in particle size (figure 1.3). The surface dependent properties mostly are scalable, changes continuously with size and extrapolate slowly to that of bulk. The surface-to-volume ratio increases proportionally to the inverse of particle size and hence in the nanoscale surface atoms constitute a considerable fraction of the total number of atoms [1, 2, 29-31]. The high proportion of surface atoms suffers unsaturation in the coordination which results in an increase in the presence of dangling bonds. The higher the number of dangling bonds greater is the surface free energy. These bonds govern largely the thermodynamic, mechanical as well as chemical functions of nanoparticles.
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The overall nanoparticle characteristics are determined by a combination of quantum and scalable effects. In general, quantum effects are superimposed on smoothly varying background of scalable effects for nanoparticles [2]. Nanoparticles are interesting intermediates between single atoms and bulk matter representing both ends at the middle. Some of the important properties of nanoparticles arising because of these effects are described below:

(i) **Electronic properties:** Electronic properties of solids in bulk depend on well defined electronic energy bands. In general, in bulk solids, there exists a valance band which is completely filled by electrons and a conduction band which is empty. The two bands are separated by an energy gap $\delta_E$. Based on the value of $\delta_E$, solids are classified as metals ($\delta_E \sim 0$), semiconductors ($\delta_E \sim 1\text{eV}$) and insulators ($\delta_E \sim 10\text{eV}$) [29, 32]. In nanometer size range, the band structure of bulk material can no more be observed as quasi continuous, instead has to be replaced by quantum mechanical levels with a size dependent spacing and band gap (figure 1.2). Single nanoparticle display an electronic structure that corresponds to an intermediate electronic structure between the band structure of the bulk and the discrete energy levels of molecules with

![Figure 1.2. Evolution of the band gap and density of states with decreasing particle size.](image)
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characteristic highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) (figure 1.2) [2, 32, 33]. Such size quantization effect may be regarded as the onset of the metal-insulator transition where the critical size at which transition occurs depends on the nature of the material. The metallic/semiconductor/insulator properties of the materials can be tuned in nanometer size range. These effects are being utilized in great extent in modern day electronics which requires miniaturization of circuit elements along with reduction in distance between them [2, 3, 28, 34]. Today’s nanolithographic fabrication techniques allow scaling down to 50 nm which open up new opportunities utilizing quantum effects.

(ii) Optical properties: Nanomaterials show novel optical properties which are remarkably different from their bulk. There are two important factors determining the optical behavior of the nanoparticles, quantum confinement and surface plasmon resonance (SPR) [2, 35]. The discretization of energy spectrum in nano size range ultimately alters optical illumination of the particles. For example, the luminescence spectra of Europium doped Y\textsubscript{2}O\textsubscript{3} show emergence of additional peaks in nanocrystalline phase [29]. This effect is most pronounced for semiconductor particles where a blue shift in the light absorption can be observed because of the increase in the band gap with reduction in size. The rate of recombination of photo-excited electron hole pair is also decreased. The surface plasmon resonance is usually observed in metal nanoparticles because of which these nanoparticles exhibit particle size dependent coloring [28, 35, 36]. SPR excitation is based on the interaction of the electromagnetic field of the incoming light with conduction electrons on the metal nanoparticle surface resulting in a collective in-phase oscillation. The frequency of these oscillations depends on the free electron density, shape and size of the material as well as surrounding dielectric medium. The SPR for noble metal nanoparticles occur throughout the visible and near-infrared region of the electromagnetic
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spectrum. Many applications in photonics, sensing and imaging industry, communication industry and in solar cells become possible due to the large enhancement of the surface electric field as well as increased detection sensitivity of the nanoparticles [35].

(iii) Magnetic properties: Essentially each atom with odd number of electrons can behave like a magnet. It is the electronic structure basically which determines the magnetic behavior. Therefore, the reduction in particle size can influence the magnetic properties of the system by altering the electronic structure, reducing the symmetry of the system and changing the boundary conditions [7, 29, 37-39]. In sufficiently small nanoparticles, magnetization can randomly flip direction. As a result, nanoparticle equivalent to single domain behave like superspins and show superparamagnetism where ferromagnetic particles become paramagnetic. The uncompensated surface spins at nanoscale leads to high magnetic moment even for small clusters of non-magnetic materials like Pd, Au and Pt [2]. The coercivety and saturation magnetization increases with decrease in particle size. A maximum coercive field is attained for the maximum size of a nanocluster that is of single magnetic domain [29]. Further, the possibility of inducing the room-temperature ferromagnetic-like behavior in ZnO nanoparticles without doping with magnetic impurities has been demonstrated where the electronic configuration of nanoparticles is altered by surface capping of organic molecule [40]. These interesting properties have shown useful potential in the fields like memory devices, batteries, magnetic resonance imaging, drug delivery etc [37-39].

(iv) Surface properties: The overall surface area increases with decrease in particle size for a fixed volume (figure 1.3). In chemical reactions involving a solid material, the surface-to-volume ratio becomes extremely important parameter for their reactivity. The high surface-to-volume ratio containing large portion of atoms/molecules at the surface of nanoparticles provides more
surface sites available for the higher activity [2, 29-32]. This can be understood from a simple example of ice melting where finely crushed ice melts faster than ice cubes. The excessively high reactivity of the surface originates from quantum mechanical atom-atom interaction that directs a strong driving force to speed up the process in the quest of minimizing the free energy. Immediately after generation, nanoparticle surface may get modified depending on the presence of reactants present, and solution conditions leading unpredictable behavior of them. On one hand, nanoparticles have a large functional surface which is able to bind, adsorb and carry other compounds such as drugs, polymers and proteins on the other hand, they also have a chemically more reactive surface that might enhance the catalytic promotion of reactions manyfold compared to their bulk analogues [44-46]. The important parameters governing the nanoparticle surface activity are surface composition, functional group present on surface, its termination, charge, surface strain and defects which are known to have strong impact on nanoparticle secondary size, solubility and affinity for other macromolecules [44].

**Figure 1.3.** Schematic of increase in surface area with decreasing particle size.
(v) **Mechanical properties:** Mechanical properties of the nanoparticles have been shown to touch the theoretical limits, which are one or two orders higher than that found in bulk [1, 29]. There are basically two factors considered responsible for governing the mechanical properties at nanometer length scale (i) strong surface forces which otherwise are less relevant and (ii) reduced probability of defects like dislocations, microtwins impurities etc [1]. These two factors together modify many mechanical properties like adhesion, contact, hardness, elastic modulus, fracture roughness, scratch resistance, deformation etc. Cutting tools formed by nanomaterials such as tungsten carbide, titanium carbide are harder, more wear-resistant, erosion-resistant and long lasting compare to their conventional bulk counterpart. Ceramic materials which otherwise are very hard, ductile, brittle and difficult to machine, can be pressed and sintered into various structures if grain size is reduced in nanoscale [29]. Moreover, the nanoparticle-polymer composites show increased reinforcement, stronger plastics nature and suitability to handle higher temperature as well as mechanical stress [41, 42]. The nanoparticles impart their properties to the polymers and as a consequence, the Young’s modulus and strength of nanocomposites increases with particle loading. Smart and sophisticated clothing can be achieved by attaching the nanoparticles to textile fibers. Many aircraft components require high fatigue strength for a longer time period. It has been shown that the fatigue strength as well as fatigue life can be enhanced by an average of 250% in nanodimensions [29].

(vi) **Thermodynamic properties:** Interesting thermal properties of nanoparticles emerge mainly because of high surface energy of the nanoparticles [43]. The nanoparticles are found to have lower melting and boiling temperature than their bulk form [2, 29]. The lowering of melting/boiling point is in general explained by the fact that the surface energy increases with the decreasing size. It has been further shown that the thermal conductivity of the nanoparticles can
be much higher. Also the nanoparticles show an intrinsic thermodynamic self-purification [1]. Any heat treatment increases the diffusion of impurities towards the nanoparticle surface causing a relatively increased perfection within the volume. Such purification has appreciable impact on other chemical and physical properties of the material. The nanoparticles provide an energy conversion through the transformation of an electromagnetic radiation into heat at the nanoscale. Therefore, the nanoparticles can also be treated as nanometric heat sources and probes for local temperature variations. For example, in plasmonic devices local heating may be used for guiding the electromagnetic wave by nanostructures. In the medical area, photo-thermal cancer therapy based on nanoparticles is a very promising technique, where nanoparticles absorb light energy, transmitted through biologic tissues and transform it into heat which diffuses toward local environment. The nanoparticles provide the possibility of sintering at lower temperatures, over shorter time scales than for larger particles [29].

Silica nanoparticles are one of the most studied model nanoparticle systems used for many applications. These nanoparticles occupy a prominent position in scientific research, because of their easy preparation, high stability, low toxicity and ability to be functionalized with a range of macromolecules [47, 48]. These are usually electrostatically stabilized suspensions of fine amorphous, nonporous, and typically spherical particles in a liquid phase. The usual particle size range is in between 10 to 100 nm in diameter. Smaller and larger particles are difficult to stabilize. Popularly, silica nanoparticles are synthesized in two ways: chemical vapor condensation (CVC) method and sol-gel process. In CVC method, silica nanoparticles are produced through high temperature flame decomposition of precursors such as silicon tetra chloride (SiCl4) with hydrogen and oxygen. Though, this method has limitations like difficulty in controlling the particle size, morphology, and phase composition but is efficiently used for
Figure 1.4. (a) A typical sol-gel process for synthesis of colloidal silica nanoparticles and (b) schematic of charged stabilized silica nanoparticles.
commercial synthesis of silica nanoparticles in powder form. The other method (sol-gel) is a multi-step process where hydrolysis and condensation of metal alkoxides [Si(OR)$_4$] such as tetraethylorthosilicate [TEOS, Si(OC$_2$H$_5$)$_4$] or inorganic salts such as sodium silicate [Na$_2$SiO$_3$] is carried out in the presence of mineral acid (e.g. HCl) or base (e.g. NH$_3$) as catalyst. The hydrolysis of silicon compound (TEOS) molecules forms silanol groups. The condensation/polymerization between the silanol groups creates siloxane bridges (Si–O–Si) that form entire silica structure in colloidal form. A general flow chart summarizing the silica nanoparticle synthesis by sol-gel process using silicon alkoxides [Si(OR)$_4$] is shown in figure 1.4(a) [49]. In aqueous solution, the hydrogen ions from the surface of colloidal silica tend to dissociate, yielding an overall high negative charge [figure 1.4 (b)]. Because of the very small size, the surface charge density becomes high. The colloidal suspension is first stabilized by adjusting the pH of the solution and then concentrated, usually by evaporation. The maximum concentration obtainable depends on the particle size. 50 nm particles can be concentrated to greater than 50 wt% solids while 10 nm particles can only be concentrated to approximately 30 wt% solids before the suspension becomes too unstable.

1.3. Different types of macromolecules

The macromolecules are very large molecules of high molecular masses and the structure of which essentially comprises the multiple units derived from molecules of lower molecular masses. Different macromolecules (e.g. polymers, synthetic fibers, surfactant micelles, proteins, DNA, lipids) possess distinct structures and are characterized by unusual physical properties [50]. For example, individual pieces of DNA in a solution can be broken into two parts simply by using an ordinary straw which is not true for smaller molecules. Another common macromolecular property that is not characterized by smaller molecules is macromolecular
crowding in which the high concentrations of macromolecules in a solution can alter the rates and equilibrium constants of the reactions of other macromolecules. Such unusual properties of the macromolecules emerge due to their large size, specific shape and chemical structure. In general, the macromolecules provide structural integrity to the many natural and synthetic systems and perform several functions in our daily life. The macromolecules can broadly be classified in the following three types:

(i) Amphiphilic molecules: The amphiphilic molecules are made up of one hydrophilic moiety (referred to as head group) which is covalently bonded to another hydrophobic moiety (generally a single or double alkyl chain also called as tail). The hydrophobicity or hydrophilicity is decided by the non-polar or polar nature of the molecule, respectively [16, 51, 52]. The common examples of amphiphilic substances are detergents, cholesterol, surfactants etc. The coexistence of two opposite type of behavior (hydrophilic and hydrophobic) inside the same molecule is the origin of the local constraints which lead to the spontaneous aggregation of amphiphilic molecules. The process is known as micellization. The hydrophilic head remains in the contact with surrounding solvent, sequestering the hydrophobic tail regions in the micelle core. The micellization occurs after a critical concentration known as critical micellar concentration (cmc). Micelles are thermodynamically stable and entropically more favorable than the segregated amphiphilic molecules.

Surfactants are one of the most important and extensively used amphiphilic molecules [51]. These are surface active substances that are known to lower the surface tension (or interfacial tension) at air and water interface and can act as wetting agents, emulsifiers, foaming agents, stabilizing agents and dispersants. The surfactants have huge importance in the diverse fields of our day-to-day life including pharmacy, food industry and cosmetic, cleaning
applications and controlled synthesis of nanostructured materials. Surfactants are classified as anionic, non-ionic, cationic or zwitterionic according to the charge nature of their polar head group. The non-ionic surfactants (e.g. decyl glucoside, polyoxyethylene glycol alkyl ether) have no charge on the head groups. The hydrophilic head of anionic surfactants (e.g. sodium dodecyl sulfate, ammonium lauryl sulfate) carry a net negative charge while charge on cationic surfactants (e.g. benzalkonium chloride, cetyltrimethylammonium bromide) is positive. The zwitterionic surfactants (e.g. cocamidopropyl hydroxysultaine) consist of a head with two oppositely charged groups. Similar to other amphiphilic molecules, surfactants also have unprecedented capacity to form self-assembled structures. Based on molecular geometry of surfactant molecule as well as solution conditions these structures may acquire different shapes such as spherical and cylindrical micelles, bilayer and vesicles (figure 1.5).

Figure 1.5. Different organized aggregates of surfactant (a) monolayer with micelles, (b) spherical micelle, (c) rod-like micelle, (d) reversed micelle, (e) bilayer and (f) vesicles.
(ii) **Biomolecules:** A biomolecule is defined as a molecule that is produced by a living organism and is involved in the maintenance and metabolism of living organisms [53-55]. The interactions of the biomolecules with each other constitute the molecular logic of life processes. The biomolecules are usually classified into four major groups, carbohydrates, proteins, nucleic acids and lipids. The carbohydrates are optically active polyhydroxy aldehydes or ketones or the compounds which produce such units on hydrolysis. The principle functions of carbohydrates include energy storage, cellular fuel, and structure formation. Proteins are made up of amino acids linked together by peptide bonds. Protein molecules can be found in every part of the body and constitute up to 75% of the dry weight of cells. The Nucleic acids are composed of nucleotides which function in the storage, utilization, and transmission of inherent genetic character. There are mainly two types of nucleic acids, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). Lipids are a diverse group of naturally occurring fatty or oily substances that are characterized by their insolubility in water and their solubility in nonpolar organic solvents. They form the major structural component of the plasma membrane and perform functions like cellular communication, signaling, storing energy etc.

Proteins are the most versatile biomolecule which underpin almost every aspect of biological activity and serve crucial role in essentially all biological processes [18, 53, 55]. Proteins perform several functions in living body such as catalytic activity, transportation, storage of other molecules, generating movement, transmitting nerve impulses and controlling growth. The function of a protein is decided by its three dimensional structure. Despite enormous functional diversity, all proteins are linear arrangement of twenty amino acid residues assembled together into a polypeptide chain. However, most proteins do not remain linear sequences of amino acids instead the polypeptide chain folds into a three dimensional characteristic shape.
spontaneously and adopts configuration that is the most stable for its particular chemical structure and environment. The protein structure may be understood in terms of four distinct conformations namely primary, secondary, tertiary, and quaternary (figure 1.6). Primary structure represents sequence of different amino acids. The secondary structure of protein molecules refers to the formation of a regular pattern of twists or kinks of the primary structure of the protein molecule stabilized by hydrogen bonds. The two most common types of secondary structure are called the α helix and β pleated sheet. Atoms in an α helix, arrange themselves in a helical pattern whereas in case of β pleated sheet instead of peptide links arranging themselves via twists and turns, they can have bond with other sheets of the polypeptide in a sheet-like fashion. The folding of secondary structure elements in a compact unit is called the tertiary structure stabilized by non-local interactions like hydrophobic interaction, salt bridging,
hydrogen bonding, disulfide bonding etc. A protein containing more than one polypeptide chain exhibits the quaternary structure. This condition arises for proteins larger than 150 residues.

(iii) Polymers and block copolymers: A polymer molecule consists of the same repeating units (sub-units), called monomers, or different but resembling units [19, 56, 57]. Polymers play a very vital role in human life as there exists lot of polymers in our body. Apart from this, other naturally occurring polymers like wood, rubber, leather and silk are of high importance in human life. Modern scientific tools have revolutionized the processing of polymers thus now synthetic polymers like useful plastics, rubbers and fiber materials are also available. The physical arrangement of monomer residues along the backbone of the chain decides the microstructure of a polymer. Polymers containing only a single type of repeat unit are known as homopolymers, whereas polymers having a mixture of repeat units are known as copolymers [figure 1.7]. The

Figure 1.7. Schematic of polymerization in (a) homopolymer and (b) copolymer.
properties of polymers are related to their constituent structural elements, their arrangement and chain length.

![Diagram of different block copolymer architectures and self-assembled micelle structure.](image)

**Figure 1.8.** Examples of (a) different block copolymer architectures and (b) self-assembled amphiphilic block copolymers into supramolecular nanostructure (micelle) in solution.

Block copolymers are one of the types of copolymers composed of two or more chemically distinct polymer chains (blocks) linked together at one or more junction points usually through covalent bonds [58, 59]. In this way, they represent a sequence of different polymer blocks connected in series. These block copolymers can be classified based on the
number of blocks and their arrangements. For example, block copolymers consisting of two blocks are called diblock whereas those with three blocks are triblock and similarly that containing more than three are called multiblock copolymer. On the basis of arrangement, the block copolymers may be categorized as linear, star-like, mixed arm and grafted polymers [figure 1.8 (a)]. As a consequence of the distinct properties of different polymer segments, block copolymers are known to shown rich phase behavior. In solution, block copolymers will form micelles when the solvent is selective for one of the blocks. Amphiphilic block copolymers that contain hydrophilic (PEO) and hydrophobic (PPO) blocks, self-assemble in aqueous solution [figure 1.8 (b)] and are capable of generating a variety of micro domain morphologies with different physical and chemical properties. The micellization process for block copolymers is mainly governed by two parameters, critical micellization temperature (CMT) and critical micellization concentration (CMC). Self assembly will not occur if either of these is not reached to the critical value and the block copolymer will remain as unimers in the solution.

The interaction of silica nanoparticles with four different macromolecules (surfactant, protein, polymer and block copolymer) has been investigated in this thesis (figure 1.9). The three types of surfactants examined are, anionic sodium dodecyl sulphate (SDS), nonionic decaoxyethylene n-dodecylether (C\textsubscript{12}E\textsubscript{10}) and cationic dodecyltrimethyl ammonium bromide (DTAB). These surfactants comprise same tail length but differ in charge on their head group. A small globular protein lysozyme is used as a model protein. It has molecular weight about 14.7 kD and iso-electric point about 11.4. The interaction of nanoparticles is examined with polymer polyethylene glycol (PEG) having different molecular weights and tri-block copolymer P85 [(EO)\textsubscript{26}(PO)\textsubscript{39}(EO)\textsubscript{26}]. The self-assembly of block copolymer is also used to tune the interaction of nanoparticle-block copolymer system.
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(a) Surfactant

Anionic surfactant sodium dodecyl sulphate (C_{12}H_{25}SO_{4}^-Na^+)

\[\text{H}_2\text{C}\]
\[\text{C} \ \text{O}\]
\[\text{S} \ \text{O} \ \text{O} \ ^+ \ \text{Na} \]

Cationic surfactant dodecyltrimethyl ammonium bromide [C_{12}H_{25}N(CH_3)_3^+ Br^-]

\[\text{H}_2\text{C}\]
\[\text{C} \ \text{O}\]
\[\text{N}^+ \ \text{CH}_3 \ \text{CH}_3 \ \text{Br}^- \]

Non-ionic surfactant decaoxyethylene n-dodecylether [CH_3(CH_2)11(CH2CH2O)10OH]

(b) Protein

Lysozyme

(c) Polymer

Polyethylene glycol (H-(O-CH_2-CH_2)_n-OH)
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(d) Block copolymer

P85 [(EO)_{26}(PO)_{39}(EO)_{26}]

Figure 1.9. Chemical structures of different macromolecules used in this thesis (a) surfactants, (b) protein, (c) polymer and (d) block copolymer.

1.4. Important interactions in nanoparticle and macromolecule systems

The nanoparticles and macromolecules individually can interact through a number of forces depending on the solution conditions. These interactions not only govern the properties of nanoparticle and macromolecule but also dictate the phase behavior of their complex system. The control over interaction parameters essentially enables the integration of the two components, implementation of complex structures for desired functions and tuning of their properties. The commonly present interactions in nanoparticles and macromolecules are

(i) Electrostatic interaction: The electrostatic interaction determines the resultant force between charged particles. In the case, if the particles are suspended in water or any other suitable solvent, dissolved ions modify the nature of electrostatic interaction and hence instead of direct electrostatic (Coulomb force) interaction, one finds a screened Coulomb force between the charged objects [60-62]. For two spheres of radius $R$ each having a charge $Z$ (expressed in units of the elementary charge) separated by a center-to-center distance $r$ in a fluid of dielectric constant $\varepsilon$ containing a concentration $n$ of monovalent ions, the screened Coulomb interaction is expressed as

$$
\frac{V(r)}{k_B T} = Z^2 \lambda_B \left( \exp(\kappa R) \right)^2 \frac{\exp(-\kappa r)}{r} \quad (1.1)
$$
where \( \lambda_B \) is the Bjerrum length and is given by \( \lambda_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_BT} \) denoting the interparticle separation at which the electrostatic interaction between the particles is comparable to the magnitude of thermal energy \( k_BT \). \( \kappa^{-1} \) is the Debye-Hückel screening length, which is expressed by \( \kappa^{-2} = 4\pi\lambda_B\varepsilon \). The strength of the force increases with the magnitude of the surface charge density or the electrical surface potential whereas range of the interaction is decided by the ionic strength of the solution [62].

The electrostatic forces are easily experienced in our daily life when hands are washed with soap, the skin becomes negatively charged by adsorption of soap molecules, and the slippery feeling is induced by the strongly repulsive screened Coulomb force. The electrostatic interaction between charged bodies (oppositely or similarly) is known to give rise to new types of versatile hybrid structures that have numerous advantages [22, 24, 63]. Many nonspecific associations especially relevant in biological systems (e.g. layer by layer self-assembly of nanoparticles and proteins in films, chromatin and protein complexes) are driven by electrostatic forces together with the other prominent processes such as formation of polyelectrolyte multilayer and coassembly of double hydrophilic block copolymers in the presence of oppositely charged species [22, 63-66].

The electrostatic forces are responsible for stability of charged colloids. According to DLVO theory the stability of a colloidal solution is determined by the sum of the van der Waals attractive \( (V_A) \) and screened Coulomb repulsive \( (V_R) \) interactions [62, 67, 68]. This theory proposes that there exists an energy barrier resulting from the repulsive force which prevents two particles approaching one another and adhering together. But if the particles collide with enough energy to overcome that barrier, the attractive force will pull them into contact where they adhere.
strongly and irreversibly together. Therefore, for dispersion to resist against flocculation it is essentiality required to have sufficiently high repulsion, and the colloidal system then only will be stable. Figure 1.9 depicts the typical variation of the total interaction energy with particle separation according to DLVO theory.

![Figure 1.9](image)

**Figure 1.9.** The variation of van der Waals attractive, electrostatic repulsive interactions and total interaction energy in a charged colloidal solution.

(ii) Steric repulsion: The stability of colloidal particles can also be achieved by steric repulsion. The addition of macromolecules such as polymer, surfactant etc. on particle surface prevents the approach of the particle cores to a separation where their mutual van der Waals attraction would cause flocculation and the particles are said to be sterically stabilized. The origin of steric repulsion lie in both volume restriction and interpenetration effects, although it is unlikely that either effect would occur in isolation to provide a repulsive force [62, 69, 70]. The two polymer covered surfaces when approach (separation distance is less than \( R_g \)) each other.
feels a repulsive interaction due to the overlap of the outer segments formed by polymer shells (figure 1.12). This repulsion results from the unfavorable entropy associated to the confinement of the polymer chains. The magnitude of the repulsion resulting from steric forces depends on the surface area of the particle occupied by the polymer and whether the polymer is reversibly or irreversibly attached to the particle’s surface.

**Figure 1.11.** Two particles sterically repelling each other through adsorbed polymer layer.

Thermodynamically, steric effects are the manifestation of an entropic contribution to the overall free energy. These effects can dictate the reaction pathways and rates in chemical synthesis due the restricted configurations in which particles/molecules can collide and successfully react. Steric forces are of paramount importance in nanotechnology where nanostructures are stabilized by coating of macromolecules [71-73]. In many cases the adsorbed macromolecules not only stabilize the nanomaterials against aggregation but also perform functions those required for different applications. For example, polymers or biomolecules adsorbed on nanoparticles apart from stabilizing the particles also interact with cell membranes during targeted drug delivery. Moreover, the steric stabilization improves the particle
sustainability in the biological milieu thus allowing prolonged circulation in blood. The coating of polyethylene glycol (PEG) is known to improve the biocompatibility of the magnetic nanoparticles while utilized in sensing tumor [72, 73].

(iii) Depletion interaction: The polymers can either stabilize colloidal particles by adsorbing on them or can destabilize the particles by remaining free in the solution. The non-adsorbing nature of polymer usually induces depletion interaction between particles. The Depletion interaction is known to arise between large colloidal particles that are suspended in a solution of smaller entities such as polymers, when the latter experience an excluded volume interaction with the former [74, 75]. The first successful model to describe the depletion interaction between two hard spheres as induced by dilute non-adsorbing polymer was developed by Asakura and Oosawa [75]. According to their theory, the mechanism that is responsible for the attraction originates from the non-adsorbing nature of the smaller particles (depletants) giving rise to a depletion layer around colloidal particles. This depletion layer can be understood as a layer around the bigger particle where smaller particle can not be found (figure 1.13). The available volume for the smaller particles increases when the depletion layers overlap. It implies that the free energy of the smaller particles is minimized in the states for which the colloidal spheres are close together. The effect of this is just as if there were an attractive force between the spheres even while the direct colloid–colloid and colloid–polymer interactions may both be repulsive. The depletion interaction is purely entropic in nature and the manifestation of the second law of thermodynamics. The gain in translational entropy of the smaller particles, owing to the increased available volume, much greater than the loss of entropy from flocculation of the colloids results into an overall positive change in entropy.
Depletion interaction leads to a variety of phase transitions in multi-component systems. For example, interesting phase transitions like vesicle-to-micelle transition of block copolymers, colloidal aggregation through macromolecules, and re-entrant solidification in colloid-polymer systems are driven by depletion interaction [76-79]. The importance of depletion interaction in many biological systems and processes has been recognized. In presence of biological macromolecules like proteins or lipids, the effects of depletion force are observed in cell membrane interactions [80]. The depletion interaction is realized as one of the responsible forces in forming helical structure in biopolymers [81]. The casein micelles are found to be becoming attractive in presence of exocellular polysaccharides [82].

**Figure 1.12.** Schematic of origin of depletion interaction.

**(iv) Hydrogen bonding:** The hydrogen bonding is a weak type of dipole-dipole attraction which occurs when a hydrogen atom bonded to a strongly electronegative atom such as nitrogen, oxygen, fluorine etc. exists in the vicinity of another electronegative atom with a lone pair of electrons [62, 83]. The electronegative atom (bonded with hydrogen) attracts the electron cloud of the hydrogen atom and by decentralizing the cloud, leaves a partial positive charge on hydrogen atom while creates a small negative charge on itself. The resulting charge on hydrogen
atom, however only partial, represents a large charge density because of the small size of hydrogen relative to other atoms. A hydrogen bond arises when this strong positive charge attracts a lone pair of electrons on another electronegative atom. These hydrogen-bond attractions can occur between different molecules (intermolecular) or within different parts of a single molecule (intramolecular). The strength of the hydrogen bond is about 5 to 40 kJ/mole which makes them relatively stronger than a van der Waals interaction, but weaker than covalent or ionic bonds.

**Figure 1.13.** Representation of various interactions including hydrogen bonding and hydrophobic interaction.

The unique and novel characteristics of water arise because of its hydrogen bonded structure. Hydrogen bonding determines the secondary and tertiary structures as well as functions of many biological molecules like DNA, lipids and proteins including enzymes and antibodies [84]. The hydrogen bonding among others is responsible for the double helical structure of DNA where hydrogen bonding between base pairs join one complementary strand to
the other. The tertiary structure of protein molecules is attained by hydrogen bonding between the backbone oxygens and amide hydrogens of the secondary structure (figure 1.13). Many synthetic polymers such as nylon attain remarkable strength due to hydrogen bonded structure within them. The hydrogen bond enables polymers sensitivity towards humidity of the atmosphere because the diffusion of water molecules can disrupt the network.

(v) **Hydrophobic interaction:** Hydrophobic interactions describe the relations between water and non-polar molecules (hydrophobes) [62, 85, 86]. The water molecules have high inclination to form hydrogen bonds with each other and this tendency influences their interactions with non-polar molecules which are incapable of forming the hydrogen bonds. The presence of such a non-polar surface into water causes interruption in the hydrogen bonding network between water molecules. The hydrogen bonds thus reorients tangentially to such surface to minimize disruption of three dimensional network of water molecules leading to a structured water "cage" around the non-polar surface. As a result, the non-polar molecules experiences an effective attraction leading to their aggregation in order to reduce the surface area exposed to water to minimize their disruptive effect. The mixing of fat and water is a good example of this particular interaction. These forces are of supreme importance in understanding surface phenomena which dependent on the properties of the non-polar solute as well as solution conditions.

Hydrophobic interaction governs many processes occurring in macromolecules such as micelle formation, protein conformation and biological membrane structure [85, 86]. The amphiphilic molecules form self-assembled structures because of hydrophobic interaction. Along with hydrogen bonding, the hydrophobic forces also contribute in the formation of folded protein structure (figure 1.13). The hydrophobic patches of alkly chains in proteins form a core where the chains are buried from water. The protein molecules while interacting with nanoparticles are
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reported to show the conformational changes possibly due to alteration in hydrophobic interactions. Similarly, other amphiphilic molecules have also been reported to show phase transitions in presence of nanoparticles. The lamellar phase formation in non-ionic surfactants has been shown to be controlled by presence of nanoparticles [87].

All or some of these forces may act in nanoparticle-macromolecule systems in a cumulative manner depending upon characteristics of nanoparticles and macromolecules as well as solution conditions. In case of interaction of anionic silica nanoparticles with charge stabilized macromolecules (e.g. proteins, ionic micelles), the resultant interaction is pre-dominantly governed by electrostatic forces. In case if the macromolecule is uncharged, the resultant interaction is a combination of non-electrostatic forces. For example, the changes in the hydrogen bonding or hydrophobic interaction present in the intermolecular structure of the macromolecule as induced by nanoparticles may lead to structural changes in the macromolecule. The adsorption of non-ionic surfactants (with groups like hydroxyl, phenolic, carboxylic) and polymers are known to driven through hydrogen bonding with variety of nanoparticles. The adsorbed macromolecules in general give rise to steric repulsion between nanoparticles. However, in many cases when macromolecules remain free, lead to depletion interaction driven phase transition in nanoparticle-macromolecule systems.

1.5. Techniques for the characterization of nanoparticle-macromolecule systems

In nanoparticle-macromolecule systems, the interest may lie in investigating the structural and interactional changes occurring in individual components as well as hybrid characteristics of their composites. For example, nanoparticle-surfactant system may either be examined for the stability of nanoparticles as influenced by surfactant or effect of nanoparticle on interfacial properties of surfactant or the resultant behavior of the complexes formed. Based
on the interest, the multi-components systems may be characterized by several techniques available in general for the characterization of materials, in one way or the other. The resulting information can be refined to yield images or spectra revealing the topographic, geometric, structural, chemical or physical details of the system. Different techniques providing complementary outcomes as per their sensitivity to the various physical parameters on different length scales are used. These techniques can be broadly classified into following four categories:

(i) **Spectroscopic techniques**: Optical spectroscopic techniques are means of studying the properties of the system by examining how the system emits and interacts with light. These techniques involve visible, ultraviolet and infrared light (alone or in combination) to extract the relevant information such as chemical compositions, bond strength and energy levels etc. The different techniques are usually based on absorption or emission of light by the material. Commonly used techniques include UV-visible spectroscopy, photoluminescence, infrared absorption and Raman scattering [20, 21, 24, 88]. While characterizing nanoparticle-macromolecule systems, the techniques generally look into the structural transitions and chemical bonding between the two components. For example, Raman and circular dichroism (CD) spectroscopy have been utilized to evaluate the extent of the protein deformation on interaction with nanoparticles [125]. Electron paramagnetic resonance (EPR) spectroscopy with spin–labeled proteins has been utilized to obtain insight into protein orientation on the nanoparticle surface [88]. Fluorescence spectroscopy has been adopted to investigate the self-assembly of the surfactants in adsorbed layers on particle surfaces and to obtain information on the polarity and viscosity of the interior of the layer as well as the aggregation number [20]. Electron spin resonance (ESR) spectroscopy and UV-Visible spectroscopy techniques have been used to calculate the adsorption isotherms of different macromolecules on nanoparticles [88].
(ii) Microscopic techniques: The microscopic techniques allow the direct visualization of the nanoparticle, macromolecules and their complex structures [89]. These techniques involves techniques like scanning electron microscopy (SEM), transmission electron microscopy (TEM), scanning tunneling microscopy (STM), and atomic force microscopy (AFM). The electron microscopic techniques involve interaction of electron beam with the specimen and the subsequent collection of transmitted or scattered electrons in order to create an image. This process may be carried out by scanning of a fine beam over the sample (e.g. scanning electron microscopy) or by wide-field irradiation of the sample (e.g. transmission electron microscopy).

One major difference between SEM and TEM is that TEM detects transmitted electrons whereas SEM detects backscattered and/or secondary electrons. While both techniques can provide topological, morphological and compositional information about the sample, TEM can provide crystallographic information as well. On the other hand, scanning probe microscopy involves the interaction of a scanning probe with the surface of the object of interest. A common characteristic of these techniques is that an atom sharp tip scans across the specimen surface and images are formed by either measuring the current flowing through the tip or the force acting on the tip. These techniques are widely used to characterize nano-scale materials including nanoparticle-macromolecule complexes. The AFM has been used to characterize protein corona around nanoparticle-surface whereas nanoparticle-DNA has been investigated by TEM [90, 91]. The major disadvantage of these techniques is the requirement of dried or frozen samples where macromolecules in general lose their native structures.

(iii) Macroscopic techniques: These techniques are widely used to measure the abrupt variation of macroscopic properties which in turn indicates the changes in microscopic properties. The mostly used macroscopic techniques are zeta-potential measurements, rheology, conductivity
measurements etc. Such techniques explore the different bulk properties of the system and hence are useful for predicting overall behavior of the nanoparticle-macromolecule systems. For example, the zeta-potential measurements provide useful information about surface charge of the particles, nanoparticle stability as directed by macromolecules and iso-electric point of the mixed system [24, 88]. If macromolecule adsorb on nanoparticles, the extent of nanoparticle coverage can also be determined by zeta potential measurements [88]. On other hand, visco-elastic properties of the macromolecules as influenced by nanoparticles can be determined by rheology [24]. The transitions in phase behavior of amphiphilic molecules like block copolymers/surfactants in presence of nanoparticles have been observed by viscosity and conductivity measurements [93].

(iv) Scattering techniques: Scattering techniques constitute powerful probes for studying nanoparticle-macromolecule systems. These techniques measure the scattered intensity as a function of wave vector transfer [93-95]. Different techniques based on different radiations (light, X-ray and neutron) have been extensively used. The important techniques used are X-ray diffraction, light scattering (static light scattering and dynamic light scattering) and small-angle scattering (small-angle X-ray scattering and small-angle neutron scattering). In each of these techniques the radiation is scattered by a sample and the resulting scattering pattern is analyzed to provide information about the structure (shape and size), interaction, ordering in the sample etc. These techniques can be applied over a wide range of length scales from 1 to 1000 nm. The different techniques are often used as a complementary tool with each other, providing detailed information about the system. Dynamic light scattering has been utilized to measure the hydrodynamic properties of the complex system. Small-angle X-ray scattering (SAXS) is useful for studying nanoparticle-macromolecule interactions where in particular at least one of the
components has higher electron density (Z value). Small-angle neutron scattering (SANS) with its unique advantage of contrast variation has been used to study multi-component complex structures at various length scales [20, 23]. This technique has also been used to study the nanoparticle-macromolecule systems in the present thesis. The details of SANS technique are provided in chapter 2.

1.6. Applications of nanoparticle-macromolecule systems

The integration of nanoparticles (having unique electronic, optical, and chemical properties) with macromolecules (which display unique recognition, catalytic, and inhibition properties) gives rise to novel hybrid functional composites possessing synergetic properties and functions. The addition of nanoparticles and macromolecules not only allows alteration in physical properties of the individual components but also implement several new features. These new and novel characteristics of the composites have been utilized in a variety of industrial and technical fields covering from biotechnology to optics to electronics. Some of important applications of nanoparticle-macromolecule systems in different areas are:

(i) Medicine: Nanoparticles due to their size which can gain access to the cells have emerged as important players in modern medicine with clinical applications ranging from contrast agents in imaging to carriers for drug and gene delivery into tumors [96, 97]. Their application to the medicine mainly comprises two objectives, the detection of the diseases by nano-scale diagnostic devices and their cure through targeted delivery system (nanomedicine). Both of these objectives require interfacing of the nanoparticles with macromolecules to carry the drugs for targeted delivery and for utilizing their sensitivity (in case of biomolecules) towards living cells during diagnosis and cure [21]. It has been now well accepted that cellular responses to materials in a biological medium deals with the adsorbed biomolecule layer, instead of the material itself but it
is only nanoparticles which takes the drug or the sensing device to the target. A drug delivery system, named as nanocell, comprising a nuclear nanoparticle functionalized with PEGylated-lipid envelope has been shown to be successfully delivering the drug to the tumor site [97]. The magnetic iron oxide nanoparticles, interfaced with a chemotherapeutic agent and guided by external magnetic fields were used to complete tumor remission [98]. A silica nanoparticle-block copolymer composite is shown to be more useful for drug delivery system compare to pure polymeric micelles [99]. In case of diagnostic devices, several types of sensors based on nanoparticle-macromolecule complexes such as chemical sensor, optical sensors, magnetic sensors etc. have been realized. A chemical nose sensor composed of nanoparticle-polymer composites has been utilized for protein detection [100]. The silver nanoparticle based nanoscale optical biosensor has been developed in order to examine the interaction between antigens and antibodies [101]. Superparamagnetic iron oxide nanoparticles functionalized with different biomolecules were used for cancer detection as magnetic sensors [102].

(ii) Electronics: The current interests in the research field of nanometer scale electronics deals with three fundamental issues, the operation of small-scale devices, schemes leading to their realization and eventual integration into useful circuits [103]. The Studies on quantum dots as well as on other nanomaterials have confirmed an increasing role for charging effects as the device size diminishes [104]. However, the construction of nanoscale circuits remains problematic, largely due to the difficulties of achieving interelement wiring and electrical interfacing to macroscopic parts of the overall circuits. In this regard, nanoparticles functionalized with different macromolecules have become prominent candidates for nanoscale electronics as the attached macromolecule can drive electrical interfacing [105]. A nanometer sized silver wire attached with DNA skeleton has been used to connect the two gold electrodes
Also the nano-clusters compositied with polymer chains have been utilized to control the electron transport between the electrodes [106]. Protein-mediated nanocrystal assembly has been demonstrated to be useful for flash memory fabrication [107]. In particular, the functionalized metal nanoparticles gathers additional attention in the electronics as they can display single-electron characteristics (e.g. quantized capacitance charging) and can be organized through external fields or through simple self-assembly methods. Nevertheless, in microelectronics and microsystems technology lithography, addition of nanosized ceramic fillers like SiO2 in to suitable photosensitive polymer based photo-resists improves the processing as well as resolution manifolds and enables the introduction of new electric properties [13].

(iii) Photonics: The surface geometry of nanoparticles (size, shape etc.) and the dielectric constant of the surrounding environment also play a crucial role in controlling the collective oscillations of the confined surface electrons (surface plasmon resonance) in metal nanoparticles [108, 109]. When a macromolecule interacts with these nanoparticles it alters the dielectric constant of the surroundings leading to the corresponding changes in the oscillation frequency of the electrons [13]. Consequently, optical properties of the nanoparticles (such as absorption and scattering) in presence of macromolecules show significant modifications which are being employed in various applications related to the photonics. For example, nanoparticles and polymer composites are shown to be useful for applications like solid state lighting, optical imaging and optical sensing. The large-area printings of optical gratings and 3-dimensional photonic crystals have also been demonstrated using nanoparticle-polymer Composites [110]. Further, it has been shown that the infiltration of nanoparticle-macromolecule in planar photonic crystals offer the opportunity to tune the photonic band gap which can be utilized for developing tunable photonic crystal based devices and hybrid light emitting diodes [111]. The interaction of
bimolecular on the surface of nanoparticles has been exploited to develop optical biosensors, which operate based on optical properties such as localized surface plasmon resonance, surface-enhanced Raman scattering and surface-enhanced fluorescence [108].

(iv) Energy: Nanoparticle-macromolecule composites also find applications in the field of energy through the systems like solar cells and batteries [13]. The use of inorganic solar cells has been limited due to the high costs imposed by fabrication procedures and other technical parameters. On the other hand, as an alternative to low cost, the organic solar cells that use organic macromolecules mostly polymers suffer to the limitation of low efficiency due to the low intrinsic carrier mobilities or low charge transport. One way to overcome these limitations is to combine organic polymers with inorganic material [13]. The nanoparticles combined with with polymers provide one of the alternatives to improve the efficiency of the solar cells. It has been shown that composites of nanoparticles like SiO$_2$, Al$_2$O$_3$, or TiO$_2$ with solar cell conductive polymers like polyaniline (PANI) and polythiophene (PTP) not only improve the efficiency of the solar cells but also provide stability against photo degradation in contrast to the case of pure polymers [112, 113]. Further, the metal nanoparticles like Ag and Au incorporated with polymers are also used to ameliorate the light adsorption capacity of the polymer cells [114]. The electrical storage systems like primary and secondary batteries also represent one of the important subsections of the field energy which has gained a worldwide significance for portable electronic devices [115]. The progress in lithium batteries relies mostly on the improvements in the electrolyte. Solid polymer electrolytes in this regard offer best desirable properties such as solid-state construction, simplicity of manufacturing, a wide variety of shapes and sizes, a higher energy density and usually inflammable etc [13, 115].
(v) **Food industry:** The protective coatings and suitable packaging of the food items are of prime importance in food industry because of their potential for increasing the shelf life of many food products [116, 117]. The materials presently used for food packaging are non-degradable, therefore generating environment related problems. Now a day, several biopolymers being eco-friendly are exploited to develop food packaging material. However, the limitations of use of biopolymers are their poor mechanical and weak barrier properties. Addition of reinforcing compounds (fillers) into these polymer matrices improves their strength by forming composites, but most of these reinforced materials have poor matrix–filler interactions which tend to increase with decreasing filler dimensions. The use of Nanoparticles having proportionally larger surface provides one of the alternatives by favoring the filler–matrix interactions and improving the performance of the resulting material. Besides nano-reinforcements, nanoparticle-polymer composites can add multiple functions, such as antimicrobial activity, enzyme immobilization, biosensing, reduce the packaging waste, preservation of fresh foods, act as reservoirs for the controlled release functions of drugs or fungicides etc.

(vi) **Miscellaneous:** The nanoparticle-macromolecule composites have also numerous applications in other areas apart from the discussed above. The nanoparticle-surfactant complexes in particular are useful in the industry related with interfacial process such as oil recovery, emulsification, paints etc [20]. The nanoparticle-polymer systems have shown their usefulness in magnetic devices like magneto-switches, charge transport and shape memory devices [13]. The chemical reactivity and catalytic process can also be controlled by these complex structures [13]. Further, these composites can be designed to have anti-fungal and bacteriostatic properties creating large positive impact on our environment and show useful contribution in our environmental sustainability [116]. The composites also known to show varying mechanical, thermal and elastic properties such as strength, thermal expansion, transition
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temperatures, elastic modulus etc. which can be of use as per requirements [13]. In all, the complexes of nanoparticle-macromolecule provide interesting systems to study them from the point of view of their wide range of fascinating applications.

1.7. Layout of the thesis

Many of the nanoparticle applications require their interfacing with macromolecules. The interfacing and resultant structure is decided by the various interactions such as electrostatic force, covalent, hydrogen bonding, non-polar and hydrophobic interactions in the system. The present thesis investigates evolution of interaction and structure of silica nanoparticles with different macromolecules (surfactant, protein, block copolymer and polymer) under varying solution conditions. These systems are characterized by small-angle neutron scattering (SANS), which is an ideal technique to study such multi-component systems. The thesis consists of seven chapters. In this chapter (chapter 1), a general introduction to nanoparticles and macromolecules, their possible interactions and applications have been presented. A brief discussion on different characterization techniques is also given in this chapter. The details of SANS technique and its usefulness are discussed in chapter 2. The Chapters 3 to 6 constitute results on the studies of silica nanoparticles interaction with different macromolecules namely surfactant, protein, block copolymer and polymer, respectively. The charged silica nanoparticles with varying size and different macromolecules with distinct properties are examined as model systems. The interaction and structure of nanoparticle with different charge state of surfactant is studied in chapter 3. Chapter 4 provides the study of protein adsorption on nanoparticles and their resultant structure. The depletion interaction between nanoparticles in presence of block copolymers is examined in chapter 5. Chapter 6 deals with the polymer dependent re-entrant phase behavior (one-phase to two-phase and back to one-phase) in nanoparticle-polymer system. The results of the thesis are summarized in chapter 7.