Wettability of Hair using Natural Surfactants in presence of Silver Nanoparticles as Additive

----

Thesis Submitted by

SANTOSH DEB BARMA (212CH1497)

In partial fulfillment for the award of the Degree of

MASTER OF TECHNOLOGY

IN

CHEMICAL ENGINEERING

Under the guidance of

Dr. SANTANU PARIA

DEPARTMENT OF CHEMICAL ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA-769008

May, 2014

CERTIFICATE

This is to certify that the thesis entitled "**Wettability of Hair using natural surfactant in presence of silver nanoparticles as additive**," submitted by Santosh Deb Barma (212CH1497) for the requirements of award of Master of Technology in Department of Chemical Engineering of National Institute of Technology, Rourkela under my supervision.

<div align="right">

Dr. Santanu Paria

National Institute of Technology

Rourkela, Orissa-769008

</div>

Date-22/05/2014

ACKNOWLEDGEMENT

I wish to express my deep sense of gratitude and indebtedness to Prof. Santanu Paria, department of Chemical Engineering, NIT Rourkela for introducing the topic and for their inspiring guidance, constructive criticism, and valuable suggestion throughout this project work.

I want to acknowledge the support and encouragement given by Mr Rajib Ghosh Chaudhuri, Mr. Siddhartha Sankar Boxi, Praneeth Rao, Rahul Purbia, Nainsi Sexana, Khushi Mukherjee and Mr. K. Jagajjanani Rao throughout the period of the my lab work.

I owe a depth of gratitude to Prof R. K Singh, H.O.D. of Chemical Engineering department, National Institute of Technology, Rourkela, and all other faculties for all the facilities provided during the course of my tenure.

I thank my parents and family members for the support, encouragement, and good wishes, without which I would not have been able to complete my thesis.

Date- 22/05/2014   **SANTOSH DEB BARMA**
                                                                                                          212CH1497

Contents   **Page No.**

ABSTRACT

The adsorption of surfactant molecules and nanoparticles at the air-liquid and solid-liquid interface play an important role in reducing surface tension and interfacial tension respectively thereby increasing wetting properties to a reasonable mark. Therefore, the combination of both i.e. surfactant as well as nanoparticles in an aqueous phase can be of great interest to investigate the wettability of hair surface. Consequently, in this report, the experimental studies were conducted to study the solution behavior of acacia (natural surfactant) solutions and its wettability on hair surface in absence and presence of silver nanoparticles (Ag NPs) as additive. Natural surfactants have been chosen over synthetic one because of its biocompatibility, biodegradable, nontoxic, and nonionic natures. The nanoparticles used in this study were synthesized by chemical route from $AgNO_3$ using $NaBH_4$ in acacia medium where $NaBH_4$ and acacia acts as a reducing and capping agent respectively. Moreover, insitu synthesis of silver nanoparticles (Ag NPs) using acacia was also done and performed wettability studies on hair and the obtained results was compared with the previous results. Characterizations of nanoparticles were performed with UV-Vis and FESEM to confirm the particles and its size. Physicochemical properties such as critical micellar concentration (CMC) and surface tension, contact angle, work of adhesion and surface energy of hair have been estimated and discussed. Characterization of hair surface was also done to study the surface roughness using AFM respectively.

.

Keywords: Acacia, wetting, Ag NPs, CMC, contact angle, work of adhesion, surface energy, surface tension

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

γ	Surface tension
Γ	Surface excess
θ	Contact angle
γ_{SV}	Interfacial tension between solid and air
γ_{SL}	Interfacial tension between solid and liquid
γ_{LV}	Interfacial tension between liquid and air
Γ_{SG}	Surface excess between solid and gas
Γ_{SL}	Surface excess between solid and liquid
Γ_{LG}	Surface excess between liquid and gas
W_A	Work of adhesion
A_{min}	Surface area per molecules
N_A	Avogadro number
R	Universal gas constant
γ_l^d and γ_l^p	Dispersion and polar components of the surface tension
γ_s^d and γ_s^p	Dispersion and polar components of the surface energy of the solid
γ_l	Surface tension of liquid
γ_S	Surface energy of solid
A_h	Hamaker constant
ΔG	Gibbs's free energy

NOMENCLATURE

CMC	Critical Micellar Concentration
DCA	Dynamic Contact Angle
OCA	Optical Contact Angle
CA	Contact Angle
Ag NPs	Silver Nanoparticles
AFM	Atomic Force Microscope
FESEM	Field Emission Scanning Electron Microscope
UV	Ultraviolet
CTAB	Cetyl Trimethyl Ammonium Bromide
AOT	Aerosol-OT
TX-100	Triton X-100
MEA	Methyl Eicosanoic Acid
DDABDT	Dimethyl Pabamidopropyllaur Dimonium Tosylate
XRD	X-ray Diffraction
TEM	Transmission Electron Microscope
ALS	Ammonium lauryl sulphate
SLS	Sodium Laureth Sulphate
SKC	Stearal Konium Chloride
BKC	Benzal Konium Chloride
DLS	Dynamic Light Scattering
OWK	Owens-Wendt-Kaelble

Chapter 1

Introduction

Abstract: This content includes the basic understanding of surfactant and its different classification, properties and application. Some of the broad areas of surfactants are briefly discussed along with their unique characteristics in this section.

1.1 Introduction to surfactants

SURFACTANT is contracted from the term <u>SURF</u>ace <u>ACT</u>ive <u>Age</u>NT which has a wide variety of utility manifested by their application in detergency, emulsification, capillary penetration, solubilization and wetting. In general, surfactant may be defined as a compound that, when present in the system at low concentration, has the ability to adsorb onto surfaces or interfaces of the system and alter its free energy to a marked degree. This change in interfacial free energy strongly reduces surface tension of the system. The property of surfactants responsible for this phenomenon is its amphiphilicity meaning they contain both hydrophilic as well as hydrophobic group/part. The hydrophobic part is a long chain hydrocarbon residue or any oxygenated hydrocarbon whereas the hydrophilic group could be an ionic or any highly polar group. The electrical charge of the head group of a surfactant may serve as a convenient basis of classification of these compounds.

1.1.1 Synthetic Surfactant: classification, properties, application

Depending on the nature of the charge, synthetic surfactants may be broadly classified as anionic, cationic, nonionic, zwitterionic, and gimini. An *anionic* surfactant is characterized by a structural balance between hydrophobic tails (e.g., paraffinic chain, alkyl substituted benzene or naphthalene ring) and negatively charged hydrophilic head (e.g., carboxyl sulfate, sulfonate or phosphate). In *cationic* surfactant, the same hydrophobic tails may be balanced with a positively charged hydrophilic head (e.g., quaternary ammonium, sulfonium, phosphonium and iodonium). *Zwitterionic* surfactant also known as "amphoteric" contains both anionic and cationic hydrophilic group attached to the same molecules. This has very less significant practical use in any application at present scenario. *Nonionic* surfactant bears no apparent ionic charge whose hydrophobic group is balanced by non-ionized hydrophilic group such as polymerized ethylene oxide or polyhydric alcohols. *Gemini* surfactant also known as "*dimeric* surfactant" is an amphiphile made up of two hydrocarbon tails and two ionic groups linked by a 'spacer'. Some of the examples of the surfactant based on the above classification are discussed below.

Table 1.1: Broad classification of surfactants based on their head charge.

Surfactants	No. of Head Group & Charges	Examples
Anionic	One head group (Negatively charge)	AOT, Alkanol B, Igepon T
Cationic	One head group (Positively charge)	CTAB, Ceepryn, LPC
Non ionic	One head group (Neutral charge)	TX-100, Igepal-630, Span 80
Gimini	Two head group (Positive, negative or neutral charge)	$[C_{12}\text{-}C_6\text{-}C_{12}]Br_2$
Zwitterionic	Both positive and negative charges	DDABS, Amino acid

Most of the surfactant shows its unique features due to different charges to its hydrophilic portion of the molecules. Most of the surfactant shows its effect in an aqueous medium. Different factors like micelles shape and size, adsorption of surfactant molecules at the interfaces, working temperature etc. decides the properties of the surfactants. Various reputed surfactant based industries had shown different, valuable, and unique properties of various surfactants. Among various industrial base surfactants, let us briefly discuss some properties of different surfactants taking three examples of mostly used surfactant from industrial point of view as follows:

Table 1.2: Properties of most commonly used synthetic surfactant (Glassman et al; 1948)

Surfactant Type	Trade Name	Manufacturer	Chemical Description	Surface Tension (Dynes/cm at 25˚C) at following concentration (in %)				
				1.0	**0.1**	**0.01**	**0.001**	**0.0001**
Anionic	Aerosol OT (AOT)	American Cyanamid	Dioctyl sodium sulfo-succinate	26.3	29.9	43.0	56.8	63.0
	Alkanol B	du Pont	Alkyl-naphthalene sulfonate	31.8	44.1	61.3	70.6	71.5
	Igepon T	General Dye-Stuff	Sodium salt of amide of oleic acid and	27.7	29.6	35.7	55.4	71.0

			methyl taurine					
Cationic	CTAB	J. T. Baker	Cetyl- trimethyl ammo- nium bromide	33.9	35.3	46.5	65.9	70.5
	Ceepryn	Merrell	Cetyl- pyridiniumchl o- ride	38.5	40.7	51.2	67.0	69.8
	LPC	Hooker	Lauryl- pyridinium chloride	40.8	38.0	55.7	68.7	71.3
Non-ionic	Triton A-20	Rohm and Haas	Polyether alcohol	33.7	36.2	43.5	59.3	71.3
	Igepal CA	General Dye- stuff	Polymerized ethylene oxide condensation	30.3	30.2	40.7	59.7	71.0
	Span 80	Atlas Powder	Sorbitan mono-oleate	29.0	29.5	30.7	57.5	71.4

Widely known applications of the surfactant has been reported in the literature which includes the broad areas like ore floatation, detergency, oil recovery, soil remediation, foam and froths, health and personal care products like shampoo, soap, conditioner and detergents, food industries, crop protection, petrochemical industries for reducing oil interfacial tension, pharmaceutical industries, oil and paint industries and so on.

1.1.2 Natural surfactant

Major classification of natural surfactants includes oleochemicals surfactant, microbial surfactant and plant surfactant. *Oleochemical surfactants* are mainly derived from plant oils (e.g. palm and coconut oil) and animal fats (e.g. tallow and fish oil) and have significant effect on cleaning, especially under mixed surfactant systems. In the recent years, vegetable oils have gained more importance over animal and fish oils. *Microbial surfactants* are membrane associated surface active agent or compound, commonly known as biosurfactants which are mainly produced by the action of yeast, fungi, and bacteria. Most of the biosurfactants are ionic as well as nonionic in nature and believed to have antiviral and antibacterial property. Biosurfactant has several advantages over synthetic surfactant which include diversity in properties, production of these biosurfactants from renewable resources, biodegradability, and biocompatibility. *Plant surfactants* are the surfactant derived from the plant fruits, stem, or seeds. It is superior over synthetic surfactants in terms of biocompatibility, biodegradability, nontoxic and nonionic nature. Among various plant based surfactant available in Indian subcontinent, acacia, reetha and shikakai are the commonly used surfactants.

1.2 Wetting and its importance

Wetting of solid substrate have been a topic of great interest in concern to its application in various industrial purpose. Wetting of the surfaces may be understood as the ability of the liquid to spread over the solid surface under the action of interfacial force at a three phase contact line. A huge number industrial applications such as froth flotation, oil recovery, oil agglomeration, solid–liquid separation in wetting medium, surface cleaning, dust abatement, coating, adhesion, printing and detergency demand a basic understanding of the wetting process, and the parameters affecting process. Wetting is directly related with the measurement of contact angle as well as surface tension of the liquid which if measured can explain the basic of wetting phenomena.

The term "wetting" commonly refers to the replacement of air with liquid over a solid surface. Wetting involves the interaction of a liquid with a solid. However, it can be the spreading of a liquid over a solid surface, the penetration of a liquid into a porous medium, or the displacement of one liquid by another. It can help to characterize surfaces and to determine

solid/liquid interactions. Wettability is most often described by putting a sessile or resting drop on solid and the contact angle (θ) as a measure of Wettability. A lower contact angle indicates better wettability where as high contact angle indicates poor wettability. When contact angle is 0°, it said to be complete wetting i.e., solid has strong affinity towards the liquid and when contact angle is about 180°, it is said to be non-wetting, i.e., solid has no affinity towards liquid. But these are ideal cases and are not found in nature, whereas in actual contact angle lies between 0°and180°.
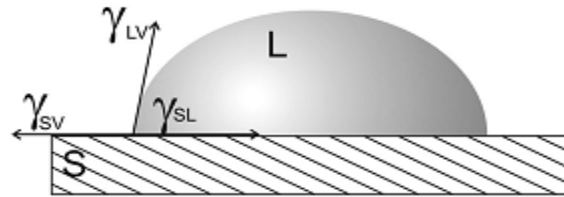
Figure 1.1: Diagrammatic representation of wetting phenomenon (Young's equation).

Young's Equation can be expressed as

$$\gamma_{LV} \cos \theta = (\gamma_{SV} - \gamma_{SL}) \tag{1}$$

θ= contact angle;

γ_{SV} = Interfacial tension between solid-air;

γ_{SL} = Interfacial tension between solid-liquid;

γ_{LV} = Interfacial tension between liquid-air;

1.3 Effect of surfactant on wettability

Extensive research has been performed on the wettability of various hydrophobic and hydrophilic surfaces using different surfactant solutions. Surfactant are composed of heterogeneous and long-chain molecule containing both hydrophilic (head group) and hydrophobic moieties (tail). When surfactant molecules are mixed in an aqueous system, the molecules tends to spread inside the aqueous system under the action of Brownian motion. Subsequently, surfactant molecules results in the formation of micelles of different shapes (e.g.

spherical, cylindrical etc.) into the system till critical micelle concentration (CMC); beyond which no further formation of micelle are possible. Eventually, some of the surfactant molecules would also go to the air water interface, hence reducing the surface tension at the air water interface. Surface tension plays an important role in wetting phenomenon. The reduction in surface tension increases wettability of hydrophobic surfaces whereas for the case of hydrophilic, wettability may increase or decrease depending upon the property of the materials. Apart from the effects of surface tension, adsorptions of surfactant at the solid liquid interface also increase the wettability of any surfaces. The adsorption of surfactant molecules at the solid-liquid interface shifts the three phase contact line thereby reducing the contact angle.

1.4 Effect of nanoparticles on wettability

Introduction of nanofluid in the surfactant solution has been studied by the many researchers where surfactants act as a capping agent. Generally nano-coatings are the favored methodology to modify surface properties like roughness and surface energy. An alternative way to improve wettability of the surface, where coating is not appropriate can be done by the use of nanoparticle suspended in fluids (nanofluid). The wetting behavior of nanofluid is more than the wetting behavior of the fluid (without nanoparticle) by itself on a given surface. The mechanism is based on the fact that the spontaneous wetting and spreading of the nanoparticles is influenced by the structural disjoining force arises due to nanoparticles ordering in the confined wedge film. This disjoining pressure is predominant at the vertex of the wedge film which shifts the position of three phase contact line and enhance spontaneous wetting. Various components of disjoining pressure gradient such as van der Waals, electrostatic and salvation forces are held responsible for dynamic mechanism of spreading. The effect of nanoparticles on surface tension and contact angle has been an important topic of research in the field of surface and colloid sciences for nearly a decade now.

Chapter 2

Background Literature

Abstract: Various literature based on wettability of hair surfaces have been studied and presented over here. The brief explanations on morphological structure of hair as well as the effects on nanoparticles on hair surface were also presented in this section. This content contains the fundamental details of wetting, parameters affecting wetting, effects of surfactants and nanoparticles on wetting and properties of the materials affecting wetting.

2.1 Wettability of hair surface

The surface wettability of hair has been an immense interest in the cosmetic and health care industry because of its profound application in manufacturing shampoo, conditioner, or other care products. The wettability of hair surface is greatly influenced by the presence of surface energy. High surface energy corresponds to high wettability whereas low surface energy corresponds to low wettability. Generally, hair surface have low surface energy and hence this corresponds to low wettability thereby conferring it to be hydrophobic. Even though some of the researchers have studied on wettability of hair surface, the actual phenomenon is still complex and complicated. In 1997, Kamath and coworkers have started working on the wettability of dark brown European ethnic based hair fiber in presence of water under different condition using wilhelmy balance method. They have shown that most of the hair fiber contains keratin protein up to 85-95 % which is hydrophobic in nature, hence responsible for the hydrophobicity of hair surface. In order to measure wettability in terms of the contact angle, a strand of hair were divided into various sections starting from the tip of the hair as A and ending at the root of the hair.

Table 2.1: Contact angle of water against hair surface measure along the length of hair fiber (Kamath et al.; 1997).

Fiber section	θ_H (degrees)	θ_V (degrees)
A	72	64
B	73	68
C	67	68
D	99	81
E	101	76
F	103	89

It can be seen from the above Table 3 that hair tip is more hydrophilic than the root of the hair. This is certainly because of damage of keratin protein by the action of ultraviolet ray of the

sun or may be due to the mechanical stress of the hair due to rubbing and combing. Among the early researcher, Kamath and his coworkers were the first to perform various experiments on the hair fiber and hence, published a series of papers explaining the different parameters affecting the hair fiber, wetting properties of keratin fiber in presence of water and its geometrical and structural explanation. Wetting force curve (advancing and receding) for human fiber in presence of water have been studied by Kamath et al and presented below.
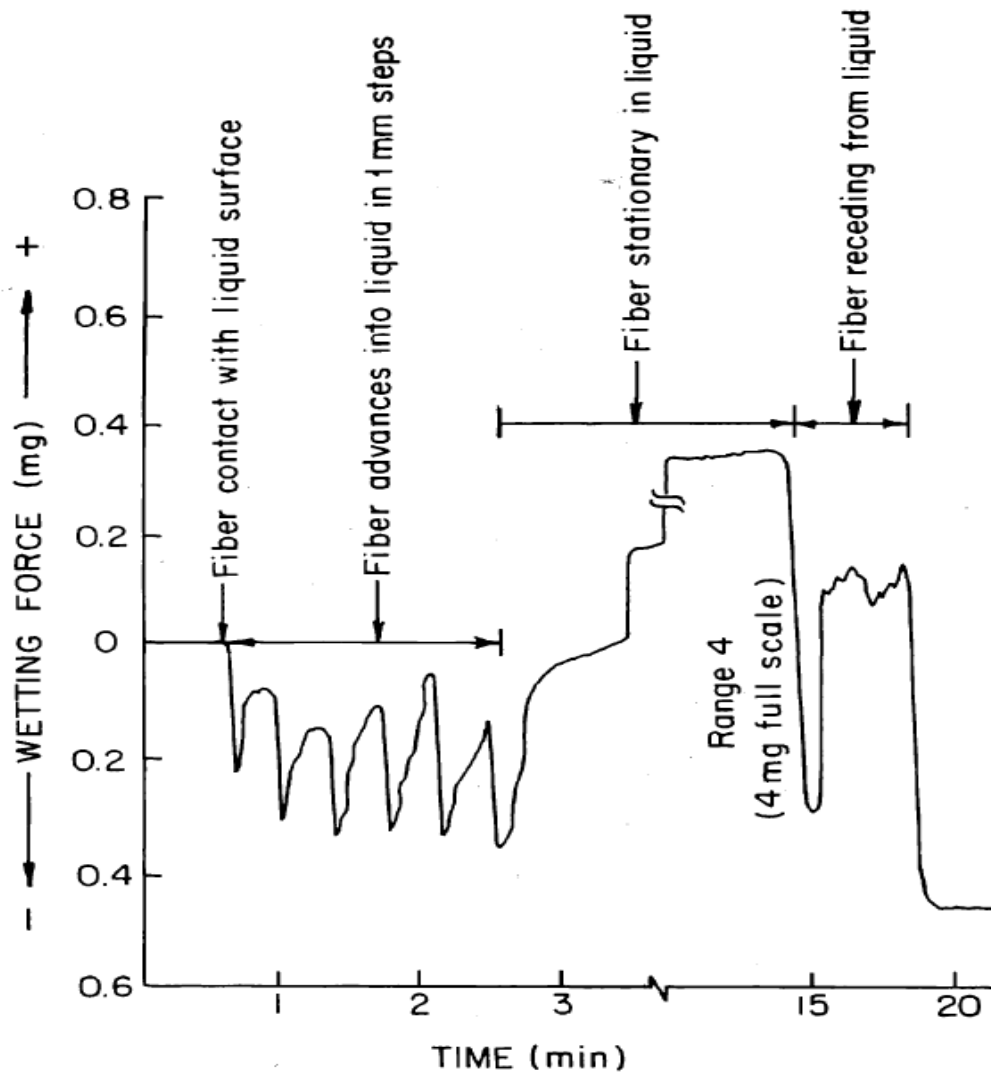
Figure 2.1: Wetting force curve (advancing and receding) for human fiber in presence of water (Kamath et al.; 1997).

Dupres et al (2006) have studied the electrical properties and wetting behavior of human hair surface using atomic force microscopy (AFM) at a nanometric scale. The topographic image of untreated hair surface explained by Duores et al (2006) are presented below
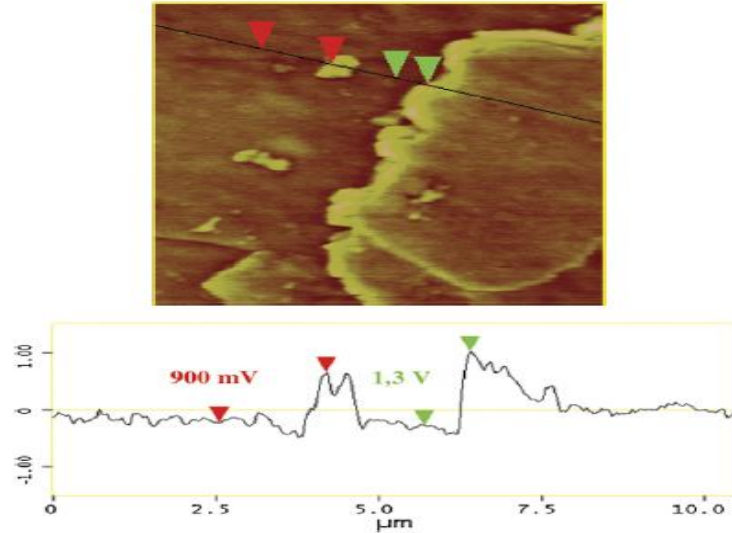
Figure 2.2: Surface potential image and corresponding cross section profile of natural untreated hair (Duores et al.; 2006).
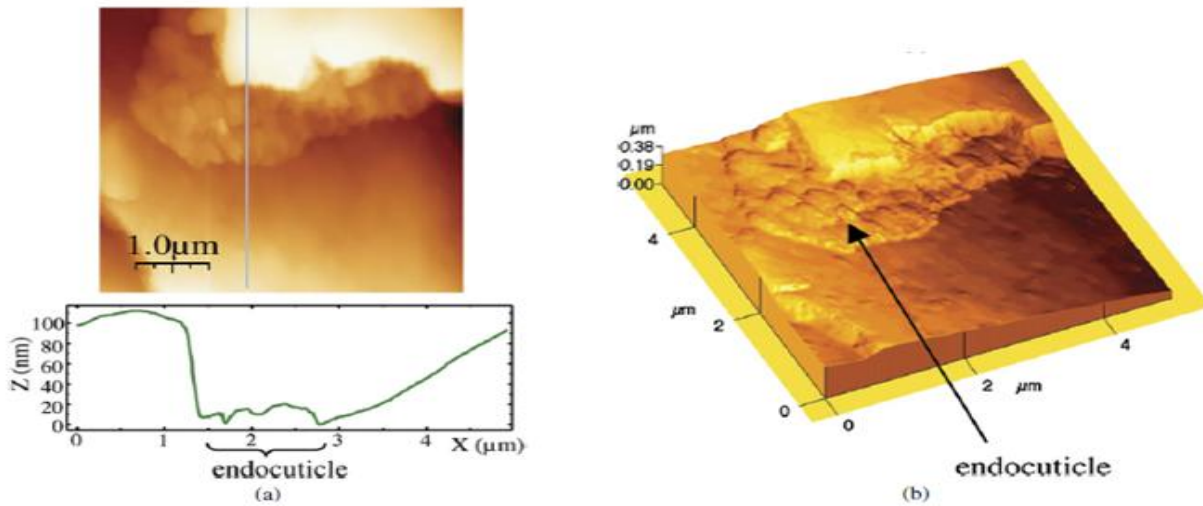
Figure 2.3: (a) A topographic image and corresponding cross section profile; (b) the three dimensional perspective associated (Duores et al.; 2006).

This studies shows that the hair fiber contains protein like 18-MEA which is responsible for the hydrophobicity of hair fiber. The removal of 18-MEA results in the hydrophilic nature of

hair surface microscopically where as it remains hydrophobic even all the other fatty acids got extracted.

The most excellent and explainable works on wettability of hair surface by means of dynamic contact angle using Wilhelmy plate method have been discussed by Lodge et al (2006). To study the contact angle of thin hair fiber, Lodge at el (2006) has found that the advancing direction is the most appropriate and reliable than receding direction. The summary of the advancing contact angle measurements measured by Lodge et al (2006) is presented below.

Table 2.2: Summary of the average advancing contact angle values on different samples (Lodge et al.; 2006).

Sample	Contact angle (θ)	
	Dry	Soaked
Virgin	103 ± 4	98 ± 2
Virgin treated	88 ± 9	92 ± 1
Chemically damaged treated (one cycle)	70 ± 7	70 ± 8
Chemically damaged treated (three cycle)	79 ± 1	84 ± 2
Asian	95 ± 4	72 ± 4
African	92 ± 11	-
Mechanically damaged	80 ± 14	-
Virgin-with scale (WS) orientation	85 ± 10	-

It can be seen from the above Table 2.2 that the initial contact angle on untreated virgin hair using pure water is found to be 103˚. This highly shows that presence of sebum (typical fatty acid) on to the hair surface. Therefore, further rigorous alcohol wash of the hair fiber shows a drastic fall of contact angle from 103˚ to 88˚. This decrease in contact angle might be due to the removal of sebum or other unwanted particles due to alcohol wash. More recent works have been done by Ran et al (2008) on the adsorption behavior of cationic surfactant on the hair fibers. In this study, dimethyl pabamidopropyllaur dimonium tosylate (DDABDT) was chosen to investigate on the wettability of human hair surface. Initially, with the increasing concentration of the DDABDT, the contact angle decreases drastically and becomes constant at CMC (0.05mM/L). The graph plot between the contact angle (θ) and equilibrium concentration (mol/l) for this study are presented in Figure 2.4 below.
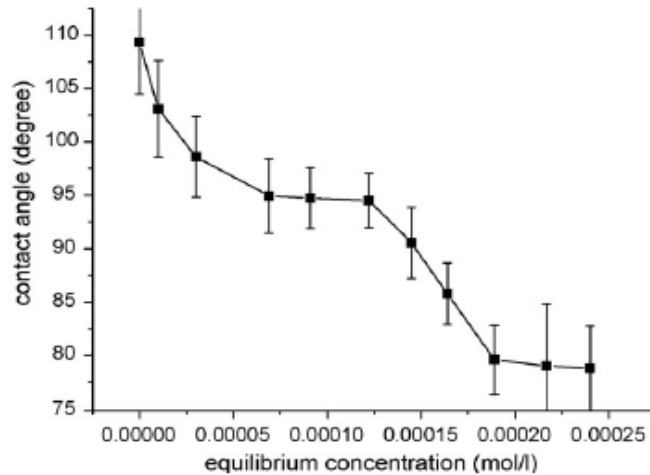
Figure 2.4: The effect of DDABDT surfactant on contact angle (Ran et al.; 2008).

2.2 Wetting behavior of nanofluids

Nanofluids are the recent hot topic of modern day because of its outstanding and unique features to modify the surface properties. Among all the technological application, nanofluids play an important role in the wetting and spreading dynamics of any solid substrates. In a broad sense, nanofluid may be defined as the suspension of nanometric-sized particles. Comparing to a pure fluid, nanofluids shows a valuable effects on the surface properties such as enhancing the optical properties of the substrate. Sefiane et al (2008) have discussed on the effect of nanofluids solution on the movement of contact angle which is possibly due to the interaction between particle-particle, particle-solid and particle fluid in a nanofluids. It has also been reported that nanoparticle concentration and size further alters the wettability to a certain large extent. Large concentration of nanoparticles highly enhances wettability by reducing the contact angle to a certain limit beyond which contact angle again increases which may be due to the agglomeration of particles resulting in large size particles. Moreover, small particle size also plays an important role in enhancing wettability by raising the structural pressure gradient from the nanoparticle ordering at the base of the solid-liquid interface.

Munshi et al (2008) have reported the effect of nanoparticle size on the contact angle where the static contact angle is measured on the indium oxide nanoparticles coated silicon substrate of different concentration. The structural property and surface morphology have been studied using the XRD method and TEM analysis respectively. Surface energy has been measure

13

using the two test liquid method (Owens method). The results obtained by Munshi et al (2008) are tabulate below as:

Table 2.3: Variation of contact angle and surface energy of the indium oxide nanoparticles of different size (Munshi et al.; 2008).

Nanoparticle size (mm)	14 ± 5	87 ± 6	210 ± 5	620 ± 4	Thin film
Contact angle with water (deg)	24	50	57	67	68
Contact angle with DEG (deg)	15	31	45	50	60
Surface free energy (10^{-3} N/m)	68.96	48.67	43.23	35	34.38
Disperse part (10^{-3} N/m)	7.86	12.28	9.26	11.71	6.67
Polar part (10^{-3} N/m)	61.09	36.39	33.97	23.28	27.7

Vafaei et al (2011) investigated and introduces the asymptotic contact angle as an important criterion which affects the wettability of the surface. This study has been performed using bismuth telluride nanoparticles coated silicon wafer and glass substrate on which the contact angles were measured. It has been found that the asymptotic contact angle does not depends on the gravity; rather it depends on the physical properties of solid, liquid, gas and nanoparticles as well. The change in asymptotic contact angle can be seen from the graph mention below.
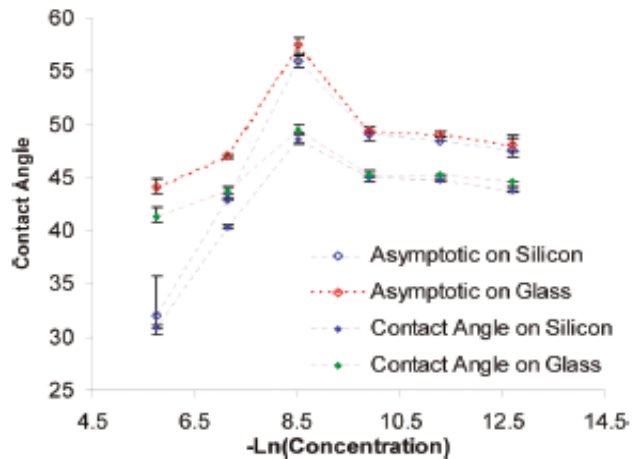
Figure 2.5: Variation of asymptotic contact angle for 2.5 nm bismuth telluride (Vafaei et al.; 2011).

According to Wasan et al (2003), spreading and adhesion of nanofluids on a solid surface modify its structural and optical properties to a great extent. In this study, the transition system has been divided mainly into two regions namely wedge region and aqueous region. When a nanofluids containing oil/liquid drop are dispersed on any solid surfaces, there exists a transition region between liquid film and bulk meniscus. This region is termed as wedge.
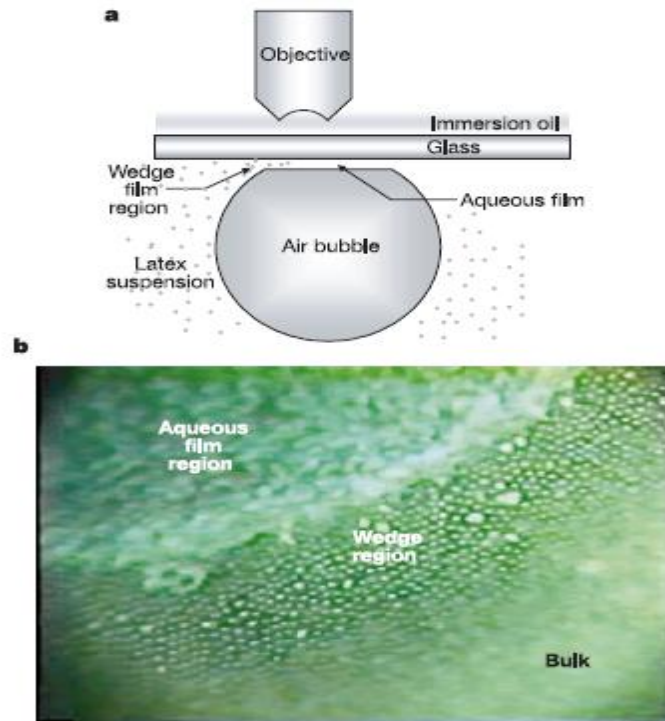
Figure 2.6: (a) Diagram of experimental set up (b) Nanoparticles structuring in a wedge region (Wasen et al.; 2003).

The mechanism is based on the fact that the wetting and spontaneous spreading of the nanoparticles is influenced by the structural disjoining force arises due to nanoparticles ordering in the confined wedge film[30]. This disjoining pressure is predominant at the vertex of the wedge film[31] which shifts the position of three phase contact line and enhance spontaneous wetting. Various components of disjoining pressure gradient such as van der Waals, electrostatic and salvation forces are held responsible for dynamic mechanism of spreading[3]. The effect of nanoparticles on surface tension and contact angle has been an important topic of research in the field of surface and colloid sciences for nearly a decade now[26, 27, 28, 30, 33].

Most recent statistical and experimental studies on wetting and spreading of nanofluids on any solid surfaces were conducted by Kondiparty et al (2011). This study explained the mechanism of spreading dynamics for the first time that the complete wetting and spreading of nanofluid which arises due the structured nanoparticles ordering in the wedge film is possible by decreasing the size of nanoparticle and interfacial tension respectively.
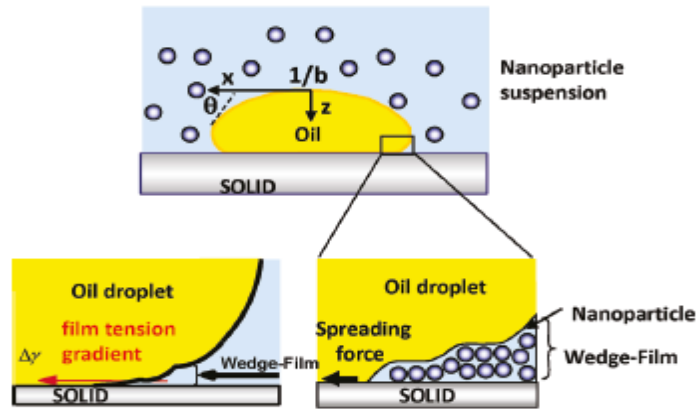
Figure 2.7: Nanoparticles structuring in the wedge film resulting in the structural pressure gradient (Kondiparty et al.; 2011).

The ordering of the nanoparticles increases the entropy of the overall dispersion to a maximum which further change the structuring of the particles. This ordered structure exert excess pressure or disjoining pressure in a film relative to bulk solution, which further separates the oil and solid surfaces confining the nanofluid. It should be noted that the disjoining pressure at the edge of the vertex of wedge film is maximum.
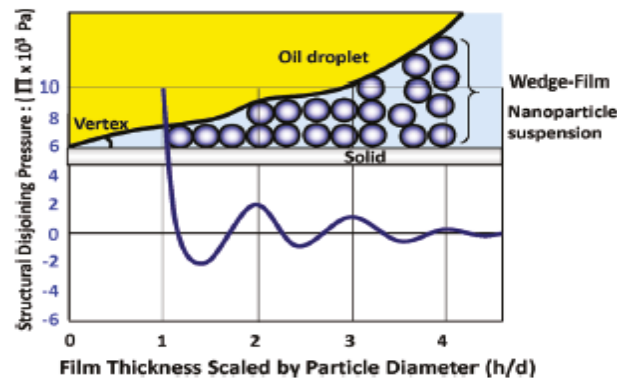
Figure 2.8: Structural pressure on the wall of wedge for 0.5˚ contact angle at the vertex (Kondiparty et al.; 2011).

2.3 Motivation of the project

Hairs are composed of keratin protein of about 90-95%, which contains negatively charged fatty acids i.e. amino acids, responsible for the hydrophobicity of hair surface. This fatty acids, sometimes known as sebum acts a protective layer over the cuticles of hair surface which protect it against ultraviolet rays and mechanical stress. However, extensive secretion of sebum onto the cuticles makes hair look dirty and greasy. Moreover, extreme accumulation of sebum causes hair strands to stick together by locking of hair strands. Dust, pollens, and dandruff may also attach with the sebum causing the hair dull and weak. Therefore, regular cleaning of hair is necessary for the healthy looks and satisfaction of the human need. This directs the researchers to study the wettability of hair in presence of various types of surfactant.

To this regards, various hair cleaning agents such a shampoo, conditioner, and fruit beer hair cleaner are available in the markets. Among all this, shampoo is the most commonly used agent for cleaning purpose. Shampoo mostly composed of various anionic surfactants like Ammonium lauryl sulphate (ALS), Sodium laureth sulphate (SLS) and so on which are more anionic than the amino acids present in the sebum, which helps in removing the hydrophobic sebum thereby making it hydrophilic. Rigorous shampoo wash remove essential natural oils needed for the hair to look good and shiny. Therefore, application of conditioners which mostly contains cationic surfactants like stearal konium chloride (SKC), benzal konium chloride (BKC) after shampoo helps in regaining the looks and shiny of the hair, thus making it easier to comb.

Most of the shampoos are composed of synthetic surfactants, which pose an environmental issue in disposal after its usage, since they are ionic in nature, non-biodegradable and non-biocompatible. Environmental unfriendly and relative high cost of the synthetic surfactants has made the researcher to find the alternative, leading to the discovery and formulation of natural surfactants based shampoos. In this regard, surfactants extracted from animal fats sources, microbial sources and plant sources have come in the limelight. However, the advantages of using plant based surfactant over surfactant extracted from microbial sources commonly known as bio-surfactants are many folds, which include easy way of extraction, cheaper cost of production, abundant resources and so on. Acacia, reetha, shikakai, neem etc were some of the plant based cleaning agents used by the people of Indian sub-continent for a very long period of time, since they does not possess any significant side-effects, by virtue of being natural products. However, Plant surfactants being organic are very prone to microbial

attack in an open environment and thus cannot be stored in solution phase for long duration of time. This demands the application of silver nanoparticles as it is known to have good anti-microbial properties.

Addition of silver nanoparticle to the surfactant solution helps in increasing the shelf life of the surfactants in the solution phase. Besides its anti-microbial property, like any surfactant solution, a nanofluid of silver nanoparticles also plays an important role in wetting of any solid surfaces which increases the wettability. This proves that the wetting is greatly affected by both surfactant as well as nanoparticles; thus, the experimental study based on the combination of both may be of great interest. Herein, we have presented an experimental study on wettability of hair surface using a natural surfactant, namely *Acacia auriculiformis* or acacia in presence of silver nanoparticles as additive. A chemical route has been followed for the synthesis of Ag NPs from $AgNO_3$ salt using a strong reducing agent, $NaBH_4$, in a surfactant medium of acacia. Acacia has been chosen to conduct the experiment because, apart from its availability, nonionic nature, and biocompatibility, acacia also acts as a reductant or reducing agent which has an ability to reduce metal ions from its respective salts.

2.4 Research objectives.

To conduct the series of experiments, it is very important to point out the research objectives for the better understanding and planning. To do so, our objectives are:

1. To compare the wettability of human hair in presence or absence of acacia in a aqueous solution.
2. To study the growth kinetics of silver nanoparticle via chemical route.
3. To characterize silver nanoparticles using UV Vis and FESEM.
4. To compare the wettability of human hair in presence or absence of silver nanofluids in acacia solution.

Chapter 3

Experimental Work

3.1 Materials

Human hair of Caucasian origin was obtained from Indian women for conducting the study. The natural surfactants used for wetting were extracted from acacia (*Acacia auriculiformis*). Extraction of saponin from acacia (MW-1765) was done according to methodology followed by Rao and Paria[10, 41]. One additional step was followed for the extraction of saponin from acacia to remove the water insoluble components from the methanol extract product. The methanol extract product was solubilized in di-ethyl ether and methanol mixture (5:1), then the soluble part was dried under vacuum to get complete water soluble component. Other chemicals, di-ethyl ether, methanol, ethanol, sodium borohydride, and silver nitride were purchased from Merck Chemicals. Ultrapure water of about 18.20 MΩ cm resistivity, 72.16 mN/m surface tension, and 6.5-7.0 pH was used for all the experiments.

Figure 3.1: Fruit of acacia [*Acacia auriculiformis*].

3.2 Cleaning and characterization of hair

Before the experiments each strand of hair was rinsed thoroughly with ultrapure water, followed by ethanol, and finally with water again to remove the unwanted deposits if any which accumulates over the cuticle over a period of time. Then after each wash, individual hair strand was dried for 3 minutes, using a hot air blower. The diameter and surface roughness of hair was characterized using atomic force microscopy (Veeco, USA).

3.3 Measurement of surface tension and CMC

The solutions were prepared freshly just before the actual measurements to avoid fungal or microbial contamination. The solutions of desired concentration (0.001-1) mM/L

were prepared from a 5 mM/L stock solution using a 50 mL volumetric flask. The surface tensions of acacia solutions (0.001-1) mM/L were measured by the Wilhelmy plate method using a surface tensiometer (Data Physic, DCAT-11EC) at 25 ± 0.5 °C, with the temperature maintained using an external constant-temperature water circulator where the motor speed was 1 mm/s, and the immersion depth of the platinum plate in the surfactant solution was maintained at 3 mm. After each concentration measurement, the platinum plate was cleaned with water and ethanol and then burned in an using spirit burner to ensure a clean surface. The CMCs of pure acacia were found to be 0.53 mM using surface tension data.

Figure 3.2: Photograph of surface Tensiometer (Data Physic, DCAT-11EC).

3.4 Measurement of surface energy and contact angle

The measurement of surface energy and contact angle was done using video based contact angle meter (Data Physics, OCA-20) by nano level dosing using sessile drop technique on a single strand of hair. The two liquid models also known as Owens-Wendt-Kaelble[36] model were used to calculate the surface energy of hair surface where water and ethylene glycol were taken as a test liquids.

Figure 3.3: Photograph of optical contact angle meter (Data Physics, OCA-20).

3.5 Method of synthesis and characterization of silver nanoparticles

In this study, the Ag NPs were synthesized chemically by the addition of freshly prepared sodium borohydride as a strong reducing agent into $AgNO_3$ solution ($NaBH_4$: $AgNO_3$ = 2:1) in the presence of acacia under stirring condition and waited for 1 h at 35 ± 3 °C. The equilibrium time for the particle formation was found to be 30 min for acacia at 35 ± 3 °C temperature. The Ag NPs were also synthesized in acacia insitu where $AgNO_3$ and acacia was maintained at the stoichiometric ratio of 1:4 to complete the reaction by trial and error method. The equilibrium time for the particle formation was found to be 6 hrs for acacia at 35 ± 3 °C temperature. Before performing characterization, sonication was carried out to supply energy to the system which in turn provides surface charge to the particles, creating a repulsive force which hampers agglomeration of particles. The formations of Ag NPs were confirmed by employing UV-vis. Spectrophotometer (UV-3600 Shimazdu). Subsequently, particle's shape and size were also confirmed using Field Emission gun based Scanning Electron Microscope (FESEM, Carl Zeiss, Neon 40).

22

Chapter 4

Characterization of hair surface

Abstract: To study the wetting behavior on hair surface, the knowledge in the domains of surface morphology of hair is very important. In this chapter, we have discussed about the internal and external structure of the hair sample briefly by preparing the schematic diagram of hair and its cross sectional area. Further, characterization of the hair sample is also done using atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM) to visualize the presence of roughness in the hair.

4.1 Introduction

Because of the huge demand of hair care products in the markets, the thorough study of morphological and physical properties of hair fiber is extremely essential before formulation of any hair care products[5, 6, 7, 8]. To understand the morphology of the hair, the schematic diagram of hair structure is shown in Figure 4.1. Majority[1] of the hair is made up of keratin fiber and appear cellular in structure which broadly consists of cortex and cuticle; cortex[2] may contain medulla at its inner central core whereas cuticle protects the cortex cell by covering its outer layer. Medulla is mostly an unstructured region which is not always present in cortex core. Cortex cell is the primary source of mechanical strength for hair and is highly structural and organized which covers majority of hair fiber composition and known to possess hydrophilic properties.
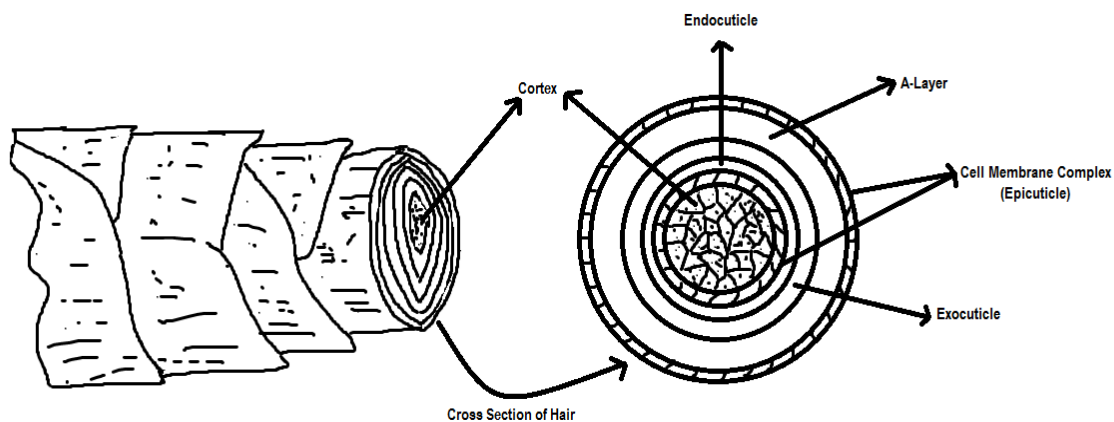
Figure 4.1: Schematic diagram showing physical structure of hair and its cross sectional representation.

The[2, 4] cuticle cell has three sub-layers namely endocuticle, exocuticle, A-layer and is collectively bounded by a cell membrane complex known as epicuticle which is hydrophobic in nature. King et al.;[3] (1986) have found that the epicuticle obtained from Merino wool consists of 78% protein, 5% lipid, and 4% ash.

Subsequently, Lodge and coworkers[4] (2006) have reported that the epicuticle primarily consists of protein matrix with some percentage of lipids. A lipid is a fatty acid consists mainly of 18-methyleicosanoic acid[2, 4] (18-MEA), is believed to be responsible for the hydrophobicity and lubricity of virgin hair. The secretion and accumulation of lipids over a period of time on epicuticle may cause hair strand sticky, greasy, and dull. Dust, pollen and other suspended particles may also adhere to sticky hair surface causing high friction and harder hair to comb[2]. To this regards, regular cleaning may be necessary for dirt less, hygienic, and healthy hair. Simply water wash of hair surface is less efficient in cleaning sticky, oily and waxy substances adhere to it due to their hydrophobic nature. Therefore, application of surfactant may be the key solution to this problem[5].

4.2 Results and discussion

4.2.1 Characterization of hair surface using Atomic force microscopy
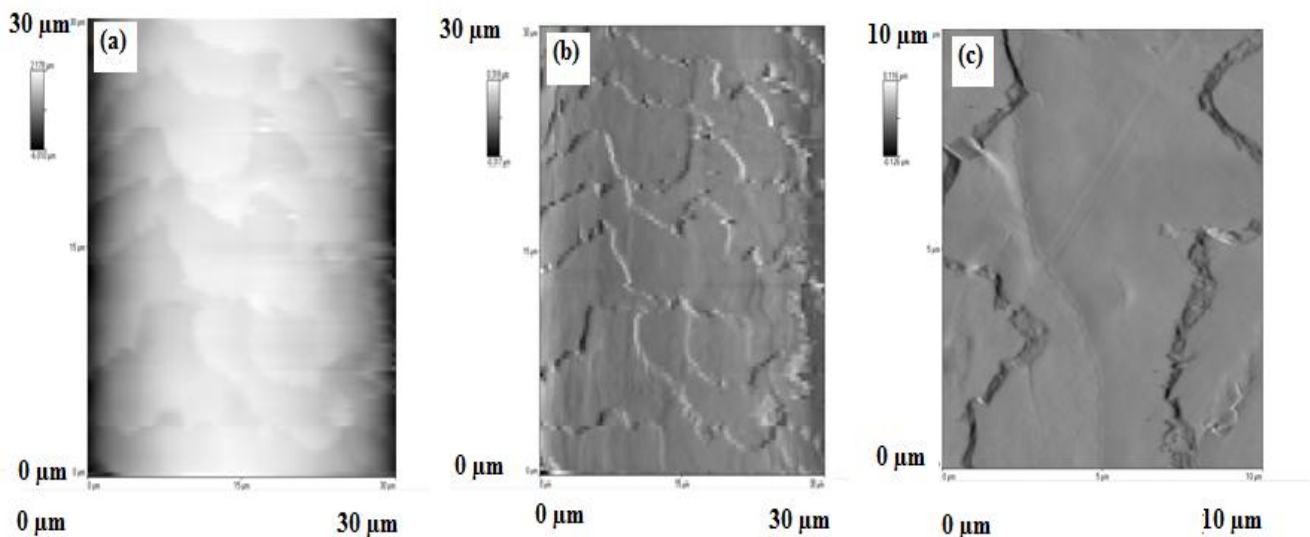
Figure 4.2: (a) AFM image of single hair strand; **(b)** and **(c)** Magnified image of hair strand showing roughness.

25

The hair surface is generally not smooth at the microscopic level, so the roughness of the hair surface used in this study has been characterized by atomic force microscopy. The diameter of a single hair strand is approximately 30 μm as seen from Figure 4.2(a). Upon further magnification the roughness of hair is evident as seen from parts b and c of Figure 4.2.

The area roughness of hair was calculated from the AFM image using SpmLab analysis software and it found to be 36.3 nm as shown in Figure 4.3(a) and the height profile of the z-axis through the lines of the inset image of Figure 4.3(b) gives the line roughness of hair, calculated as 39.4 nm. Since the line and area roughness are very close, it can be concluded that the heterogeneity is more or less uniformly distributed.

(a)

.

(b)
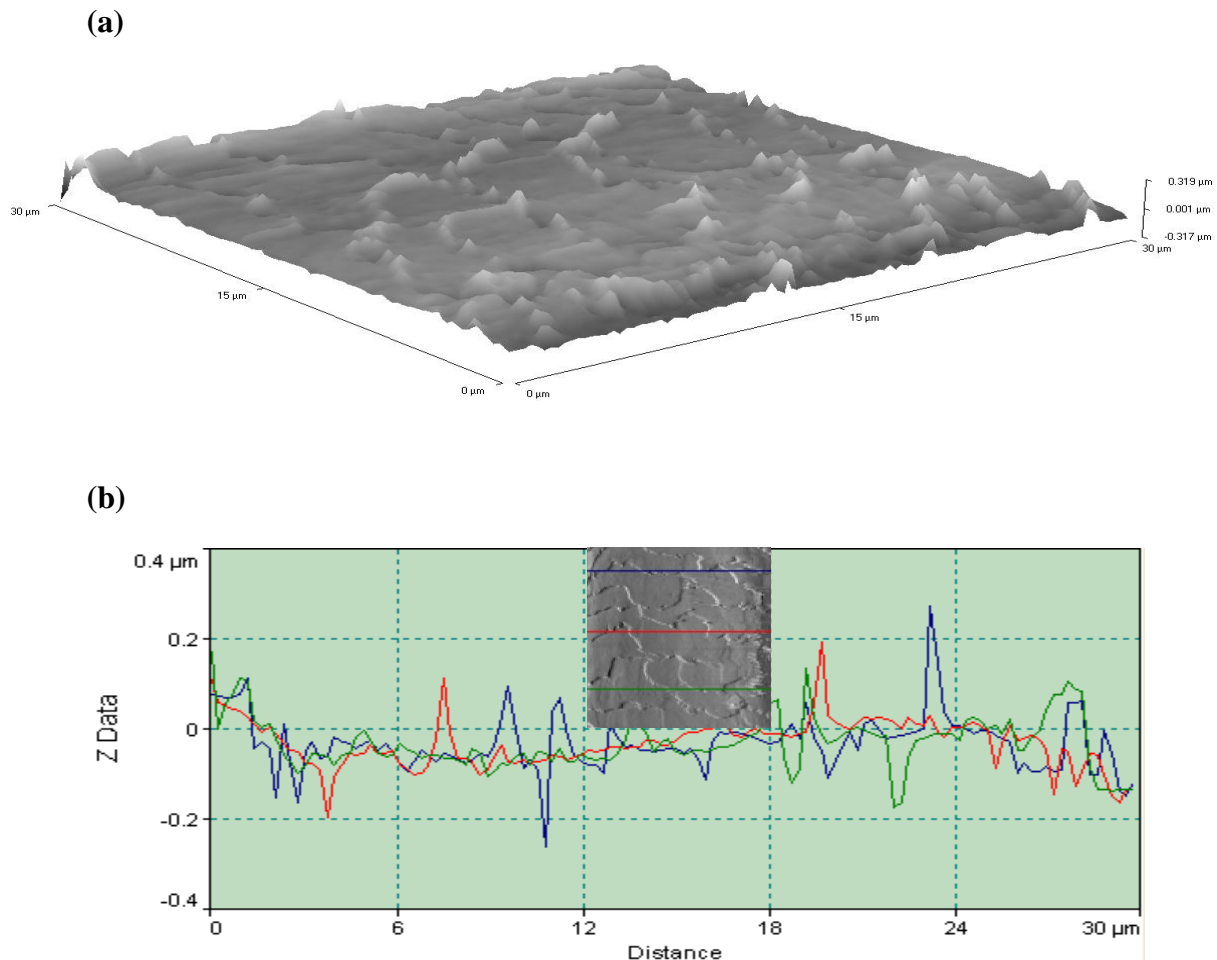
Figure 4.3: (a) Surface topography of a hair strand generated by AFM; **(b)** Height profile of the surface along the z-axis.

26

4.2.2 Characterization of hair surface using FESEM analysis

Further, to confirm the roughness present in the hair surface, field emission scanning electron microscopy (FESEM) was used for the investigation. Before the FESEM analysis, a sample of untreated virgin hair strand was treated with ultrapure water followed by ethanol and again with pure water. This is done to remove the unwanted materials (sebum or lipids) coated onto the cuticle over a period of time. From the Figure 4.4, it can be clearly seen that the surface roughness is uniform along the length of the hair strand. Moreover, the picture also shows that the some portions of the hair surface are believed to have damaged due to mechanical stress. This image is generated at a magnification of 1000x and at a nanometric range of 50 μm.
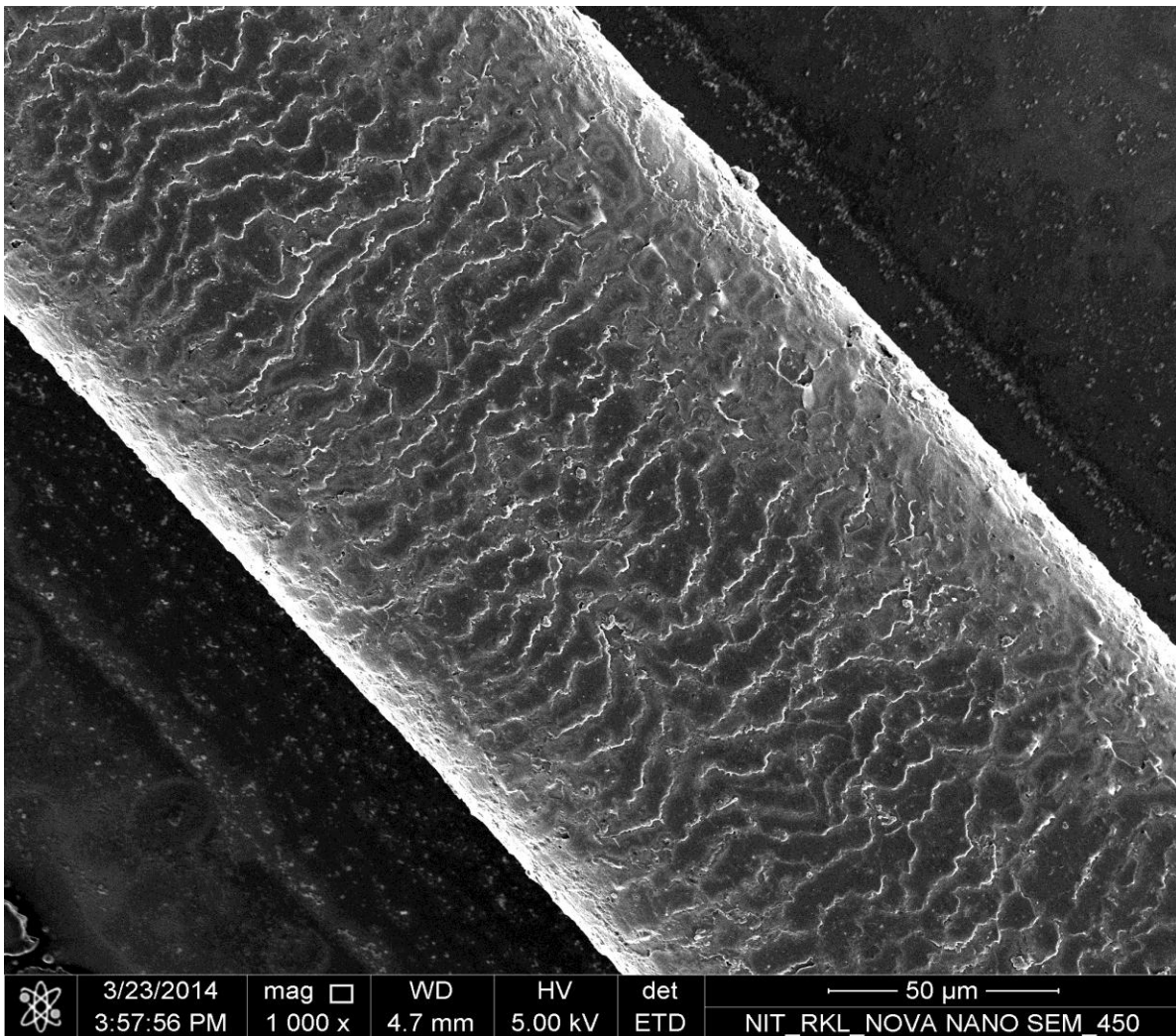
Figure 4.4: Image of a hair strand characterized by FESEM analysis.

4.3 Conclusion

In this chapter, the characterizations of a single hair strand were performed using atomic force microscopy (AFM) and field emission scanning electron microscopy (FESEM). Both analysis shows that the surface of hair is uneven and rough along the length of the hair. This roughness has major effects on the wettability of hair which has been explained in the later part of the report. Roughness at a nanometric scale of any solid surface plays an important role in determining the hydrophilicity or hydrophobicity of the surface which further decides the wettability of the surface. Higher the roughness, higher is the hydrophobicity of the surface. Therefore, we can conclude that hydrophobicity of hair surface is due to the presence of roughness at a microscopic level.

Chapter 5

Measurement of surface energy

Abstract: Among various available methodologies for calculating surface energy, the most commonly used are Owens-Wendt-Kaelble model. This model has been used to estimate the surface energy of hydrophobic hair surface. To compare the obtained results with hydrophilic surface, the surface energy of glass surface were also calculated.

5.1 Introduction

Surface Energy is the determination of the amount of energy which exists in a unit area of air-solid interface (mJ/m^2). Among various available models, Owens-Wendt-Kaelble model also known as two liquid model is the most common method to calculate the surface energy of solid surfaces. To understand its theoretical background[35, 36, 37, 38], the Young–Dupre equation has been used which can represented as

$$W_A = \gamma_l (\cos\theta + 1) \tag{2}$$

Where γ_l is the surface tension of liquid and θ is the contact angle. The work of adhesion, W_A can be expressed in terms of the polar and dispersion components of the surface energy as

$$W_A = 2[(\gamma_l^d)(\gamma_s^d)]^{1/2} + 2[(\gamma_l^p)(\gamma_s^p)]^{1/2} \tag{3}$$

where, γ_l^d and γ_l^p are the dispersion and polar components of the surface tension of the test liquid respectively; γ_s^d and γ_s^p are the dispersion and polar components of the surface energy of the solid respectively. Combining equation (2) and equation (3) gives

$$\gamma_l(1+\cos\theta) = 2[(\gamma_l^d)(\gamma_s^d)]^{1/2} + 2[(\gamma_l^p)(\gamma_s^p)]^{1/2} \tag{4}$$

It is possible to measure the surface tension of liquid γ_l in terms of its polar and dispersion components of equation (4). As the values of γ_l^d and γ_l^p are known, the contact angle can be measured to determine the unknown value of γ_s^d and γ_s^p. Since γ_s^d and γ_s^p are two unknown quantities, we need to measure the contact angle with two liquids in order to have two independent equations. Therefore, by considering polar and non-polar liquid as a test liquid, equation (4) can be written separately for two test liquids m and n as,

$$\gamma_{lm}(1+\cos\theta_m)=2[(\gamma_{lm}{}^d)(\gamma_s{}^d)]^{1/2}+2[(\gamma_{lm}{}^p)(\gamma_s{}^p)]^{1/2} \tag{5}$$

and

$$\gamma_{ln}(1+\cos\theta_n)=2[(\gamma_{ln}{}^d)(\gamma_s{}^d)]^{1/2}+2[(\gamma_{ln}{}^p)(\gamma_s{}^p)]^{1/2} \tag{6}$$

The two unknown components of surface free energy of the solid, $\gamma_s{}^d$ and $\gamma_s{}^p$, can be calculated by solving equation (5) and (6). The summation of these two components finally gives the total surface energy of the any solid.

5.2 Results and discussion

5.2.1 Measurement of surface energy using Owens-Wendt-Kaelble model

In this study, total surface energy of hydrophobic hair in form of polar and dispersion component has been determined using the two liquids model, widely known as Owens-Wendt-Kaelble model. This calculation after measuring the contact angle on solid surface and by choosing water and ethylene glycol as a test liquid are shown as below in Table 6.

Table 5.1: Surface energy and its polar and dispersion components of glass and hair surface using OWK method.

Material	$\gamma_s{}^d$	$\gamma_s{}^p$	γ_s (mJ/m^2)
Hair	0.21	31.90	32.11
Glass	2.07	62.02	64.06

It is interesting to note from the Table 6 that the polar component in comparison to the dispersion component of surface energy of hair is larger. This component values are dependable on the type of test liquids to be used. It can be seen from the Table 6 that the surface energy of hair is obtained to be 32.11mJ/m^2 is much lower than the hydrophilic solids. To compare these estimated values with the hydrophilic solid, surface energy of glass surface were determined using the same methodology used for hair surface. The comparative study clearly shows that the surface energy of glass surface (hydrophilic) is much more than that of hair surface (hydrophobic). This is because that the molecules in the glass are held by a strong molecular force of attraction.

5.3 Conclusion

In this content, measurements of surface energy for hair strand in terms of polar and dispersion components using Owens-Wendt-Kaelble model were determined by two test liquids. To validate the results, these results were also compared with the glass surface which is hydrophilic in nature. The calculation shows that the surface energy is more for hydrophilic surface than that of hydrophobic surface. Therefore, we can say that 32.11mJ/m^2 of energy is present on the hair surface whereas 64.06mJ/m^2 of energy is present on the glass surface per unit area of air-solid interface

Chapter 6

Wettability of hair using pure surfactant

Abstract: The wettability of any solid surfaces is estimated in terms of contact angle. Solution parameters like surface tension and CMC plays an important role in reducing contact angle. Therefore, in this chapter, the solution behavior of pure surfactant (acacia) solution was studied experimentally to estimate surface tension and CMC values using surface tensiometer. Moreover, to check the wettability of hair surface, contact angle was also measured using contact angle meter.

6.1 Introduction

The wetting of any solid surfaces depends on various factors such as the solution behavior (surface tension and CMC), property/nature of the material (hydrophobicity and hydrophilicity), surfactant adsorption at solid-liquid interface, work of adhesion and so on. The solution behavior can be studied by measuring surface tension of the surfactant solution of different concentration. Therefore, using the surface tension data, one can easily calculate CMC form a graph plotted between surface tension and logarithmic of surfactant concentration. The property of solid surface is also of great important which decides the wettability of any solid surface. Mostly, the solid surface of hydrophilic nature shows more wettability than that of the hydrophobic nature. Generally, our concern is to increase wettability of the hydrophobic surface by the application of surfactant system. Surfactant plays a significant role in reducing surface tension and contact angle. The surfactant molecules adsorbed at the air-liquid and solid-liquid interfaces are responsible for the reduction of surface tension and contact angle. The molecules of the surfactant tend to disperse in the aqueous system under the action of Brownian motion and forms micelles of different shapes and sizes till CMC beyond which no further micelles forms. Some of the molecules tend to adsorb in the air-liquid interface thereby reducing the surface tension of the system. While measuring contact angle on any solid surface, a drop of specific volume taken on the surface also contains adsorbed surfactant moieties which further reduces the solid-liquid interfacial tension.

6.2 Results and discussion

6.2.1 Solution behavior of pure surfactant

Adsorption of surfactant at air-water interface strongly reduces the surface tension by replacing the water molecules at the interface with the surfactant molecules. To see the effect of

surfactant adsorption, let us plot a graph of the surface tension values of acacia solution versus logarithm of concentration (Log c) presented in Figure 6.1.
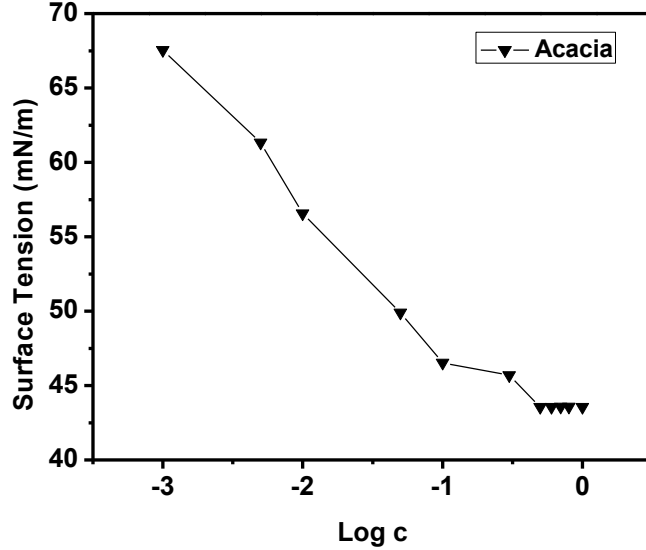
Figure 6.1: Change in surface tension (mN/m) with logarithm of concentration (Log c) of acacia solution.

It is clear from Figure 6.1 that the surface tension at air-water interface decreases gradually with increasing concentration of acacia and becomes constant beyond CMC. The CMC and corresponding surface tension value were found to be 0.53mM/L and 43.5mN/m respectively. Then, quantitatively to get an idea about the adsorption of surfactants at the air-water interface, the concentration of surfactant or surface excess concentration at the air-water interface may be calculated from surface tension data by use of the appropriate Gibbs equation as given below.

$$\Gamma = -\frac{1}{n \times 2.303 \, RT} \frac{d\gamma}{d \log c} \tag{7}$$

$$A_{min} = \frac{1}{N_A \Gamma_{max}} \tag{8}$$

where, Γ is surface excess in mole/m^2, A_{min} is surface area per molecule in nm^2, R is universal gas constant (8314 m^3 Pa/kg mole K), T is absolute temperature and N_A is Avogadro number (6.023×10^{23}). The value of n is 1 for non-ionic surfactants. Generally, to calculate A_{min}, Γ_{max} is

approximated as Γ, for places where linear dependence between surface tension and log c exists. The value of $d\gamma/d\log c$ was obtained from the slope of the plot of surface tension vs. logarithm of concentration (Log c), measured at a constant temperature of 298 K. The experimental values for surface tension at CMC (γ_{CMC}), CMCs, surface excess, and molecular areas acacia are presented in Table 7.

Table 6.1: Experimental values of surface tension at CMC (γ_{CMC}), CMC, surface excess (Γ_{max}) and molecular areas (A_{min}) for acacia surfactant solution.

Surfactant	γ_{CMC}(mN/m)	CMC (mM)	Γ_{max} (mole/m^2) $\times 10^6$	A_{min} (nm^2)
Acacia	43.5623	0.53	1.9394	0.85605

6.2.2 Contact angle measurement on hair surface

The contact angle of pure water and surfactant solutions on the hair surface measured by sessile drop technique is presented in Figure 6.2. Virgin untreated hair surface shows a contact angle value of 105 ± 5° using ultrapure water. The value obtained is in good agreement with the value of 103 ± 4° measured by Lodge et al[4]., (2006). After the alcohol wash contact angle decreases to 87° may be because of removal of oily components from the hair surface. The change in sessile drop contact angle on a single hair strand was studied and plotted in Figure 6.2. It can be clearly seen from Figure 6.2, that there is a gradual decrease in contact angle with increasing surfactant concentration until the CMCs of respective surfactants, beyond which there is no further reduction of contact angle with increasing surfactant concentration.
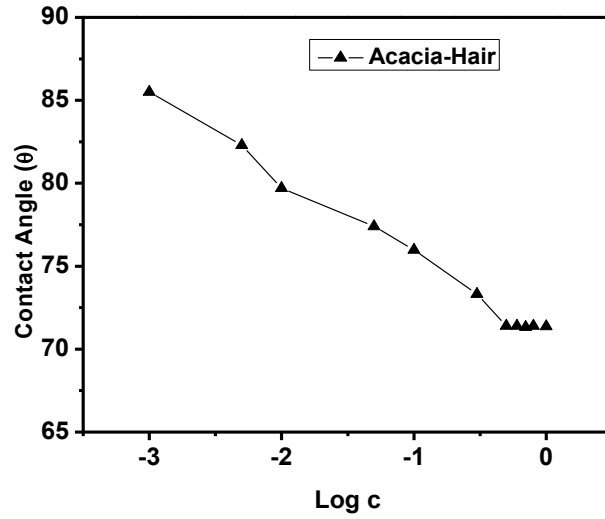
Figure 6.2: Change in contact angle (θ) with logarithm of concentration (Log c) of acacia solution on hair.

The contact angle value changes from 87° (pure water) to 71.3° for acacia solution. The present study shows that the plant surfactants have a large contact angle on hair which hardly affects wettability of the surface. In general, wetting property of surfactant solutions can be enhanced by the addition of additive (electrolytes, alcohol etc) or using a mixed surfactant system, so we have studied the effect of Ag NPs as additive on the wetting behavior. This may have some advantages in practical applications such as enhancement of self life of the surfactants inhibiting from microbial attract, act as anti dandruff agent, apart from the enhancement of wetting property.

6.2.3 Work of adhesion of surfactant solution

The work of adhesion of a liquid to solid, W_A, is defined by the reversible work required to separate a unit area of liquid from a solid surface and can be calculated by using the following equation

$$W_A = \gamma_{LG} + \gamma_{SG} - \gamma_{SL} \tag{9}$$

Introducing the Young equation,

$$W_A = \gamma_{LG}(\cos\theta + 1) \tag{10}$$

The work of adhesion of surfactant solutions on hair surfaces was calculated by putting the contact angle and surface tension values in equation 10 and is presented in Figure 6.3. It is obvious from the Figure 6.3 that the work of adhesion (W_A) decreases abruptly with increasing concentration of surfactants on hair surfaces till CMC. Initially, the work of adhesion of pure water for hair surface is found to be 73.927mJ/m^2 which is comparatively larger. Therefore, addition of surfactant reduces the amount of work of adhesion.

At a very low concentration of 0.001mM of surfactant, the W_A is about 72.89mJ/m^2 and on further increasing the surfactant concentration till CMC, W_A is found to be 57.48mJ/m^2 which is the minimum work of adhesion value obtained. Beyond CMC, the work of adhesion increases slightly in decimals further to some extent and then becomes constant. This shows that the work of adhesion is dependent on the amount of surfactant concentration. More addition of surfactant in the solution would decrease the surface tension thereby decreasing the contact angle which ultimately is responsible in the decrease in work of adhesion.
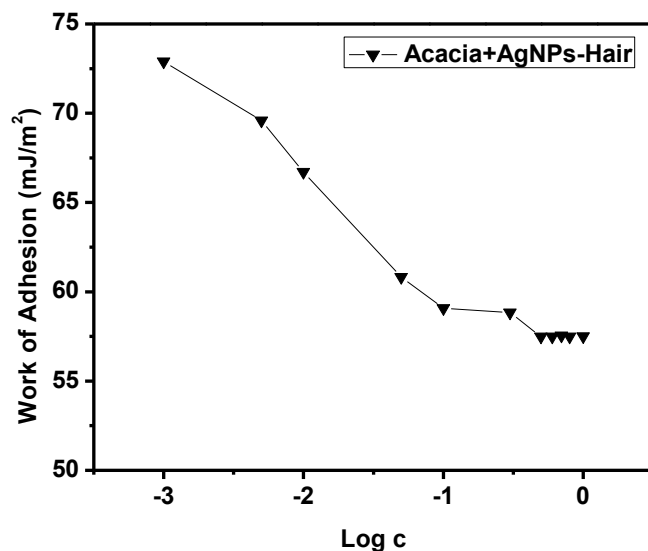
Figure 6.3: Change in work of adhesion (W_A) with the concentration (Log c) of acacia solution.

6.3 Conclusion

The contact angle of pure water on untreated virgin hair was measured to be 105± 5˚, which after ethanol treatment has reduced to a value of 87˚. The large contact angle obtained

elucidates the hydrophobicity of hair due to the presence of lipids coating to its surface. The study of solution behavior of pure acacia shows that the minimum surface tension and corresponding CMC values are 43.5 mN/m and 0.53 mM respectively. This change in parameters of the surfactant solution shows an adverse effect on the measurement of contact angle on hair. The plot between contact angle and logarithm of concentration (Log c) for pure acacia shows the dependency of the contact angle on the hair surfaces significantly with varying surfactant concentration. The minimum contact angle of pure acacia on ethanol treated hair was then obtained to be 71.3˚ which is 15.7˚ less than that of pure water on ethanol treated hair which is 87˚. This certainly confirms the wetting of hair surface which may be due to the adsorption of surfactant molecules at the solid-liquid interface of the system.

Chapter 7

Chemical synthesis of silver nanoparticles

Abstract: This section consists of the synthesis of silver nanoparticles using by a chemical route in presence of sodium borohydride under acacia medium. Herein, Sodium borohydride act as a strong reducing agent whereas acacia act as a capping agent. To confirm the formation of silver nanoparticles and its size, UV vis and FESEM analysis has been done.

7.1 Introduction

Nanotechnology has taken over its application almost in all fields of science and technological areas. Various metals at its nanometric scale especially in the range of 1 to 100 nm shows a unique characteristic in optical, electrical, and catalytic property. Large spectrums of research have been done by various researchers to study the effects of particle size and concentration of various metals at a nanosized level on its optical, electrical, chemical, physical, and catalytic property. The proliferation of nano-science and technology merges with a new venture in the advanced synthesization of different metallic nanoparticles with a controlled shape and size. Controlled shape and size of the nanoparticles is very crucial to enhance the nanometric properties. Some of the researcher has shown that the silver nanoparticles can be synthesized chemically using sodium borohydride as strong reducing agent with a fixed size [Solanki et al., 2011, Shameli et al., 2010] as well as variable size such as prism [Dong et al., 2010] and sphere [Lu et al., 2011]. According to Shameli et al., (2010), silver nanoparticle of spherical shape can be prepared by adding $NaBH_4$ to $AgNO_3$ solution till their molar ratio becomes 1:4 under the action of continuous stirring. As the $AgNO_3/NaBH_4$ molar ratio increases, the particles size becomes small and more dispersion can be achieved. Song et al., (2009) also studied the synthesis of silver nanoparticles under the variation of $NaBH_4$ to $AgNO_3$ concentration (0.5-15), initial concentration of $AgNO_3$, and different surfactant concentration (SDS). It is also observed that the intensity of surface Plasmon peak is weak at low $AgNO_3$ concentration while the intensity increases as the $AgNO_3$ concentration increases which elucidates that the formation of silver nanoparticles as the concentration of $AgNO_3$ increases. This confirms that the degree of dispersion of nanoparticles would be better if the absorption peak is held narrow. When the molar ratios of $NaBH_4/AgNO_3$ is in the range of (2-5), the absorption peak goes broad while the molar ratios of $NaBH_4/AgNO_3$ is in the range of (10-15), the absorption peak goes narrow. This clearly shows that at higher initial concentration of $AgNO_3$, silver nanoparticles are better dispersed compared to the lower concentration. There are various factors which affect the

formation of synthesis of silver nanoparticles which includes the initial concentration of $AgNO_3$, amount of $NaBH_4$ used, temperature of the system and capping agent used if any. The capping agent is normally known to prevent the agglomeration of the nanoparticles. Apart from this, it also has some reducing ability and thus helps in reducing the un-reacted reactants. It is also possible to synthesize silver nanoparticles by using surfactant solution in absence of any reducing agent. This methodology is quite environmental friendly and biocompatible. But it has a disadvantage that one cannot have control over the shape and size of the particles whereas this size control can be achieve in chemical route.

7.2 Results and discussion

7.2.1 Synthesis and characterization of silver nanoparticle in acacia medium

Ag NPs could be prepared conveniently by chemical reduction method with controlled particle shape and size. In this study, Ag NPs were synthesized by chemical route in acacia medium in presence of strong chemical reducing agent i.e. Sodium borohydride ($NaBH_4$) where acacia act as a capping agent and reductant as well. The role of capping agent i.e. acacia is to avoid particles agglomeration by dispersing the particles uniformly in the bulk medium. To prepare the nanofluid samples, at first, $AgNO_3$ solution (1mM) was added with $NaBH_4$ drop by drop so that the final molar concentration of $AgNO_3$: $NaBH_4$ becomes 1:2, subsequently, resulting in the formation of desired Ag NPs. Thereafter, acacia solution of different concentration ranging from (0.001-1) mM/L was added to the Ag nanofluids so formed which further reduces the unconverted $AgNO_3$ to Ag NPs and keeps the particles well dispersed. The Ag NPs so formed is maintained at a concentration of 0.33mM/L for all the samples used in the series of experiments. The particle size is affected due to various parameters like initial $AgNO_3$ concentration, surfactant (capping agent), reaction temperature, and $NaBH_4$ concentration. The resulting nanoparticle synthesis from $AgNO_3$ solution using sodium borohydride occurs by the following given equation:

$$Ag^+ + BH_4^- + 3\ H_2O \rightarrow Ag^o + B\ (OH)_3 + 3.5\ H_2 \tag{11}$$

The reaction is instantaneous and the colour of the solutions depends on the concentration of added $AgNO_3$ solutions, surfactant type and its concentration and concentration of reducing agent. So as to confirm the formation of Ag NPs in absence and presence of capping agent, UV

spectrophotometer analysis was performed. To ascertain the nanoparticle formation the absorption spectra was taken and the silver surface plasmon resonance bands were detected at around 406-420 nm as shown in Figure 7.1.
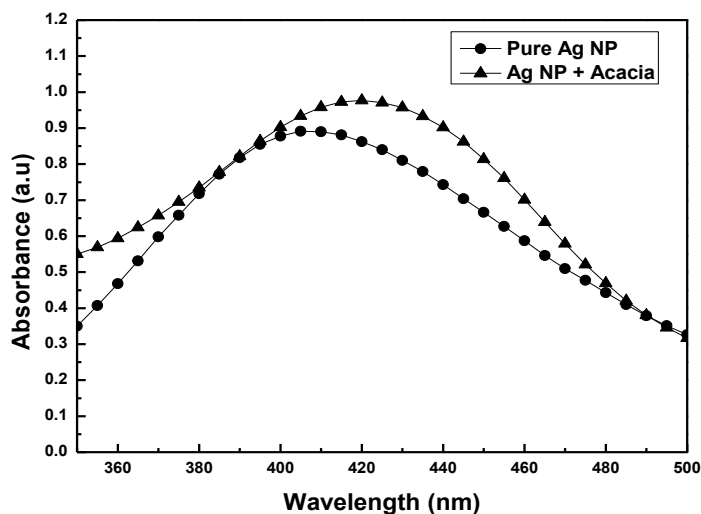
Figure 7.1: UV-Vis Absorption spectra of Ag NPs formation in pure form and in surfactant (acacia) solution at 0.5 mM.
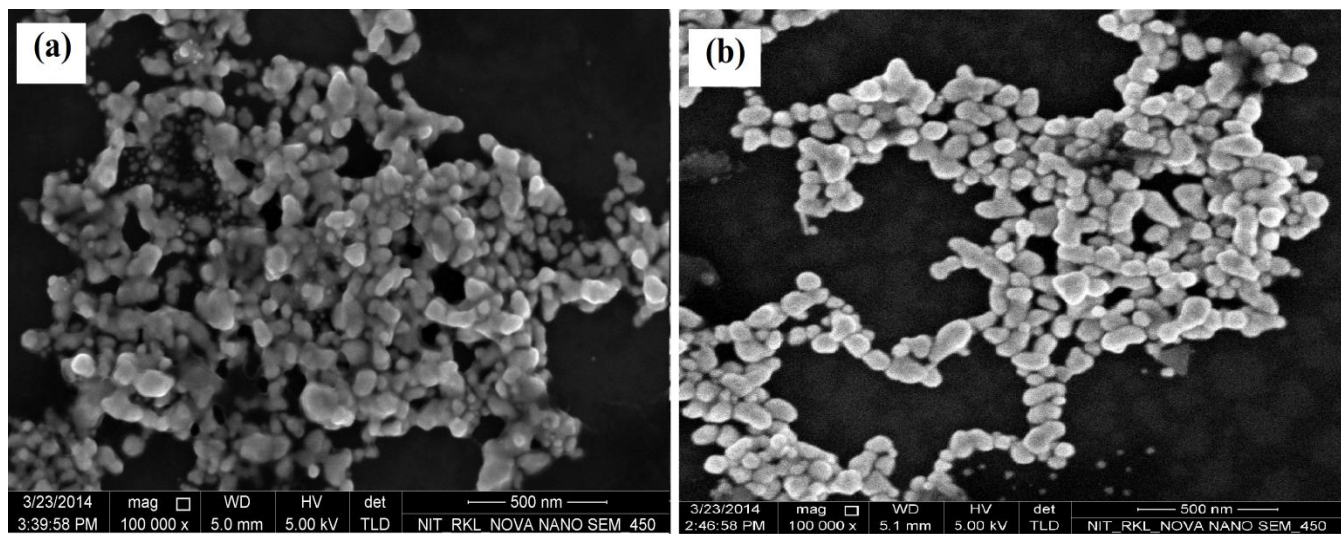
Figure 7.2: FESEM image of Ag NPs at 0.33 mM concentration (a) without capping agent and (b) with capping agent (acacia) at 0.5 mM concentration.

The formations of Ag NPs were confirmed by FESEM images as shown in Figure 7.2. It is clear from the image of Figure 7.2(a) that the particles so formed without capping agent has an affinity to attract with each other resulting in the agglomeration of the particles. Figure 7.2(b) shows the dispersion of particles in the system in presence of capping agent. The resulting image shows the formation of large number of Ag NPs with a particle size in the range (40-60) nm.

7.3 Conclusion

The silver nanoparticles (Ag NPs) have been synthesized chemically using sodium borohydride ($NaBH_4$) which act as a strong reducing agent. The formations of silver nanoparticles were confirmed by the help of UV vis spectroscopy. The spectroscopy analysis shows that the maximum absorption peak for Ag NPs in absence of acacia is 402nm whereas the maximum absorption peak for Ag NPs in presence of acacia is 402nm at 0.5mM concentration of acacia solution. Finally FESEM analysis confirms the presence of silver nanoparticles along with its shapes and sizes. An average of 50 nm particles size was confirmed form the FESEM image.

Chapter 8

Wettability of hair using nanofluid synthesized chemically

Abstract: As the plant surfactant is prone to fungal attack in an open environment, silver nanoparticles has been added to the surfactant solution to increase its shelf life. This so formed nanofluid has been used to check the wettability of hair using contact angle meter in this section. It is observed that the there is a sudden fall in contact angle on addition of nanoparticles. The experiments have been conducted by keeping the nanoparticles concentration constant at 0.33mM throughout the entire duration of the work. Solution behavior has also been studied to estimate the effect of nanoparticles on the surface tension.

8.1 Introduction

Wetting of solid surfaces by nanofluids is a complex phenomena where the interections between particles in nanofluid and solid surface takes place and subsequently enhance dynamic spreading and wetting under the action of disjoining pressure gradient. For a given volume of fluid, the spreading is increased if the equilibrium contact angle becomes less. So, nanoparticles in fluid suspension decreases the contact angle and thus aid in enhanced spreading of the nanofluid on the hair surface. The determination of nanofluid wettability can be done effectively by probing the individual as well as combinational effects of environment, nature of base liquid, characteristic of nanoparticle and also the substrate material. Kondiparty et al.;[31] (2011) found out experimentally that the deformation of fluid wedge tip occurs under the action of structural film disjoining pressure, which develops in thin liquid film (less than 10 nm thick) when its two surfaces attract or repel each other through van der Waals and electrostatic forces. The disparity amongst van der Waals and electrostatic forces causes fluid flow towards or away from the wedge tip; hence causing wetting or dewetting, depending upon the flow. Thus, capillary and disjoining pressure are of paramount significance for establishing the stability of thin curved films.

The structural film disjoining pressure is more towards the edge of the liquid film than at the centre, since disjoining pressure increases with the decrease in film thickness. Wasan et al.; [28] (2003) also applied the concept of the structural disjoining pressure gradient or film tension gradient to explain the spreading of nanofluids on solid surfaces. According to Sefiane et al.;[26] (2008),disjoining pressure has three important components: molecular (Π_m), electrostatic (Π_e) and structural (Π_s). Depending on the attractive or repulsive nature of the

disjoining pressure, the calculated hamaker constant can either be positive (repulsive forces) or negative (attractive forces).

Disjoining pressure $\Pi(h)$ = molecular $\Pi_m(h)$+ electrostatic $\Pi_e(h)$ structural $\Pi_s(h)$ (12)

Each of the compnents can be calculated separately to determine the overall disjoining pressure. While DLVO theory explains the electrostatic $\Pi_e(h)$ and structural $\Pi_s(h)$ forces, the molecular component can be calculated by London–van der walls molecular interactions as:

$$\Pi_m(h) = \frac{A_h}{6\pi h^3}$$
(13)

where A_h is a constant referred to as Hamaker constant and h is the liquid film thickness.

8.2 Results and discussion

8.2.1 Solution behavior of nanofluid

The solution behaviour of silver nanofluid in acacia medium were studied by the measurement of surface tension and CMC. The parameters affecting the solution properties of nanofluids mainly include the concentration of nanoparticles, size and shape of nanoparticle and nature of the base solution. Here, base solution is a acacia solution which act as a capping agent. Since nanoparticles has a tendency to self-agglomerate due to presence of opposite surface charge on it, base solution helps in avoiding those agglomeration of particles by dispersing it uniformly throughout the solution. Besides this advantage, base solution also has the ability to reduce surface tension of the solution as it is a surfactant by nature. Therefore, nanoparticles in presence of capping agent can effectively decrease the solid-liquid and liquid-air interface tension respectively by shifting the three phase contact line and thus increases the wettability of the nanofluid.

In this experiment, surface tension measurements were done for Ag NP in acacia medium where nanoparticles concentration was kept constant at 0.33mM/L throughout with varying concentration of acacia solution ranging from (0.001-1) mM/L.
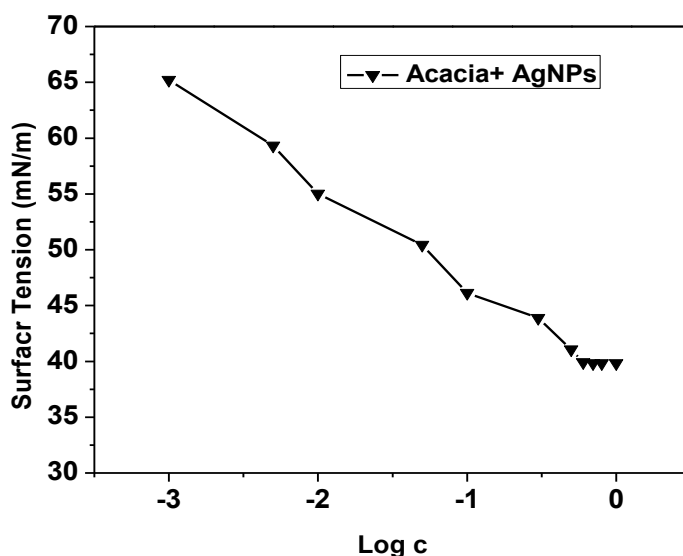
Figure 8.1: Change in surface tension (mN/m) with logarithm of concentration (Log c) of Ag NP in acacia solution.

Our previous result shows that the surface tension value gradually decreases with increasing concentration of acacia until CMC value; beyond which the surface tension remains constant. But addition of Ag NP in acacia surfactant soution shows a sharp decrease in surface tension than the values exhibited by the surfactant in their pure forms. The change in surface tension values were plotted against logarithm of concentration (Log c) in the Figure 8.1.

From Figure 8.1, it can be seen that the surface tension of Ag NPs in acacia at CMC is 39.8 mN/m which is comparatively less than that of the results obtained by the pure one which is 43.5 mN/m. The nanoparticles itself have less effects on the interfacial properties, since they hardly reduce the surface tension. But, in conjuction with surfactant system they play an important role in changing the properties of the base liquid. Nanoparticles remain dispersed in the surfactant system under the action of brownian motion and moves towards the air-water interface as well as bulk phase, thus, reducing the surface tension at the interface by influencing cohesive force of water molecules. Therefore, with increasing the surfactant concentration even above the CMC value, the surface tension decreses apprecaibly because of the particle diffusion from the bulk solution to the interface. Thus, an irreversible transfer of

nanoparticles occurs to the interface due to the continuous increase of the amount of absorption taking place at the interface affecting the surface tension of the solution.

8.2.2 Contact angle measurement on hair surface

Herein, the Ag NP sythesised by the chemcial reduction of $AgNO_3$ using $NaBH_4$ acacia medium has been employed for performing wettability studies of the concerned nanofluid on the hair. In this study, Ag NPs concentration is kept constant at 0.33mM/L for all the samples with varying acacia concentration ranging from (0.001-1)mM/L. Low concentration of Ag NPs is desirable to avoid increase in particle size and particles agglomeration. A graph is ploted in Figure 8.2 to discuss the effect of wetting on hair by acacia in presence of Ag NPs. Intially, the contact angle decreases with increasing concentration till 0.6 mM/L (log C = -0.22) of surfactants solution and then becomes constant beyond which further decrease in contact angle is not posible.
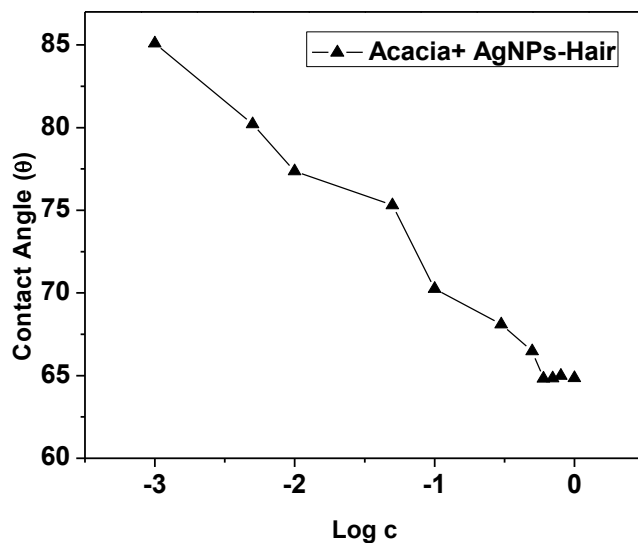
Figure 8.2: Change in contact angle (θ) with logarithm of concentration (Log c) of acacia solution on hair.
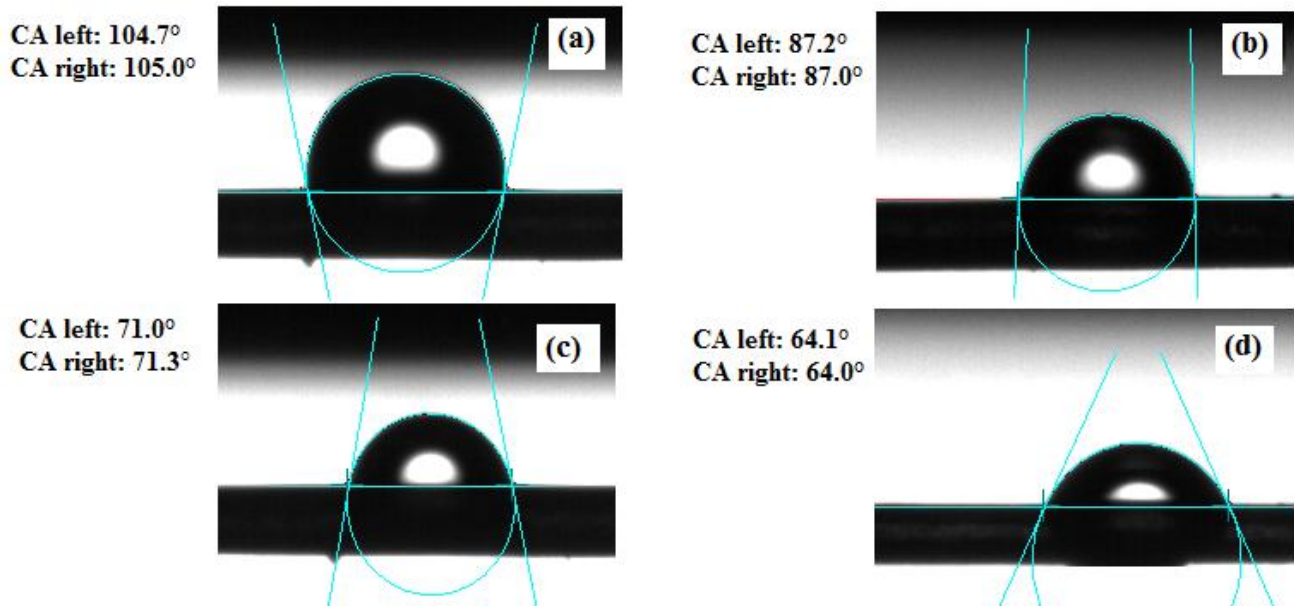
Figure 8.3: Optical image of (a) water droplet on untreated virgin hair, (b) water droplet on ethanol treated hair, (c) droplet of pure acacia solution at a concentration of 0.53 mM (CMC of pure acacia) on ethanol treated hair and (d) droplet of nanofluid in the presence of acacia at 0.6 mM concentration.

It is noteworthy to remember from the previous results that the contact angle of alcohol treated hair changes from 87° (pure water) to 71.3° with increasing concentration of pure acacia. But, the presence of Ag NPs in the surfactant solution leads to a further increase in wettability of the surfactant on the hair surface. At CMC, the contact angle given by the Ag NPs in acacia is 66.4°, nearly 4.9° lesser than that given by the pure acacia solution which is 71.3°. Moreover, a fall in contact from 66.4˚ (values at CMC) to 64˚ can also be seen above CMC value from the Figure 8.3, which is the minimum contact angle obtained experimentally. This clearly shows the effect of nanoparticles on hair surface and its key role in dynamic wetting and spreading phenomena. It is believed that the presence of self-structured nanoparticles near the three-phase contact line shifts the the contact line further, enabling dynamic wetting due to increase of disjoining pressure. Thus, the combination of both surfactant as well as nanoparticles has shown an effective methodology to reduce the contact angle enhancing wettability of the hair surface.

8.3 Conclusion

Ag NPs are known for its antimicrobial property which increases the shelf life of acacia solution as plant surfactant are very prone to fungal attack in open environment. Additionally, nanoparticles also have the ability to affects wettability. Therefore, Ag NP has been synthesized by chemical route in acacia medium, to see its effects on wettability of hair. Characterization shows that the average particle size is about 50 nm. The so formed nanofluids of constant concentration in presence of varying acacia concentration shows a minimum surface tension of about 39.8 mN/m which indicates the drastic fall of surface tension due to the adsorption of particles which further influence and alter the cohesive fore at the air-water interface. This further affects the contact angle by reducing it from 71.3˚ (pure acacia) to 64˚ which is the lowest contact angle obtained. The possible reason for this reduction might be due to disjoining pressure held at the vertex of the wedge film which further shifts the three phase contact line, thereby, enhancing wettability. The presence of acacia in the nanofluids is also held responsible for the reduction of surface tension and contact angle. Acacia in the nanofluid acts as a capping agent which keeps the particles well disperse throughout the system by preventing agglomeration. Furthermore, acacia is also believed to have known as reductant which has the affinity to convert unconverted $AgNO_3$ to Ag NP further.

Insitu synthesis of silver nanoparticles

Abstract: This section consists of the synthesis of silver nanoparticles using by a green route under acacia medium. Herein, acacia act as a strong reducing agent as well as a capping agent. To confirm the formation of silver nanoparticles and its size, FESEM analysis has been done.

9.1 Introduction

To minimize the environmental impact, many researchers had come up with the various alternatives to synthesize metal ions from metal salts. Among various metal salts, silver nanoparticles are the most common metal used in various applications such as medicine, food industries and so on. Silver nanoparticles can be synthesized insitu using various plant surfactants which includes reetha, shikakai, gum kondagogu, camellia sinenis, jatropha curcas etc. Synthesis any metal salts insitu has many advantages over chemical synthesis which includes environmental friendly process, less chemicals required, easy way to separate particles from the solution and so on. Apart from these advantages, plant surfactants are also biodegradable, easily available, low cost, and easy way to extract from its fruits. In this process, plant surfactant acts as a mild reducing agent as well as capping agent.

9.2 Results and discussion
9.2.1 Synthesis and characterization of silver nanoparticle in acacia medium

Ag NPs could be prepared conveniently by green method with controlled particle shape and size. In this study, Ag NPs were synthesized by green route in acacia medium insitu where acacia act as a capping agent and reductant as well. The role of acacia is to avoid particles agglomeration by dispersing the particles uniformly in the bulk medium. To prepare the nanofluid samples, at first, $AgNO_3$ solution (1mM) was added with acacia (4mM) so that the final molar concentration of $AgNO_3$: acacia becomes 1:4 and kept the solution in a dark room at $35\pm 3°C$ for 6 hours, subsequently, resulting in the formation of desired Ag NPs. Thereafter, the final stock of 4mM acacia solution so formed was diluted with different concentration ranging from (0.001-1) mM/L. The Ag NPs so formed is maintained at a concentration of 0.25mM/L for all the samples used in the series of experiments.
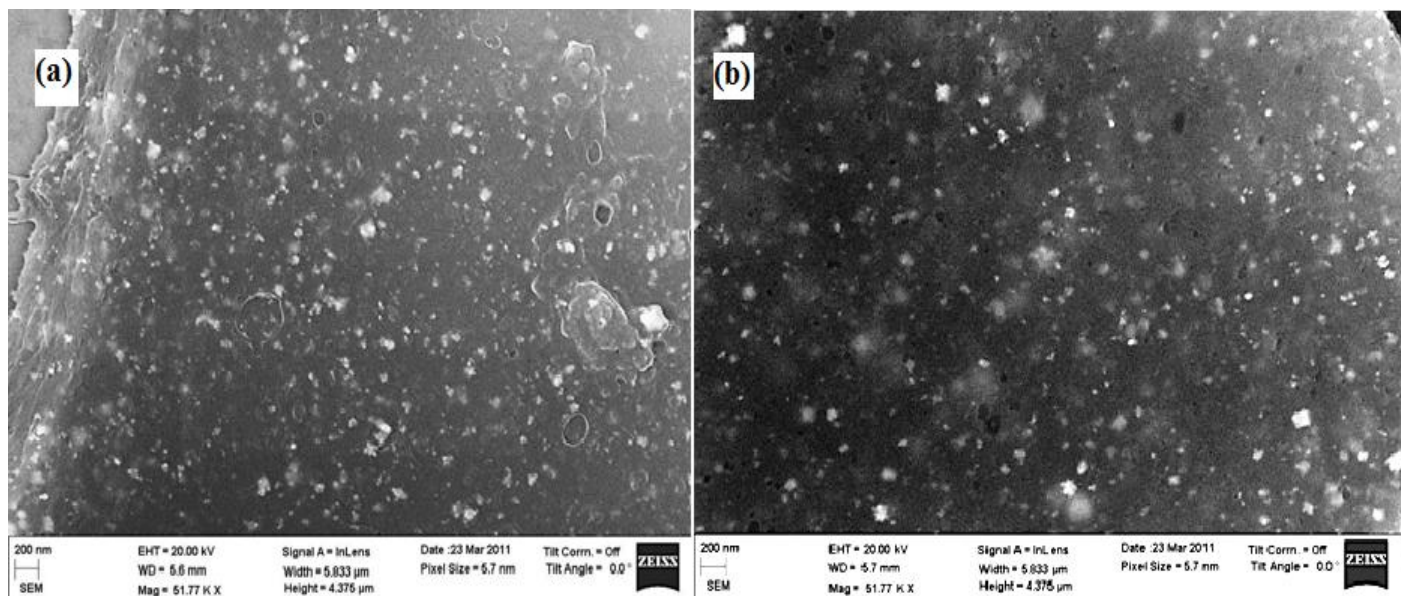
Figure 9.1: FESEM image of Ag NPs at 0.25 mM concentration shown in Figure (a) and (b) in acacia medium (4mM).

The formations of Ag NPs were confirmed by FESEM images as shown in Figure 9.1. It is clear from the image of Figure 9.1 that the dispersion of particles in the system in presence of acacia is significant. The resulting image shows the formation of large number of Ag NPs with a particle size in the range (30-50) nm.

9.3 Conclusion

The silver nanoparticles (Ag NPs) have been synthesized insitu using acacia which act as a reducing agent and capping agent as well. The formations of silver nanoparticles were confirmed by the help of UV vis spectroscopy. The spectroscopy analysis shows that the maximum absorption peak for Ag NPs in acacia medium is 418nm. Finally FESEM analysis confirms the presence of silver nanoparticles along with its shapes and sizes. An average of 40 nm particles size was confirmed form the FESEM image.

Chapter 10

Wettability of hair using nanofluid synthesized insitu

Abstract: In this content, wettability of nanofluids synthesized insitu in acacia medium was studied. The obtained contact angle from this study has been compared with the wettability obtained from the pure surfactant as well as chemically synthesized nanofluid. The solution behavior for the nanofluid has also been studied in terms of surface tension.

10.1 Introduction

In the previous section, we have studied about the wettability of hair using silver nanofluid synthesized by chemical route. But chemical synthesis poses a severe environmental impact and hence required a methodology alternative to it. The best alternative is the insitu synthesis in which the nanoparticles forms inside the reaction mixtures. This methodology is green in nature and is not a matter of environmental concern. There are many available plant surfactants which could reduce the silver nanoparticles such as reetha, shikakai, neem, acacia and many more. Among these available plant surfactants, acacia is chosen because of its biocompatibility with environment. In the present study, silver nanoparticles have been synthesized insitu in acacia medium and the so formed nanofluid has been used to check the wetting studies on hair surface. The obtained results has been compared with the earlier results obtained with chemically synthesized Ag nanofluid.

10.2 Results and discussion

10.2.1 Solution behavior of nanofluid

The solution behaviour of silver nanoparticles in acacia medium were studied by the measurement of surface tension. The parameters affecting the solution properties of nanofluids mainly include the concentration of nanoparticles, size and shape of nanoparticle and nature of the base solution. Here, acacia which act as a both reducing and capping agent. Acacia also has the ability to reduce surface tension of the solution as it is a surfactant by nature. Since nanoparticles has a tendency to self-agglomerate due to presence of opposite surface charge on it, acacia as a capping agent helps in avoiding those agglomeration of particles by dispersing it uniformly throughout the solution. Therefore, nanoparticles in presence of capping agent can effectively decrease the solid-liquid and liquid-air interface tension respectively by shifting the three phase contact line and thus increases the wettability of the nanofluid.

In this experiment, surface tension measurements were done for Ag NP in acacia medium where nanoparticles concentration was kept constant at 0.25mM/L throughout with varying concentration of acacia solution ranging from (0.001-1) mM/L.
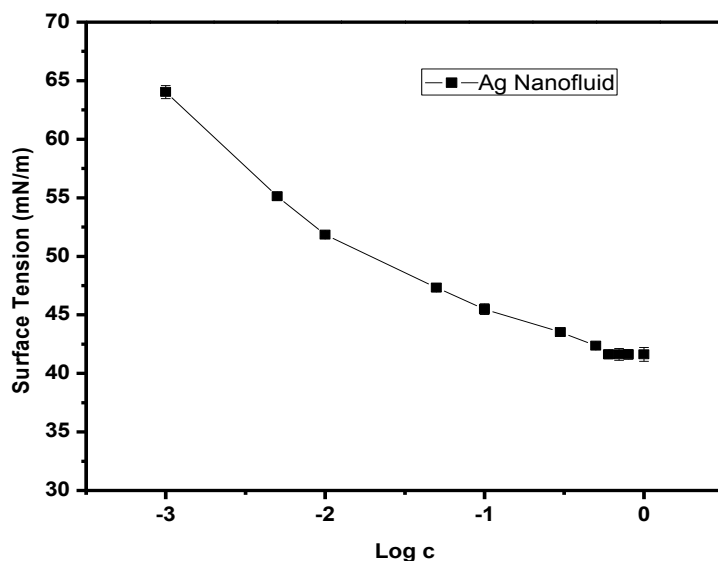
Figure 10.1: Change in surface tension (mN/m) with logarithm of concentration (Log c) of Ag nanofluid synthesized by green route.

Addition of Ag NP in acacia surfactant soution shows a sharp decrease in surface tension than the values exhibited by the surfactant in their pure forms. The change in surface tension values were plotted against logarithm of concentration (Log c) in the Figure 10.1.

From Figure 10.1, it can be seen that the minimum surface tension of Ag NPs in acacia is 41.62 mN/m which is comparatively less than that of the results obtained by the pure one which is 43.5 mN/m. The nanoparticles itself have less effects on the interfacial properties, since they hardly reduce the surface tension. But, in conjuction with surfactant system they play an important role in changing the properties of the base liquid. Nanoparticles remain dispersed in the surfactant system under the action of brownian motion and moves towards the air-water interface as well as bulk phase, thus, reducing the surface tension at the interface by influencing cohesive force of water molecules. Therefore, with increasing the surfactant concentration even above the CMC value, the surface tension decreses apprecaibly because of the particle diffusion

from the bulk solution to the interface. Thus, an irreversible transfer of nanoparticles occurs to the interface due to the continuous increase of the amount of absorption taking place at the interface affecting the surface tension of the solution.

10.2.2 Contact angle measurement on hair surface

Herein, the Ag NP sythesised by bio-synthesis route from $AgNO_3$ salt using acacia has been employed for performing wettability studies of the concerned nanofluid on the hair. In this study, Ag NPs concentration is kept constant at 0.25mM/L for all the samples with varying acacia concentration ranging from (0.001-1)mM/L. A graph is ploted in Figure 10.2 to discuss the effect of wetting on hair by acacia in presence of Ag NPs. Intially, the contact angle decreases with increasing concentration till 0.6 mM/L (log C = -0.22) of surfactants solution and then becomes constant beyond which further decrease in contact angle is not posible.
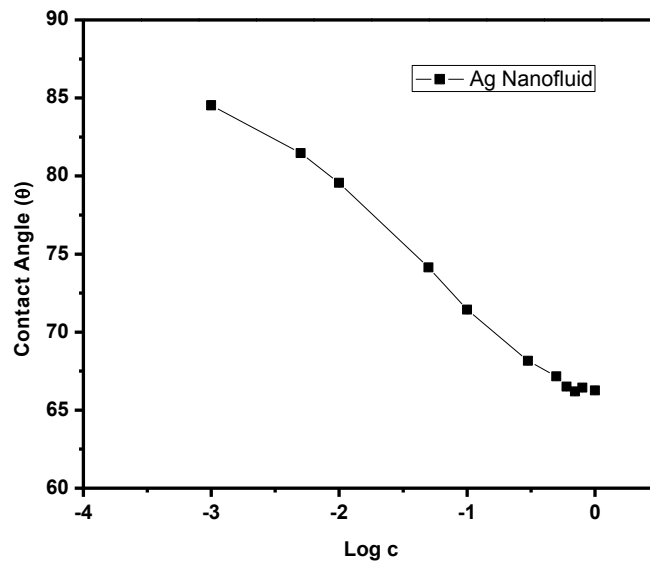
Figure 10.2: Change in contact angle (θ) with logarithm of concentration (Log c) of Ag nanofluid containing acacia.

The presence of Ag NPs in the surfactant solution leads to a further increase in wettability of the surfactant on the hair surface. At CMC, the contact angle given by the Ag NPs in acacia is 67°, nearly 4.3° lesser than that given by the pure acacia solution which is 71.3°. Moreover, a fall in contact from 67˚ (values at CMC) to 66˚ can also be seen above CMC value from the Figure 10.2, which is the minimum contact angle obtained experimentally. This clearly shows the effect of nanoparticles on hair surface and its key role in dynamic wetting and spreading phenomena. It is believed that the presence of self-structured nanoparticles near the three-phase contact line shifts the the contact line further, enabling dynamic wetting due to increase of disjoining pressure.

10.3 Conclusion

It has been seen that the wettability of hair increases compared to that of pure acacia. The surface tension found in the case of pure acacia was 43.5mN/m which is then reduced to 41.62mN/m using nanofluid synthesized insitu. Further decrease in contact angle was also seen from 87˚ to 66.3˚ which is possibly due to the adsorption of surfactant molecules as well as nanoparticles at the interface which influence the cohesive forces and reduces surface tension thereby increasing wettability. Comparatively with the Ag nanofluid synthesized by chemical route, the insitu synthesized is a bit inferior. The wettability of hair is less for the case of Ag nanofluid synthesized by insitu methodology compared to the chemically synthesized nanofluid.

<div align="right">

Chapter 11

</div>

Conclusion and suggestion for future work

11.1 Conclusion

The wettability of human hair has been studied experimentally using acacia solution in the absence and presence of Ag NPs by sessile drop techniques. The conclusions are summarized as follows:

1. The contact angle of pure water on untreated virgin hair was measured to be 105± 5˚, which after ethanol treatment has reduced to a value of 87˚. The large contact angle obtained elucidates the hydrophobicity of hair due to the presence of lipids coating to its surface.

2. The study of solution behavior of pure acacia shows that the minimum surface tension and corresponding CMC values are 43.5 mN/m and 0.53 mM respectively. This change in parameters of the surfactant solution shows an adverse effect on the measurement of contact angle on hair. The plot between contact angle and logarithm of concentration (Log c) for pure acacia shows the dependency of the contact angle on the hair surfaces significantly with varying surfactant concentration. The minimum contact angle of pure acacia on ethanol treated hair was then obtained to be 71.3˚ which is 15.7˚ less than that of pure water on ethanol treated hair which is 87˚. This certainly confirms the wetting of hair surface which may be due to the adsorption of surfactant molecules at the solid-liquid interface of the system.

3. Ag NPs are known for its antimicrobial property which increases the shelf life of acacia solution as plant surfactant are very prone to fungal attack in open environment. Additionally, nanoparticles also have the ability to affects wettability. Therefore, Ag NP has been synthesized by chemical route in acacia medium, to see its effects on wettability of hair. Characterization shows that the average particle size is about 50 nm. The so formed nanofluids of constant concentration in presence of varying acacia concentration shows a minimum surface tension of about 39.8 mN/m which indicates the drastic fall of surface tension due to the adsorption of particles which further influence and alter the cohesive fore at the air-water interface. This further affects the contact angle by reducing it from 71.3˚ (pure acacia) to 64˚ which is the lowest contact angle obtained. The possible reason for this reduction might be due to disjoining pressure held at the vertex of the wedge film which further shifts the three phase contact line, thereby, enhancing wettability.

4. The presence of acacia in the nanofluids is also held responsible for the reduction of surface tension and contact angle. Acacia in the nanofluid acts as a capping agent which keeps the particles well disperse throughout the system by preventing agglomeration. Furthermore, acacia is also believed to have known as reductant which has the affinity to convert unconverted $AgNO_3$ to Ag NP further.

5. Insitu synthesized nanofluid shows a reduction in surface tension with a minimum surface tension of 41.62mN/m beyond CMC. The minimum contact angle on hair is found to be 66.3° which is also superior to that of the pure acacia on hair. But comparatively, the insitu synthesized nanofluid shows inferior wetting behavior than that of chemically synthesized nanofluid.

11.2 Suggestion for future work

1. In this wettability studies, the experimental work for the measurement of contact angle has been performed using static contact angle measurement. However, similar work can be performed using dynamic contact angle measurement and validate the results obtained.

2. The experimental work has been performed on a virgin Caucasian origin. However, similar studies may be performed using hairs of different ethnics and compare with our obtained results.

3. Acacia has been used as a natural surfactant for the system. However, other available natural surfactants may be used to perform the experiments.

Chapter 12

Reference and research publication

12.1 References

1. Kamath, Y.K.; Dansizer, C.J.; Weigmann, H.D. Wettability of Keratin Fiber Surfaces. *J Soc. Cosmet. Chem*. **1977**, 28,273.

2. Torre, C.L.; Bhushan, B.;Yang, J.Z. Nanotribological Effects of Silicone Type, Silicone Deposition Level, and Surfactant Type on Human Hair using Atomic Force Microscopy. *J. Appl. Polym. Sci*. **2006**, 57, 37.

3. King, N. L. R.; Bradbury, J. H. The Chemical Composition of Wool. Part V, The Epicutcle. *Aust. J. Bio. Sci*. **1968**, 21, 375.

4. Lodge, R.A.; Bhushan, B.Wetting Properties of Human Hair by Means of Dynamic Contact Angle Measurement. *J. Appl. Polym. Sci*. **2006**, 102, 5255.

5. Kamath, Y.K.; Dansizer, C.J.Weigmann, H.D.; Marangoni Effect in the Water Wetting of Surfactant Coated Human Hair Fibers. *J Colloid Interf. Sci*. **1984**, 102, 164.

6. Khenniche, S.; Bouali, B.; Lanteri, P. Scalp Hair: A Model for the Evaluation of Cosmetic Formulations Intended for Depilation. *Polym. Int*. **2003**, 52, 563.

7. Wortmann, F.J.; Wortmann, G.; Wiesche, E.S.Z. Spatial Probing of the Properties of the Human Hair Surface using Wilhelmy Force Profiles. *Langmuir*. **2010**, 26, 7365.

8. Baghdadli, N.; Luengo, G.S. A Closer Look at the Complex Hydrophilic / Hydrophobic Interactions Forces at the Human Hair Surface. *J. Phys. Conf. Ser*. **2008**, 100, 052034.

9. Ahmad, N.; Sharma, S.; Alam, M.K.; Singh, V.N.; Shamsi, S.F.; Mehta, B.R.; Fatma, A. Rapid Synthesis of Silver Nanoparticles using Dried Medicinal Plant of Basil. *Colloid Surface B*. **2010**, 81, 81.

10. Rao, K.J.; Paria, S. Solubilization of Naphthalene in the Presence of Plant-Synthetic Mixed Surfactant Systems. *J. Phys. Chem. B*. **2009**, 113, 474.

11. Shameli, K.; Ahmad, M.B.; Yunus, W.Z.W.; Ibrahim, N.A.; Darroudi, M. Synthesis and Characterization of Silver/Talc Nanocomposites using the Wet Chemical Reduction Method. *Int.J. Nanomed.* **2010**, 5, 743.

12. Solanki, J.N.; Murthy, Z.V.P. Reduction of Nitro Aromatic Compounds over Ag/Al_2O_3 Nanocatalyst Prepared in Water-in-Oil Microemulsion: Effects of Water-to-Surfactant Mole Ratio and Type of Reducing Agent. *Ind. Eng. Chem. Res*. **2011**, 50, 7338.

13. Bar, H.; Bhui, D.K.; Sahoo, G.P.; Sarkar, P.; De, S.P.; Misra, A. Green Synthesis of Silver Nanoparticles using Latex of Jatrophacurcas. *Colloid Surface A*. **2009***, 339, 134.

14. Bar, H.; Bhui, D.K.; Sahoo, G.P.; Sarkar, P.; Pyne, S.; Misra, A. Green Synthesis of Silver Nanoparticles using Seed Extract of Jatrophacurcas. *Colloid Surface A*. **2009**, 348, 212.

15. Begum.N.A.; Mondal.S.; Basu.S.; Laskar.R.A.; Mandal. D. Biogenic Synthesis of Au and Ag Nanoparticles using Aqueous Solutions of Black Tea Leaf Extracts. *Colloid Surface B*. **2009**, 71, 113.

16. Dong, X.; Ji, X.; Jing, J.; Li, M.; Li, J.; Yang, W. Synthesis of Triangular Silver Nanoprisms by Stepwise Reduction of Sodium Borohydride and Trisodium Citrate. J. *Phys. Chem. C*. **2010**, 114, 2070.

17. Dwivedi, A.D.; Gopal, K. Biosynthesis of Silver and Gold Nanoparticles using *Chenopodium Album* Leaf Extract. *Colloid Surface A*. **2010**, 369, 27.

18. Kumar, V.; Yadav, S.D. Plant-Mediated Synthesis of Silver and Gold Nanoparticles and their Applications. *J. Chem. Technol. Biotechnol.* **2009**, 84, 151.

19. Song, K.C.; Lee, S.M.; Park, T.S.; Lee, B.S. Preparation of Colloidal Silver Nanoparticles by Chemical Reduction Method. *Korean J. Chem. Eng*. **2009**, 26, 2009, 153.

20. Krishnaraj, C.; Jagan, E.G.; Rajasekar, S.; P. Selvakumar, P.; Kalaichelvan, P.T.; Mohan, N. Synthesis of Silver Nanoparticles using Acalyphaindica Leaf Extracts and its Antibacterial Activity against Water Borne Pathogens. *Colloids Surf. B*. **2010**, 76, 50.

21. Garai, S.; Mahato, S.B. Isolation and Structure Elucidation of Three Triterpenoidsaponins from Acacia Auriculiformis. *Phytochemistry*, **1997**, 44, 137.

22. Holmberg, K. Natural surfactants. *Curr.Opin. Colloid In.* **2001**, 6, 148.

23. Tezuka, Y.; Honda, K.; Banskota, A.H.; Thet, M.M.; Kadota, S. Kinmoonosides A-C, Three New Cytotoxic Saponins from the Fruits of Acacia Concinna, A Medicinal Plant Collected in Myanmar. *J. Nat. Prod*. **2006**, 63, 1658.

24. Pal, D.; Chakraborty, P.; Ray, H.N.; Pal, B.C.; Mitra, D.; Kabir, S.N. Acaciaside-B-Enriched Fraction of Acacia Auriculiformis is a Prospective Spermicide with no Mutagenic Property. *Reproductio.* **2009**, 138, 453.

25. Rao, K.J.; Paria, S. Green synthesis of silver nanoparticles from aqueous Aeglemarmelos leaf extract. *Mat. Res. Bull*. **2013**, 48, 628.

26. Sefiane, K.; Skilling, J.; MacGillivray, J. Contact Line Motion and Dynamic Wetting of Nanofluid Solutions. *Adv. Colloid Interfac.* **2008**, 138, 101.

27. Vafaei, S; Wen, D.; Borca-Tasciuc, T. Nanofluid Surface Wettability through Asymptotic Contact Angle. *Langmuir.* **2011**, 27, 2211.

28. Wasan, D.; Nikolov, A. Spreading of nanofluids on solids. *Nature.* **2003**, 423, 156.

29. Xia, Y.; Qin, D.; Yin, Y. Surface Patterning and its Application in Wetting/Dewetting Studies. *Curr. Opin. Colloid In.* **2001**, 6, 54.

30. Chaudhury, M.K. Spread the word about Nanofluids. *Nature.* **2003**, 423, 131.

31. Kondiparty, K.; Nikolov, A.; Wu, S.; Wasan, D. Wetting and Spreading of Nanofluids on Solid Surfaces Driven by the Structural Disjoining Pressure: Statics Analysis and Experiments. *Langmuir.* **2011**, 27, 3324.

32. Munshi, A.M.; Singh, V.N.; Kumar, M.; Singh, J. P. Effect of Nanoparticle Size on Sessile Droplet Contact Angle. *J. Appl. Phys.* **2008**, 103, 084315.

33. Rao, Y. Nanofluids: Stability, Phase Diagram, Rheology and Applications. *Particuology.* **2010**, 8, 549.

34. Sobac, B.; Brutin, D. Triple-Line Behavior and Wettability Controlled by Nanocoated Substrates: Influence on Sessile Drop Evaporation. *Langmuir.* **2011**, 27, 14999.

35. Otami, M.; Saito, M.; Yabe, A. Surface Energy Analysis of the Detergency Process - Surface Tension Components of Binary Mixtures of Organic Liquids and Aqueous Solutions of Surfactants, *Textile Res. J.* **1985**, 55, 582.

36. Żenkiewicz, M. Methods for the calculation of surface free energy of solids. *J. Ach. Mat. Man. Engg.* **2007**, 24, 137.

37. Tarasevich, Y. I. The Surface Energy of Hydrophilic and Hydrophobic Adsorbents. *Colloid Journal.* **2007**, 69, 212.

38. Chibowski, E. Surface free energy of a solid from contact angle hysteresis. *Adv. Colloid Interfac.* **2003**, 103, 149.

39. Ivan, S.; Sondi, B.S. Silver nanoparticles as antimicrobial agent: a case study on *E. coli as* a model for Gram-negative bacteria. *J. colloid interface sci.* **2004**, 275, 177.

40. Paria, S. Surfactant-enhanced remediation of organic contaminated soil and water. *Adv. Colloid Interfac.* **2008**, 138, 24.

41. Rao, K.J.; Chaudhuri, R.G.; Paria. S. Naphthalene Degradation in the Presence of Natural-Synthetic Surfactants Mixture by Mixed Cultures. *J. Env. Chem. Engg.* **2014**, 2, 826.

12.2 Research Publication.

Original research paper (to be communicated)

1. Santosh Deb Barma and Santanu Paria. *"Wettability of hair using natural and synthetic surfactant in presence of silver nanoparticles as additive".*

Conference Proceedings

1. Santosh Deb Barma and Santanu Paria. **"Wettability of Glass and Hair Surfaces using Nonionic Surfactant Solutions"**. **CHEMCON-2013** (ICT, Mumbai), December 27-30, 2013