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The Effect of Starch Interactions with Soap or Surfactants Studied by the Ternary Phase Diagram

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THE EFFECT OF STARCH INTERACTIONS WITH SOAP OR SURFACTANTS STUDIED BY THE TERNARY PHASE DIAGRAM

A Dissertation Submitted to the Department of Applied Chemistry and Chemical Engineering, University of Rajshahi, Bangladesh for the
Degree of Doctor of Philosophy

BY

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February, 2014

DECLARATION

I do hereby declare that the entire research work submitted as the thesis entitled **"THE EFFECT OF STARCH INTERACTIONS WITH SOAP OR SURFACTANTS STUDIED BY THE TERNARY PHASE DIAGRAM"** under the supervision of **Professor Dr. Md. Ibrahim H. Mondal and Professor Dr. A. T. M Kamrul Hasan** towards the fulfillment for the degree of Doctor of Philosophy in the Department of Applied Chemistry & Chemical Engineering, University of Rajshahi is based on the results of my own investigation and has not ever been submitted before in any form for any other degree at any place.

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Certificate of Research

This is to certify that the Ph.D thesis entitled **"The Effect of Starch Interactions with Soap or Surfactants Studied by the Ternary Phase Diagram"** submitted by **Md. Mohsin Hossain,** Roll No. 07303, Registration No.3560, Session: 2007-2008, Department of Applied Chemistry & Chemical Engineering, University of Rajshahi, Rajshahi, Bangladesh has been completed under our supervision. This is a bonafide record of the research carried out by the candidate.

To the best of our knowledge, this thesis has not been submitted for the award of any degree elsewhere.

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Dedicated

To

**ZAINAH MANHA SUHA, ZANNATUL
MAWOA MOHONA, FARIDA YASMIN**

And

The memory of Late Mojahar Mollah &

My Beloved Mother Syeda Sorifun Nesa

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MD. MOHSIN HOSSAIN
February, 2014

ABSTRACT

MD. MOHSIN HOSSAIN

(Under the Supervision of Professor Dr. Md. Ibrahim H. Mondal
& Professor Dr. A.T. M. Kamrul Hasan)

Starch interactions with various surfactants have been studied for the investigation of ability and cleansing activity of starch-surfactant-water system. The surfactants investigated were sodium dodecyl sulphate (SDS), cetyltrimethyl ammonium bromide (CTAB), Triton-X-100, Brij-30 and tween-20. The Degree of substitution of starch is 0.8 and the concentration of starch was varied from 0.01 to 1% w/v. The effect of mixing on the micellisation of the ternary surfactant solutions can be described to a good approximation by taking into account only the effects of the volume difference between the hydrocarbon chains length. Mixed micelle formation with starch depends on the chain-length difference in the same way as for starch-surfactant micelle. Aggregation of the mixed micelles of the surfactants and the polymer coils produced a gel-like complex phase. The water content of the gel phase in equilibrium with aqueous solution increased when the chain-length difference between the two surfactants increased. The more surface-active component is strongly enriched in the polymer complexes of gels and it showed maximum cleansing activity of respective surfactant. From the experimental results of viscosity, surface tension and other physical properties it indicated that adding starch in surfactant as soap filler these properties have been changed. Starch mixed surfactant systems have the potential to impart controlled combinations of functionality and pore structure to mesoporous phase. Here, we combined various ionic and non-ionic surfactants with starch. Polymer that readily forms liquid crystalline meso-phases. The phase diagram for the ternary systems CTAB /H_2O /starch, SDS/ H_2O/ starch, TritonX-100/ H_2O/ starch, Brij-30/ H_2O/ starch and Tween-20/ H_2O/ starch at 50°C is measured using polarized optical microscopy. At this temperature, the binary starch/H_2O system forms disordered micellar solutions up to 72 wt% starch, and there is no hexagonal phase. With the addition of CTAB, we identified a large area of hexagonal phase, as well as cubic, lamellar and solid surfactant phases. The ternary phase diagram was used to predict the synthesis of thick meso-porous silica films via a direct liquid crystal tin plating technique. By changing the relative concentration of mixed surfactants as well as inorganic salts, surfactant /starch meso-structured thick films can be synthesized with variable water content. A 2D hexagonal, cubic and lamellar structure has been found by XRD instrumental analysis. The domains over which different meso-phases were prepared correspond well with those of the ternary phase diagram if the hydrophilic inorganic species is assumed to act as an equivalent volume of water. The effect of starch on surfactant like Brij-30, Twen-20, CTAB, Titron-X-100 and SDS were studied by the surface tension, viscosity measurement and the ternary phase diagram with these surfactants. The surface tension and viscosity of all of the surfactant solutions decreased with increasing concentration. For both non-ionic and ionic surfactants, the surface tension and viscosity decreased with increasing concentration of surfactants. However, in presence of starch solutions and starch paste, an increase in surfactant concentration resulted in decrease in the surface tension and reduced viscosity with increasing concentration of surfactants. For both cationic (CTAB) and anionic (SDS) surfactants, the surface tension and reduced viscosity of water decreased in the presence of starch. Critical association concentrations (CAC) occurred at surfactant concentrations well below the critical micelle concentrations (CMC) of the surfactants, at the lowest starch concentrations investigated (0.1 w%). The surface tensions of starch/surfactant solutions decreased strongly below the CAC. This is attributed to the formation of surface active associates by ion condensation. Associative phase separation of gels formed by starch and surfactant took place at extremely low concentrations when the surfactant/polymer charge ratio was somewhat larger than 1. The gel was highly viscous and contains 40–60% water, depending on the concentration of the surfactant hydrocarbon chain length and the nature of the polar head of the surfactant. The concentration at which the phase separation occurred decreased with increasing surfactant chain length and the concentration of simple electrolyte factors that promote micelle formation. This indicated that the gels were formed by association of starch to surfactant micelles. When surfactant well in excess of charge equivalence was added, the gels dissolved because the starch /surfactant complexes acquired a high charge. The complexes were analyzed and characterized by FTIR, XRD and SEM. Some of the complexes exhibited excellent emulsifying efficiency and surfactants performance properties with this polymeric starch.

THE EFFECT OF STARCH INTERACTIONS WITH SOAP OR SURFACTANTS STUDIED BY THE TERNARY PHASE DIAGRAM

CONTENTS

LIST OF ABBREVIATIONS

The following acronyms and abbreviations are used throughout this thesis:

AM	amylose
AMP	amylopectin
AHG	anhydroglucose
AOT	Sodium diethylhexylsulfosuccinate
CTAB	Cyltrimethylammonium bromide
CAC	Critical association concentration
CEC	Critical electrolyte concentration
CMC	Critical micellisation concentration
$C_n(EO)_m$	Alkyl poly (oxoethylene ether)
DDBS	Sodium dodecyl benzene sulphonate
DLS	Dynamic light scattering
DMSO	Dimethyl sulfoxide
DP	Degree of polymerization
DS	Degree of substitution
NaOct	Sodium octanoate
NaOl	Sodium cis-9-octadecenoate (sodium oleate)
NaPa	Sodium poly(acrylate)
NMR	Nuclear magnetic resonance
PAA	Poly(acrylic acid)
PAMPS	Poly[2-(acrylamido)-2-methylpropanesulphonic
PDADMAC	Poly(diallylmethylammonium chloride)
PEO	Poly(ethylene oxide)
PMAA /NIPAM	Poly(sodium methacrylate-co-N-isopropylacrylamide)
PMAA	Poly(sodium methacrylate)
Polymer JR	Cellulose, 2-hydroxyethyl 2-[2-hydroxy-3-(trimethylammonio)propoxy]
PVAc	Poly(vinyl alcohol)
PS1	Poly(maleic acid-co-methyl vinyl ether)
PS4	Poly(maleic acid-co-butyl vinyl ether)

PSS	Poly(styrene sulphonate)
PVP	Poly(vinyl pyrrolidone)
PVS	Poly(vinyl sulphate)
SANS	Small Angle Neutron Scattering
SAXS	Small Angle X-ray Scattering
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscopy
SHS	Sodium hexadecylsulphate
SOS	Sodium octylsulphate
STS	Sodium tetradecylsulphate
TEM	Transmission electron microscopy
XRD	X-ray Diffraction

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1. General Introduction

Today’s consumer interest in biodegradable materials has grown as a consequence of increasing social awareness to reduce environmental degradation by selecting more environmental-friendly products. Due to this fact, globally, the development of polymers and their derived products is a high priority from the standpoint of environmental preservation. In this race, synthetic natural products (like starch, sorbitol, sugar, etc.) based polymers and their allied products are being increasingly explored because of their potential applications. In the last five decades there is common trend to use petroleum products as active and useful ingredients in commercial products like liquid powder detergents, paints, printing inks, cosmetics and textile auxiliaries. Commercial detergent powder use LABS in range of 15-20%. There is a need to synthesis novel products based on vegetable origin which are eco-friendly. Efforts are necessary to substitute petroleum based product by novel polymers. The present generation of surfactant is based on LABS or similar materials, which are obtained from crude petroleum. We must develop renewable vegetative based biodegradable alternatives for these conventional petroleum based surfactant.

The present research work is aimed at developing a polymeric surfactants based on starch and various surfactant mixture. As the polymeric surfactant is based on starch it will have certain characteristics. It is used in the detergent formulation as partial substitute for linear alkyl benzene sulphonate (LABS). We aimed at formulating detergent consisting of dolomite, silicate with minimum use of STPP from the statistical study of production of starch (potato) in Bangladesh. It is observed that surplus amount of potato is left behind after its supply to the required areas. The cost of starch source (potato) is only USD 0.25 per kg, so it will be economical and sensible if this excess of remaining starch is utilized in the synthesis of some commercial products of reasonable price which are required by common man in his day to day life.

The present understanding of polymer/surfactant interactions in aqueous solutions have been summarized in several reviews, for example, Goddard and Ananthapadmanadhan [1993], Hayakawa and Kwak [1991], Saito [1991] and Robb [1981]. Many investigations have focused on aggregate structure in dilute solution, i.e., systems in which phase separation does not occur. The general picture emerging from these studies is that in dilute solution the surfactant molecules adsorb to polymer chains as micellar or micelle-like clusters. A general phenomenon in systems of polyelectrolyte and oppositely charged surfactant is that complexes of these components separate as a water-swollen phase in equilibrium with very dilute aqueous solution. Generally, the rich phase behavior of surfactants in water is also characteristic of polyelectrolyte-surfactant complexes in contact with water. In an early paper, Harada and Nozakura [1984] described the formation of layered structures in poly-vinyl sulfate (PVS)/ cetyltrimethylammonium bromide and 1-4-ionene/sodium dodecyl sulfate (SDS) systems. More extensive studies of x,y-ionene/ SDS and PVS/n-alkylpyridinium surfactants systems have recently been reported in a series of papers Chen et al. [1998] and Kim et al. [1999]. Kabanov et al. [1994], Khandurina [1994] and Bakeev et al. [1994] reported that complexes of sodium poly (acrylate) gel and alkyltrimethyl ammonium bromides form lamellar structures. Hanssonet and Langmuir [1998] found that a cubic phase was formed by sodium poly-(acrylate) and dodecyltrimethylammonium bromide. Ilekti et al. [1998] studied sodium poly(acrylate)/cetyltrimethylammonium bromide complexes and found that they form hexagonal structures and that the ionic compositions of the concentrated and dilute phase have significant effect on the phase behavior. [Kosmella et al. [1996] and Ruppelt et al. [1997] found that the intercalation of sodium poly(acrylate) into mesophases formed by alkyltrimethylammonium bromides induced some disordering, but did not substantially affect the phase structures. Recently, Zhou et al. [1998] observed long-range order in complexes of poly(sodium methacrylate-co-N-isopropylacrylamide) and poly(styrenesulfonate) with tetradecyl-, hexadecyl-, or odecyltrimethylammonium bromide. Zhou et al. [1999] discussed a characteristic of starch-surfactant complexes which contains a very hydrophilic carbohydrate polymer associated with oppositely charged surfactants. Thus, we expect the predominant driving forces for the self-assembly of surfactant molecules in these complexes to be hydrophobic interactions between the hydrocarbon chains of the surfactant and electrostatic interactions between charged segments of the polymer and the headgroups of the surfactant. Previously, it has been reported on interactions by Merta and Stenius [1995] aggregate formation Merta and Stenius [1997] and rheological properties of the complex phase in these systems. Merta et al. [1999] have also reported that their goal is to evaluate the structure of the phases in equilibrium with very dilute aqueous solution. Goddard and Hannan [1976] investigated that the interactions between surfactants with cationized cellulose were identified and the rheology of the complexes Goddard and Hannan [1977] but to our knowledge this study is the first investigation for starch and all type of surfactant systems. In the ternary phase, systems containing water, ionic or non-ionic surfactants and water-soluble polymer have been a subject of extensive investigations in last ten years aimed at a fundamental understanding of their properties as well as at evaluation of their use in various technical applications.

A polymer that has been relatively little studied in spite of its technical importance, starch, which is widely used in paper processing as flocculation and retention aid. Potato starch is a better retention aid than native starch, because due to the cellulose fibre/ starch attraction, it retains very effectively to the fibers and doesn't concentrate to the circulation water as badly as native starch. It is not only the fibers that are involved but also fines and soap-detergent fillers, which are much smaller particles than fibers. Their retention to the fiber network is extremely important. Fibers, fines and fillers are all negatively charged and therefore repel each other. Large cationic, anionic polyelectrolyte (surfactant) with starch can adsorb on these negatively/positively charged particles and collect them by formation H-bond between them. In this way, it is possible to effectively flocculate and also retain the fines and fillers. Optimal retention improves the wet strength of paper, and also important, the waste of these components decreases radically. Starch has also been proved to improve the dry strength of paper, making the inter-fiber bonding stronger. It is added to the process between refiner and the headbox. Starch is also used as a size on uncoated papers. It improves the printability, prevents the dusting of paper and makes the paper surface smooth. Starches have a high degree of substitution (>0.8) are also used in the paper coatings as well as in the headbox of paper machines, among other things in order to collect harmful cationic/anionic compounds from the water circle. This so-called “cationic/anionic trash” consists mainly of dissolved hemicelluloses, fatty and resin acids, and their salts, which are components of wood extracts. Starch that is used as a retention aid can also produce, together with wood extracts very harmful precipitates, which can disturb the whole paper processing. The cationic starch-cellulose fibre interactions are extensively studied in the thesis of van Steeg [1992] however; nothing has been published about interactions of starch with surfactants. Thus, it is very important to get information about the interactions of these two substances. For example, interactions of surfactants with cationized cellulose, has been studied by Goddard et al. [1976, 1977] and nonionic cellulose ethers have been subject of extensive studies by Piculell, Lindman et al.

[1992].

The structure of starch is very similar to cellulose, but the difference on the bindings, which link the mono glucose units to form the polymer, makes their chemical behaviour very different. The polymeric chains in starch are much more flexible than in cellulose, making the polymer more soluble in different solvents. The polymer chains of amylopectin are also branched, whereas cellulose has completely straight chain. Thus, actually starch is very different material to cellulose despite of their chemical similarity. The aim of this research work is to form better understanding about interactions between starch and all type of surfactants: What are the parameters affecting these interactions and how can these systems be modelled. Another important part of this study was the determination of the structure of these complexes and how these structures might be modified. Over the last few years, there has been an increasing interest in biodegradable materials. This interest was also a motivating factor in these studies, because chemicals used in these studies are nearly all derived from nature and also non-toxic and biodegradable. Starch is produced in huge amounts all around the world so it would be important to try to find new applications for its use instead of synthetic non-biodegradable polymers where possible. Surfactants constitute the most important group of detergent components. Generally, these are water-soluble surface-active agents comprised of a hydrophobic portion, usually a long alkyl chain, attached to hydrophilic or water solubility enhancing functional groups. To meet highest demands for quality, we offer a wide range of detergents and surfactants. Surfactants can be categorized according to the charge present in the hydrophilic portion of the species (after dissociation in aqueous solution): anionic surfactants, nonionic surfactants, cationic surfactants and ampholytic surfactants. All surfactants possess the common property of lowering surface tension/reduced viscosity when added to water in small amounts, the characteristic discontinuity in the plots of surface tension/reduced viscosity against surfactant concentration can be experimentally determined. The corresponding surfactant concentration at this discontinuity corresponds to the CMC. At surfactant concentrations below the CMC, the surfactant species are loosely integrated into the starch structure (monomer). In the region of the CMC, the surfactant-water structure is changed in such a way that the surfactant molecules begin to build up their own structures (micelles in the interior and monolayer at the surface). Due to the limited solubility of surfactants in water, aggregates are formed in which the hydrophobic or hydrophilic sections of the surfactant are stuck together. The micelle may be represented as a globular cylindrical or ellipsoidal cluster of individual surfactant molecules in equilibrium with its monomers. The reverse orientation of the hydrophilic and hydrophobic portion of the surfactant in a hydrocarbon medium leads to reversed micelles. Planar bilayers or small unilamellar vesicles are also formed .The extraordinary variety of the phase behavior of surfactants in solution can further be broadened by the inclusion of additives or co-surfactants The micelle formation process can be described by the following equation: $m * S <=> S_{m,}$ where m is the average association number, S is the concentration of monomeric surfactant and S_m is the critical micelle concentrations. The formation of micelles, critical micelles is shown in **Fig.** 1.1

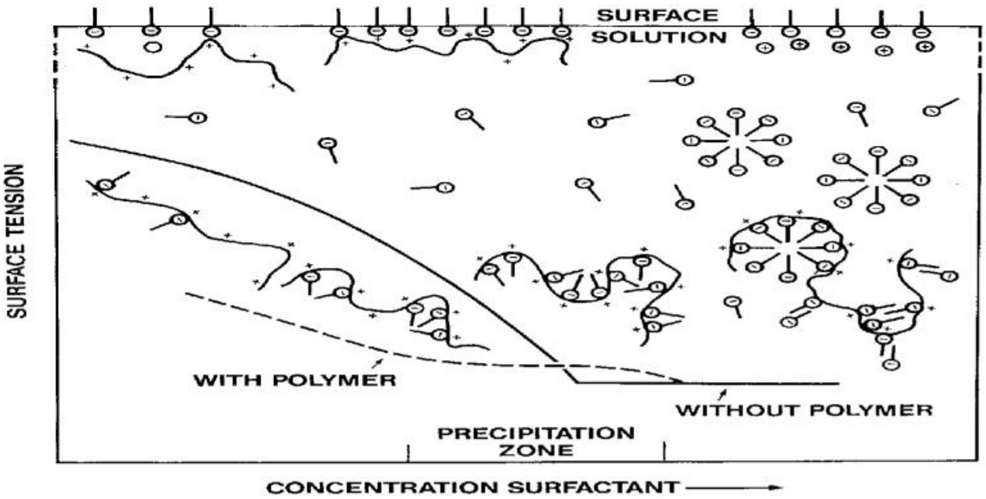


Fig.1.1: Formation of micelles and critical micelles and lowering of surface tension value of water at CMC point.

1.1 Starch

A naturally abundant nutrient carbohydrate, $(C_6H_{10}O_5)_n$, found chiefly in the seeds, fruits, tubers, roots and stem pith of plants, notably in corn, potatoes, wheat, and rice, and varying widely in appearance according to source but commonly prepared as a white amorphous tasteless powder. The structural formula of starch molecule has been given

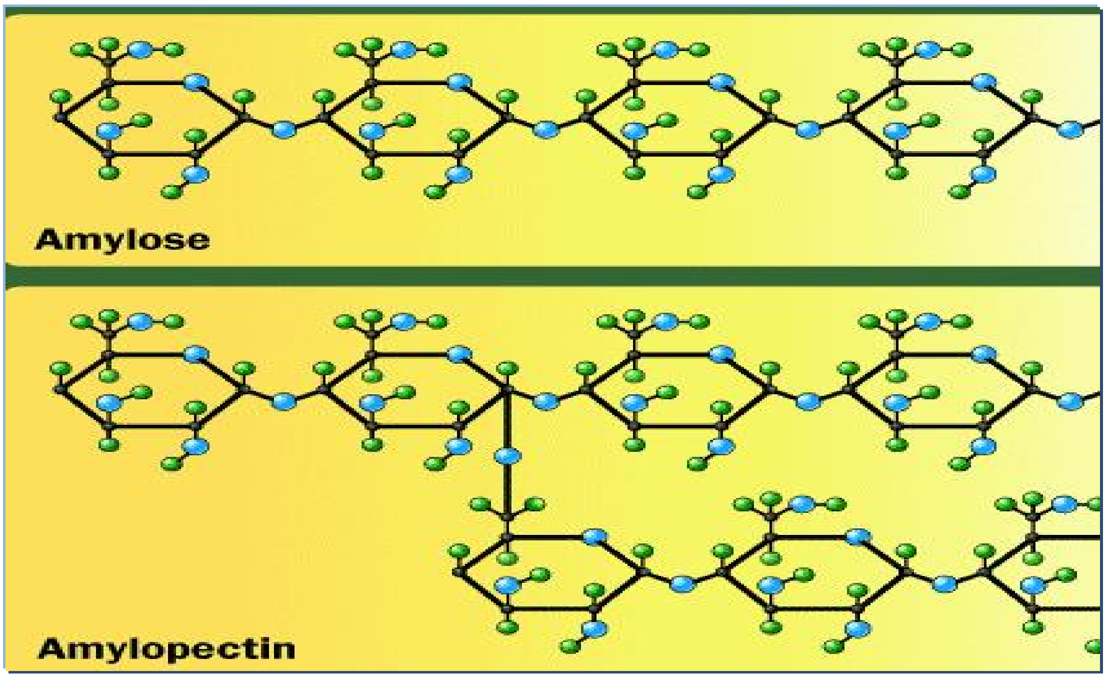


Fig: 1.2**: Structure of starch molecule containing two part amylose and amylopectin.**

Starch is a polymer consisting of anhydroglucose (AHG) units (see **Fig.** 1.2) Wurzburg [1986]. Two types of AHG polymers are usually present in starch: amylose and amylopectin Wurzburg [1986], Young [1984] and Nawrath et al. [1995] reported that amylose is essentially a linear polymer in which AHG units are predominantly connected through α-D-(1,4)-glucosidic bonds. The molecular weight of amylose is a function of the plant source and processing method, but usually in the range of 1.6-7 x 10^5 Da Whistler and Daniel [2005]. Amylopectin is a branched polymer, containing periodic branches linked with Whistler and Daniel [2005] the backbones through α-D-(1,6)-glucosidic bonds Wurzburg [1986]. Each branch contains about 20-30 anhydroglucose units. The molecular weight of amylopectin is higher than that of amylose and is typically 4-5 x 10^8 Da Whistler and Daniel [2005] the content of amylose and amylopectine in starch varies and largely depends on the starch source. Typically, the amylose content is between 18-28% Whistler and Daniel [2005] the amylose content of several common starches is given in **Table 1.1**

Table 1.1: Amylose content of common starches Younng, [1984]

Starch	Amylose (%)
Arrowroot	20.5
Corn	28
Hybrid amylomaize Class V	52
Hybrid amylomaize Class VII	70-75
Oat	27
Manioc	15.7
Potato	20
Rice	18.5
Sago	25.8
Sweet potato	17.8
Tapioca	16.7
Wheat	26

1.1.1 Properties of Starch

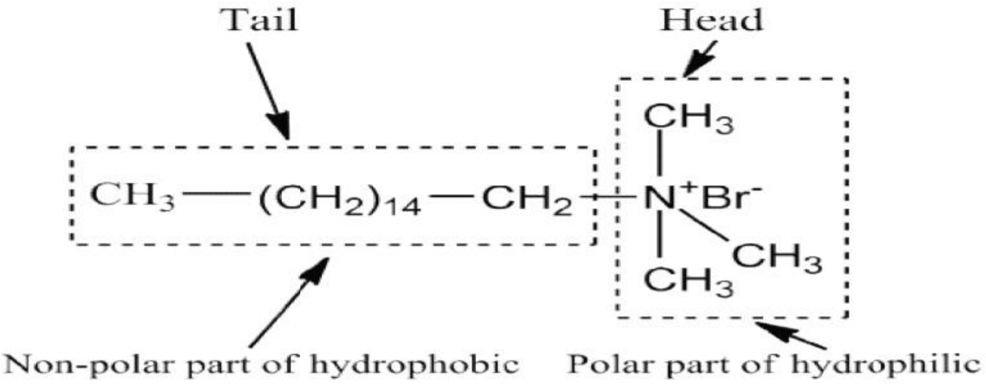
Starch is insoluble in cold water, but it is very hygroscopic in nature and binds with water reversibly. Heating starch solution leads to loss of hydrogen bonding in the interior of the starch granule and the starch will start to gelatinize. The starch granules will swell rapidly to many times of its original volume. The linear amylose molecules leach out of the granules into the solution. The resulting suspension contains a mixture of linear amylose molecules, swollen granules, and granule fragments, and, depending on the amount of water present, will form a thick paste or gel. The gelatinization temperature range can be defined as the temperature at which granular swelling begins until the temperature when nearly 100% of the granules are gelatinized Whistler and Daniel [2005]. The gelatinization temperature ranges of various starch sources is given in **Table 1.2**.

Table 1.2: Starch gelatinization temperature range Whistler and Daniel [2005]

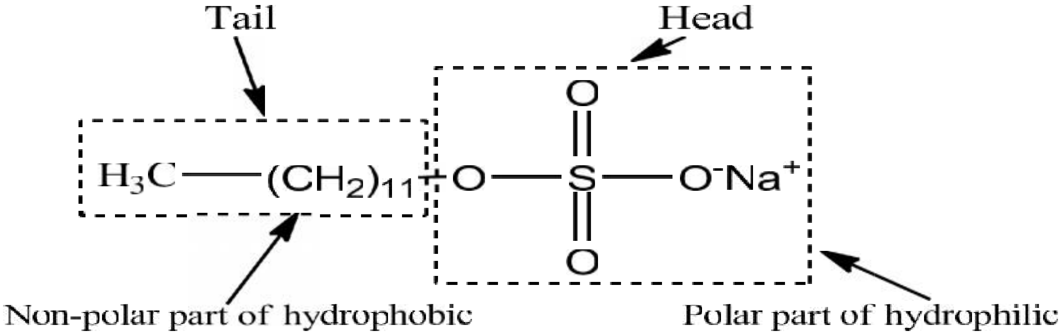
Starch	Gelatinization Temperature Range[^{o} C]
Potato	59-60
Tapioca	58.5-70
Corn	62-72
Waxy corn	63-72
Wheat	58-64

1.2 Surfactant

Surfactants constitute the most important group of detergent components. Generally, these are water-soluble surface-active agents comprised of a hydrophobic portion, usually a long alkyl chain, attached to hydrophilic or water solubility enhancing functional groups. a cleansing substance; specific, a surface-active chemical preparation, as, now especially, a linear alkyl sulfonate, that is capable of emulsifying dirt or oil.. As an additive pertaining to a substance, it (or "detersive") means "cleaning" or "having cleaning properties"; "detergency" indicates presence or degree of cleaning property. a cleansing agent: as a: SOAP b: any of numerous synthetic water-soluble or liquid organic preparations that are chemically different from soaps but are able to emulsify oils, hold dirt in suspension, and act as wetting agents c: an oil-soluble substance that holds insoluble foreign matter in suspension and is used in lubricating oils and dry-cleaning solvents few surfactant species are shown **Fig.**1.3.



Cationic surfactant (CTAB)



Anionic surfactant (SDS)

Fig.1.3: Structure of cationic and anionic surfactant species containing long alkyl chain

1.2.1 Properties of surfactant:

Surfactants are wetting agents that lower the surface tension of a liquid, allowing easier spreading, and lower the interfacial tension between two liquids. The term 'surfactant' is a blend of "surface acting agent". Surfactants are usually organic compounds that are amphiphilic, meaning they contain both hydrophobic groups (their "tails") and hydrophilic groups their "heads". Therefore, they are soluble in both organic solvents and water. For the more general meaning, "surface active agent" is the heading. This phenomenon is shown in the **Fig.**1.4.The most common biological example of surfactant is that coating the surfaces of the alveoli, the small air sacs of the lungs that serve as the site of gas exchange. Surfactants reduce the surface tension of water by adsorbing at the liquid-gas interface. They also reduce the interfacial tension between oil and water by adsorbing at the liquid-liquid interface. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles are formed in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil. Surfactants are also often classified into four primary groups; anionic, cationic, non-ionic, and zwitterionic (dual charge). Thermodynamics of the surfactant systems are of great

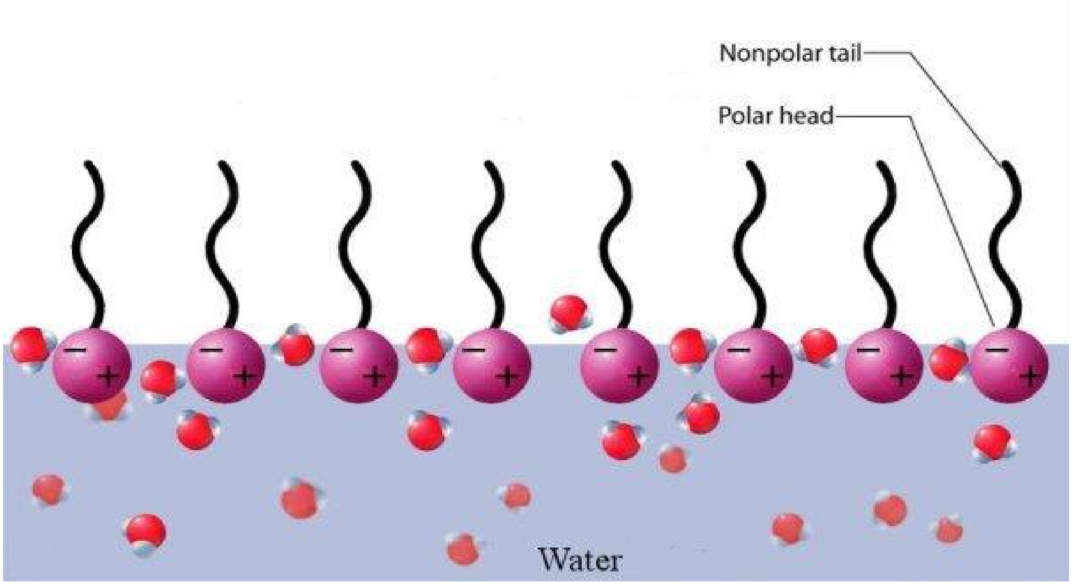


Fig.1.4: Surfactant species in water containing head and tail importance, theoretically and practically. This is because surfactant systems represent systems between ordered and disordered states of matter. Surfactant solutions may contain an ordered phase (micelles) and a disordered phase (free surfactant molecules and/or ions in the solution).

1.2.2 Classifications of surfactants

Generally, surfactant species consists of two parts having different properties: a ‘head group’ (hydrophilic) with a strong affinity for the solvent and a ‘tail’ (hydrophobic) with less affinity for the solvent. The head group may carry a negative or positive charge, giving rise to anionic or cationic surfactants, respectively. Alternatively, it may contain ethylene oxide chains or sugar or saccharide type groups, as is the case with nonionic surfactants. The tail part of the molecule is usually a hydrocarbon chain, but may contain aromatic groups. Besides, there is the class of ‘zwitterionic’ surfactants which alter their ionic behavior according to pH-value of the solvent. Depending on the molecular structure and type, a balance between hydrophilicity and hydrophobicity exists in the surfactant molecule. This is called hydrophobic-lipophilic-balance or HLB, which is important in categorizing surfactants as emulsifiers, detergents, wetting agents, solubilizing agents, micelle forming types, etc.

1.2.2.1 Anionic surfactants

When the head group of the surfactant species carries an anion, the surfactant is referred to as an anionic surfactant. Anionic surfactants are most widely used for laundering, dishwashing liquid and shampoos because of their excellent cleaning properties. Important types of anionic surfactants are carboxylates, suffocates, sulfates and phosphates. SDS is well known anionic surfactants which have a wide range of applications.

1.2.2.2 Cationic surfactants

Surfactants which carry a cationic head group are referred to as cationic surfactants. Cationic surfactants play an important role as antiseptic agents in cosmetics, as general fungicides and germicides, corrosion inhibitors, fuel and lubricating oil additives and in a number of bulk chemical applications. Two common types of cationic surfactants are long chain amines and quaternary amine salts. Alkyl amines chain length C_8 to C_{18} are the most important surfactants in this category. In the pharmaceutical area, cationic surfactants with pyridinium and piperidinium groups are also used. Pure cationic surfactants such as CTAB have been extensively studied in terms of the fundamental physical chemistry of surface active components.

1.2.2.3 Zwitterionic surfactants

These surfactants are very mild to personal use, making them particularly suited for use in personal care and household cleaning products. Zwitterionic surfactants are compatible with all other classes of surfactants and are soluble and effective in the presence of high concentrations of electrolytes, acids and alkalies. They exhibit cationic behavior near or below their isoelectric points and anionic behavior at higher pH. The isoelectric point depends on the structure of the surfactant. These surfactants contain two charged groups of different sign. Whereas the positive charge is almost always ammonium, the source of the negative charge may vary (carboxylate, sulphate, sulphonate). These surfactants have excellent dermatological properties. They are frequently used in shampoos and other cosmetic product and also in hand dishwashing liquids because of their high foaming properties.

1.2.2.4 Nonionic surfactants

Nonionic surfactants do not carry any electrical charge. They are more stable over the entire pH range. They show lower sensitivity to the presence of electrolytes in the system and they are compatible with other surfactants. They are excellent grease removers used in laundry products, household cleaners, and hand dishwashing liquids. The amphiphilic nature of these surfactants is expressed in terms of an empirical HLB Water-soluble surfactants have an HLB value higher than 13 and those with poor or no dispersibility in water have HLB values less than 6. Pentaethylene glycol
mono dodecyl ether ($C_{12}E_5$) is an example for a nonionic surfactant.

1.3 Theoretical Background

1.3.1 Surface Tension

Surface tension is a measure of force that holds the molecules together in both liquids and solids. Thus liquid droplets tend to assume spherical shape exposing minimum surface. Owing to surface tension that the liquid expose minimum surface area which is due to the fact that the cohesive energies existing the molecules in the sphere. To explain this phenomenon let us embark on the following discussion. Let us have a look into the situation existing in a liquid when taken in a container as shown in **Fig**.1.5

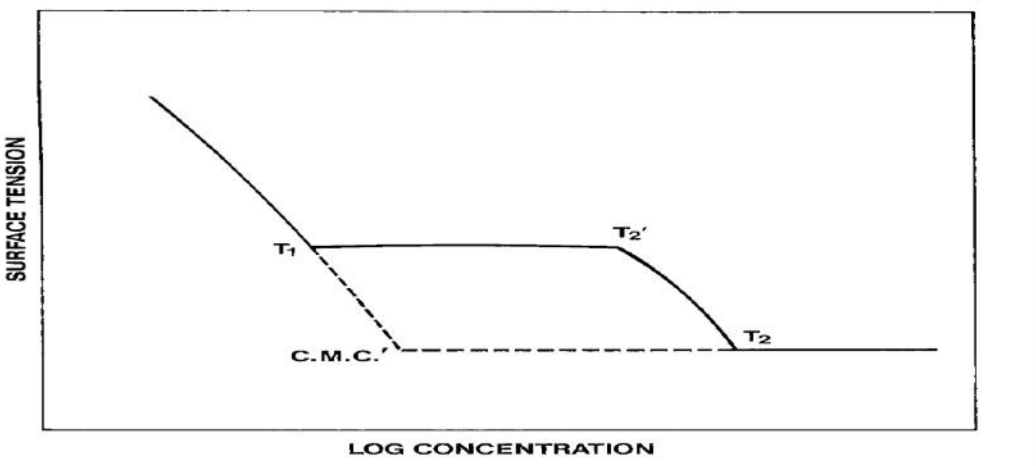


Fig.1.5: Diagrammatic surface tension/concentration plot of a surfactant in the presence of complexing polymer from Goddard and Anabthapadmanadhan [1993].

A system which has been widely studied by the surface tension method is poly (vinyl pyrrolidone) (PVP)/SDS as illustrated in the works of Lange [1971] and Murata et al. [1973]. Another system which is much studied by surface tension method is the system of Polymer JR (cationic hydroxyethyl cellulose derivate)/SDS, studied by Goddard et al. [1976]. They detected:

1) A synergistic lowering of the surface tension at very low surfactant concentration, implying the formation of highly surface active complexes;

2) The persistence of a low surface tension even in the zone of high precipitation where most of the originally added SDS is out of the solution;

3) Eventual coincidence with the surface tension curve of the polymer-free surfactant system in the micellar region. The observed phenomena can be explained in terms of the diagrams shown in **Fig**.1.5, representing progressive uptake of surfactant by the polymer.

CHAPTER-2: Objective of the present work

2.1 Objectives

For the last few decades several efforts have been made for starch interactions with soap or surfactants studied but still although many researcher have reported during the last several decades on the interactions, bond formations and others chemical reactions of starch with mentioned surfactants. In spite of half century of great effort, many academic aspects concerning the origin of interactions of starch with all types of surfactants are being emphasized for further exploration and discussion.

Based on the above mentioned importance on the mechanisms and H-bond formations through starch–surfactant complexes interaction, measuring by surface tension, reduced viscosity & to observe ternary phase diagram are being expected to be our experimental results. Finally, some literature had been survey before the research work started.

Solubilization is an important phenomenon both from theoretical and practical purposes. The most common application of solubilization is in cleaning and washing, where it is observed. It is also important in synthetic detergent industry, emulsion, polymerization, some of foods we eat, cloths we wear, regenerated fillers, preparation of vitamin and antibiotics and the stabilization of colloids which is important not only in the functioning of the detergent but also for the continued existence of biological organisms. The large scale application of solubilization dramatically emphasizes the need for a clearer understanding of the phenomenon.

The most reviews available in the literature have confined to a description of the experimental facts and the theoretical treatment of the solvent action has been lacking, especially on

i. Effect of chain length of surfactants;
ii. Mature of ionic head (size and chemical environment);
iii. Effects of chemical structure of the solubilizers and solubilizates;
iv. Effects of heat and concentration etc.

Few studies concern for ionic and nonionic systems which focus mainly as:-

1. The mixed surfactants from mixed micelle
2. Ionic surfactants are effective in solubilization of oil and organic compound in aqueous solution of nonionic surfactants and also to raise their solubilization temperature

3. Dependence of solubilization temperature on mixing ratio of the surfactants

From the above review of the solubilization in general it is obvious that although a great deal of information in the literature, there are many aspects of the process which are yet to be undated.

Salt effect in the different ternary system has already been observed in the literature, which includes studies is also available as:-

i. Non electrolytic detergents which are associative in aqueous solution.
ii. The ions which are opposite in sign to that of the aggregate are effective in lowering the critical concentration.
iii. The common ions and counter ions effect in micelle formation.
iv. The effect of alkynes and alkaline earth metal on surfactants in solution

2.2 Motivation

The aim of this research work is to use FTIR, SEM and XRD to characterize the starch/surfactant aggregation at a single molecule level. Moreover, we shall demonstrate the potential of SEM, XRD to access the macroscopic as well as microscopic properties of complex systems in detail. As a model system complex formation between non-ionic polymer (starch) and the anionic surfactant sodium dodecyl sulfate /cationic surfactant CTAB in water was chosen for investigation. We shall show that SEM and XRD can follow the motion of individual SDS, CTAB micelles and single starch/SDS and starch/CTAB aggregates. Rheology (surface tension, viscosity and ternary phase) is used to follow the macroscopic properties of the polymer/surfactant systems which will then be compared to the SEM and XRD measurements. Starch tends to undergo a sol-gel transition at elevated temperature. Therefore temperature dependence measurements are performed by both SEM and rheology. The additives SDS, CTAB and salts will normally change.

2.3 Present Problem

The cleansing activity of soap-detergent is one of the most important phenomena in daily life for the modern society. Thus, the improvement of activity of soap-detergent is obviously needed for the better quality and performance. Many investigations of starch/surfactant interactions in aqueous systems have focused on aggregate structures in dilute solutions. Very few observations of the properties of starch /surfactant systems are available. There still exist many unsolved problems including chemistry, chemical reactions and bond formations on the effect of starch interactions with non-ionic surfactants in our research.

2.4 Objective of the present research

The purpose of the present study is to explore the effect of starch interaction with various surfactants and for better understanding the mechanism between starch & surfactants complexes by the ternary phase, interfacial surface tension, viscosity and some instrumental analysis (XRD, SEM and FT-IR). Solubilization is an important phenomenon both from theoretical and practical purposes. The most common application is in cleaning and washing, where it is observed. It is also important, in synthetic detergent industry, emulsion, polymerization, some of foods we eat, cloths we wear, regenerated fillers, preparation of vitamin and antibiotics. The stabilization of colloids which is important not only in the functioning of the detergent but also for the continued existence of biological organisms. The large scale application of solubilization dramatically emphasizes the need for a clearer understanding of the phenomenon. The most ancient reviews have confined to a description of the experimental facts and the theoretical treatment of the solvent action has been lacking. Such as:-

1. Effect of chain length of surfactants
2. Mature of ionic head (size and chemical environment)
3. Effects of chemical structure of the solubilizers and solubilizates and.
4. Effects of heat and concentration etc.

A few workers have been reported for anionic, nonionic and cationic systems. These are given in brief as follows:

1. The mixed surfactants from mixed micelle
2. Ionic surfactants are effective in solubillization of oil and organic compound in aqueous solution of nonionic surfactants and also to raise their solubilization temperature.
3. Solubilization temperature is dependent on mixing ratio of the surfactants

From the above review of the solubilization in general it is obvious that although a great deal of information is irritable in the literature, there are many aspects of the process which are yet to be undated. From the review it is clear that salt effect in the different ternary system has already been observed. The information are:

a. Non-electrolytic detergents are associative in aqueous solution.
b. The ions which are opposite in sign to that of the aggregate are effective in lowering the critical concentration.
c. The common ions and counter ions effect in micelle formation and
d. The effect of alkaline and alkaline earth metal on surfactants in solution.

2.5 Thesis Outline

The objective of this thesis is to study starch interactions with various surfactants by some physical properties such as interfacial surface tension, viscosities, and to do the ternary phase diagram. Three routes have been studied in detail: starch-surfactant interactions, starch/ surfactant/ water mixtures crystalinity and starch-surfactant H-bond formations by H-atom.

There are also some studies about the effect of adding starch solution to the liquid crystalline phase of some surfactants. Kosmella et al. [1996] and Ruppelt et al. [1997] found that the intercalation of sodium polyacrylate into mesophases formed by alkyl trimethylammonium bromides induced some disordering but did not substantially affect the phase structures. These studies can be summarized as follows:

1) Alkyl chain length of the surfactant affects the formation and transition of highly ordered structures inside Starch/surfactant complexes. The longer the chain length, the stronger are the hydrophobic interactions between surfactant and starch chains and the smaller the volume ratio of polar-to-apolar moieties of surfactant, both of which determine the self-assembly behaviour of the surfactant inside the complexes.

2) Both electrostatic and hydrophobic interactions are very important for inducing the highly ordered self-assembly of surfactant molecules. The longer the surfactant chain length, the lower the charge density and the weaker is the hydrophobicity of polyelectrolyte chains are required to form ordered structures.

3) The charge density of the polyelectrolyte is an important parameter determines the structures formed. When the charge density of polyelectrolyte chains decreases the structures of the resulting complexes become less ordered. Both the aggregation number and the radius of the micelles inside the complexes decrease with decreasing charge density of the polymer.

4) The flexibility of polyelectrolyte chains affects the shape of structural elements formed by the self-assembly of polymer-bound surfactant molecules. The surfactant molecules bound by stiff polymer chains prefer to form the structural element of cylinders, while those bound by more flexible polymer chains can form spheres.

5) Temperature has also a clear effect on the stability of the ordered structures. At higher temperatures ordered structures with lower stability are formed, and above certain temperatures, the formation of highly ordered structures inside the complexes can be totally prevented.

The details of the chapters are discussed as follows:

Chapter 2 provides a detailed discussion about the polymers and the surfactants. Polymer-surfactant interactions are dealt with followed by a discussion about the techniques required to characterize such interactions. A brief literature review on the polymer-surfactant system investigated in this thesis is given at the end of the chapter.

Chapter 3 focuses on the materials under study and experimental methods. The basics, experimental setup, and theory of the SEM, XRD and IR technique are discussed. To analyze the macroscopic properties, rheological and turbidity measurements are done which is also discussed at a later stage of this chapter followed by details about the SEM measurements.

Chapter 4 summarizes the results obtained from Ternary phase diagram and other techniques as well as the detailed discussions of all the relevant observations. The first part of this chapter is focused on the Starch concentration dependence studies followed by the discussions on temperature dependent measurements. The surface tension and reduced viscosity results to understand the polymer-surfactant interactions are further supported by rheological data. To view the aggregations, SEM images are shown and discussed. The effect of temperature on the gelatinazation of starch with additives of surfactants is also discussed with XRD, rheology and surface tension measurements and viscosity was also discussed.

In Chapter 5, 6 and 7, the structure of starch-surfactant is reported. The method applied basically consists of three steps H-bond formation identification, complexes crystalinity determination and surface smoothness by the complexes formation. *A* preliminary study on the effect of starch on surfactant variables (reactant ratio, addition and application of different concentration) on starch Chapter 3 based on these preliminary results, a systematic experimental study on the effect of starch variables on the surfactant concentration has been performed. The results were quantified using a statistical methods i.e. surface tension and viscosity calculation from chapter 3 & 8. The complexes, together with the mechanical and thermal properties of the synthesized starch –surfactants complexes .The effect of temperature on structure of amylase-surfactant complexes had been studied in chapter: 3 and 8 also increasing temperature within the ranges of 35-75^{o}C.

CHAPTER-3: Literature Review

1. Interactions of surfactants with cationized cellulose has been studied by Goddard et al. [1976, 1977] and nonionic cellulose ethers have been subject of extensive studies by Piculell, Lindman et al. [1992]. The structure of starch is very similar to cellulose, but the difference on the bindings, which link the monoglucose units to form the polymer, makes their chemical behavior is very different. The polymer chains in starch are much more flexible than in cellulose, making the polymer more soluble in different solvents. The polymer chains of amylopectin are also branched, whereas cellulose has completely straight chain. Thus, actually starch is very different material to cellulose despite of their chemical similarity.

2. Over the last few years, there has been an increasing interest in biodegradable materials. This interest was also a motivating factor in these studies, because chemicals used in these studies are nearly all derived from nature and also non-toxic and biodegradable. Starch is produced in huge amounts all around the world so it would be important to try to find new applications for its use instead of synthetic non-biodegradable polymers where possible.

3. The isotherm has a marked sigmoid shape, which is an indication of cooperative binding, and the onset of the surfactant binding often occurs at a certain, rather well defined, surfactant concentration. This concentration is called the critical aggregation (or association) concentration (CMC). This notion, which was introduced by Chu and Thomas [1986], indicates that the surfactant molecules form aggregates upon interacting with the polymer chains. The leveling out of the binding isotherm at higher surfactant concentrations is due to saturation of the polymer with surfactant, and indicates the maximum amount of surfactant that can be bound per polymer unit. For many systems, this level is not reached due to phase separation, or is obscured by the formation of free micelles.

4. It was observed for the binding of C_{10}TAB to Hy, which has a relatively low charge density by Thalberg and Lindman [1989], Thalberg et al.[1990a, 1991a]. Thus, the cooperativeness also depends on other features of the polyelectrolyte, such as the flexibility of the chains and hydrophobic character of the repeating units.

5. Above the CAC by Goddard [1986a, b] and Goddard and Ananthapadamabhan, [1993] found that the concentrated phase could be a solid or a highly viscous gel-like

solution. Addition of large amount of salt inhibits the phase separation and a redissolution of the complex phase takes place when an excess of surfactant is added.

6. Several references may be found in the literature to the compaction of polyelectrolytes on binding of oppositely charged surfactants by Musabekov et al. [1983] also reported viscosity measurements have been carried out by Abuin and Scaiano [1984] on mixtures of PSS of M_w of 130 000 and DTAB. When added to solution of 0.36 w% PSS, DTAB in the pre-precipitation zone brought about a progressive reduction in the viscosity of the solutions. For example, 5.8 mM DTAB was found to drop the reduced viscosity of PSS by a factor of ten, far exceeding the reduction effected by addition of the simple analog "surfactant", tetra decyl trimethyl ammonium bromide. The explanation offered was that coiling of the flexible "vinyl" backboned poly electrolyte occurs around small clusters of the surfactant, which form under these conditions. Similar effects had been obtained by Bekturov et al. [1984], who studied the viscosity characteristics of a series of amphoteric polymers on addition of anionic (SDS) or cationic (CTAB) surfactants to their solutions.

7. Goddard et al. [1982] and Leung and Goddard [1985] had reported viscosimetric and rheological studies on two cationic polymers, viz. a cationic cellulosic (Polymer JR) and an acrylamide/methacryloxyethyltrimethylammonium chloride copolymer (Reten, Hercules) within a range of polymer and added SDS concentrations. Considerable differences in behaviour between the two polymers were found. At the 1% Reten level, no change was detectable in viscosity at all levels of added SDS but, by contrast, the viscosity of 1% Polymer JR solutions increased over 200-fold.

8. Experimental evidence for this behaviour has been given by Koene et al. [1983 a, b, c] for solutions of poly(styrenesulphonate) (NaPSS) and Smits et al. [1993] for solutions of linear poly(ethyleneimine) chloride (LPEI). Due to these difficulties, light-scattering techniques have seldom been employed to elucidate changes in systems of polymers and surfactants.

9. Dubin and co-workers Dubin et al. [1988, 1990] had described light-scattering measurements on a negatively charged surfactant in solution with a neutral polymer, and on the complex formed between mixed micelles and an oppositely charged polyelectrolyte. There is also an article by Fundin et al. [1994] found where

polymer/surfactant interactions in a system of sodium poly (styrenesulfonate) and CTAB are studied by light-scattering measurements.

10. A study of poly(acrylate-co-acrylamide) had been done by Ranganathan and Kwak [1996] where the ionization of the polymer was varied. The experiment of varying the charge density of the micelles by mixing in non-ionic surfactant has also been made Li and Dubin [1995]. As expected, reducing the micellar charge density or the charge density of the polymer markedly reduces the extent of the phase separation.

11. The use of fluorescence techniques has contributed to the establishment of this structure, but also different NMR techniques have been used. The first report of aggregation numbers in polyeletrolyte/surfactant system is repoted by Abuin and Scaiano, [1984]. They studied the system of PSS and C_{12}TAB and found that the surfactant forms small clusters of only up to 10 monomers absorbed into the polymer chains. Zhen and Tung [1992] studied extensively interactions of NaCMA (sodium carboxy methylamylose) with SDS.

12. The concentration of the bound surfactant, studied byHansson and Almgren [1994, 1995]. This behaviour has been illustrated by the studies of Anthony and Zana [1996]. They studied binding of C_{12}TAC to PS1 (poly(maleic acid-co-methyl vinyl ether) and PS4 (poly(maleic acid-co-butyl vinyl ether). The constancy of N_{agg} indicates that the surfactant binding to poly-ions results in the formation of aggregates of constant composition and, thus, involving a constant length of polyion, in number increasing with C_b.

13. For the longer surfactant by Kiefer et al. [1992] also observed an increase of N_{agg} with " in the system of PAA/C_{14}TAB in the presence of 10mM KBr. The N_{agg} values for polyelectrolyte-bound aggregates increase with the surfactant chain length as in polymer-free systems observed by Almgren et al. [1992], but decrease with temperature Hansson and Almgren [1995]found that the independent of the nature of the surfactant counterion. Where Hansson and Almgren [1994] reported about the added electrolyte and Hansson and Almgren [1995] explained the series of results in contrast with the behaviour of polymer-free surfactant solutions.

14. Recently scattering studies with SANS and SAXS have provided further information. A decrease in the dimensions of the polyelectrolyte coils was observed for

NaPA-C_nTAB solutions by Thalberg et al. [1991c]. Certainly, coiling of the chains can be expected both for electrostatic reasons, as polyelectrolyte chains in pure water are extended, and for topological reasons, i.e., in order to create a large contact area between polymer chain and the micelle. Herslöf and Sundel[1992] studied the viscosity in dilute solution for NaHy-C_{16}TAB system after addition of salt (NaBr).

15. Monte Carlo simulations have been applied to investigate complex formation between micelles and hydrophilic polyelectrolytes by Wallin and Linse [1995] studied. The scope of these studies was to study how different system parameters as flexibility and linear charge density of the polymer, and the chain length of the surfactant affect the cac/CMC ratio.

16. It has for a long time been known that amylose forms helical inclusion complexes with a variety of organic compounds such as lipids studied by Snape et al. [1998], and Codet et al. [1993] and different surfactants studied by Yamamoto et al.[1983]. The helical coil formed by the amylose/lipid inclusion complex in aqueous solution has been demonstrated to comprise from 6 to 8 repeating glucose units per helical turn. Amylose takes so-called V-form conformation when forming the inclusion complexes. The V amylose is a generic name for crystalline amyloses, obtained as single helices co-crystallized with compounds such as water, iodine, DMSO, alcohols or fatty acids. In the V-form, a single chain of amylose forms a helix with a relatively large cavity. The central cavities of the V-forms have a pitch of about 8Å per turn. A detailed X-ray conformational analysis of the hydrated helix with a guest molecule inside has been reported by Rappenecker et al. [1981] and Yamamoto et al., [1983] found that the binding of sodium alkyl sulphates to amylose is cooperative when the DP of polymer is big enough, and that its cooperativeness depends on the carbon chain length of the surfactant. Also, the outer branches of the amylopectin molecule are assumed to form the same kind of inclusion complexes with suitable lipids studied by Kubik et al. [1995], Thomasik et al. [1995] and Eliasson et al. [1995].

17. Polyelectrolyte-surfactant complexes have known for some years to form ordered complexes in organic solvents and in the solid state. For a review, observed by Ober and Wegner [1997] and Antonietti et al.[1994] have observed that complexes that precipitate out when aqueous solution of NaPSS and alkyltrimethylammonium

bromides are mixed together can be redissolved in organic solvents such as dimethylformamide, tetrahydrofuran or ethanol, where they behave like polyelectrolytes. Cast films of some of these complexes showed highly ordered mesophases of the lamellar type Antonietti et al. [1995]. Such structures appear to be of a general character since they were observed with several polyion/surfactant ion complexes: copolymers of 2-acrylamido-2-methyl-1-propanesulphonic acid with N-octadecylacrylamide, at different ratios of the two monomers with $C_{16}TAB$ reported by Antonietti et al. [1996], and poly (dimethyl diallyl ammonium chloride) / natural lipid reported by Antonietti et al. [1998].

18. Kabanov et al. [1994,1995] investigated complexes of polycations and polyanions with the anionic surfactant AOT (sodium diethylhexylsulfosuccinate) in organic solvents in the presence of water. The complexation of polyelectrolytes of the ionomer type (partially sulfonated polystyrene) by AOT in m-xylene resulted in a partial disruption of the aggregates formed by the ionomer reported by Kabanov et al. [1994]. Poly(N-ethyl-4-vinylpyridinium bromide was found to be soluble in octane and hexane in the presence of AOT studied by Kabanov et al. [1995] and in the presence of water pools formed by AOT, where it adopted a rather compact conformation by Kabanov et al. [1994]. At low water content, the authors proposed a comb-like model for the complex.

19. In the first reported study, as expected Harada and Nozakura [1984] described electron microscope (TEM) studies of polyelectrolyte complexes made from poly(vinyl sulphate), PVS, with $C_{16}TAB$. By mixing dilute aqueous solutions of the potassium salt of PVS with $C_{16}TAB$.

20. Osada et al. [1994] made extensive studies of x,y-ionene/SDS and PVS or PAMPS (poly[2-(acrylamido)-2-methylpropanesulphonic acid]/n-alkylpyridinium surfactants systems Chen et al. [1998] and Kim et al. [1999] alsoreported that the results showed that n-alkylpyridinium surfactants form lamellar mesophases in the complexes of NaPSS, but hexagonal close-packed of spherical micelles with PAMPS. They assumed that the reason for these different structures might be the more rigid chains of NaPSS, which may inhibit the folding of polymer chains around the micelles. Kabanov et al. [1995] studied the NaPA-gel/ alkyltrimethyl ammonium bromide complexes supported by Khandurina et al. [1994 a, b, c]. The complexes

were found to have lamellar structure when the chain length of the surfactant was long enough (>14). The NaPA complexes with C_{14}TAB and C_{12}TAB were amorphous without any long-range order. Benjamin Chu and his co-workers have extensively studied ordered polyelectrolyte/surfactant structures. They studied poly(diallylmethyl-ammonium chloride, PDADMAC) gels with different sodium alkyl sulphates. Sokolov et al. [1996, 1998] found that these complexes have structure of hexagonal close-packed of cylindrical micelles with SDS, STS, and SHS. The SDS complex was found to have a cubic structure.

21. There are also some studies about the effect of adding polyelectrolyte to the liquid crystalline phase of some surfactants by Kosmella et al. [1996] and Ruppelt et al. [1997] found that the intercalation of sodium polyacrylate into mesophases formed by alkyltrimethylammonium bromides induced some disordering, but did not substantially affect the phase structures.

22. These studies can be summarized as follows:

i) Alkyl chain length of the surfactant affects the formation and transition of highly ordered structures inside polyelectrolyte/surfactant complexes. The longer the chain length, the stronger are the hydrophobic interactions between surfactant and polymer chains and the smaller the volume ratio of polar-to-apolar moieties of surfactant, both of which determine the self-assembly behaviour of the surfactant inside the complexes.

ii) Both electrostatic and hydrophobic interactions are very important for inducing the highly ordered self-assembly of surfactant molecules. The longer the surfactant chain length, the lower the charge density and the weaker is the hydrophobicity of polyelectrolyte chains are required to form ordered structures.

iii) The charge density of the polyelectrolyte is an important parameter determines the structures formed. When the charge density of polyelectrolyte chains decreases the structures of the resulting complexes become less ordered. Both the aggregation number and the radius of the micelles inside the complexes decrease with decreasing charge density of the polymer.

iv) The flexibility of polyelectrolyte chains affects the shape of structural elements formed by the self-assembly of polymer-bound surfactant molecules. The surfactant molecules bound by stiff polymer chains prefer to form the structural element of cylinders, while those bound by more flexible polymer chains can form spheres.

v) Temperature has also a clear effect on the stability of the ordered structures. At higher temperatures ordered structures with lower stability are formed, and above certain temperatures, the formation of highly ordered structures inside the complexes can be totally prevented.

23. It was reported by Jones [1967] who studied the properties of mixed poly(ethylene oxide) (PEO)/sodium dodecyl sulphate (SDS) systems and first formalised the concept, in a system of fixed polymer concentration and increasing amounts of surfactant, using two critical concentrations.

24. A system which has been widely studied by the surface tension method is poly (vinyl pyrrolidone) (PVP)/SDS as illustrated in the worked by Lange, [1971] and Murata et al. [1973] . Another system which is much studied by surface tension method is the system of Polymer JR (cationic hydroxyethyl cellulose derivate)/SDS, studied by Goddard et al. [1976]. They detected:

i) A synergistic lowering of the surface tension at very low surfactant concentration, implying the formation of a highly surface active complex;

ii) The persistence of a low surface tension even in the zone of high precipitation where most of the originally added SDS is out of the solution;

iii) Eventual coincidence with the surface tension curve of the polymer-free surfactant system in the micellar region.

25. Lange [1971] observed an increase in viscosity of PVP on addition of SDS. In this case, the effect was recorded as an increase in specific viscosity that occurred in the vicinity of T_1 for this system. These results clearly imply a change in polymer conformation, viz. an expansion of the polymer coils, on association with the charged surfactant, as reported also by Nagaran and Kalpakci of PEO/SDS systems but Nagaran et al.[1982], and Tadros [1974] studied for PVAc/DDBS systems, respectively. A systematic investigation of the variation of the viscosity of PEO solutions, covering a range of molecular weight and concentration as a function of

added SDS concentration, has been described by Francois et al. [1985].

26. Several references may be found in the literature to the compaction of polyelectrolytes on binding of oppositely charged surfactants by Musabekov et al. [1983]. Viscosity measurements have been carried out by Abuin and Scaiano [1984] on mixtures of PSS of M_w of 130 000 and DTAB.

27. Goddard et al. [1982] and Leung and Goddard [1985] had reported viscosimetric and rheological studies on two cationic polymers, viz. a cationic cellulosic (Polymer JR) and an acrylamide/methacryloxyethyl trimethylammonium chloride copolymer (Reten, Hercules)

The above mentioned huge number of research had been done before starting my work.

Chapter 4: *Experimental*

4.1 Materials

- 4.1.1 Starch Powder
- 4.1.2 Various Surfactants
- 4.1.3. Other chemical

4.2 Methods

- 4.2.1 Methods of surface Tension determination
- 4.2.2 Methods of Viscosity determination

4.1. Materials

The chemicals used in this experiment are listed as:-

4.1.1. Starch

This product was purchased from UNI-CHEM. Chemical Reagents Made by China. The degree of substitution (DS) was 0.80. The Starch was dissolved by heating the starch/ water mixture in an autoclave or 30 min. at 120°C .All solutions were prepared at least 24 h before measurement were performed.

4.1.2. Various surfactants

The surfactants used were commercial grade Sodium dodecyl sulphate (SDS) N-cetyl- N,N,N-trimethyl Ammonium Bromide (CTAB), Triton-X-100, Brij-30, Brij-35, Tween-20) and NaOct were analytical grade made from LOBA.

4.1.3. Other chemical

The water was ion exchanged and distilled. Its conductivity, reduced viscosity were 2.0 µs, 4.0 dm^3/mol and its surface tension was 71.5± 0.5 mN/m at 30°C. All other chemicals were analytical grade and were used without further purification.

4.2 Methods

4.2.1. Surface and interfacial tension measurement

Methods for the determination of surface tension:

There are several methods available for the determination of surface tension which is shown below:

(a) Capillary rise method.

(b) Drop weight and drop volume method.

(c) Ring method.

(d) Bubble pressure method.

(e) Pendant drop method.

(f) Sessile drop method.

(g) Hanging plate method.

(h) Surface potential method.

(i) Method based on the spreading of oils.

(j) Method of ripples etc.

Of the above mentionable methods, I have chosen the drop weight method to determine surface tensions.

Surface tension has long been recognized as an important physical characteristic of fluids and colloids that can affect biological processes. Scientists sought ways to measure this phenomenon, but reproducible results were difficult to obtain. Two approaches, developed to measure this subtle force, are displayed here.

The process of drop formation by liquids is, in part, controlled by the surface tension of the fluid. To determine surface tension, the stalogometer used a drop weight method, in which the number and weight of drops were compared to those from a reference liquid. Seemingly simple, the stalogometer nevertheless required considerable skill and absolute cleanliness for readings to be meaningful. An instrument for measuring the size of drops suspended from a capillary tube, used in the drop-weight method. Also known as stactometer; stalogometer. Tubes are available in 2.5mL, 3.5mL and 5.0mL sizes.

If the drops which stay at the end of a tip were cylindrical and of the same diameter as the tip, it is evident the maximum weight of drops which could be supported would be exactly equal to the weight of the liquid uphold in a capillary tube of the same diameter, because in both cases, the force of surface tension, acts on a line $2\pi r$ long, so the force is $2\pi r\gamma$

or $W=mg = 2vr\gamma$

$$\boxed{\gamma = \frac{mg}{2\circledR r f^{\frac{1}{3}}}}$$

A drop of the weight (m) given by the above equation has been designated by [Harkins and Brown, 1948] as the ideal drop. This method is directly applicable to the determination of the interfacial tension of oils or mercury against the aqueous phase. In the calculation of surface tension, the correction factors of Huh and Mason [Huh, C. and Mason S.G., 1995.] were used. The reproducibility between measurements on the same sample was ±0.5 mN/m. This was probably due to the very low concentrations of starch (0.01 wt.%). The results of the surface tension measurement were presented as (g) values calculated from $\gamma = \frac{mg}{2\pi rf}$ where f is equal to $\frac{1}{v^3}$, v being the volume of the drop and r its radius, m the weight of falling drop g and γ its surface tension. A drop of the weight (m) given by the above equation has been designated as the ideal drop. Repeat measurements (2—4) were conducted on each sample from which equilibrium surface or interfacial tension values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to running tests with the starch solutions, the instrument was calibrated with water and then checked by measuring the interfacial tension between water and pure starch.

IV) DEPENDENCE OF SURFACE TENSION:

The surface tension of a solution has been found to depend on several parameters which are as follows:

a. Concentration: The surface tensions of solutions were found to depend of concentration. Thus for lyophilic colloids the surfactants were found to decrease the surface tension to a considerable extent and then above a specific concentration the surface tension was found to become fairly constant.

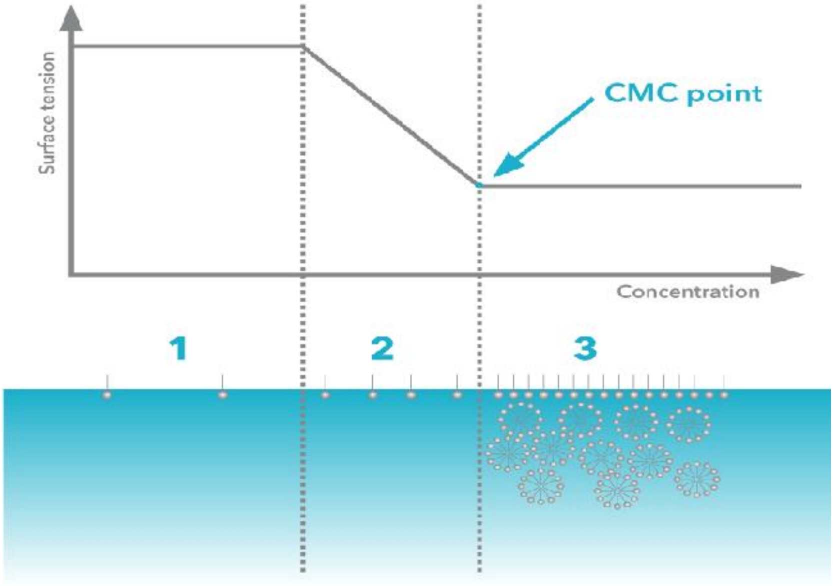


Fig. 4.1 Surface concentration curve for micelle formation

b. **pH:** The effect of pH on surface tension of surfactant have been studied by Nutting and Harkins [1976] that the surface tension was observed to be high in basic and low in neutral solutions The surface tension of fatty acids, such as sodium or potassium salts of oleic, lauric and myristic acids were studied at 20°C in the presence of atmospheric carbon dioxide.

The change of surface tension produced by added alkali and by changes in pH in general, has been investigated. It was observed that small changes in pH at the solution produced to large changes in surface tension. The lariats were particularly sensitive. The influence of carbon-dioxide on the surface tension of surfactant can be correlated with changes of pH produced by the atmospheric carbon dioxide.

c. **Time:** The surface tension of a liquid has been found to decrease with time. Washburn and Bigelow, [1964] noticed that the surface tension of surfactant solution has been found to decrease with time and after a considerable period maintained a constant **or** weakly constant value. The magnitude of lowering the surface tension of the two solutions to be different. This means that after the ageing of solutions, the solute becomes more surface active.

d. Temperature: Powney and Addition, [1956] have studied the surface tension of SDS solution in little with the temperature and concentration. Unfortunately owing to their sample being impure they obtained surface minimum in their surface tension concentration curves. Matijevic and Pathicali, [1965] also studied the surface tension minima of SDS solution and explained it to be occurring due to the presence of dodecanal in the sample. They also studied the effect of temperature and electrolytes on the surface tension and surface tension was found to decrease with temperature.

4.2.2 Methods of Viscosity determination

The property of fluid by virtue of which opposes the relative motion between its different layers is called viscosity, which expressed in poises. On the other hand, viscosity may be defined as the frictional resistance of a fluid in two different layers. Viscosity of a fluid is expressed by the symbol η (eta). Now poisecillies equation is used to determine the viscosity of liquid. The mathematical expression of poisecelles equation is used to determine the viscosity of a liquid. The mathematical expression of poiseulles equation governs the flow of a liquid though a capillary may be written as-

$$\eta = \frac{\pi pr4t}{8lv} \text{ .... (1)}$$

Where, η = Viscosity of the solution used.
p = Driving pressure causing the flow
v = Volume of the liquid flowing at time t.
r = Radius of the capillary tube
l = Length of the capillary

But we know that driving pressure is related with density and height of the liquid with respcct to the acceleration due to gravity. The relation of them mentioned below.

$$p = h\rho g \text{........................ (2)}$$

Where, h = Average height of the liquid
ρ = Density of the liquid
g = Acceleration due to gravity.

Putting the value of p in the equation as; we get the following expression- i.e.

$$\eta = \frac{h^\circ g \times ® r^4 t}{8lv} \qquad [\because h\rho g = p]$$

$$\therefore \qquad \eta = \frac{h^\circ g ® r^4 t}{8lv} \text{ .... } (3)$$

Equation (3) behaves satisfactory when the time of flow is very high i.e. the liquid flows at a very slow rate. But it the time of flow is low correction for less of kinetic energy has to be applied. When this effect is taken in the account the expression becomes

$$\eta = \frac{h^\circ g ® r^4 t}{8lv} - \frac{mv^\circ}{8®lt} \quad \text{.................}(4)$$

When m is constant and may have positive values up to 1.5 for a particular viscometer the values of h, g. l, m, r and v are constant and hence equation (4) can be written as

$$\eta = A\rho t - \frac{B\rho}{t} \text{ ....}(5)$$

$$\text{Where } A = \frac{hg®r^4}{8lv} \text{ and } B = \frac{mv}{8®l}$$

$\frac{B}{t}$ is the kinetic energy correction term. It is reported that if the efflux time for a liquid is greater than 100 seconds, the kinetics energy correction term may be neglected. For dilute solution, the density of a solution can be taken as equal that of the solvent. The relative viscosity is therefore

$$\eta_r = \frac{¦}{¦_0} = \frac{t}{t_0} \text{ ....}(6)$$

The derivation of the above equation (6) are mentioned below by neglecting the kinetic energy term of equation (5) we get

$$\eta = A\rho t \qquad \text{(for solution).................. (m)}$$

Again the equation can be written for solvent

$$\eta_0 = A\rho t_0 \text{ -------------- (n)}$$

Now dividing the equation (m) by (n) we get

$$\frac{n}{n_0} = \frac{A^\circ t}{A^\circ t_0} = \frac{n}{n_0} = \frac{t}{t_0}$$

Where, η = viscosity of the solution

η_0 = viscosity of the solvent

t = Falling time of solution

t_0 = Falling time of solvent

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0} \qquad [\eta_r = \frac{\eta}{\eta_0}]$$

Therefore the equation (6) is determined.

From the equation (6) the specific viscosity can be calculated by the following way the calculation mentioned below-

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

$$\Rightarrow \eta_r - 1 = \frac{\eta}{\eta_0} - 1 = \frac{t}{t_0} - 1 \text{ [In both side 1 is subtracted]}$$

$$\Rightarrow \eta_r - 1 = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0}$$

$$\Rightarrow \eta_{sp} = \frac{\eta - \eta_0}{\eta_0} = \frac{t - t_0}{t_0} \text{ ....(7)}$$

Where, η_{sp} = specific viscosity

η_0 = Viscosity of the solvent

t & t_0 = time flow of sol^n & solvent respectively.

Reduced viscosities were determined with an Ostwald viscometer of British standard controlled (the fisher Scientific TM 200) with fluctuation of ± 0.1^o C was used. The flow of time was recorded by a timer accurate up to ± 0.01second. At certain surfactant/starch ratios the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements. The results of the viscosity values calculated from $\eta_{red} = \frac{\frac{(t - t_0)}{t_0}}{c}$ where, t is the measured efflux time of solutions and t_0 is the efflux time of the pure solvent (water) and c is the weight concentration of the surfactant, starch & surfactants mixed polymer.

Necessary Chemicals

The following chemicals are used for the determined of reduced viscosity of polymeric samples by viscosity method.

1. Solvent as H_2O (pure distilled water)
2. Chromic Acid ($H_2SO_4+K_2Cr_2O_7$)
3. Acetone (CH_3-CO-CH_3)
4. Polyethylene Glycol. $[-CH_2-CH_2O]_n$

NECESSARY APPARATUS:

The following apparatus are to needed for the determination of reduced viscosity of polymeric samples (starch, surfactant and complexes).

1. Ostwald viscometer
2. Stop watch
3. Electric balance
4. Volumetric flux (100 ml)
5. Beaker
6. Pipette
7. Burette
8. Dropper
9. Funnel
10. Distilled water pot.
11. Magnetic stirrer

Preparation of starch solution in H_2O:

For the preparation of starch solution six volumetric flask (100ml) are properly washed and dried. Next of starch powder was taken in a 100 ml. volumetric flask and added distilled H_2O as solvent into that volumetric flask up to the mark. The starch is dissolved completely then 0.1%; 0.2%; 0.4% 0.6% and 0.8% solution were prepared by diluting the original starch solution. In another method directly weight out of starch mixed surfactant and was taken in a level volumetric flask and pure distilled water added to the mark 100 cc. Next another 5 solution were prepared from the original solution. It the starch samples are not easily dissolved than it completely dissolved by casing electrical, magnetic stirrer, therefore these are the methods of preparation of sample solution.

Calculation for the preparation sample sol^n:

Step-1

Preparation of 0.6% sample of sol^n from 0.8% original sol^n:

Considering volume of original sol^n $V_1 = ?$

Concentration of original sol^n $S_1 = 0.8\%$

Volume of the required sol^n $V_2 = 100ml$

Concentration of required sol^n $S_2 = 0.6\%$

Now We know that $V_1 S_1 = V_2 S_2$

$$\Rightarrow V_1 = \frac{V_2 S_2}{S_1}$$

$$\Rightarrow V_1 = \frac{100 \times 0.6\ (\%)}{0.8\ (\%)}$$

$$V_1 = 75ml.$$

Step-2

Preparation of 0.4% sample sol^n from 0.6% sample sol^n:

Considering

Volume 0.6% sol^n $V_1 = ?$

Concentration of 0.6% sol^n $S_1 = 0.6$

Volume of 0.4% Sol^n $V_2 = 100$

Concentration of 0.4% sol^n $S_2 = 0.4$

Now we know that $V_1 S_1 = V_2 S_2$

$$\Rightarrow V_1 = \frac{V_1 S_1}{S_1}$$

$$\Rightarrow V_1 = \frac{100 \times 0.4}{0.6}$$

$$V_1 = 66.66 \text{ ml.}$$

100ml 0.4% sample sol^n = 0.6% 66.66 ml sample sol^n +33.33 ml pure Distilled H_2O

Step-3

Preparation of 0.2 % sample sol^n from 0.4% sample sol^n:

Considering, Volume of 0.4% sample sol^n $V_1 = ?$

Concentration of this sol^n $S_1 = 0.4$

Volume of Required sol^n $V_2 = 100$

Concentration of required sol^n $S_2 = 0.2$

Now we know that $V_1 S_1 = V_2S_2$

$$\Rightarrow V_1 = \frac{V_1S_1}{S_1}$$

$$\Rightarrow V_1 = \frac{100 \times 0.2}{0.4}$$

$$V_1 = 50$$

100 ml 0.2% sample sol^n = 50 ml 0.4% sample sol^n +50 ml pure Distilled water.

Step-4

Preparation of 0.1 % sample sol^n from 0.2% sample sol^n:

Considering

Volume of Required sol^n $V_2 = 100$

Concentration of required sol^n $S_2 = 0.1$

Volume of 0.4% sample sol^n $V_1 = ?$

Concentration of this sol^n $S_1 = 0.2$

Now we know that $V_1 S_1 = V_2S_2$

$$\Rightarrow V_1 = \frac{V_1S_1}{S_1}$$

$$\Rightarrow V_1 = \frac{100 \times 0.1}{0.2} = 50 \text{ ml}$$

100 ml 0.1% sample sol^n = 0.2% 50 ml sol^n +50 ml pure Distilled water.

Experimental techniques or procedure:

Measurement of viscosity is carried out in an ubbelohde suspended level viscometer at 25°C in a water bath. Generally we are the Ostwald viscometer for the determination of the reduced viscosity of polymeric materials or natural polymer. At first we recorded the falling time of the solvent (pure distilled H_2O) from stop watch by using the Ostwald viscometer and recorded the reading in table. Next the sample solution was taken in viscometer (13 cc) by pipette and determined of falling time. In this way the falling time of different solutions were recorded by viscometer & stop watch. To remember that in each stage during the determination of falling time the viscometer was rinsed with cromic acid and next with acetone and finally was dried. The viscosity of the pure water was determined from the time difference between solvent and sample solution. Next the Relative viscosity of the sample & solution is determined by the following equation-

$$\eta_r = \frac{\eta\ solution}{\eta_0\ solvent} \text{ ....(11)}$$

Then the specific viscosity of the solution will be

$$\eta_{sp} = \eta_r - 1 \quad [\eta_{sp} = \text{specific viscosity}]$$

Reduced viscosity is obtained by dividing η_{sp} by concentration C and, where c is the concentration in gm/$_{100cc}$ of the solution. From the measured reduced viscosity the following equation. i. e.

$$\eta_{red} = \frac{\frac{(t - t_0)}{t_0}}{c}$$

Chapter: 5 *Surface Properties of Starch, Surfactant and their mixtures by the Physical property of surface tension*

5.1 Surface tension

Surface tension is a property of the surface of a liquid that causes it to behave as an elastic sheet. An everyday observation of surface tension is the formation of water droplets on various surfaces or raindrops. The physical and chemical behavior of liquids cannot be understood without taking surface tension into account. It governs the shape that small masses of liquid can assume and the degree of contact a liquid can make with another substance. Surface tension has the dimension of force per unit length or of energy per unit area. The surface tension of water is 72×10^{-3} N-m/m at 25°C. It would take a force of 72 neutons to break a surface film of water 0.01m long. The surface tension of water decreases significantly with temperature as shown in the graph. The surface tension arises from the polar nature of the water molecule.

Hot water is a better cleansing agent because the lower surface tension makes it a better "wetting agent" to get into pores and fissures rather than bridging them with surface tension. Soaps and detergents further lower the surface tension.

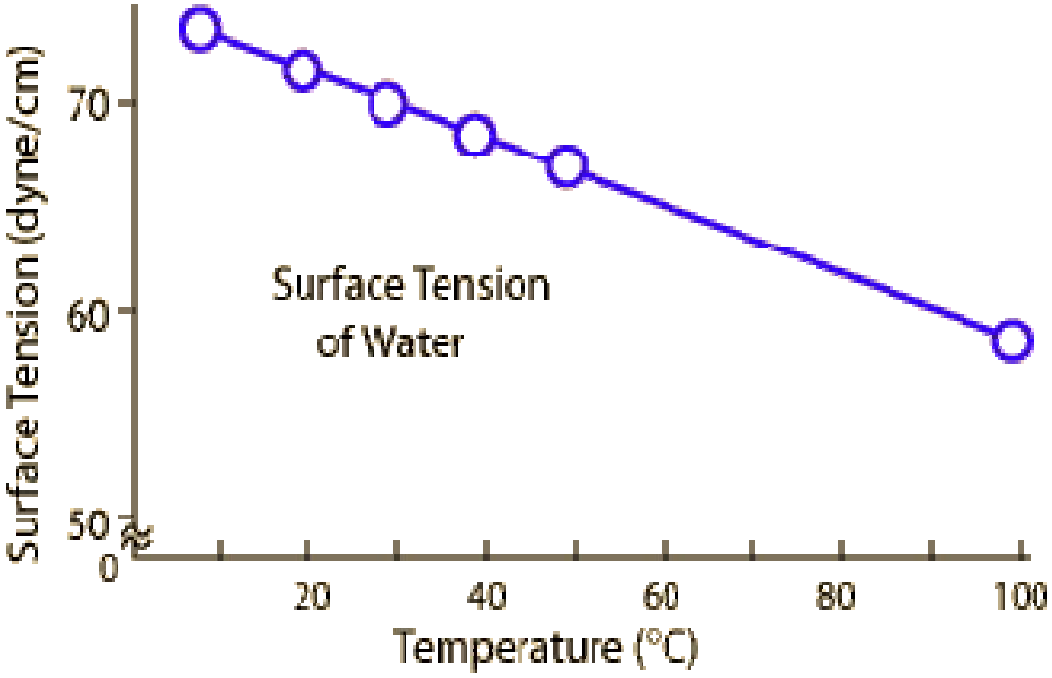


Fig. 5.1 Temperature vs. surface tension curve of water.

5.2 Lyophilic colloids

Lyophilic colloids are those which have much of an affinity for the solvent; they have some unique properties in which they differ from lyophobic colloids such as scattering of light, low osmotic pressure, slow diffusion, electrophoresis dialysis, high viscosity, reversibility and in some cases moderate sensitivity to electrolytes. The surface active substances as the soaps and surfactants all lower the surface tension of water. They have also the properties to aggregate in presence of solvents.

5.3 Characteristic of polyelectrolyte

Polyelectrolytes such as starch have some special properties which distinguished them from uncharged polymers. First, the mutual repulsion of their charges causes expansion of the chain far beyond the expansion from changes from poor to good solvents with ordinary polymers. The size of the polyelectrolyte random coil is, moreover, a function of the concentrations of polymer and added salt, since both influences the degree of ionization. Secondly, the ionization of the electrolyte groups leads to a variety of unusual effects in the presence of small amounts of salt. The intensity of the light scattering decreases because of the ordering of the molecules in solution, while osmotic pressure and ultra centrifugation behavior are determined predominantly by the total charge on the molecule (Donnan effect From this equation, it is clearly seen that the electrostatic persistence length decreases linearly with salt concentration and increases with the square of the charge density along the backbone. Counterion condensation advanced as a model and studied extensively by Manning [1977-79], Fixman [1979] and Anderson et al. [1982], is a phenomenon that regulates the effective charge density on a polyelectrolyte chain. The maximum supportable charge density on the poly-ion is controlled by it.

5.4 Surface-active agents

Surfactants are characterized by the presence of two moieties in the same molecule, one polar and the other non-polar. The behavior of surfactants in aqueous solution is determined by their tendency to move their hydrophobic part away from the solution and their hydrophilic part towards the solutions. This dual tendency is responsible for adsorption of surfactants at interfaces and for the formation of such aggregates as micelles. Surfactant molecules adsorb at the water/air interface with their hydrophobic groups away from the water and their hydrophilic groups in solution. A consequence of this is that some of the water molecules at the interface will be replaced by hydrocarbon or other non-polar groups. Since the interaction force between water molecules decreases, the adsorption of surfactants at the interface results in a reduction in the surface tension of the solution.

5.5 Micelle formation in aqueous solutions:

Above a certain concentration, the so-called CMC, almost all of the added surfactant molecules are consumed in micelle formation, and the monomer concentration does not increase. Since only the surfactant monomers adsorb at the interface, the surface tension remains constant above the CMC. As mentioned above, surfactant species in aqueous solutions at concentrations above their CMC aggregate to form uniform sized structures referred to as micelles. Well-studied micelles like those of SDS have a near-spherical geometry over a wide range above the CMC. Evidence also exists for the formation of cylindrical and other shapes in certain systems. It has been found that surfactants with bulky hydrophilic groups and long, thin hydrophobic groups tend to form spherical/globular micelles in aqueous solutions. In contrast to this, surfactants with bulky hydrophobic groups and small hydrophilic groups tend to form lamellar or cylindrical micelles. The shape of a micelle is related to its size. The size is normally expressed in terms of an aggregation number. Typical aggregation numbers obtained for commonly used surfactants varied from 30 to 90. The size and aggregation number of surfactants change markedly with such variables as ionic strength and temperature.

5.6 Factors affecting the CMC and aggregation number

By increasing in the length of the hydrocarbon chain it decreases the CMC. Linear hydrocarbon surfactants tend to have much lower CMC than their branched-chain counterparts. The presence of a double bond in the chain increases the CMC. Ionic surfactants have a much higher CMC than nonionic surfactants with a corresponding hydrocarbon chain length. Correspondingly, as the number of ionizing groups increases in a surfactant molecule the CMC increases. As the position of the ionic group changes from the terminal position to more central positions, the CMC increases.

Counter ions adsorb at the ionic micelle surface and stabilize it; the extent of adsorption is dependent on the micelle charge density. The higher adsorption of counter ions lowers the CMC. An increase in the valences of counter ion decreases the CMC. An increase in hydrated radius, on the other hand, increases the CMC. Electrolytes have a significant effect on the CMC of ionic surfactants reported by Corrin et al. [1947]. An increase in the concentration of the electrolytes progressively contracts the electrical double layer around the micelle and in the process stabilizes the micelle. This is manifested as a reduction in CMC with electrolyte concentration. Lindman, [1984] showed that the process of micellization itself is dependent on temperature in a complex way. For example, cooling of a micellar solution of SDS below 12^{oC}, results in the precipitation of the surfactant. Here the concentration of the surfactant is equal to the CMC. This temperature, referred to as the Krafft temperature or Krafft point, is the temperature at which the solubility of the surfactant equals the CMC, and above this temperature, the total solubility of the surfactant increases markedly because of the formation of micelles. Below this temperature, only surfactant monomers exist in solution and, therefore, the total solubility is drastically limited. The Krafft point of surfactants depends upon the chain length of the hydrophobe as well as the type, valence, and concentration of counter ions. The Krafft point, in general, increases with alkyl chain length.

5.7 Mixed micellization

In solutions containing mixtures of surfactants, the tendency to form regated structures can be substantially different from that in solutions containing only the pure surfactants. The tendency for components to distribute between a non-aggregated state and an aggregate may vary from component to component for mixtures. Therefore, the surfactant composition of a micelle may differ greatly from the composition of the non-aggregated surfactants.

5.8 Polymer-surfactant interactions

The interactions responsible for association phenomena in polymer-surfactant systems are mainly:

1. Hydrophobic interactions between polymer and surfactant molecules. This kind of interaction will be particularly important for hydrophobically modified polymers.
2. Hydrophobic interactions between hydrophobic parts of surfactant molecules.
3. Hydrophobic interactions between polymer molecules.
4. Electrostatic interactions between polymer molecules.
5. Electrostatic interactions between polymer and surfactant molecules; they may be repulsive or attractive, depending on whether the molecules have similar or opposite charges.
6. Electrostatic interactions among the hydrophilic parts of surfactant molecules. These repulsive interactions are strongly unfavorable for surfactant micellization. For the different interactions mentioned, the main driving force of association in polymer surfactant systems in general comes from the hydrophobic interactions between surfactant molecules. For hydrophobic polymers, the hydrophobic interaction between polymer and surfactant alkyl chains, will contribute more or less strongly, depending on the system. Because of delicate energy balances, even quite small contributions from the other interactions can have dramatic influences on the self-assembly and induce important surfactant-polymer interactions. Ionic surfactant micellization will, because of the electrostatic interactions, be particularly susceptible to changes. There is obviously an interrelation between specificity and co-operatively such, that for a higher degree of specificity, co-operativity will be less important and smaller aggregates may form. The variation in driving forces will have its counterpart in the structural description. For many polyelectrolyte-ionic surfactant systems, there will be just a long-range effect on micellization, and the polymers chains and the surfactant micelles may remain at some distance.

5.9 Polyelectrolyte/surfactant complexes

5.9.1 Phase behavior of hydrophilic polymers with pure surfactant micelles:

Hydrophilic non-ionic polymers are well soluble in water. There are no hydrophobic interactions between these polymers and surfactants. In most cases, the phase separation is segregative, but if the polymer and the surfactants are oppositely charged, associative phase separation of the complexes may occur. Adding a certain amount of salt will suppress the association and eventually lead to a segregative phase separation.

5.9.2 Oppositely charged mixtures

High-charged polymers differ strongly from the corresponding non-ionic species. There is a strong enrichment of counter ions close to the polyelectrolyte and this uneven counter ion distribution lowers the entropy markedly. For ionic surfactants, this entropic effect strongly counteracts micellization. This is the major reason for the much higher CMC of ionic surfactants compared to non-ionic suggested by Evans et al.,[1994]. In the presence of electrolytes, micelles are stabilized; the higher is the valence of the oppositely charged ion. This polyelectrolyte induced lowering of the CMC of oppositely charged surfactants is also referred to as a cooperative binding of the surfactant to the polyelectrolyte. Another observation by Goddard 1986a, b, Goddard and Ananthapadamabhan [1993] is that in oppositely charged mixtures associative phase separation occurs at quite low surfactant concentrations, often only slightly above the CAC The concentrated phase could be a solid or a highly viscous gel-like solution. Addition of large amount of salt inhibits the phase separation and a redissolution of the complex phase takes place when an excess of surfactant is added. The phase behaviour of oppositely charged surfactant and hydrophilic polyelectrolyte depends on the choices of polyelectrolyte, surfactant and simple salt. The minimum concentration of surfactant required for phase separation decreases strongly as its chain length increases, i.e. as CMC decreases. This observation supports the notion that associative phase separation involves the poly-ion and the self-associated surfactant. The redissolution concentration is less dependent on the surfactant chain length. An increase in the simple salt concentration leads to shrinkage of the two-phase area. The amount of salt needed to give redissolution, the critical electrolyte concentration (CEC), increases with increasing surfactant chain length and is strongly dependent on the surfactant concentration. CEC also depends on the nature of the added salt, the anion in particular. Increasing the valance of a simple ion lowers counter-ion entropy effects and decreases the entropic gain of poly-ion-micelle association. This reduces the tendency to associative phase separation. The salt effects have been confirmed for mixtures of cationic with NaPa (sodium poly(acrylate)) by Hansson and Almgren, 1994]. They suggested that the increasing CEC with increasing surfactant chain length could be attributed to a larger aggregation number of micelles. Tendency to association increases strongly with increasing charge density of the polyelectrolyte. This is nicely shown in a study of poly(acrylate-co-acrylamide) by Ranganathan and Kwak, [1996] reported where the ionisation of the polymer was varied. The experiment of varying the charge density of the micelles by mixing in non-ionic surfactant has also been made by Li and Dubin, [1995]. As expected, reducing the micellar charge density or the charge density of the polymer markedly reduces the extent of the phase separation.

5.10 Methods for the determination of surface tension

There are several methods available for the determination of surface tension which are shown below:

(a) Capillary rise method.
(b) Drop weight and drop volume method.
(c) Ring method.
(d) Bubble pressure method.
(e) Pendant drop method.
(f) Sessile drop method.
(g) Hanging plate method.
(h) Surface potential method.
(i) Method based on the spreading of oils.
(j) Method of ripples etc.

Of the above mentioned methods, I have chosen the drop weight method to determine our surface tensions. The drop weight and drop volume methods :

Fig. 5.2 Stalagmometer Instrument for determination of surface tension

Surface tension has long been recognized as an important physical characteristic of fluids and colloids that can affect biological processes. Scientists sought ways to measure this phenomenon, but reproducible results were difficult to obtain. Two approaches, developed to measure this subtle force, are displayed here. The process of drop formation by liquids is, in part, controlled by the surface tension of the fluid. To determine surface tension, the stalagmometer used a drop weight method, in which the number and weight of drops were compared to those from a reference liquid. Seemingly simple, the stalagmometer nevertheless required considerable skill and absolute cleanliness for readings to be meaningful. An instrument for measuring the size of drops suspended from a capillary tube, used in the drop-weight method. Also known as stactometer; stalogometer. Tubes are available in 2.5mL, 3.5mL and 5.0mL sizes.

If the drops which stay at the end of a tip were cylindrical and of the same diameter as the tip, it is evident the maximum weight of drops which could be supported would be exactly equal to the weight of the liquid uphold in a capillary tube of the same diameter, because in both cases, the force of surface tension, acts on a line $2\pi r$ long, so the force is $2\pi r\gamma$

$$\text{or } W = mg = 2vr\gamma \qquad \gamma = \frac{mg}{2\text{®}rf^{\frac{1}{3}}}$$

A drop of the weight (m) given by the above equation has been designated by Harkins and Brown [1948] as the ideal drop. This method is directly applicable to the determination of the interfacial tension of oils or mercury against the aqueous phase.

5.11 Surface tension of different types of surfactants:

(a) Anionic surfactants
(b) Cationic surfactants
(c) Non-ionic surfactants

Anionic surfactants

Anionic surfactants or surface active agents are those that commonly contain carboxylate, sulphonate and sulphate ions. The carboxylate ions containing surface active agents are known as soaps. Most soap has sodium or potassium or ammonium cations and the fatty acid chain length range from 12 to 18. The solubility of soaps or surfactants in water is vary dependent on alkyl chain length and the presence of double in the alkyl chains. When the surfactants contain multivalent cations their water insolubility increases. Thus surfactant containing Ca or Mg ions are more insoluble in water than those containing Na or K or NH_4^+ ions when surfactants are subjected to hydrolysis they form free fatty acids and hydroxide demise particularly in more concentrated solutions.

Lowering of surface tension in vary dilute solution occurs because the molecules of the surface active substances absorbed and specifically oriented at the interface.

Cationic Surfactants

Amine salts and quaternary ammonium salts having long hydrocarbon chain are included in this class. Decreasing of surface tension occurs also on increasing the concentration of the surfactants is vary in dilute solution

Nonionic surfactants

The nonionic surface active agents getting importance with the lapse as time owing to their decreasing cost of by increasing application in many fields. The nonionic emulsifiers may be divided into two groups:

The water soluble groups comprise the long chain fatty alcohols; they are water insoluble derivatives which are as follows:

1) Fatty alcohols e.g lauryl, palmityl and stearyl,
2) Glyceryl ester e.g. naturally occurring mono, di and triglycerides
3) Fatty acids, esters of fatty alcohols and other alcohols propylene glycol, polyethylene glycol, sorbitol, sucrose and cholesterol. In second group of nonionic surface active agents there are compounds containing polyoxyethylene groups that are added other linkage with one of their alcohol groups.

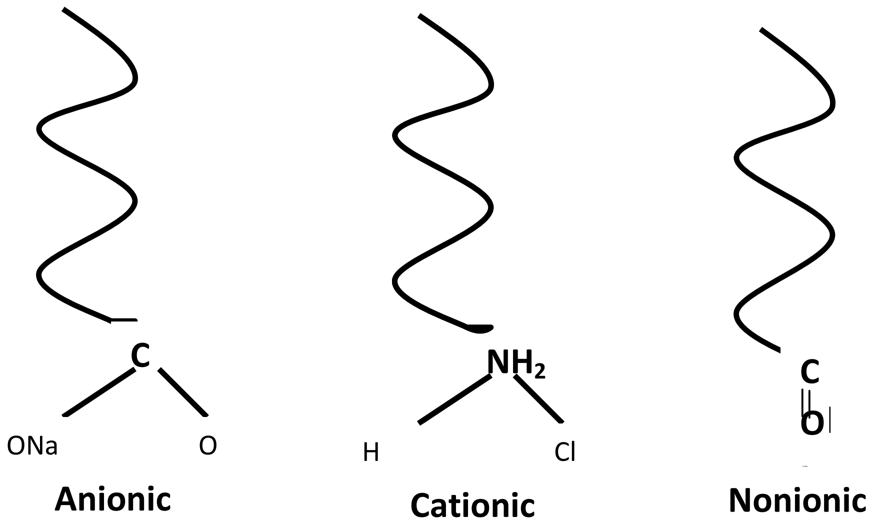


Fig. 5.3 Structural diagram of surface active agents represents the hydrocarbon chain.

5.12 Experimental

Apparatus used for surface tension measurements

Surface tension was determined by drop weight method. In this a tube for dropping liquids was used which was constructed at one end of narrow end from which the liquid was ejected used to have diameter 0.125cm. The upper part of the tube was connected to rubber tubing for sucking up the liquids. To the rubber tubing was attached a pinch cock for controlling the fall of drops.

5.12.1 Preparation of triple distilled water

The surface tension of ordinary single distilled water in this laboratory was 73.306×10^{-3} N/m at temperature 28°C. This water was redistilled from alkaline potassium permanganate solution and sodium hydroxide pellets. A soda lime guard tube was used to present the entry of carbon dioxide. The first and last fractions of the distillate were rejected. The surface tension of this double distilled water was about 73.103×10^{-3} at temp. 24.5^{o}C. This water was again distilled from alkaline potassium permanganate solution and sodium hydroxide pelletes. The surface tension of this third distilled water was about 72.417×10^{-3}N/m, at temp. 24.8°C The water was stored in a glass flask and was used.

5.12.2 Materials

1. The following equipments and chemicals which I mention under below to conduct my experimental research: starch (powder form) Product from UNI-CHEM China.
2. soap/surfactants (CTAB, Tween-20, Tween-80, SDS, Brij-30, Triton-X-100)

Cationic Surfactants

Cetyel trimethyl Ammonium bromide (CTAB) product of BDH Chemicals Ltd

Anionic Suractants

Sodium dodecyl sulphate (SDS) a product of BDH Chemicals Ltd.

Nonionic Surfactants

Triton X-100 ((Polyoxyethylne iooctylphenol) product of BDH Chemicals Ltd.

Instrument

The instruments which we needed in my research: (i) Electronic balance (ii) Volumetric flask (iii) Pipettes (iv) Beakers (v) Glass rods (vi) Dropper (vii) Thermostat box (viii) Test tubes with robber corks (ix) Micro pipette (x) Spatula (xi) Reagent bottle.(XII) Stralaglometer (measuring surface tension) (Xiii) Wing Bottle (XIV) Pipette filler Conductance, Balance (Satories Electrical Micro Balance), Volumetric flask, other relevant things such as pipettes, beakers, glass rods, dropper, desicator, spatula etc.)

5.12.3 Measurement of surface tension and determination of the CMC of aqueous solutions of surfactant with different amounts of added starch and surfactant

A number of surfactant solutions of different Concentration were prepared from the respective stock solutions of starch and various surfactants. The surface tension was determined by the drop weight method. The CMC of aqueous solutions of surfactant for each solution were obtained from the plot of surface tension against log of concentration of surfactant solution. The concentration corresponding to the break points of the curves give the CMC.

The drop weight method apparatus was cleaned with chromic acid mixture (chromic acid + H_2SO_4) and rinsed with acetone and dried. Then the sample solution was drawn into the clamped tube with a rubber tube stopped the flowing of experimental solution with the drop controlling system and attached with rubber tube, the rate of fall of drops from the graduated tube was controlled by adjusting the screw so that the minimum time required between two consecutive drops was 1.5 minutes. 15-20 such drops were allowed to fall from the tube and the volume of these drops was determined very accurately. This process was repeated three times for experimental solution and the average volume (v) of single drop was calculated, the outer radius (r) of the tip of the tube was measured at the position where drop was formed. Then the value of $\frac{v}{r^{\frac{1}{3}}}$ for experimental solution and density of experimental solution and solvent was determined. The surface tension (¥) of experimental solution and solvent was calculated from the weight (w) of single drop by the relation.

$$\text{¥} = \frac{mg}{2\text{®}rf^{\frac{1}{3}}}$$

Where, m is the mass of single drop, g is the acceleration due to gravity,
r = 0.125 cm, r is the radius of the tip of the tube; f is the correction factor and γ is the surface tension. The value of the correction factor, for experimental solution was calculated from the plot of standard value of f against $\frac{r}{v^{\frac{1}{3}}}$ of the Table 5.4.

Table 5.1 The value of the correction factor f for each solution was calculated from the plot of standard value of f against $\frac{r}{v^{\frac{1}{3}}}$ of the table.

$\frac{r}{v^{\frac{1}{3}}}$	f	$\frac{r}{v^{\frac{1}{3}}}$	f
0.00	1.0000	0.85	0.5992
0.03	0.7256	0.90	0.5998
0.35	0.7011	0.95	0.6034
0.40	0.6828	1.00	0.6098
0.45	0.6669	1.05	0.6179
0.50	0.6515	1.10	0.6280
0.55	0.6362	1.15	0.6407
0.60	0.6250	1.20	0.6535
0.65	0.6171	1.25	0.6560
0.70	0.6093	1.30	0.6400
0.75	0.6032	1.35	0.6230
0.80	0.6000		

5.13 Results and Discussion from surface tension

The effect of starch on the CMCs formation was observed. Addition of starch with surfactant brought about decrease in CMC at all concentrations but starch is surface inactive. We are now interested to see what type of interactions occurred in between starch and surfactant complexes. Surface tension was studied by the drop weight method. The magnitude of surface tension was found to be reduced by the addition of starch. In all cases, the CMC was found to be reduced as determined by the surface tension method. In the surface tension method the CMC was identified from the break point in the curve. When log concentration value of starch mixed surfactant vs. surface tension value were plotted in a graph paper the log concentration of starch mixed surfactants solution showed a gradual fall. (Show the list of **Fig. 5.4- Fig. 5.5**) but after a certain concentration the level become off ,which indicated the CMC's formed and maximum interaction occurred of the starch-surfactant complexes at that definite concentration ranges (CMC point) then the value of surface tension values are gradually increasing. The surface tension of aqueous solution of CTAB with variation concentration (wt.%) added starch is shown in the **Fig. 5.4**

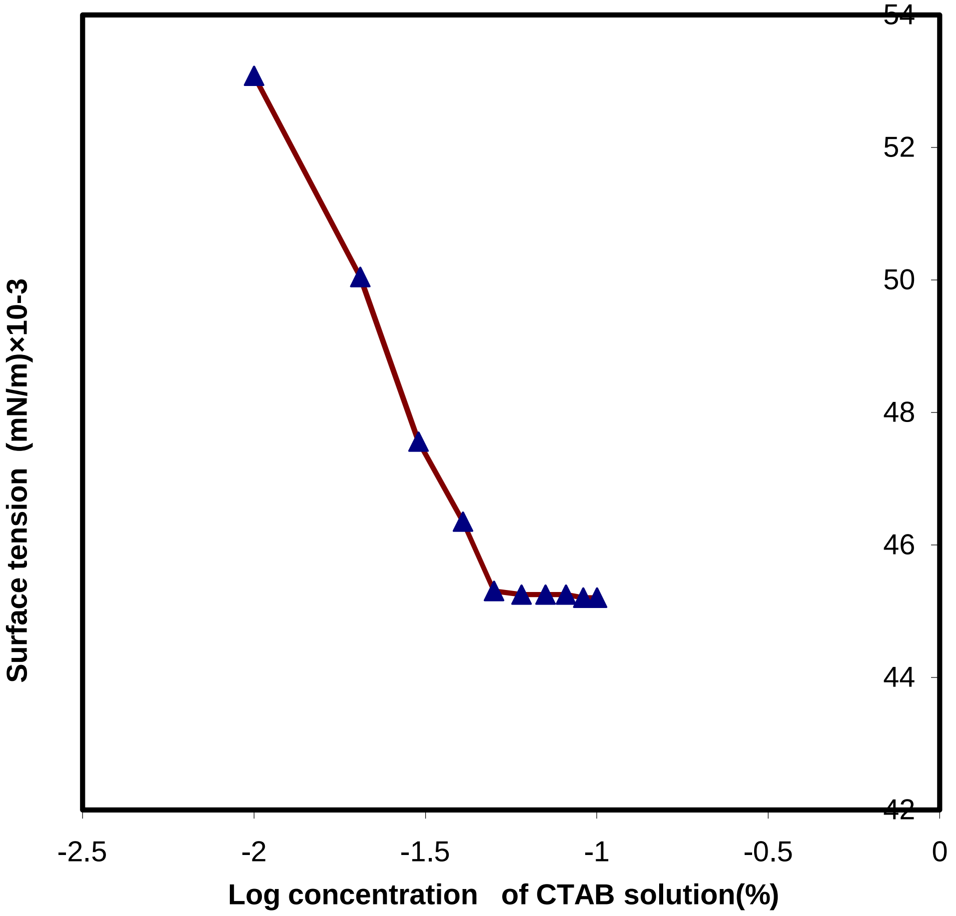


Fig. 5.4 The surface tension of aqueous solution of CTAB with variation concentration (wt.%) of added starch

The surface tension of aqueous solution of SDS with variation concentration (wt.%) added starch is shown in the **Fig. 5.5**

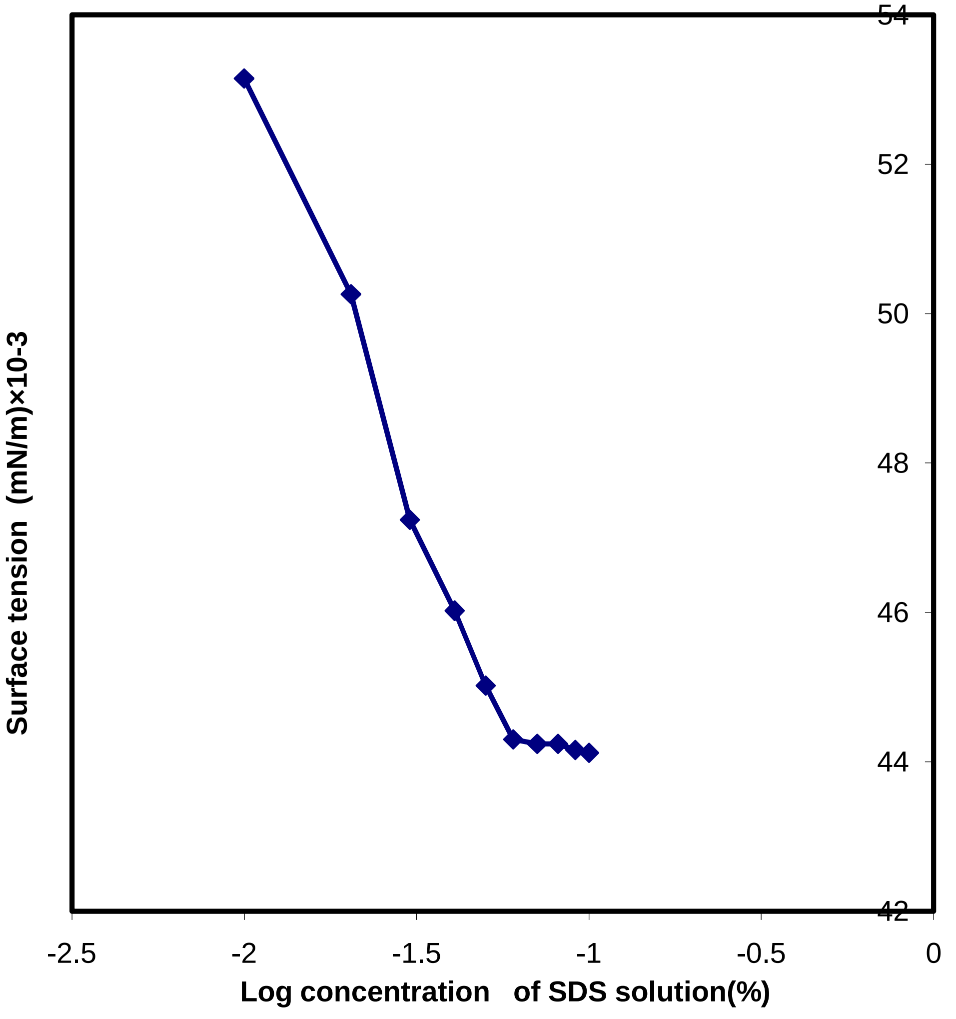


Fig. 5.5 The surface tension of aqueous solution of SDS with variation concentration (wt.%) of added starch

The surface tension of aqueous solution of Tween-20 with variation concentration (wt.%) added starch is shown in the **Fig. 5.6.**

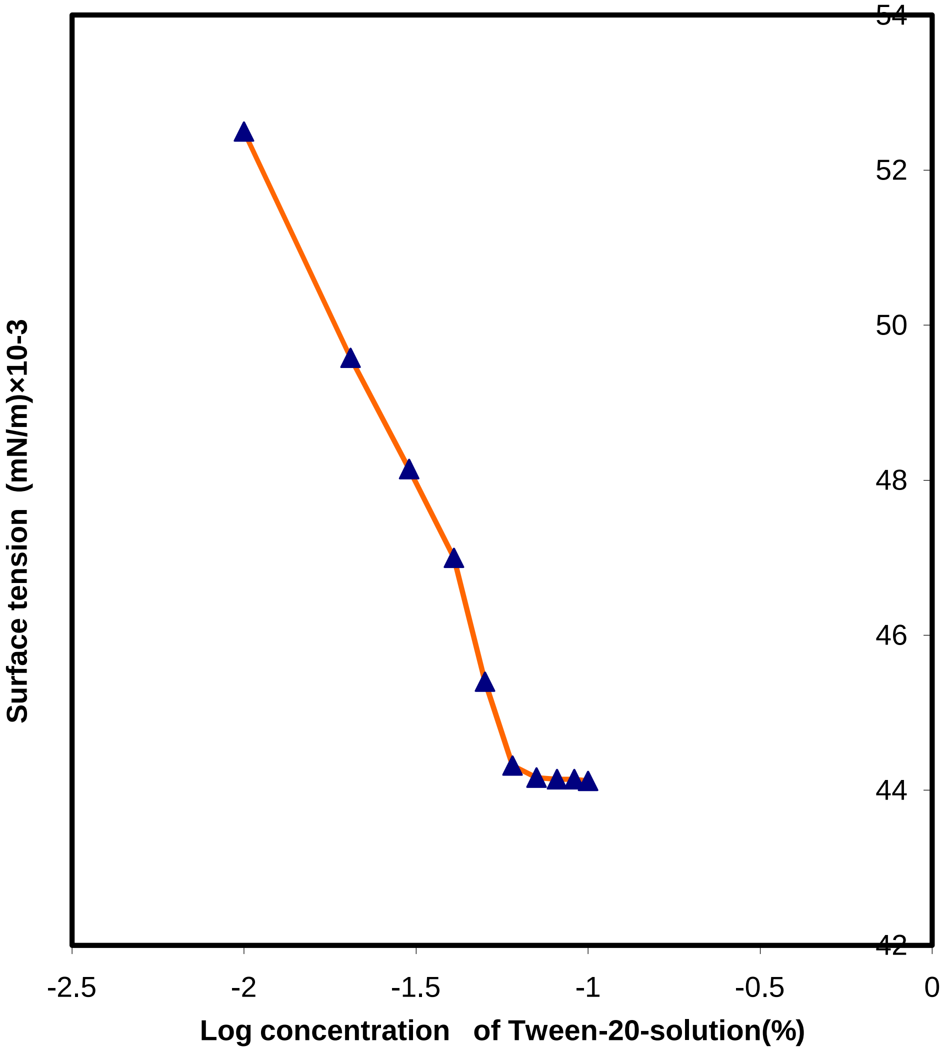


Fig. 5.6 The surface tension of aqueous solution of Tween-20 with variation concentration (wt.%) of added starch

The surface tension of aqueous solution of Tween-80 with variation concentration (wt.%) added starch is shown in the **Fig. 5.7**

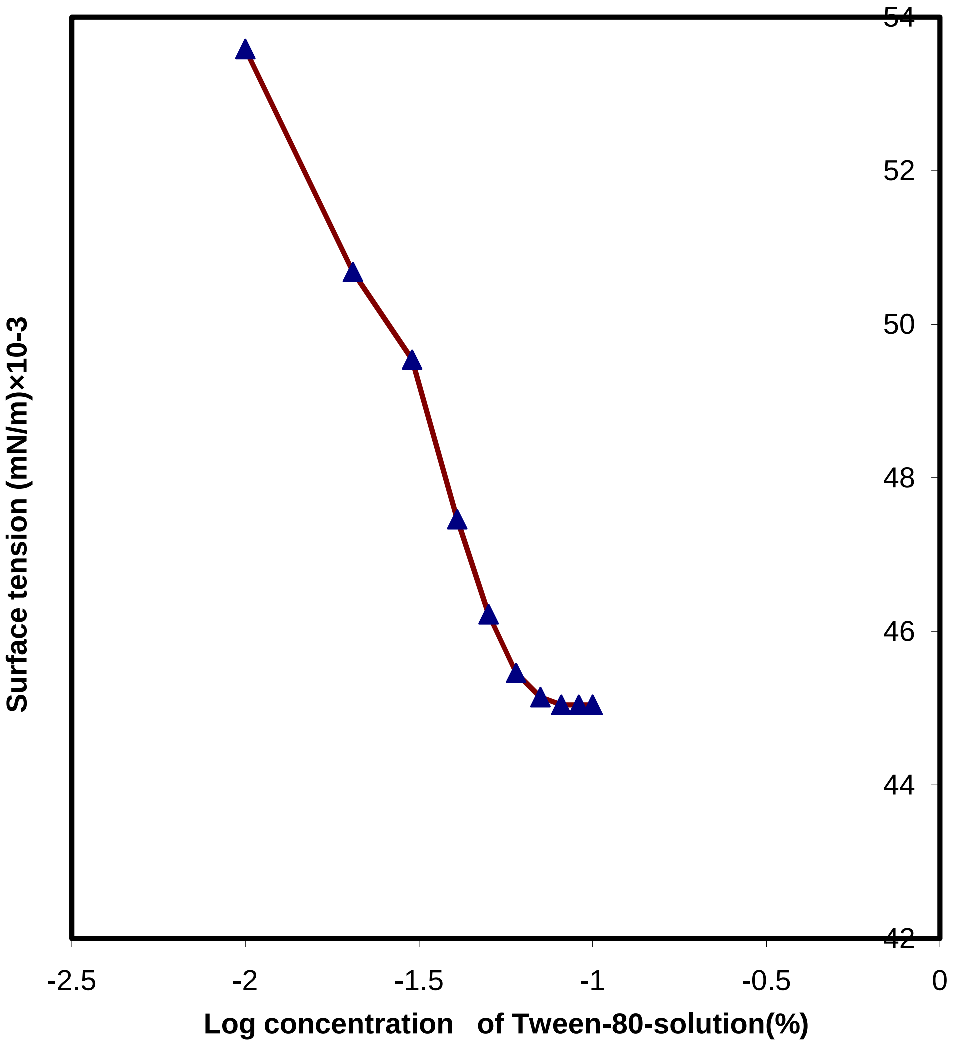


Fig. 5.7 The surface tension of aqueous solution of Tween-80 with variation concentration (wt.%) of added starch

The surface tension of aqueous solution of Triton-X-100 with variation concentration (wt.%) added starch is shown in the **Fig. 5.8**

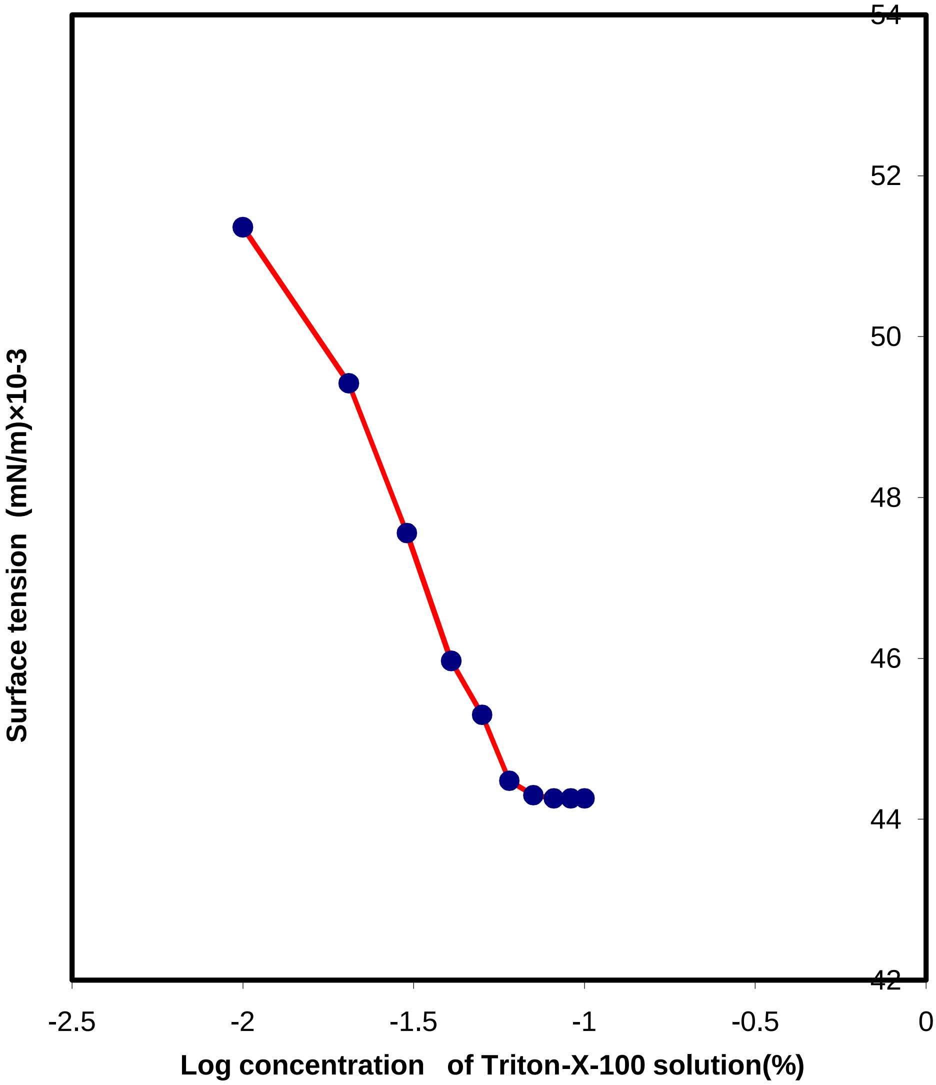


Fig. 5.8 The surface tension of aqueous solution of Triton-X-100 with variation concentration (wt.%) of added starch

The surface tension of aqueous solution of Brij-30 with variation concentration (wt.%) added starch is shown in the **Fig. 5.9**

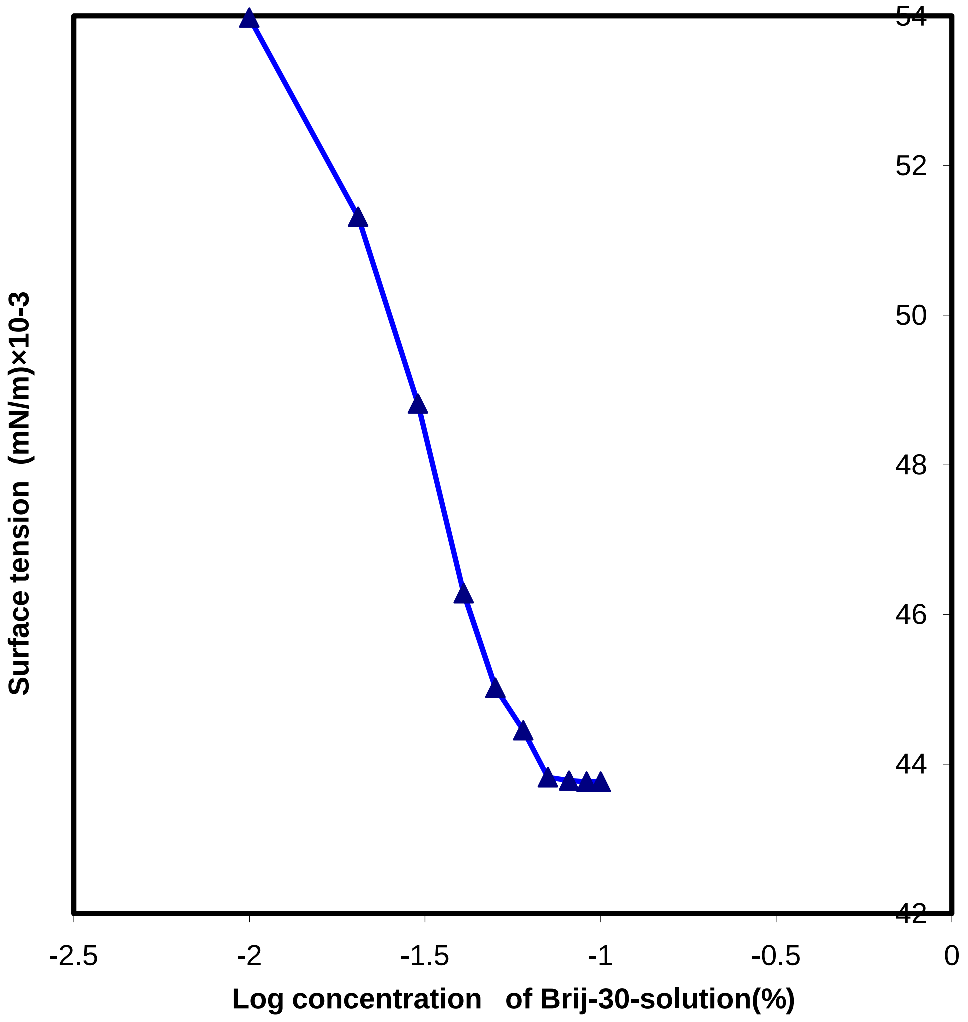


Fig. 5.9 The surface tension of aqueous solution of Brij-30 with variation concentration (wt.%) of added starch

The surface tension of aqueous solution of NaOct with variation concentration (wt.%) added starch is shown in the **Fig. 5.10**

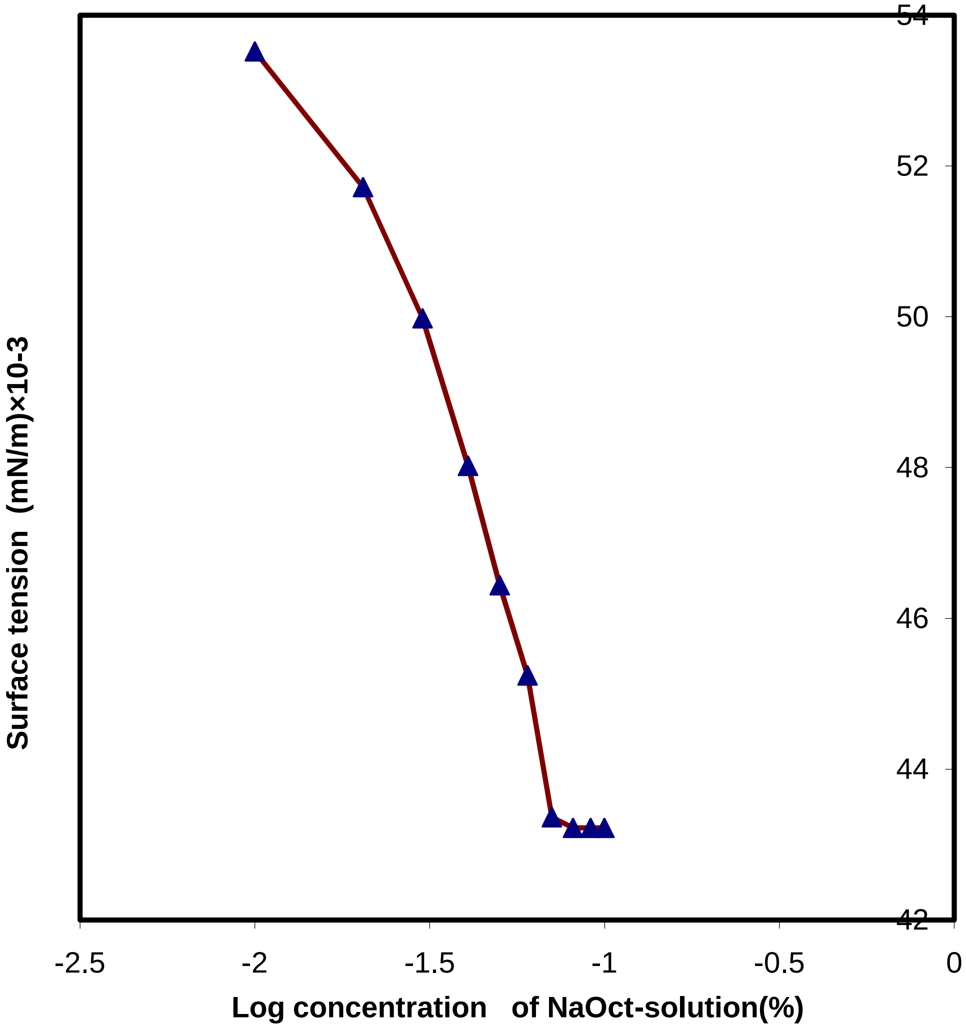


Fig. 5.10 The surface tension of aqueous solution of NaOct with variation concentration (wt.%) of added starch

Solubility of starch is very negligible. It is within 0.5%, but not more. This amounts of` starch is solubilized in the soap and surfactant solutions and has the remarkable effect on the CMC of soaps and surfactants which we have studied here by surface tension. When log Concentration of surfactant Vs surface tension is plotted different slopes are obtained from different concentration of detergent which on extrapolation gives a decisive break point indicative of the critical micelle concentration. There on extrapolation the two straight lines of different slopes at a point, the concentration that corresponds to the break point is known as the critical micelle concentration. Although starch, by itself, is surface inactive but when added to both soaps and surfactants makes the foam more surface active, a fact, which has direct relevance to the detergent. This can be visualized from our results. Above are the discussions on the results. Now we will go into the explanation of the experimental results from theory point of view.

5.13.1 Interactions between Surfactants and Amylose in Solution

The ability of a surfactant such as SDS to enhance granule swelling while long-chain (C_{16}- C_{18}) monoglycerides have the opposite effect, have previously been attributed to differences in solubility of a surface layer on the granules built of amylose-surfactant complexes formed as AM leached from the granule during gelatinisation. Eliasson [1985] was suggested that the high hydrophilicity of charged surfactant head groups to be responsible for the water solubility of the complex which in turn was believed to favourable water uptake by the granule. In fact, poor water solubility of inclusion complexes of amylose and surfactants has been reported to be associated with the absence of electrostatic stabilization, either because the surfactant is non- ionic, or because the concentration of non-complexed surfactant or added salt is sufficiently high to screen electrostatic effects which were suggested by Karkalas and Raphaelides [1986]. As it has already been discussed, the results from previous investigations of Isabel et al. [2006] indicated that the swelling-enhancing/ restricting effect of different surfactants can not be entirely attributed to the water solubility of complexes formed between amylose and ionic surfactants. Moreover, preliminary investigations on the solubility of complexes of amylose and a series of short (C_{12}) and long-chain (C_{16}) surfactants indicated that, contrary to what had been expected, the solubility of the amylose-surfactant complexes was not entirely governed by the presence of a charged surfactant head group. This finding indicated that a better understanding on the solution properties of these complexes was required.

This section summarizes the results from the investigations presented in Papers Hossain et al.[2012] on the solubility of complexes of AM and short-

(C_{12}) and long-chain (C_{16}) non-ionic (Tween-20) and anionic (SDS) surfactants. A prerequisite for the establishment of comparisons between different AM-surfactant complexes was the determination of the overall binding capacity of the AM molecule in solution. In this respect, studies of crystalline AM-fatty acids complexes have revealed that the stoichimetry of the complex varies with the chain length of the complexing agent. Godet et al. [1988] have also been found in studies on the binding capacity of AM in solution where it was reported that the amount of a fatty acid salt required to saturate AM decreased with increasing alkyl chain length of the fatty acid which was found by Karkalas and Raphaelides [1986] Furthermore, results from various studies on the binding of different surfactants to amylose in solution Eliasson Krog [1985], Lundqvist,et al. [2002], Bulpin et al. [1982] and Svensson et al. [1996] suggested that the characteristics of the surfactant head group could also affect the overall binding capacity of the amilose of starch molecules by studying the association of surfactants to amylose in solution, i.e. under conditions where the amylose molecule has no conformational constraints, it is also possible to retrieve information on the characteristic features of the association process between different surfactants and this polysaccharide.

5.13.2 Binding of surfactants to AM in solution as studied by means of surface tension

The ability of a polymer to alter the surface tension of a surfactant solution, particularly when the polymer is not surface active in itself, is an indication of the occurrence of interactions (association) between the surfactant and the polymer in bulk. Under these conditions, it is usually assumed that surfactants bound to the polymer do not contribute to the surface tension. Thus, by comparing the surface tension of surfactant solutions with and without polymer, it is possible to estimate the amount of surfactant bound to the polymer at any given surfactant concentration. As starch is in itself a non-surface active polymer, the binding of surfactants to starch in solution can, in principle, be conveniently estimated by means of surface tension determinations.

5.14 Results and Discussions

From **Table [5.5-5.10]** shows the surface tension curve (surface tension vs. surfactant concentration) of the nonionic surfactant shows [**Table 5.7- 5.11**] minimum interaction i.e. maximum surface tension compared to ionic surfactant [**Table 5.5-5.6**] could be found minimum surface tension i.e. maximum interaction with starch which clearly indicates starch polymer has some cleansing property when it is added with surfactants, especially in ionic surfactant both cationic and anionic.

Table 5.2 The surface tension of aqueous solution of (SDS) with different amounts of added starch solution (%) at room temperature

Concentration of Starch solution X10^{-2}	Log concentration of Starch solution (%)	Surface tension of SDS solution (N/m)×10^{-3}			
		.05%	0.10%	0.15%	0.20%
1.00	-2.00	48.42	48.11	47.81	47.21
2.00	-1.69	48.02	47.37	46.72	46.61
3.00	-1.52	47.21	46.91	46.62	46.52
4.00	-1.39	46.82	46.71	46.61	46.45
5.00	-1.30	46.81	46.62	46.43	46.15
6.00	-1.22	46.81	46.62	46.43	46.08
7.00	-1.15	46.81	46.61	46.43	46.00
8.00	-1.09	46.81	46.61	46.42	46.00
9.00	-1.04	46.81	46.61	46.42	46.00
10.00	-1.00	46.91	46.81	46.67	46.45

Table 5.3 The surface tension of aqueous solution of Cetyltrimethyl ammonium bromide (CTAB) with different amounts of added starch solution (%)

Concentration of Starch solution X10^{-2}	Log concentration of Starch solution (%)	Surface tension of CTAB solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	50.00	49.56	49.41	48.86
2.00	-1.69	49.30	49.06	48.12	48.00
3.00	-1.52	48.80	48.58	47.96	47.83
4.00	-1.39	48.61	48.34	47.90	47.76
5.00	-1.30	48.48	48.28	47.88	47.67
6.00	-1.22	48.42	48.20	47.82	47.52
7.00	-1.15	48.42	48.20	47.80	47.52
8.00	-1.09	48.40	48.20	47.80	47.50
9.00	-1.04	48.40	48.20	47.80	47.50
10.00	-1.00	48.90	48.70	48.50	48.20

Table 5.4 The surface tension of aqueous solution of Tween-20 with different amounts of added starch solution (%).

Concentration of Starch solution X10^{-2}	Log Concentration of Starch solution	Surface tension of Tween-20 solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	49.29	48.82	48.72	48.56
2.00	-1.69	48.26	47.84	47.30	47.28
3.00	-1.52	47.68	47.30	47.24	47.20
4.00	-1.39	46.54	46.28	46.20	46.14
5.00	-1.30	46.34	46.18	46.00	45.92
6.00	-1.22	46.34	46.08	45.94	45.76
7.00	-1.15	46.30	46.08	45.72	45.66
8.00	-1.09	46.30	46.08	45.72	45.64
9.00	-1.04	46.30	46.08	45.72	45.64
10.00	-1.00	46.30	46.08	45.72	45.64

Table 5.5 The surface tension of aqueous solution of Brij-30 with different amounts of added starch solution (%).

Concentration of Starch solution X10^{-2}	Log concentration of Starch solution (%)	Surface tension of Brij-30 solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	49.98	49.82	49.66	49.28
2.00	-1.69	49.32	49.24	48.88	48.82
3.00	-1.52	49.18	49.06	48.72	48.64
4.00	-1.39	49.06	49.04	48.44	48.32
5.00	-1.30	49.00	48.98	48.34	48.20
6.00	-1.22	48.56	48.44	48.12	48.00
7.00	-1.15	48.56	48.20	48.00	47.70
8.00	-1.09	48.56	48.20	48.00	47.70
9.00	-1.04	48.56	48.20	48.00	67.70
10.00	-1.00	48.56	48.20	48.00	47.70

Table 5.6 The surface tension of aqueous solution of Triton–X-100 with different amounts of added starch solution (%).

Concentration of Starch solution X10^{-2}	Log concentration of Starch solution (%)	Surface tension of Triton-X-100 solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	48.92	48.74	48.26	48.06
2.00	-1.69	48.16	47.42	47.22	47.00
3.00	-1.52	47.28	47.18	46.14	45.94
4.00	-1.39	46.24	46.15	46.02	45.83
5.00	-1.30	46.20	46.15	46.00	45.74
6.00	-1.22	46.20	46.06	45.92	45.70
7.00	-1.15	46.20	46.06	45.68	45.46
8.00	-1.09	46.20	46.06	45.68	45.46
9.00	-1.04	46.20	46.06	45.68	45.46
10.00	-1.00	46.20	46.06	45.68	45.46

Table 5.7 The surface tension of aqueous solution of Tween-80 with different amounts of added starch solution (%).

Concentration of starch solution X10^{-2}	Log Concentration of starch solution	Surface tension of Tween-20 solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	50.29	49.82	49.72	49.56
2.00	-1.69	49.26	48.84	48.30	48.28
3.00	-1.52	48.68	48.30	48.24	48.20
4.00	-1.39	47.54	47.28	47.20	47.14
5.00	-1.30	47.34	47.18	47.00	46.92
6.00	-1.22	47.34	47.08	46.94	46.76
7.00	-1.15	47.30	47.08	46.72	46.66
8.00	-1.09	47.30	47.08	46.72	46.64
9.00	-1.04	47.30	47.08	46.72	46.64
10.00	-1.00	47.30	47.08	46.72	46.64

The surface tension isotherm of CTAB or SDS in the presence of starch exhibits the familiar features of minimum surface tension clearly proves maximum interaction that of a surfactant in the presence of a non-surface active polymer and allows the identification of different association regimes which is found from **Table** [3.5-3.6] Between points high to low the higher surface tension of the system with respect to that of the surfactant alone indicates that only a fraction of the total amount of added surfactant remains free. Beyond point high up to point CMC, the surface tension of the system remains unchanged, thus indicating that within this concentration range [0.05-0.20] essentially for all the added surfactant binds to amylase of starch molecule where excessive concentrated solution is not appropriate for the experiment. **Table 3.10-3.17** shows the surface tension isotherm of Ionic, non-ionic and in the presence and absence of starch at definite temperature. The surface tension isotherm of SDS in the presence of starch is characterized by the occurrence of two clear break points: one occurring at high surface tension values and another occurring at low ones. Beyond the first break point (0.3 mM), the surface tension falls below that of the pure surfactant, and the low-surface-tension break point takes place well below the CMC of the surfactant in the absence of starch Thus, beyond the first break point, a synergistic adsorption of polymer-surfactant entities at the liquid-air interface takes place.

As both the surfactant and the polymer contribute to the surface tension in this concentration region, the surface tension of the system cannot be used to provide an estimate of the free surfactant concentration in solution. However, a comparison of the surface tension isotherms of the SDS and starch-SDS systems in the presence and absence of electrolyte [SEE **Table** 3.10-3.17], revealed that the first break point in the isotherm could be used as an indication of the concentration up to which the surfactant would bind to amylose of starch molecule through the formation of non-surface active complexes.

Table 5.8 The surface tension of aqueous solution of Sodium octanoate-(NaOct) with different amounts of added starch solution (%)

Concentration of Starch solution X10^{-2}	Log Concentration of Starch solution	Surface tension of NaOct solution (N/m)×10^{-3}			
		0.05%	0.10%	0.15%	0.20%
1.00	-2.00	49.52	49.04	49.00	48.46
2.00	-1.69	48.72	47.55	47.42	47.34
3.00	-1.52	47.98	47.45	46.82	46.08
4.00	-1.39	46.96	46.40	46.22	46.02
5.00	-1.30	46.44	46.15	46.00	45.26
6.00	-1.22	45.20	45.16	45.02	44.32
7.00	-1.15	45.20	44.96	44.32	44.22
8.00	-1.09	45.20	44.96	44.32	44.22
9.00	-1.04	45.20	44.96	44.32	44.22
10.00	-1.00	45.20	44.96	44.32	44.22

Table 5.9 The surface tension of aqueous solution of only SDS with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of SDS solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	53.15
0.02	-1.69	50.26
0.03	-1.52	47.24
0.04	-1.39	46.02
0.05	-1.30	45.02
0.06	-1.22	44.84
0.07	-1.15	44.62
0.08	-1.09	44.24
0.09	-1.04	44.16
0.10	-1.00	44.08

Table 5.10 The surface tension of aqueous solution of only CTAB with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of CTAB solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	53.08
0.02	-1.69	50.04
0.03	-1.52	48.56
0.04	-1.39	47.78
0.05	-1.30	47.04
0.06	-1.22	46.26
0.07	-1.15	45.58
0.08	-1.09	45.25
0.09	-1.04	45.20
0.10	-1.00	45.20

Table 5.11 The surface tension of aqueous solution of only Triton-X-100 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Triton-X-100 solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	51.36
0.02	-1.69	49.42
0.03	-1.52	47.56
0.04	-1.39	45.97
0.05	-1.30	45.52
0.06	-1.22	44.89
0.07	-1.15	44.58
0.08	-1.09	44.03
0.09	-1.04	44.03
0.10	-1.00	43.56

Table 5.12 The surface tension of aqueous solution of only Tween-20 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Tween-20-solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	52.5
0.02	-1.69	49.58
0.03	-1.52	48.14
0.04	-1.39	47.00
0.05	-1.30	46.02
0.06	-1.22	45.43
0.07	-1.15	44.24
0.08	-1.09	44.14
0.09	-1.04	44.14
0.10	-1.00	44.06

Table 5.13 The surface tension of aqueous solution of only Tween-80 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Tween-80-solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	53.58
0.02	-1.69	50.68
0.03	-1.52	49.54
0.04	-1.39	48.30
0.05	-1.30	46.22
0.06	-1.22	46.03
0.07	-1.15	45.14
0.08	-1.09	45.04
0.09	-1.04	45.04
0.10	-1.00	45.04

Table 5.14 The surface tension of aqueous solution of only Brij-30 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Brij-30-solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	52.98
0.02	-1.69	51.32
0.03	-1.52	48.82
0.04	-1.39	46.28
0.05	-1.30	45.02
0.06	-1.22	44.45
0.07	-1.15	43.82
0.08	-1.09	43.78
0.09	1.04	43.76
0.10	-1.00	43.70

Table 5.15 The surface tension of aqueous solution of only NaOct with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of NaOct-solution (%)	Surface tension (N/m)×10^{-3}
0.01	-2.00	53.52
0.02	-1.69	51.72
0.03	-1.52	49.98
0.04	-1.39	48.02
0.05	-1.30	47.44
0.06	-1.22	46.88
0.07	-1.15	45.62
0.08	-1.09	44.22
0.09	-1.04	44.20
0.10	-1.00	44.20

Table 5.16 The surface tension at CMC point of aqueous solution of SDS with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of SDS solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	48.40
0.10	-1.00	48.20
0.15	-.82	47.80
0.20	-0.69	47.50
0.25	-0.60	47.15
0.30	-0.52	46.76

Table 5.17 The surface tension at CMC point of aqueous solution of CTAB with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of CTAB solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	48.40
0.10	-1.00	48.20
0.15	-.82	47.80
0.20	-0.69	47.50
0.25	-0.60	47.15
0.30	-0.52	46.76

Table 5.18 The surface tension at CMC point of aqueous solution of Tween-20 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Tween-20 solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	46.30
0.10	-1.00	46.08
0.15	-.82	45.72
0.20	-0.69	45.64
0.25	-0.60	45.30
0.30	-0.52	45.00

Table 5.19 The surface tension at CMC point of aqueous solution of Brij-30 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Brij-30 solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	48.56
0.10	-1.00	48.20
0.15	-.82	48.00
0.20	-0.69	47.70
0.25	-0.60	47.45
0.30	-0.52	47.05

Table 5.20 The surface tension at CMC point of aqueous solution of Triton-X-100 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Triton-X-100 solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	46.20
0.10	-1.00	46.06
0.15	-.82	45.68
0.20	-0.69	45.46
0.25	-0.60	45.08
0.30	-0.52	44.74

Table 5.21 The surface tension at CMC point of aqueous solution solution of NaOct with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of NaOct solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	45.20
0.10	-1.00	44.96
0.15	-.82	44.32
0.20	-0.69	44.22
0.25	-0.60	43.84
0.30	-0.52	43.62

Table 5.22 The surface tension at CMC point of aqueous solution of Tween-80 with variation of concentration (%)

Concentration of Surfactant solution X10^{-2}	Log concentration of Tween-80 solution (%)	Surface tension at CMC point (N/m×10^{-3})
0.05	-1.30	45.50
0.10	-1.00	45.28
0.15	-.82	44.92
0.20	-0.69	44.84
0.25	-0.60	44.50
0.30	-0.52	44.20

As observed in **Table 5.5**, the surface tension isotherm of SDS in the presence of AM and electrolyte is characterized by the occurrence of one clear break point at high surface tensions and another one occurring at low surface tension values. Up to the surfactant concentration at which the first point takes place, hardly any change in surface tension is observed upon addition of surfactant. By contrast, in the absence of polymer, a significant lowering of the surface tension occurs in this SDS concentration range. Thus, this first break point in the isotherm can be unambiguously ascribed to the concentration up to which essentially all the added surfactant binds to the AM and form complexes with no surface activity. Results from binding studies of various surfactants to AM in aqueous solution have indicated that such a distinctive break point in the surface tension isotherm of the surfactant in the presence of AM denotes the end of a highly cooperative association process of the surfactant to the polymer, which seems to involve the formation of helical inclusion complexes. As observed in Figure 25 B, the first break point in the surface tension isotherm of SDS in the presence of AM takes place at the same SDS concentration (ca. 0.3 mM) both in the presence and absence of electrolyte, demonstrating that the presence of electrolyte does not exert any significant influence on the interactions between SDS and AM up to this point. Thus, we propose that, by analogy, also in the absence of electrolyte all the added SDS binds to AM via formation of non-surface active helical inclusion complexes up to this concentration. Overall, as discussed bellow, the surface activity of the complexes formed between AM and the two sodium alkyl sulphates (SDS and NaOct) within certain conditions and concentration ranges, limited the quantitative information that could be extracted from the surface tension isotherms. However, the information that surface active amylose-SDS complexes form, whereas no surface active complexes are detected in the AM-maltoside systems, is intriguing and would be worth further studies.

Table 5.23 Determination of surface tension of starch mixed surfactant (SDS) 0.05% solution at different temperature (Ranges: 30-75^oC)

Conc. Of starch mixed surfactant (SDS) solution	Temperature (^oC)	Surface tension (N/m)×10^{-3}
0.05%	30	50.98
0.05%	35	50.74
0.05%	40	48.97
0.05%	45	46.63
0.05%	50	45.12
0.05%	55	44.32
0.05%	60	43.07
0.05%	65	42.92
0.05%	70	42.90
0.05%	75	42.90

Table 5.24 Determination of surface tension of starch mixed surfactant (CTAB) 0.05% solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (CTAB) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.05%	30	51.90
0.05%	35	50.54
0.05%	40	49.87
0.05%	45	47.43
0.05%	50	46.32
0.05%	55	45.38
0.05%	60	43.07
0.05%	65	43.52
0.05%	70	43.50
0.05%	75	43.50

Table 5.25 Determination of surface tension of starch mixed surfactant (Tween-20) 0.05% solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (Tween-20) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.05%	30	49.98
0.05%	35	48.56
0.05%	40	47.84
0.05%	45	45.49
0.05%	50	44.36
0.05%	55	43.36
0.05%	60	41.87
0.05%	65	41.72
0.05%	70	41.70
0.05%	75	41.70

Table 5.26 Determination of surface tension of starch mixed surfactant (Tween-80) 0.05% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Tween-80) solution	Temperature.(^{o}C)	Surface tension (N/m)$\times 10^{-3}$
0.05%	30	49.08
0.05%	35	48.16
0.05%	40	47.24
0.05%	45	45.69
0.05%	50	44.05
0.05%	55	43.38
0.05%	60	41.86
0.05%	65	41.48
0.05%	70	41.40
0.05%	75	41.40

Table 5.27 Determination of surface tension of starch mixed surfactant (Brij-30) 0.05% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Brij-30) solution	Temperature.(^{o}C)	Surface tension (N/m)$\times 10^{-3}$
0.05%	30	48.96
0.05%	35	47.54
0.05%	40	46.88
0.05%	45	46.45
0.05%	50	45.35
0.05%	55	44.32
0.05%	60	43.24
0.05%	65	43.22
0.05%	70	43.20
0.05%	75	43.20

Table 5.28 Determination of surface tension of starch mixed surfactant (Triton-X 100) 0.05% solution at different temperature (Ranges: 30-750°C)

Conc. Of starch mixed surfactant (Triton-X-100) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.05%	30	50.90
0.05%	35	49.52
0.05%	40	48.80
0.05%	45	46.99
0.05%	50	45.56
0.05%	55	44.86
0.05%	60	42.79
0.05%	65	42.62
0.05%	70	42.60
0.05%	75	42.60

Table 5.29 Determination of surface tension of starch mixed surfactant (NaOct) 0.05% solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (NaOct) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.05%	30	52.76
0.05%	35	50.66
0.05%	40	49.54
0.05%	45	47.50
0.05%	50	47.22
0.05%	55	45.86
0.05%	60	43.88
0.05%	65	43.68
0.05%	70	43.66
0.05%	75	43.66

Table 5.30 Determination of surface tension of starch mixed surfactant (SDS) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (SDS) solution	Temperature (^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	49.58
0.10%	35	49.34
0.10%	40	47.57
0.10%	45	45.23
0.10%	50	44.12
0.10%	55	43.02
0.10%	60	42.07
0.10%	65	41.52
0.10%	70	41.50
0.10%	75	41.50

Table 5.31 Determination of surface tension of starch mixed surfactant (CTAB) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of mixed starch & surfactant(CTAB) sol^{n}	Temperature.(^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	50.50
0.10%	35	49.14
0.10%	40	48.47
0.10%	45	46.03
0.10%	50	44.92
0.10%	55	44.08
0.10%	60	42.07
0.10%	65	42.00
0.10%	70	42.00
0.10%	75	42.00

Table 5.32 Determination of surface tension of starch mixed surfactant (Tween-20) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Tween-20t) solution	Temperature.(^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	48.48
0.10%	35	47.06
0.10%	40	46.34
0.10%	45	43.00
0.10%	50	42.98
0.10%	55	41.88
0.10%	60	40.47
0.10%	65	40.42
0.10%	70	40.42
0.10%	75	40.42

Table 5.33 Determination of surface tension of starch mixed surfactant (Tween-80) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Tween-80) solution	Temperature (^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	47.76
0.10%	35	46.52
0.10%	40	45.92
0.10%	45	44.87
0.10%	50	43.05
0.10%	55	42.08
0.10%	60	40.36
0.10%	65	40.00
0.10%	70	40.00
0.10%	75	40.00

Table 5.34 Determination of surface tension of starch mixed surfactant (Brij-30) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Brij-30) solution	Temperature.(^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	47.90
0.10%	35	46.48
0.10%	40	45.82
0.10%	45	45.39
0.10%	50	44.30
0.10%	55	43.30
0.10%	60	42.04
0.10%	65	42.02
0.10%	70	42.02
0.10%	75	42.02

Table 5.35 Determination of surface tension of starch mixed surfactant (Triton-X-100) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Triton-X-100) solution	Temperature (^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	49.50
0.10%	35	48.56
0.10%	40	47.90
0.10%	45	45.92
0.10%	50	44.42
0.10%	55	43.84
0.10%	60	42.96
0.10%	65	42.28
0.10%	70	42.28
0.10%	75	42.28

Table 5.36 Determination of surface tension of starch mixed surfactant (NaOct) 0.10% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (NaOct) solution	Temperature.(^{o}C)	Surface tension (N/m)×10^{-3}
0.10%	30	50.78
0.10%	35	48.64
0.10%	40	47.52
0.10%	45	45.40
0.10%	50	45.02
0.10%	55	44.82
0.10%	60	43.04
0.10%	65	43.00
0.10%	70	43.00
0.10%	75	43.00

Table 5.37 Determination of surface tension of starch mixed surfactant (SDS) 0.15% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (SDS) solution	Temperature.(^{o}C)	Surface tension (N/m)×10^{-3}
0.15%	30	47.90
0.15%	35	47.02
0.15%	40	46.22
0.15%	45	44.62
0.15%	50	44.02
0.15%	55	42.82
0.15%	60	41.34
0.15%	65	41.10
0.15%	70	41.06
0.15%	75	41.06

Table 5.38 Determination of surface tension of starch mixed surfactant (CTAB) 0.15%solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (CTAB) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.15%	30	49.60
0.15%	35	48.58
0.15%	40	46.64
0.15%	45	45.40
0.15%	50	43.92
0.15%	55	44.02
0.15%	60	41.56
0.15%	65	41.50
0.15%	70	41.50
0.15%	75	41.50

Table 5.39 Determination of surface tension of starch mixed surfactant (Tween-20) 0.15% solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (Tween-20) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.15%	30	47.56
0.15%	35	46.82
0.15%	40	45.98
0.15%	45	42.86
0.15%	50	41.88
0.15%	55	41.44
0.15%	60	40.02
0.15%	65	40.02
0.15%	70	40.02
0.15%	75	40.02

Table 5.40 Determination of surface tension of starch mixed surfactant (Tween-80) 0.15% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Tween-80) solution	Temperature.(^{o}C)	Surface tension (N/m)×10^{-3}
0.15%	30	47.04
0.15%	35	46.08
0.15%	40	45.24
0.15%	45	44.56
0.15%	50	42.98
0.15%	55	41.82
0.15%	60	40.12
0.15%	65	39.92
0.15%	70	39.92
0.15%	75	39.92

Table 5.41 Determination of surface tension of starch mixed surfactant (Brij-30) 0.15% solution at different temperature (Ranges: 30-75^{o}C)

Conc. Of starch mixed surfactant (Brij-30) solution	Temperature (^{o}C)	Surface tension (N/m)×10^{-3}
0.15%	30	47.46
0.15%	35	46.08
0.15%	40	45.44
0.15%	45	45.06
0.15%	50	44.02
0.15%	55	43.06
0.15%	60	42.42
0.15%	65	41.90
0.15%	70	41.90
0.15%	75	41.90

Table 5.42 Determination of surface tension of starch mixed surfactant (Triton-X 100) 0.15% solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (Triton-X-100) solution	Temperature.(°C)	Surface tension (N/m)×10^{-3}
0.15%	30	49.06
0.15%	35	48.08
0.15%	40	47.62
0.15%	45	45.44
0.15%	50	44.02
0.15%	55	43.46
0.15%	60	42.42
0.15%	65	42.04
0.15%	70	42.04
0.15%	75	42.04

Table 5.43 Determination of surface tension of starch mixed surfactant (NaOct) 0.15% solution at different temperature (Ranges: 30-75°C)

Conc. Of starch mixed surfactant (NaOct) solution	Temperature (°C)	Surface tension (N/m)×10^{-3}
0.15%	30	50.06
0.15%	35	48.08
0.15%	40	47.02
0.15%	45	45.00
0.15%	50	44.96
0.15%	55	44.28
0.15%	60	42.96
0.15%	65	42.48
0.15%	70	42.48
0.15%	75	42.48

From **Table** [5.27-5.44] it has been found at temperature range 30°C to 75°C and various concentrations (0.05 to 0.45%) the value of surface tension is remarkable. Here it is found at low concentration and at low temperature the surface tension value is high which indicates from our results minimum interactions occurred but at concentration at CMC and maximum temperature 75°C the surface tension value shows minimum which clearly proves maximum interaction within the amylose of starch molecule and surfactants. The results indicate our concept and aim of the experiment is successful. From **Table** [5.17-5.23] the used surfactant with or without starch mixture the CMC value is obtained where the maximum interaction in between them indicates the maximum reaction in this concentration (CMC).

From Table 5.XII shows the effect of interaction of surfactant (CTAB) and starch by the surface tension measurement it is found that the values of surface tension Vs log concentration of CTAB (%) solutions plot shows a definite break point. The obtained break point indicates CMC the critical concentrations above which micelles are formed is called CMC. (the list of **Fig. 5.5**). From the **Table** 5.12 it is found by increasing concentration of CTAB surfactant decreases the surface tension value but at certain point of low concentration (.07%) where CMC formed the value of surface tension is unchangeable.

From **Fig. 5.7** shows the effect of interaction of surfactant (Tween-20) and starch by the surface tension measurement it is found that the values of surface tension Vs log concentration of Tween-20 (wt.%) solutions plot shows a definite break point . The obtained break point indicates CMC the critical concentrations above which micelles are formed is called CMC (the list of **Figure**-5.7). From the **Table**-5.13 it is found by increasing concentration of Tween-20 surfactant decreases the surface tension value but at certain point of low concentration (.08%) where CMC are formed the value of surface tension is unchangeable.

CHAPTER-6: *Starch –Surfactant interactions by viscometric properties*

6.1. Experimental techniques or procedure

6.2 Results and discussion

6.1. Experimental techniques or procedure

Measurement of viscosity is carried out in an ubbelohde suspended level viscometer at 25°C in a water bath. Generally, we use the Ostwald viscometer for the determination of the molecular weight of polymeric materials or Natural polymer. At first we recorded the falling time of the solvent (pure distilled H_2O) by using the Ostwald viscometer and recorded the reading value in table from stop watch with vary early. Next the sample solution is taken in viscometer (13 cc) by pipette and determined of falling time. In this way, the falling time of the different solution is recorded by viscometer & stop watch. To remember that in each stage during the determination of falling time the viscometer is rinsed with chromic acid next acetone and finally drying in own gradually. The viscosity of the pure water is determined and count the time different from sample solution. Next the Relative viscosity of the sample & solution is determined by the following equation-

$$\eta_r = \frac{\text{¦}\ solution}{\text{¦}_0\ solvent} \text{.....................................(1)}$$

Then the specific viscosity of the solution will be

$\eta_{sp} = \eta_r - 1$ [η_{sp} = specific viscosity]

Intrinsic viscosity is obtained by plotting $\eta_{sp}/_c$ against concentration C and extra plotting to zero concentration, where c is the concentration in gm/$_{100cc}$ of the solution. From the measured intrinsic viscosity the molecular weight of supplied polymeric sample Starch mixed surfactant is calculated by the following equation. i.e.

$[\eta] = KM^a$....................................(2)

From the intercept of the plot log [η] against log [M] value of K and from the slope value of a are found. Finally ploting the value of K. a and [η] in (12) No equation we get the molecular weight of the sample Starch mixed surfactant.

6.2 Results and discussion

The solutions showed a Newtonian behavior within the range of shear rate used in this work.

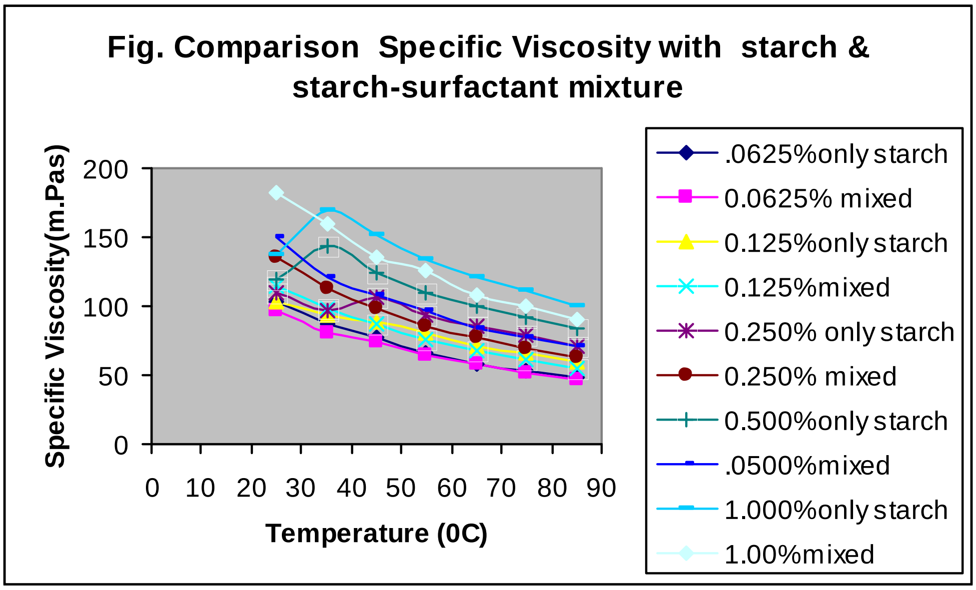


Fig. 6.1 Temperature Vs Specific Viscosity of starch and starch –surfactant mixture

Fig. 6.1 shows the dependence of specific viscosity on the concentration for starch-surfactant-water solutions, at different temperatures. There is a master curve, which encompasses all the temperatures (ranges from 25^{o}C to 85^{o}C) used in this work, although data fit is poorer for lower concentrations. **Fig**. 6.1 also shows that, regarding concentration dependence, there are two regions, which can be characterized by the two different slopes in the double-logarithmic plot. They have already been characterized in literature as a consequence of two kinds of behavior: one in which the individual polymer (starch) molecules are present as isolated coils, which is related to the line with a lower slope; another one in which the total hydrodynamic volume of individual chains exceeds the volume of the solution; suggested by Morris et al. [1986] As a consequence, there is significant coil overlap and inter-penetration, which results in stronger polymer—polymer interactions and higher viscosity.

More specifically, it reinforces already established theories which claim that random coil polymers obey a universal behavior expressed through the existence of a unique log ¦ $_{SP}$ vs. log C[¦] master curves (where ¦ $_{SP}$ and [¦] are the specific and intrinsic viscosities, respectively). Deviations from this master curves are attributed to specific molecular interactions creating "hyper-entanglements" Moris et al. [1986] Since the analysis carried out in this work was of phenomenological character, it is not possible to assert what kind of specific interaction we have, apart from that (for higher concentrations) its occurrence is a function of temperature, as we will subsequently show in this work, by an analysis of the apparent flow energy of activation by Launay et al. [1997] have suggested that there are two critical concentrations, c", the point from which there is an initial departure from linearly (C*[¦] « 0.80) and c" (C**[¦] ~ 6) which delimit three regimes: dilute (c < c*), semidilute (c" < c < c**), and concentrated (c > c*). It can be seen that there is a discontinuity in the curve at c ~ 0.015 g/ ml, which, in a master curve would correspond to a value of C[¦] = 0.8; this concentration would correspond, therefore, to the transition from the dilute to the semidilute regime. The highest concentration used in this work corresponded to a value of C [¦] = 1.0 ± 0.3; that would explain the absence of c" in this plot. Since, in the present case, intrinsic viscosity was not necessary to build the master curve, it follows that, for this system, $[¦_{sp}]$ is independent of temperature. Its value was calculated according to Mark-Huggins equation (Eq. (5))[8] as 50 ± 2 ml/g.

$$\frac{¦_{sp}}{c} = [¦] + k'[¦]^2 c \,. \text{ -------------------(3)}$$

Values of intrinsic viscosity for starch, amylopectin and amylose in different solvent conditions can be found in literature by Salemis and Rinaudo [1984] and a value in the same range has been found for an amylose sample ([¦] ~ 60 ml/g and Surfactant/water solvent composition = 66/34) Eq. (i), adequately described the viscosity-temperature dependence for all the concentrations analyzed in this work. It is, therefore, reasonable to plot the apparent energy of activation (E_A) against concentration. Fig. 6.1 shows that the value of E_A is constant below c = 0.125 g/dl, continuously rising, afterwards. A constant value of E_A reflects the fact that, in the dilute regime, viscosity is solely a function of starch-solvent and solvent-solvent interactions. At concentrations above c', E_A is expected to change, due to occurrence of starch entanglement: a new type of interaction starts playing its role and as concentration is increased, starch-surfactant interactions become more significant and, as a result, there is a continuous increase in E_A.

A more quantitative approach can be carried out if one takes Mark-Huggins equation as the starting point. Rearranging Eq. (3) in terms of solution viscosity, $¦_{sp}$ (c), and solvent viscosity, ¦ (0), it follows that

$$¦(c) = \left[1 + [¦]c + k'([¦]c)^2\right]¦(0) \text{ .------------------(4)}$$

The superposition of the points in Fig.6.1 showed that neither [¦] nor k', significantly varies with temperature. Consequently, TJ (C, T) can be expressed, when in the dilute solution regime, according to Eq. (i), where

$$¦_0 = ¦_0(c) = \left[1 + [¦]c + k'([¦]c)^2\right]¦_0(0); E_A = E_A(0) \text{ --------------(5)}$$

Here, E_A (0) and $¦_0$(0), respectively are the values of the apparent activation energy and pre-exponential constant for the pure solvent, a change in the value of E_A indicating a change in the flow regime.

Table 6.1 at temperature range (25^o-85^{o}C) solution viscosity of starch mixed surfactant (SDS) compounds

Temp ^{o}C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.500%	1.000%
25	1644.528	813.616	411.320	213.134	116.297	1549.392	912.256	539.508	298.854	182.692
35	1385.072	823.416	481.496	288.598	170.153	1298.592	786.768	454.012	240.734	159.576
45	1229.392	718.792	426.532	247.572	151.884	1177.504	703.104	392.944	216.802	135.538
55	1065.072	645.592	374.624	218.512	133.615	1021.824	608.992	344.088	192.870	125.923
65	926.688	572.392	341.036	201.418	121.115	918.048	541.016	307.448	168.940	108.615
75	857.504	525.328	313.556	184.324	110.538	822.912	488.728	279.968	155.264	99.961
85	771.024	478.272	286.076	168.94	99.961	753.728	441.672	252.488	141.588	90.346

Finally, values obtained for $¦_0$ are plotted against concentration in **Fig.** 6.2 as well as the graphical representation of Eq. (5) for this system. The curve was built using the experimentally obtained values of [¦], k'[¦]^2 (the slope of the $¦_{sp}$/c vs. c plot) and ¦ (0). It can be seen that ¦ $_{O}$ ceases to be a function of c, as described by Eq, (5), at approximately the same concentration, indicating a change in the flow regime, which is consistent with what has been found from the ¦ $_{sp}$ vs. C and E_A vs. C data.

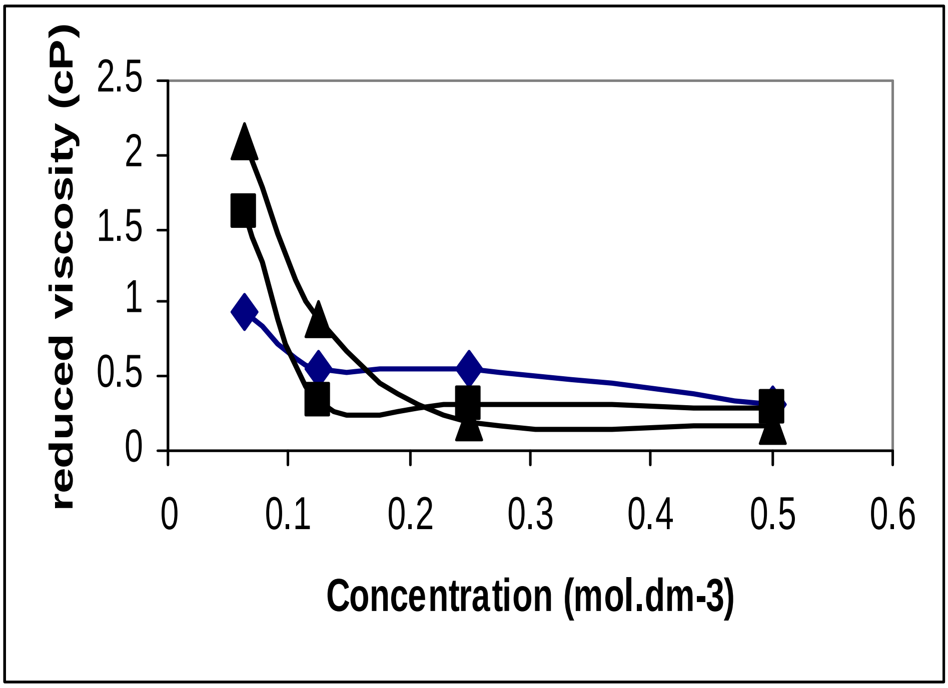


Fig. 6.2 Reduced viscosity vs. concentration curve of SDS-starch complexes

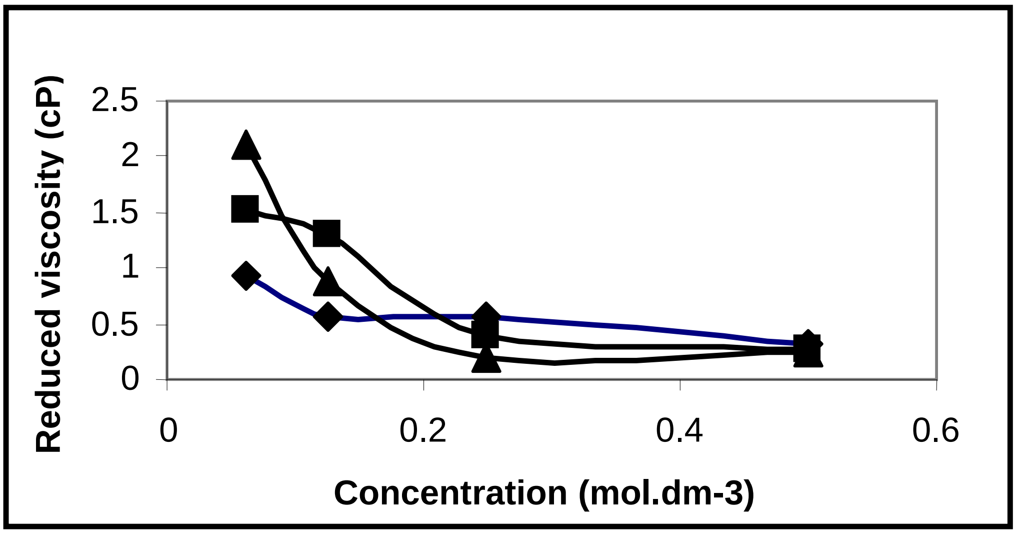


Fig. **6.3** Reduced viscosity vs. concentration curve of CTAB-starch complexes

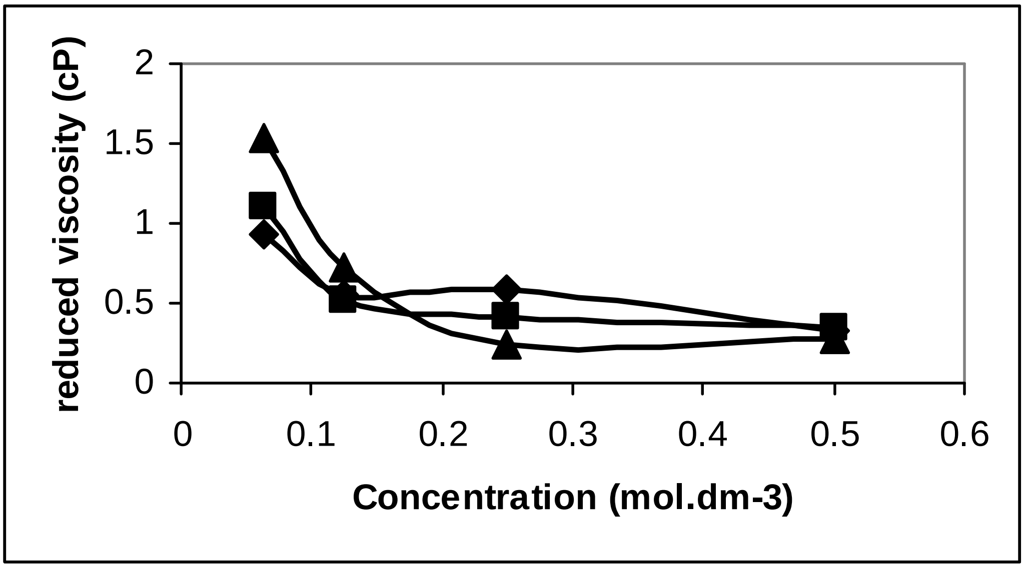


Fig. **6.4** Reduced viscosity vs. concentration curve of Twen-20-starch complexes

From results analysis it has found at lower concentration the reduced viscosity value are high but at CMC point the curve become level off but after increasing concentration the reduced viscosity value increased slowly in all cases but in case of ionic surfactant (SDS, CTAB) the changing is remarkable due to maximum interactions occurred with starch polymer. Here, we mentioned that temperature has a remarkable effect in the complexes of starch-ionic surfactant, here it is obtained according to Arrhenius rule increasing temperature reduced viscosity and specific viscosity is reduced due to the freeness of solution.

Table 6.2: Specific viscosity of starch-CTAB complex solution with or without polymer.

Temp °C	Specific Viscosity (polymer)					Specific Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.500%	1.00%
25	102.783	103.702	109.783	119.567	136.297	96.837	114.032	134.877	149.427	181.692
35	86.567	92.921	96.374	144.299	170.153	81.162	98.346	113.503	120.367	159.576
45	76.837	88.849	106.633	123.786	151.884	73.594	87.888	98.236	108.401	135.538
55	66.567	80.699	93.656	109.256	133.615	63.864	76.124	86.022	96.435	125.923
65	57.918	71.549	85.259	100.709	121.115	57.378	67.627	76.862	84.470	108.615
75	53.594	65.666	78.389	92.162	110.538	51.432	61.091	69.992	77.632	99.961
85	48.189	59.784	71.519	84.470	99.961	47.108	55.209	63.122	70.794	90.346

Table 6.3 at temperature range (25°C-85°C) solution viscosity of starch mixed CTAB

Temp °C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.50%	1.00%
25	1644.528	813.616	411.320	213.134	116.297	1549.392	912.256	539.508	298.854	182.692
35	1385.072	823.416	481.496	288.598	170.153	1298.592	786.768	454.012	240.734	159.576
45	1229.392	718.792	426.532	247.572	151.884	1177.504	703.104	392.944	216.802	135.538
55	1065.072	645.592	374.624	218.512	133.615	1021.824	608.992	344.088	192.870	125.923
65	926.688	572.392	341.036	201.418	121.115	918.048	541.016	307.448	168.940	108.615
75	857.504	525.328	313.556	184.324	110.538	822.912	488.728	279.968	155.264	99.961
85	771.024	478.272	286.076	168.94	99.961	753.728	441.672	252.488	141.588	90.346

Table 6.4 at temperature range (25^{o}-85^{o}C) solution viscosity of starch mixed surfactant Triton X-100

Temp ^{o}C	Reduced Viscosity (polymer)						reduced Viscosity (polymer-surfactant mixture)			
	0.0625%		0.125%		0.250%		0.500%		1.000%	
25	102.783	96.837	101.702	114.032	102.783	134.877	106.567	149.427	116.297	171.765
35	86.567	81.162	102.921	98.346	120.374	113.503	144.299	120.367	170.153	157.970
45	76.837	73.594	89.849	87.888	106.633	98.236	123.786	108.401	151.884	135.538
55	66.567	63.864	80.699	76.124	93.656	86.022	109.256	96.435	133.615	123.843
65	57.918	57.378	71.549	67.627	85.259	76.862	100.709	84.470	121.115	107.654
75	53.594	51.432	65.666	61.091	78.389	69.992	92.162	77.632	110.538	98.976
85	48.189	47.108	59.784	55.209	71.519	63.122	84.470	70.794	99.961	87.378

Table 6.5 at temperature range (25^{o}-85^{o}C) solution viscosity of starch mixed surfactant Tween-20

Temp ^{o}C	Reduced Viscosity (polymer)					reduced Viscosity (polymer-surfactant mixture)				
	0.0625%	0.125%	0.250%	0.500%	1.000%	0.0625%	0.125%	0.250%	0.50%	1.00%
25	1646.523	810.610	417.380	211.138	118.299	1545.397	910.251	534.509	288.451	181.678
35	1380.073	821.446	471.486	289.594	180.150	1291.595	756.736	414.092	248.744	148.577
45	1214.395	778.756	421.537	248.772	161.830	1171.504	700.102	332.947	226.806	133.513
55	1073.070	640.599	364.620	238.510	130.618	1011.823	603.996	366.086	182.870	124.723
65	920.668	571.382	381.039	208.818	128.119	911.044	546.011	367.442	158.340	103.614
75	847.704	529.308	319.558	184.321	114.533	812.917	468.325	249.969	155.254	98.761
85	746.026	478.272	286.076	168.94	99.961	753.728	441.672	252.488	141.588	89.447

Several references may be found in the literature to the compaction of polyelectrolytes on binding of oppositely charged surfactants Musabekov et al. [1983]. Viscosity measurements have been carried out by Abuin and Scaiano [1984] on mixtures of PSS of M_w of 130 000 and DTAB. When added to solution of 0.36 w% PSS, DTAB in the pre-precipitation zone brought about a progressive reduction in the viscosity of the solutions.

For example, 5.8 mM DTAB was found to drop the reduced viscosity of PSS by a factor of ten, far exceeding the reduction effected by addition of the simple analog "surfactant", tetradecyltrimethylammonium bromide. The explanation offered was that coiling of the flexible "vinyl" backboned polyelectrolyte occurs around small clusters of the surfactant, which form under these conditions. Similar effects have been obtained by Bekturov et al. [1984, who studied the viscosity characteristics of a series of amphoteric polymers on addition of anionic (SDS) or cationic (CTAB) surfactants to their solutions. Goddard et al. [1982] and Leung and Goddard [1985] have reported viscosimetric and rheological studies on two cationic polymers, viz. a cationic cellulosic (Polymer JR) and an acrylamide/methacryl oxyethyl trimethylammonium chloride co-polymer (Reten, Hercules) within a range of polymer and added SDS concentrations. Considerable differences in behaviour between the two polymers were found.

Our motivation for the present study is not only scientific interest. Polysoaps are present in the wash liquor where they might form microdomains. Amphiphilic molecules may bind to these domains, and the concomitant reduction of free surfactant in solution may adversely affect wash performance of surfactants. The **Fig**.6.5 of non-ionic surfactant under the region given where it has been seen that the non ionic Tween -20 molecule is totally di-pole absent so, there is no chance to make bond formation through H atom by hydrogen bonding with starch molecule.

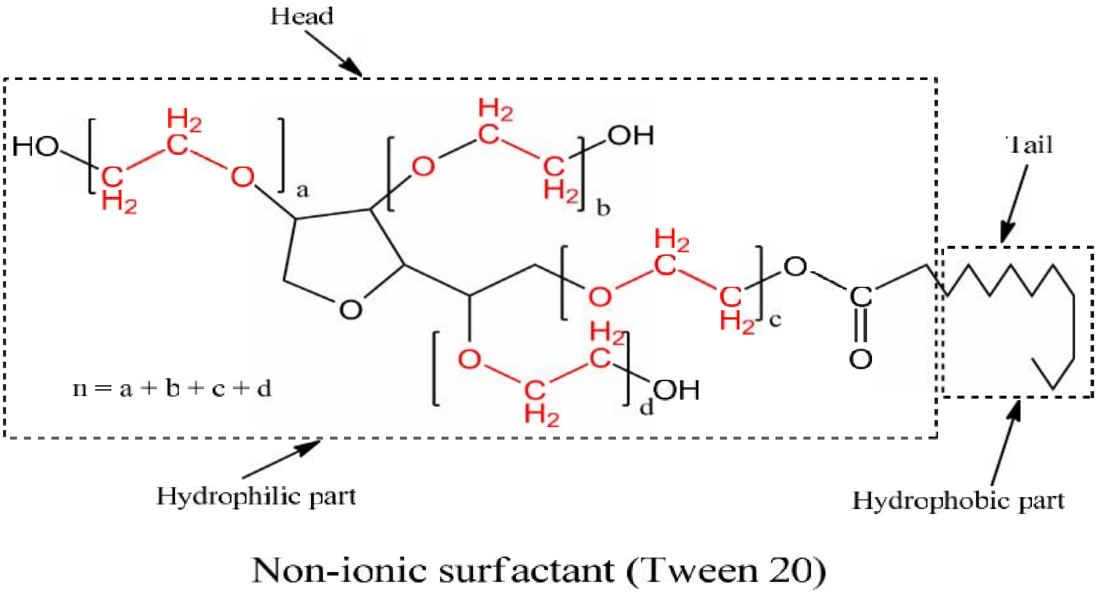


Fig. **6.5** Structure of non-ionic surfactant absence of H-bond formation

From results analysis it has found at lower concentration the reduced viscosity value are high but at CMC point the curve become level off but after increasing concentration the reduced viscosity value increased slowly in all cases but in case of ionic surfactant (SDS, CTAB) the changing is remarkable due to maximum interactions occurred with starch polymer. Here, we mentioned that temperature has a remarkable effect in the complexes of starch-ionic surfactant, here it is obtained according to Arrhenius rule increasing temperature reduced viscosity and specific viscosity is reduced due to the freeness of solution.

From Viscometric analysis The viscosity of the larger scale formation of complexation were measured at 100 rpm was lower than the experimental-scale (13.5 ml starch solution) but not significant difference (P 0.05) with an approximately 1,785.15 ± 13.18 and 1,790.50 ± 12.21cP, respectively. The lower the viscosity, the less was tendency for any further spontaneous reduction with surfactant mixture.

Viscosity is the flow property of a material, or the resistance of the material to flow under a mechanical stress expressed in units of centipoises (cp) Elgun et al. [1998] found that solutions with viscosity of less than 1,000 cp are freely flowing liquids. Between 1,000 and 3,000 cp they have a thick, soup-like consistency, and at higher viscosities, the gruels become progressively thicker suggested by Hsu and Huang [2000] . From the **Tables** 6.1 to 6.5 we are trying to identify the differences among the ionic and non-ionic surfactants in presence of polymeric starch the results show different between the respective two types surfactants. Not only this Triton-X-100 and Tween-20 are the non ionic but SDS and CTAB are ionic. Comparable study Ionic surfactants showed excellent results as reduced viscosities value and specific viscosities values. Here, we have been found that the increasing temperature the values of reduced viscosity and specific viscosity has decreased due to freeness of bonding in the complexes as a inclusion compound in between starch and ionic surfactants but in case of Triton –X-100 and Tween-20 no bond formation is formed due to the absence of dipole in that respective two non ionic surfactants (**Fig**.6.5).

CHAPTER-7: *Surface Properties of Starch, Surfactant and their mixtures by the Physical property of the Ternary Phase.*

7.1 Solubilization
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7.2 Importance of solubilization
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  7.5.1 Representation the Phases
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7.1 Solubilization:

When two compounds that are insoluble or sparingly soluble in water are mixed together they will remain separated into two layers. Adding a small amount of a surface active agent (emulsifier) makes it a suitable structure which may stabilize a state in which one of the liquids is dispersed in small droplets. The droplets have the size of one micron than the two soluble compounds spontaneously form a solution that is clear to eye and is further thermodynamically stable. Mc Bain and Meltan [1948] states that the phenomena of solubilization is the process by which two insoluble or sparingly soluble substances can be made soluble by the addition of a suitable third substance.

7.1.1 The mechanism of solubilization:

The solubilization begins at critical micelle concentration (CMC) which indicates that the solubilization molecules are taken up in way by the micelles. Three modes of solubilization have been proposed for ionic surfactant. These are:-

1. Incorporation in the hydrocarbon center of the micelle;
2. Incorporation in to the polished layer of the micelle;
3. Adsorption on the surface of the micelle

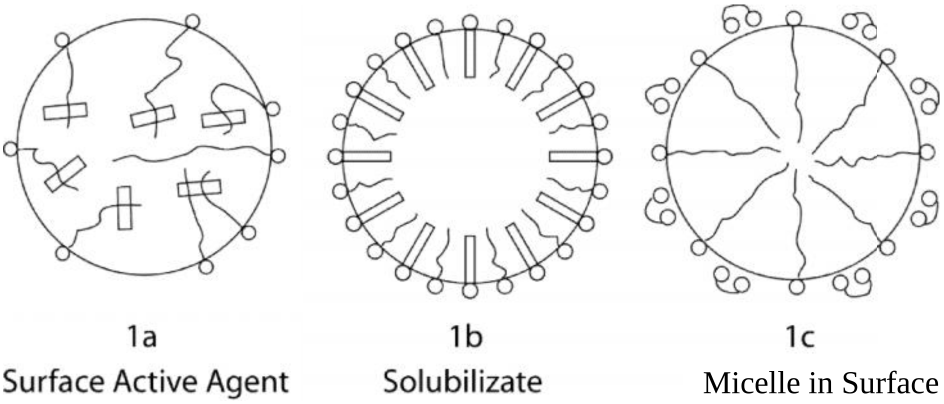

Fig. 7.1 a,b,c Schematic diagram of three modes of solubilization.

7.2 Importance of solubilization

1. Incorporation into the hydrocarbon center

There is direct evidence that the addition of hydrocarbons to a solution involves penetration of these additives into the hydrocarbon centre of the micelles. Where, the hydrocarbon tails of the aggregate molecules serve as the solvent. The X-ray work of Hess and Gunderrnaum [1937] indicated that (from the increase in long X-ray spacing upon the adding of hydrocarbons) the solubilizate enters the hydrocarbon center of the micelles. The long X-ray spacing was supposed to appear from the layer of surfactant bundles plus a portion of the water layer. In this process the rate of solubilization increases with the increasing concentration of surfactant when the solubilization are liquid paraffin’s and benzene etc. but the process is reversed when the solubilization were long chain alcohol’s and amines.

2. Penetration into the palisade layer of the micelle

It is an oriented solubilization process. In this process, the solubilization molecules orient in such a manner that it is aligned with orientation of the soap or surfactant molecules. Orient in such a manner that it is aligned with the orientation of the soap molecules, polar molecule consists of a hydrocarbon chain and a weak hydrophilic group e.g. long chain amines and alcohol's. The hydrocarbon tails in the palisade layer of the micelle and hydrophilic heads producing into the aqueous medium of the micelle periphery. It has been indicated by the characteristic X-ray studies that there is no increase but at times decrease in X-ray spacing and this supports that solubilization to take place in the palisade layer of the soap or surfactant micelle.

c. Adsorption by the micelle:

There are some solubilizate molecules that are insoluble in both hydrocarbon and hydrophilic ends.; these are believed to adsorb in the surface of the micelle e.g. dimethylpthalete, McBain and BcBain [1936] have recently showed that a marked increase in the solubility of dimethylpthalete in soap solution over that in water. They postulate an adsorption on the micelle surface. Riegelman et al. [1958] have examined the spectra of several organic molecules in aqueous solution of ionic and nonionic surfactant. He has compared the spectra with those in water, water in ethanol, acetone and easter. It is observed that the wave length of maximum absorption of organic molecules changes slightly, accompanied by an increased degree of fine structure, as the polarity of the environment is decreased. This fact was utilized to infer the loci of solubilization. Thus solubiliztion was considered to occur at four sites:

1) Inclusion into the hydrocarbon interior of the micelle.
2) Deep penetration into the palisade layer
3. Short penetration into the palisade layer
4) Adsorption on the surface of the micelles.

The absorption spectra of all the solubilization examined were quite similar for anionic, cationic & non- ionic surfactants suggesting similar loci of solubilization for these cases. For non-ionic surfactant containing polyoxyethylene group, another mode of stabilization was found to occur. In this type of surfactant, the micelle contains two parts on inner core of hydrocarbon tails and an outer shell of hydrated polyoxyethylene. The concentration in outer regions of polyoxyethylene groups must be considerably higher than the overall concentration. Organic compounds having a strong affinity to a polyoxyethylene groups may be incorporated into this region as shown below.

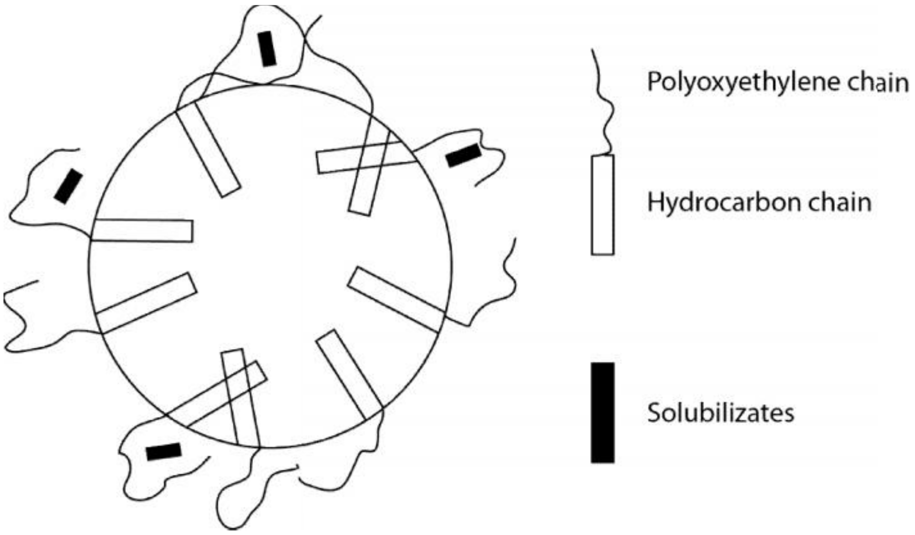

Fig. 7.2 Schematic diagram of another possible mode of solubilization.

This type of solubilization is classified as inclusion into the polyoxyethylene exterior of the micelle rather than as adsorption on the surface of the micelle. From theoretical studies that compounds formed complex with Polyoxyethylene glycol, and combined some way in certain cases by hydrogen bonding.

Early investigators Fontell, K. et al. [1985] postulated that non-polar solubilization could be interposed between the ends of hydrocarbon tails of the surfactant molecules which are arranged in the lamellar micelle. Figure under below:-

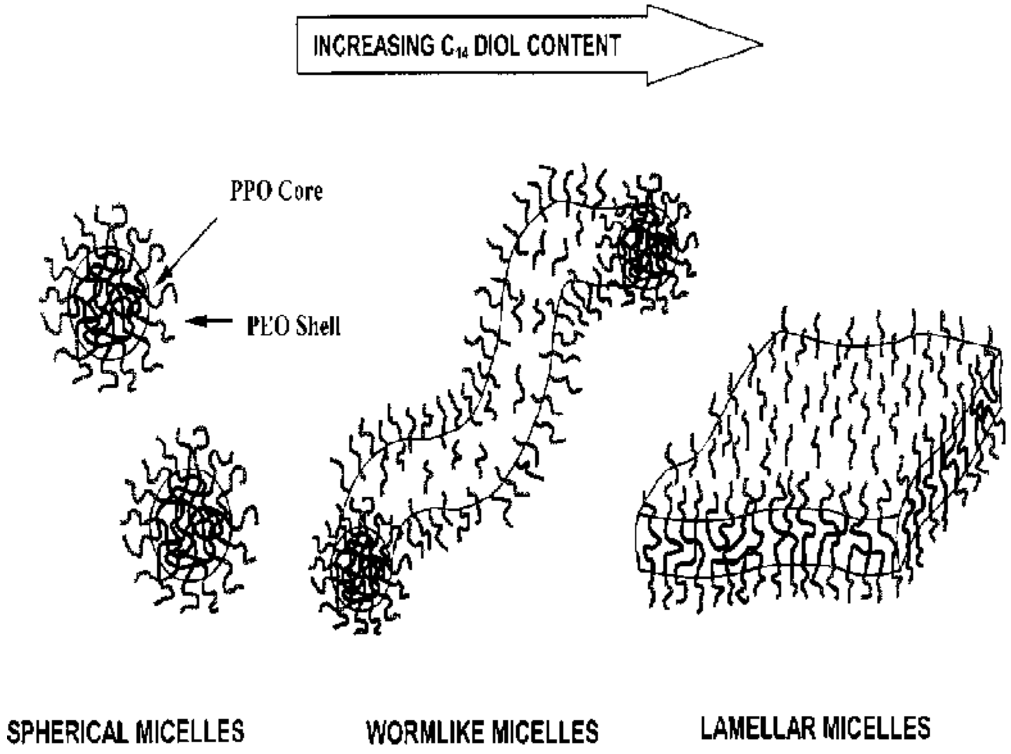

Fig. 7.3 Schematic diagram of spherical, wormlike and lamellar micelle

3. Temperature dependence of solubilization:

When a solution containing non-ionic surfactant is heated gradually, it shows turbidity at a certain state of temperature which is called the cloud point. After further heating the solution becomes separated into two phases; one is enriched in surfactant concentration whereas the other one is depleted. The presence of solutilization and its effect on both cloud point and the phase separation temperature due to appropriate crystalline phase has formed. The sign (increases or decreases) and magnitude of which depends on are amounts of solubilizate and the species. Thus, in some cases a progressive addition of solubilizate causes clouding and before reaching phase separation, the limit of solulibization is in the usual meaning. In such cases, the phase is separated from the solution containing a mixture of water, solubilizate and especially rich in surfactant. When solulibization limit is overcome almost pure solubilizate is separated out.

It is experimentally shown in **Fig.7.5** and **5.4** that (by diffusion viscosity, by light scattering [Cotton, J. P. (1991)], ultra centrifugal) the micellar weight of a polyoxyethylene type of nonionic surfactant is increased by the elevation of temperature. As the cloud point is approached the micellar weight will become more and larger. Finally, it comes to a point where the micelle becomes so large that it will be noticeable even to the naked eye. Further, growth will cause the separation of a surfactant rich phase. This interpretation says that the cloud point is accompanied by the formation of giant molecules. After the phase separation has been completed, the concentration of the surfactant is low in the co-existing water rich phase because there are no or few micelles present. It is believed that the hydration of other oxygen of the polyoxyethelene group is, generally to be the main factor in keeping the non-ionic surfactant in solution. Then increase in temperature causes partial dehydration and finally results in the separation of the surfactant rich phase. Non-ionic having a longer polyoxyethelene groups which shown in **Fig.7.5**, a higher cloud point by virtue of a greater capacity to hydrate. But recent investigations Murata, M. and Arai, H. [973] have thrown a doubt on the idea that the increase in temperature decreases in hydration. The discrepancy (at least partially) is due to the different definition of hydration. The water hydration bond to ether oxygen's will decrease with rising temperature, whereas the water trapped in polyoxyethylene mesh may increase. The cloud point is influenced by the presence of certain additive but in sensitive to the surfactant concentration certain substances do not depress the cloud point, on the other hand some other depress, which is due to the different mode of incorporation of the stabilization, as seen in the following figure electrolytes suppress.

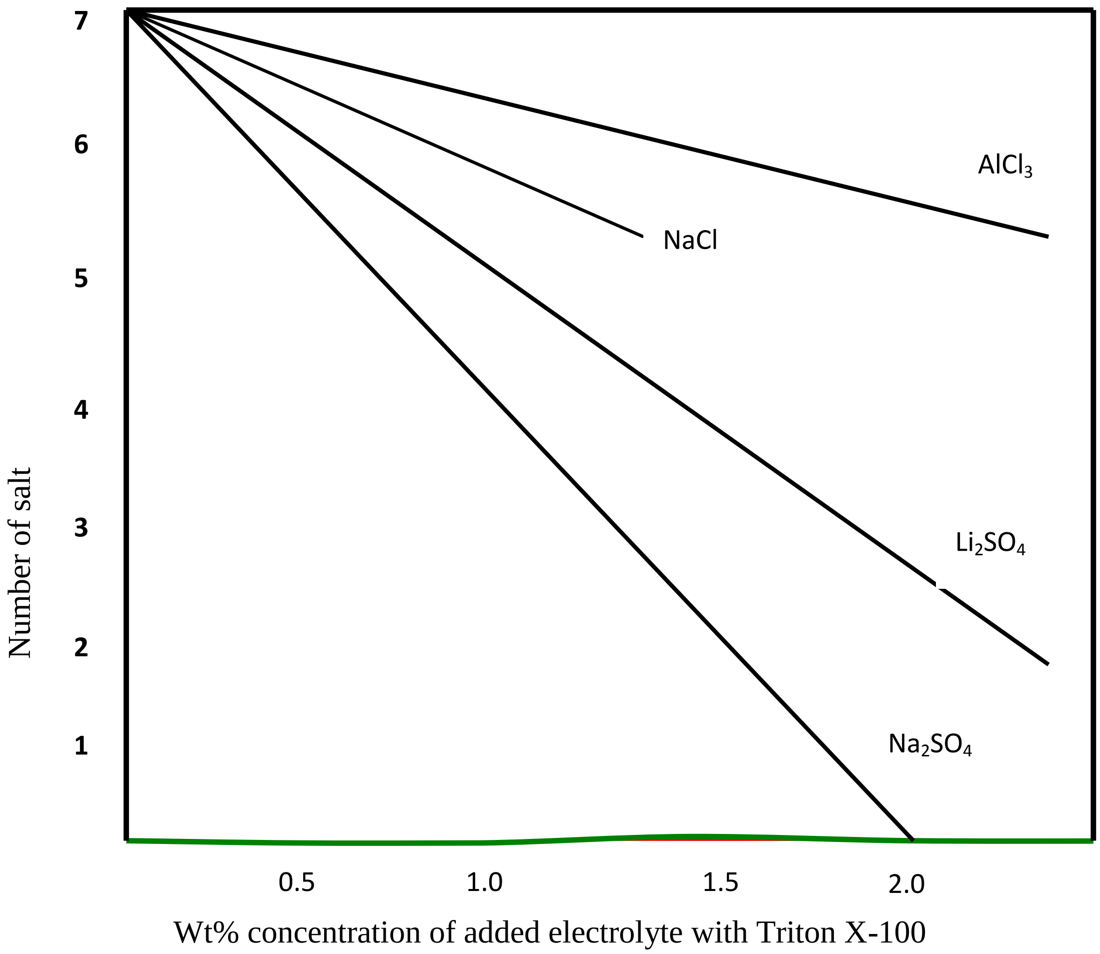

Fig. **7.4** Effect of added electrolytes on the cloud point of 2% triton X- 100 solution

The cloud point which is proportional to their concentrations. An electrolytes lower lyotropic number depresses the cloud point remarkably; There are again two cloud points for the commercial or impure surfactants due to extra additives addition.

4. Solubilization in concentrated solution

In a concentrated solution the solubilization phenomenon is some what different from that of dilute system. The solution can no longer be considered as system in which globular micelles having liquid like inner structure and monomolecular dispersed surfactant molecules are randomly distributed in an aqueous medium.

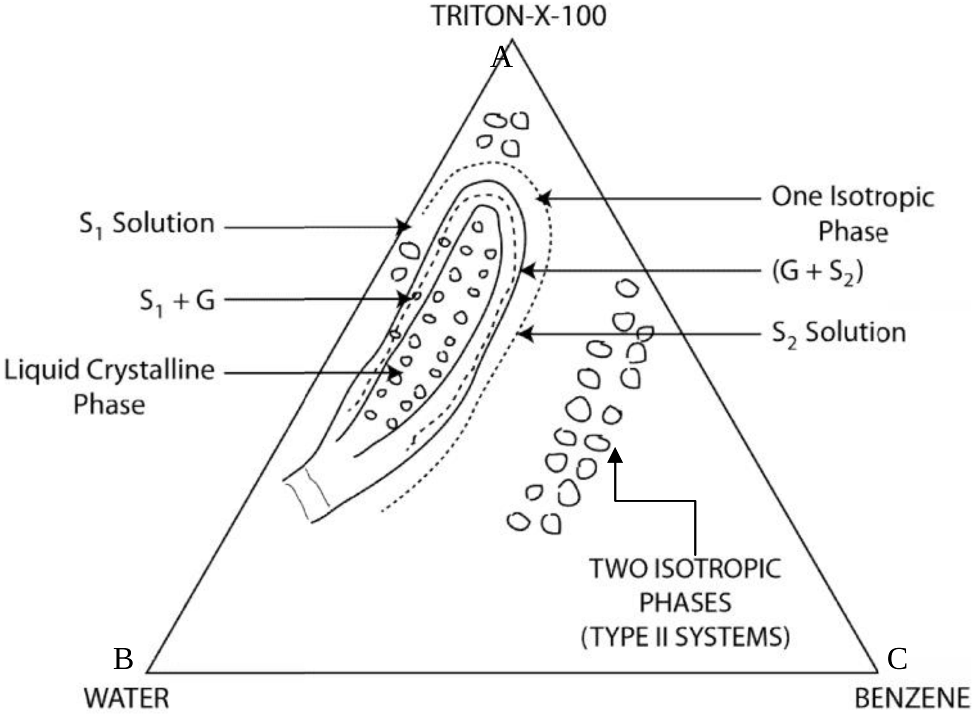

Fig. **7.5** Phase diagram of the Triton X-100(poplyoxyethlene isooctylphenol) /Benzene /water system.

On adding progressively more benzene to a suitable (e.g. 50 percent aqueous medium of Triton X-100 one phases through the phase sequence. From fig.7.5 it had been seen that:-Isotropic solution (S_1) → (S_1+G) → liquid crystalline solution (G) → (G+S_2_ → isotropic solution (S_2) → two isotropic solution (S_2+aqueous phase.) Sample in the liquid crystal phase are generally quite viscous, highly birefringence and beautifully colored on examination in a polarizing microscope. They give long spacing in X-ray patterns which are indicating of a high degree of orientation. These findings suggest the presence of a lamellar structure for this phase. By following a different route ACB, one may pass continuously from S_1 to S_2 always through the isotropic region. For simple understanding of the phenomenon lyophilic, let us consider a ternary mixture composed of water of substance and an amphiphilic compound. The amphiphilic compounds serve as a monolayer between the aqueous and the organic environments. The convenes of monolayer towards either aqueous or organic phase give O/W or W/O type structure.

Increasing the amount of benzene to an aqueous solution of Triton X-100 the system will pass from S_1 throughout G to S_2. The liquid crystalline state G is, however, not always encountered. In absence of liquid crystalline state between O/W and W/O structure, the stability of the planar amphiphilic monolayer or the existence of an extended lamellar structure depends upon the composition and temperature of the system. This is illustrated by Fig.7.5. The above explanation predict the solubilization phenomenon qualitatively. Because it is not formulated. Fig.7.5 Schematic illustration of the mean foam of the C region in isotropic (S_1 and S_2) and anisotropic (G) in terms of numerically measurable quantities having clearly defined physical meaning by the theory of temperature effect can be clearly explained from the mentioned ternary phases at different area at different type of phases due their individual properties.

7.3 Materials

7.3.1 Instruments

1. An equilateral triangular wooden frame consisting of 228 holes.
2. Electrical microbalance
3. Test tubes with rubber corks
4. Thermostat box
5. A polarizing microscopes
6. Other relevant such as micro pipettes reagent bottles, desicator glass, beakers, measuring flask, cylinder, glass rods, spatula etc.

7.3.2 Chemicals

Cationic Surfactants

Cetye trimethyl Ammonium bromide (CTAB)
(N – Cetyl- N,N,N – trim ethylAmmonium bromrde)
A product of BDH Chemicals Ltd.

Anionic Suractants

Sodium dodecyl sulphate (SDS)

(Dodecyl hydrogen sulfate sodium salt)

A product of BDH Chemicals Ltd.

It was used without further purification.

Nonionic Surfactants

Triton X-100, (polyoxyethylne iooctylphenol) A product of E. Merck
Brij – 30, A product of E. Merck.
Tween -20 A product of E. Merck,

7.4. Experimental Methods

7.4.1 Sample Preparation

For the development of ternary phase diagrams, the sample components were taken into the test tube by varying composition in such a way that the total composition remains 100%. The components were added by varying weight or volumes. The samples were prepared by varying 5% composition of two components simultaneously keeping the third component constant, alternatively in a test tube. The open end of the test tube was then closed with rubber cork in such a way that the vapour would come out and would enter into the test tube, here the cork reacted with the sample. The samples were then shaken for well mixing of the components and placed into the diagram are put according to the composition and mark. After completion of the 228 samples according to the diagram on the wooden frame. The open end of the test tube was then closed tightly with cork, so that this would remain no leakage or the lower part of the cork did not touch the sample solution and after that these samples were then left to equilibrate in a thermostat box at 30°C for at least ten days and would be shaken from time to time. The equilibrium was established within this period.

7.4.2 Graphical representation of the three components (Ternary) System:

For system of three components, it is possible to have four degrees of freedom since temperature, pressure and the concentrations of two components may be independently variable. In order to simplify the graphical representation of the conditions of equilibrium for three components, the procedure usually adopted was to consider a condensed system that was the vapor but was ignored, this reduced the number of degrees of freedom to three and hence a three dimensional model can be used to represent the compositions of a system of three independent components. For this purpose, it is the common practice to use a diagram consisting of an equilateral triangle. The property which was utilized the sum of the distances from any point within this triangle drawn perpendicular to the three sides is always equal to the height of the triangle. By taking this length as unity and the amounts of the three components of a given system are expressed as fraction of the whole. It is possible to represent the composition of any system by a point in the diagram. To facilitate the plotting of the points corresponding to various compositions on the triangular diagram, the height is divided into twenty equal parts and a series of line are drawn parallel to the three sides, thus has predicted a net work of small equilateral trainees within the larger one. Special graph paper, based on these principles can be purchased for use by plotting the experimental results for three component system.

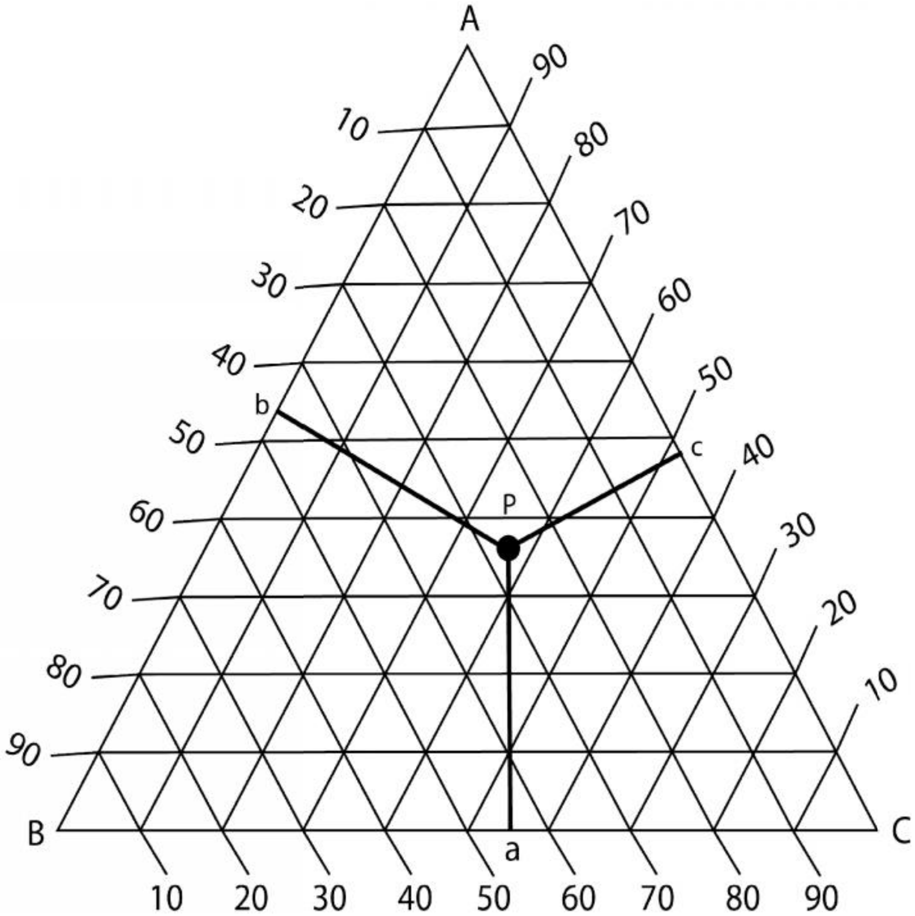

Fig. **7.6** Schematic Triangular diagram for three component system.

From Fig.7.6 the corners A, B and C of the triangle represent the pure components of A (Water), B (Surfactant) and C (Starch) respectively. The perpendicular distance from a point P to any sides gives the proportion of the component occupying the opposite corner. Thus, the distances Pa, Pb and Pc give the fractional amounts of A, B and C respectively. In the system represented by the point P, where the compositions are seen to be 0.3A, 0.4B and 0.3C in weight fractions multiplied by 100, become weight percent respectively. It is perpendicular distance from AB, BC and CA. Any point of the line AB, BC and CA represents two components, where the third one is zero, but a point within the triangle indicates a system of three components.

7.5. Identification of the samples:

The physical states of the samples were determined by the polarizing microscope.

The phases of the samples were then plotted into a triangular graph paper against composition in weight percent phase boundaries and thus a ternary phase diagram was developed.

7.5.1 Representation of the phases:

In ternary phase diagram the significance of the symbols used to explain the ternary phase as above mentioned as follows:-

1L =The one liquid phase. This is a completely miscible solution of two or three components.

2L=The two liquid phase. Two liquids remain side by side, i.e. two immiscible liquid form two distinct layers.

L_1 & L_2 = The liquid one and the liquid two phases. If the system forms two isotropic solutions it is noted as L_1 and L_2 the two solutions. The L_1 phase is rich in water and the L_2 phase is rich in third components (Surfactant). L_1 phase contains the normal micelle and the L_2 phase is the reversed micelle.

LC= The liquid crystal phase, which possesses a transparent viscous region. The LC phase is highly birefringence and beautifully colored on examination under a polarizing microscope, this is called optical birefringence.

In a ternary system, water, amphilic monolayer and surfactants tend to orient in a parallel and repeated manner resulting in a liquid crystalline structure.

S + L = The solid + Liquid phase. In this phase the solid and liquid remain side by side without much of interaction.

S+ LC = The solid + Liquid crystal phase.

L+C = The liquid + Crystal phase.

E = The emulsion phase.

S = The solid phase.

7.6 Results and Discussion

From the various ternary phase diagrams such as anionic, cationic and non-ionic surfactants were used to do the phase preparation in present research. As three component system (water, surfactant and polymer) phases were identified by the polarizing microscope and scanning electron microscope. the following mentioned ternary phase diagram have been done for better understanding the chemical reactions and H- bonding through surfactant-polymer(starch) complexes. This was confirmed by the FT-IR spectroscopy.

7.6.1 Phase diagrams with Starch/Water/SDS:

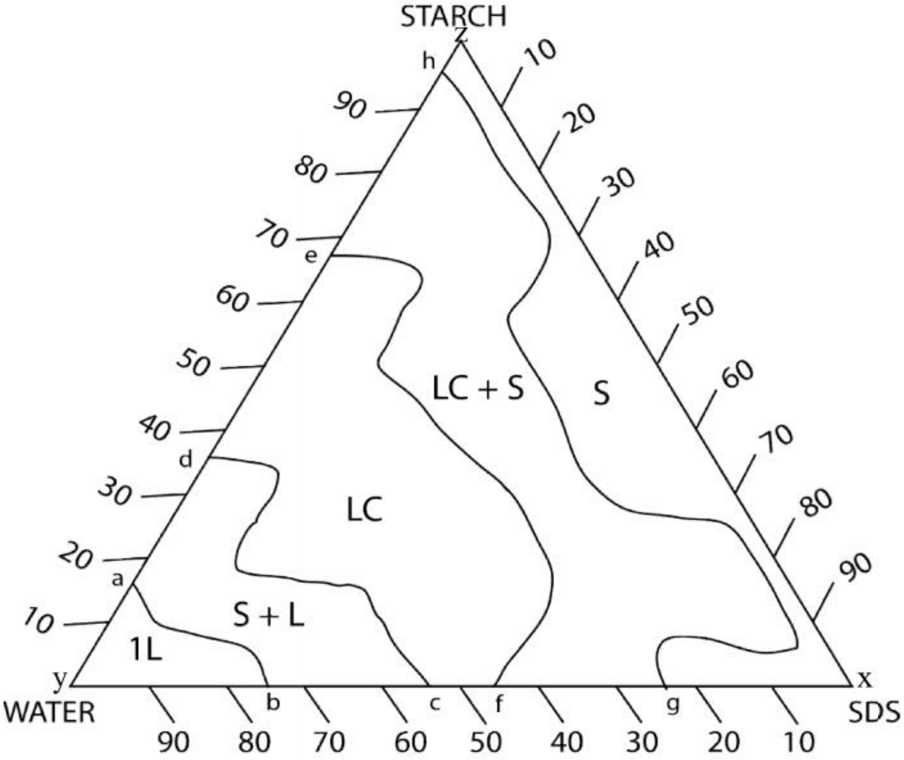

Fig. 7.7 Starch-anionic surfactant (SDS) -H_2O as the ternary phase system diagram

From this figure, it has been seen five distinct phases and they are 1L, S+L, LC, LC+S and S. The clear explanation has been given below:-

1. The one liquid phase (1L) has shown in the area ayb. This phase indicates 17% of starch is solubilized in starch/water boundary line. The boundary line of water / SDS shows that 25% of SDS has solubilized in the 1L phase.
2. The solid + liquid phase (S+L) is denoted by abcd. The S+L phase formed is relatively small.
3. The most important and interesting liquid crystal phase (LC) is denoted by the region cdef. In the LC phase 35 to 36% of starch is solubilized in the water /starch

boundary line and less than 9 to 10% SDS is solubilized in this phase.

4. The remaining big region denoted by efgh is the liquid crystal and solid phase. In this phase, water / SDS boundary line shows to 54 to 55% SDS and starch / water boundary line shows 65 to 95% starch is solubilized in this phase.

5. The remaining region gxzh is the solid phase, S which is unreacted area.

7.6.2 Phase Diagrams with Starch/Water/CTAB

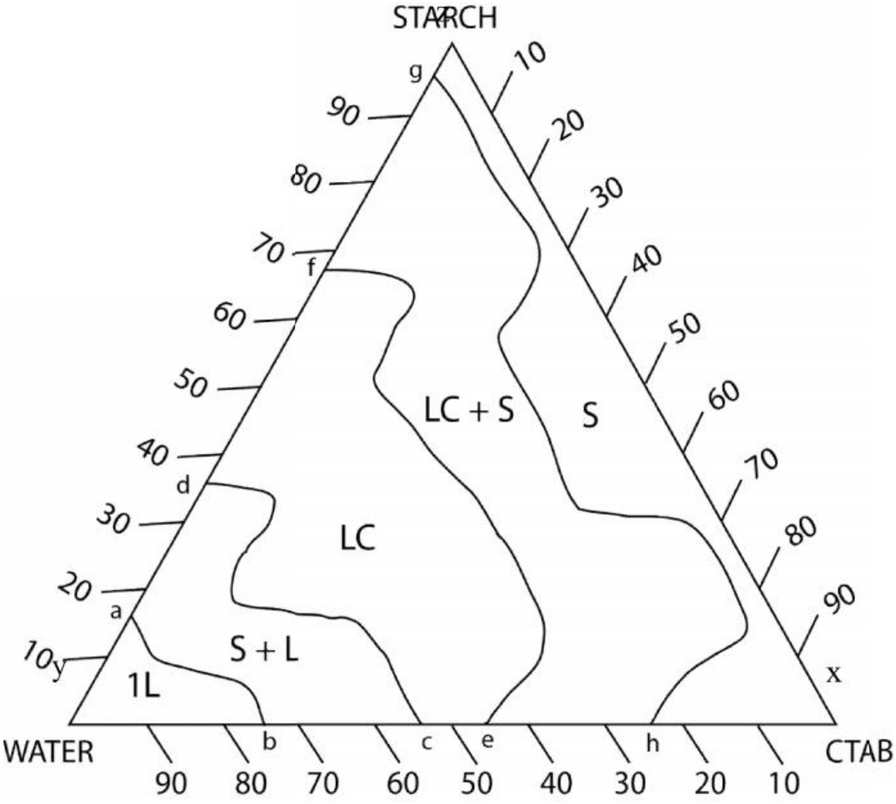

Fig. **7.8** Starch-cationic surfactant (CTAB) -H_2O as the ternary phase system

From the figure, it has been seen five distinct phases and they are 1L, S+L, LC, LC+S and S

1. The one liquid phase is shown in the area ayb. This phase indicates 15% starch is solubilized in water / starch boundary line. The boundary line of CTAB / water indicates 25% of CTAB solubilized in this phase.

2. The Solid + liquid phases are described by the area abcd. In the S+L phase water/CTAB boundary line, CTAB is 55 to 75% solubilized and starch is 25 to 65% solubilized in this phase.

3. The most important and interesting liquid crystal phase (LC) is denoted by the region dcef. in the LC phase. 45 to 55% of CTAB is solubilized on the water/CTAB boundary line and also starch is 35 to 65% solubilized on the water/starch boundary line.
4. LC+S phase: In this phase is shown in the area efgh. It is the big region and CTAB is 25 to 45% solubilized in the water/CTAB boundary line and starch is 65 to 95% solubilized on the water/starch boundary line.
5. In the corners of starch and CTAB the Solid phase is formed. The region of this phase is ghxz. S, The solid phase waists toward CTAB and starch corner but this area is most inactive where no interactions occur.

7.6.3 **Phase Diagrams with Starch/Water/Brij-30**

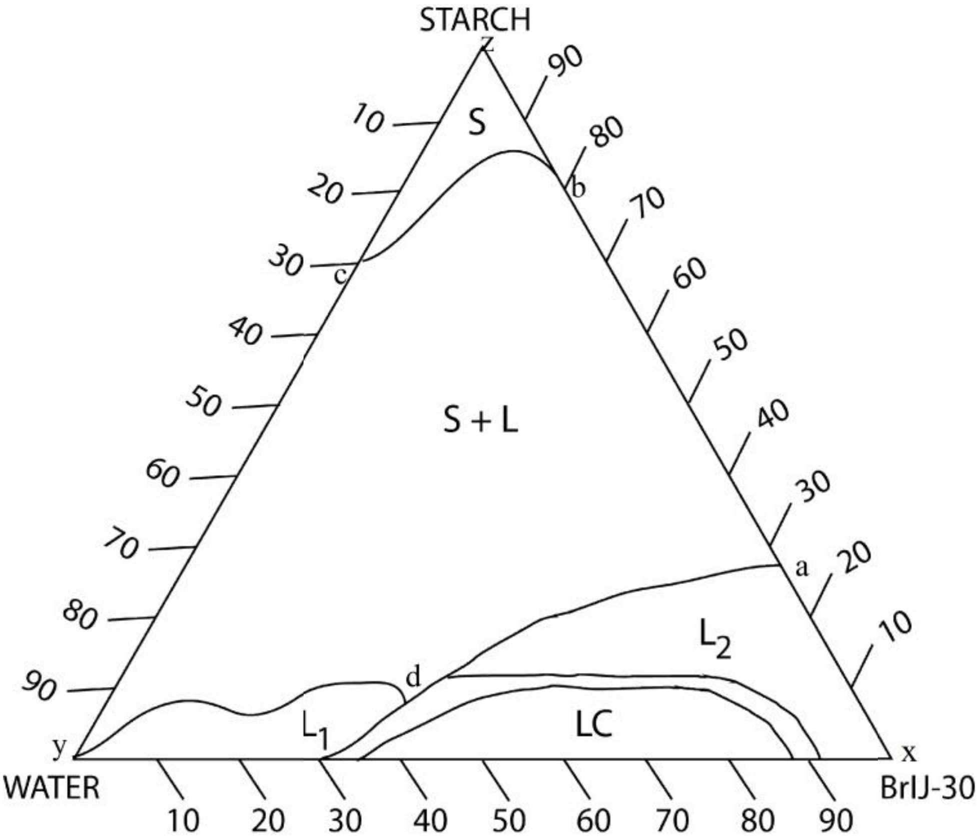

Fig. **7.9** Starch-Brij-30(nonionic)-H_2O as the ternary phase system diagram

From the **Fig**.7.9 shows five distinct phases and they are L_1 LC, L_2 S+L and S. Now the clear explanations are given below in details:-

1. The boundary line of binary components of water/Brij-30 shows the L_1, LC and L_2 phases. In this line 30% Brij-30 forms the 1L phase and from 32 to 88% Brij-30 forms LC phase and then the L_2 phase is formed the region is adx.

2. In the 1L phase 7% of starch is solubilized. In the LC phase the maximum solubilization of Brij -30 is 65%, the corresponding composition of 12% of starch.

3. In the L_2 phase maximum of 26% of starch is solubilized. Above these three phases a big region of S+L phase is observed. Here it is notify that as nonionic surfactant Brij-30 is liquid substance, so its physical appearance intensifies to form liquid phase. Here, it has been seen from this ternary phase an exceptional region abcy as large areas are unreacted due to non bonding starch-Brij-30 complexes.

4. In the S+L phases is described by the area ydabc, the S+L phase water/starch boundary line, starch is 75 to 80% solubilized and Brij-30 is 25 to 65% solubilized in this phase.

5. In the corner of starch the Solid phase is formed. The region of this phase is zbc S, The solid phase waists towards starch corner. This phase is only 10 to 15%

7.6.4 Phase Diagrams with Starch/Water/Tween-20

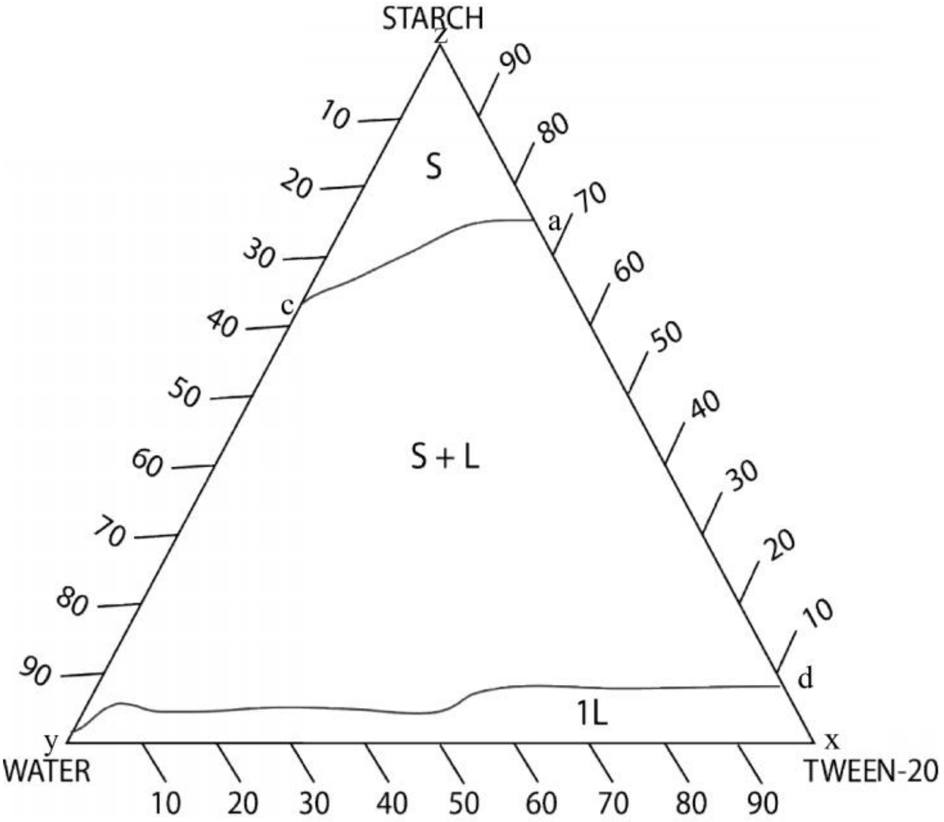

Fig. 7.10 Starch-nonionic surfactant -H_2O as the Ternary Phase system

Fig. 7. 10 shows three distinct phases and there are:- 1L, S+L and S

(1) In the 1L phase 7.5% starch is solubilized.

(2) Above the 1L phase a large region ydac of S+L phase is formed. In the S+L phase the maximum of starch is 75%

(3) In the region azc is the small area where only solid phase, S is found. The phase area is minimum. Though Tween-20 is liquid sustenance, its interaction is different from other ionic (CTAB, SDS) surfactant with natural polymeric starch. In this ternary phase there is no crystalline phase due the non ionic surfactant of Tween-20**.** In this phase there is no change in the region ydx, here any type of chemical reaction did not occur due to non-ionic surfactant of Tween-20. From **Fig.**7.10 it have been seen that as a non ionic surfactant of Tween-20 any chemical reactions, H-bond formations, crystalinity did not form which support Tween -20 have no effect on starch like polymer for better interactions.

7.6.5 Phase Diagrams with Starch/Water/Triton X-100

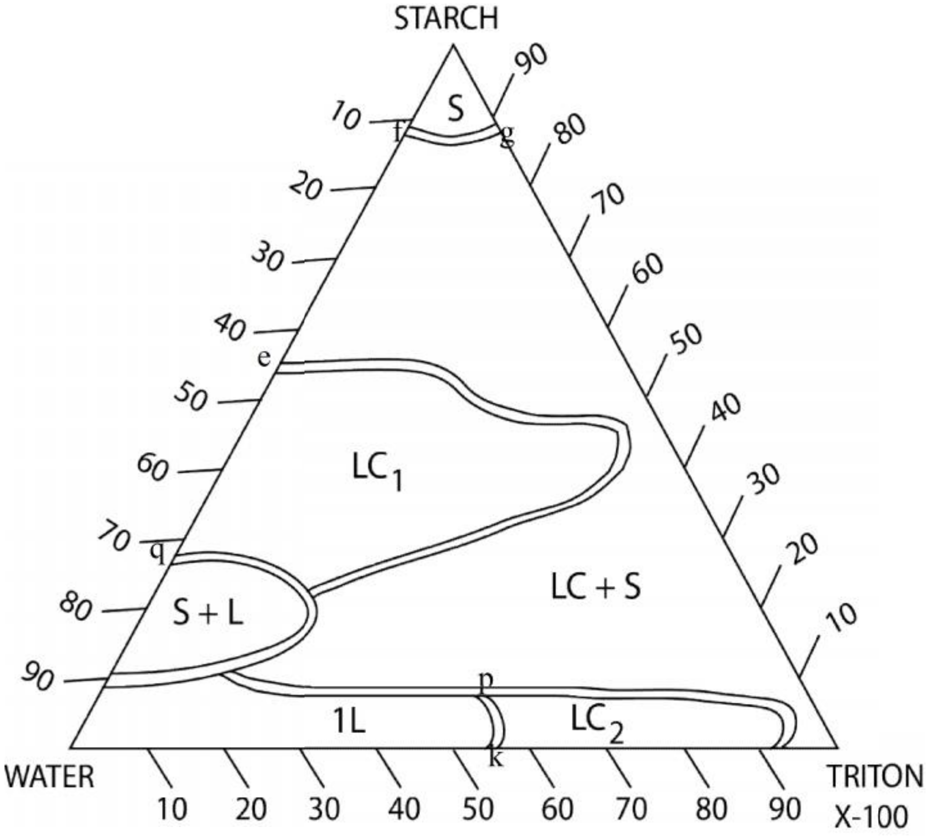

Fig. **7.11** Starch-Triton-X-100 -H_2O as the Ternary Phase system

From **Fig**.7.11 has been observed six distinct phases and there are:-1L, LC_1, S+L, LC+S, LC_2 and S. Among the all six Ternary phases, this phase diagram has showed maximum phases.

1. The boundary line of binary components of water/Triton-X-100 show the 1L and LC_1 phases. In this line 55% Triton-X-100 forms the 1L phase and from 40 to 45%Triton-X-100 forms LC_2 phase formed the region is pkb.

2. In the S+L phase 20% of starch is solubilized. In the S+L phase the minimum solubilization of Triton-X-100 is 15% the corresponding composition of 20% of starch.

3. In the LC_1 phase maximum of 30% of starch is solubilized. Above these three phases a big region of LC+S phase is observed. In the big region LC+S phase is fedcbxg.

4. In the LC_2 liquid crystalline phase is described by the area bkp. In the LC_2 phase water/ Triton-X-100 boundary line, starch is only 10% solubilized and Triton-X-100 is 25 to 35% solubilized in this phase.

5. A big region of LC+S phase is observed, which is most interaction region in between starch-Triton-X-100 and water system.

6. In the corner of starch the Solid phase is formed. The region of this phase is zfg S, the solid phase waists towards starch corner. This phase is only 10 to 12%

Now, from experimental analysis the overall discussion in starch-surfactant-water as a ternary phase, it has been seen from polarizing microscope and scanning electron microscopy, It has been found in **Fig.** 7.7 -7.11 illustrates the phase diagram for this ternary system at the temperature of 30^{o}C. In this diagram the notation is L_1, aqueous micellar solution ; L_2 , micro emulsion ; 2L, two liquid phase or emulsion; LC, liquid crystalline phase; L+LC, liquid crystal in equilibrium with solution; LC+S, liquid crystal in equilibrium with crystal; With these samples of various phase regions having various chemical compositions, the flow properties were measured by Oswald viscometer. With others corresponding samples the surface tensions were measured by Stalagmometer at 30^{o}C. The region L_1 is not broad in this system owing to the small solubility of the ionic surfactant (CTAB & SDS) in water. The region L_2 is visually homogeneous but if we observe through polarizing microscope it will be seen as heterogeneous are called micro emulsion. Different phases are identified by SEM analysis.

CHAPTER-8:*Structural analysis by FT-IR Spectroscopy*

Chapter-8 Structural analysis by FT-IR spectroscopy

8.1 Introduction:

The Infrared spectra of starch and related compounds have been studied for a long time by a number of authors Rowen and co-worker Rowen et al. [1947] and Forziati et al. [1987] studied the infrared spectra in the detection of chemical changes in starch and some other starch-surfactant derivatives and investigated the effect of Hydrogen bonding and change in crystalline structure on the infrared spectrum of starch. Starch-surfactants complex interactions of H- atom of starch within the surfactant molecule by the H-bonding process are now subject to IR absorption of the functional groups which may vary over a wide range. However, it has been found that many functional groups give characteristic IR absorption at specific, narrow frequency ranges regardless of their relationship with the rest of the molecule. Generalized Table 8.1 of the positions and relative intensities of absorption bands (Fig.8.1, 8.2 & 8.3) have been established and used to determine the functional groups present or absent in a molecule. The CRC Handbook of Chemistry and Physics Lide [1994] and Silverstein et.al. [1981]'s book and a number of other publications all contain useful correlation charts. Multiple functional groups may absorb at one particular frequency range, but a functional group often gives rise to multiple-characteristic absorption. Thus, the spectral interpretations should not be confined to one or two bands and the whole spectrum should be examined. To confirm or better elucidate the structure of an unknown substance, other analytical information provided by nuclear magnetic resonance (NMR), mass spectrometry (MS), or other chemical analysis should also be used where possible. For systematic evaluation, the IR spectrum is commonly divided into three regions:-

I. The Functional Group Region, 4000 to 1300 cm^{-1}, where the appearance of strong absorption bands in the region of 4000 to 2500 cm^{-1} usually comes from stretching vibrations between hydrogen and some other atoms with a mass of 19 or less.

II. The O-H and N-H stretching frequencies fall in the 3700 to 2500 cm^{-1} region, with various intensities. Hydrogen bonding has a significant influence on the peak shape and intensity, generally causing peak broadening and shifts in absorption to lower frequencies. The C- H stretching bands occur in the region of 3300 to 2800 cm^{-1}. The acetylene C-H exhibits strong absorption at about 3300 cm^{-1}. Alkene and aromatic C-H stretch vibrations absorb at 3100 to 3000 cm^{-1} Most aliphatic (saturated) C-H stretching bands occur at 3000 to 2850 cm^{-1}, with generally prominent intensities that are proportional to the number of C-H bonds. Aldehyde often show two sharp aldehydic C-H stretching absorption bands at 2900 to 2700 cm^{-1}.The absorption bands at the 2700 to 1850 cm^{-1} region usually come only from triple bonds and other limited types of functional groups, such as C triple bond C at 2260 to 2100 cm^{-1}, C triple bond N at 2260 to 2220 cm^{-1}, diazonium salts $-N^{+}$ triple bond N at approximately 2260 cm^{-1}. The 1950 to 1450 cm^{-1} region exhibits IR absorption from a wide variety of double-bonded functional groups.

III. Almost all the carbonyl C=O stretching bands are strong and occur at 1870 to 1550 cm^{-1}. Acid chlorides and acid anhydrides give rise to IR bands at 1850 to 1750 cm^{-1}. Whereas ketones, aldehydes, carboxylic acids, amides and esters generally show IR absorption at 1750 to 1650 cm^{-1}, carboxylate ions usually display stretching bands at 1610 to 1550 and 1420 to 1300 cm^{-1}. Conjugation, ring size, hydrogen bonding, and steric and electronic effects often result in significant shifts in absorption frequencies. Aromatic compounds contain delocalized electrons from the resonance-stabilized double bonds, showing skeletal vibrations (including C-C stretching's within the ring) in the 1650 to 1400 cm^{-1} region and weak combination and overtone bands in the 2000 to 1650 cm^{-1} region. Valuable information about the substitution pattern on an aromatic ring can be obtained by careful examination of absorption bands in these two regions. Molecules containing NO_2 groups, such as nitro compounds, nitrates, and nitramines, commonly exhibit asymmetric and symmetric stretching vibrations of the NO_2 group at 1660 to 1500 and 1390 to 1260 cm^{-1} region.

The fingerprint Region, 1300 to 910 cm^{-1} Absorptions in this region include the contributions from complex interacting vibrations, giving rise to the generally unique fingerprint for each compound. A good match between the IR spectra of two compounds in all frequency ranges, particularly in the fingerprint region, strongly indicates that they have the same molecular structures. Detailed interpretation of IR bands in this region is difficult.

However, some assignments of bands in the fingerprint region to a few important vibrational frequencies of functional groups can be done when IR absorptions in other regions are correlated together. For example, esters not only show their carbonyl C=O stretch at 1750 to 1735 cm^{-1}, but also exhibit their characteristic absorption at 1300 to 1000 cm^{-1} from the couplings of C-O and C-C stretches. The Aromatic Region, 910 to 650 cm^{-1} The IR bands in this region does not necessarily come from the aromatic compounds,

but the absence of strong absorption in the 910 to 650 cm^{-1} region usually indicates the lack of aromatic characters. The out-of-plane bending of ring C-H bonds of aromatic and hetero aromatic compounds gives rise to strong IR bands in the range between 910 and 650 cm^{-1}. As previously studied, certain non-aromatic molecules such as amines and amide salt of soap or surfactant can also contribute absorption in this region. From above band spectrum starch ,surfactant alone but mixture specially, ionic surfactant (SDS, CTAB) formed with starch molecule by the Intra or Inter molecular H-bond in between them .However ,the purpose of the present study is to attempt to evaluate the real mechanism of starch-surfactant bond formation through FT-IR analysis and as well as the structure of the complexes.

8.2 Experimental:

8.2.1 Materials

Powder sample of starch, Powder samples of CTAB, SDS and Tween-20 and Powder samples of starch mixed CTAB, SDS and Tween-20

8.3 Preparation of the various samples of starch, surfactant and mixture for FT-IR

Preparation of Starch for IR

Potato starch from Loba Chemical, India near about 2g is taken by electric balance and then dried in an electric oven at a temperature of about 105^{o}C for half an hour then kept in a deciccator. Samples should therefore be ground in a mortar to reduce the average particle size to 10 to 20 µm. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate, With a gentle circular and back-and-forth rubbing motion of the two windows, evenly distribute the mixture between the plates. The mixture should appear slightly translucent, with no bubbles, when properly prepared. Later this white powdery substance was used for IR spectrum study. Infrared spectrum of the precipitated salt was taken suspending it in Nujol and in KBr optics with SHIMADZU IR-470 infra-red spectrophotometer.

Preparation of Surfactant (CTAB, SDS and Tween-20) for individual IR

Cetyltrimethylammonium bromide (CTAB) as a cationic surfactant crystalline sample from Loba Chemical, India near about 2g is taken by weighting with a electric balance and then dried in an electric oven at a temperature of about 105^{o}C for half an hour then kept in a deciccator. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate Later this white fine powder substance was used for IR spectrum study. Infrared spectrum of the precipitated salt was taken suspending it in Nujol and in KBr optics with SHIMADZU IR-470 infra-red spectrophotometer.

Sodium dodecyl Sulphate (SDS) as a anionic surfactant which is also crystalline particle sample fram Loba Chemical, India near about 2g is taken by weighting with a electric balance and then dried in a micro oven at a temperature of about 105^{o}C for half an hour then kept in a deciccator. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate Later this white fine powder substance was used for IR spectrum study. Infrared spectrum of the precipitated salt was taken suspending it in Nujol and in KBr optics with SHIMADZU IR-470 infra-red spectrophotometer.

Tween-20 is a non-Ionic Surfactant made by BDS which is high viscous liquid solution near about 10ml sample was taken into glass tray and mixed with KBr then dried in an electric oven at a temperature of about 105^{o}C for two hours then kept in a deciccator. After proper dried the mixture then Samples should therefore be ground in a mortar to reduce the average particle size to 1o to 20 µm. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate Later this white fine powder substance was used for IR spectrum study. Infrared spectrum of the precipitated salt was taken suspending it in Nujol and in KBr optics with SHIMADZU IR-470 infra-red spectrophotometer.

For mixture at the same ratio of starch and surfactant individual (CTAB, SDS and Tween-20) are prepared for IR .In the presence of starch, same ratio of individual surfactant mixed with the starch and dried by the electric oven at a temperature of about 105^{o}C for two hours then kept in a deciccator. After proper dried the mixture then Samples should therefore be ground in a mortar to reduce the average particle size to 10 to 20 µm. About 5 to 10 mg of finely ground sample are then placed onto the face of a KBr plate Later this white fine powder substance was used for IR spectrum study .Much care was taken to make the uniform surface of the mixture and the thickness of the dried sample was controlled to 10 to 20 µm. Otherwise its spectra were not so good to analyse.

8.4 IR Spectra Measurements:

An IR spectrum of dried sample was obtained with SHIMADZU IR-470 infra-red spectrophotometer. After drying the sample with KBr plate at room temperature, it was again at 60^{o}C for 1h under reduced pressure and then its individual IR spectra were measured. In case of sample crystalline (Tween-20) IR spectra was measured on the Teflone plate at controlled temperature and pressure.

8.5 Determination of H-bond through starch–surfactant interaction

For determination of H-bonding starch molecule with only ionic surfactant by the FTIR band analysis suggested by Mann and Marrinan [1977] based on the observed polarization and the effect of surfactant on starch molecule by the way of counter ion condensation through H-bond formation indicating identification band 3600cm^{-1}. clearly proved the Intra- molecular H-bonding in between starch and CTAB surfactant. the structure is shown **Fig**.8.1 The IR spectra of starch, surfactant and starch-surfactants are shown in **Fig**. 8.2, 8.3 and 8.4 respectively

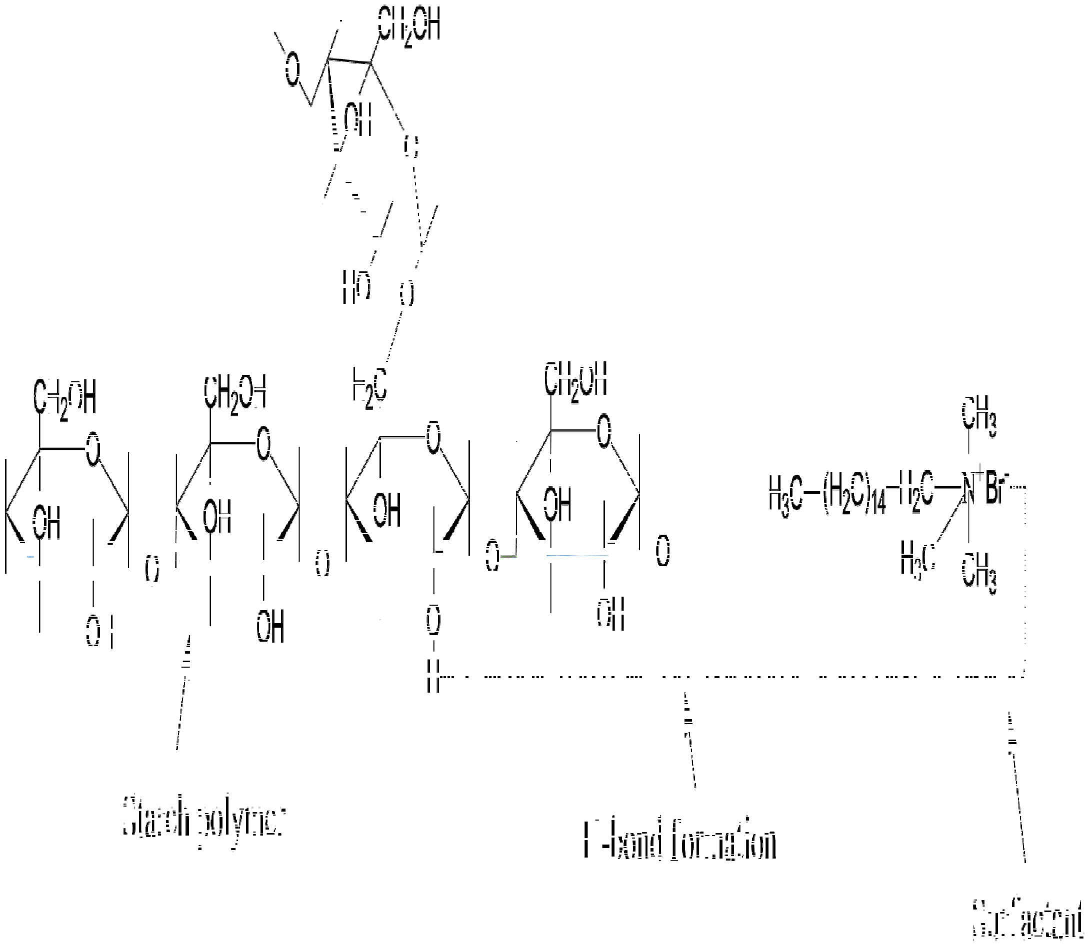

Fig.8.1 Inter molecular H-bond formation within the complexes of starch and CTAB

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13.2 List of publications

List of publications from this Ph.D thesis (1, 2, 3)

Md.Mohsin Hossain, Md.I.H. Mondal & A.T.M. Kamrul Hasan,
Interactions between Starch and Surfactants by Ternary Phase Diagram, *Canadian Journal of Scientific and Industrial Research (CJSIR*), Canada, Vol. 3 No.4, May 2012, p.246-253

Md.Mohsin Hossain, Md.I.H Mondal,
Eco-friendly Biodegradable Polymeric Surfactants from Starch for Cleansing *Proceedings of the International Conference on Engineering Research, Innovation and Education 2013 ICERIE 2013*, SUST, Sylhet, Bangladesh.ICERIE, Nov. 2012.

Md.Mohsin Hossain, Md.I.H. Mondal & A.T.M. Kamrul Hasan
Viscosity-Temperature-Concentration Relationship for Starch-Surfactant-Water Solutions, *Canadian Journal on Chemical Engineering*, Canada, Vol.3 No.4, December 2012. pp.74-79

M.R. Khan & Md.I.H. Mondal & Md.Mohsin Hossain,
Modification of Denim Garment with the Treatment of Bleaching Powder *Canadian Journal on Chemical Engineering*, Canada, Vol.3 No.2, March 2012, p.30-37

A. B.M. Fakrul Alam, Md.I.H. Mondal & Md.Mohsin Hossain,

Synthesis and Characterization of Cellulose Nitrate from Environmental Pollutant Textile Wastes, Canadian *Journal of Scientific and Industrial Research (CJSIR)*, Canada, Jan. 2012, Vol.3 No.3, March 2012,p.92-97

Manuscript pending for publication:

Md.I.H Mondal, Md.Mohsin Hossain, & A.T.M kamrul Hasan,

Structure of Starch-Ionic Surfactant Complexes Studied by ternary phase, XRD and Scanning Electron Microscopy,

Submission processing, Journal of American Chemical society.

Md.Mohsin Hossain, Md.I.H. Mondal & A.T.M. Kamrul Hasan,

The eco-friendly biodegradable starch interaction with various surfactants Submitted to Supervisors for publication in reputed International Journal.

Md.Mohsin Hossain, Md.I.H. Mondal & A.T.M. Kamrul Hasan,

Surface Properties of Water Soluble Surfactants, Starch and Their Complexes by Various Methods. Submission and processing by the Supervisor

13.3 List of ABSTRACT

Eco-friendly Biodegradable Polymeric Surfactants from Starch for Cleansing

ICERIE, Nov. 2012.

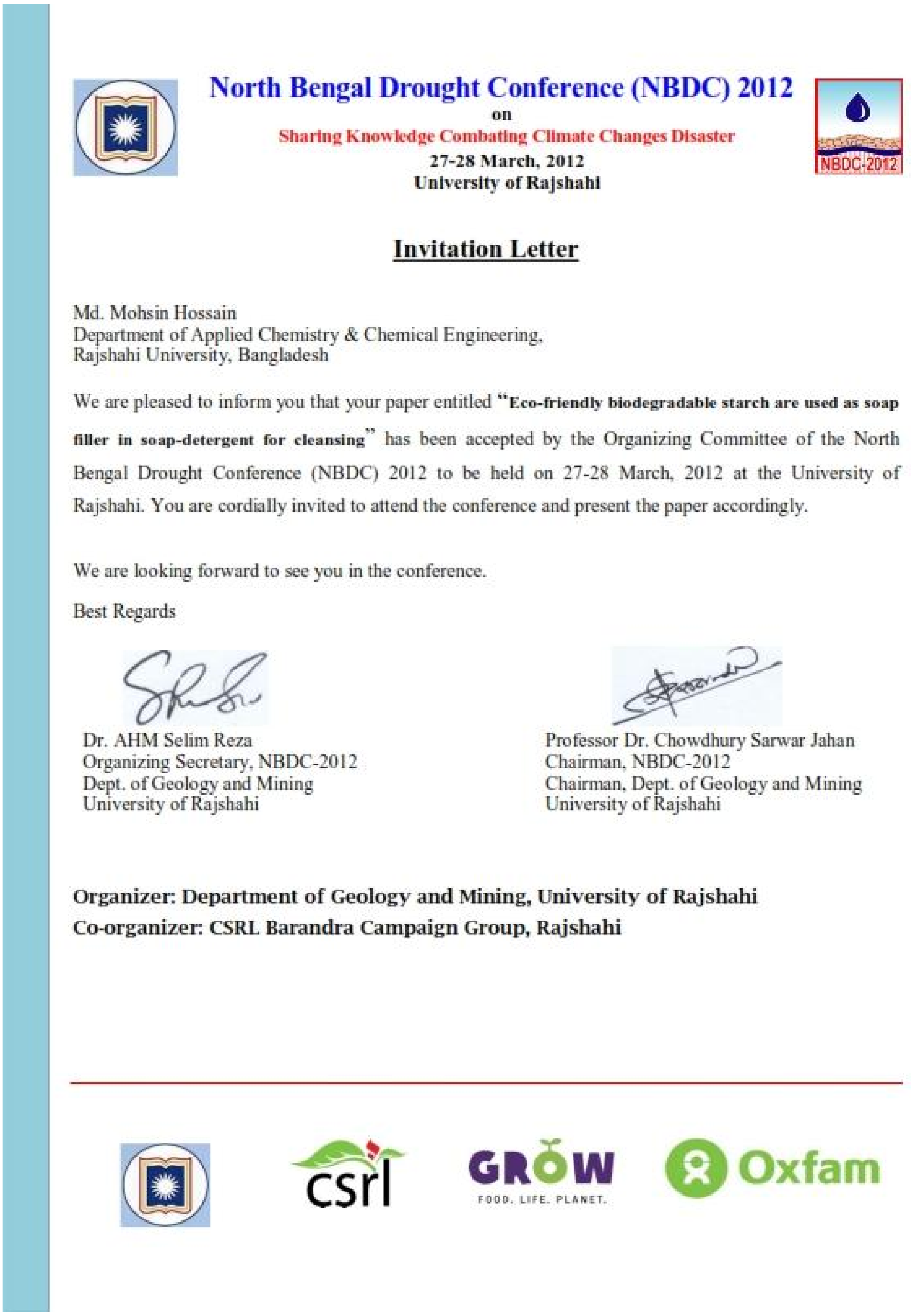
Eco friendly biodegradable starches are used as soap filler in soap-detergent for cleansing. NBDC-2012

Starch Interaction with surfactant studies by ternary phase diagram, BCC, Dhaka University.

13.4 List of Conference Presentations

1. *Bangladesh Chemical Congress, 2008 Oral presentation, Dhaka University.*
2. *Poster presentation in Senate Vhaban, Dhaka University, 2010*
3. *South Asian Regional Conference, University of Rajshahi & University of Khulna, Oral presentation, 2012*
4. *Oral presentation in Gallery at Jahangirnagor University, Savar, Dhaka, 2011*
5. *Shahajalal University of Science and Technology, Oral presentation, ICERIE -2013*
6. *Oral presentation in BCSIR and Dhaka University, 2013*

13.5 Conference Invitation and in details thesis related manuscripts



North Bengal Drought Conference (NBDC) 2012
on
Sharing Knowledge Combating Climate Changes Disaster
27-28 March, 2012
University of Rajshahi

Invitation Letter

Md. Mohsin Hossain
Department of Applied Chemistry & Chemical Engineering,
Rajshahi University, Bangladesh

We are pleased to inform you that your paper entitled "**Eco-friendly biodegradable starch are used as soap filler in soap-detergent for cleansing**" has been accepted by the Organizing Committee of the North Bengal Drought Conference (NBDC) 2012 to be held on 27-28 March, 2012 at the University of Rajshahi. You are cordially invited to attend the conference and present the paper accordingly.

We are looking forward to see you in the conference.

Best Regards

Dr. AHM Selim Reza
Organizing Secretary, NBDC-2012
Dept. of Geology and Mining
University of Rajshahi

Professor Dr. Chowdhury Sarwar Jahan
Chairman, NBDC-2012
Chairman, Dept. of Geology and Mining
University of Rajshahi

Organizer: Department of Geology and Mining, University of Rajshahi
Co-organizer: CSRL Barandra Campaign Group, Rajshahi

South Asian Regional Conference on
Natural Resource Conservation in the Developing Countries Under the Changing Climate
28-29 February & 01 March 2012, Rajshahi University, Bangladesh

Prof. Sowdagar Mahfuzar Rahman
Chairman, Organizing Committee &
Chairman, Zoology Department, Rajshahi University
Rajshahi-6205, Bangladesh
Tel: 88-0721-711119 (Office); 88-0721-760765 (Res)
Fax : 88-0721-750064 (Common)

Dr. Bidhan Chandra Das
Organizing Secretary &
Lead Coordinator, DelPHE R-4 and
Professor, Department of Zoology
Rajshahi University, Bangladesh
Email: bidhan@ru.ac.bd; Cell: +88 01556308987
Tel:+88-0721-711944 (Office)

8 February 2012

Md. Mohsin Hossain
Ph.D. Fellow
Department of Applied Chemistry & Chemical Engineering
Rajshahi University

Subject: Invitation to attend a conference

Dear Mr. Hossain,
We are pleased to inform you that your paper entitled, "Viscosity-temperature-concentration relationship for starch-surfactant-water solutions" has been accepted by the Organizing Committee of the South Asian Regional Conference on "Natural Resource Conservation in the Developing Countries Under the Changing Climate" to be held from 28-29 February to 01 March 2012 at the Rajshahi University, Bangladesh. Accordingly, you are invited to attend the conference and present your paper (oral/poster, depending on the space and time available to the event and number of accepted articles).

You have also been listed as one of the participants for Sundarbans trip for which you need to pay Tk 5,500.00 (subsidized fee).

Look forward to seeing you at our conference hall soon.

With best regards,

(Prof. Sowdagar Mahfuzar Rahman)
Chairman, Organizing Committee &
Chairman, Department of Zoology Rajshahi University, Rajshahi-6205 Bangladesh

(Dr. Bidhan Chandra Das)
Organizing Secretary &
Lead Coordinator, DelPHE R-4 and
Professor, Department of Zoology
Rajshahi University, Bangladesh

Certificate of Attendance

This is to certify that

Mr. Md. Mohsin Hossain

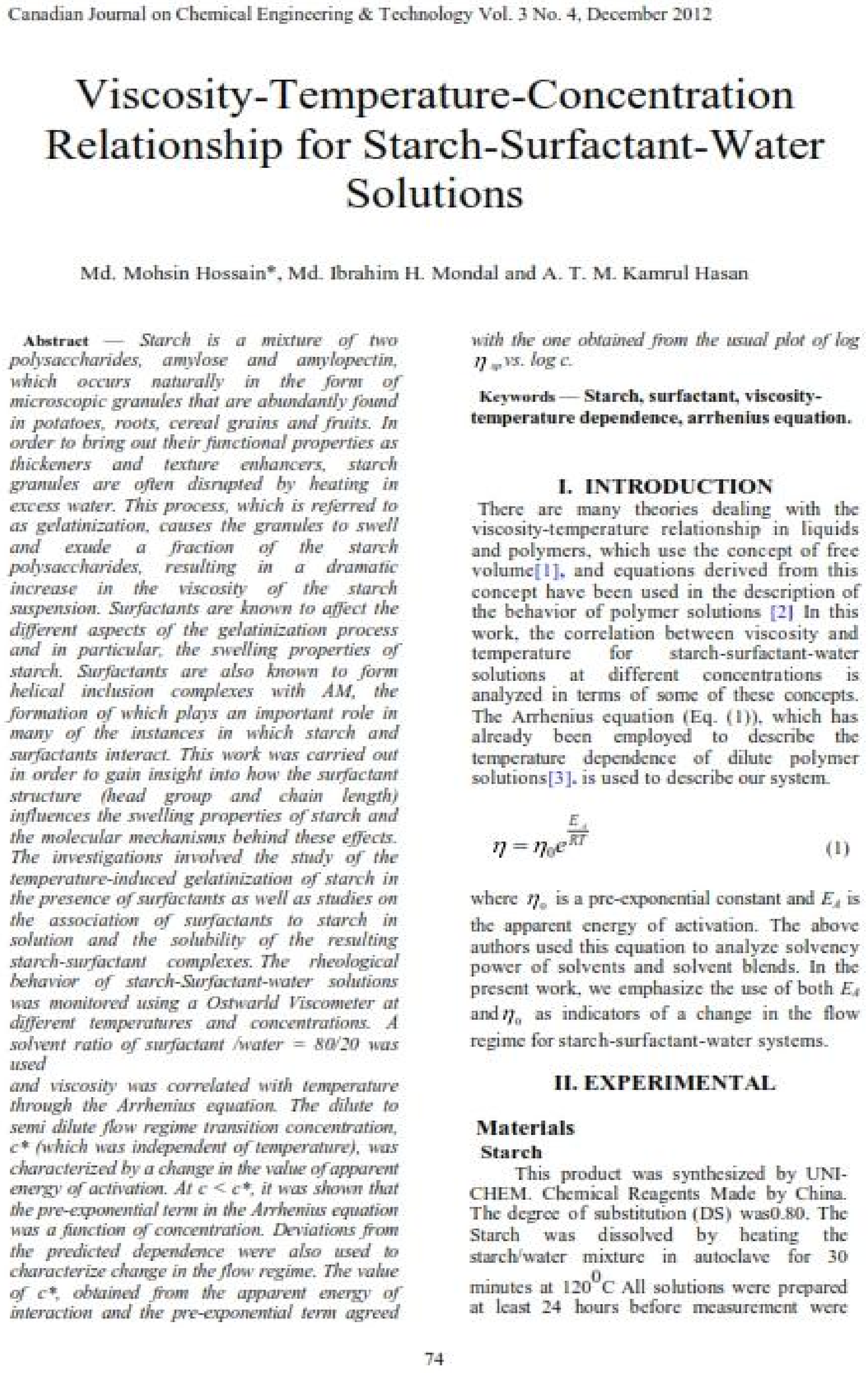
Attended the

International Conference on Engineering Research, Innovation and Education (ICERIE 2013) on 11-13 January, 2013

held at Shahjalal University of Science and Technology, Sylhet, Bangladesh

Prof. Dr. M. Aktarul Islam Chowdhury
Convener, ICERIE 2013

Dr. Md. Mozammel Hoque
Member Secretary, ICERIE 2013



Canadian Journal on Chemical Engineering & Technology Vol. 3 No. 4, December 2012

Viscosity-Temperature-Concentration Relationship for Starch-Surfactant-Water Solutions

Md. Mohsin Hossain*, Md. Ibrahim H. Mondal and A. T. M. Kamrul Hasan

Abstract — *Starch is a mixture of two polysaccharides, amylose and amylopectin, which occurs naturally in the form of microscopic granules that are abundantly found in potatoes, roots, cereal grains and fruits. In order to bring out their functional properties as thickeners and texture enhancers, starch granules are often disrupted by heating in excess water. This process, which is referred to as gelatinization, causes the granules to swell and exude a fraction of the starch polysaccharides, resulting in a dramatic increase in the viscosity of the starch suspension. Surfactants are known to affect the different aspects of the gelatinization process and in particular, the swelling properties of starch. Surfactants are also known to form helical inclusion complexes with AM, the formation of which plays an important role in many of the instances in which starch and surfactants interact. This work was carried out in order to gain insight into how the surfactant structure (head group and chain length) influences the swelling properties of starch and the molecular mechanisms behind these effects. The investigations involved the study of the temperature-induced gelatinization of starch in the presence of surfactants as well as studies on the association of surfactants to starch in solution and the solubility of the resulting starch-surfactant complexes. The rheological behavior of starch-Surfactant-water solutions was monitored using a Ostwarld Viscometer at different temperatures and concentrations. A solvent ratio of surfactant /water = 80/20 was used and viscosity was correlated with temperature through the Arrhenius equation. The dilute to semi dilute flow regime transition concentration, c* (which was independent of temperature), was characterized by a change in the value of apparent energy of activation. At c < c*, it was shown that the pre-exponential term in the Arrhenius equation was a function of concentration. Deviations from the predicted dependence were also used to characterize change in the flow regime. The value of c*, obtained from the apparent energy of interaction and the pre-exponential term agreed with the one obtained from the usual plot of log η_{sp} vs. log c.*

Keywords — **Starch, surfactant, viscosity-temperature dependence, arrhenius equation.**

I. INTRODUCTION

There are many theories dealing with the viscosity-temperature relationship in liquids and polymers, which use the concept of free volume[1], and equations derived from this concept have been used in the description of the behavior of polymer solutions [2] In this work, the correlation between viscosity and temperature for starch-surfactant-water solutions at different concentrations is analyzed in terms of some of these concepts. The Arrhenius equation (Eq. (1)), which has already been employed to describe the temperature dependence of dilute polymer solutions[3], is used to describe our system.

$$\eta = \eta_0 e^{\frac{E_A}{RT}} \qquad (1)$$

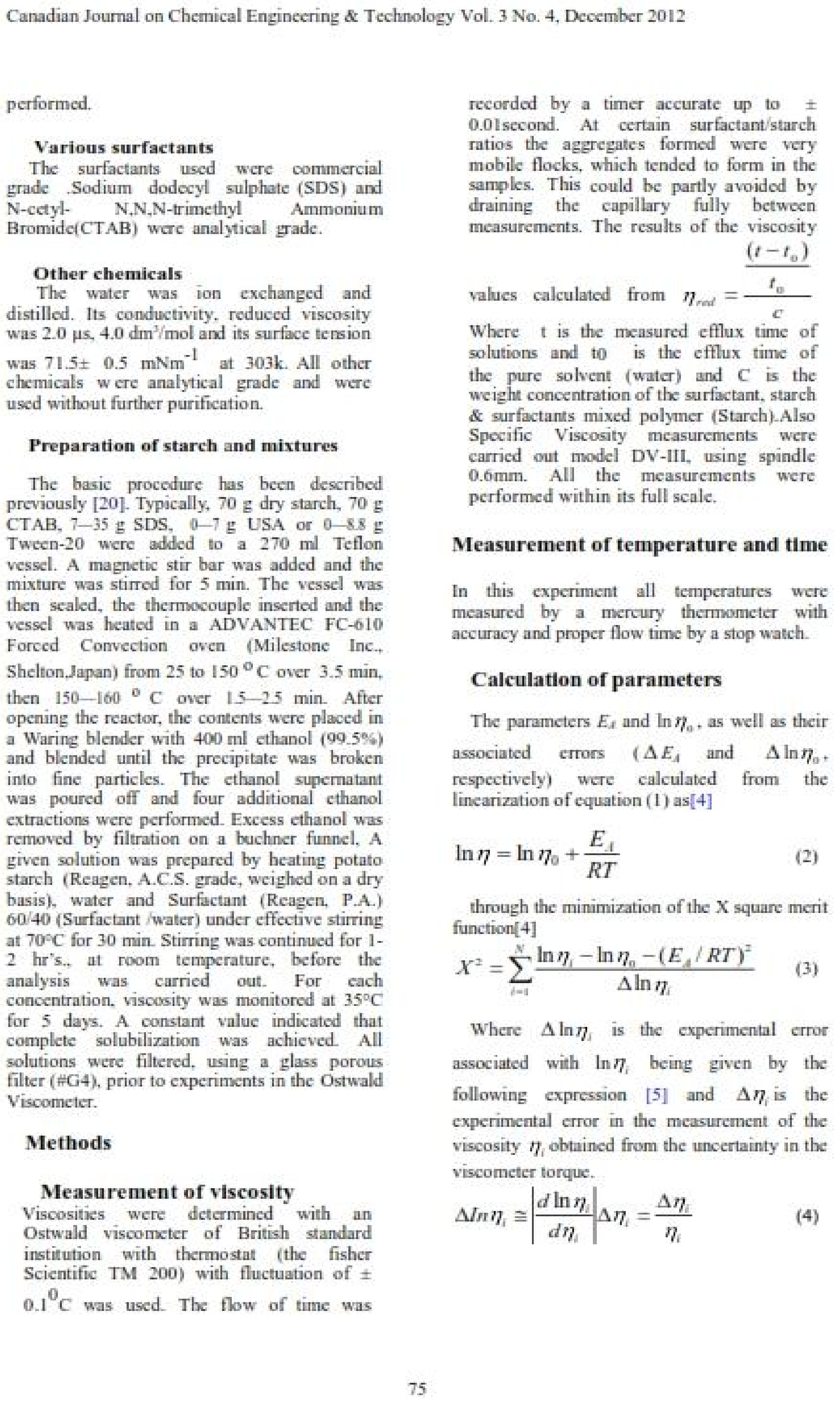
where η_0 is a pre-exponential constant and E_A is the apparent energy of activation. The above authors used this equation to analyze solvency power of solvents and solvent blends. In the present work, we emphasize the use of both E_A and η_0 as indicators of a change in the flow regime for starch-surfactant-water systems.

II. EXPERIMENTAL

Materials

Starch

This product was synthesized by UNI-CHEM. Chemical Reagents Made by China. The degree of substitution (DS) was0.80. The Starch was dissolved by heating the starch/water mixture in autoclave for 30 minutes at 120^0C All solutions were prepared at least 24 hours before measurement were



performed.

Various surfactants

The surfactants used were commercial grade .Sodium dodecyl sulphate (SDS) and N-cetyl- N,N,N-trimethyl Ammonium Bromide(CTAB) were analytical grade.

Other chemicals

The water was ion exchanged and distilled. Its conductivity, reduced viscosity was 2.0 μs, 4.0 dm^3/mol and its surface tension was 71.5± 0.5 mNm^{-1} at 303k. All other chemicals were analytical grade and were used without further purification.

Preparation of starch and mixtures

The basic procedure has been described previously [20]. Typically, 70 g dry starch, 70 g CTAB, 7—35 g SDS, 0—7 g USA or 0—8.8 g Tween-20 were added to a 270 ml Teflon vessel. A magnetic stir bar was added and the mixture was stirred for 5 min. The vessel was then sealed, the thermocouple inserted and the vessel was heated in a ADVANTEC FC-610 Forced Convection oven (Milestone Inc., Shelton,Japan) from 25 to 150 ^{o}C over 3.5 min, then 150—160 ^{o} C over 1.5—2.5 min. After opening the reactor, the contents were placed in a Waring blender with 400 ml ethanol (99.5%) and blended until the precipitate was broken into fine particles. The ethanol supernatant was poured off and four additional ethanol extractions were performed. Excess ethanol was removed by filtration on a buchner funnel, A given solution was prepared by heating potato starch (Reagen, A.C.S. grade, weighed on a dry basis), water and Surfactant (Reagen, P.A.) 60/40 (Surfactant /water) under effective stirring at 70°C for 30 min. Stirring was continued for 1-2 hr's., at room temperature, before the analysis was carried out. For each concentration, viscosity was monitored at 35°C for 5 days. A constant value indicated that complete solubilization was achieved. All solutions were filtered, using a glass porous filter (#G4), prior to experiments in the Ostwald Viscometer.

Methods

Measurement of viscosity

Viscosities were determined with an Ostwald viscometer of British standard institution with thermostat (the fisher Scientific TM 200) with fluctuation of ± 0.1^{0}C was used. The flow of time was recorded by a timer accurate up to ± 0.01second. At certain surfactant/starch ratios the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements. The results of the viscosity values calculated from $\eta_{red} = \frac{\frac{(t-t_0)}{t_0}}{c}$

Where t is the measured efflux time of solutions and t0 is the efflux time of the pure solvent (water) and C is the weight concentration of the surfactant, starch & surfactants mixed polymer (Starch).Also Specific Viscosity measurements were carried out model DV-III, using spindle 0.6mm. All the measurements were performed within its full scale.

Measurement of temperature and time

In this experiment all temperatures were measured by a mercury thermometer with accuracy and proper flow time by a stop watch.

Calculation of parameters

The parameters E_A and $\ln \eta_0$, as well as their associated errors (ΔE_A and $\Delta \ln \eta_0$, respectively) were calculated from the linearization of equation (1) as[4]

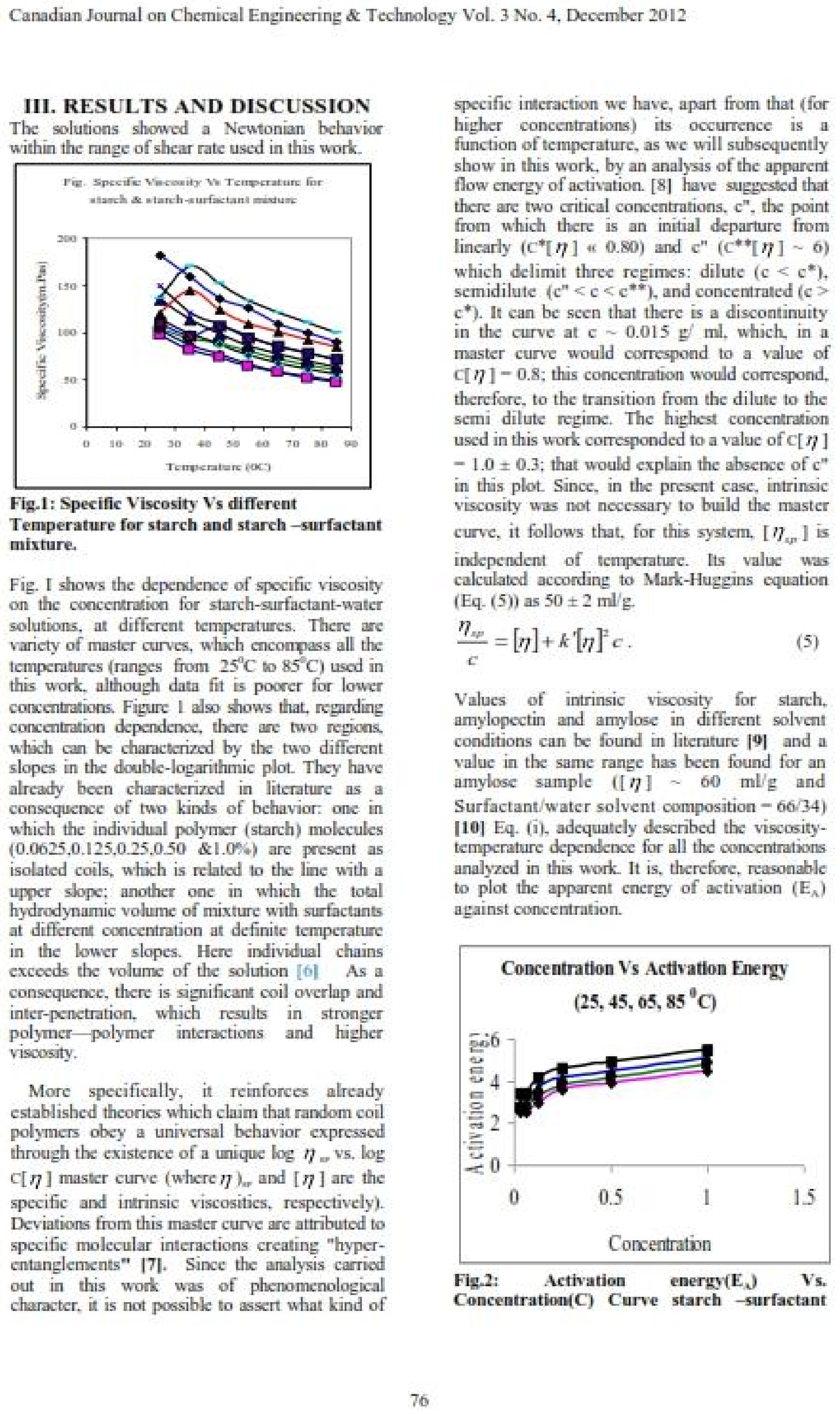
$$\ln \eta = \ln \eta_0 + \frac{E_A}{RT} \qquad (2)$$

through the minimization of the X square merit function[4]

$$X^2 = \sum_{i=1}^{N} \frac{\ln \eta_i - \ln \eta_0 - (E_A / RT)^2}{\Delta \ln \eta_i} \qquad (3)$$

Where $\Delta \ln \eta_i$ is the experimental error associated with $\ln \eta_i$ being given by the following expression [5] and $\Delta \eta_i$ is the experimental error in the measurement of the viscosity η_i obtained from the uncertainty in the viscometer torque.

$$\Delta ln \eta_i \cong \left| \frac{d \ln \eta_i}{d \eta_i} \right| \Delta \eta_i = \frac{\Delta \eta_i}{\eta_i} \qquad (4)$$



Canadian Journal on Chemical Engineering & Technology Vol. 3 No. 4, December 2012

III. RESULTS AND DISCUSSION

The solutions showed a Newtonian behavior within the range of shear rate used in this work.

Fig.1: Specific Viscosity Vs different Temperature for starch and starch –surfactant mixture.

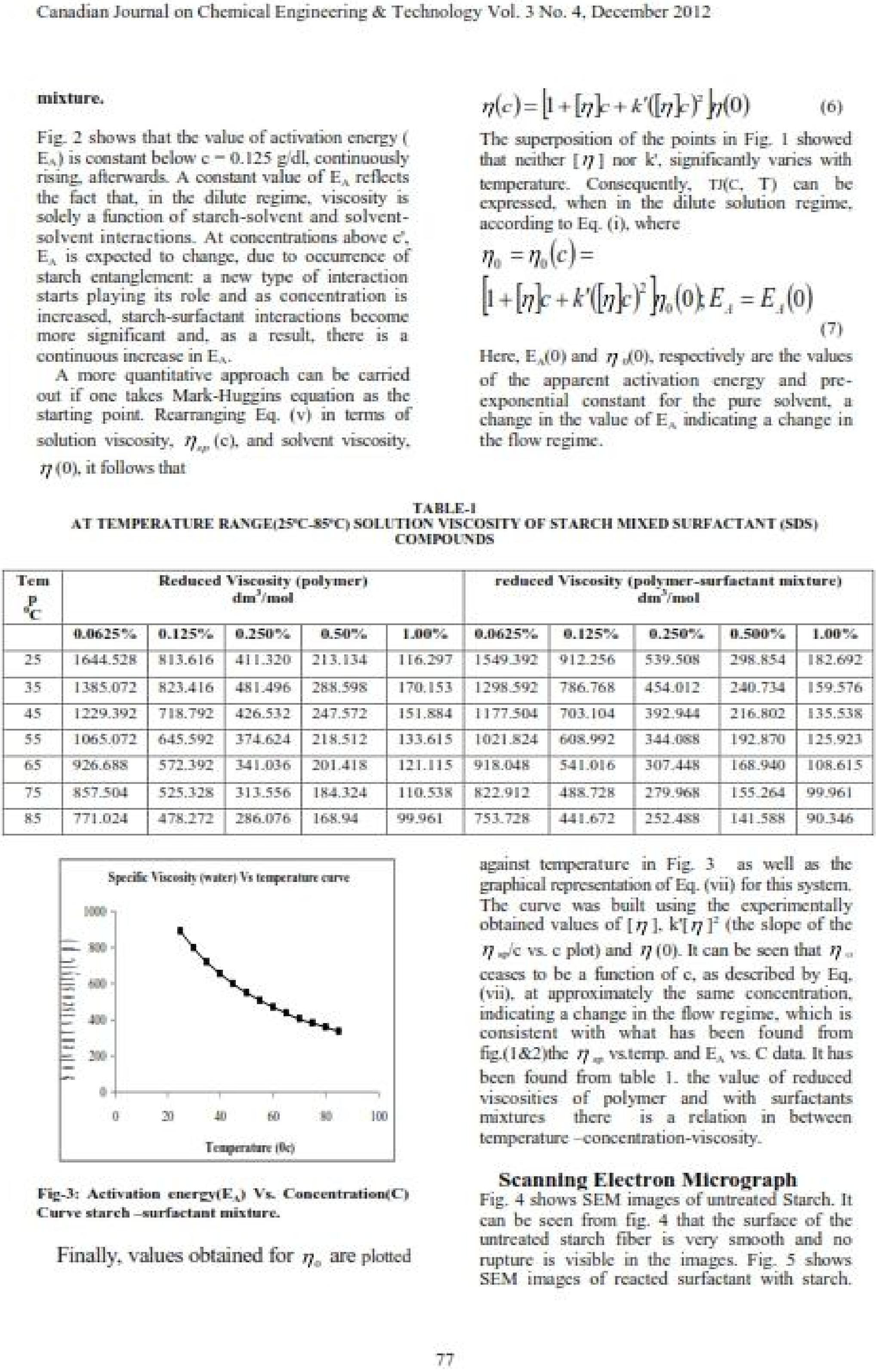
Fig. I shows the dependence of specific viscosity on the concentration for starch-surfactant-water solutions, at different temperatures. There are variety of master curves, which encompass all the temperatures (ranges from 25°C to 85°C) used in this work, although data fit is poorer for lower concentrations. Figure 1 also shows that, regarding concentration dependence, there are two regions, which can be characterized by the two different slopes in the double-logarithmic plot. They have already been characterized in literature as a consequence of two kinds of behavior: one in which the individual polymer (starch) molecules (0.0625,0.125,0.25,0.50 &1.0%) are present as isolated coils, which is related to the line with a upper slope; another one in which the total hydrodynamic volume of mixture with surfactants at different concentration at definite temperature in the lower slopes. Here individual chains exceeds the volume of the solution [6] As a consequence, there is significant coil overlap and inter-penetration, which results in stronger polymer—polymer interactions and higher viscosity.

More specifically, it reinforces already established theories which claim that random coil polymers obey a universal behavior expressed through the existence of a unique log η_{sp} vs. log C[η] master curve (where η)$_{sp}$ and [η] are the specific and intrinsic viscosities, respectively). Deviations from this master curve are attributed to specific molecular interactions creating "hyper-entanglements" **[7]**. Since the analysis carried out in this work was of phenomenological character, it is not possible to assert what kind of specific interaction we have, apart from that (for higher concentrations) its occurrence is a function of temperature, as we will subsequently show in this work, by an analysis of the apparent flow energy of activation. [8] have suggested that there are two critical concentrations, c", the point from which there is an initial departure from linearly (C*[η] « 0.80) and c" (C**[η] ~ 6) which delimit three regimes: dilute (c < c*), semidilute (c" < c < c**), and concentrated (c > c*). It can be seen that there is a discontinuity in the curve at c ~ 0.015 g/ ml, which, in a master curve would correspond to a value of C[η] ~ 0.8; this concentration would correspond, therefore, to the transition from the dilute to the semi dilute regime. The highest concentration used in this work corresponded to a value of C[η] ~ 1.0 ± 0.3; that would explain the absence of c" in this plot. Since, in the present case, intrinsic viscosity was not necessary to build the master curve, it follows that, for this system, [η_{sp}] is independent of temperature. Its value was calculated according to Mark-Huggins equation (Eq. (5)) as 50 ± 2 ml/g.

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 c . \qquad (5)$$

Values of intrinsic viscosity for starch, amylopectin and amylose in different solvent conditions can be found in literature **[9]** and a value in the same range has been found for an amylose sample ([η] ~ 60 ml/g and Surfactant/water solvent composition = 66/34) **[10]** Eq. (i), adequately described the viscosity-temperature dependence for all the concentrations analyzed in this work. It is, therefore, reasonable to plot the apparent energy of activation (E_A) against concentration.

Fig.2: Activation energy(E_A) Vs. Concentration(C) Curve starch –surfactant



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mixture.

Fig. 2 shows that the value of activation energy (E_A) is constant below c = 0.125 g/dl, continuously rising, afterwards. A constant value of E_A reflects the fact that, in the dilute regime, viscosity is solely a function of starch-solvent and solvent-solvent interactions. At concentrations above c', E_A is expected to change, due to occurrence of starch entanglement: a new type of interaction starts playing its role and as concentration is increased, starch-surfactant interactions become more significant and, as a result, there is a continuous increase in E_A.

A more quantitative approach can be carried out if one takes Mark-Huggins equation as the starting point. Rearranging Eq. (v) in terms of solution viscosity, η_{sp} (c), and solvent viscosity, η (0), it follows that

$$\eta(c)=\left[1+[\eta]c+k'([\eta]c)^2\right]\eta(0) \qquad (6)$$

The superposition of the points in Fig. 1 showed that neither [η] nor k', significantly varies with temperature. Consequently, TJ(C, T) can be expressed, when in the dilute solution regime, according to Eq. (i), where

$$\eta_0=\eta_0(c)=\left[1+[\eta]c+k'([\eta]c)^2\right]\eta_0(0); E_A=E_A(0) \qquad (7)$$

Here, $E_A(0)$ and $\eta_0(0)$, respectively are the values of the apparent activation energy and pre-exponential constant for the pure solvent, a change in the value of E_A indicating a change in the flow regime.

TABLE-1
AT TEMPERATURE RANGE(25°C-85°C) SOLUTION VISCOSITY OF STARCH MIXED SURFACTANT (SDS) COMPOUNDS

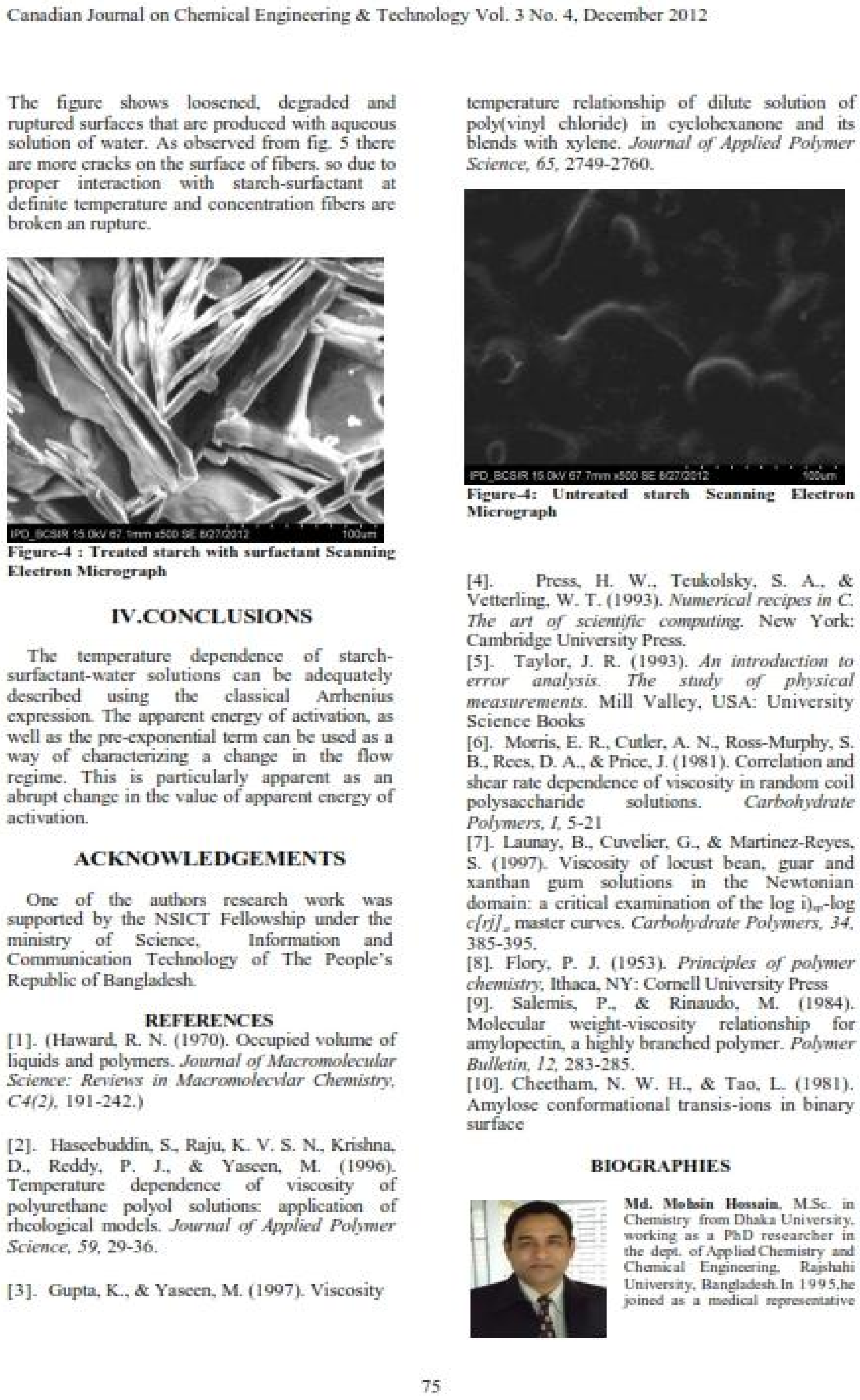
Temp °C	Reduced Viscosity (polymer) dm³/mol					reduced Viscosity (polymer-surfactant mixture) dm³/mol				
	0.0625%	**0.125%**	**0.250%**	**0.50%**	**1.00%**	**0.0625%**	**0.125%**	**0.250%**	**0.500%**	**1.00%**
25	1644.528	813.616	411.320	213.134	116.297	1549.392	912.256	539.508	298.854	182.692
35	1385.072	823.416	481.496	288.598	170.153	1298.592	786.768	454.012	240.734	159.576
45	1229.392	718.792	426.532	247.572	151.884	1177.504	703.104	392.944	216.802	135.538
55	1065.072	645.592	374.624	218.512	133.615	1021.824	608.992	344.088	192.870	125.923
65	926.688	572.392	341.036	201.418	121.115	918.048	541.016	307.448	168.940	108.615
75	857.504	525.328	313.556	184.324	110.538	822.912	488.728	279.968	155.264	99.961
85	771.024	478.272	286.076	168.94	99.961	753.728	441.672	252.488	141.588	90.346

Fig-3: Activation energy(E_A) Vs. Concentration(C) Curve starch –surfactant mixture.

Finally, values obtained for η_o are plotted against temperature in Fig. 3 as well as the graphical representation of Eq. (vii) for this system. The curve was built using the experimentally obtained values of [η], k'[η]^2 (the slope of the η_{sp}/c vs. c plot) and η (0). It can be seen that η_o ceases to be a function of c, as described by Eq. (vii), at approximately the same concentration, indicating a change in the flow regime, which is consistent with what has been found from fig.(1&2)the η_{sp} vs.temp. and E_A vs. C data. It has been found from table 1. the value of reduced viscosities of polymer and with surfactants mixtures there is a relation in between temperature –concentration-viscosity.

Scanning Electron Micrograph

Fig. 4 shows SEM images of untreated Starch. It can be seen from fig. 4 that the surface of the untreated starch fiber is very smooth and no rupture is visible in the images. Fig. 5 shows SEM images of reacted surfactant with starch.



The figure shows loosened, degraded and ruptured surfaces that are produced with aqueous solution of water. As observed from fig. 5 there are more cracks on the surface of fibers. so due to proper interaction with starch-surfactant at definite temperature and concentration fibers are broken an rupture.

Figure-4 : Treated starch with surfactant Scanning Electron Micrograph

IV.CONCLUSIONS

The temperature dependence of starch-surfactant-water solutions can be adequately described using the classical Arrhenius expression. The apparent energy of activation, as well as the pre-exponential term can be used as a way of characterizing a change in the flow regime. This is particularly apparent as an abrupt change in the value of apparent energy of activation.

ACKNOWLEDGEMENTS

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Figure-4: Untreated starch Scanning Electron Micrograph

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Interactions between Starch and Surfactants by Ternary Phase Diagram

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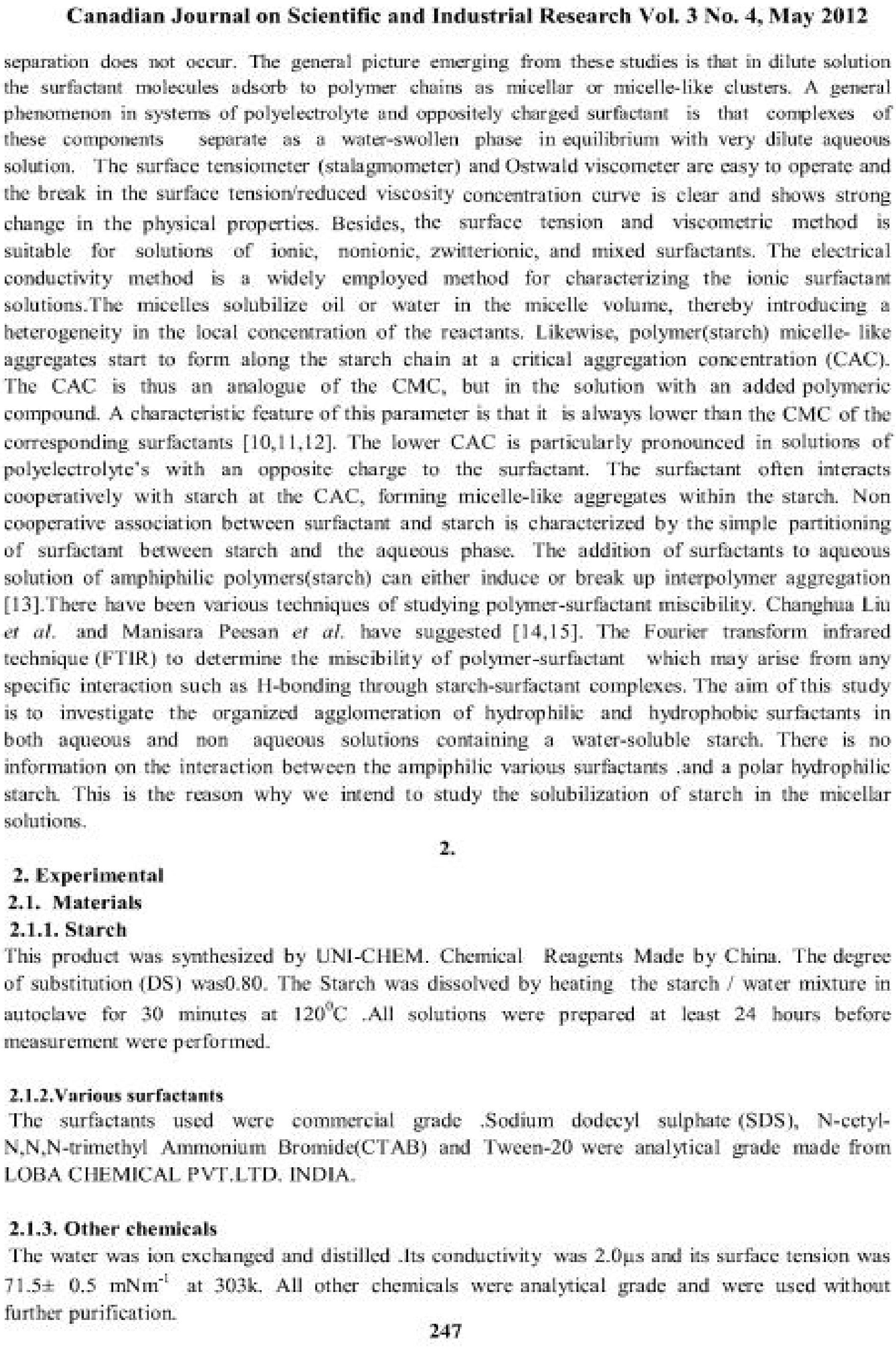
Abstract: *Studies were carried out to find out the cleansing activity of starch in various surfactants using surface tensiometry, viscometry and FTIR method. In this study the formation of complexes between surfactants and the helical chains of amylopectins was confirmed. Three types of surfactants with hydrophobic and hydrophilic groups of appropriate size and chemical structure enhanced the swelling and gelatinization process of starch granules. Hydrophobic groups from complexes with the amylase and linear chains of amylopectin by becoming inserted into the hydrophobic inner area of helical structures. Among the anionic surfactant (SDS) caused maximum swelling and gelatinization peaks. The hydrophobic alkyl chains of anionic and cationic surfactants fix to the edge of the starch molecular chains by forming inclusion complexes with the helical chains of the amylopectin. The surface tension and reduced viscosity were used to study the association behavior of amphiphiles. The surface tension/viscosity vs. concentration curve was described by a curve with minimum at the critical micelle concentration(CMC) . The addition of starch on various surfactant concentrations influence the shape of surface tension /viscosity curve indicated strong intermolecular interaction among starch-surfactant-water complexes which strongly indicated the cleansing activity of starch as a filler in surfactant. This intermolecular H-bond formation of surfactants with starch was clarified by FTIR analysis. Critical association Concentration (CAC) were observed at concentrations well below the CMCs of surfactants.*

Keywords: Starch-surfactant interaction, surface tension, viscosity, complexations, FTIR, CMC.

1. 1. Introduction

From 1957 onwards [1]. the interaction between micelles and water soluble neutral homopolymers have been studied in detail. The interaction of starch with various surfactants (Cationic, Anionic & nonionic) micelles have been to particular interest. The main features of these "classical" polymer-surfactant interactions have been summarized in excellent review articles [2]. Solutions of surface-active materials such as all type of surfactants (CTAB,SDS,Tween-20) exhibit special and useful property called the critical micelle concentration (CMC), at which micelles first appear in the solution. At the CMC abrupt changes in some physical properties, such as viscosity, conductivity, surface tension, turbidity, osmotic pressure, etc. take place [3]..The surface tension, viscosity and conductivity are the most popular methods for the characterization of micellar colloidal solutions [4,5]. For example. [6,7,8,9]. Many investigations have focused on aggregate structure in dilute solution, i.e. systems in which phase



separation does not occur. The general picture emerging from these studies is that in dilute solution the surfactant molecules adsorb to polymer chains as micellar or micelle-like clusters. A general phenomenon in systems of polyelectrolyte and oppositely charged surfactant is that complexes of these components separate as a water-swollen phase in equilibrium with very dilute aqueous solution. The surface tensiometer (stalagmometer) and Ostwald viscometer are easy to operate and the break in the surface tension/reduced viscosity concentration curve is clear and shows strong change in the physical properties. Besides, the surface tension and viscometric method is suitable for solutions of ionic, nonionic, zwitterionic, and mixed surfactants. The electrical conductivity method is a widely employed method for characterizing the ionic surfactant solutions.The micelles solubilize oil or water in the micelle volume, thereby introducing a heterogeneity in the local concentration of the reactants. Likewise, polymer(starch) micelle- like aggregates start to form along the starch chain at a critical aggregation concentration (CAC). The CAC is thus an analogue of the CMC, but in the solution with an added polymeric compound. A characteristic feature of this parameter is that it is always lower than the CMC of the corresponding surfactants [10,11,12]. The lower CAC is particularly pronounced in solutions of polyelectrolyte's with an opposite charge to the surfactant. The surfactant often interacts cooperatively with starch at the CAC, forming micelle-like aggregates within the starch. Non cooperative association between surfactant and starch is characterized by the simple partitioning of surfactant between starch and the aqueous phase. The addition of surfactants to aqueous solution of amphiphilic polymers(starch) can either induce or break up interpolymer aggregation [13].There have been various techniques of studying polymer-surfactant miscibility. Changhua Liu *et al.* and Manisara Peesan *et al.* have suggested [14,15]. The Fourier transform infrared technique (FTIR) to determine the miscibility of polymer-surfactant which may arise from any specific interaction such as H-bonding through starch-surfactant complexes. The aim of this study is to investigate the organized agglomeration of hydrophilic and hydrophobic surfactants in both aqueous and non aqueous solutions containing a water-soluble starch. There is no information on the interaction between the ampiphilic various surfactants .and a polar hydrophilic starch. This is the reason why we intend to study the solubilization of starch in the micellar solutions.

2.

2. Experimental

2.1. Materials

2.1.1. Starch

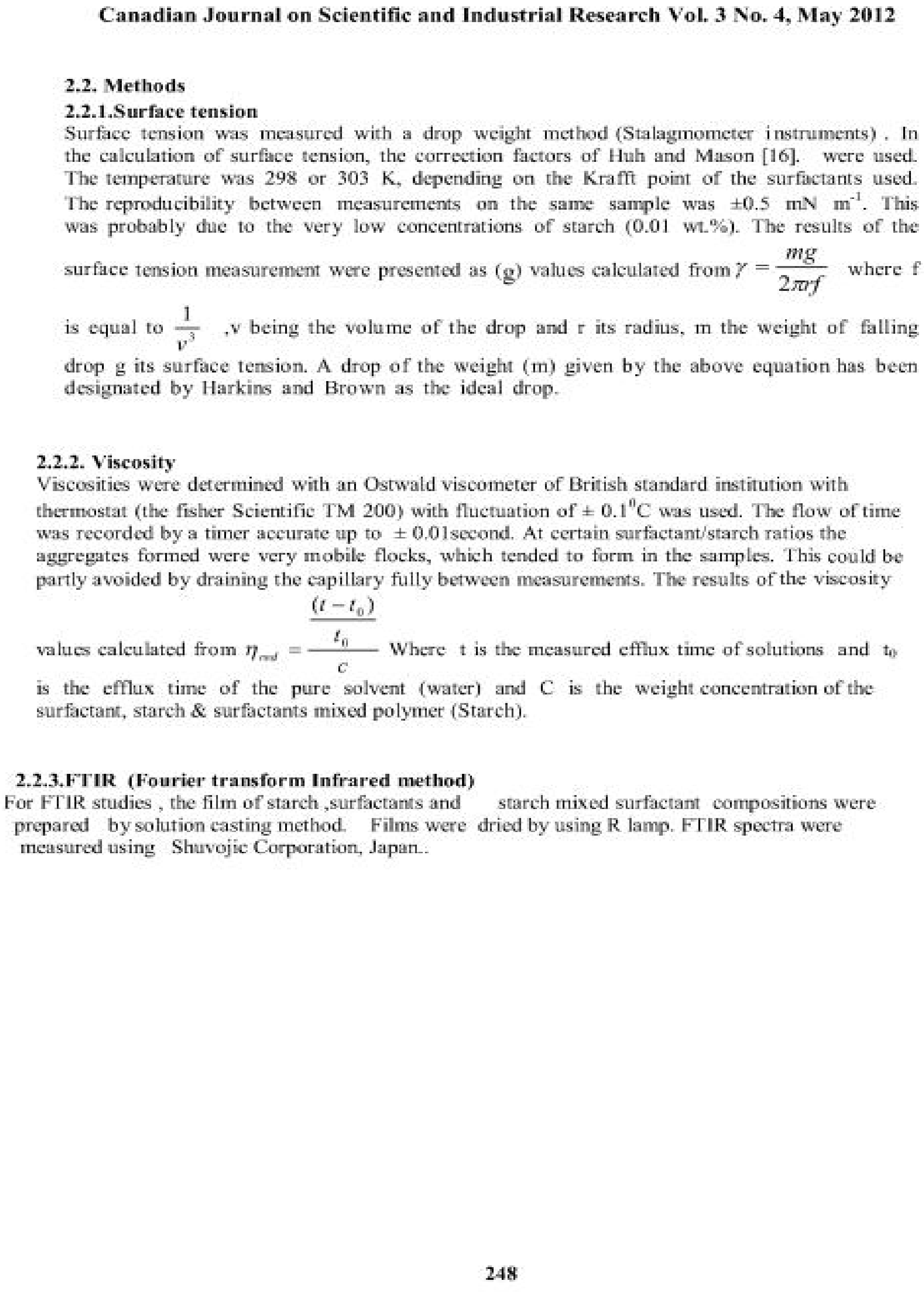
This product was synthesized by UNI-CHEM. Chemical Reagents Made by China. The degree of substitution (DS) was0.80. The Starch was dissolved by heating the starch / water mixture in autoclave for 30 minutes at 120^{0}C .All solutions were prepared at least 24 hours before measurement were performed.

2.1.2.Various surfactants

The surfactants used were commercial grade .Sodium dodecyl sulphate (SDS), N-cetyl-N,N,N-trimethyl Ammonium Bromide(CTAB) and Tween-20 were analytical grade made from LOBA CHEMICAL PVT.LTD. INDIA.

2.1.3. Other chemicals

The water was ion exchanged and distilled .Its conductivity was 2.0μs and its surface tension was 71.5± 0.5 mNm^{-1} at 303k. All other chemicals were analytical grade and were used without further purification.



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2.2. Methods

2.2.1.Surface tension

Surface tension was measured with a drop weight method (Stalagmometer instruments) . In the calculation of surface tension, the correction factors of Huh and Mason [16]. were used. The temperature was 298 or 303 K, depending on the Krafft point of the surfactants used. The reproducibility between measurements on the same sample was ±0.5 mN m^{-1}. This was probably due to the very low concentrations of starch (0.01 wt.%). The results of the surface tension measurement were presented as (g) values calculated from $\gamma = \frac{mg}{2\pi r f}$ where f is equal to $\frac{1}{v^{3}}$,v being the volume of the drop and r its radius, m the weight of falling drop g its surface tension. A drop of the weight (m) given by the above equation has been designated by Harkins and Brown as the ideal drop.

2.2.2. Viscosity

Viscosities were determined with an Ostwald viscometer of British standard institution with thermostat (the fisher Scientific TM 200) with fluctuation of ± 0.1^{0}C was used. The flow of time was recorded by a timer accurate up to ± 0.01second. At certain surfactant/starch ratios the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements. The results of the viscosity values calculated from $\eta_{red} = \frac{\frac{(t - t_0)}{t_0}}{C}$ Where t is the measured efflux time of solutions and t_0 is the efflux time of the pure solvent (water) and C is the weight concentration of the surfactant, starch & surfactants mixed polymer (Starch).

2.2.3.FTIR (Fourier transform Infrared method)

For FTIR studies , the film of starch ,surfactants and starch mixed surfactant compositions were prepared by solution casting method. Films were dried by using R lamp. FTIR spectra were measured using Shuvojic Corporation, Japan..

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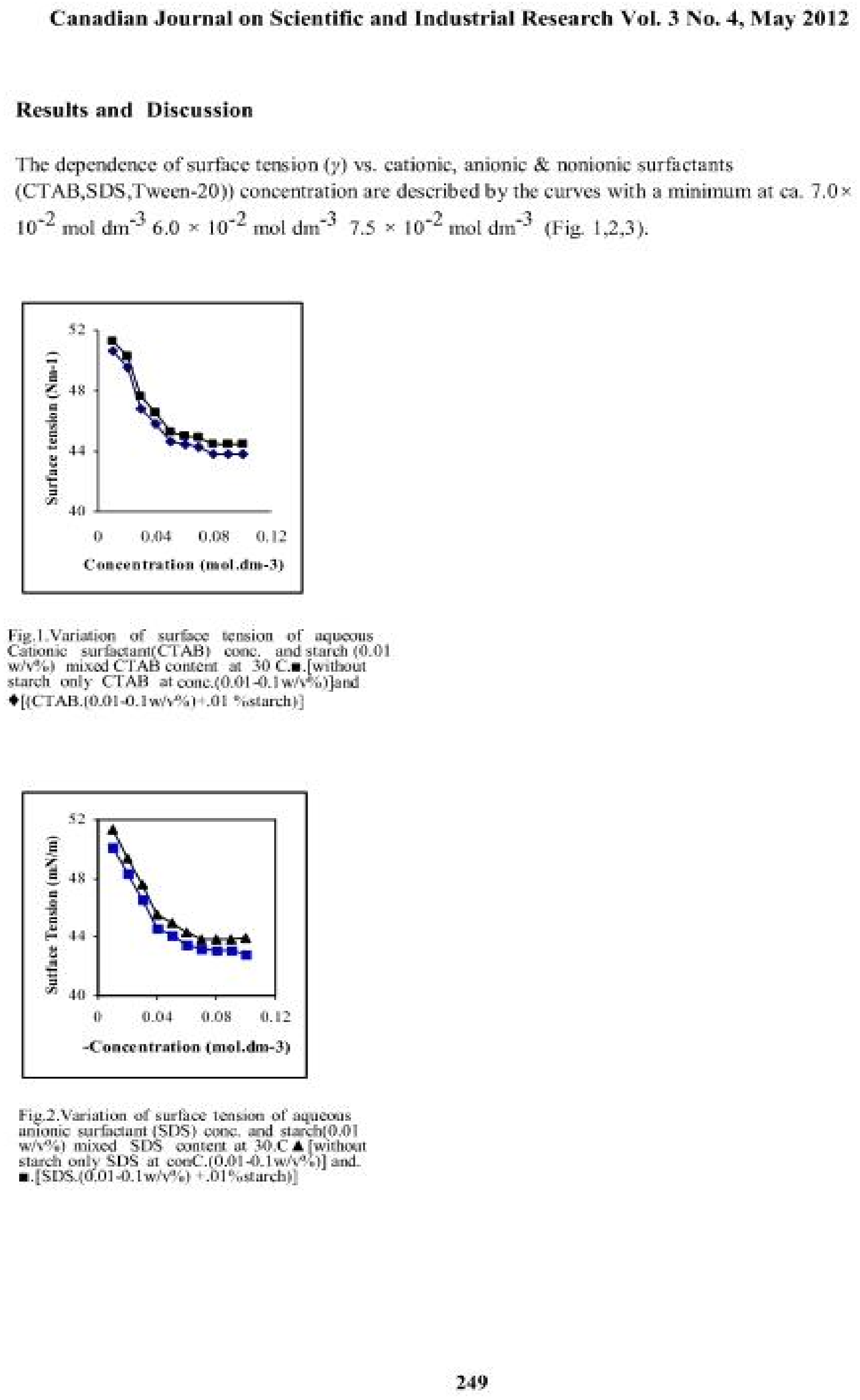

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Results and Discussion

The dependence of surface tension (γ) vs. cationic, anionic & nonionic surfactants (CTAB,SDS,Tween-20)) concentration are described by the curves with a minimum at ca. 7.0×10^{-2} mol dm^{-3} 6.0×10^{-2} mol dm^{-3} 7.5×10^{-2} mol dm^{-3} (Fig. 1,2,3).

Fig.1.Variation of surface tension of aqueous Cationic surfactant(CTAB) conc. and starch (0.01 w/v%) mixed CTAB content at 30 C.■.[without starch only CTAB at conc.(0.01-0.1w/v%)]and ◆[(CTAB.(0.01-0.1w/v%)+.01 %starch)]

Fig.2.Variation of surface tension of aqueous anionic surfactant (SDS) conc. and starch(0.01 w/v%) mixed SDS content at 30.C ▲ [without starch only SDS at conC.(0.01-0.1w/v%)] and. ■.[SDS.(0.01-0.1w/v%) +.01%starch)]

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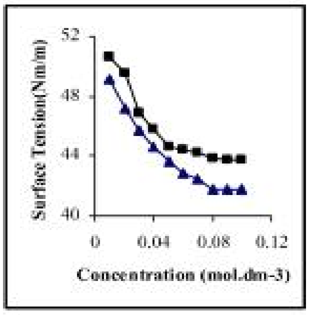


Fig.3.Variation of surface tension of aqueous Nonionic surfactant conc. and starch (0.01 w/v%) mixed Tween-20 content at 30C. ■. [without starch only Tween-20 at conC.(0.01-0.1w/v%)] and ▲[Tween-20.(0.01-0.1w/v%) +.01%starch]

First the surface tension of the aqueous solution decreases with increasing the surfactants (CTAB,SDS, Tween-20) concentration from ca. 8.0×10^{-2} mol dm^{-3} 7.0×10^{-2} mol dm^{-3} and then it starts to increase above ca.. 7.5×10^{-2} mol dm^{-3} From fig 1,2,3 it had been found at CMC point the value of surface tension were 44.0, 44.1 & 44.3 mNm^{-1} in surfactants respectively, whereas in mixture it were near to 43.5, 43 & 42.5 mNm^{-1} This results indicate though starch itself surface inactive but it reduced the surface tension of surfactant which clearly represented the cleansing property when it was mixed with any type of surfactants.

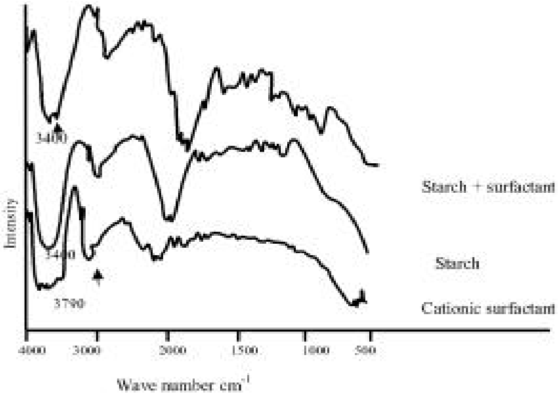


Fig. 4: IR Spectra of Cationic surfactant, Starch and their mixed sample film

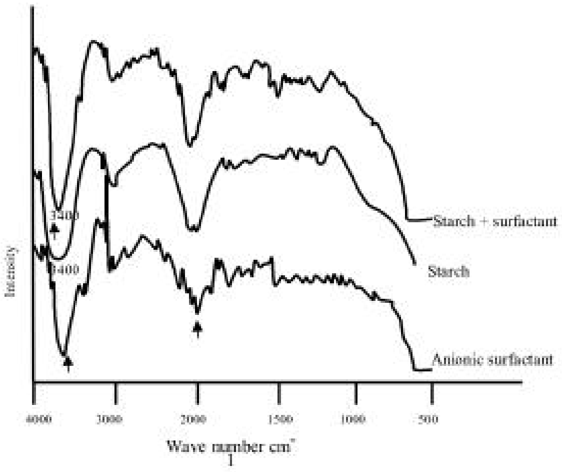


Fig.5: IR Spectra of Anionic surfactant, Starch and their mixed sample film

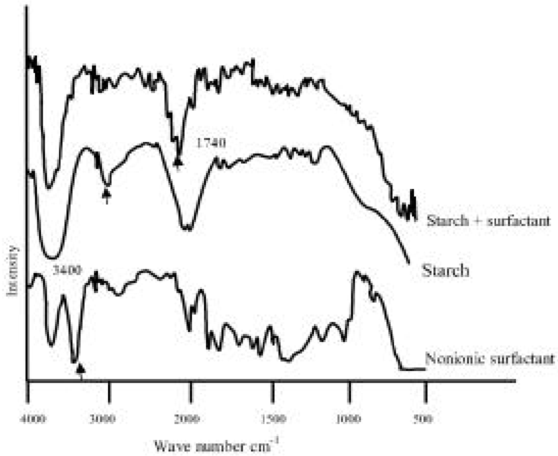
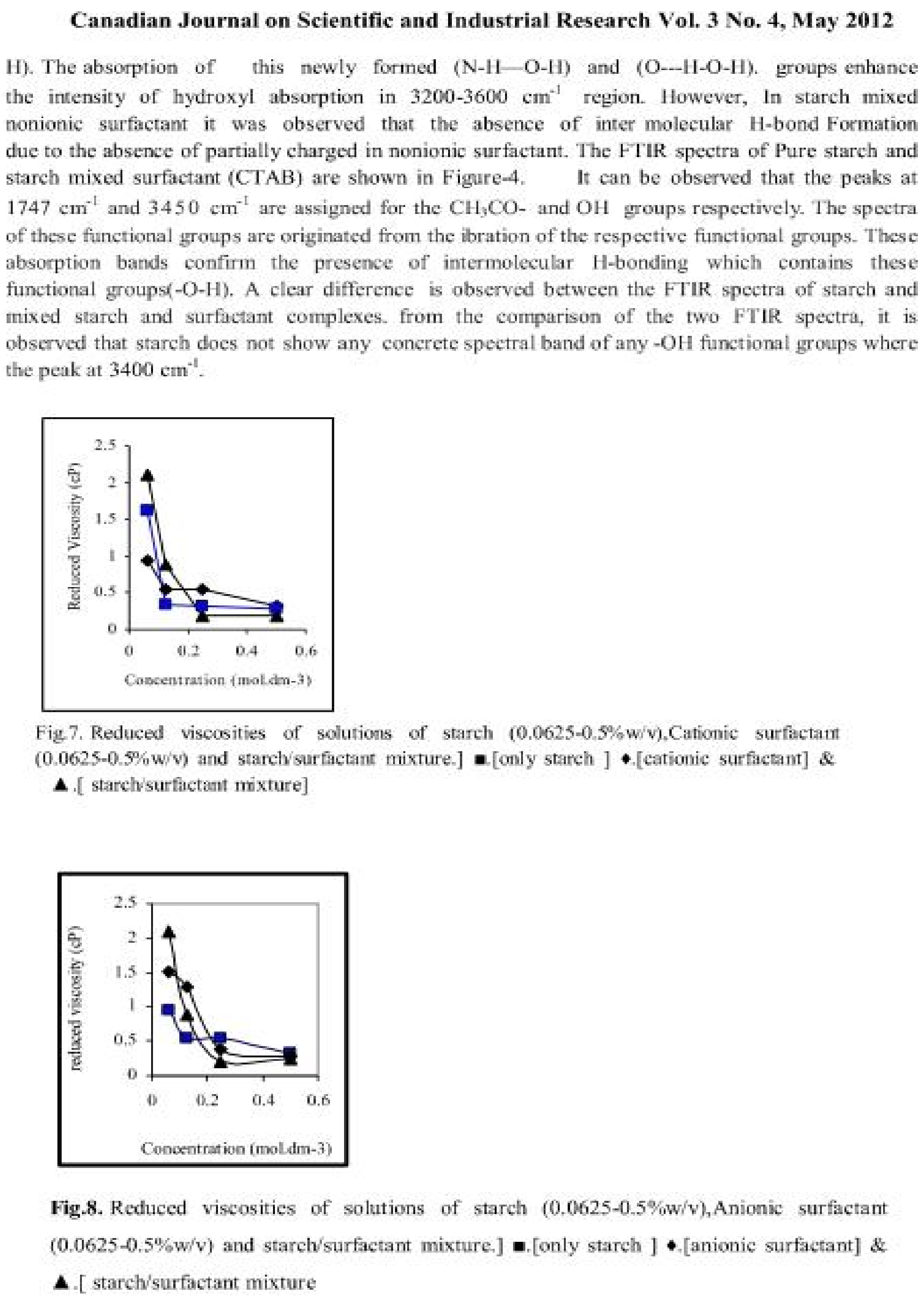


Fig.6: IR Spectra of Nonionic surfactant, Starch and their mixed sample film

The IR-Spectra of pure starch, various surfactants and their mixed sample film were recorded by Shimadzu FTIR-8900 Spectrophotometer for BCSIR Lab Dhaka. The infrared spectra of starch, various surfactants (cationic, anionic & nonionic) and their mixed films are shown in Fig. 4, 5 & 6 respectively. From the Fig. 4, 5 & 6 it is observed that the broad absorption band (3200-3600 cm^{-1}) represents the hydroxyl (-OH) in starch molecule but in SDS (anionic) and CTAB(cationic) surfactants absorption peak of hydroxyl group which is absent but during mixing of starch with this two types of surfactants broad peak of hydroxyl group is found .It is indicated that obviously inter molecular Hydrogen bond formation with polar(head group) hydrophilic part of mentioned types surfactants. CTAB and ether group of SDS react with the hydroxyl group starchl-OH) and form a intra –molecular H-bond (N-H—O-H) and (O---H-O-



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H). The absorption of this newly formed (N-H—O-H) and (O---H-O-H). groups enhance the intensity of hydroxyl absorption in 3200-3600 cm^{-1} region. However, In starch mixed nonionic surfactant it was observed that the absence of inter molecular H-bond Formation due to the absence of partially charged in nonionic surfactant. The FTIR spectra of Pure starch and starch mixed surfactant (CTAB) are shown in Figure-4. It can be observed that the peaks at 1747 cm^{-1} and 3450 cm^{-1} are assigned for the CH_3CO- and OH groups respectively. The spectra of these functional groups are originated from the ibration of the respective functional groups. These absorption bands confirm the presence of intermolecular H-bonding which contains these functional groups(-O-H). A clear difference is observed between the FTIR spectra of starch and mixed starch and surfactant complexes. from the comparison of the two FTIR spectra, it is observed that starch does not show any concrete spectral band of any -OH functional groups where the peak at 3400 cm^{-1}.

Fig.7. Reduced viscosities of solutions of starch (0.0625-0.5%w/v),Cationic surfactant (0.0625-0.5%w/v) and starch/surfactant mixture.] ■.[only starch] ♦.[cationic surfactant] & ▲.[starch/surfactant mixture]

Fig.8. Reduced viscosities of solutions of starch (0.0625-0.5%w/v),Anionic surfactant (0.0625-0.5%w/v) and starch/surfactant mixture.] ■.[only starch] ♦.[anionic surfactant] & ▲.[starch/surfactant mixture

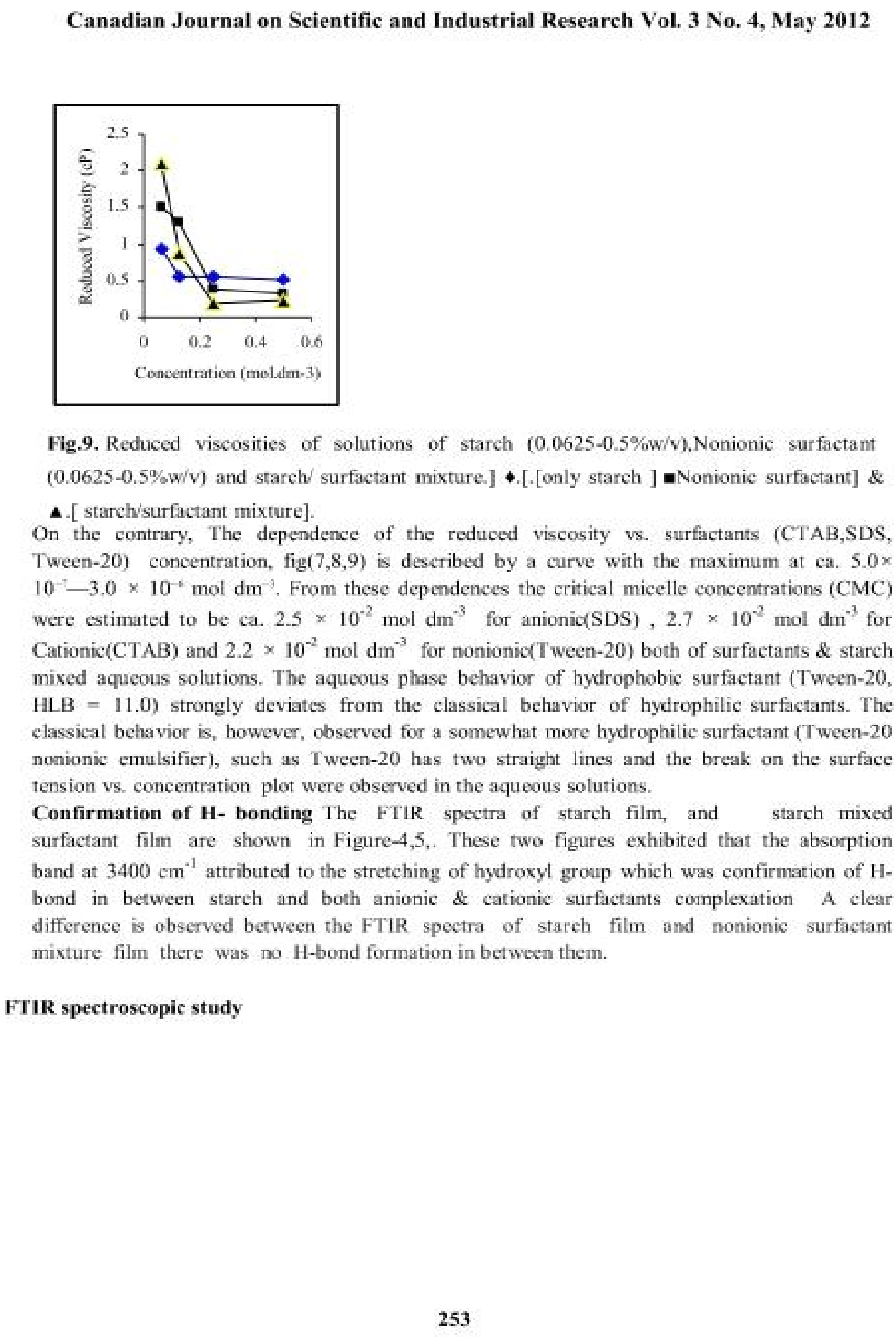
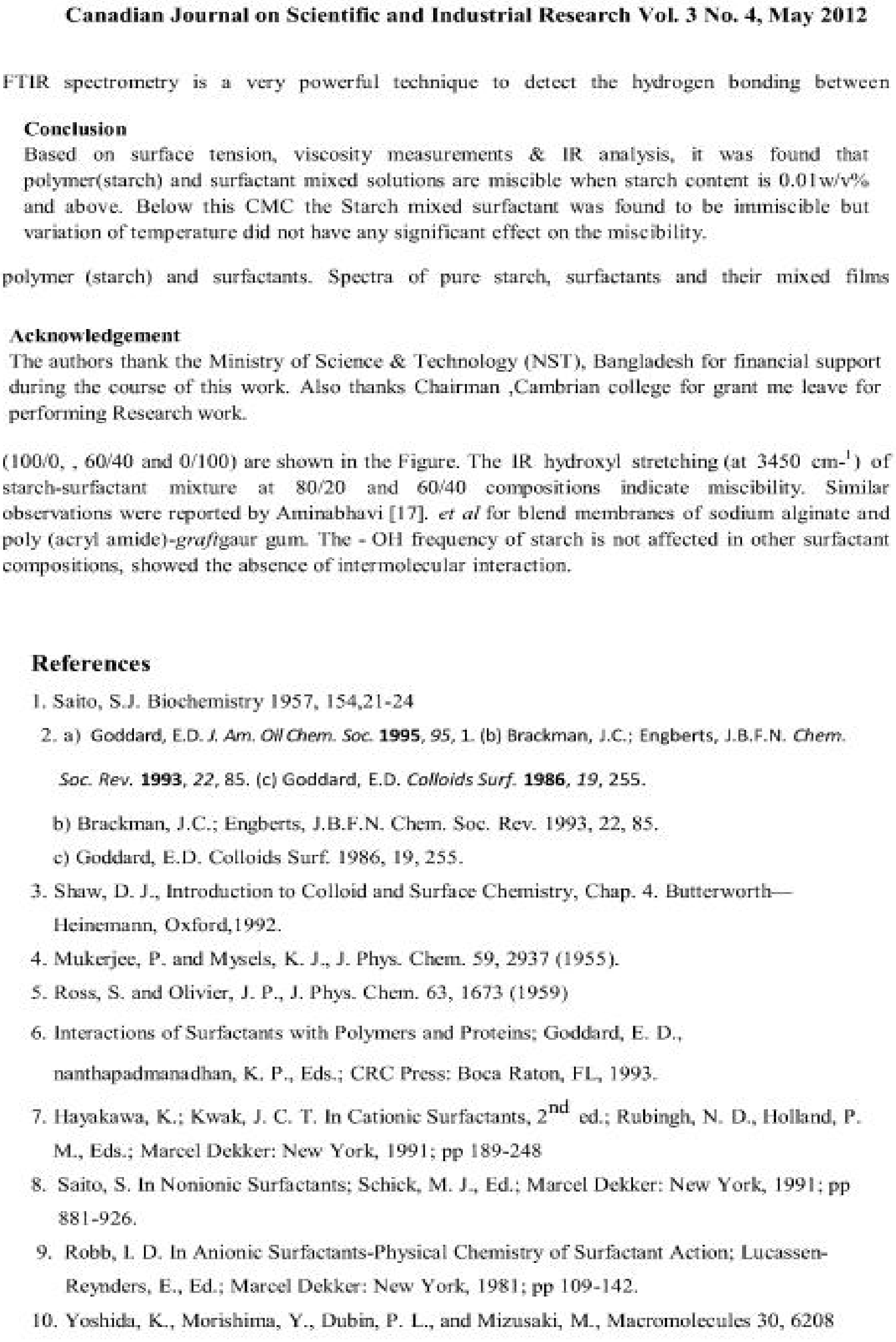


Fig.9. Reduced viscosities of solutions of starch (0.0625-0.5%w/v),Nonionic surfactant (0.0625-0.5%w/v) and starch/ surfactant mixture.] ♦.[.[only starch] ■Nonionic surfactant] & ▲.[starch/surfactant mixture].

On the contrary, The dependence of the reduced viscosity vs. surfactants (CTAB,SDS, Tween-20) concentration, fig(7,8,9) is described by a curve with the maximum at ca. 5.0×10^{-7}—3.0×10^{-4} mol dm^{-3}. From these dependences the critical micelle concentrations (CMC) were estimated to be ca. 2.5×10^{-2} mol dm^{-3} for anionic(SDS) , 2.7×10^{-2} mol dm^{-3} for Cationic(CTAB) and 2.2×10^{-2} mol dm^{-3} for nonionic(Tween-20) both of surfactants & starch mixed aqueous solutions. The aqueous phase behavior of hydrophobic surfactant (Tween-20, HLB = 11.0) strongly deviates from the classical behavior of hydrophilic surfactants. The classical behavior is, however, observed for a somewhat more hydrophilic surfactant (Tween-20 nonionic emulsifier), such as Tween-20 has two straight lines and the break on the surface tension vs. concentration plot were observed in the aqueous solutions.

Confirmation of H- bonding The FTIR spectra of starch film, and starch mixed surfactant film are shown in Figure-4,5,. These two figures exhibited that the absorption band at 3400 cm^{-1} attributed to the stretching of hydroxyl group which was confirmation of H-bond in between starch and both anionic & cationic surfactants complexation A clear difference is observed between the FTIR spectra of starch film and nonionic surfactant mixture film there was no H-bond formation in between them.

FTIR spectroscopic study



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FTIR spectrometry is a very powerful technique to detect the hydrogen bonding between

Conclusion

Based on surface tension, viscosity measurements & IR analysis, it was found that polymer(starch) and surfactant mixed solutions are miscible when starch content is 0.01w/v% and above. Below this CMC the Starch mixed surfactant was found to be immiscible but variation of temperature did not have any significant effect on the miscibility.

polymer (starch) and surfactants. Spectra of pure starch, surfactants and their mixed films

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(100/0, , 60/40 and 0/100) are shown in the Figure. The IR hydroxyl stretching (at 3450 cm-^{1}) of starch-surfactant mixture at 80/20 and 60/40 compositions indicate miscibility. Similar observations were reported by Aminabhavi [17]. *et al* for blend membranes of sodium alginate and poly (acryl amide)-*grafi*gaur gum. The - OH frequency of starch is not affected in other surfactant compositions, showed the absence of intermolecular interaction.

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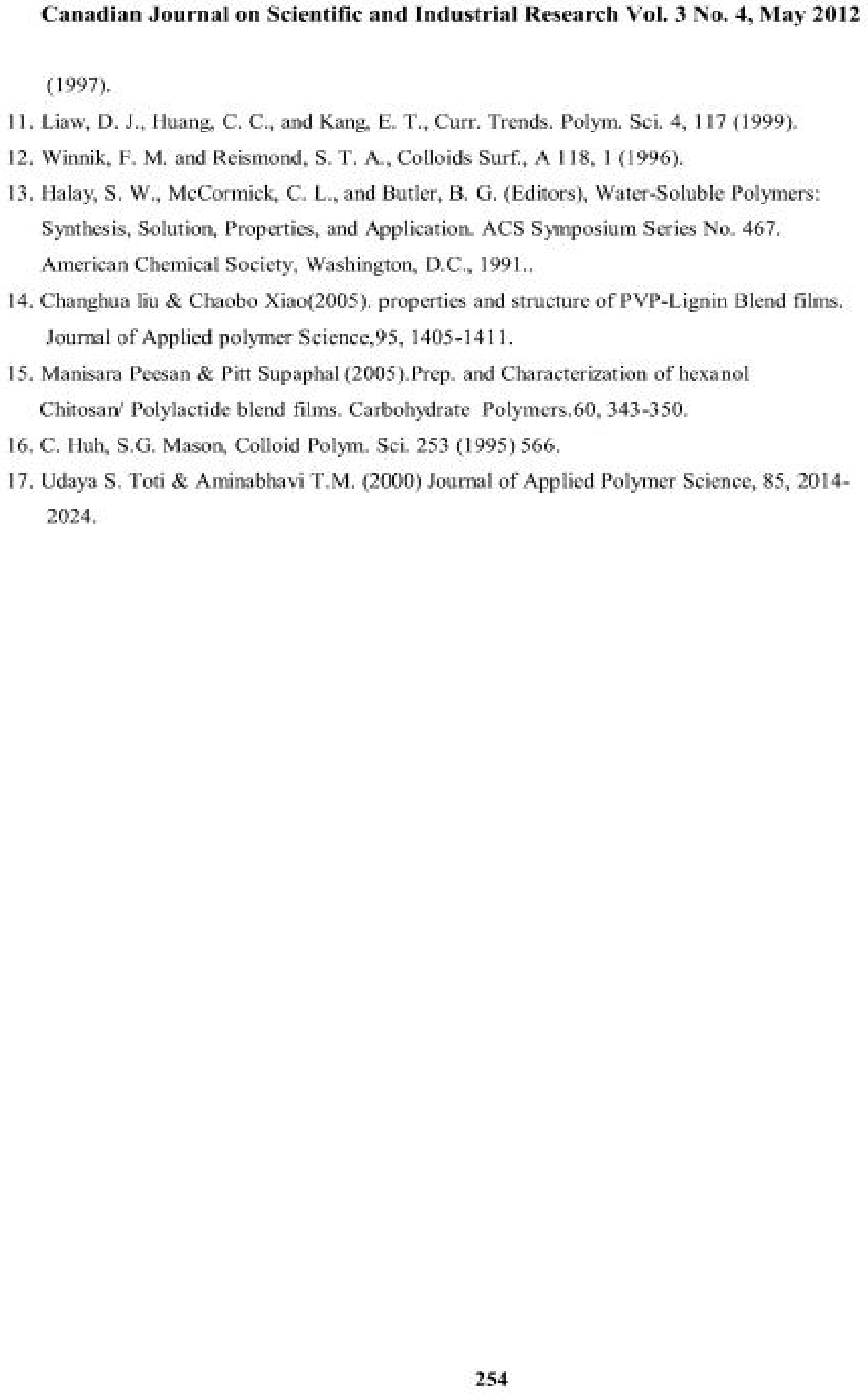

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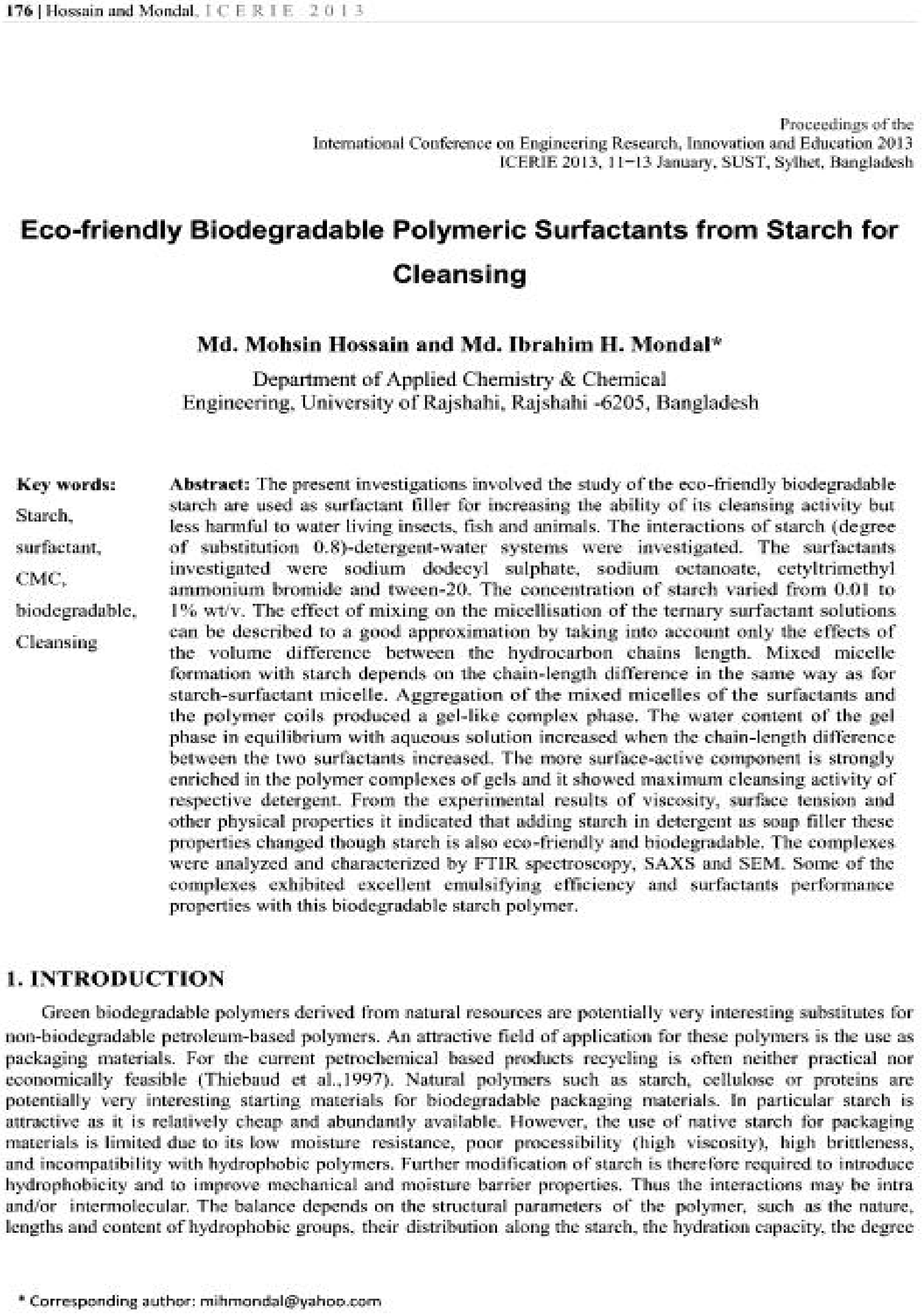

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Eco-friendly Biodegradable Polymeric Surfactants from Starch for Cleansing

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Key words:
Starch,
surfactant,
CMC,
biodegradable,
Cleansing

Abstract: The present investigations involved the study of the eco-friendly biodegradable starch are used as surfactant filler for increasing the ability of its cleansing activity but less harmful to water living insects, fish and animals. The interactions of starch (degree of substitution 0.8)-detergent-water systems were investigated. The surfactants investigated were sodium dodecyl sulphate, sodium octanoate, cetyltrimethyl ammonium bromide and tween-20. The concentration of starch varied from 0.01 to 1% wt/v. The effect of mixing on the micellisation of the ternary surfactant solutions can be described to a good approximation by taking into account only the effects of the volume difference between the hydrocarbon chains length. Mixed micelle formation with starch depends on the chain-length difference in the same way as for starch-surfactant micelle. Aggregation of the mixed micelles of the surfactants and the polymer coils produced a gel-like complex phase. The water content of the gel phase in equilibrium with aqueous solution increased when the chain-length difference between the two surfactants increased. The more surface-active component is strongly enriched in the polymer complexes of gels and it showed maximum cleansing activity of respective detergent. From the experimental results of viscosity, surface tension and other physical properties it indicated that adding starch in detergent as soap filler these properties changed though starch is also eco-friendly and biodegradable. The complexes were analyzed and characterized by FTIR spectroscopy, SAXS and SEM. Some of the complexes exhibited excellent emulsifying efficiency and surfactants performance properties with this biodegradable starch polymer.

1. INTRODUCTION

Green biodegradable polymers derived from natural resources are potentially very interesting substitutes for non-biodegradable petroleum-based polymers. An attractive field of application for these polymers is the use as packaging materials. For the current petrochemical based products recycling is often neither practical nor economically feasible (Thiebaud et al.,1997). Natural polymers such as starch, cellulose or proteins are potentially very interesting starting materials for biodegradable packaging materials. In particular starch is attractive as it is relatively cheap and abundantly available. However, the use of native starch for packaging materials is limited due to its low moisture resistance, poor processibility (high viscosity), high brittleness, and incompatibility with hydrophobic polymers. Further modification of starch is therefore required to introduce hydrophobicity and to improve mechanical and moisture barrier properties. Thus the interactions may be intra and/or intermolecular. The balance depends on the structural parameters of the polymer, such as the nature, lengths and content of hydrophobic groups, their distribution along the starch, the hydration capacity, the degree

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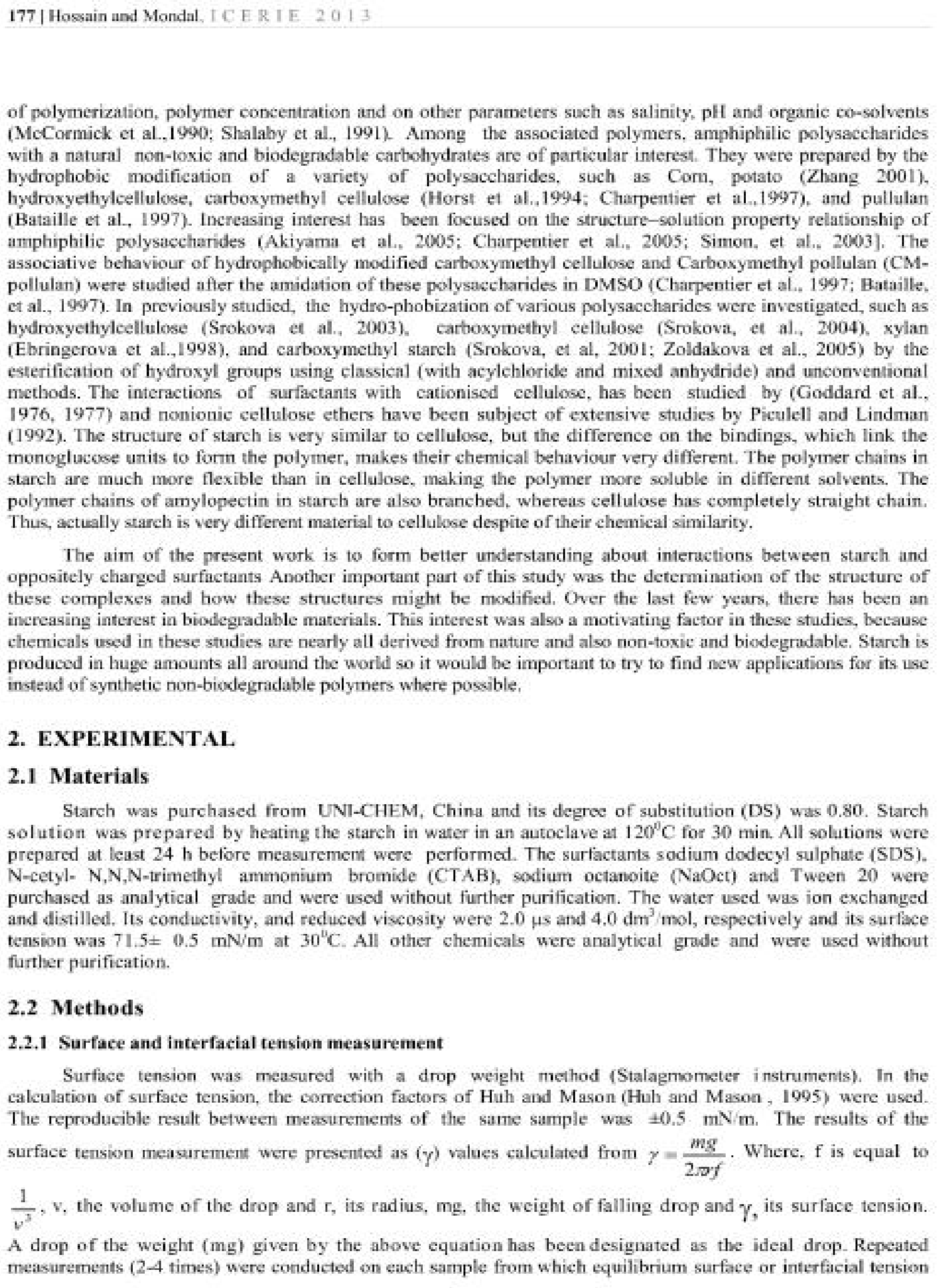


of polymerization, polymer concentration and on other parameters such as salinity, pH and organic co-solvents (McCormick et al.,1990; Shalaby et al., 1991). Among the associated polymers, amphiphilic polysaccharides with a natural non-toxic and biodegradable carbohydrates are of particular interest. They were prepared by the hydrophobic modification of a variety of polysaccharides, such as Corn, potato (Zhang 2001), hydroxyethylcellulose, carboxymethyl cellulose (Horst et al.,1994; Charpentier et al.,1997), and pullulan (Bataille et al., 1997). Increasing interest has been focused on the structure–solution property relationship of amphiphilic polysaccharides (Akiyama et al., 2005; Charpentier et al., 2005; Simon, et al., 2003]. The associative behaviour of hydrophobically modified carboxymethyl cellulose and Carboxymethyl pollulan (CM-pollulan) were studied after the amidation of these polysaccharides in DMSO (Charpentier et al., 1997; Bataille, et al., 1997). In previously studied, the hydro-phobization of various polysaccharides were investigated, such as hydroxyethylcellulose (Srokova et al., 2003), carboxymethyl cellulose (Srokova, et al., 2004), xylan (Ebringerova et al.,1998), and carboxymethyl starch (Srokova, et al, 2001; Zoldakova et al., 2005) by the esterification of hydroxyl groups using classical (with acylchloride and mixed anhydride) and unconventional methods. The interactions of surfactants with cationised cellulose, has been studied by (Goddard et al., 1976, 1977) and nonionic cellulose ethers have been subject of extensive studies by Piculell and Lindman (1992). The structure of starch is very similar to cellulose, but the difference on the bindings, which link the monoglucose units to form the polymer, makes their chemical behaviour very different. The polymer chains in starch are much more flexible than in cellulose, making the polymer more soluble in different solvents. The polymer chains of amylopectin in starch are also branched, whereas cellulose has completely straight chain. Thus, actually starch is very different material to cellulose despite of their chemical similarity.

The aim of the present work is to form better understanding about interactions between starch and oppositely charged surfactants Another important part of this study was the determination of the structure of these complexes and how these structures might be modified. Over the last few years, there has been an increasing interest in biodegradable materials. This interest was also a motivating factor in these studies, because chemicals used in these studies are nearly all derived from nature and also non-toxic and biodegradable. Starch is produced in huge amounts all around the world so it would be important to try to find new applications for its use instead of synthetic non-biodegradable polymers where possible.

2. EXPERIMENTAL

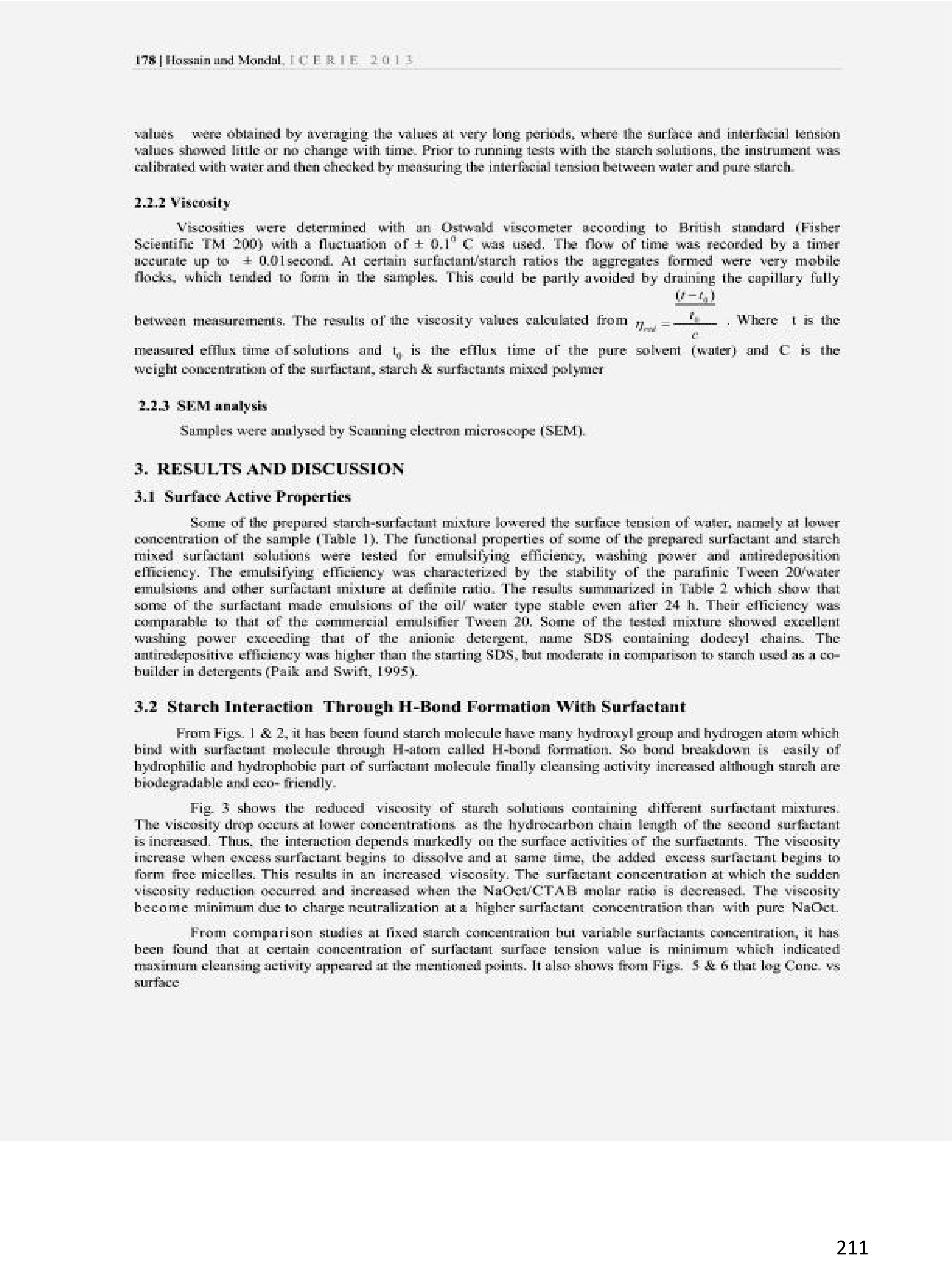
2.1 Materials

Starch was purchased from UNI-CHEM, China and its degree of substitution (DS) was 0.80. Starch solution was prepared by heating the starch in water in an autoclave at 120^0C for 30 min. All solutions were prepared at least 24 h before measurement were performed. The surfactants sodium dodecyl sulphate (SDS), N-cetyl- N,N,N-trimethyl ammonium bromide (CTAB), sodium octanoite (NaOct) and Tween 20 were purchased as analytical grade and were used without further purification. The water used was ion exchanged and distilled. Its conductivity, and reduced viscosity were 2.0 µs and 4.0 dm^3/mol, respectively and its surface tension was 71.5± 0.5 mN/m at 30^0C. All other chemicals were analytical grade and were used without further purification.

2.2 Methods

2.2.1 Surface and interfacial tension measurement

Surface tension was measured with a drop weight method (Stalagmometer instruments). In the calculation of surface tension, the correction factors of Huh and Mason (Huh and Mason , 1995) were used. The reproducible result between measurements of the same sample was ±0.5 mN/m. The results of the surface tension measurement were presented as (γ) values calculated from $\gamma = \frac{mg}{2\pi r f}$. Where, f is equal to $\frac{1}{v^3}$, v, the volume of the drop and r, its radius, mg, the weight of falling drop and γ, its surface tension. A drop of the weight (mg) given by the above equation has been designated as the ideal drop. Repeated measurements (2-4 times) were conducted on each sample from which equilibrium surface or interfacial tension



values were obtained by averaging the values at very long periods, where the surface and interfacial tension values showed little or no change with time. Prior to running tests with the starch solutions, the instrument was calibrated with water and then checked by measuring the interfacial tension between water and pure starch.

2.2.2 Viscosity

Viscosities were determined with an Ostwald viscometer according to British standard (Fisher Scientific TM 200) with a fluctuation of ± 0.1^0 C was used. The flow of time was recorded by a timer accurate up to ± 0.01second. At certain surfactant/starch ratios the aggregates formed were very mobile flocks, which tended to form in the samples. This could be partly avoided by draining the capillary fully between measurements. The results of the viscosity values calculated from $\eta_{red} = \frac{\frac{(t-t_0)}{t_0}}{c}$. Where t is the measured efflux time of solutions and t_0 is the efflux time of the pure solvent (water) and C is the weight concentration of the surfactant, starch & surfactants mixed polymer

2.2.3 SEM analysis

Samples were analysed by Scanning electron microscope (SEM).

3. RESULTS AND DISCUSSION

3.1 Surface Active Properties

Some of the prepared starch-surfactant mixture lowered the surface tension of water, namely at lower concentration of the sample (Table 1). The functional properties of some of the prepared surfactant and starch mixed surfactant solutions were tested for emulsifying efficiency, washing power and antiredeposition efficiency. The emulsifying efficiency was characterized by the stability of the parafinic Tween 20/water emulsions and other surfactant mixture at definite ratio. The results summarized in Table 2 which show that some of the surfactant made emulsions of the oil/ water type stable even after 24 h. Their efficiency was comparable to that of the commercial emulsifier Tween 20. Some of the tested mixture showed excellent washing power exceeding that of the anionic detergent, name SDS containing dodecyl chains. The antiredepositive efficiency was higher than the starting SDS, but moderate in comparison to starch used as a co-builder in detergents (Paik and Swift, 1995).

3.2 Starch Interaction Through H-Bond Formation With Surfactant

From Figs. 1 & 2, it has been found starch molecule have many hydroxyl group and hydrogen atom which bind with surfactant molecule through H-atom called H-bond formation. So bond breakdown is easily of hydrophilic and hydrophobic part of surfactant molecule finally cleansing activity increased although starch are biodegradable and eco- friendly.

Fig. 3 shows the reduced viscosity of starch solutions containing different surfactant mixtures. The viscosity drop occurs at lower concentrations as the hydrocarbon chain length of the second surfactant is increased. Thus, the interaction depends markedly on the surface activities of the surfactants. The viscosity increase when excess surfactant begins to dissolve and at same time, the added excess surfactant begins to form free micelles. This results in an increased viscosity. The surfactant concentration at which the sudden viscosity reduction occurred and increased when the NaOct/CTAB molar ratio is decreased. The viscosity become minimum due to charge neutralization at a higher surfactant concentration than with pure NaOct.

From comparison studies at fixed starch concentration but variable surfactants concentration, it has been found that at certain concentration of surfactant surface tension value is minimum which indicated maximum cleansing activity appeared at the mentioned points. It also shows from Figs. 5 & 6 that log Conc. vs surface

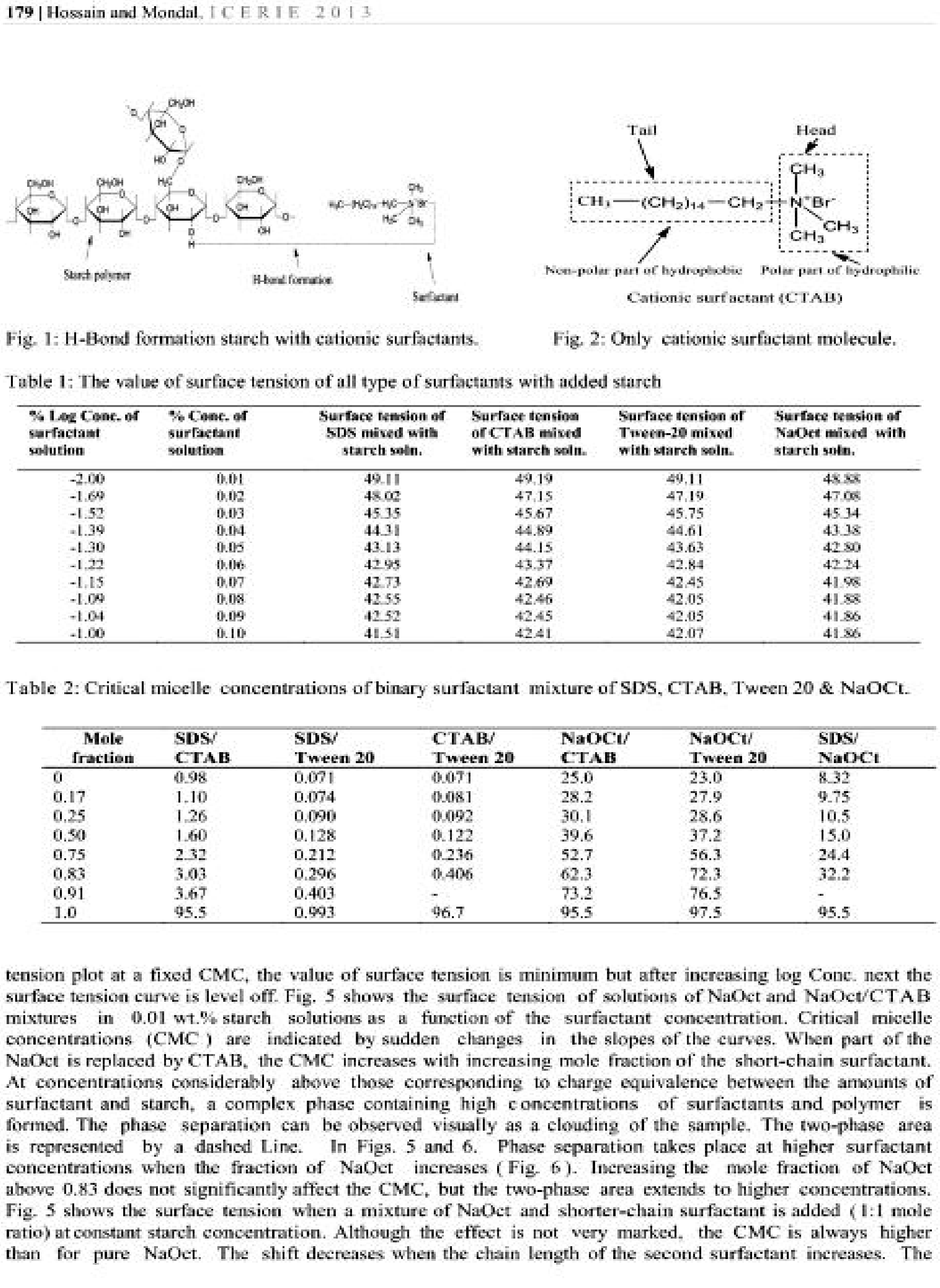


Fig. 1: H-Bond formation starch with cationic surfactants.

Fig. 2: Only cationic surfactant molecule.

Table 1: The value of surface tension of all type of surfactants with added starch

% Log Conc. of surfactant solution	% Conc. of surfactant solution	Surface tension of SDS mixed with starch soln.	Surface tension of CTAB mixed with starch soln.	Surface tension of Tween-20 mixed with starch soln.	Surface tension of NaOct mixed with starch soln.
-2.00	0.01	49.11	49.19	49.11	48.88
-1.69	0.02	48.02	47.15	47.19	47.08
-1.52	0.03	45.35	45.67	45.75	45.34
-1.39	0.04	44.31	44.89	44.61	43.38
-1.30	0.05	43.13	44.15	43.63	42.80
-1.22	0.06	42.95	43.37	42.84	42.24
-1.15	0.07	42.73	42.69	42.45	41.98
-1.09	0.08	42.55	42.46	42.05	41.88
-1.04	0.09	42.52	42.45	42.05	41.86
-1.00	0.10	41.51	42.41	42.07	41.86

Table 2: Critical micelle concentrations of binary surfactant mixture of SDS, CTAB, Tween 20 & NaOCt.

Mole fraction	SDS/ CTAB	SDS/ Tween 20	CTAB/ Tween 20	NaOCt/ CTAB	NaOCt/ Tween 20	SDS/ NaOCt
0	0.98	0.071	0.071	25.0	23.0	8.32
0.17	1.10	0.074	0.081	28.2	27.9	9.75
0.25	1.26	0.090	0.092	30.1	28.6	10.5
0.50	1.60	0.128	0.122	39.6	37.2	15.0
0.75	2.32	0.212	0.236	52.7	56.3	24.4
0.83	3.03	0.296	0.406	62.3	72.3	32.2
0.91	3.67	0.403	-	73.2	76.5	-
1.0	95.5	0.993	96.7	95.5	97.5	95.5

tension plot at a fixed CMC, the value of surface tension is minimum but after increasing log Conc. next the surface tension curve is level off. Fig. 5 shows the surface tension of solutions of NaOct and NaOct/CTAB mixtures in 0.01 wt.% starch solutions as a function of the surfactant concentration. Critical micelle concentrations (CMC) are indicated by sudden changes in the slopes of the curves. When part of the NaOct is replaced by CTAB, the CMC increases with increasing mole fraction of the short-chain surfactant. At concentrations considerably above those corresponding to charge equivalence between the amounts of surfactant and starch, a complex phase containing high concentrations of surfactants and polymer is formed. The phase separation can be observed visually as a clouding of the sample. The two-phase area is represented by a dashed Line. In Figs. 5 and 6. Phase separation takes place at higher surfactant concentrations when the fraction of NaOct increases (Fig. 6). Increasing the mole fraction of NaOct above 0.83 does not significantly affect the CMC, but the two-phase area extends to higher concentrations. Fig. 5 shows the surface tension when a mixture of NaOct and shorter-chain surfactant is added (1:1 mole ratio) at constant starch concentration. Although the effect is not very marked, the CMC is always higher than for pure NaOct. The shift decreases when the chain length of the second surfactant increases. The concentration at which the gel phase separates increases in the order NaOct<CTAB<SDS<Tween 20. Redissolution, which is not complete with this highly charged starch (DS=0.80), also takes place at a slightly higher concentration the shorter is the chain length of the second surfactant. Here it is mention that starch is obtained from nature but detergent is chemical substance which is harmful for water living organism not only this starch is biodegradable so it is eco-friendly.

3.3 Scanning Electron Micrograph

Fig.7. a and b show SEM images of only Starch and only surfactant suface. It can be seen from Fig. 7a and b that the surface of the starch and surfactant is quite different from that of surface of starch-SDS product. So, at a certain temperature and concentration, starch interact with the surfactant through the formation of micelle.

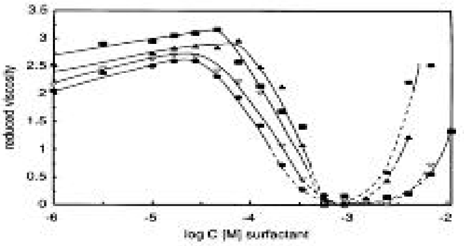


Fig. 3: Reduced viscosities of solutions of potato starch (0.01 wt.%, DS=0.80) and NaOct/ second sur-factant mixtures. The surfactants were NaOct (⬬), NaOct /CTAB (▼), NaOct/SDS (◆) and NaOct/Tween-20 (▲). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The two-phase domain is indicated by the dotted line.

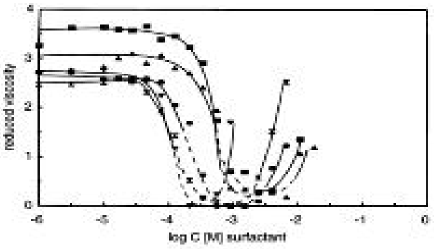


Fig. 4: Reduced viscosities of solutions of starch (0.01 wt. %, DS=0.80) and SDS/CTAB mixture. The molar ratios of the surfactants were 1:0 (▼), 3:1 (⧗), 1:1 (⬬), 1:3 (▲) and 1:5 (◆). The two-phase domain is indicated by the dotted line.

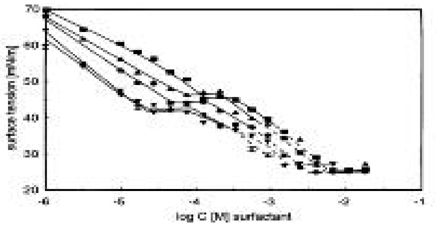


Fig. 5: Surface tensions of solutions of potato starch (0.01 wt.%, DS=0.80) and SDS/CTAB mixture. The molar ratios of the surfactants were 1:1 (⬬), 3:1 (⧗), 1:0 (▼)1:3(▲) and 1:5 (◆). The two-phase domain is indicated by the dotted line.

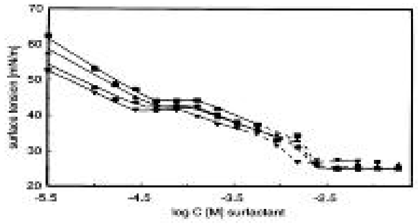


Fig. 6: Surface tension of solutions of potato starch (0.01 wt.%, DS=0.80) and NaOct/second surfactant mixtures. The surfactants were NaOct (⬬), NaOct/CTAB (▼), NaOct/SDS (◆) and NaOct/ Tween-20 (▲). The molar ratio of the surfactants in the surfactant mixtures was 1:1. The two-phase domain is indicated by the dotted line.

4. CONCLUSION

The investigations presented in this paper show that strong ionic interaction occurs between cationic and anionic surfactants (CTAB, SDS, NaOct) except non ionic surfactant (Tween-20) and starch polymer, leads to phase separation and precipitation of the formed amorphous complexes. Complex formation on starch depends on the chain length difference in exactly in the same way as for free mixed micelles .The separated complex phase is a hydrophobic, highly viscous and gel like containing 40 to 60% water. The highly and low water content of the complex phase indicates that the interactions between the starch and ionic surfactants are very strong and they are capable more effective cleansing than normal detergent available our indoor market but also biodegradable and eco-friendly for environment. The Ionic surfactants (CTAB, SDS, NaOct) at concentrations above its critical micelle concentration reduces the inter-polymer association through micelles formation around hydrophobic (alkyl group) groups. The presence of a miscible starch molecule also reduces inter-polymer association by preferential solvation of the hydrophobic groups.

(a) starch (b)Surfactant (SDS) (C) starch with SDS mixture

Fig. 7. SEM Image of (a) starch, (b) Surfactant (SDS) and (c) starch with SDS mixture

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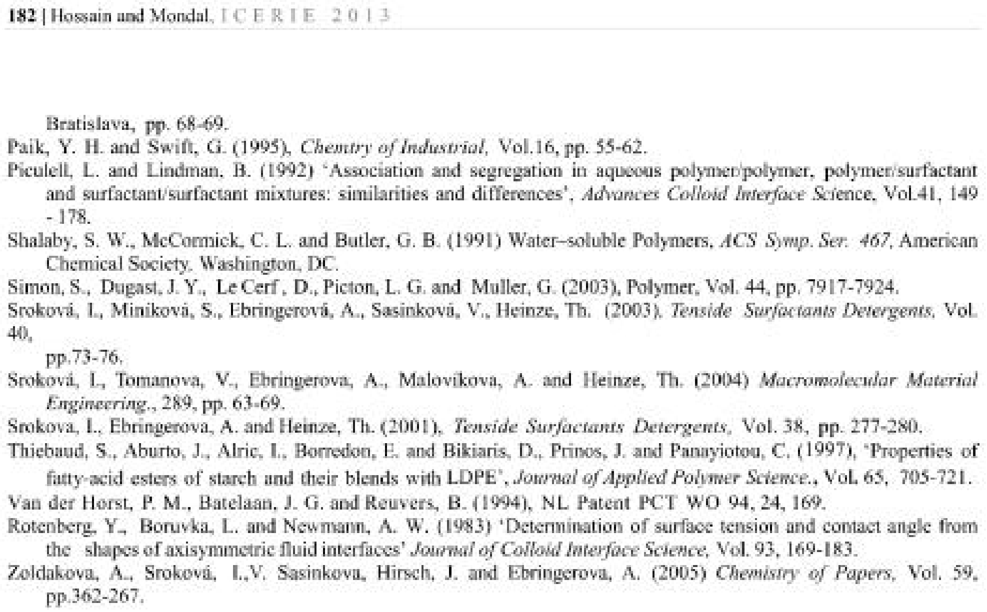

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13.6 CURRICULUM VITAE

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SCHOLARSHIP: Primary and Junior Scholarship in 1979 and 1982

FELLOWSHIP: **NSICT fellowship** from Ministry of Science, Information and Technology, **The People Republic of Bangladesh**, three fiscal year (2008, 2009 and 2010)