CHAPTER 1

Introduction
1.1. **Introduction:** According to Barber the earliest mention of sugarcane is found in India writing of the period 1400-1000 B.C., and asserted that no such references have been found in ancient Chinese or European records. While agriculture can be traced back to 8000 years, crude sugar was developed by 400 B.C.\(^{1,2}\) Chaturvedi dates the introduction in China from India around 8000 B.C. However, Chinese\(^{1,3,4}\) literature records sugarcane as early as 475 B.C. Cane culture\(^{4}\) spread slowly reaching Persia by A.D.500. Egypt by A.D.710, Southern Spain (A.D.755), Sicily (A.D. 950), Madeira, Canary Island, Mexico, Brazil and Peru, West Indian Islands, Mauritius, Hawaii, Australia, Fiji and South Africa.\(^{3}\)

India is known\(^{5}\) as the original home of sugar and sugarcane. Indian mythology supports the above fact, as it contains legends showing the origin of sugarcane. India is the second largest producer of sugarcane next to Brazil. Presently, about 4 million hectares of land is under sugarcane with an average yield of 70 tonnes per hectare. India is the largest single producer of sugar including traditional cane sugar sweeteners Khandasari and Gur equivalent to 26 million tones raw value followed by Brazil in the second place at 18.5 million tones.

"Cane sugar" is the non technical chemical name for the substance whose technical name is **sucrose**. It occurs\(^{6}\) in all parts of the sugarcane plant and is more abundant in the cane stalk. The scientific name of sugarcane\(^{1-4}\) is **Saccharum Officinarum**. Sugarcane is tropical grass belonging to the cane tribe (Andropogoneae) as sorghum, Johnsongrass and corn maize. The sugarcane is a complex hybrid of more than hundred species of the genus saccharum; sugarcane cultivation methods, area and
production have undergone innumerable changes in this country. At present sugar industry is a second largest agro-based industry in India.

Among sugar producing plants, sugar cane is responsible for about 70% of the world sugar production; the remaining 30% is coming from sugar beet, a temperate zone crop. Sugarcane cultivated mainly in tropics though, it is also grown in subtropical area in India. Sugarcane crop plays a vital role in the national economy, as it is one of the most commercial crops for the extraction of sucrose. Sugar industries play a major role in Indian economy.

Sugarcane grows in all tropical and subtropical countries. A hot, moist climate with a dry ripening season is suitable for its growth, while a very low temperature or suddenly lowering temperature may affect adversely. The sugarcane consists of roots, stalk and leaves, the roots penetrate into the soil to a considerable extent especially in search of water, minerals and nutrients. The stalk of cane is built up of a series of inter nodes separated from one another by hard portion wall called the nodes. The stalk of cane may run up to 12 feet. The outer shell of the cane is hard and it is called the rind of the cane. The surface of the rind coated to a greater or a lesser extent with a kind of wax and the inside is called pith. The pith, a soft fibrous part of the cane that contains bulk of the juice in its cellular structure. In the pith of the cells, the fibrous strand or fibro vascular bundles, that run lengthwise, serve as channels along with them water and nutrients from the roots reach the leaves and the sugar products formed by the process of photosynthesis in leaves will pass down through them into the stream. The rind is hard and tough while the nodes are hard and woody, at each node a bud appears. This forms the basis of future germination of the cane.
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Sugar and sugar polymers\textsuperscript{3,10} are synthesized in plants and used by plants and animals as convenient source of energy. A metabolic relationship exists between the amount of sugar in an organism and its stored condensed energy from polysaccharide. The organism produces more or less sugar out of the polysaccharide energy store according to its environment and stage of growth.

1.2. History of Sugar Industry: The sugar industry is one of the largest food industry in India, with more than 500 sugar mills presently in operation in different parts of the country. Production of plantation\textsuperscript{11} white sugar or mill white sugar was first introduced in Java in 19\textsuperscript{th} century by \textit{carbonation process}. In the beginning of the present century, use of sulphur dioxide was introduced, which brought down the consumption of lime in cane juice clarification in the process of manufacture of white sugar from sugar cane. Purification of juice employing sulphur dioxide\textsuperscript{5,6,11-13} and lime is termed as \textit{"sulphitation process"}. In India this process was introduced in the year 1930.

Almost 85-90\% of white crystal sugar is produced by vacuum pan method. In India sugar is manufactured by sulphitation process.\textsuperscript{11,19-21} India is the major sugar producing country, employing sulphitation on an extensive scale for manufacture of white sugar.

1.3. Manufacture of Sugar: There are various processes\textsuperscript{14,15} used for sugar manufacturing world widely. Some of the important processes are:

1. Plantation white sugar manufacturing process by double carbonation and double sulphitation
2. Plantation white sugar manufacturing process by middle juice carbonation.
3. Plantation white sugar manufacturing process by liming and sulphitation
4. Raw sugar manufacturing processes
5. Refined sugar manufacturing processes.
1.4. **Plantation White Sugar by Double Sulphitation:** Juice is extracted from sugar cane. The raw juice after heating about 65°-75°C is treated with phosphoric acid, sulphur dioxide and dilute lime solution known as milk of lime for removal of impurities in suspension in a continuously working apparatus. The sulphur dioxide is generated by combustion of sulphur, while lime is either produced in lime klin from limestone or brought as such and stored in store room. The treated juice on boiling fed to continuous clarifier from which the clear juice is decanted, while the settled impurities known as mud. These mud or sludge separated in a clarifier, with the purified juice being withdrawn from the top, while the muddy solution at the bottom is further vacuum filtered to recycle the filtrate juice.

The clarified juice obtained from this process still contains bacterial remnants as well as macro molecular impurities, like dextran, starch, fat and waxes in the colloidal form. This gives the juice a dark, cloudy appearance that has an adverse effect upon the quality of the final product. The undesired materials were removed by filtration.

The clear juice with about 73-75% water is concentrated in a multiple effect evaporator under vacuum to yield syrup with about 37-43% water content. The syrup as again treated with sulfur dioxide before being sent to the pan station for crystallization of sugar. It is at vacuum pan boiling stage that the sugar crystal appears. The crystal containing the *mother liquor* is dropped from the pan in crystalliser and subsequently centrifuged in centrifugal machine for isolating sugar crystals from mother liquor, which again is sent to pan for boiling and recrystallisation. Repeated recrystallisation process ensures crystallization of white sugar from the molasses to maximum extent. The molasses an uncrystaliable sugar is separated and was used in the production of rectified spirit by fermentation process.
1.5. Flow Chart of Double Sulphitation Method:

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1.5. Flow Chart of Double Sulphitation Method:

1. Cane
   100 Tonnes
   Cane preparation

2. Immibition water
   10Bx 15Be
   Milk of lime (0.15T)
   Sulphur 0.05T

3. Cane
   100 Tonnes
   Milling
   Bagasse (30T)

4. Raw juice heating
   (100 T) 30°C
   Juice sulphitor
   (100 T) 65°C
   Juice sulphited heating
   (113.5 T) 105°C
   DORR Clarifier
   98.5 T 98°C
   Clear juice heating
   98.5 T 115°C (15Bx)
   Evaporator
   24.6525 T 60Bx
   Syrup sulphitor
   Vacuum pan
   Crystaliser
   De sugarisation in step

5. To distillery
   Final Molasses
   4 T
   Centrifugals
   Sugar white sugar (10T-13T)

6. Godown
   Bagging
   Grader

7. Bagasse saving 5T
   Boiler
   Steam

8. Condensate 48 T
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Some work has been done on the clarification processes in double sulphitation methods.\textsuperscript{6,15,16,20-22}

1. Juice is treated to pH 9.5 and then sulphited to neutrality in the cold
2. Juice is first sulphited to nearly 4.2 pH and then limed to neutrality
3. Juice is heated to 50° C limed to 9.5 pH and then sulphited to neutrality
4. Juice is heated to 70°C, limed to nearly 8.5 pH and then sulphited to simultaneously neutrality

Among these last method has been adopted as standard sulphitation process due to different merits claimed over them. Some technologists had studied the effect of pre liming and claimed certain advantages in the formation of good flocculation swelling, hydration, reduction in viscosity, faster settling etc.,

Necessarily the cane juice will be in acidic condition\textsuperscript{6,7} and the pH ranging 4.9-6.6. The acidity or alkalinity\textsuperscript{15} of cane juice in practice is not measured by actual titration but in terms of “Hydrogen ion concentration” by a logarithmic scale known as pH. The difference in these two methods is that while the titration gives the total acidity, the hydrogen ion concentration gives the active acidity.

The addition of milk of lime in the cold\textsuperscript{16,21} is to give an alkaline reaction, some colloids are precipitated by the formation of what may be termed a calcium floc and precipitated form consisting of mainly of calcium phosphate, iron and aluminum hydroxides. A calcium phosphate precipitate\textsuperscript{24-26} is a flocculent precipitate and remove certain colloids by adsorption. The settling screens our mechanically some of the coagulation is accelerated due to the heat and further precipitation of colloids occurs due to dehydration.

1.6. **Composition of Cane and Cane Juice:** The composition of sugarcane depends on the variety of cane,\textsuperscript{3,6} its maturity, the condition of the soil, the climatic condition
and also on agricultural practice. Sugarcane contains, in addition to sucrose, many other dissolved substances and cellulose or woody fiber. The composition of sugarcane varies from field to field and region to region but the typical composition of sugarcane is as follows.

### 1.6.1 Composition of sugarcane (in percentage):

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>74.50</td>
</tr>
<tr>
<td>Ash</td>
<td>0.50</td>
</tr>
<tr>
<td>Fiber</td>
<td>10.00</td>
</tr>
<tr>
<td>Sugars</td>
<td>14.0</td>
</tr>
<tr>
<td>Nitrogenous Bodies, Total N=0.06%</td>
<td>0.40</td>
</tr>
<tr>
<td>Fate and wax</td>
<td>0.20</td>
</tr>
<tr>
<td>Pectin (Gums)</td>
<td>0.20</td>
</tr>
<tr>
<td>Free acids</td>
<td>0.08</td>
</tr>
<tr>
<td>Combined acids</td>
<td>0.12</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>74.50</td>
</tr>
<tr>
<td>Ash</td>
<td>0.50</td>
</tr>
<tr>
<td>Fiber</td>
<td>10.00</td>
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</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

- **Silica SiO₂**: 0.25
- **Potash K₂O**: 0.12
- **Soda Na₂O**: 0.01
- **Lime CaO**: 0.02
- **Magnesia Mgo**: 0.01
- **Iron Fe₂O₃**: Trace
- **Phosphoric acid P₂O₅**: 0.07
- **Sulphuric acid SO₃**: 0.02
- **Cellulose**: 5.50
- **Pentosans Xylan**: 2.00
- **Cane-gum Araban**: 0.50
- **Lignin bodies etc.,**: 2.00
- **Sucrose**: 12.50
- **Dextrose**: 0.90
- **Levulose**: 0.60
- **Albuminods**: 0.12
- **Amides (as asparagin)**: 0.07
- **Amido acids (as aspartic)**: 0.20
- **Nitric acid**: 0.01
- **Ammonia**: Trace
- **Xanthin bodies**: Trace

7
### Composition of Non sugars in raw cane juice (in percentage)

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>69-75</td>
</tr>
<tr>
<td>Sucrose</td>
<td>8-16</td>
</tr>
<tr>
<td>Reducing Sugars (Dextrose, Levulose)</td>
<td>(0.5 - 2.0)</td>
</tr>
<tr>
<td>Hemicelluloses and pentosans (Xylan)</td>
<td>8.5</td>
</tr>
<tr>
<td>Pectins</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Organic Nitrogen compounds</strong></td>
<td></td>
</tr>
<tr>
<td>Higher Proteins (Albumin)</td>
<td>7.0</td>
</tr>
<tr>
<td>Simple proteins (Albuminoses &amp; peptoses)</td>
<td>2.0</td>
</tr>
<tr>
<td>Amino Acids (Glycine, Aspartic Acid)</td>
<td>9.5</td>
</tr>
<tr>
<td>Acid Amides (Asparagine, Glutamine)</td>
<td>15.5</td>
</tr>
<tr>
<td><strong>Organic Acids</strong> (other than Amino, Aconitic, Oxalic, Succinic, Glycolic, Malic)</td>
<td>13.05</td>
</tr>
<tr>
<td><strong>Colouring matter</strong></td>
<td></td>
</tr>
<tr>
<td>Chlorophyll, Anthocyan, Saccharatin, Tannins</td>
<td>17.0</td>
</tr>
<tr>
<td>Waxes Fats &amp; soaps cane wax</td>
<td>17.05</td>
</tr>
<tr>
<td><strong>Inorganic salts</strong></td>
<td></td>
</tr>
<tr>
<td>Phosphates, chlorides, sulfates, nitrates of sodium</td>
<td></td>
</tr>
<tr>
<td>Potassium, calcium, magnesium, Aluminum and</td>
<td>7.0</td>
</tr>
<tr>
<td>Iron chiefly</td>
<td>2.0</td>
</tr>
<tr>
<td>Silica</td>
<td></td>
</tr>
</tbody>
</table>

Although, the cane juice comprises the 3% non-sucrose (non-crystallisable solids). The principal non-crystallisable components are of the composition, invert sugars (1.5%), inorganic ash (0.5%) and organic compounds (1%) on the total juice percent. These constituents are considerable effect on juice clarification. The inorganic that are found normally in sugarcane juice are phosphate, sulphate, chloride as anions and silica, iron aluminum, calcium, magnesium, potassium and sodium as cat ions. Maximum inorganic constituents are found in juice obtained from immature cane tops.
The concentration of these ions decrease gradually from cane tops to lower portion of the plant. As a result, the cane tops are avoided for milling. Inorganic salts of cane that are extracted into juice are partially removed by normal clarification method. For instance, when juice is rich in phosphate, that could be brought down to 250-300mg/l by clarification.

The cane juice is opaque owing\(^6\) to the presence of colloids such as waxes, proteins, pentosans, gums, starch and silica. The colloids are particles existing in a permanent state of fine dispersion and they impart turbidity to the juice. These colloids do not settle ordinarily unless conditions are altered. The application of heat and addition of clarification bring about flocculation and coagulation. They may be coagulated\(^{16,27,28}\) by the action of electric current and adsorption by sucrose attraction using porous or flocculent material. Some colloids are flocculated easily while others do so with great difficulty. Each colloid has a characteristic pH at which flocculation occurs most easily. It is known as the ‘iso-electric point’ of the colloid. The quality of the product mainly depends on the efficiency of clarification.

Cane juice consists of dissolved and suspended impurities and can be classified into two sub-groups known as lyophobic and lyophillic. Their removal is of great importance from better sugar quality point of view. Lyophillic colloids are organic characterised by a strong attraction for the liquids. This property is manifested by degree of hydration, settling and high viscosity.

Lyophobic colloids\(^{18,27,29}\) are those less hydrated, more unstable in dispersion media and are characterized by a little effect on viscosity which include fats, waxes and other foreign particles which come from milling operation. These colloids have a great tendency towards micro-bios and forms glucosans and levuosans of lyophillic and
mucilaginous character. The quantum of colloids adhere in cane juice are 0.02-0.29% and the clarification may increase or decrease this quantity but removal have been reported from 10-15%.

It is clear from the foregoing discussion, the clarification is the main unit operation, where impurities react with clarificants to form precipitate and are eliminated form the process. During the clarification of the juice using alkaline chemicals or flocculating agents. It is to effect either a better clarified juice or a faster settling of mud and obtain a very good quality of final product.

Earlier to these, only natural flocculants such as algin, soybean extract, gum Arabic etc., were employed for the clarification. These are now, completely replaced by synthetic polymers (poly electrolytes).

The synthetic and modified natural polymer segment market is growing at a higher rate than the total water-soluble polymer market, this is because, they are not only displaying the natural polymers in many application, but are also creating entirely new end-use areas\(^{30,31}\). Their higher priced, they are replacing natural products because of

i. Greater efficiency: much lower dosage are needed to do a given job

ii. Increased versatility: they can be tailored a serve better a given need.

iii. Lower biological oxygen demand: important where stream pollution is a critical consideration

Synthetic high polymers are polyamines and are either poly acrylates\(^{31,33}\) (Sodium salts of acrylic acid with acrylamide). They exist in the form of thread like long chains and the molecular weight is the region of 3,000,000 necessarily. The molecule should be long enough to bridge the gap between two adjacent molecules of suspended matter.
1.7. **Classification of Polyelectrolytes:** During the last four decades, polyelectrolytes have been investigated intensively but still knowledge about their conformations, structuring and interactions with other molecules is rather poor, when compared to their natural analogues.\(^\text{34,35}\) In spite of a relatively poor understanding of polyelectrolytes, industrial applications is enormous and cover almost all segments of human life, e.g. from food to material and pharmaceutical technology.\(^\text{34,36,37}\) Recently, a special design hybrid of polyelectrolytes and inorganic particles promises to yield new materials for molecular electronics, drug delivery and nano technology.\(^\text{36}\) In biotechnology polyelectrolyte structures are used for the immobilization of enzymes and everyday the number of possible applications of polyelectrolytes increases.\(^\text{34,36,38,39}\)

Polyelectrolytes are water soluble polymer carrying ionic charge along the polymer chain.\(^\text{40,41}\) Depending upon the charge, these polymers are anionic or cationic. Polyelectrolytes are available in a wide range of molecular weights and charge densities. Polyelectrolytes have got a wide range of applications right from water purification, oil recovery,\(^\text{42}\) colour removal, sugar processing etc., Polyelectrolytes\(^\text{43,44}\) are both flocculants as well as deflocculants depending upon the molecular weight. A flocculant is essentially a solid liquid separating agent while a deflocculant is a dispersing agent.

Flocculants are also used for solid liquid separation in other industries such as the sugar industry. Flocculation is a process of bringing together small particles to form large particles,\(^\text{44}\) often highly porous in nature. The initial fine particles are usually thought of as being too small to be seen with the naked eye; They settle or are filterable only slowly. The flocculation process produces a large particle, a floc, that can be distinguished by the naked eye. In flocculation the final structure of floc is usually a
loose, three dimensional net work, resulting from the bridging of macromolecular flocculants between particles.

The macromolecules that carry covalently bound charged\textsuperscript{34,35} groups (cationic or anionic) and low molecules counter ions are called polyelectrolytes. However, every neutral polymer can be transformed into a polyelectrolyte by covalently attaching an appropriate number of ionic groups.\textsuperscript{41} A special class of polyelectrolytes called “Polyampholytes” macromolecules that carry both anionic and cationic groups covalently bound to the polymer chain. Polyelectrolytes are mostly produced by free radical, ionic, stepwise polymerization methods\textsuperscript{34,37,45} as well as by chemical modification of neutral polymers.

1.8. Working of Flocculants: Stoke’s Law predicts that spherical particles suspended in a fluid medium settle at a rate proportional to the fourth power of the particle radius. Thus large particles will settle much faster than smaller ones. Most particles while suspended in aqueous solution have a net negative surface charge.

- Unequal distribution of constituent ions on the particle surface.
- Ionisation of surface groups pH effect
- Specific adsorption on the particle surface of ions from solution
- Isomorphous substitution of silicone atoms by aluminum atoms in an alumino silicate mineral lattice (inorganic clays)

The above factors causes an electrical double layer around each particle and colloidal particle in aqueous solution will not settle very quickly. Interparticle interactions will cause repulsion and in spite of Brownian motion trying to bring them together the suspension becomes stable. The particles do not aggregate unless they are forced.\textsuperscript{21} The first phenomenon taking place in the process of flocculation is the neutralization of the net charge carried by each particle. Once charge neutralization takes place several
particles come together which will result in coagulation. Flocculation is the stage whereby the destabilized particles are induced to collect into larger aggregates. The aggregation is followed by rapid settling as per Stoke's law.

There are two possible mechanisms given for the phenomena of polyelectrolyte induced coagulation and flocculation.

1.9. **Types of Polyelectrolytes:** Polyelectrolyte flocculants can be generally divided into two groups, depending on their molecular character and mode of operation. Polyelectrolytes are both inorganic and organic exhibiting both flocculation and deflocculation properties. Inorganic polyelectrolytes exhibiting sedimentation property and are coagulants rather than flocculants. Whereas organic polyelectrolytes, exhibiting sedimentation property, and are invariably high molecular weight synthetic polymers. Inorganic flocculants are salt of multivalent metals like aluminum and iron that shows different mechanism in the process of sedimentation in comparison with organic polyelectrolytes. Polelectrolyte are classified into:

- Anionic (Negatively charged)
- Cationic (Positively charged)
- Non ionic (No charge)

In analogy to the low molecular electrolytes one distinguishes between weak and strong polyelectrolytes. The distinction is based on the charge distribution along the polymer chain. On the basis of molecular architecture polyelectrolytes are divided into linear and branched polyelectrolytes.

1.9.1. **Linear Polyelectrolytes:** The class of polyelectrolytes where a large number of atoms are connected together in order to make a chain called the backbone. The
backbone is linear in a topological sense, but the actual shape of the polymers in solution is quite different.\textsuperscript{35,46}

1.9.2. Branched Polyelectrolytes: These are the chains which are not linear in topological sense. However, the physical of branched molecules is less known in comparison with linear analogues.\textsuperscript{34,37,47-50} Various branched structures are known such as comb, stars, (regular and non regular), H-shape, super H-shaped polymers and dendrimers. The dendrimers\textsuperscript{37,38} are macromolecules consisting of a polyfunctional central core covalently linked to layers of repeating units (generations) and a number of terminal groups.\textsuperscript{37,50}

A special class of polyelectrolytes is presented by amphiphilic polyelectrolyte.\textsuperscript{37,51} The conformation and structuring of these polymers is much more affected by the quality of solvents since the different solubility of the monomer unit generates the appearance of polyelectrolyte supramolecular structure in solution.

1.10. Polyelectrolyte Conformation: In water\textsuperscript{34,35,52} the polyelectrolyte is dissociated into macro ions (charged polymer) and small ions (counter ions). The amount of macro ions and counter ions has to be equal in order to satisfy electrical neutrality of the solution. The charges along the chain generate long range. The electrostatic interaction along and between polymers chains. The electrostatic interaction depends on the effective charge density per chain, which is given by the interplay of formal charge density and counter ion density. Since the persistence length* (* persistence length – orientation correlation function which describes correlation between two segments of chain) of a polyelectrolyte chain is strongly influenced by long range electrostatic interaction, the polyelectrolyte chains are much more extended than their linear
The persistence length of a polymer chain is the parameter which determines the chain stiffness and it is used to describe the conformation of single polymer chains.

The charge density (formal charge density) of polyelectrolytes are partially screened by counter-ions. The difficulties in the description of counter-ions in the vicinity of a polyelectrolyte show that polyelectrolytes cannot be considered as simple combinations of the neutral macromolecules and electrolytes. The behaviour of the counter-ions in the vicinity of polyelectrolyte chains cannot be described satisfactorily by the Debye Huckel theory because of the presence of strong electrostatic fields in the vicinity of the chains even in dilute solution. Energetically, it is much more favorable that a fraction of the counter ions is condensed at chains. This so called counter-ion condensation and has been explained by Manning. The physical background of the counter-ion condensation is related to the competition between the gain of energy in the electrostatic interaction and a loss of entropy the free energy.

More precisely when the distance between charges is smaller than the Bjerrum length [Eq 1.2] for the strongly charged chain the Manning condensation must be taken into account. The Manning theory describes quantitatively and successfully the process of counter-ion condensation only for DNA and rod like polyelectrolytes. The counter-ion condensation are investigated with different experimental and theoretical methods but still many questions are open. Up to date the process of counter-ion condensation on flexible coils is not described properly on a quantitative level and direct application of the Manning theory should be considered a very cautiously.

The first theoretical model, which describes conformation of polyelectrolyte, was developed by Flory. The model of flory describes conformation of a single
He described a chain of charged and uncharged units in the dielectric continuum which replace the solvent. The model is not a very realistic one because polyelectrolytes are hydrated in water and the structure of the hydration shell as well as the interaction between polyelectrolyte and solvent depends on the local solvent structure.

In Flory’s model the total Hamiltonian of the polyelectrolyte isolated chain with N monomers is described as the energy of a neutral chain with corrections for electrostatic interaction equation 1.1

\[ H = H_0 + \frac{1}{2} k_B T \sum_{i=j,N} \sum_{j \neq i} l_B Z_i Z_j / |r_i - r_j| \] (1.1)

Where \( H_0 \) is the Hamiltonian of the neutral polymer, \( Z \) is charge, \( T \) is the absolute temperature and \( l_B \) is the Bjerum length. The energy of the covalent bond and short range excluded volume interaction are included in the Hamiltonian of the neutral chain \( H_0 \). The Bjerum length \( l_B \) equation 1.2 represents the strength of the electrostatic interaction in the corresponding solvent.

\[ l_B = \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r k_B T} \] (1.2)

\( \varepsilon_0, \varepsilon_r \) refers to the dielectric constant of vacuum and polymer respectively in water at \( T=300K \), \( l_B \) is approximately 0.7 nm.

The Flory’s theory describes the conformation of one single polyelectrolyte chain. In practice it is difficult to measure the properties of one chain in solution since polyelectrolyte chain start to overlap\(^{34,56,57}\) at very low concentrations. The overlapping of chains and the electrostatic interactions between them cause the appearance of
mesoscopic ordering (structuring) in solution. De Gennes proposed a model\textsuperscript{56,57} which describes the structuring of the polyelectrolyte in solution.

1.11. Semi Dilute Region and Scaling Concept of Linear Polyelectrolytes: The properties of polymers, charged and uncharged in the semi dilute region is explained by the scaling theory which was developed from Des Cloiseaux\textsuperscript{35,56,57} work. De Gennes extended his concept and developed a theory which describes the properties of polymers at finite concentration.

The dilute solution is defined as the concentration region in which polymer chains are isolated and do not interact with other chains. In dilute solution, polyelectrolytes have a large overall size and rather stiff local conformation\textsuperscript{35} but when salt is added or the concentration increase, they become more flexible. With increasing polymer concentration the chains start to overlap and the conformation of single chain is strongly modified (Fig. 1.1). The concentration at which chains start to overlap is called the overlap concentration and is marked with $c^\ast$. The critical overlap concentration is very low for long polyelectrolyte chains.
The semi dilution region, the region which is doubtless more realistic to the experimental conditions presents the main interest of this thesis. In the semi dilute regime above the overlap concentration the structuring of chains begins and de Gennes proposed that at the overlap concentration the chains form an isotropic transient network like structure (figure 1.2). One chain can be part of different meshes.

The correlation length $\xi$ corresponds to the mesh size

The network of chain could be described as network of blobs. Inside one blob, the part of the chain of $n$ segments behaves as an isolated chain under excluded
volume effect.\textsuperscript{34,35} Outside the blob the chain can be considered as an ideal chain of \( g \) (\( g = N/n \)) segments (\( g \) blobs where each blob contains \( n \) segments, \( N \) represents degree of polymerization)

The correlation length determine the properties of the network, it is related to the monomer concentration

\[
\xi = R(0) \left[ c^* / c \right]^{1/6} = \left[ 1 / (ca) \right]^{1/2}
\]

\( a \) = distance between charges

The correlation length must satisfy the following requirement:

At fixed \( c \), \( (c > c^*) \), the correlation length must be independent of \( N \) (local properties)

Both \( c^* \) and \( R \) radius of single chain depend on \( N \) (degree of polymerization) but \( \xi \) itself must not.

This scaling\textsuperscript{34,45,56,57} concept was developed for polymer chains in good solvents. In poor solvents the situation is more complicated and attractive interaction can overcome repulsive forces and phase separation can occur. Result from many experimental investigations (mainly scattering measurement) support de Gennes idea of a transient network and the correlation length calculated from experimental results is in good agreement with the theory.

1.12. Scaling Theory of Branched Polyelectrolytes: The scaling theory is also used to describe structuring of branched polyelectrolyte. In the pioneering work of Zimm and Stockmayer branched polyelectrolytes\textsuperscript{48} were described ideally disregarding any interactions between monomer and taking into account only the branched topology of the macromolecules. A new approach takes into account intermolecular excluded volume interaction and poly disparity of the branched chains.\textsuperscript{45,48,49,57} The branched architecture influences strongly the distribution of counter-ions which becomes non
uniform. Very often electrostatic swelling of branches is determined by the osmotic pressure of the trapped ions inside the branched core.\textsuperscript{48,49}

However scaling approaches for branched polyelectrolyte are more complex in comparison to its linear analogues and more system dependent.\textsuperscript{45,48,49} In our investigation we were interested in a special class of branched polyelectrolytes that is used in clarification process in sugar industry.

In the first approximation these branched polyelectrolytes in semi dilute solution are described as charged colloid spherical particles\textsuperscript{38,39,48,49,58,59} and structuring of these particles in semi dilute solution is:

\[ \xi \sim C^{-1/3} \]

The characteristic length is related to the diameter of spheres enlarged by the Debye screening length. The experimental results for irregular branched polyelectrolytes as well as for polydisperse dendrimers of high generation confirm this model.

The same model describes the structuring of different spherical systems as micelles or particles.\textsuperscript{49} However, structuring of the irregular branched polyelectrolytes is not investigated as linear analogous and many experiments and theoretical simulations are needed before the structuring of these polymers could be completely described.

1.13. Review of Literature: Since the sugarcane clarification is the major process in sugar industry. Clarification of the mud settling is the major topic of this thesis, only a short overview important research works done in this field of sugar industry, is presented in this section.
Flocculating agents (usually in the form of natural or synthetic poly-electrolytes of high molecular weight, interconnects) underwent fast development during the 1980's which has led to a remarkable improvement in the use and performance of many types of separation equipments.

In the last few decades quite number of poly-electrolytes have been used by various workers to improve the clarity of juice, reduce the viscosity of the liquid and to improve the settling rate during cane juice clarification. During 1967-68, 1968-69 crushing season, number of sugar mill in India faced serious mud trouble. In sulphitation sugar mills this problem is generally observed during peak recovery period. During 4-5 decades number of workers tried to overcome this problems. The review various attempts is as below.

Bose.\(^{60}\) et al reported the study regarding the use of califloc A as flocculating agent. They claimed 2ppm optimum dose of califloc A and increased mud settling rate about 3 times.

Pawar.\(^{24}\) stated that use of sedipur TF\(_2\) incrased settling rate and reduced mud volume by 20-25%. He also listed various measures to overcome mud problem.

Chen.\(^{61}\) et al established a particle method of evaluating polymer flocculants. They demonstrated that the effectiveness of a flocculant is not only in the rate of sedimentation but rather in the clarity of the clarified juice. The normal dosage of polymer in juice clarification is 2-4 ppm on weight of juice.

Cress \(^{40}\) et al studied the effects of thermal mechanical and chemical degradation on molecular weight (MW) and settling rate, and found both chain breakage and reduction in settling rate occurred with temperature rise from 30\(^\circ\) (to 50\(^\circ\)-80\(^\circ\)C) in the case of flocculants of MW 21 X10\(^6\) and MW 10.5X10\(^6\). But the one of MW
3.7 \times 10^6 \text{ at } 30^\circ \text{ C under went no change with temperature rise, nor in settling rate, they found that the problem was attributed to radicals formed by oxygen and ferrous ions, which further reacted with flocculant to initiate such degradation. To solve the problems is to increase the pH of solution greater than 9 and to line (or paint) the tank to avoid the metal ions (or just to use a stainless steel tank). The higher MW polymers suffered more rapidly from mechanical degradation caused by shear stress due to poor design in the mixture devices.}

Cressol, Hale\textsuperscript{62} et al reported that the theory of flocculants and the problem mode of action of flocculants. The formation of a bridged three dimensional net work produces faster settling rate and clearer supernatants as the floc are much larger and include the very small particles which of otherwise will not settle, in filtration of the floc structure improves the porosity because of the fact that considerable void space is available with in the flocs and improves the retention of small particles with in the space.

Synthetic high polymers are poly anions and are either poly-acrylates, poly acrylamides partially hydrolyzed poly acrylonitriles or co-polymers of vinyl acetate and maleic anhydride they exist in the form of thread like long chains and the molecular weight in the region of 3000 is necessary, for the molecule should be long enough to bridge the gap between two adjacent molecules of suspended matter. These synthetic poly electrolytes are effective in very minute doses.

James C.P.Chen and Chung Chi Chou\textsuperscript{63} stated that bearing various trade name have come into general factory use. The action of these poly electrolytes is to produce the secondary flocculation. Generally a good flocculant improve flocculation increases
settlings rate, reduces mud volume decreases pol in cake, and most important, increases the clarity of the clarified juice.

Jahn\textsuperscript{64} reported a spectrum of plant materials with flocculating properties. For instance, the stem of Abelmoschus esculentus(L), Moench., commonly known as ladies’ finger or okra, the gum from Lannea coromandelica (Anacardiaceae), and the bark from Triumfetta lappula (Tiliaceae) have all been used for cane juice clarification. The well-known and efficient natural coagulant “Floccotan” is produced from tannins in schinopsis wattle bark in Argentina. In developing counties, the clarifying property of the seeds of Moringa oleifera (moringaceae) for food and water purification processes is well known.

John\textsuperscript{65} studied removal of suspended matter from juice before clarification. In the treatment of juice after heating, polyelectrolytes offer promise of economic utility in cases where poor settling is encountered. The mechanism of the varied behavior of juice is not understood. It would appear, however, that polyelectrolytes of the cationic type would be more effective than the anionic polyelectrolytes.

Khan\textsuperscript{66} described the flotation process of treatment of filtrate, treating the filtrate with phosphoric acid and followed by aeration with the neutralizing with milk of lime followed by action with the help of flocculent. Calcium, phosphate scum is removed together with suspended and colloidal impurities. The process claims removal of 95% of turbidity.

Lwong Sak Hoi and S.tse chi shum\textsuperscript{56} stated that there is a continual quest for a natural flocculant for juice clarification in the production of organic sugar as the use of synthetic polyelectrolytes is batted. The clarifying property of the seeds of drumstick tree (Moringa oleifera) in food and water purification processes is well known in rural
areas of developing countries and has been recently exploited in full scale water treatment plants in Africa. Laboratory tests showed that a sieved solution of crushed seeds of Moringa oleirera, when applied at 0.16% on limed juice produced a solution (52%) clearer than one without a flocculant, but the mud produced was twice in volume. The latter could be reduced by 10% by using bentonite at 0.05% on juice, with the added benefit of reducing the juice turbidity by 10%.

The clarifying properties of the edible fruit of cordia myxa were also investigated. Laboratory tests showed that when solution of cordia myxa fruit was added between 0.016 and 0.04% on limed juice. Up to 42% clearer solution could be obtained with a reduction in mud volume. Pilot tests confirmed that Cordia myxa solution applied for one hour at 0.02% on limed juice actually withheld the rising tendency in the clear juice turbidity during that period.

Morales\textsuperscript{68} studied the process of treatment of filtrate from vacuum filter the process consists the treatment of filtrate with milk of lime and addition of organic flocculent. The liming of filtrate is done at 7.5 pH and flocculent addition at the rate of 8 ppm dose. Removal of solids to the extent of 30-40% was claimed.

Rao and Sinha\textsuperscript{69} have reported study regarding used califloc A flocculant, 3ppm dose of califloc was reported effective in making settling rate faster & lower mud level.

Suresh chandra Gupta. and Ramaiah\textsuperscript{70} reported the use of seed extract of strychmos potatorum as settling agent, they found that seed extract alone is not useful for improving rate of settling but the mixture of 4 ppm seed extract with 6ppm separan AP-30 resulted in better settling rate.
Suresh Chandra Gupta et al reported the study regarding use of floccal Tmn-40. The optimum dose used was 2ppm added to various stages in sulphitation process. The best results were obtained when the floc was added to the limed and sulphited juice before it was heated to boiling. This treatment reduced the mud volume significantly and the mud could conveniently handled in continuous clarifier.

Larraghondo studied the primary objective of the clarification process in sugar production is to obtain a juice with good colour and low turbidity by removing the maximum amount of the impurities (dissolved and or in suspension). Clarification is done by adding synthetic anionic polyelectrolytes, which are not acceptable for producing organic sugar. For this reason, this research evaluated aqueous or mucilaginous extracts from the fruits of the plant Cordia lutea (fam. Boraginaceae) and chitosan as possible flocculating agents to clarify cane juice. Two polysaccharides, which are responsible for the flocculant properties that contribute to the removal of impurities in the cane juices, were found in the aqueous fraction of C. lutea, bound to an insoluble lignocellulosic portion. The general sedimentation trials on a lab scale and the conditions for using both the extract of C. lutea and chitosan as flocculating agents in cane juices are discussed in this paper.

1.14. Objectives and Scope of the Present Work: Indian sugar industry is a typical mix of relatively small capacity, old plants and new plants, which have limited influence of modern concepts in sugar cane processing. Therefore, modernization of Indian sugar industry offers challenging prospects right from juice extraction, its clarification and subsequent process operations. A better understanding of the role of additive (poly electrolyte), pH and temperature control including mechanics of settling at
the juice clarifier should enable a rational approach to the design and operation of a clarifier, perhaps the membrane cell technology for juice clarification and concentration may provide a break-through. Further the phenomenon of boiling nucleation for the onset of crystallization at the vacuum pan is a dynamic situation with a highly complex interplay of simultaneous heat and mass transfer, continuous crystallizers with appropriate viscosity control are likely to enhance productivity. The use of ion-exchanger for complete de-ashing of the clarified juice will produce “edible molasses” which may be put to several non-traditional uses. Though the scope of technology innovations is enormous.

In the light of the above observations of the effect of non-sugars and colloidal constituents and colouring matters gathered from the literature survey these are removal by settling of cane juice. Certain chemicals already applied for the removing the non-sugar and mud particles in clarification process.

Cane juice in addition to sucrose, contain non-sugars colloids, inorganic salts, colouring matters, gums, pectin’s etc.. These constituents impart turbidity, colour to juice. In order to remove these matters, different flocculants (poly-electrolytes) are used during the clarification process. Generally, the quality of sugar depends mainly on efficiency of clarification; clarification is nothing but juice “Departiculization”. Thus clarification is very important process in a sugar factory. At present two main methods are in practice. They are, settling separation and flotation separation.

Poly-electrolytes act as a flocculating and alkalizing agents. Generally water soluble poly-electrolytes are used for improving the separation of colloids from liquid. These polymer flocculants are of high molecular weight were studied for the rate of
settling as function of molecular weight which demonstrated that settling rate increased with increasing molecular weight.

However, molecular weight is not the only criterion, it also depends on degree of hydrolysis. Many poly-electrolytes are synthetic organic resinous polymers of anionic, cationic or non-ionic characters. Because of difference in molecular weight and molecular structure of polymers variation of local conditions and cane varieties, the sedimentation polymers bearing various trade names have come into generally use in the factories, the action of these poly-electrolytes have given better results. The present investigation explores the prospect of employing new synthesis polymer solution (poly-electrolyte) introduced for cane juice clarification in the Indian sugar industry. synthesized polyelectrolytes flocculent that is synthetic water-soluble polymers to develop a new flocculent, which enhance performance characteristic and improved properties during clarification of juice. These synthesized polyelectrolytes exhibit superior performance and require shorter time to achieve better performance. The prepared blend is added to cane juice during clarification to achieve high clarification efficiency with reduced cost.

In spite of extensive laboratory investigation on this subject, steps towards large-scale application of this technology have been taken up only in this decade.

The long-chained high molecular weights of co-polymers of sodium salt of acrylic acid with acrylamide are generally termed as poly acrylamides and poly styrene sulfonic acid. These two synthesized electrolytes are anionic polyelectrolytes. The synthesized water-soluble polymer solutions are added to the juice before sending into the clarifiers (2 to 4 ppm). These low concentration polymer solutions are sufficiently effective for better, clarification and settling of mud.
CHAPTER 1

Introduction

The Scope of the present work is:
* To eliminate the maximum non-sugars and maximum removal of colour constituents
* To improve the clarified juice colour
* To reduce the mud volume and turbidity
* To increase the settling rate.
* To chose cheaper and effective clarificants