

Theoretical Study

Basic Mechanism of Coagulation

It is important to a discussion of coagulation for the removal from water of turbidity which may be either organic or in-organic, organic color, or the sludges resulting from lime or lime-soda softening are the basic mechanisms involved. The substances that cause turbidity in water are colloids, and it is necessary that the water chemist familiarizes himself with the properties and behaviours of colloids.

Properties of Colloids.

Colloids chemistry was originally defined as the physico-chemical phenomena of particles within a certain size range of about 5-200 μ . This definition, however was soon found to be too confining, for the most important properties of colloids are surface effects at interfaces and the surface areas involved are extremely great. If a 1-cm. cube of pure gold is placed into a 1-litre beaker filled with distilled water, the surface area of the gold is 6 sq. cm. The brightly polished gold surface reflects practically all the incident light, and the properties of the water and of the gold are affected to only a minute degree by virtue of their physical contact. If the gold cube is dissolved in aqua regia and induced under proper conditions with tannic acid or sodium formate, the result is dramatically different, - a purple solution. Long known as "the purple of Cassias" it may be filtered unchanged through analytical grade filter paper. It may be kept under proper conditions, for years without settling. Much of the light entering the

solution is scattered. ~~The~~ coligative properties of the system, its boiling point, freezing point osmotic pressure, and vapor pressure have all been slightly but measurably changed. Perhaps most important of all, when the solution is placed in an electrical field between charged poles, the particales migrate to the ~~anode~~, indicating that they posses a negative charge. The size of particles in the solution. In within the limits stated before, and the surface area of the 10-mu. particles made from the 1-cm. gold cube has now increased to 6,000,000 sq.cm. more than twice the area of a tennis court. The properties of the turbidity, organic color, and softening sludges which are to be removed by coagulation in water treatment are in general, the properties of this solution. ~~It~~ is important, therefore to understand the forces that surround the particles of such solutions and give the particles their remarkable properties. (Black, 1960)

Instability and Stability Factors.

The two most important instability factors are the Brownian movement and the Van der Waals forces of attraction. The Brownian movement is the movement imparted to the suspended solution particles because of their impact with invisible, rapidly moving particles of the medium. It is, therefore, essentially a thermal effect that tends to drive particles closer to each other and even causes them to penetrate the force fields surrounding each particle. Although the nature of the Van der Waals forces is not well understood, they may be described as molecular cohesive forces that increase in

intensity as the particles approach each other. They become more effective with decreasing particle size.

The most important stabilizing factors are hydration and the zeta potential. Hydration is the property possessed by some particles to attract relative by large numbers of solvent molecules to the surface. When the solvent is water, such particles are called Hydrophilic and as has been said, contact between particles is hindered by the solvent "sandwich"

Nature of Zeta Potential

Zeta Potential refers to a surface charge of colloidal particles which causes the particles to migrate in an electrical field to the pole of opposite charge. Zeta Potential may be the result of selective absorption of ions from the solution or of residual valence forces, or both. The original Helmholtz picture of a charged colloidal particle showed a closely held double layer of charge of opposite sign. Electrophoresis the movement of charged particles in an electrical field - could not, however, be explained by such a picture, Gouy (1910) and Stern (1958) proposed the diffuse-double-layer theory, which picture a stationary layer of ions on the surface of the particle surrounded by a movable diffuse layer extending out into the solution a rapid drop in potential occurs between the particle and the stationary layer, and a much more gradual potential drop occurs between the stationary layer and a point in the solution at which electroneutrality exists. The overall potential is called the chemical or Nernst potential whereas the lesser potential between the stationary layer and the

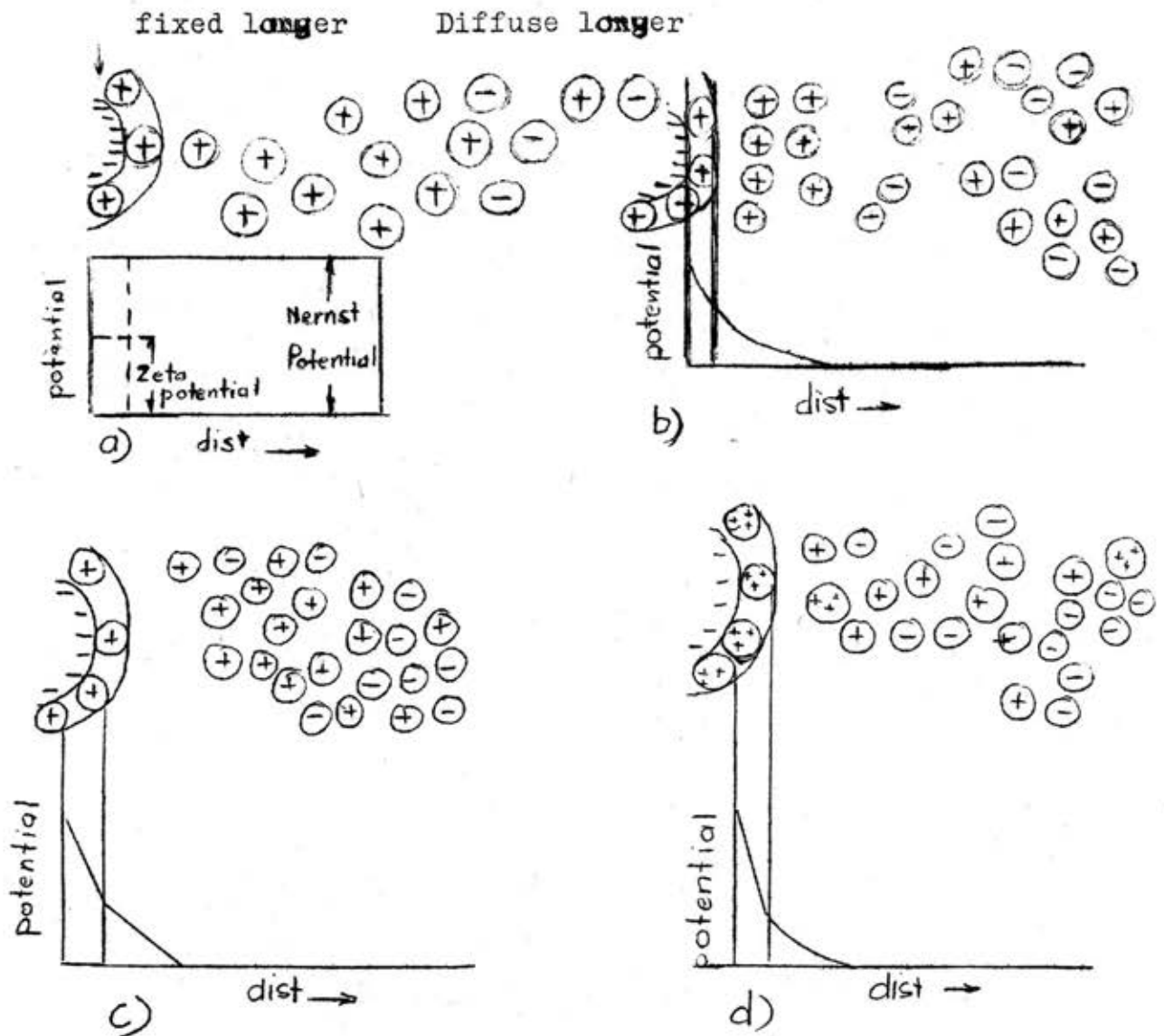
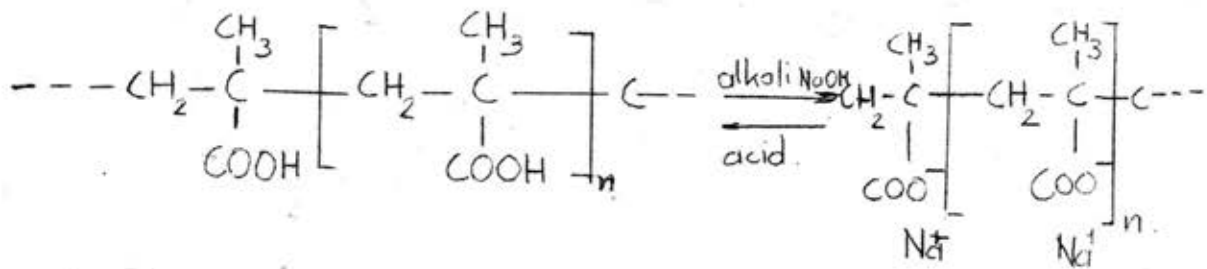


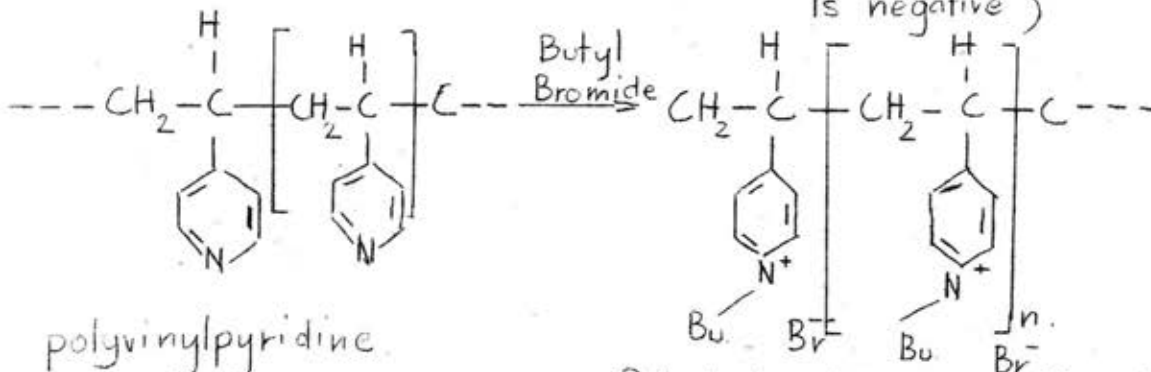
Fig 1. Source of Zeta Potential and Effect of Ions of opposite Charge (Black, 1960)

1.a represents a negative colloidal particle in a low concentration increases from that in 1.b. to that in 1.c, more positive ions enter the fixed double layer, and the zeta potential is reduced. In 1.d, a trivalent positive ion has entered the fixed double layer and so reduced the zeta potential that coagulation would probably result.



polymethacrylic acid
(uncharged polymer)

Sod. Polymethyl
acrylate (charged
polyelectrolyte chain
is negative)



polyvinylpyridine
(uncharged polymer)

Polyvinylpyridinium Butyl Bromide
(charged polyelectrolyte
chain is positive.)

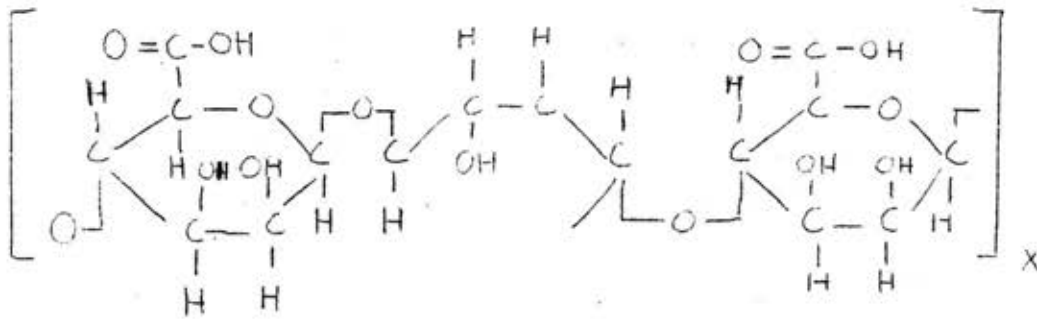
Fig 2. Anionic and cationic polyelectrolytes

Each dissociating sodium ion leaves a negative charge site along the chain of sodium Polymethyl acrylate. Each dissociated bromide ion leaves a positive charge site along the chain of polyvinylpyridinium Butyl Bromide.
(Black, 1960)

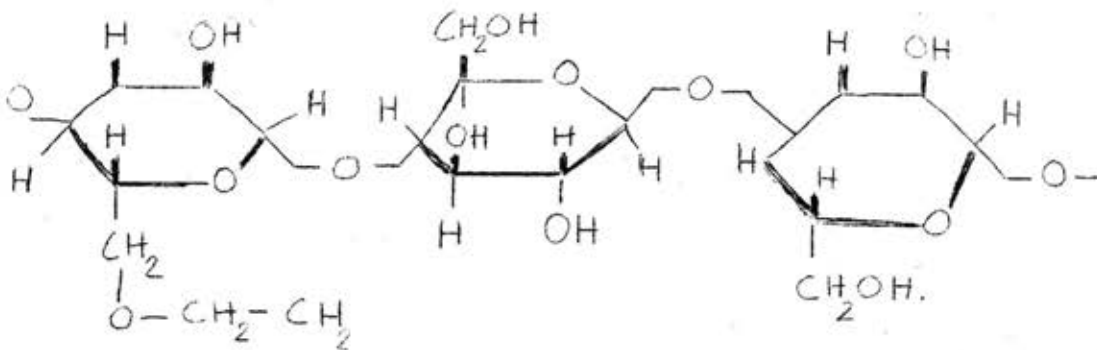
solution is called the zeta potential. The latter makes it possible for the particle to move within a charged electrical field (Fig 1 a). Because the motion of charged particles in an electrical field is independent of their size or shape and dependent mainly on the Zeta potential, the measurement of particle mobilities affords a rapid and accurate method of Zeta potentials. Because all the particles of a given solution possess the same Zeta potential, it acts as a repulsive force preventing the individual particles from approaching each other.

Coagulation of Colloids

With the foregoing explanation of colloidal systems as a basis for discussion, the next step is to understand the mechanism of coagulation of solution particles. Colloid chemists long ago showed that coagulation results when ions with a charge opposite to the charge of the colloidal solution are added to the colloidal solution. The ionic atmosphere of the diffuse layer surrounding each particle expands and contracts as the salt content of the solution is decreased and increased. As the concentration of the added ion increased, the diffuse layer is contracted until a point is reached when the Van der Waals attractive forces are stronger than the repulsive forces of the Zeta potential, and coagulation results (Fig 1, b and c) the valence of the ion of opposite charge is all important, and the observed effects in general, follow the Schulze-Hardy rule, which states that a



a).



b).

Fig 3. Recurring Molecular Units of natural and synthetic polymers. (Black, 1960)

Fig 3 a) shows the structural formula of alginic acid, derived from kelp; 3 b shows hydroxyethylcellulose, a substituted natural polymer. See Fig 4 for other molecular units.

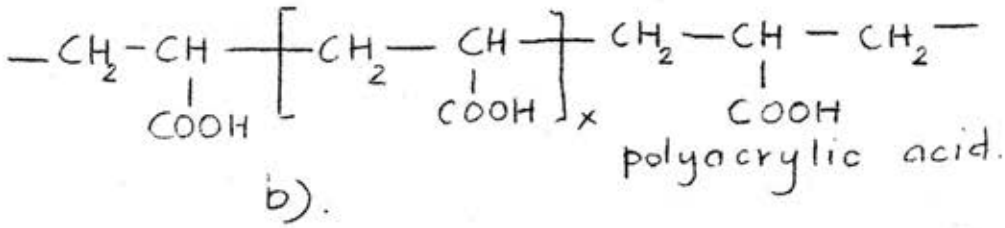
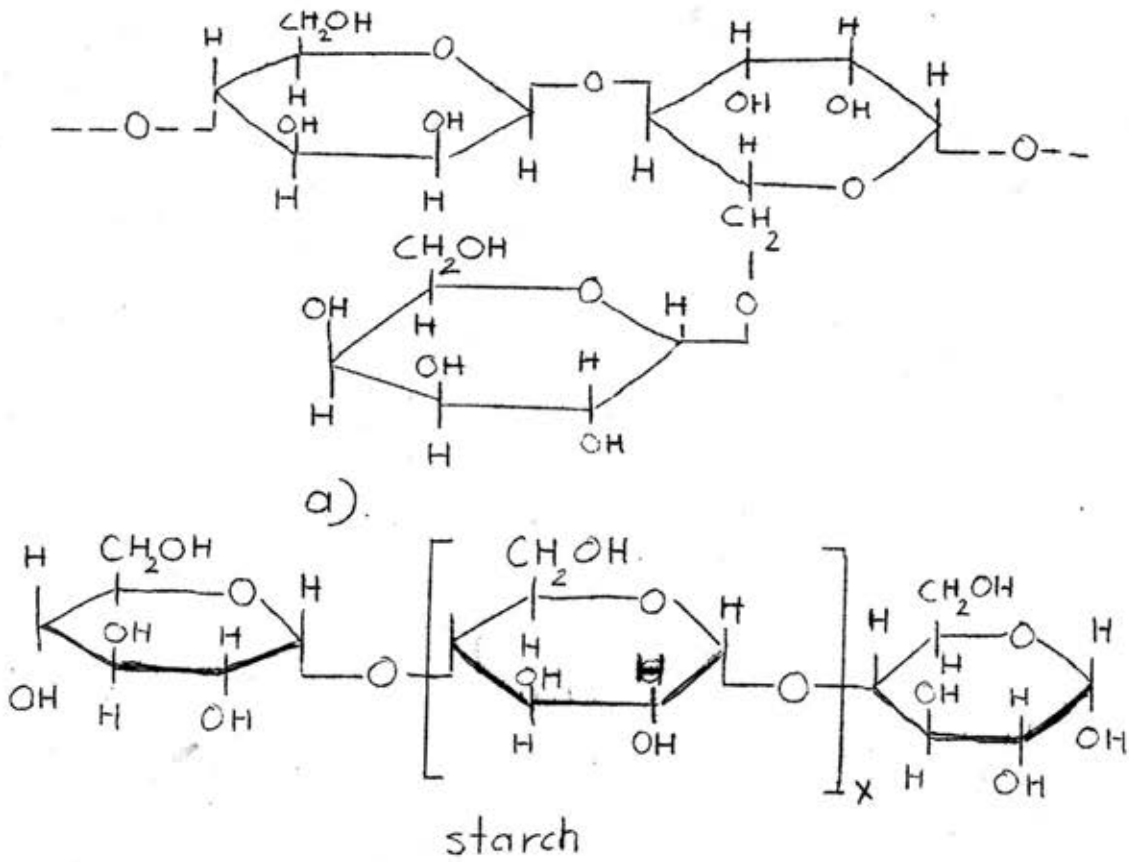


Fig 4. Recurring Molecular Units of Natural and Synthetic Polymers. (Black,1960)

Fig 4 a shows the structural formula of a galactomannan, derived from guar gum. In 4b. a natural polymer, starch is compared with a synthetic polymer; polyacrylic.

bevalent ion is 50-60 times more effective than a monovalent ion, and a trivalent ion 700-1000 times more effective than a monovalent ion (Fig 1 d) A colloid may also be precipitated by the addition of the colloid of opposite sign. This is called mutual coagulation.

The observed facts of water coagulation can be interpreted in terms of these colloidal phenomena, the two coagulants most widely used in water treatment are aluminium and ferric sulfate. Both supply trivalent cations. In as much as it has been shown that, in general both turbidity and organic color in water are present as negative colloids, the significance and importance of the trivalent positive charge becomes immediately apparent. Secondly, when either aluminium or ferric sulfate is added to a water in the pH. range of optimum coagulation, hydrolysis takes place. The formation of insoluble colloidal basic salts probably precedes the formation of colloidal aluminium oxide solutions. Both possess positive Zeta potentials and have the ability to precipitate negatively charged color or turbidity by mutual coagulation.

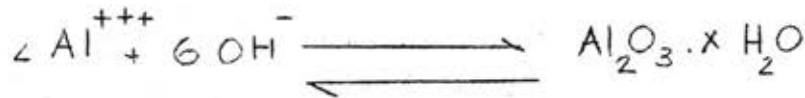
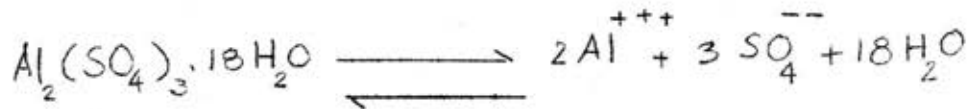
Colloids chemists have long recognized that rapid coagulation of a colloid solution usually takes place shortly before the Zeta potential has been completely neutralized. Electrophoretic studies show that this is generally true where either alum or ferric sulfate is being used for the coagulation of either organic color or turbidity. When turbidity is present as clay, a further factor must be considered. It has been shown that the metallic ions in the diffuse double layer

surrounding a clay particle constitute an ion-exchange system and that an equilibrium exist between them and other ion exchange facilitates the substitution of the positively charged aluminium or ferric ions in the diffuse double layer surrounding the clay particle, and, together with the number and size of the particles involved, governs the coagulant dosage.

Chemical Coagulants

Chemical coagulants are obtained by adding the floc forming chemicals for the purpose of emmeshing or combining with, settleable, but more particularly with non-settleable, suspended and colloidal matters. Rapidly settling aggregates, or flocs, are created. The added chemicals, called coagulants, are soluble, but they are precipitated by reacting with substances in or added to the water or waste water. In water purification, the floc that has not been removed by sedimentation is generally removed by filtration; in waste-water treatment, the floc is removed by filtration or by biological treatment. The most common coagulants are aluminium and iron salts while the ^{precipitating} substances are, usually, naturally present alkalinity or, more rarely, added alkalinity releaved by substances such as soda ash. (Fair, G.M. and Gayer, J.C., 1956)

The reaction of alum are:-



The second reaction is the combination with OH. ions available by the alkalinity of water. If the alkalinity of water is inadequate, it must be increased by adding substances such as hydrated lime, $\text{Ca}(\text{OH})_2$, Na_2CO_3 , NaHCO_3 or NaOH . In practice, more than the amount required for reaction is added in order to leave a residual of unreacted alkalinity in the water.

Polyelectrolytes.

The ability of such natural substances as starch, gelatin, and vegetable gums to act as coagulant aids has long been known. Recent years have witnessed the introduction of synthetic polyelectrolyte coagulant aids. Their use has stimulated an increased interest in the older natural products. Some of these materials have been found to be effective in extremely low concentrations and to produce spectacular results in many situations involving coagulation. It is necessary, therefore, to examine the nature and

properties of these material, in order to learn about their mode of action.

The term "Polyelectrolyte" was introduced by Fuoss(1947) to include those polymers which, by some ion producing mechanism, can become converted to a polymer molecule having electrical charges. (ionized sites) along its length (Fig 2)

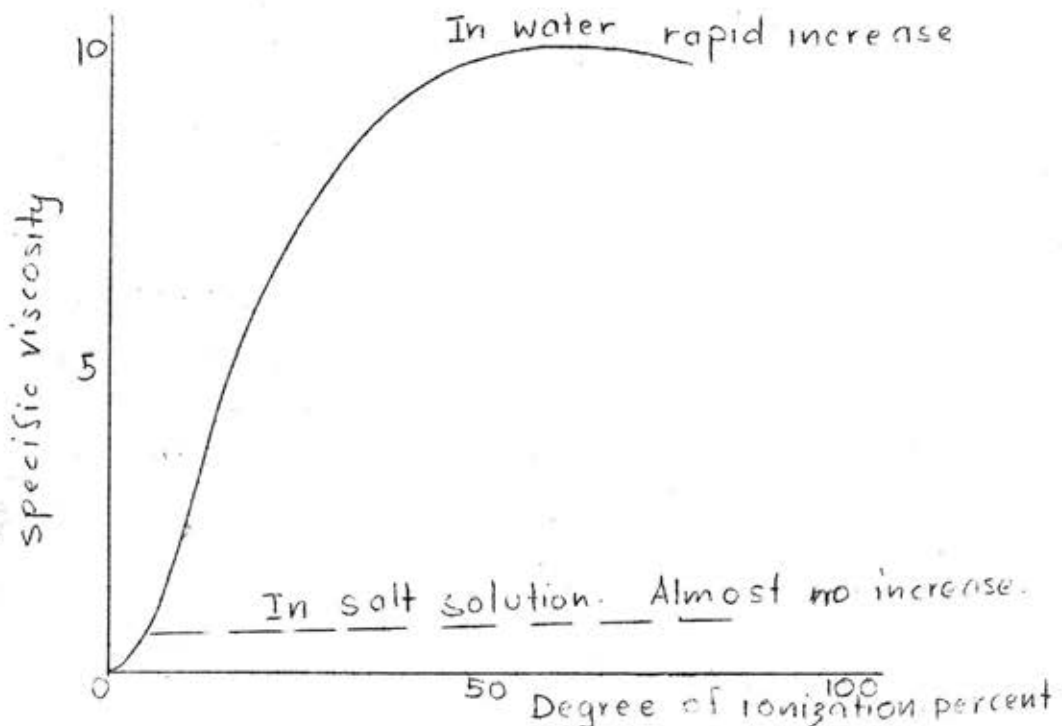
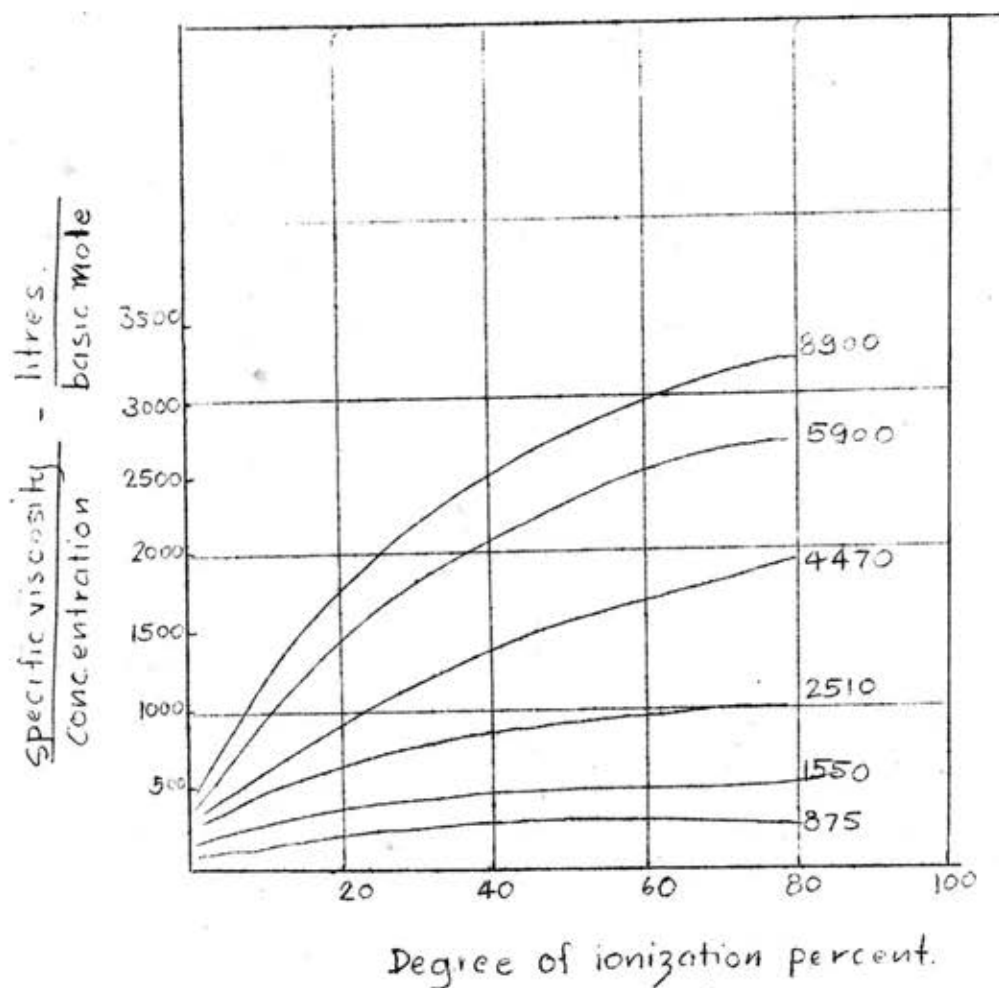


Fig 5 Effect of Degree of ionization of a polyelectrolyte on the viscosity of its solution.(Black,1960)

If the chain is formed by linking molecules of one molecular species, the compound is called a polymer, if the chain is formed by linking two or more different molecules, it is called a copolymer. Starch is an example of a natural polymer involving the linkage of a simple molecular unit (Fig 3 and 4.) Proteins are polyelectrolytes involving the linkage of several amino-acids. Proteins



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Fig 6. Effect of Molecular Weight and Degree of Ionization on Viscosity. (Black, 1960)

The relationship of specific viscosity to concentration is plotted against degree of ionization for six polymethylacrylic acids. The number near each curve indicates the number of simple molecules per macromolecule. The respective molecular weights would, therefore be these numbers multiplied by 86, the molecular weight of the monomer.

may also have both positively and negatively charged sites. The behavior of solutions of polymethylacrylic acid provides information on the possible mode of action of polyelectrolytes as coagulant aids. When sodium hydroxide is gradually added to a water suspension of this acid, the specific viscosity is found to increase rapidly as the acid is neutralized, a maximum being reached at approximately 50 - 60 percent neutralization (Fig 5). The viscosity is found to increase with the square of the molecular weight, so that polymers of high molecular weight provide solutions of much greater viscosity than do polymers of low molecular weight (Fig 6)

Mechanism of Polyelectrolyte Section.



The uncharged Polyelectrolyte may be compared to a coiled spring. This shape is the result of the random forces surrounding the polyelectrolyte. As a basic polymer neutralized with acid or an acid polymer neutralized with base, the ions of the neutralized acid or base dissociate from the chain, leaving charges at the points of dissociation. For example, if polymethylacrylic acid is 10 percent neutralized with base, each tenth molecule in the long chain will have a negative charge. These charges will repel each other; the polymer chain will begin to uncoil and the molecule to stretch with consequent increase in viscosity, (Fig 7). As neutralization proceeds and more charge sites

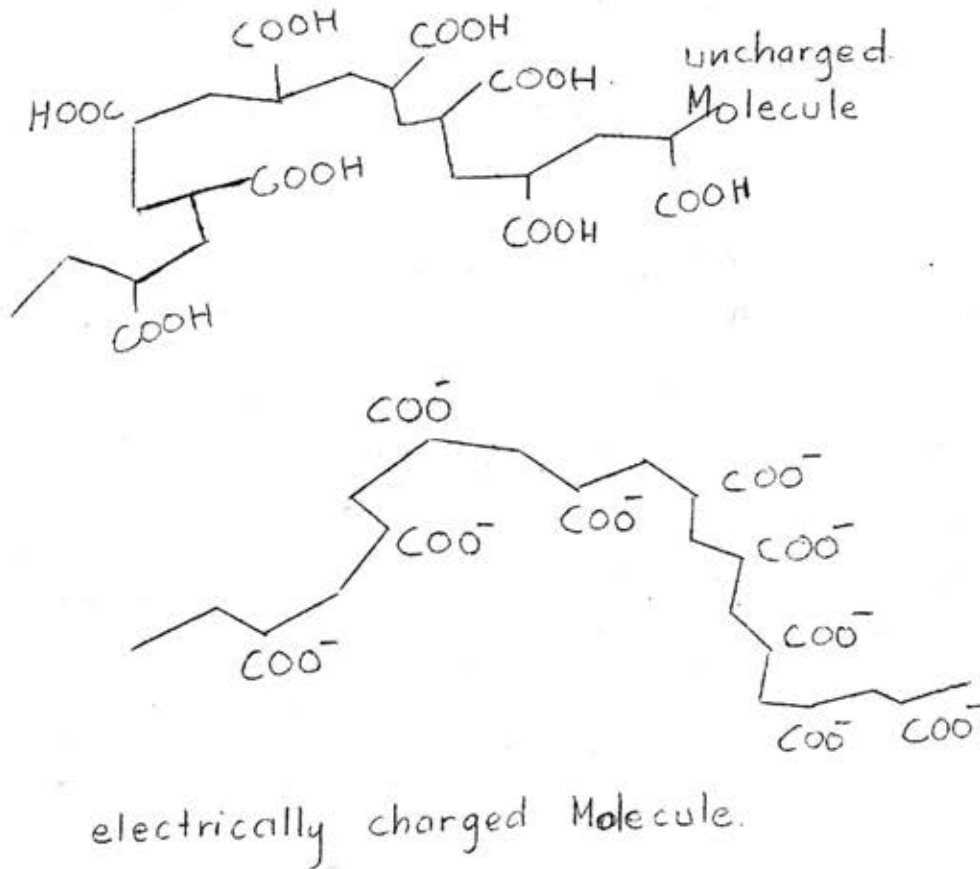


Fig 7. Effect of Electric Charge on the shape of a Molecule in Solution. (Black,1960)

The uncharged molecule is like a contracted chain, which might even be coiled or looped. The electrically charged chain has expanded and Lengthened owing mutual repulsion of charged sites along the chain.

are placed on the molecule, it uncoils more and more and finally straightens out, reaching maximum viscosity. The charged sites on the polymer chain can attract ions or colloids of opposite charge or can cross link with other polymers of opposite charge Fig (8)

Mechano - Chemical Effect.

The behavior of polymer molecules provides a possible means of converting chemical energy directly into mechanically energy. Fibers of a poly acid soil-conditioning agent are drawn from a concentrated solution and heat treated so that they become insoluble in water. One end of a bundle of these fiber is attached to the inside bottom of a glass cylinder that can be filled with acid or alkali as desired. The other end of the fiber bundle is attached to one beam of a chemical balance, and a balancing weight is added to the opposite pan. The balance pointer indicates any physical change taking place in the system. If the cylinder is then filled alternately with 5 percent hydrochloric acid and 5 percent Sodium Hydroxide, the fibers will expand in the alkali, owing to the mutual repulsion of charged sites, and contract in the acid. With fibers about a foot in length and counterpoise weight of 10 gm, the movement of the pointer may be as much as 2-3 in this so-called "mechano-chemical" effect is remarkably similar to that involved in the contraction of muscle fibers in the human body the protein myosin, a main constituent of muscle fiber is a very long protein molecule possessing ionized

or ionizable sites. If, be enzyme action, the electrostatic energy of these molecules is suddenly diminished, the result might be a muscle twitch more rapid than, but similar in nature to, the change that has just been described. One may imagine the long chains of natural or synthetic polyelectrolyte coagulant aids as tiny muscles suspended in water which actually attract and draw together, by muscle action, tiny colloidal particles and agglomerate them into the visible flocs than can be removed by settling. If this is the true explanation of their action, then the name "polyelectrolyte coagulants aids" is consistent with their behavior. Also one would expect that their maximum activity would expect that their maximum activity would be exerted right after the preliminary phase of coagulation. In actual practice, it has been found that the aid being used should, in most instances, be added after and not before the coagulant. The number of those "little muscles" available for floc building even at the minute dosages at which some of these aids are effective, is very large. For example, a dosage of only 0.2 ppm. of a polyelectrolyte having a molecular weight of 100,000 would provide 120 trillion active chains per liter of water treated.

Although the above mechanism may possibly explain the action of some of the natural polyelectrolytes as coagulant aids, it fails to explain the action of others. The high viscosity of aqueous solution of the nonionic natural materials, such as starch and guar gum, is probably the result of the ready hydration of the highly hydrophylic

molecules. Cationic starch, however, has recently been produced and is now commercially available. Lamer, (1956) in his study of the flocculation of phosphate slimes, found potato starches to be much more effective than those derived from corn or other sources. He attributes their effectiveness to their phosphate content, and suggests that specific cross-linking between the phosphate radicals which normally occurs in potato starch molecules, with calcium or other cations forming insoluble phosphates is responsible for the specific flocculating power of potato starch and its derivatives. He further found that whereas electrolytes will coagulate colloiddally dispersed matter, in the absence of electrolytes, will preferentially coagulate the coarse particles. The metallic salts of alginic acid, derived from Kelp, have been shown to have ion-exchange properties.

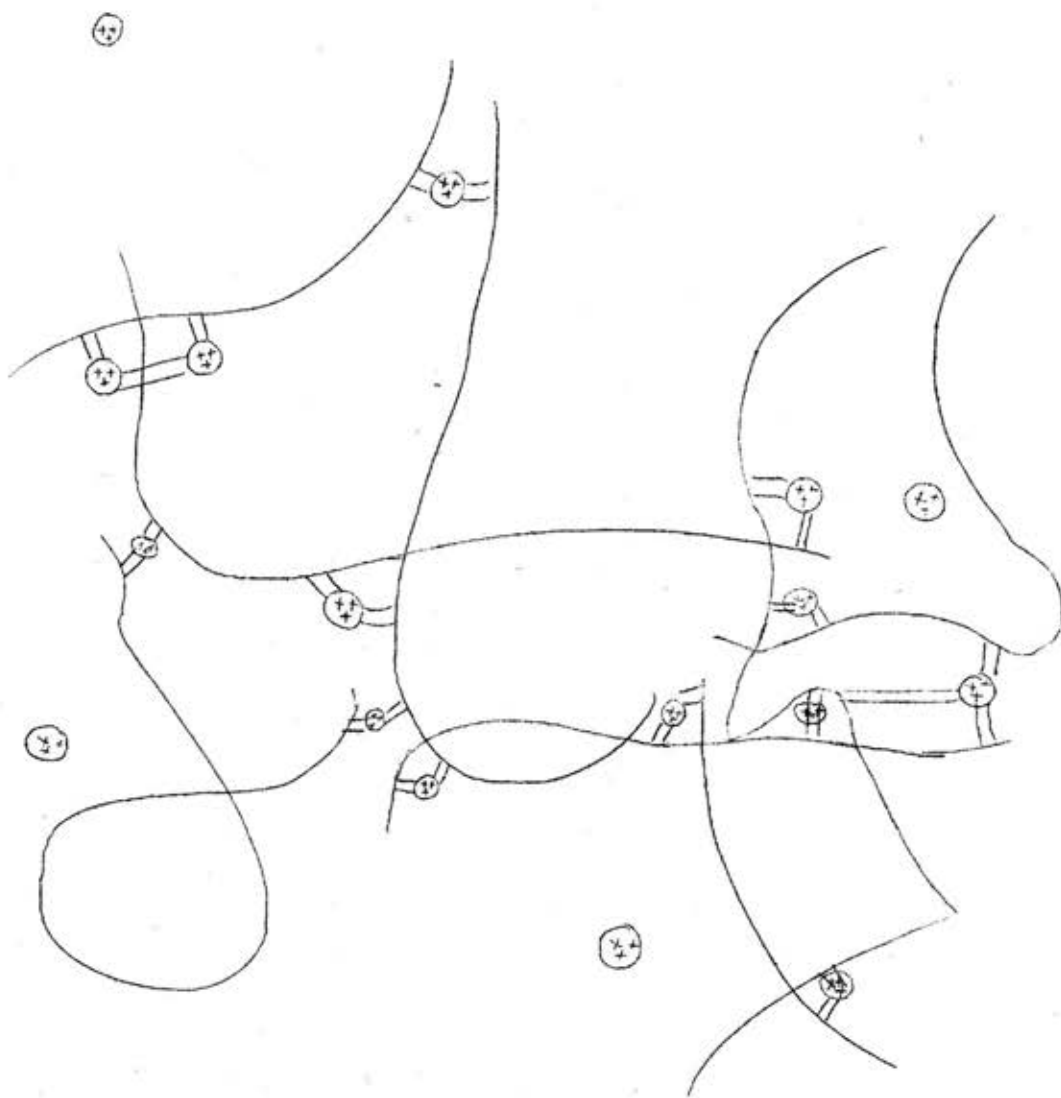


Fig 8. Electrostatic Cross-linking of Polymer Chains by trivalent Ion.(Black,1960)

The diagram represents a gel of an acidic polyelectrolyte formed with polyvalent. Cations by electrostatic cross-linking.