

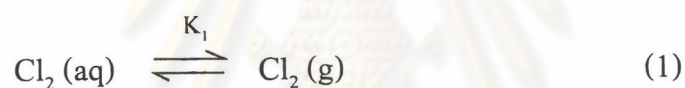
## Chapter II

### Theoretical consideration

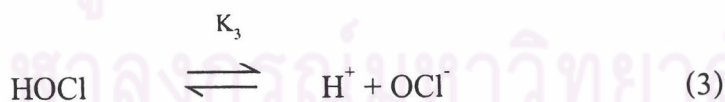
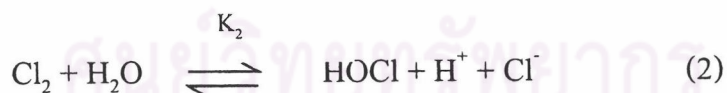
#### 2.1 Chlorine chemistry<sup>1</sup>

The most commonly used chlorine compounds in water treatment are chlorine gas ( $\text{Cl}_2$ ), calcium hypochlorite [ $\text{Ca}(\text{OCl})_2$ ], sodium hypochlorite ( $\text{NaOCl}$ ) and chlorine dioxide ( $\text{ClO}_2$ ).

Henry's law describes the equilibrium relationship between gaseous state and liquid state of chlorine.



The loss of chlorine by volatilization is minimal because chlorine can rapidly hydrolyze in water according to the following reactions. The reaction in equation(2) occurs in a fraction of a second at  $20^\circ\text{C}$  and takes only a few seconds at  $0^\circ\text{C}$ .



Hypochlorous acid (HOCl) is also volatile but it is in the order of  $1.28 \times 10^5$  less volatile than  $\text{Cl}_2$ . The Henry's law constant of hypochlorous acid is  $1.28 \times 10^5$  larger than that of  $\text{Cl}_2$ .

The equilibrium expression for reactions (2) and (3) are as follows.

$$K_2 = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} = 4.5 \times 10^{-4} \quad (\text{at } 25^\circ\text{C}) \quad (4)$$

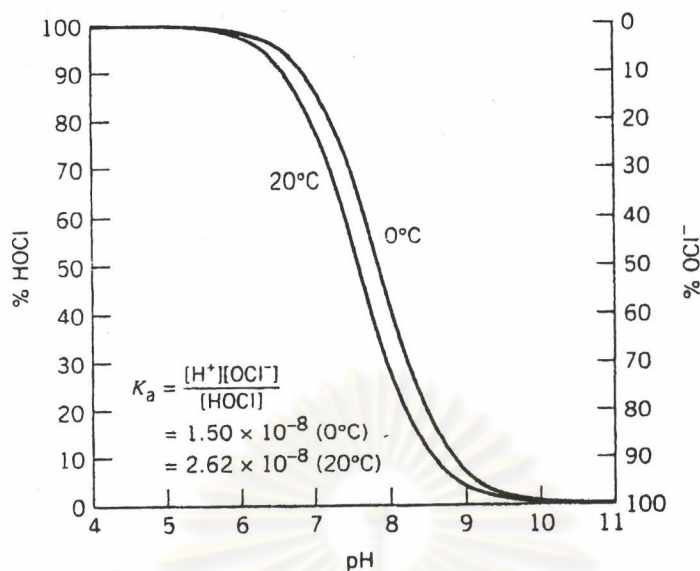
$$K_3 = \frac{[\text{H}^+][\text{OCl}^-]}{[\text{HOCl}]} = 2.9 \times 10^{-8} \quad (\text{at } 25^\circ\text{C}) \quad (5)$$

The  $K_i$  value is temperature dependent and its variation is reported in Table 2.1

**Table 2.1** Values of the ionization constant of hypochlorous acid at different temperature.<sup>2</sup>

Temperature ( °C )	$K_i \times 10^8$
0	1.49
5	1.75
10	2.03
15	2.32
20	2.62
25	2.90

From equation (4), it can be seen that  $\text{Cl}_2$  is much less than 1% of the total moles of chlorine species ( $\text{Cl}_2$ , HOCl and  $\text{OCl}^-$ ) in the pH range of 6-9 of treated water. Free available chlorine is in the form of  $\text{Cl}_2$ , HOCl and  $\text{OCl}^-$ . The dissociation of HOCl (equation 5) is also temperature and pH dependent as shown in Figure 2.1.



**Figure 2.1** Distribution<sup>1</sup> of HOCl and OCl<sup>-</sup>

Table 2.2 The variation of pKa in equation (5) as a function of temperature follows the following equation:

$$pK_a = 3000.00/T - 10.0686 + 0.0253T \quad (6)$$

where T is in Kelvin.

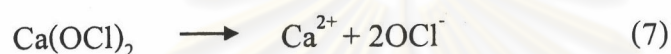
**Table 2.2** Dissociation of hypochlorous acid with pH and temperature.<sup>2</sup>

pH	% HOCl		pH	% HOCl	
	0°C	20°C		0°C	20°C
4	100	100	8	40.1	27.6
5	99.9	99.7	9	6.3	3.7
6	98.5	97.4	10	0.7	0.4
7	86.9	79.2	11	0.07	0.04

The following observations made from Figure 2.1 and Table 2.2 indicate that the dissociation of hypochlorous acid depends on pH and temperature. Almost all chlorine is in the form of HOCl at pH 5.0 or below while almost all chlorine is in the

form of  $\text{OCl}^-$  at pH 10.0 or above. It is noted that the percentage of  $\text{HOCl}$  at  $0^\circ\text{C}$  is higher than at  $20^\circ\text{C}$ .

$\text{HOCl}$  is a very strong disinfectant, about 80-200 times higher than  $\text{OCl}^-$ . Since pH greatly affects the dissociation of  $\text{HOCl}$ , it has a strong influence on the effectiveness of chlorine availability.  $\text{HOCl}$  reacts with the enzymes essential to the metabolic processes of living cells. If hypochlorite salt are used, the following reactions take place to generate hypochlorous acid.



When calcium hypochlorite is used in the industrial process, the calcium ion tends to form calcium carbonate which will clog the metering pumps and valves. A lot of researchers had attempted to correct this problem. One of the best methods is to use the chelating agents to chelate with the calcium ion. This thesis will thoroughly study a variety of chelating agents and various effects on the chelation.

## 2.2 The chelate effect<sup>9</sup>

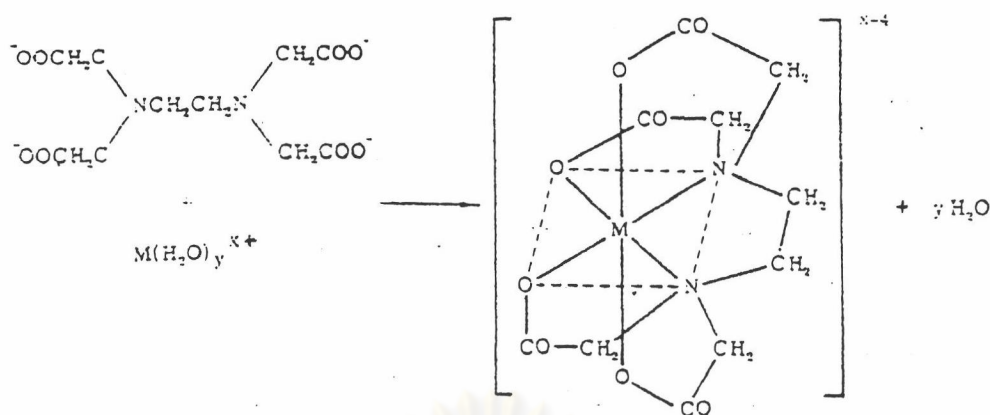
The chelate effect deals with the entropy of the chelating systems. The entropy of these complex systems may be considered from two points of view which have equivalent statistical and probabilistic nature. However they look at the problem from different aspects. One is simply to consider the difference between the dissociation of ethylenediamine complexes and ammonia complexes, for example, in terms of the effect of the structure of ethylenediamine versus ammonia. The electronic effects of both ligands are practically identical since they both contain lone pair electrons on nitrogen which chelate to the metal ions. If a molecule of ammonia dissociates from

the complex, it is quickly swept off into the solution and the probability of its returning to its former site is not likely. On the other hand, if one of the amino groups of ethylenediamine dissociates from a complex, it is retained by the other end. Consequently, the molecule of ethylenediamine is still attached to the metal. The nitrogen atom can move only a few hundred picometers away and can swing back and attach to the metal again. The complex has less probability of dissociating and is therefore experimentally found to be stable towards the dissociation.

A more sophisticated explanation would be to consider the equilibrium of the displacement reaction of ammonia by ethylenediamine in term of the enthalpy and entropy. Since the bondings of nitrogen and cobalt in ammonia complex and ethylenediamine complex are very similar, we expect  $\Delta H$  of this reaction to be close to zero. The entropy change of this reaction is proportional to the difference of the number of particles present in the system. The reaction proceeds to the right hand side with an increase in the number of particles according to the third law of thermodynamics and hence the entropy factor favors the production of the chelate system instead of the hexaamine.



The chelate effect is amplified in the case of polydentate ligands forming several rings with a single metal atom. The extreme of this form of stabilization is found in hexadentate ligands such as ethylenediaminetetraacetic acid [EDTA,  $(\text{HOOCCH}_2)_2\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_2\text{COOH})_2$ ], in which its anion has six coordinating atoms. EDTA forms very stable complexes with many metals with the ratio of metal ion chelated to EDTA of 1:1. The structure of EDTA-metal complex is octahedron with a coordination number of 6 as shown in Figure 2.2. The charge of the resulting complex is less than the starting metal ion by four.



**Figure 2.2** Complex formation of Calcium ion with EDTA<sup>10</sup>

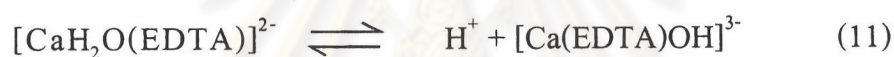
The high stability of  $Ca(II)$  chelated with EDTA has stimulated research on this complex, especially with regard to its stereochemistry. The white crystalline compounds;  $K_2[Ca(EDTA)]$  and  $Na_2[Ca(EDTA)].6H_2O$  are readily soluble in water. Pfeiffer and Simons<sup>11</sup> studied the stereochemistry of  $Na_2[Ca(EDTA)].6H_2O$ . It was thought at first that EDTA is quadridentate with a square-planar distribution of bonds through two nitrogen and two oxygen atoms. To test this theory an attempt was made to prepare the calcium chelate of  $HOOCCH_2(CH_3)NCH_2CH_2N(CH_3)CH_2COOH$ , a quadridentate ligand. Upon addition of oxalate ions, calcium oxalate precipitated out of the solution. This demonstrated that calcium cannot form complexes with a quadridentate ligand. Thus, EDTA forms complex with calcium ion with six coordination number. The other evidence which can support the structure of the  $Ca-EDTA$  chelate is to isolate the complex formed. However, if the chelate were quinquedentate or quadridentate the complex could also be resolved, so that even a successful resolution would not prove the hexadentate function of the EDTA. The only symmetrical structure is the meso form of the square-planar configuration. Although the brucine salt could be easily crystallized and no resolution was effected. This was to be expected, as whatever the structure of the calcium chelate, the interactions between the alkaline earth ions and the nitrogen and oxygen atoms of the  $(EDTA)^{4-}$  anion would be expected to be essentially electrostatic. The fact that the EDTA complexes of

calcium, strontium and barium exchange almost instantaneously with radioactive calcium ion makes the chances of resolution very remote.

Since this early work by Pfeiffer and Simons<sup>11</sup>, opinion has oscillated between a square-planar and an octahedral structure for the calcium chelate. They have also proposed that a water molecule occupies one of the octahedral positions since the complex shows a slight tendency to take up hydroxyl ion in solution.



The pK value of 11.39 was observed for the following reaction.



The aquo complexes can dissociate and give up protons. It is shown that the complex is an extremely weak acid since it has a high pKa. This slight uptake of OH<sup>-</sup> might also be explained if one carboxyl group of the hexadentate EDTA detaches at high pH. Hydroxyl ion could then coordinate to the calcium in the unoccupied octahedral position.

It is difficult to detect various species of Ca-EDTA complexes such as [Ca(EDTA)OH]<sup>3-</sup> since these complexes are colorless. However, the highly colored complexes, e.g., [Co(EDTA)]<sup>-</sup> and [Co(EDTA)OH]<sup>2-</sup> can be observed. It will be a good evidence to be able to obtain the complete crystal structure. Nevertheless it is not impossible that a modified species can exist in solution. It has been shown that the nitrogen atoms of EDTA are coordinated to the calcium. The failure to observe the complex formation of the compound HOOCCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>NCH<sub>2</sub>CH<sub>2</sub>N(CH<sub>3</sub>)CH<sub>2</sub>COOH with calcium suggests that the geometry of Ca-EDTA complex is an octahedral. The

pH values in the titration of  $\text{Ca}^{2+}$  with  $\text{H}_4\text{EDTA}$  are increased considerably when proton acceptors in the form of acetate ions are added. If two of the carboxyl groups of EDTA were not coordinated, little change would be expected. These results suggest strongly that the geometry of  $[\text{Ca}(\text{EDTA})]^{2-}$  complex is an octahedron containing hexadentate EDTA in the solid state and in solution at pH 5-10.

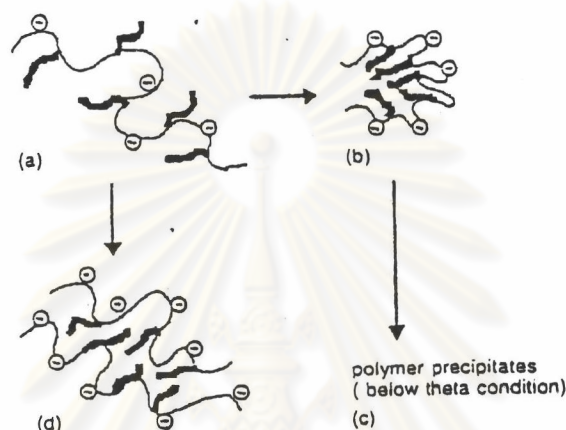
Even though EDTA can form stable complexes with calcium ion, many researches demonstrate that the new developed chelating polymers possess many attractive properties. They can be modified structurally to suit any particular purpose. These polymers can offer high selectivities and fast chelation to the metal ions. Because of these advantages, these polymers have been widely used worldwide. Acrylate polymers are well known chelating polymers which have a lot of applications. They can be classified as water - soluble dispersible polymers and polyelectrolytes.

### 2.3 Water-soluble and dispersible polymers<sup>12</sup>

Homopolymers and copolymers derived from ionic and hydrophobic monomers can be solubilized in aqueous media and display a variety of polymer chain characteristics. Figure 2.3 shows the configurational changes of those polymers in dilute and concentrated aqueous solutions. For example, an extended-coil configuration with large end-to-end dimensions is normally observed in water or dilute aqueous solutions (<1%) at low ionic strength for a homopolymer of sodium acrylate or for a hydrophobic polyelectrolyte copolymer of ethyl acrylate and sodium acrylate, as shown in Figure 2.3a. Each polymer coil is stabilized in the aqueous media through electrostatic repulsion among the charge of the hydrophilic groups. Neutralization of the charges upon addition of salt results in the formation of a more compact coil structure as depicted in Figure 2.3b. In general, an optically clear solution of such compact coils can be obtained even for high-molecular-weight synthetic



polyelectrolytes. Further increase in ionic strength reduces the coil size of polymer and causes the onset of precipitation. At such ionic strength, the polymer has reached its “theta condition” and is characterized by a zero second polymer phase. Beyond the theta point the polymer generally leads to formation of intrachain and interchain aggregates (Figure 2.3c).



**Figure 2.3** Configurational changes of polymers containing ionic and hydrophobic side chains: a) the extended coil in dilute polymer solution at low ionic strength; b) the compact coil at high ionic strength; c) intrachain or interchain aggregates below theta condition; d) interchain aggregates in concentrated polymer solution.<sup>12</sup>

Interchain aggregation can also occur in concentrated polymer solutions (>10%), even though the polymer can molecularly dissolve in a dilute concentration (1%). Such interchain aggregation, as shown in Figure 2.3d, is attributed to a chain association due to the concentration effect. A small interchain aggregation may retain its stability in the solution, provided that sufficient charges are available on the surface of the aggregate. This electrostatic stability may be greatly reduced, however, if a sufficient number of hydrophobic moieties are present along the chain, polymer precipitation and phase separation can take place. Long alkyl or aromatic substituents linked at the side

chains of poly(carboxylic acids) increase the hydrophobic moieties in the polymer chain. Counterions also play a role in controlling the stability of the aggregate.

On the contrary to the instability of ion-containing polymers, improvement in the stability of the macromolecular aggregates may be achieved by several means; i.e., the control of particle diameters to submicrometers with low-molecular-weight polymers; the increase in charge density, and the steric stabilization provided by terminally attached or surface-adsorbed hydrophilic chains. To distinguish such stable interchain macromolecular aggregates from those of the individually dispersed soluble polymer chains as shown in Figure 2.3a, 2.3b, the terms “polymeric dispersion” and ‘polymeric colloid” are frequently used.

## 2.4 Dispersion<sup>13</sup>

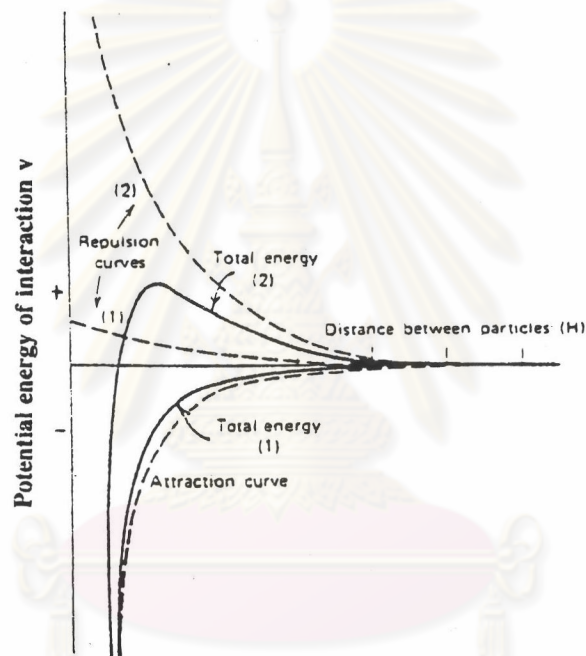
When finely divided solid is immersed in a liquid, it often does not form a stable dispersion. Many of the particles remain attached (aggregated) in the form of clumps and those particles that do disperse in the liquid very often clump together and form larger aggregates that settle out of the suspensions. In addition when the particles do disperse in the liquid, the mixture may be viscous or thin and the particles may remain dispersed for different lengths of time due to the sensitivity of the dispersions to the molecular environmental conditions (pH, temperature, additives) which may vary greatly. The stability of the dispersion can be explained by DLVO theory which assumes a balance between the repulsive and the attractive potential energies of the interaction of the dispersed particles. The repulsive interactions are believed to be due either to the similarly charged electrical double layers surrounding the particles or to the particle-solvent interactions. The attractive interactions are believed to be due mainly to the Van der Waals forces between the particles. To disperse the particles ,

the repulsive interactions must be increased to the level which can overcome the attractive interactions.

The total potential energy of the interaction  $V$  is the sum of the potential energy of the attraction  $V_a$  and the repulsion  $V_r$ :

$$V = V_a + V_r$$

(12)



**Figure 2.4** Total interaction energy curves (obtained by summation of attraction and repulsion curves) for two repulsion curves of different heights.<sup>13</sup>

#### 2.4.1 Role of the surfactant in the dispersion process

The dispersion of a solid in a liquid has been described as a three-stage process.

### 2.4.1.1 Wetting of the powder

For a liquid to disperse a finely divided solid, it must first wet each particle cluster completely. This will involve, at least in the final stage of wetting, a spreading type of wetting, which the air is completely displaced from the surface by the wetting medium. The driving force for this process, as we have seen, is the spreading coefficient,  $S_{L/S}$ . In the case of spontaneously spreading wetting,

$$S_{L/S} = \gamma_{SA} - \gamma_{SL} - \gamma_{LA} \quad (13)$$

This quantity must be positive producing a contact angle of zero degree. The wetting agents are therefore added to the liquid to lower  $\gamma_{SL}$  and/or  $\gamma_{LA}$  by adsorption at those interfaces, especially in the case where a liquid of high  $\gamma_{LA}$ , such as water, is the dispersion medium. The reduction of contact angle has been correlated with the increased dispersibility in an aqueous medium.

### 2.4.1.2 Deaggregation of fragmentation of particle clusters

Once the particle clusters have been wet by the suspending liquid, they must disperse in it. This may be accomplished by the surface-active agent in a number of ways. a) By being adsorbed in “macrocracks” in the solid, the surface-active agent may reduce the mechanical work needed to fragment the particles of solid. These microcracks are believed to form in crystals under stress, but are self-healing and disappear when the stress is removed. The adsorption of surface-action agents onto the surfaces of these microcracks may increase their depth and reduce their self-healing ability and thus reduce the energy required to rupture solid particles mechanically. b) The adsorption of an ionic surfactant onto the particles in a cluster may cause the

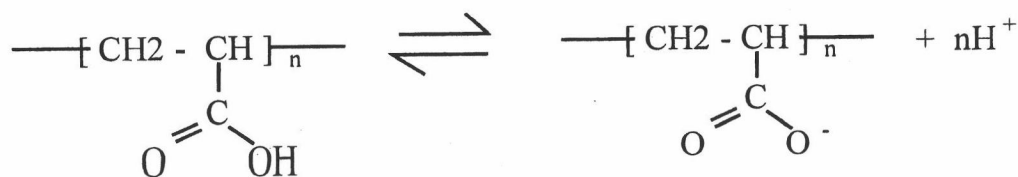
individual particles in the cluster to acquire the same electrical charge, resulting in their mutual repulsion and dispersion in the liquid phase.

### 2.4.1.3 Prevention of reaggregation

Once the solid has dispersed in the liquid, it is necessary to prevent the individual dispersed particles from coming together once again to form aggregates. The reduction of the thermodynamic instability of the dispersion ( $\gamma_{SL} \times \Delta A$ , where  $\Delta A$  is the increase in the interfacial area as a result of the dispersion) relative to the aggregated state is reduced, although probably not eliminated, by the adsorption of surfactants. In the case of aqueous dispersions, this means the adsorption of the surfactant with the hydrophilic group oriented toward the aqueous phase. The tendency for the dispersed particles to aggregate can be further reduced by the adsorption of the surfactant onto the dispersed particles in such a fashion as to increase or produce the energy barriers to the aggregation. These energy barriers may be electrical or nonelectrical in nature. In both case, the solvation of the lyophilic heads probably plays an important role.

## 2.5 Polyelectrolytes<sup>14</sup>

The term “ polyelectrolyte” is employed for the polymer system consisting of a “macroion”. Poly(acrylic acids) are usually classified as polyelectrolytes. They can dissociate to polyion-counterion system as shown in Figure 2.5.



**Figure 2.5** Dissociation equilibrium of poly(acrylic acid).

In principle, any macromolecular chemical structure can be transformed into a polyelectrolyte structure by covalently attaching a reasonable number of ionic groups to the polymer backbone. The resulting linear or branched macromolecules can dissolve in an aqueous medium at appropriate pH after introducing a sufficient number of ionic groups. While in the case of a crosslinked polymer, its swellability in aqueous media is enhanced by transferring into a polyelectrolyte. The remarkable varieties of the polyelectrolyte chemical structures are as follows;

- anionic and cationic polysaccharides and polysaccharidic derivatives
- nucleic acids
- gelatin
- polyacrylic and polymethacrylic acid and its copolymers
- maleic acid anhydride copolymers
- polystyrene sulfonic acid
- polyethylene imine
- polyamines and polyamidamines
- homo- and copolymers of cationic acrylic acid esters

### **2.5.1 Structure formation by interaction of polyelectrolyte with low molecular weight inorganic counterions.**

The solubility of the polyelectrolyte in an aqueous system is largely determined by the counterion species and the ionic strength of the system. In general, an increase of the ionic strength of the system influences the solubility, mainly due to a change of the conformation of the polyelectrolyte in solution via a screening effect as

well as a thermodynamically controlled salting out effect by deterioration of solvent quality. At a definite ionic strength the kind of counterion is of special interest with regard to the structure formation process in solution. The valency of the counterion employed and the state of hydration can be of great importance.

In the case of the monovalent counterions in particular, their state of hydration plays a major part. In the presence of the divalent or multivalent counterions these can act as the centers of cross-linking via intra- and/or intermolecular bridges.

The structure formation processes of the polyelectrolyte solutions in the presence of the monovalent and divalent counterions will be explained.

#### 2.5.1.1 Monovalent

The aggregation process of polyelectrolyte with monovalent counterions is a spontaneous and thermoreversible gelation phenomenon. By treating ionically modified polysaccharides with monovalent counterions, e.g.,  $K^+$ ,  $Na^+$  such phenomena can be observed due to predominantly Coulombic interactions between the more rigid polysaccharides and the counterion species. It is reported that hydration of the counterion plays an important role. In the presence of  $NH_4^+$ ,  $Rb^+$  and  $Cs^+$ , especially  $K^+$ , the phenomenon of gelation of different carrageenan solutions can be observed at a polymer concentration of 0.125M. On the other hand, the monovalent counterion  $Na^+$  behaves differently in the state of hydration.

Cellulosesulfates, obtained by different procedures of synthesis, show a more complex gelation behavior. Highly substituted cellulosesulfates synthesized by Schweiger show an increase of the gel strength in the order  $K^+$ ,  $Cs^+$ ,  $Rb^+$  in contrast to products of low charge density, where an increase of viscosity is

found only in the presence of multivalent counterions. Using another procedure of sulfation synthesized cellulosesulfates in a rather small range of low charge density, showing thermoreversible gelation behavior only in the presence of  $K^+$ . These results demonstrate the important role of the degree of substitution as well as the distribution of the charge centers along the backbone chain and the anhydroglucose unit with regard to the gelation behavior of such polyelectrolytes in the presence of monovalent counterions.

### 2.5.1.2 Divalent

Coulombic interactions of divalent or multivalent cation with polyanions (PEL) leads to an interionic cross-linking, resulting in gel formation from aqueous solution. In addition, an intramolecular interaction of the counterions with more than one anionic site along the chain has to be considered. Comprehensive investigations acidic polysaccharide and  $Ca^{2+}$  ion.  $Ca^{2+}$  alginate gels being an example of practical relevance.

### 2.5.2 Application of Polyelectrolyte

The processes of complex formation between polyelectrolyte and metal ions can be used to remove metal ion from dilute solutions (wastewater). They are economical and safe to the ecological system.

The anionic polyelectrolyte such as polyacrylic acid and acrylic acid copolymers have been used in many applications such as,

- for stabilizing coal suspensions in the electrode manufacturer .
- for the suspensions of  $Al_2O_3$  and SiC in the production of whiskers.
- for dispersing pigment in coating preparation.



- for stabilizing polymer lattices and stabilizing colloid dispersions result from the fact that the colloid particles predominantly carry negative surface charges and coagulation of the system is therefore impeded by macroions with charge sites of the same sign.

Polyelectrolyte as dispersing agents and stabilizers of colloidal system due to intermolecular interactions with the suspended particles. And polyelectrolyte can inhibition of crystal growth. Anionic acrylic as a drilling sludge stabilizer, employing water-soluble, high molecular acrylic terpolymers compared of acrylic acid and some acrylate ester are preferred for this purpose.

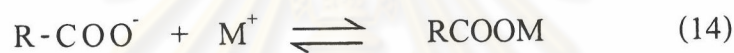
## 2.6 Literature Review

H.S. Wu, H.C. Jone and J.W. Hwang<sup>15,16</sup> studied the kinetics of the reactions of poly(acrylic acid) with various metal oxides (ZnO, CaO, CuO, Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>) by infrared spectroscopic technique. The factors such as the amount of metal oxide, reaction time, solvents, the kind of metal oxides and the temperature were investigated to derive the optimum condition for these reactions. They reported that the reactions of Cr<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> were far from complete. Furthermore, the reactivity of the reaction increased by using the hydrophilic solvent particularly water or methanol and the solubility of poly(acrylic acid) and metal oxide in the solution increased. In case of temperature, the reaction rate increased when temperature decreased.

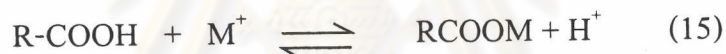
SM.Rabie, A.Sawaby, M.A.Moharam, A.M.Nassar and K.H.Tahon<sup>17</sup> studied the temperature dependence of the reaction between metal oxides (MgO, ZnO, PbO, Bi<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub>, NiO, CuO, Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and SnO<sub>2</sub>) and an aqueous solution of poly(acrylic acid), by using the infrared spectroscopy. The obtained data indicated that the divalent metal oxides MgO, ZnO and PbO react rapidly with the poly(acrylic acid) and

form carboxylate salt. The bonding between the acid groups and these metals is purely ionic in character. The reactivity between these metals and the carboxylic acid is inversely proportional to the radius of metal ions. The reaction of  $\text{Bi}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$  or  $\text{Tl}_2\text{O}_3$  is far from complete. The rate of reaction between some metal oxides and poly(acrylic acid) depends on the temperature of the reaction. The reaction rate increases while the temperature is lowered.

H.P. Gregor, L.B. Luttinger and E.M. Loebel<sup>18</sup> studied metal-polyelectrolyte complexes [the poly(acrylic acid)-copper complexes]. They explained that the reaction of poly(acrylic acid) with metal ion can occur in the form of free carboxylate ion or carboxylic acid .



or



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