

CHAPTER II

LITERATURE REVIEW

2.1 Concentration of Food Liquids

Most of the liquids encountered in everyday life are aqueous solutions or suspensions. In many cases, it is desirable to remove some, or all, of water from these aqueous solutions (Muller, 1967). Therefore, liquid foods are required to be concentrated in order to: reduce energy consumption during subsequent drying; induce crystallization; reduce weight and volume of products, thereby reduce packaging, transportation, and storage costs; reduce water activity so as to enhance storage stability; recover by-products; or remove pollutants from waste streams (Schwartzberg, 1977).

The most widely used techniques to concentrate liquid foods included distillation and evaporation. In the evaporating process, water from aqueous solutions is removed as vapor. By employing this technique, the volatiles responsible for flavor and aroma are driven off. While equipment has been developed to condense and return these volatiles back to the system, the recombined end product is inferior to the starting material. Distillation or evaporation takes place at an elevated temperature. Accordingly, the chemical structure of food liquids could be broken down, thus causing the flavor changes, and some losses of vitamin contents and other nutritive values (Muller, 1967).

Pervaporation, direct osmosis, and reverse osmosis are the methods for removing water from aqueous liquids, using selective permeable membranes. The pervaporation technique has many drawbacks, such as high-energy consumption, low dewatering capacity, long retention time in process apparatus, and high capital investment. Direct osmosis can be operated at a low temperature. In addition, it is an easy and economic method of preparing flavorful fruit juice concentrates. Reverse osmosis offers advantages of low operating temperature and selective dewatering. In this process, an excessive pressure is required to reach concentrations that are used for most liquid food concentrates (Deshpande *et al.*, 1982). Ultrafiltration is used to concentrate solutions containing high molecular weight solutes; however, it cannot be used to concentrate solutions containing low molecular weight solutes. In addition, for high molecular weight solutes, gel formation limits the maximum concentration that can be obtained and thus reduces water removal fluxes to uneconomically low levels as the solute concentration increases. Moreover, reverse osmosis and ultrafiltration require long holdup times and involve flow geometries, which are conducive to microbial growth unless countermeasures are taken (Schwartzberg, 1977).

2.2 Freeze Concentration

Freeze concentration is an alternative to overcome the drawbacks associated with evaporation. It is capable of concentrating comestible liquids without appreciable changes in flavor, aroma, color, or nutritive value (Muller, 1967).

Concentration of fluid foods by freezing can lower the temperature of the product in a sufficiently controlled manner to partially freeze product, resulting in

a slurry of ice crystals in a concentrated solution. Under the suitable conditions, highly pure ice crystals can be obtained. The product will be incorporated within the ice crystals. The ice crystals are then removed with a minimum of liquid carryover. As a result, the product is concentrated (Hartel, 1992).

The degree of concentration in a freeze concentrator depends on the amount of ice frozen in the product slurry. Accordingly, it is often necessary to determine the quantity of water, which must be removed from a liquid to raise a solid concentration from the initial value to the desired value. The relationship of the quantities is independent of the concentration process and of the aqueous liquid being handled. Material balances and algebraic manipulations lead to the following equation (Muller, 1967):

$$w_i = (C_p - C_f) / (C_p - C_i), \quad (2.1)$$

where: w_i is grams of water removed as ice per grams of feed solution,
 C_p is the concentration of solids in the final product; grams of solids per gram of solution,
 C_f is the concentration of solids in the feed liquid; grams of solids per gram of solution,
 C_i is the concentration of solids in ice; grams of solid per gram of ice.

Since the solids lost in ice can be neglected, Eq. (2.1) becomes:

$$w_i = 1 - C_f/C_p \quad (2.2)$$

2.2.1 Principles of Freeze Concentration

Separation by freezing is based on solid-liquid phase equilibrium. The solution to be concentrated contains a large number of soluble components dissolved in water. However, for all practical purposes, it is considered as a pseudo binary system where all substances dissolved in water are considered as one component.

A simple phase diagram of a binary mixture is shown in Figure 2.1. If a binary mixture is cooled under conditions allowing equilibrium to be attained, pure ice crystals then separate out at a point that corresponds to composition W_A and the freezing point of this solution (T_A). Further cooling results in more ice crystals separating out, while liquid composition follows the line $[(W_A T_A)(W_B T_B)]$. At W_E the crystallizing solid has the same composition as the supernatant liquid (Deshpande *et al.*, 1982).

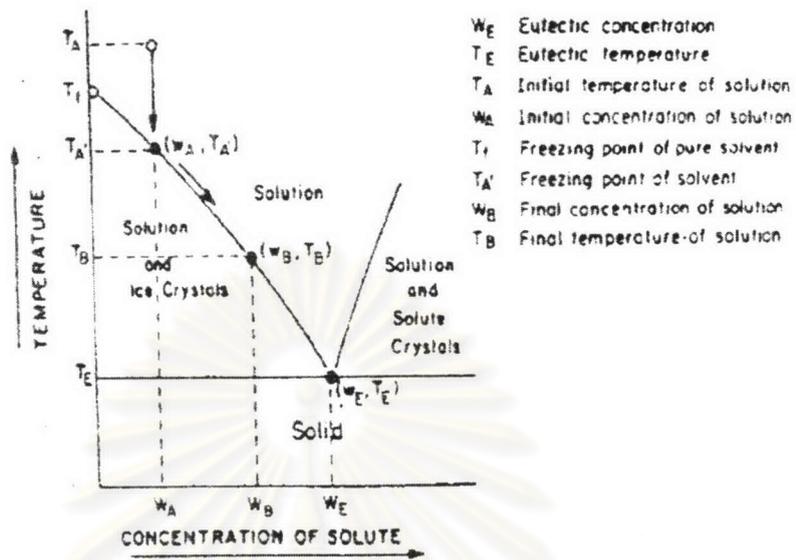


Fig. 2.1 Phase diagram for a binary system (Deshpande *et al.*, 1982)

Freezing-point curves generated experimentally can be utilized for determining the operating conditions of a freeze-concentration system. Figure 2.2 shows freezing-point curves for milk and sugar solutions. This figure indicates that the freezing temperature decreases when the solid content increases. This information is crucial to the design of the freeze-concentration system since the refrigeration requirements and operating conditions are specified to a large extent by the freezing temperature.

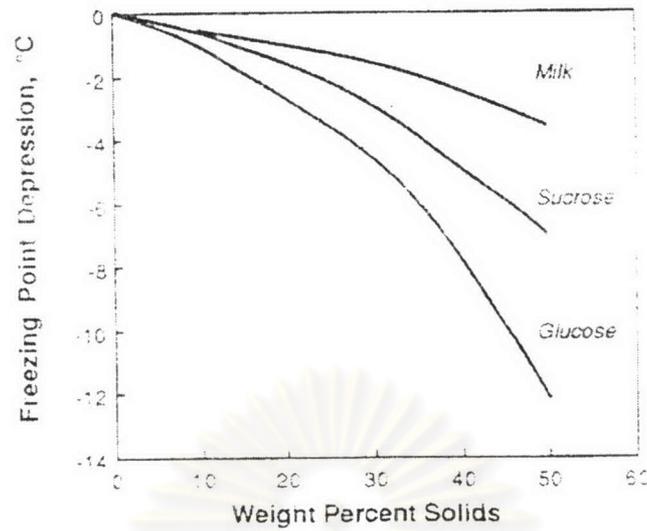


Fig. 2.2 Freezing point curves for milk and sugar solutions

(Hartel, 1992).

If the freezing process occurs at a very low temperature or the concentration of solute in a solution increases, ice will not be crystallized in pure form, but a solid mixture will rather be formed at the eutectic temperature. Below this eutectic temperature, the solid phase will have the same composition as the liquid phase, thus resulting in a termination of separation (Hartel, 1992).

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2.3 Freeze Concentration of Liquid Foods

There are mainly two methods of freeze concentration: suspension crystallization and progressive freeze-concentration.

2.3.1 Suspension Crystallization Method

At industrial scales, suspension crystallization has been extensively employed because of its potential for scale-up. The suspension crystallization technique or the conventional freeze-concentration system consists of three fundamental components, including

1. The ice nucleation

In this stage, the feed stream is supercooled below its freezing point to allow water to separate as ice crystals (many small ice crystals are formed). The formation of the solid phase can occur in one of the several mechanisms. At very high subcooling, nuclei will form by a molecular accretion mechanism known as homogeneous nucleation. This mechanism does not generally occur in most food systems because it requires high energy levels (subcoolings). In addition, most solutions of interest contain microscopic particles that can catalyze the formation of nuclei at low energy levels. The formation of nuclei on such a foreign surface is termed heterogeneous nucleation. Nuclei may be formed either on the surface of a particle in suspension or, alternatively, on the wall of the vessel, in which the solution contained. The final mechanism of crystal nucleation requires the presence of the surface. This surface can cause the formation of new nuclei by some contact or fluid shear mechanism under appropriate conditions. This mechanism is

contact or fluid shear mechanism under appropriate conditions. This mechanism is called secondary or contact nucleation. In suspension crystallizers, ice crystals are formed by a combination of heterogeneous and secondary nucleation mechanisms. The rate of nucleation in a suspension crystallizer is affected by various parameters, including the subcooling temperature, the presence of existing ice crystals, the level of agitation, and the types and concentrations of various solutes. Nucleation has been found to have a second order dependence on the subcooling at lower subcooling values (0.01 to 0.2 °C), whereas a first-order dependence is found at higher subcoolings (0.25 to 1.0 °C). The nucleation rate has also been found to increase as the number of crystals in suspension increase. The agitation rate may affect the nucleation rate in several ways. At low agitation rates, where the suspension is not well mixed, an increase in the agitation rate may lower the effective nucleation rate by reducing the pockets of extreme subcoolings. At higher agitation rates, however, an increase in agitation increases the number of contacts between crystals, and thus results in a higher secondary nucleation rate. The effects of solute molecules on the crystallization parameters are important for the freeze concentration of food. In general, sugar (except, perhaps, lactose) has been found to enhance the nucleation rate of ice, compared to pure solutions. However, other components, such as salts, protein, polymers, and pectin, have shown a negative effect on the nucleation rate in the suspension crystallizers (Hartel, 1992).

2. The ice crystal growth

The very large crystals are preferred in the freeze concentration process because they can be more readily separated from the liquid. This also reduces the loss of mother liquid due to occlusions and adherence to the crystals (Deshpande *et al.*, 1982). The supercooling is the driving force responsible

for the growth of existing crystals and creates the new crystals nuclei. At high degrees of supercooling, most of the supercooling is released in creating a shower of tiny new crystals. At low degrees of supercooling, little or no nucleation occurs, and the bulk of supercooling is released on the existing crystals (Muller, 1967). The important steps in the ice crystal growth include:

- the diffusion of water molecules (or growth units) to the crystal surface and subsequent counter-diffusion of any solute molecules;
- the incorporation of the water molecules into the crystal lattice; and
- the transfer of the latent heat of formation away from the crystal surface into the bulk solution.

It is generally accepted that, for the ice crystallization from fluid food products, the growing step is limited by a combination of heat transfer and counter-diffusion of solute molecules (Hartel, 1992). A ripening crystallizer has been developed to a commercial scale. The slurry containing small ice-crystals is fed continuously to the ripening crystallizer. Ripening is based on the fact that the mean bulk temperatures of the liquid settle to the values between the extreme temperatures of the crystals and those of nuclei, when the small ice crystals are mixed in the suspension. This results in a driving force for the growth of larger crystals and for the melting of smaller crystals (Ramteke *et al.*, 1993). Kobayashi and Shirai (1996) proposed a method of agglomerated ice crystals to produce a large ice crystal in glucose solution for freeze concentration. Keys to making large agglomerated ice crystals are to keep the initial supercooling temperature (or the temperature difference between the lowest temperature and the freezing point of the solution) to less than 0.2

the ice crystallization. Introducing seed ice crystals before the temperature of the crystallizer approaches the freezing point of the solution controls the initial supercooling. In addition, the study of the influence of the concentration of glucose solution, ranging from 10 to 30% (w/w), on the formation of agglomerated ice crystals at 2 hours after introducing seed ice crystals shows that the concentration of the glucose solution affected the agglomerated ice crystals. In the 10% (w/w) glucose solution, large agglomerated ice crystals were produced, whereas ice crystals formed in the 20% (w/w) glucose solution were not agglomerated, and a lot of very small ice crystals (0.41 mm diameter on average) were produced around the seed ice crystals even under the condition adopted in the ice crystallization to produce perfect agglomerated ice crystals in the 10% (w/w) glucose solution. The same results were found in the 30% (w/w) glucose solution. These results suggest that ice crystals were not agglomerated in glucose solutions with the concentration higher than 20% (w/w).

3. The ice crystals separation

The purpose of this separation step is to remove ice from the concentrated slurry. It should be done in such a way that only a few solids are carried over into the separated ice stream (Hartel, 1992). The commercial applicability of freeze concentration considerably depends on the effectiveness of ice-concentrate separation. The separation is carried out in filter presses, centrifuges, wash columns, or a combination of these devices. Filter presses have proved to be slightly effective for crystal separation. The loss of dissolved solids is primarily determined by the amount of liquid that remains occluded in the compressed ice cakes. A wash process cannot remove dissolved solids easily even after girding the cake (Ramteke *et al.*, 1993).

Centrifuges can provide forces of at least 1,000 times that of gravity by which the ice-crystals are separated from the concentrate due to the density difference between liquid and solid phase. The efficient separation crystalline materials with centrifugation should be as follows:

- Crystals should be as large as possible. The larger the crystal, the fewer points of contact per unit volume;
- Crystals should be uniform in size. A variation in crystal size means that small crystals will lodge between the large crystals, resulting in a larger number of contact points per unit volume; and
- Crystal's shape should approach the sphere as closely as the laws of nature will permit. Contiguous spheres always touch at a point. No contact lines are involved, as is the case with crystals having a cylindrical shape. No contact areas are involved, as is the case with crystals having a flat surface.

Under these circumstances, a small quantity remains as a very thin film adhered to the surface of the crystal and as a thicker liquid wedge held by capillary attraction between two adjacent contiguous crystals. Upon melting of the ice, the food solids in this residual may represent a sizable monetary loss (Muller, 1967).

Both presses and centrifuges present problems with carryover of the product, whereas wash columns have developed to the point where the carryover has been reduced to less than 100 ppm. Accordingly, wash columns are used exclusively in freeze concentration systems for food products (Hartel, 1992).

Wash columns provide a perfect separation of ice and liquid without any dilution. Since this process is operated in a close system without headspace, aroma losses are virtually zero. For the ice-concentrate separation, the slurry is forced through one end of the column, where the ice crystals are separated from the concentrate by creating a counter-current motion between melting crystals and the crystallizing liquid (Ramteke *et al.*, 1993).

In summary, the utilization of the suspension crystallization method is limited. The freeze concentration based on this method required a complicated system, comprising ice nucleation, ice crystal growth, and ice crystals separation. This complicated system makes the freeze concentration process to be the most expensive technique among the other solid-liquid separation techniques. Therefore, the practical application of freeze concentration is very limited in food industries (Miyawaki *et al.*, 2003).

2.3.2 Progressive Freeze-concentration

Progressive freeze-concentration is a freeze-concentration method of liquid food based on a concept completely different from the conventional method. In the progressive freezing or normal freezing, freeze-concentration occurs in the freezing process with the ice phase growing from one to the other end. Freeze-concentration proceeds at the moving ice front and only a single ice crystal is formed as a sheet on a cooling surface in a freezing vessel immersed in coolant. The schematics of ice crystal formed in suspension crystallization and progressive freeze-concentration methods are shown in Figure 2.3.

method, the separation of ice crystals from the mother solution is much easier, and thus the system is much simpler (Lui *et al.*, 1997).

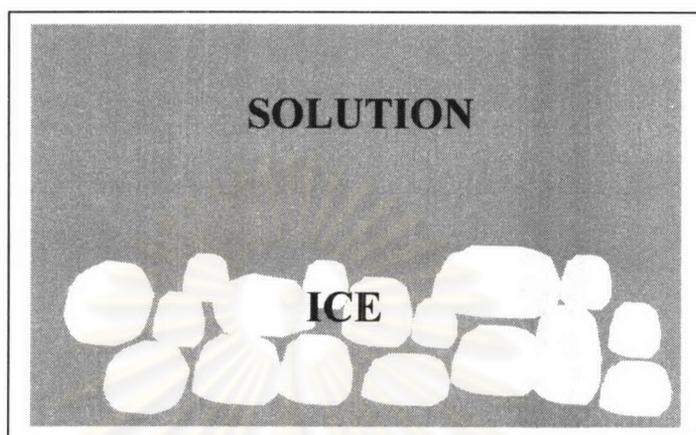


Fig. 2.3 The ice crystal formed in suspension crystallization method.

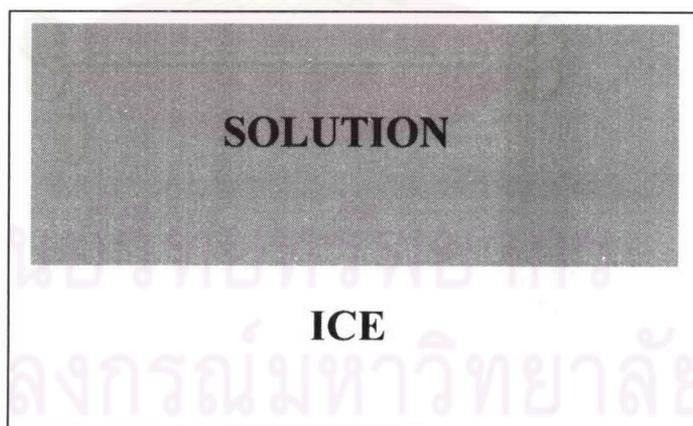


Fig.2.4 The ice crystal formed in progressive freeze-concentration method.

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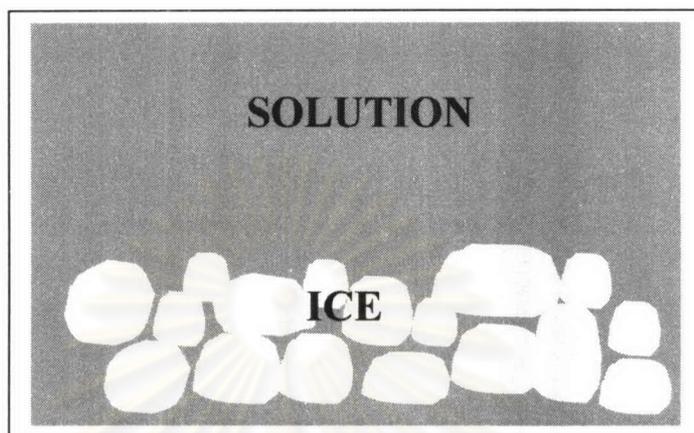


Fig. 2.3 The ice crystal formed in suspension crystallization method.

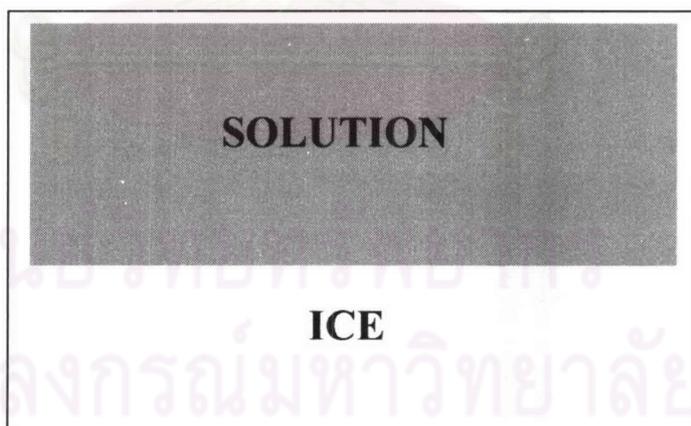


Fig.2.4 The ice crystal formed in progressive freeze-concentration method.

2.4 Principles of Progressive Freeze-concentration

In the progressive freeze-concentration process, water in a solution is frozen on a cooling surface. Water molecules must flow through the solution to the ice-liquid interface and find an energetic favorable spot in the crystal lattice. At the same time, the solute must be transported away from the interface in order to achieve a pure ice layer (Flesland, 1995). The regulations of the progressive freeze-concentration are composed of:

- slow-freezing at the only one side; and
- exclusion of solute molecules from the advancing ice front.

2.4.1 Slow-freezing at the Only One Side

To make a large single ice crystal formed as a normal layer on a cooling surface, the solution has to be frozen slowly at the only one side. Fennema (1996) stated that very slow freezing results in close conformance to solid-liquid equilibrium and maximum freeze concentration. A mechanism for increasing the size of ice crystals by the usual growth process is governed by heat and mass transfer resistance (Flesland, 1995). The difference between the lowest temperature, the freezing point, and the initial subcooling, is the driving force for the growth and nucleation of the ice crystal. The growth rate of ice crystals is proportional to the subcooling, whereas the nucleation rate is proportional to the second power of the subcooling. Therefore, the greater the initial subcooling, the smaller the initial ice crystal occurs (Shirai *et al.*, 1987). In addition, the small crystals were created by a

heat exchanger at a high rate of secondary nucleation and a short resident time of nuclei in a heat exchanger. By applying a high flux of heat withdrawal, the high nucleation rate was occurred (Huige, and Thijssen, 1972). Besides, the ice layer concentration gives a measure of solute loss. The ice layer concentration and the maximum ice production (or the ice growth rate) are the most important parameters for commercial plants. The higher the ice growth rates the higher the loss of solute. This is due to increased concentration at the interface (Flesland, 1995). Halde (1979) demonstrated that air is a solute rejected by freezing water. It accumulates in the advancing interface until its concentration is high enough for bubbles to nucleate. Once a bubble has formed, it grows because air diffuses into it. If the ice-water interface moves forward, the bubble cannot grow laterally, and it grows to form cylindrical bubbles called ice worm. Fast freezing suppresses the formation of ice worms, because insufficient air diffuses into bubbles due to less time for diffusions, and ice contains the large number of small bubbles. Very slow freezing permits the rejected air to diffuse away from the interface and neither bubbles nor ice worms appear.

2.4.2 Exclusion of Solute Molecules from the Advancing of Ice Front

Halde (1979) described the fundamental phenomenon of the interaction between a solute (or a suspended particle) and an ice water interface during freezing. In the freezing of solutions, water is apparently unique among substances in such a way that it expands in volume as it approaches freezing. In other substances, solid is more dense than liquid because the atoms become more closely pack in the crystal. The structure of the ice crystal has regularity and symmetry.

molecules without very severe local strain, practically every solute in the water is rejected by the advancing surface of a growth in ice crystal. The hypertonic solution at the surface slows down the freezing part of the liquid-solid molecular exchanges, by decreasing the availability of water molecules. Consequently, the temperature is lower to a depression of freezing point at which the freezing and the melting are in equilibrium.

When freezing the suspensions at sufficiently small growth velocities, particles of nearly all materials are rejected by a moving solid-liquid interface. Thus, they are pushed ahead into the liquid, traveling along with the interface as it advances. The pushing demands both force preventing incorporation of the impurity in the solid and the feeding of a fresh matrix material to the region behind the particle. Forces, such as gravity and viscous drag promoting contact, act upon an inner particle in front of a growing interface. If the particle is an ideal sphere it will be in single contact with the ideal curved solid-liquid interface. There is one point for the development of force to push the particle. On the other hand, if the particle is in contact with the interface at more than one points, the share of force developed at each point will be less than the total force required when there was only one point of contact. This results in a less distorted surface and easier diffusion at each point of contact. The larger particle diameter, regardless of the particle type, the lower the critical velocity for particle trapping. An increase in contact area at a constant particle size causes increased migration.

The layer of water continuously present between the particle and the ice front is more easily replenished when the viscosity is low and the particle surface is rough. However, even though the force that the interface is capable of exerting is sufficient to push one particle, a pile-up may be extensive enough to

of exerting is sufficient to push one particle, a pail-up may be extensive enough to overcome this force. The particles may also form layers so that the channels between adjacent particles become too narrow to allow sufficient water transfer to the interface.

In a sample of sewage sludge placed upon a cold surface, the freezing isotherm moves slowly up the sample as the water in the system freezes. This is schematically shown in Figure 2.5. If the resistance to flow through the accumulated solids and the concentration in the freezing isotherm remain low, the ice may push the solid until they finally reach the top of the sample, leaving pure or nearly pure ice below. Under a high resistance condition, the cake buildup and sludge to be dewatered forms a layer of solid, which may be trapped by the ice. The trapping is often repeated numerous times and is referred to as the rhythmic banding (Halde, 1979).

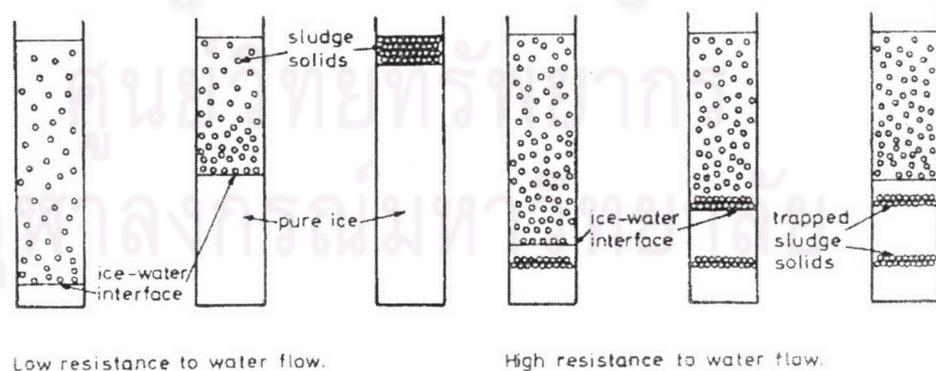


Fig.2.5 Vertical migration of particles in front of a freezing plane
(Logsdon and Edgerley, 1971).

When the concentration of a dissolved substance is high, the solute remains even more concentrated near the ice water interface, thus resulting in a depression of the freezing point of the liquid. The temperature falls below the freezing point of the rest of the solution, and a subsequent breakdown of the constitution supercooling causes freezing at some distance from ice-water interface and trapping the layer high in solute.

Chen, Chen, and Free (1998) studied factors affecting the solute inclusion in the ice formed from sucrose solutions on a sub-cooled surface. They found that the solute inclusion in the ice layer is governed by three factors, comprising average ice growth rate, solution velocity, and concentration of solute, as described by the following equation:

$$K = -0.145 + 2.056 \omega_{s,\infty} + 0.139(v_{ice}) / (u_{s,\infty})^{0.5}, \quad (2.3)$$

where K is the ratio of solute inclusion in ice and in the bulk solution, $\omega_{s,\infty}$ is the mass fraction of solute in bulk solution (w/w), v_{ice} is the average ice growth rate ($\mu\text{m/s}$), and $u_{s,\infty}$ is the solution velocity (m/s). From this equation, the higher the ice growth rate, the more impurities would be entrained in the ice. This is because the speed of ice moving front can become too high to take over the solute outward movement. In addition, the increasing solution velocity and/or reducing solution viscosity, by decreasing solute concentration, can increase the mass transfer coefficient, in order to help solute at ice-solution interface to be transported into the bulk flow (Chen *et al.*, 1998).

Chen, Chen, and Free (1999) studied the solute inclusions in ice formed from falling films flows on a subcooled surface. Sucrose

solution at the concentration of 11%(w/w), fresh whole milk, and reconstituted whole milk with the concentration between 10 and 25%(w/w), were used. This study suggested that the ice growth rate increases with increasing difference in temperature between the entering sucrose solution and the cooling plate. At a lower coolant temperature, the supercooling (*i.e.* the driving force of ice growth) was larger. For this reason, solute inclusion in ice was higher at the higher ice growth rate. In addition, the fresh whole milk gave similar solute incursion in ice with the reconstituted whole milk at the same concentration.

Halde (1979) studied the effect of stirring speed, freezing rate, impurity size, and impurity concentration on the purification of solution by progressive freezing. Considerable purification was obtained if the liquid phase was stirred vigorously at a rate of 2000 rpm to avoid accretion of impurities layer at the interface. The application of different rate of stirring revealed that a more intense stirring rendered a higher degree of purification. The effectiveness of the purification is slightly affected by increasing the rate of freezing from 10 to 30 mm/h. The result of the impurity size revealed the fact that coarser particles like CaCO_3 are easier to separate than the finer clay particles, and the glucose solution is easier to concentrate than the dissolved NaCl. Suspensions with higher initial concentrations were more difficult to purify. The purification of NaCl solution proved to be more sensitive to variations of the initial concentration than the purification of a glucose solution. A marked depression of freezing point caused by the NaCl rendered experimental work in the possible high concentration range. Since the colligative property depends upon the number of particle rather than the type of the particle, this small impurity causes deepest depression.

2.5 The Efficiency of the Progressive Freeze-Concentration

In the progressive freeze-concentration, the efficiency of concentration is exclusion of solute molecules from the advancing ice front and the interface between the ice and the solution phase. Liu *et al.* (1997) defined the effective partition coefficient (K) of solute between the ice and bulk liquid phase as:

$$K = C_S/C_L, \quad (2.4)$$

where C_S (% (w/w)) and C_L (% (w/w)) are solute concentrations in solid and liquid phases, respectively. The value of K varies between 0 and 1. The K value of zero means the complete freeze concentration or highest efficiency of this process. The K value of 1 means that there is the equilibrium of the solute concentration in ice and in solution phases, and thus no freeze concentration occurs. At the moment when the solute volume is V_L in the progressive freeze concentration process, assume a small volume increase ($-dV_L$) in the ice phase. Then, the solute concentration increase in solution phase by dC_L and the following equation is obtained from the mass balance of solute by assuming complete mixing in the solution phase and no mixing in the ice phase:

$$C_L V_L = C_S(-dV_L) + (C_L + dC_L)(V_L + dV_L). \quad (2.5)$$

Combining Eq.(2.4) and Eq. (2.5) yields

$$(dC_L/C_L) / (dV_L/V_L) = K - 1 \quad (2.6)$$

Eq. (2.6) is combined with the following boundary conditions:

$$V = V_0 \quad \text{at} \quad C = C_0,$$

$$V = V_L \quad \text{at} \quad C = C_L,$$

where V_0 and C_0 (%w/w) are the volume and the solute concentration at the beginning of the solution phase, respectively. Eq.(2.6) can then be integrated as:

$$\log(C_0/C_L) = (1 - K) \log(V_L/V_0) \quad (2.7)$$

The relationship between the relative concentration (C_0/C_L) in the solution phase and the volume ratio of the unfrozen phase (V_L/V_0) based on Eq. (2.7) is linear. Therefore, the apparent partition coefficient defined by Eq. (2.4), in the range of concentration between C_0 and C_L , can easily be determined from the slope of a plot between $\log(V_L/V_0)$ and $\log(C_0/C_L)$.

Liu *et al.* (1997) studied the effect of operating conditions on the apparent partition coefficient in the progressive freeze-concentration of model liquid food that contained glucose (5% w/w) and/or blue dextran (0.006% w/w). The stirring speed (N_r) at 0-1400 rpm and the moving speed of ice front (u) at 0.5-2.0 cm/h were studied. The result of this study showed that the concentration of mixed solution

of glucose and blue dextran with the stirring speed at 600 rpm and the moving speed of 2.0 cm/h in ice phase slightly changed with time and were much lower than those in the solution phase while the concentration of solutes in the solution phase increased with time, showing that the concentration process effectively proceeded.

In addition, the study concerning the effect of the stirring speed on the apparent partition coefficient showed that a higher stirring speed produced a higher freeze-concentration ratio. In the single component solutions, the partition coefficient of blue dextran was much lower than that of glucose. In the mixed solution, however, the partition coefficient of glucose was lower than that of blue dextran, suggesting that there were some mechanisms of discrimination between the two components at ice solution phase.

As for the effect of the moving speed of freezing front on the apparent partition coefficient, the lower moving speed of the freezing front was found to yield the higher concentration efficiency, or the higher purity in the ice phase, for glucose and blue dextran. Although the absolute values of the apparent partition coefficients were different between the concentration of glucose and blue dextran, the partition coefficient increased with an increase in the moving speed of the freezing front.

As a result, at the optimum operating condition, at which a stirring speed at the ice-solution interface is high and a growth speed of ice crystal is low, the freeze-concentration efficiency was found to be high.

Liu *et al.* (1999) applied the progressive freeze-concentration to concentrate tomato juice with the initial concentration of 5% (w/w). The juice was stirred at the speed ranging from 300 to 1400 rpm, and the advance rate of ice front

was in the range of 0.5 to 2 cm/h. It was found that high purity ice crystals could be obtained under appropriate operating conditions.

The stirring speed at the ice front affected the concentration of total solid and KCl-equivalent salts of tomato juice in the solution phase (C_L). A large difference between C_L and C_S and increase in C_L with an increase in ice fraction was observed, showing the effectiveness of this technique to concentrate the juice. An increase in the stirring speed at the ice-solution interface caused an increase in purity of the ice phase and subsequent higher efficiency of the freeze concentration.

The advance rate of the ice front affected the change in concentration of total solid and KCl-equivalent salts in the solution and the ice phase in the progressive freeze-concentration with a fixed stirring speed of 1400 rpm. A decrease in advance rate of ice front caused an increase in the ice purity.

In addition, a good linear relationship between $\log(V_L/V_0)$ and $\log(C_0/C_L)$ was found in both total solid and salts. From the slope of the linear lines, the effective partition coefficients were determined. When a stirring speed was higher than 600 rpm, the slope of the plot was close to 1, which corresponded to the K value of zero, indicating a good freeze concentration effect for solid contents. However, the slopes for salts were lower than 1, which corresponded to the K value above zero. This means that salts are more easily incorporated into the ice phase at the ice front than is total solid.

It could be concluded that there are differences between the effective partition coefficient of total solid and salts, probably due to a difference in the mechanism of the partition phenomenon between the two components. In both cases, however, the higher stirring speed along with the slower advance rate of ice front

decreased the partition coefficient between the solid and liquid phases, thus leading to the better freeze concentration performance.

Miyawaki, Liu, and Nakamura (1998) used the concentration polarization model to describe the effects of the stirring speed and the advance rate on the effective partition coefficient. As the ice phase grows at a speed of u into the liquid phase in the progressive freeze-concentration, a solute flux of uC_s from the liquid to solid phases exists when the x -axis is fixed on the ice front to the liquid phase, as shown in Figure 2.6.

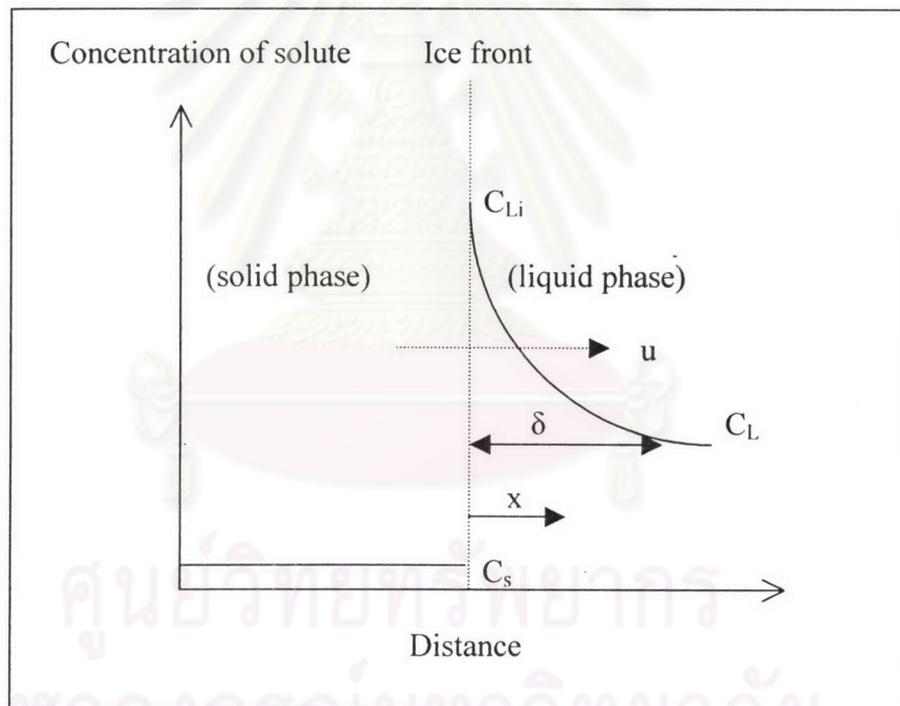


Fig 2.6 Concentration polarization at the ice front in progressive freeze-concentration (Miyawaki, Liu, and Nakamura, 1998).

Then a mass balance equation of solute will be

$$D(dC/dx) + uC_s = uC, \quad (2.8)$$

where C is the solute concentration in the liquid boundary layer, C_s is the concentration at $x = 0$ in the solid phase, and D is diffusion coefficient of the solute.

Eq. (2.8) is combined with the following boundary conditions:

$$C = C_{Li} \quad \text{at } x = 0 \quad (\text{in the liquid phase}) \quad (2.9)$$

$$C = C_L \quad \text{at } x = \delta, \quad (2.10)$$

where δ is the boundary layer thickness. Eq. (2.8) can then be integrated as:

$$\ln[(C_{Li}-C_s)/(C_L-C_s)] = u\delta/D. \quad (2.11)$$

The limiting partition coefficient (K_0) is defined by:

$$K_0 = C_s / C_{Li}. \quad (2.12)$$

From Eqs. (2.4), (2.11), and (2.12), the following expression will be obtained for the effective partition constant:

$$K = K_0 / [K_0 + (1 - K_0)\exp(-u/k)], \quad (2.13)$$

where k is the mass transfer coefficient in the boundary layer defined as

$$k = D/\delta. \quad (2.14)$$

The mass transfer coefficient is related to the stirring speed, N_r , as the following equation:

$$k = aN_r^{0.2}, \quad (2.15)$$

where a is an experimentally determined constant. Eqs. (2.13) and (2.15) give the theoretical basis of the effect of operating conditions on the concentration performance in progressive freeze-concentration, as the following equation:

$$K = K_0 / [K_0 + (1 - K_0)\exp(-u/ aN_r^{0.2})]. \quad (2.16)$$

By these equations, the effective partition coefficient of solute between ice and liquid phase is strongly dependent on the ice growth rate and the mass transfer at the ice-liquid interface. The effective partition coefficient is not equal to the limiting partition coefficient of solute at the ice-liquid interface. Moreover, the limiting partition coefficient has been found to be an important parameter in progressive freeze-concentration. The limiting partition coefficient corresponds to the value of the partition coefficient at the infinitesimal advance rate of ice front ($u \rightarrow 0$) and/or at infinite mass transfer coefficient ($k \rightarrow \infty$) because at this condition, $K = K_0$, as shown in Eq. (2.13).

2.6 Water-Solute interaction

Water is a polar molecule, because of the unequal charge distribution. An individual H_2O molecule is V-shaped, with an H-O-H angle of about 105° as shown in Figure 2.7. The oxygen atom gains a slight excess of negative charge, and the hydrogen atom become slightly positive. It is this polarity that gives water its great ability to dissolve compounds (Zumdahl, 1995).

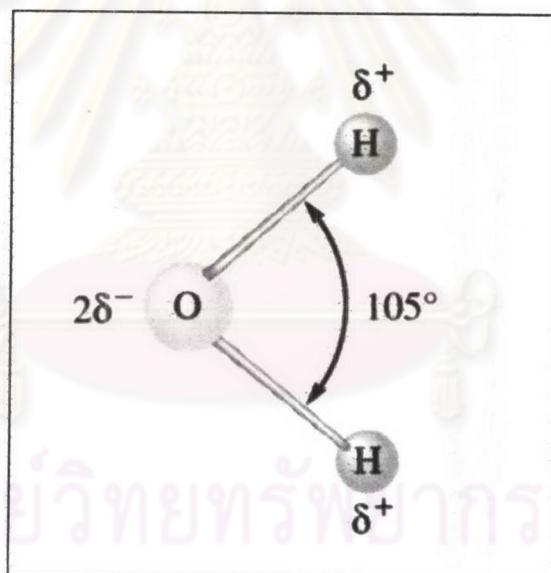


Fig. 2.7 The polar water molecule (Zumdahl, 1995)

Polarity of this magnitude produces intermolecular attractive forces, and water molecules therefore associate with considerable tenacity. Water's large intermolecular attractive forces can be explained quite adequately in terms of its ability to engage in multiple hydrogen bonding on a three-dimensional basis (Fennema, 1996), as shown in Figure 2.8.

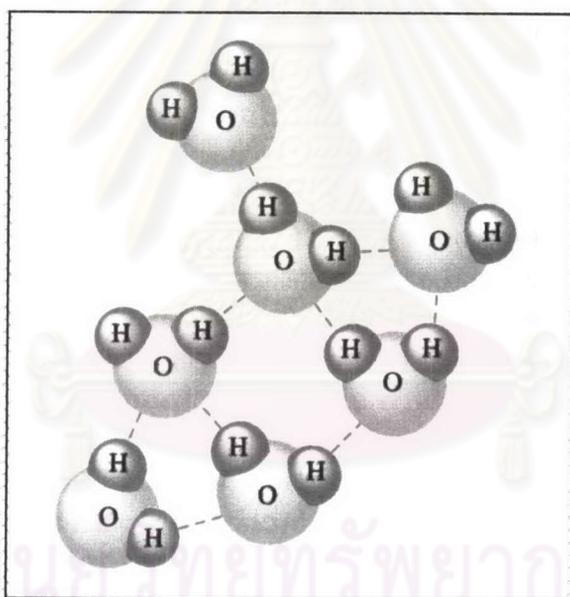


Fig. 2.8 Hydrogen bonding among water molecules (Zumdahl, 1995)

2.6.1 Interaction of water with ionic solutes

A schematic of an ionic solid dissolving in water is shown in Figure. 2.9. Note that the “positive ends” of the water molecules are attracted to the negative charge anions, and the “negative ends” of the water molecules are attracted to the positive charge cations. The process is called hydration. The hydration of its ions tends to cause a salt to “fall apart” of water, or dissolve. The strong forces present among the positive and negative ions of the solid are replaced by strong water-ion interactions. In addition, when ionic substances dissolve in water, they break up into the individual cations and anions floating around independently, as shown in Figure 2.10. The solubility of ionic substances in water varies greatly. The differences in solubility of ionic compounds in water typically depend on the relative affinities of the ions for each other (these forces hold the solid together) and the affinities of ions for water molecules (Zumdahl, 1995).

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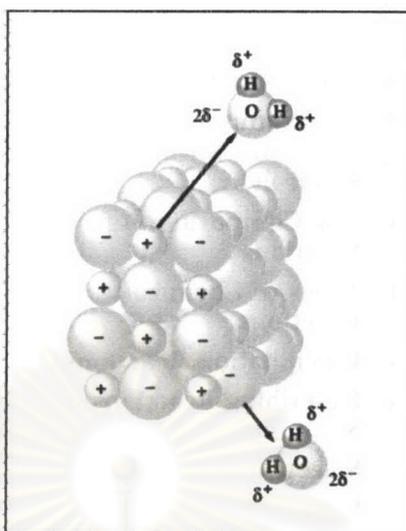


Fig. 2.9 Polar water molecules interact with the ionic substances
(Zumdahl, 1995).

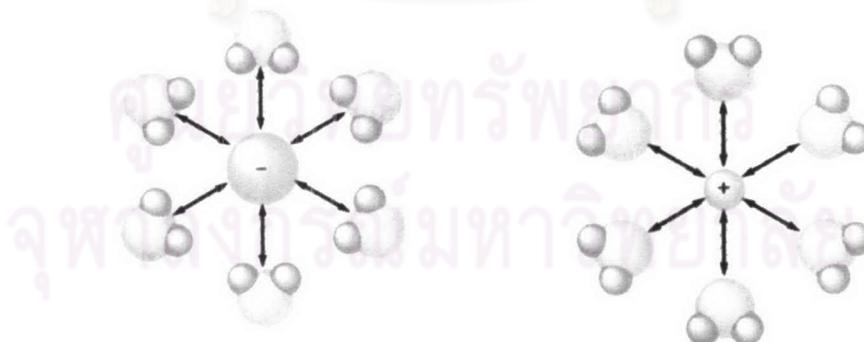


Fig. 2.10 The hydrated cation and anion (Zumdahl, 1995).

Cussler(1997) stated that the hydration correlated to diffusion coefficients of ions in water as following equation:

$$D_0 = (k_B T) / (6 \mu R_0), \quad (2.17)$$

where D_0 is a diffusion coefficient, μ is solvent viscosity, R_0 is the solute radius, k_B is the Boltzmann's constant, and T is temperature. In solution, the solute radius, R_0 , much be that of the hydrated species. This can be related to the true solute radius, R'_0 , by the equation:

$$(4/3)\pi(R_0)^3 = (4/3)\pi(R'_0)^3 + n [(V_{H_2O})/N], \quad (2.18)$$

where V_{H_2O} is molar volume of water, and n is the "hydration number" which is the number of water molecules bound to a solute. If the diffusion coefficient is known, R_0 can be calculated. R'_0 can be estimated from crystallographic data, and n can be calculated.

The data in Table 2.1 illustrates the hydration numbers and the diffusion coefficients of various ions. This suggests that the radii of diffusing solutes are in the order $Li^+ > Na^+ > K^+ > Cs^+$, exactly the reverse of the ionic radii found in the solid state. Such inverted behavior seems to be the result of hydration.

Table 2.1 The diffusion coefficients of various ions in water and the hydration numbers at 25°C.

Ion	Diffusion Coefficient* (X 10 ⁻⁵ cm ² /sec.)	Hydration numbers*
Li ⁺	1.03	2.8
Na ⁺	1.34	1.2
K ⁺	1.96	0.9
Cs ⁺	2.06	0.5
Cl ⁻	2.03	0
Br ⁻	2.08	0.2
I ⁻	2.04	0.7

Note: * Data of Robinson and Stokes (1960)

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2.6.2 Interaction of water with non-ionic solutes

Interactions between water and non-ionic, hydrophilic solutes are weaker than water-ion interactions and about the same strength as those of water-water hydrogen bonds (Fennema, 1996). Non-ionic substances dissolve in water but do not produce any ions. Since the molecules do not break up into ions, the resulting solution does not conduct an electric current. Ethanol (C_2H_5OH) or sucrose ($C_{12}H_{22}O_{11}$), for example, are very soluble in water but produce no ions when they dissolve. The molecules of these substances as shown in Figure 2.11, contain the polar O-H bond like those in water, which make them very compatible with water. The interaction of water with ethanol is represented in Figure 2.12.

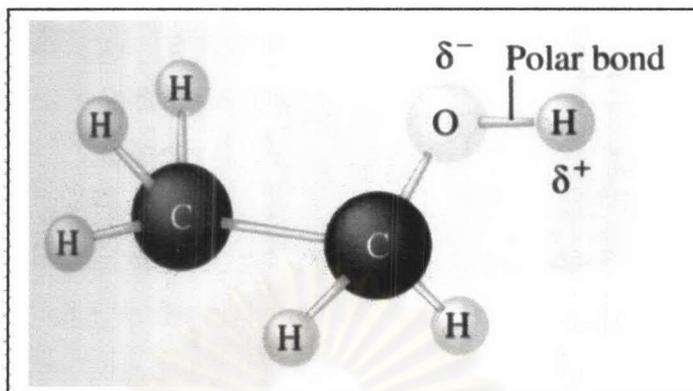


Fig. 2.11 The non-ionic molecule contains a polar O-H
(Zumdahl, 1995).

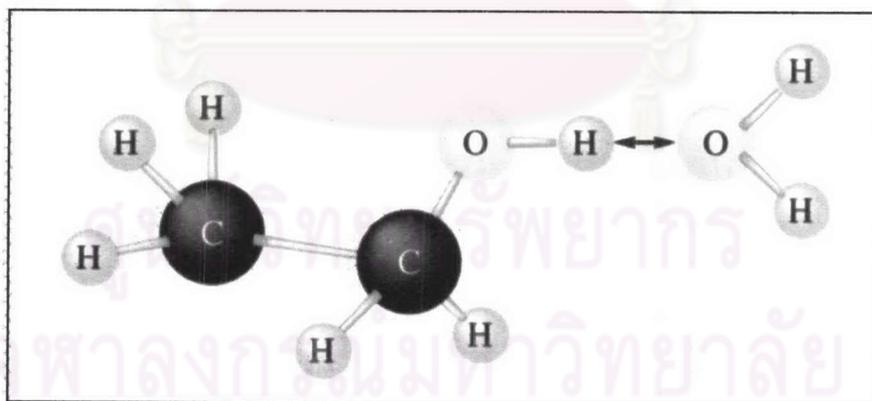


Fig.2.12 The polar water molecule interacts with the polar O-H bond
(Zumdahl, 1995).

2.6.3 Interaction of water with colloidal particles

A suspension of tiny particles in medium is called colloid. The suspended particles can be single, large molecules, aggregates of molecules or ions ranging in size from 10 nm to almost 1 mm. A colloid, like all other macroscopic substances, is electrically neutral. In an aqueous environment, the center of a colloidal particle (a tiny ionic charge, a group of molecules, or a single large molecules) attracts from the medium a layer of ions, all of the same charge. This group of ions in turn attracts another layer of oppositely charge ions, as shown in Figure 2.13 (Zumdahl, 1995).

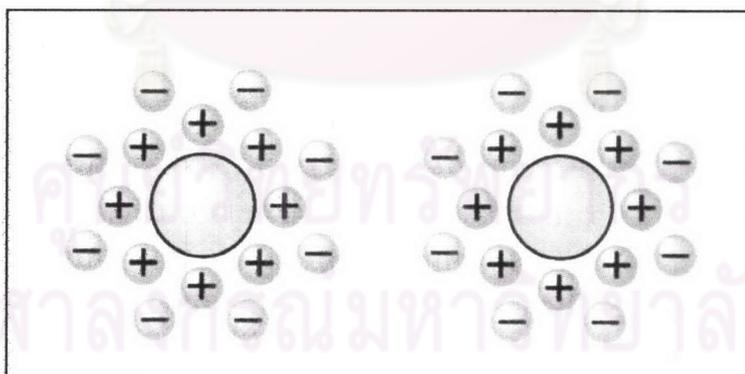


Fig. 2.13 A representation of two colloidal particles (Zumdahl, 1995).