

CHAPTER II

HISTORICAL BACKGROUND

2.1 Polyelectrolyte - Enhanced Ultrafiltration

Colloid - enhanced ultrafiltration is effective and economical method. Micellar - enhanced ultrafiltration (MEUF) involves the addition of surfactants to water. The micelles have a hydrophobic interior and the hydrophilic portion of the surfactants forms the surface of the micelle. Dissolved organics in the solution will tend to dissolve in the micelle. The solution is then treated in an ultrafiltration to reject the micelles and the solution passing through membrane can be pure (Scamehorn *et. al.*,1990). Polyelectrolyte - Enhanced Ultrafiltration (PEUF) is one of Colloid Enhanced Ultrafiltration process, which is a pressure - driven filtration separation occurring on a molecular scale, by adding water - soluble polymer or polyelectrolyte of opposite charge to waste streams containing ionic material in order to bond target ions (Sriratana *et. al.*,1996). It was improved to solve the problem from Micellar - Enhanced Ultrafiltration (MEUF) by using polyelectrolytes instead of micelles. The advantages of substituting polymer macroions for ionic micelles are that the low concentration in water of polyelectrolyte can remove trace quantities of highly poisonous or valuable multivalent counters and not dissociate into monomers. But ionic micellar solutions contain increasing fractions of monomers as the total surfactant concentration is diminished toward the critical micelle concentration (CMC), which is cause of loss surfactant monomers because they are small enough to pass through the ultrafiltration membrane. It leads to a small continuous depletion of the micelle for

separation (Tucker *et.al.*,1992) whereas it is not appeared in the case of the polyelectrolyte. On the other hand, MEUF can be used to remove both nonionic organics, while PEUF can remove only ions of opposite charge to the polyelectrolyte (Tabatabai *et. al.*,1995). In PEUF process, the retentate - based rejection, R , of a given species in a solution is defined by:

$$R_i (\%) = \left(1 - \frac{[\text{per}]_i}{[\text{ret}]_i} \right) \times 100$$

where $[\text{per}]_i$ is the concentration of species i in the permeate and $[\text{ret}]_i$ is the concentration of species i in the retentate

2.2 Precipitation

Most frequently the precipitation is the separation of solid phase, which is an insoluble substance, from a liquid phase. The desired constituents may be present in either the solid or liquid phase. According to Von Weimarn reference, the stages in precipitation process taking place in a solution of electrolytes are followed: (1) the collision of ions to form associated ions; (2) the aggregation of these associated ions to form a disperse colloidal system; (3) the further aggregation of colloidal particles to form visible particles; (4) the precipitation of the colloidally dispersed particles by the residual ions in solution; and (5) further changes, in the course of which the particles become larger to form a filterable precipitate and, in some cases, undergo a transformation to a more stable and less impure modification. Many factors should be concerned for formation of a given precipitate. They are the following: (1) the conditions of reaction e.g. the temperature, the concentrations of reactants, and the mixing solution; (2) the speed of reaction which has great effect on the nature of the precipitate obtained and which is in

large degree controlled by the conditions of the reaction; (3) the products formed, including the weight relationships, whether stoichiometric or empirical between the reactants and products, and the purity of the products.

2.2.1 Colloidal Phenomena

A colloid system consists of one substance, of suitable particle size, dispersed in another in which it is relatively insoluble. The former is called the dispersed phase and the latter the dispersing medium. Table 2.1 is shown the classification of disperse systems by size of the particles dispersed and some properties.

Table 2.1 Classification of disperse systems

True solution	Colloids	Suspensions
Diameter < 1.0 m μ	Diameter: 1.0m μ to 0.1 μ	Diameter:>0.1 μ
Not filterable	Not filterable	Filterable
Nonmicroscopic	Ultramicroscopic	Microscopic
Diffuse through membrane	Don't diffuse through membrane	Don't diffuse through membrane

The colloids are between the true solution and suspensions. They do not settle out and the dispersed phase cannot be separated by filtration because the particles are small enough to pass through the finest filters. Colloids are stable and exhibit the Tyndall effect and Brownian movement which is the random motion. The Tyndall effect which refers the path of a beam of light through a colloid can be seen since the particles are large enough to reflect light even though they are too small to be seen by eyes.

2.2.2 Equilibria in Mixtures of Precipitate and Solution

In the fact that the solutions forming an insoluble substance on reacting with each other may have no visible evidence of formation of the precipitate. An invisible substance is attributable to the formation either of a clear colloidal dispersion or a supersaturated solution. Moreover, a possibility is that not enough product to saturate the solvent may have been formed. As the results, the analyst is concerned with the equilibria, which is involved in the overall transformation of ions into insoluble particles of precipitate. At a given temperature a state of equilibrium is attained where there is not further change in the concentration of the solution in contact with solvent.

At equilibrium, there are two reactions:



Applying the equilibrium expression at any given temperature;

$$\frac{[X]_{\text{Dissolved}}}{[X]_{\text{Solid}}} = K$$

since the thermodynamic activity of a solid is constant for a given temperature, $[X]_{\text{Solid}}$ is constant. As the result,

$$[X]_{\text{Dissolved}} = [X]_{\text{Solid}} * K = K_{sp}$$

where K_{sp} is the solubility constant ,

$[X]_{\text{Dissolved}}$ is the concentration of ion product in saturated solution

$[X]_{\text{Solid}}$ is the concentration of precipitate in saturated solution.

When the solid is being formed in the solution, precipitation should occur as soon as the value of K_{sp} is exceeded, unless a state of supersaturation or a colloidal dispersion intervenes.

The solubility constant is used as a reference in order to compare with ion concentration products (ICP) for demonstration the possibility of the precipitation. ICP is the product of ion concentration in a solution. The precipitation takes place when the ion concentration product is higher than K_{sp} . On the other hand, the precipitation is not appeared in the solution.

For a saturated solution of a slightly soluble product, the expression shows that (1) the product of the concentrations of the ions has a definite value, characteristic of the solute at a given temperature; (2) there will be no precipitation of a given compound until the product of the concentration of its ions exceeds the solubility constant; and (3) the compound will dissolve in the solvent until the product of the concentration of the ions reaches the value of the ion product constant.