



CHAPTER II

BACKGROUND AND LITERATURE SURVEY

There are several ways to remove organic compounds from wastewater such as distillation and liquid extraction. However, these conventional separations still have some disadvantages; for examples, the distillation consumes a lot of energy and some liquid extraction process uses hazardous solvent. To overcome these problems, surfactant-based separation technique has been proposed because it consumes low energy and, generally, surfactant is not harmful. One of the interesting surfactant-based separations is cloud point extraction (CPE), which utilizes nonionic surfactant as a mass separating agent.

2.1 Principle of Cloud Point Extraction

Nonionic surfactant solution will become turbid when it is heated above a well-defined temperature, often called cloud point (CP) or a lower consolute temperature (LCT). The cloud point is depended on the type and concentration of surfactant. Moreover, the presence of other surfactants, acids or bases, salts and organic additives can also alter the cloud point. This cloudy solution can be separated into two phases under gravity or in a centrifuge. These two phases are coacervate phase and dilute phase. The coacervate phase is generally dense with micellar surfactants, while the dilute phase is lean in micellar surfactants. The cloud point extraction or coacervate-liquid extraction can separate the organic compounds from contaminated water by phase partitioning. Above the cloud point, volatile organic solute in the nonionic solution (or zwitterionic) tends to be solubilized and concentrated in micelles or micellar-like aggregates in the coacervate phase.

2.2 Surfactant Regeneration Processes

In order to make the CPE economically practical, the surfactants, which serve as a solvent in the extraction process, have to be recovered. Various technologies available for the surfactant regeneration are as follows.

2.2.1 Air Stripping in Packed Column

A packed column can be utilized to remove the volatile contaminants from water by air stripping at atmospheric pressure (Byers and Morton, 1985). Air can be injected either countercurrent or co-current into the column. The contaminant is transferred from aqueous phase to air due to a concentration gradient. This contaminated air stream needs to be treated either by incineration or adsorption using granular activated carbon (GAC) beds, which then need to be regenerated. When surfactant solution contacts with a gas phase, it leads to excessive foaming in the air stripper which could make the process inoperable (Lipe, 1993; Choori, 1994).

2.2.2 Steam Stripping in Packed Column

This is similar to air stripping except that steam is the vapor feed instead of air. The advantage of steam stripping over air stripping is that the contaminated gaseous stream can be treated just by condensing the steam. The organic contaminant separates out as an organic phase which can be separated from water by a liquid-liquid separator (Hwang et al., 1992a, 1992b). The disadvantage of this process is that it would lead to excessive foaming (Roberts, 1993).

2.2.3 Spraying

In spraying, area for mass transfer is generated by spraying the aqueous phase into small droplets. Rough vacuum can also be applied. This process also seems to be promising for surfactant regeneration if foaming can be suppressed (Choori, 1994).

2.2.4 Pervaporation

Pervaporation is a process in which a liquid stream containing VOCs is placed in contact with one side of a nonporous polymeric membrane while a vacuum or gas purge is applied to the other side. The components in the liquid stream adsorb into the membrane, permeate through the membrane, and evaporate into the vapor phase. The permeate vapor is then condensed. By using a membrane which is VOC-selective, the material on the vapor permeate side of the membrane will contain VOCs with concentrations significantly higher than those on the liquid side of the

membrane. Further, the permeate composition may differ widely from that of the vapor evolved after a free vapor-liquid equilibrium process (L. M. Vane et al., 2000). The advantage of this process is no foaming occurred but it is quite more expensive than stripping process (L. M. Vane, 2002).

2.2.5 Flash Vacuum Stripping in Packed Column

Vacuum stripping has been practiced for years for removing volatile compounds from water in the chemical and petroleum industry. It is used to remove hydrogen and ammonia from sour water, in removal of refrigerants (such as butane, propane) from water in desalination processes, in vacuum degassing of carbon dioxide and oxygen from water (Rasquin et al., 1977) and in de-aeration of water for injection into oil reservoirs. In addition, Tackie and Rice (1991) shown that vacuum stripping is feasible for stripping emulsions of an immisible volatile organic compound with water in several processes such as the waste brine streams from the secondary refrigerant freezing process, raffinate streams from extraction processes using solvents more volatile than water, waste streams from dry cleaning industries, and leachat streams from hazardous waste sites containing volatile organics.

In vacuum stripping there is no external vapor phase introduced but a very small volume of vapor phase is generated by flashing the aqueous feed stream at the top of the column (Rasquin et al., 1977, 1978). The column can be operated at temperature close to the boiling point of water at that pressure. The column operates under rough vacuum. Foaming is reduced considerably because of the reduced volume of the vapor phase. The contaminant can be recovered easily by condensing the vapor phase. The column can be operated in countercurrent or co-current mode. The co-current column is a single stage process. This process seems to be the most promising for removal of volatile organic compounds from surfactant solutions.

Rasquin et al. (1977) found that, in a mathematical model, the removal of sparingly soluble gases from aqueous solutions can be accomplished economically by a multistage vacuum stripping with the co-current operation rather than a single stage countercurrent with or without stripping steam operation. In addition, the advantage of co-current operation is that flooding is eliminated totally and the column can be operated at a much higher liquid rate. Excessive foaming that

accompanies the stripping of surfactant solution can be reduced by employing a co-current column (Lydersen, 1991).

2.3 Surfactant and Solubilization

Surfactants are one of the most widely used class of chemicals in the chemical process industry under a variety of names such as detergents, coagulants, dispersants, emulsifiers, de-emulsifiers, foaming agents, and defoamers. They are used in diverse products such as detergents, paints, pharmaceuticals, and motor oil. Moreover, surfactants have found applications in such high technology areas as magnetic recording, microelectronics, biotechnology, and viral research

‘Surfactants’ is an acronym of ‘Surface Active Agents’. Surfactant is a molecule, which alters the interfacial properties of any two phases by concentrating at the interface and thereby changing the interfacial free energy of the interface. This interfacial activity is due to the presence of two types of molecular groups (called head and tail groups) in one single molecule, one of which is lyophilic (solvent liking) and the other one is lyophobic (solvent disliking). This is known as the amphipathic structure. If the surfactant is present in an aqueous solution, then the lyophobic group (hydrophobic group) is the tail portion of the surfactant, which could be a hydrocarbon or a fluorocarbon. The lyophobic group (hydrophilic group) is the head portion of the surfactant, which could be an anion (such as sulfate or sulfonate), a cation (such as ammonium) or a nonionic group (such as a polyethoxylate).

2.3.1 Micelle Formation

One of the most fundamental and extremely important properties of surfactants is micelle formation. Micellization is an important phenomenon in detergency and solubilization.

When surfactants are present in water at low concentration, the hydrophobic group distorts the structure of the water and increases the free energy of the system. One way to minimize the system free energy would be to reorient the surfactant monomers so that their hydrophobic groups are directed away from the

water. Therefore monomers concentrate at the interface, leading to surface tension reduction. If the surfactant concentration is increased beyond the point at which the interface is completely covered with surfactant monomers then the free energy of the system can be reduced by the aggregation of the surfactant monomers into clusters with their hydrophobic groups oriented towards the interior of the cluster and their hydrophilic groups directed towards the solvent (water). These tiny clusters containing 50 to 500 monomers are called micelles. The phenomenon is called micellization, and the surfactant concentration at which the micellization begins to occur is called critical micelle concentration (CMC). Above the CMC the total monomer concentration remains at the CMC, but additional surfactant added forms micelles. At the CMC a drastic change in solution properties such as conductivity, surface tension, osmotic pressure, detergency, solubilization, light scattering and refractive index can be observed.

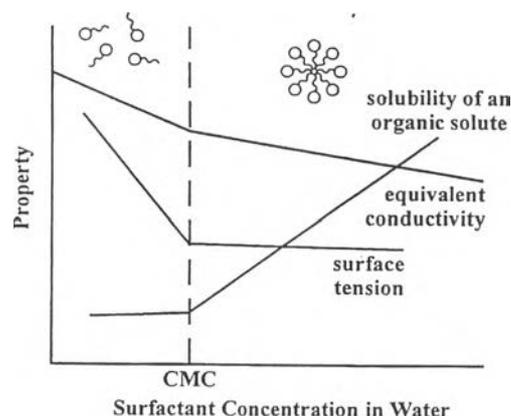


Figure 2.1 Plot of solution properties versus the bulk phase concentration for an aqueous solution of a surfactant.

2.3.2 Solubilization

When a hydrophobic organic molecule is added to a micellar solution, it tends to concentrate in the nonpolar interior of the micelles, which are more oil-like, rather than going into the more polar aqueous phase, a phenomenon called solubilization (Dunaway et al. 1995). The distribution of the solute between the micelles and the aqueous phase is described by a solubilization constant which is defined as follows:

$$K_s = \frac{C_{sol}}{C_u (C_m + C_{sol})} \quad (2.1)$$

Where K_s is the solubilization constant; C_{sol} is solubilized organic solute concentration; C_u is the unsolubilized organic solute concentration; and C_m is the surfactant concentration in micellar form.

In ground water treatment processes, where the concentration of solutes in the micellar phase is often much smaller than the concentration of surfactant in the micellar phase ($C_{sol} \ll C_m$), Equation 2.1 simplifies to:

$$K_s = \frac{C_{sol}}{C_u C_m} \quad (2.2)$$

where:

$$C_{sol} = C_{Total\ solute} - C_u$$

$$C_m = C_{Total\ surfactant} - CMC$$

$C_{Total\ solute}$ is total organic solute concentration and $C_{Total\ surfactant}$ is total surfactant concentration.

At a low enough solute concentration, the value of K_s is essentially equal to its infinite dilution value and is independent of solute concentration.

2.4 Mass Transfer in Surfactant Solutions

According to the thin film theory, the resistance to mass transfer consists of the individual resistances of the two phases and the resistance of the interface itself. The interfacial resistance of a clean surface is very small. The presence of surfactants and polymeric substances reduces the mass transfer rates in both gas-liquid and liquid-liquid systems as reported by many investigators (Koide et al., 1976). Koide et al. (1976) studied the mass transfer of CO_2 from single bubbles in

aliphatic alcohol solutions. In all these studies, the concentration of surfactants is either below or close to the critical micelle concentration.

The reduction in mass transfer coefficient due to the presence of surfactants is explained by two different mechanisms: the hydrodynamic mechanism and the barrier mechanism. Both mechanisms can probably act simultaneously. According to the hydrodynamic mechanism, the surfactants adsorbed at the interface retard the surface flow by a surface tension gradient, which is assumed to be indicated by the apparent increase in the viscosity of the dispersed phase (Koide, 1976). This accounts for the change in the mass transfer resistance of the bulk phases. In the barrier mechanism, the adsorbed surfactants act as barrier to the passage of solute molecules, which affects the interface resistance.

2.5 Equilibrium Data

The most important physical property data required for the design of absorbers and strippers are gas-liquid equilibrium. Since equilibrium represents the limiting condition for any gas-liquid contact, such data are needed to define the maximum gas purity and rich solution concentration attainable in absorbers and the maximum lean solution purity attainable in strippers. Equilibrium data also are needed to establish the mass transfer driving force, which can be simply defined as the difference between the actual and equilibrium condition at any point in a contactor.

In order to know the extent of removal of a solute from a solvent, it is necessary to know the equilibrium solubility of the solute in the solvent at a given temperature and pressure. When a solute and a solvent are completely soluble, and form an ideal solution, the vapor-liquid equilibrium can be described by Raoult's law. If a solute is sparingly soluble (mole fraction less than 0.01) in a solvent, then Henry's law can be used to define the equilibrium solubility at a given temperature and pressure. Henry's law is defined as follows:

$$P = H.C \quad (2.3)$$

where:

P = partial pressure of the contaminant in the vapor phase

H = Henry's law constant at a given temperature

C = concentration of the contaminant in the liquid phase.

If the Henry's law constant is expressed in dimensionless form, the above equation becomes:

$$y = H'.x \quad (2.4)$$

where H' is a dimensionless Henry's law constant based on mole fraction.

2.5.1 Measurement of Henry's Law Constant Using a Headspace Autosampler

A number of methods to determine Henry's law constant have been presented in the literature. They include (i) calculation from vapor pressure and solubility data; (ii) direct measurement of equilibrium concentrations in air and liquid; (iii) equilibrium partitioning in closed systems (EPICs); (iv) bubbled column technique; (v) multiple equilibration of a closed system; (vi) quantitative structure-activity relationship techniques (QSAR model); and (vii) wetted-well column technique. In this research, a method using a headspace autosampler is developed to measure Henry's law constant. (Peng and Wan, 1997)

A method using a headspace autosampler and gas chromatograph (GC) is developed to measure Henry's law constant of volatile organic compounds (VOCs). Equilibrium of VOCs between gas and liquid is established in the 22 ml headspace glass vials sealed with Teflon-faced silicone septa and cramp aluminum caps. Equilibration, sampling, and chemical concentration analysis by a high precision headspace autosampler-GC system minimize sample losses due to volatilization and give accurate results. With data of the chemical concentration in gas versus in liquid, Henry's law constant is determined by mass balance principle and ideal gas law.

2.6 Thermodynamics of Flash Vacuum Stripping

2.6.1 The Henry's and Modified Henry's Law Constant

Henry's law constant is one of the most important physical properties of VOCs to determine the partitioning of the chemical between air and water which

sometimes called True Henry's law constant. However, when surfactants are present above their CMC, they will form micelles and organic solutes will solubilize in the micelles. The presence of a micellar phase can be taken into account by modifying the Henry's law constant.

True Henry's law constant:

$$H_{Tr} = \frac{P_i}{C_u} \quad (2.5)$$

where:

P_i = partial pressure of the component i in vapor phase.

Henry's law constant for toluene in water at 30°C is 0.0062363 atm.m³/mol (Vane and Giroux, 2000).

Modified Henry's law constant (or Apparent Henry's law constant):

$$H_m = \frac{P_i}{(C_u + C_{sol})} \quad (2.6)$$

where,

C_u = unsolubilized solute concentration

C_{sol} = solubilized solute concentration.

Substitute P_i from equation 2.5 into equation 2.6

$$H_m = \frac{H_{Tr} \cdot C_u}{(C_u + C_{sol})}$$

$$H_m = \frac{H_{Tr}}{\left(1 + \frac{C_{sol}}{C_u}\right)} \quad (2.7)$$

Substitute K_s from equation 2.2 into equation 2.7

$$H_m = \frac{H_{Tr}}{(1 + K_s C_m)} \quad (2.8)$$

2.6.2 The Vapor-liquid Equilibrium Partition Coefficient (K)

In dimensionless form, the partition coefficient is defined as

$$K = \frac{y_i^*}{x_i^*} \quad (2.9)$$

where,

y_i^* = mole fraction of component 'i' in vapor phase at equilibrium condition

x_i^* = mole fraction of component 'i' in liquid phase at equilibrium condition

For solute (pollutant)

$$y_p^* = \frac{H_{Tr} C_u}{P} \quad (2.10)$$

$$x_p^* = \frac{C_u + C_{sol}}{C_{Tot}} \quad (2.11)$$

where,

C_{Tot} = total concentration of all components in the liquid phase (solute, water, and surfactant)

P = total pressure in vapor phase.

Therefore,

$$K_p = \frac{y_p^*}{x_p^*} = \frac{H_{Tr} C_u C_{Tot}}{P(C_u + C_{sol})} \quad (2.12)$$

Combining equation 2.2 with equation 2.12 yields:

$$K_p = \frac{H_{Tr} C_{Tot}}{P(1 + K_s C_m)} \quad (2.13)$$

In case of C_{sol} is much higher than C_u , equation 2.12 simplifies to

$$K_p = \frac{H_{Tr} C_u C_{Tot}}{P C_{sol}} \quad (2.14)$$

Combining with equation 2.2

$$K_p = \frac{H_{Tr} C_{Tot}}{P K_s C_m} \quad (2.15)$$

For water

$$y_w^* = \frac{P_w}{P_w + P_p} \quad (2.16)$$

$$x_w^* = \frac{C_w}{C_{Tot}} \quad (2.17)$$

where,

- P_w = partial pressure of water at equilibrium condition
- P_p = partial pressure of solute at equilibrium condition
- C_w = concentration of water in liquid phase at equilibrium condition.

In case of ground water treatment process, where the concentration of solutes in the liquid phase is dilute enough to obey Henry's law, water which acts as diluent and solvent is a major component. So, the partial pressure of water is assumed to be described adequately by Raoult's law and the mole fraction of water in liquid phase at equilibrium condition can be assumed to equal with 1. So, from Raoult's law,

$$P_w = x_w^* P_w^0 \quad (2.18)$$

where,

$$P_w^0 = \text{pure water vapor pressure.}$$

And, from the assumption that $x_w^* \sim 1$. So, we can conclude that

$$P_w = P_w^0 \quad (2.19)$$

In addition, total pressure in vapor phase at equilibrium condition can be calculated from

$$P = P_p + P_w^0 \quad (2.20)$$

So, the partition coefficient of water simplifies to

$$K_w = \frac{P_w^0}{P_w^0 + P_p} \quad (2.21)$$

2.7 Flash Calculations

Co-current flash vacuum stripping is, in effect, a single stage flashing operation. Hence, given the pressure and temperature of the system, from mass balance and partition coefficients, the final equilibrium concentration of the contaminant can be calculated.

Total mole balance

$$F = L + V \quad (2.22)$$

Component mole balance

$$z_i F = x_i L + y_i V \quad (2.23)$$

where,

- F = total mole in feed solution
- L = total mole in liquid phase after flashing at equilibrium condition
- V = total mole in vapor phase after flashing at equilibrium condition

- z_i = mole fraction of component i in feed
 x_i^* = mole fraction of component i in liquid phase after flashing at equilibrium condition
 y_i^* = mole fraction of component i in vapor phase after flashing at equilibrium condition.

The vapor-liquid equilibrium partition coefficient

$$K_i = \frac{y_i}{x_i} \quad (2.24)$$

Equation 2.22, 2.23, and 2.24 can be combined to give

$$x_i^* = \frac{z_i}{1 + \frac{V}{F}(K_i - 1)} \quad (2.25)$$

$$y_i^* = \frac{K_i z_i}{1 + \frac{V}{F}(K_i - 1)} \quad (2.26)$$

Since $\sum x_i^* - \sum y_i^* = 0$,

$$\sum_{n=1}^{n=i} \frac{z_i(1-K_i)}{1 + \frac{V}{F}(K_i - 1)} = 0 \quad (2.27)$$

2.8 Rate of Mass Transfer in Flash Vacuum Stripping

In order to design a packed stripping column, it is necessary to know the mass transfer coefficient of solute (pollutant). The mass transfer coefficient is a function of temperature, pressure, liquid and vapor flow rates, physical properties of liquid and vapor, packing size and type, and concentrations of solute and surfactant.

There are a number of correlation such as Sherwood and Holloway, Shulman, and Onda-Correlation available to predict mass transfer coefficients in air stripping.

In case of stripping a diluted liquid solution, mass balance of solute across a thin section of length dZ was derived as equation A.3 in appendix A

$$Z_0 = \frac{L}{K_x a} \int_{x_{ua}}^{x_{ub}} \frac{1}{x_u - x_u^*} dx \quad (2.28)$$

or

$$Z_0 = \text{HTU} \cdot \text{NTU} \quad (2.29)$$

where,

Z_0 = a height of packed column

HTU = a height of a transfer unit

NTU = a number of transfer unit.

Integrating equation 2.28 and rearranging and defining the number of transfer units (NTU) as

$$\text{NTU} = \frac{Z_0 K_x a}{L} = \ln \frac{x_{ub} - x_u^*}{x_{ua} - x_u^*} \quad (2.30)$$

where,

x_{ua} = the final unsolubilized liquid phase mole fraction of solute (in product)

x_{ub} = the initial unsolubilized liquid phase mole fraction of solute (in feed)

x_u^* = the equilibrium mole fraction of solute at that temperature and pressure.

Here it is assumed that x_u^* remains constant along the length of the column; i.e., pressure and temperature remain constant in the column. If the initial and final mole fraction of toluene are known, then the NTU and overall liquid phase mass transfer coefficient can be calculated.