Chapter 2

Theory

2.1 Pervaporation process

Pervaporation is a method for separation of liquid mixtures by partial vaporization through a non-porous membrane. The membrane acts as a selective barrier between liquid phase feed and vapor phase permeate. It allows the desired component(s) of liquid feed to transfer through it by vaporization. Typically, upstream side of the membrane is at ambient pressure and downstream side is under vacuum to allow evaporation of the selective component after permeation through the membrane. The fractionation process is mainly due to polarity differences, and not to volatility difference of the components in the feed. The word "pervaporation" is derived from two basic steps which are permeation of component(s) through the membrane and then evaporation into vapor phase. This process is used by a number of industries for several different applications, including purification and analysis, due to its simplicity and in-line nature.

The driving force for transport of different components is provided by chemical potential difference between liquid feed (retentate) and vapor permeate at each side of the membrane. The retentate is the remainder of the feed leaving the permeation cell, which is not permeated through the membrane. The chemical potential can be expressed in terms of fugacity, given by Raoults law for a liquid and by Daltons law for (an ideal) gas (Wikipedia, 2006). The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing partial pressure gradient is to sweep an inert gas over the permeate side of the membrane. These methods are described as vacuum and sweep gas pervaporation, respectively (Mahesh, 2006).

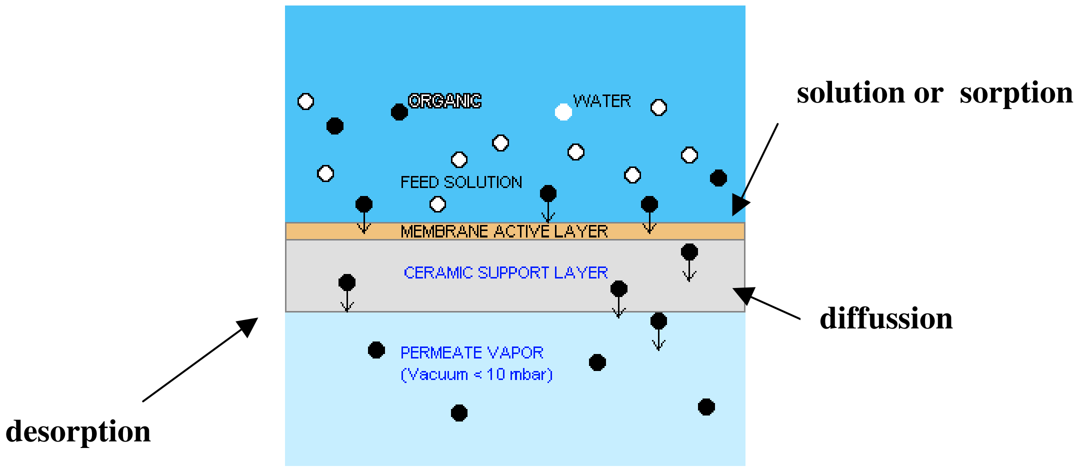

Figure 2.1 Schematic diagram of solution-diffusion model (www.chemelab.ucsd.edu/pervap/images/prevapmac.gif).

Separation of components (*e.g.* water and ethanol) is based on difference in transport rate of individual components through the membrane. This transport mechanism can be described using the solution-diffusion model (Wikipedia, 2006). The steps included are (1) sorption of the components at the interface of solution feed and membrane, (2) diffusion across the membrane due to concentration gradients (rate determining steps), and (3) desorption into vapor phase at the permeate side of the membrane. The solution-diffusion model is shown in Figure 2.1. The first two steps are primarily responsible for the permselectivity. As material passes through the membrane a "swelling" effect makes the membrane more permeable, but less selective, until a point of unacceptable selectivity is reached and the membrane must be regenerated.

Performance of Pervaporation Process

Pervaporation performance of the membrane is evaluated by three parameters; flux, separation factor and separation index.

Flux

In pervaporation, flux is the amount of permeate per unit area per unit time for a given membrane.

$$J = \frac{Q}{A \times t} \qquad (2\text{-}1)$$

where,
- J = Flux (g/m^{2}h)
- Q = Weight of permeate (g)
- A = Effective membrane area (m^2)
- t = Time (h)

Separation factor

Separation factor is the ratio of concentrations of components in the permeate to that in the feed, as given below:

$$\alpha = \frac{X_i^p / X_j^p}{X_i^f / X_j^f} \qquad (2\text{-}2)$$

where,
- α = Separation factor
- X^p_i and X^p_j = The weight fraction of the preferential and secondary, respectively, in the permeate
- X^f_i and X^f_j = The weight fraction of the preferential and secondary, respectively, in the feed

Separation index

Pervaporation separation index (PSI), which is a relative measure of the separation ability of a membrane, has been defined as the product of total flux and separation factor (Kariduraganavar et al., 2005). This index can be used as a relative guideline index for the design of pervaporation membrane separation process and also to select a membrane with an optimal combination of flux and separation factor. Separation index (PSI) was calculated as follow:

$$PSI = J(\alpha - 1) \tag{2-3}$$

where, PSI = Separation index

J = Flux (g/m^{2}h)

α = Separation factor

Membrane characterization

Swelling ratio

Swelling ratio is an important property of membrane as well as permeability and mechanical properties. Knowledge gained from such investigation between a polymer and water/organic mixture would be of considerable interest to many applications using membranes. The membrane swelling , as a result of interaction between penetrant and polymer, is a very important factor in transport through membranes. Swelling ratio can be calculated as follow :

$$R = \frac{l - l_0}{l_0} \tag{2-4}$$

where, R = Swelling ratio

l = Length of swollen membrane

l_0 = Length of dried membrane

Sorption selectivity

In pervaporation process, permeation of permeants through dense membranes follows a three-step course: sorption of permeating molecules into, diffusion through, and desorption out of the membrane. Incorporation of an adsorptive filler to the membrane can effectively improve the separation properties of membrane by enhancing the sorption capacity for the desired component. Sorption selectivity is calculated by the following equation.

$$\alpha_{sorp} = \frac{Y_i / Y_j}{X_i / X_j} \qquad (2\text{-}5)$$

where, α_{sorp} = Sorption Selectivity

X_i , X_j = The weight fraction of the preferential and secondary, respectively, in the feed

Y_i , Y_j = The weight fraction of the preferential and secondary, respectively, in the membrane

Tensile strength

Many polymer properties such as solvent, chemical, and electrical resistance and gas permeability are important in determining the use of a specific polymer in a specific application. However, the prime consideration in determining the general utility of a polymer is its mechanical behavior, that is, its deformation and flow characteristics under stress. The mechanical behavior of a polymer can be characterized by its stress-strain properties. Stress, in materials, is defined as the load per unit cross section of area. If a bar of any material is loaded by forces pulling it in opposite directions, the bar is said to be in tension. If the load or force pulling on the material is divided by the cross-sectional area of the bar, the result is the tensile stress applied to the sample. The maximum stress is known as the tensile strength. Tensile strength is usually expressed in newtons per square centimeter (N/cm^2) or megapascals (MPa). The equation for tensile strength is

$$tensile\ strength = \frac{load}{area} \tag{2-6}$$

2.2 Response Surface Methodology

Response surface methodology, or RSM, is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables and the objective is to optimize this response (Douglas, 2001). For the most of the response surfaces, the functions for the approximations are polynomials because of simplicity, though the functions are not limited to the polynomials (Todoroki, 2006). For polynomial equation is described as follows:

$$Y = b_0 + \sum_{i=1}^{k} b_i x_i + \sum_{i=1}^{k} b_{ii} x_2^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} b_{ij} x_i x_j \tag{2-7}$$

Where

Y	=	Response or interested property
x	=	Independent variables
b	=	Coefficient of independent variables which indicates the magnitude of effect that ensure from each independent variable which may be positive or negative
k	=	Number of independent variables

In the case of two variables, the response surface is expressed as follows:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_{11} x^2_1 + b_{22} x^2_2 + b_{12} x_1 x_2$$

In the case of three variables, the response surface is expressed as follows:

$$Y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{11} x^2_1 + b_{22} x^2_2 + b_{33} x^3_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3$$

RSM STEPS ;

1. Assign number of independent variables and range of each variable.
2. Calculate scale of variable (S) from

$$S = \frac{Range}{2a} = \frac{Max\ value - Min\ value}{2a} \qquad (2\text{-}8)$$

$$a = 2^{(k/4)}$$

Where, k = Number of independent variables.

3. Calculate natural variable from

Natural variable = S x coded variable + Mean (2-9)

Where, coded variable are -a, -1, 0 +1, -a and shown in Table 2.1.

Table 2.1 Coded variables of independent variables

Number of independent variable	Coded variables				
	-a	-1	0	+1	+a
2	-1.414	-1	0	+1	+1.414
3	-1.682	-1	0	+1	+1.682
4	-2.000	-1	0	+1	+2.000
5	-2.378	-1	0	+1	+2.378
6	-2.828	-1	0	+1	+2.828

4. Carry out experiments using natural variables calculated from equation (2-9).

5. From experimental results, determine the coefficients of independent variables (b_0, b_i, b_{ii}, b_{ij}), standard error (SE) and polynomial equation using essential linear regression program.

6. Create contour curve of response to locate the optimization.