일반강연 1-7

Preferential Sorption and Its Role on Pervaporation of Organic Liquid Mixtures

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The unique feature of pervaporation is the mass transfer from a liquid phase to a vapor phase through a non-porous polymeric membrane. When a liquid mixture is brought into contact with a membrane at one side, it is sorbed into the membrane. Due to a driving force applied across the membrane, the sorbed liquid molecules permeate through the membrane and evaporate at the downstream side of the membrane. In pervaporation the permeated species are usually removed from the downstream side under a relatively low vapor pressure, for example by evacuation with a vacuum pump. As far as this condition is fulfilled, the evaporation step can be considered to be much faster than sorption or diffusion. Hence evaporation does not contribute to permselectivity. Therefore the separation by pervaporation results from the differences in the preferential sorption of the individual components of a mixture into the membrane together with the diffusion rates through the membrane. This postulation implies that both sorption and diffusion phenomena have to be accounted for to understand the physico-chemical nature of the pervaporation separation process.

It is impossible to investigate experimentally sorption and diffusion processes separately because they take place simultaneously. Based on the above consideration, however, the results of thermodynamic equilibrium sorption experiments can be used to obtain information on the sorption process during pervaporation. The sorption of a binary liquid mixture in a polymer is characterized by two parameters; (i) overall sorption and (ii) preferential sorption. The overall sorption represents the total amount of liquid inside the polymer. The preferential sorption is a measure for the difference of the liquid compositions in the binary liquid phase compared to that in the polymer phase.

When a polymer is in contact with a binary liquid mixture, normally one of the mixture components is preferentially sorbed into the polymer. This preferential sorption phenomenon is

of special interest in the pervaporation process. Many authors have assumed an ideal additive behavior for component solubilities. In this case, the amount of each component sorbed in the polymeric membrane Q_i^m is assumed to be proportional to its activity a_i in the liquid mixture and the single liquid solubility Q_i° in the membrane: $Q_i^m = a_i * Q_i^\circ$. This equation implies that ideal preferential sorption occurs, which can be derived from pure component sorption data. However deviations from an ideal sorption are usually observed experimentally for the sorption of various liquid mixtures in polymers. Furthermore it is quite often observed that the component that is sorbed preferentially also permeates preferentially. In other words, preferential sorption is the leading factor in selective transport.

In order to obtain more information on the separation mechanism in pervaporation, equilibrium sorption experiments were carried out. The overall and preferential sorption of alcohol-toluene mixtures in homogeneous blends of poly(acrylic acid) and poly(vinyl alcohol) were determined to investigate the influence of liquid mixture composition. The sorption measurements with methanol-toluene and ethanol-toluene liquid mixtures showed that the varying liquid mixture composition had a strong influence on the overall and preferential sorption. The overall solubility in the poly(acrylic acid)-poly(vinyl alcohol) blends increased very much with increasing alcohol concentration in the liquid mixtures. In contrast, although alcohols were preferentially sorbed over the whole liquid composition range, the sorption selectivity decreased for all tested blends containing poly(vinyl alcohol) 10 to 40 wt.%.

The equilibrium sorption results were compared with the pervaporation results to evaluate the influence of sorption and diffusion on the overall pervaporation process. It could be deduced from this comparison that preferential sorption dominates the pervaporation selectivity in the membrane-liquid mixture systems studied.