

Effect of Temperature on Pervaporation Dehydration of Water-Acetic Acid Binary Mixture

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Dehydration of acetic acid was carried out in a small scale pervaporation pilot plant unit using commercial polyvinyl alcohol (PVA) membrane supported on polyether sulfone (PES). The hydrophilic membrane was able to selectively transport water molecules from the acetic-acid water mixture. It was observed that PVA membrane swelled significantly when the acetic acid concentration was increased in the feed solution. With increase in feed temperature degree of swelling decreased marginally. At 25°C the maximum degree of swelling was found out to be 46.3%, which reduced to 39.5% at 65°C. Although the pervaporation flux increased with increasing temperature of the liquid feed mixture, the separation factor decreased. From the temperature dependence of diffusion and permeation values, the Arrhenius apparent activation parameters have been estimated. The resulting activation energy values, obtained for water permeation being lower than those of acetic acid permeation values, suggest that the membranes have higher separation efficiency.

Keywords: Pervaporation, Acetic acid, PVA, Swelling, Flux, Activation energy

Introduction

Although the mixtures containing acetic acid and water do not form an azeotrope; their separation using distillation is constrained with associated high costs due to the requirement of large number of plates which are as many as 45-60¹. This separation is energy intensive because the relative volatility between water and HAc is close to unity. Cost-minimization and increase of separation efficiency are the major challenges of this separation. Pervaporation is recognized as a separation process in which a liquid mixture is separated by partial vaporization through membrane film. The feed liquid is brought into contact with a membrane and one component preferentially permeates the membrane in the form of vapor either by a sweeping carrier gas or by applying a vacuum. Pervaporative separation of aqueous HAc solution has been reported by several researchers, however with different membranes¹⁻⁵. While a number of researchers have studied the effects of process conditions on pervaporation system^{3,8}, correlating separation performance with temperature and intrinsic separation characteristics of commercial PVA membranes remain to be an underexploited area of research. Keeping this in mind the effect of temperature on the separation performance during pervaporation of

binary mixture of HAc-water in a pilot plant has been studied. A commercial hydrophilized PVA-PES composite membrane was employed for separation of water-HAc mixture. Pervaporation flux, separation factor, and selectivity were evaluated under different experimental conditions. From the temperature dependence of the permeation flux the Arrhenius activation parameters were estimated. Studies covered the entire concentration range of 10-90 vol% of HAc.

Materials and methods

Chemicals and membranes

Acetic acid (AR grade) was purchased from S D.fine-chem, Mumbai, India and used as received without further purification. Preparation of stock solutions was carried out with deionized water, having a conductivity of 20 μ S/cm, produced from a reverse osmosis system. Hydrophilized and flat sheet polyvinyl alcohol (PVA) membrane of thickness 115 μ m, with polyether sulfone (PES) support and crosslinked with glutaraldehyde was used in the study. The asymmetric PVA-PES composite membrane was supplied by M/s Permionics Membrane Pvt. Ltd, Baroda, India.

Pervaporation experiment

Pervaporation experiments were conducted in a small pilot plant assembly as shown in Fig. 1. The permeation cell consisted of two detachable stainless

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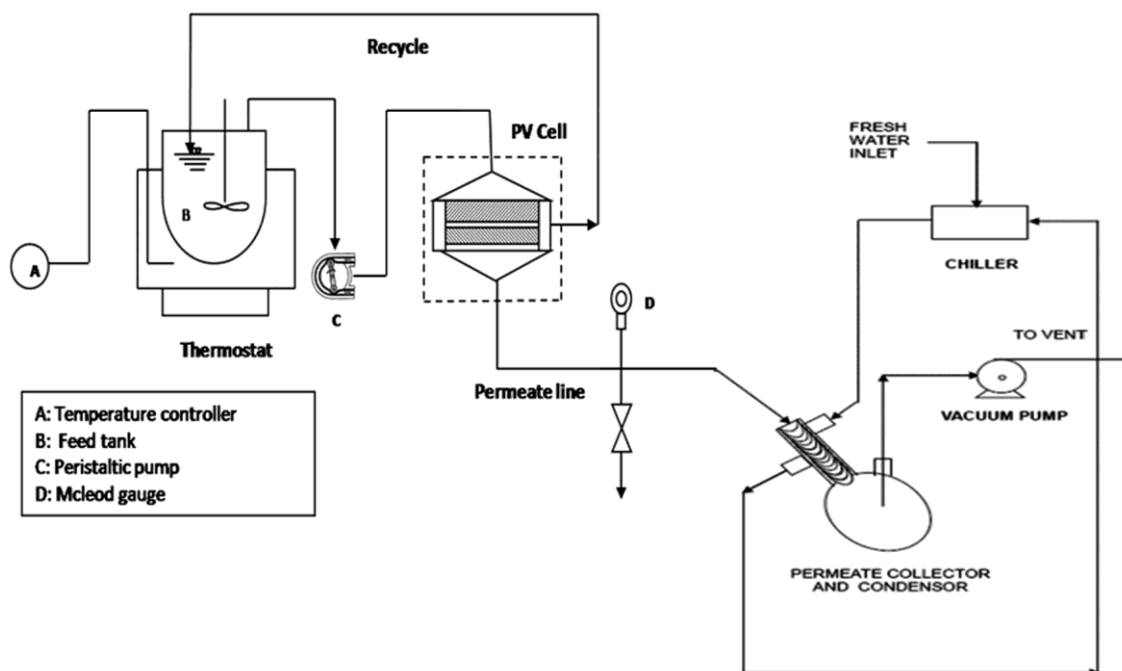


Fig. 1—Schematic diagram of experimental set-up for pervaporation used in the present study.

steel (SS 316) parts which were provided with inlet and outlet openings for the flow of feed solution and an outlet opening for the withdrawal of permeated product. The liquid feed-mixture is circulated in contact with the membrane using a peristaltic pump (capacity 180 l/h) from a feed tank, equipped with an overhead condenser to prevent any loss of feed due to evaporation.

The constant temperature of feed was maintained by using a thermostat bath and controlled on the inlet and outlet of cell according to the need of the experiment. The optimal operating pressure above the active layer of the membrane was atmospheric^{4, 8}. This condition was thought to avoid partial vaporization of the feed; thus, a pressure of 1 atm was used in this work. Before starting the PV experiments, test membranes were equilibrated for 1 h with the feed mixture. The pervaporate compositions were analyzed by measuring its refractive index with an accuracy of ± 0.0005 units using a refractometer. The obtained refractive index was then compared to a standard curve for acetic acid and water mixtures. Each experiment was repeated twice and the results were averaged to minimize error. The experimental data points were reproducible and the errors inherent in the pervaporation measurements were less than 3%.

Swelling study

Degree of swelling of the membrane was estimated by immersing the membrane samples into deionized water at a particular temperature for 24 h to ensure

equilibrium. Subsequently, the samples were taken out and removed the residual water on surfaces and weighed immediately. The samples were then dried in vacuum at 80°C for 24 h and weighed again. The water uptake was calculated in terms of swelling ratio as given by the following equation

$$S_R = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \quad \dots (1)$$

Where W_{dry} and W_{wet} are the weight of dry and swollen membrane, respectively,

Flux and separation factor

Flux and separation factor are two important performance indices of any pervaporation process. Pervaporation data are usually reported in terms of membrane separation factor and flux. The trans membrane flux in pervaporation is generally expressed as mass flux (J_i) with typical unit $\text{kg/m}^2 \text{ h}$. It can be determined for any species (say 'i', i.e. J_i) as Eq. (2)⁸:

$$P_i^G / l = J_i / (\gamma x_i P^{\text{sat}} - \gamma_i P_p) \quad \dots (2)$$

Where P_i is the membrane permeability, l is the membrane thickness and γ is the activity coefficient, which may be calculated using Van Laar equation. The mole fraction in the feed solution is denoted as x , P^{sat} is the saturated vapor pressure calculated with Antoine's equation, y is the mole fraction in the permeate and P_p is the permeate pressure obtained for

the component during the PV experiment. In gas separation, flux is normally given as a molar flux (J_i) with units $\text{cm}^3(\text{STP})/\text{cm}^2 \text{ s}$ or $\text{m}^3(\text{STP})/\text{m}^2 \text{ s}$. Ignoring simple numerical conversion terms (m^2 to cm^2 , h to s) this means:

$$J_i = j_i (m_i/v_i^G) \quad \dots (3)$$

Where v_i^G is the molar volume of gas I ($22.4 \text{ l}(\text{STP})/\text{mol}$) and m_i is the molecular weight of component 'i'. The membrane separation factor (β) can be defined as the ratio of the molar component concentrations in the fluids on either side of the membrane. Hence:

$$\beta = y(1-x)/x(1-y) \quad \dots (4)$$

Where 'x' and 'y' represent the feed and permeate mole fractions of the faster permeating component i which is water in the present case.

Permeability and selectivity

The membrane permeability, (P_i^G) (or permeability coefficient) is a component flux normalized for membrane thickness and driving force⁷. It is defined as the transport flux of material through the membrane per unit driving force per unit membrane thickness, given as Eq. (5)

$$P_i^G = j_i \times l / (\gamma_i x_i P_{\text{sat}} - y_i P_p) \quad \dots (5)$$

It is generally denoted as Barrers ($1 \text{ Barrer} = 1 \times 10^{-10} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ s cm Hg}$) for the gas separation. Alternatively, when the membrane thickness is not known, membrane permeance (P_i^G/l), ratio of membrane permeability to membrane thickness can be used. Permeance is most commonly reported as gas permeation unit (gpu) ($1 \text{ gpu} = 1 \times 10^{-6} \text{ cm}^3(\text{STP})/\text{cm}^2 \text{ s cm Hg}$). Membrane selectivity (α_{mem}), defined as the ratio of the permeabilities or permeances of components i and j through the membrane is given by Eq. (6)

$$\alpha_{\text{mem}} = p_i^G / p_j^G \quad \dots (6)$$

Results and Discussion

Membrane swelling

Pervaporation performance is affected by the extent of membrane swelling. Degree of swelling of the PVA-PES composite membrane used in the present study at three different temperatures viz. 25, 45 and 65°C for different concentration of acetic acid are presented in Fig. 2. In general it was observed that per cent degree of swelling decreased gradually with

increase in water concentration of the binary (water-acetic acid) feed mixture irrespective of temperature. Moreover, with increase in feed temperature degree of swelling decreased marginally. At 25°C the maximum degree of swelling was found out to be 46.3%, which reduced to 39.5% at 65°C . The sorption (swelling) mechanism of pervaporation membranes depends on many factors, such as membrane morphology, affinities of the components towards membrane and their mutual interaction^{8, 9}. This was due to an increase of preferential sorption of water. Water molecules absorbed by the hydrophilic groups, such as, $-\text{NH}_2$, $-\text{COO}^-$, or $-\text{OH}$ in the membrane resulted in the swelling of the membrane thereby assisting transport through the membrane. As the acetic acid concentration in the feed mixture increases because of a strong interaction between acetic acid and membrane, the membranes may become more swollen. This further result in more flexibility of polymeric chains and transport may become easier. Since the molar mass of HAc (60.05 g/mol) is higher than that of water (18.01 g/mol), the total degree of swelling of PVA-PES membrane was higher in HAc compared to water². It merits mentioning that the study of degree of swelling based on weight measurements is unable to justify differences in sorption on both sides of the membrane. Thus under present experimental setup swelling was thought to take place on the top PVA layer of membrane only. As a glassy polymer PES does not absorb water. Equilibrium mass uptake is a strong function of acetic acid concentration and also depends weakly on temperature. It is what causes PVA-PES composite membrane to swell among other things. Both

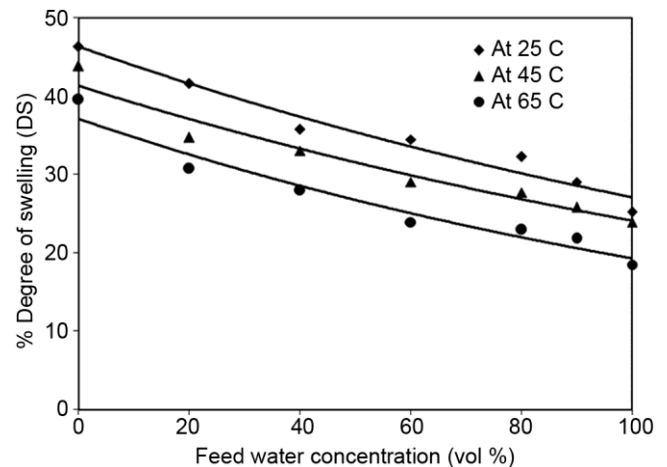


Fig. 2—Degree of swelling as function of feed water concentration at different feed temperature

temperature and solvent activity strongly affect the viscoelastic response of the membrane. In general creep increases significantly with increasing temperature. This is because bonding strength between polymer chains decreases with increasing temperature. However, combined effects of temperature and solvent activity are complicated. Acetic acid concentration strongly affects the viscoelastic response of membrane at all temperature¹⁰. It was shown at room temperature increased acetic acid concentration had increased the creep as well. The swelling from the high acetic acid concentration feed increased the free volume thereby changing the free volume distribution. The HAc-induced plasticization helped itself through the membrane much more than water, resulting in the low membrane selectivity.

Flux and separation factor

The temperature dependence of pervaporation data was investigated over a temperature range from 50 to 90°C with a constant feed concentration of 50% by volume acetic acid. These are presented in Fig. 3, which indicates that molar fluxes of both water and acetic acid increased with increasing temperatures. Generally, temperature influences both the permeate transport behavior and the ease of swelling by the polymer chain in the membrane structure. At higher temperature, frequency and amplitude of segmental motion of the polymeric chains increases with increased free volume and lower degree of swelling. This increased free volume facilitates transport of permeants. Further, vapor pressure of the permeating molecules also increases at higher temperature. The

combined effects of increased free volume and driving force (vapor pressure difference) result in the increased flux at higher temperature irrespective of concentrations. It is worth mentioning that the rate of increase of molar flux of water with temperature was found to be substantially higher than the rate of increase of acetic acid molar flux. At 70°C the molar flux of water was found out to be 0.3342 m³(STP)/m²h, whereas the acetic acid flux was 0.0526 m³(STP)/m²h, almost about seven fold lower. Although the pervaporation flux increased with increasing temperature of the liquid feed mixture, the separation factor decreased. At 50°C the separation factor was estimated to be 2.3, which decreased to 1.52 and 1.35 at 80°C and 90°C respectively. These results can be explained following the free volume theory. The thermal motion of polymer chains in the amorphous regions randomly produces free volume. As temperature increase, the frequency and amplitude of the chain jumping increase and the resulting free volumes become larger. The diffusion rate of isolated permeating molecules and associated permeating molecules are high when the temperature is high, so that total permeation rate is high and the separation factor is low¹⁰.

Permeability and selectivity

Intrinsic membrane permeability of acetic acid and water as a function of temperature is presented in Fig. 4. A perusal of Fig.4 indicates that permeabilities of both water and acetic acid increase with increase in temperature, although the magnitude of permeability of water was higher than that of acetic acid. It was observed (data not shown) that the membrane selectivity decreased with increase in temperature. At 90°C the selectivity was found out to be 44 % of that

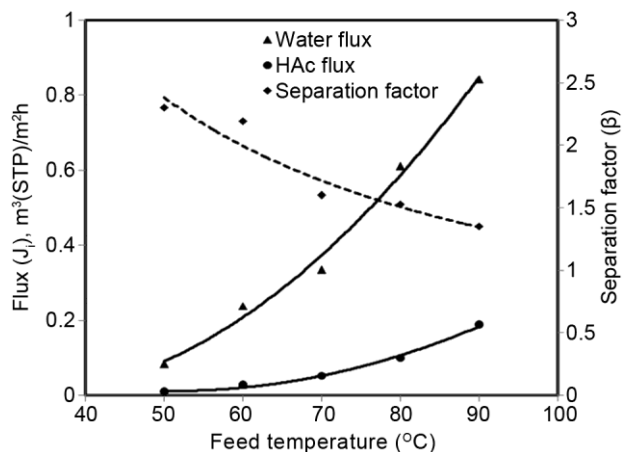


Fig. 3—Molar flux and separation factor as a function of feed temperature during pervaporative separation of acetic acid-water mixture.

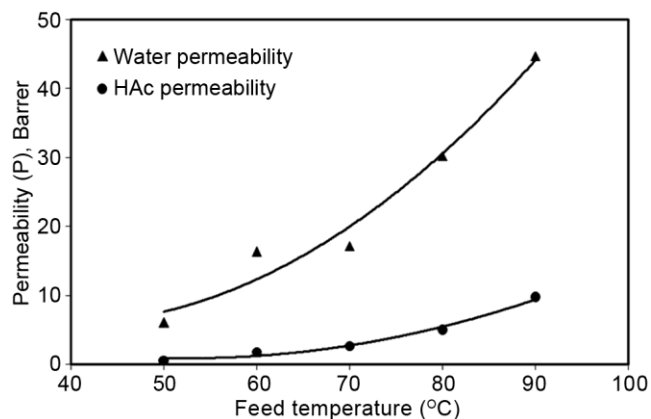


Fig. 4—Water and acetic acid permeability as a function of feed temperature during pervaporation in the present study.

obtained at 50°C. The HAc solubility in the polymer plays an important role in the membrane selectivity in contrast to the almost negligible water sorption. The swelled polymer chains due to the high HAc concentration feed favour more HAc sorption into the polymer (solubility). This swelling, in turn, enables large increase in diffusivity and permeability. In other words, the HAc permeability and solubility can increase significantly in high HAc concentration solutions. Nevertheless, the membrane selectivity decreases since the water permeability exhibits a rather limited increment under the HAc-induced swelling condition. This is believed to occur, since the swelling effect benefits the larger penetrant more than the smaller one¹¹. Thus, the PVA-PES membrane used in the present study may be suitably used at higher temperature with increased flux, however at the cost of a considerable decrease in membrane selectivity.

Activation energy

The relationship of flux or permeance of a penetrant across a membrane with operating temperature can be described by the Arrhenius equation¹². The results indicate that the apparent activation energy of water permeation (56.82 kJ/mol) was significantly lower than those of acetic acid permeation (79.35 kJ/mol), suggesting a higher separation efficiency of the membranes. If the activation energy is positive, the permeation flux increases with an increase in temperature¹². The present study also corroborates the same observation. As the water content in the feed decreases the polymeric membrane become less swollen and the mobility of chain segments decreases, thus increasing the energy required for the diffusive jump of acetic acid molecules. The interaction between permeants is thought to have an enhancing effect on the permeation activation energy because associated molecules require more energy for permeation than isolated molecules. In contrast, the plasticization action diminishes the activation energy by making the polymeric chain segments more flexible¹³.

Conclusion

Effect of temperature on molar flux, selectivity and intrinsic membrane permeability was investigated with a commercial PVA-PES composite membrane cross-linked with glutaraldehyde during the pervaporation of water-acetic acid binary mixture over a wide concentration range. The degree of swelling increased almost linearly with increasing

acetic acid concentration in the feed mixture ultimately resulting in an increase of the total flux. With increase in feed temperature degree of swelling decreased marginally. At 25°C the maximum degree of swelling was found out to be 46.3%, which reduced to 39.5% at 65°C. The rate of increase of molar flux of water with temperature was found to be substantially higher than the rate of increase of acetic acid molar flux. At 70°C the molar flux of water was found out to be 0.3342 m³(STP)/m²h, whereas the acetic acid flux was 0.0526 m³(STP)/m²h, almost about seven fold lower. However the separation factor decreased with increasing temperature. At 50°C the separation factor was estimated to be 2.3, which decreased to 1.52 and 1.35 at 80°C and 90°C respectively. The apparent activation energy value of water permeation was significantly lower than that of acetic acid permeation, indicating a higher separation efficiency of the membrane. The membrane used in the present study could tolerate highly concentrated corrosive acetic acid, thus may be useful for dehydration of other organics. However, further efforts for flux enhancement are needed in the future.

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