Comparison of the Separation Characteristics of Polyvinyl Alcohol Membrane in Dehydration of Benzene and Toluene Using Pervaporation

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ABSTRACT

Pervaporation (PV) is a well-established membrane technique used in separation; especially dehydration of organic solvents. Along with other parameters such as permeate pressure and feed temperature; feed composition is an important parameter, which affects separation characteristics and membrane performance in pervaporation. In this paper, the separation characteristics of a hydrophilic polyvinyl alcohol (PVA) membrane in the dehydration of benzene and toluene by pervaporation in the temperature range of 30-60 °C and permeate pressure of 7 mmHg have been compared. The results show that the difference in the molecular sizes of benzene and toluene and their mutual solubilities with water cause differences in separation parameters, so that for example at 50 °C, in dehydration of benzene water flux and water concentration in the permeate are 0.53 (g/hm^2) and 2.03 (wt.%) respectively, while the corresponding values in toluene dehydration are 0.61 (g/hm^2) and 3.19 (wt.%) respectively. Therefore these amounts result in higher pervaporation separation index (PSI) for toluene compared to benzene.

Keywords: Pervaporation, Benzene, Toluene, Dehydration, Poly (vinyl alcohol).

INTRODUCTION

In order to avoid deactivation of catalyst and/ or corrosion of equipment, it is often necessary to remove water from solvents during their application in chemical processing industries. The traditional processes for dehydration of solvents such as distillation have operational difficulties and consume large amounts of energy [1]. Pervaporation is an efficient membrane-based process used in the economical separation of liquid mixtures given some of its advantages including highly effective separation, no pollution, less installation space and energy saving [2]. This method has attracted the attention of specialists in chemical and related fields such as biochemical and petrochemical industries. Separation of liquid mixtures by partial vaporization through a membrane (non-porous or porous) is the separation principle in pervaporation. The driving force for the pervaporation process is the difference in chemical potential, corresponding to the concentration gradient between phases on the opposite sides of the interfacial barrier. The

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separation in PV occurs because of the different rates of sorption and diffusion of the feed components through the membrane [3]. The main industrial application of pervaporation even today is the dehydration of organic liquids; especially low molecular weight alcohols such as ethanol and isopropanol [4-6]. However, water removal from other solvents has also been considered in recent years [7-8].

Among aromatic compounds, dehydration of benzene using pervaporation has been focused on. Yu Lixin et al. have used PVA hydrophilic membrane in benzene dehydration at a temperature of 70° C and pressure of 800 (Pa) [9]. In addition, Gutch et al. have used aromatic polyamide membranes for the same purpose [10]. Li et al. have studied benzene dehydration in laboratory and pilot scales using modified hydrophilic membranes in 2002 [11]. Khatinzadeh et al. have studied benzene dehydration at low permeate pressures [12].

In dehydration of organic solvents by PV, the membrane should have sufficient affinity for water molecules so that water can be preferentially sorbed and transported at a rapid rate affecting an efficient separation. Due to high hydrophilicity, PVA has a greater tendency for polar water molecules than less polar organic molecules [13].

Although the solubility and permeability of water molecules in the membrane play fundamental and determining roles in the performance of hydrophilic membranes, the nature of organic solvent molecules can considerably affect these parameters. For example, in the dehydration of tetrahydrofuran and 1,4-dioxane using several hydrophilic membranes, Vijaya Kumar Naidu et al. found out that water flux values are higher for water+THF mixtures than water+1,4-dioxane

mixtures. They concluded that the flux for water increases steadily for water+THF mixtures probably due to a higher preferential interaction of water with the membrane in the presence of THF compared with 1,4-dioxane [14]. In other words, the differences between the properties of 1,4- dioxane and THF in the presence of water lead to varying interactions of water molecules with the membrane, resulting in the difference in the selectivity of the membrane to water molecules. This effect has been considered in water removal from benzene and toluene by pervaporation using polyvinyl alcohol membrane in this work. Although benzene and toluene possess very similar chemical properties, the difference in their molecular sizes and water solubility may affect membrane selectivity to water molecules in the presence of these solvents. The roles of the latter parameters have not been studied much in previous works on dehydration of aromatic solvents. In addition, the effect of temperature, a very effective parameter on membrane performance, has been studied in this work.

EXPERIMENTAL PROCEDURES

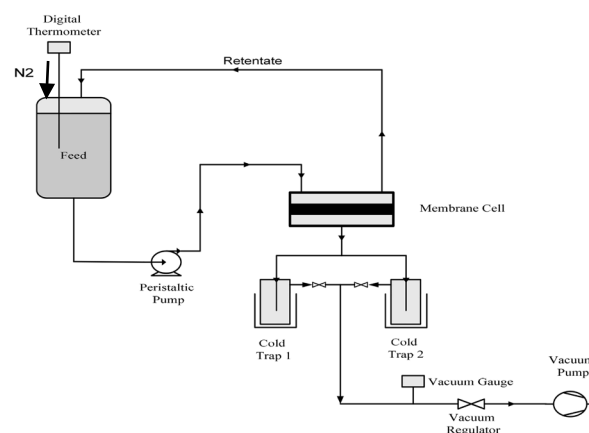Figure 1 shows the experimental set-up used in pervaporation experiments.

Figure 1: Schematic diagram of the experimental apparatus.

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The membrane module used in this study was of a plate-frame type made of stainless steel, and the membrane was supported on a porous disc with an effective membrane area of 177 cm². In all experiments, a commercially available membrane from Sulzer Chemtech (PERVAP 2201) was used. The membrane was a composite one with a hydrophilic top layer of PVA (thickness=2 μm) on a polyacrylonitrile (PAN) porous support (thickness=80 μm). Before starting the PV experiments, the test membrane was equilibrated with the feed solutions for about 3 hrs. In all pervaporation experiments, the feed was circulated over the membrane with a flow rate of 1.1 L/min using a peristaltic pump. A temperature probe attached to the feed tank was used to monitor the temperature during each run. The feed tank was maintained in the 30-60 °C temperature range by using a temperature controller. The permeate side of the membrane was maintained at the desired pressure using a vacuum pump. The permeate samples were condensed and collected in cold traps immersed in a liquid nitrogen bath. The water content of the samples including feeds permeates and retentates was determined by Karl Fischer method (ASTM D1533) using a Metrohom-831 KF Coulometer. Permeate fluxes (g/hm²) were gravimetrically obtained using Eq. (1):

$$J=M/At \hspace{3cm} (1)$$

where J is the permeate flux, M is the permeate weight (g), A (m²) is the membrane area and t (hr) is operation time. Separation factor (α) was evaluated using Eq. (2):

$$\alpha = \frac{Y_W / Y_B}{X_W / X_B} \hspace{2cm} (2)$$

where α is the separation factor and X and Y are the mass fractions of the feed and the permeate, respectively. Subscripts W and B stand for water and benzene or toluene, respectively.

Benzene and toluene used in these experiments were provided by Isfahan Petrochemical Complex and contained 150 ppm of water, as determined by Karl Fischer method. All experiments were carried out in N_2 atmosphere in order to prevent moisture from entering the system.

RESULTS AND DISCUSSION

Figure 2 shows the performance of the membranes in the dehydration of benzene and toluene in terms of water concentration in the permeate at different feed temperatures and constant permeate pressure (7 mmHg). As observed, the water concentration in the permeate is markedly higher than that in the feed. Therefore, the membrane is more selective toward water than benzene and toluene molecules.
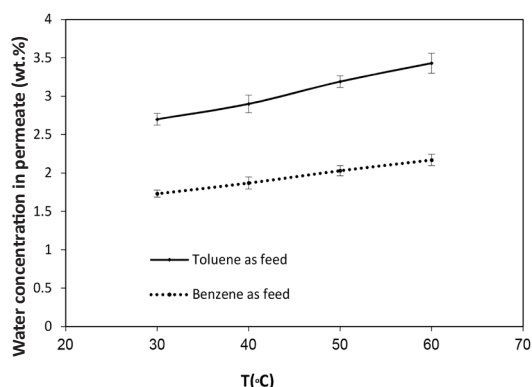

Figure 2: Water concentration in the permeate as a function of feed temperature (permeate pressure: 7 mmHg).

It is well known that hydrophilic membranes such as PVA can develop hydrogen bond interactions with water leading to preferential sorption and diffusion of water through the barrier membrane compared to organic solvents [15]. Furthermore,

Figure 2 shows well that water concentration in the permeate in toluene dehydration is greater than that of benzene dehydration. In other words, the membrane exhibits higher selectivity to water molecules in the presence of toluene compared with benzene. The investigation of water flux values also verifies this.

The water fluxes in the dehydration of toluene and the benzene as a function of temperature are shown in Figure 3. Water flux values are higher for toluene compared with benzene.
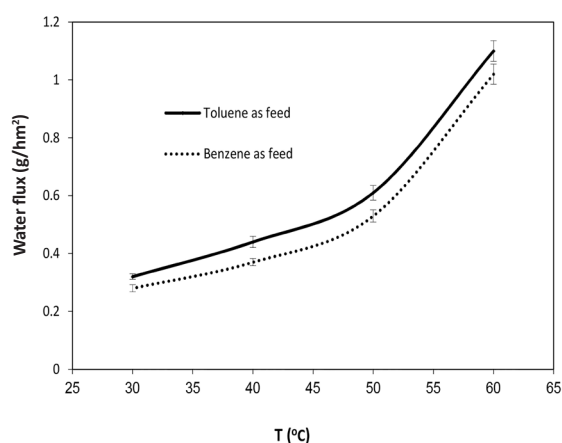

Figure 3: Water fluxes as a function of feed temperature (permeate pressure: 7 mmHg).

The transport of components of a mixture across the membrane in pervaporation is described by solution-diffusion model resulting from these processes in series: (1) solution of component molecules in the upstream surface of the membrane, (2) diffusion of the dissolved species across the membrane matrix and (3) desorption of the dissolved species in the downstream face of the membrane. These three fundamental processes also govern the mass transport across pervaporation membranes [16]. Therefore, according to the solution-diffusion mechanism, the permselective

properties of pervaporation membranes are determined by solubility and diffusivity of the permeating components in the membrane [17].

Permeability (P) = solubility (S) × diffusivity (D)   (3)

The solubility of a compound is the amount sorbed by the membrane under equilibrium conditions and is hence a thermodynamic parameter unlike diffusivity, which is a kinetic parameter quantifying the rate of permeation through the membrane. Solubility and diffusivity affect the selectivity as well as flux. Since both sorption and diffusion phenomena are dependent on the composition of the liquid mixture, the permeation properties are strongly influenced by the feed composition.

Therefore, the difference in the selectivity of the membrane to water molecules in the presence of benzene and toluene can be investigated from both solubility and diffusivity aspects. From the viewpoint of the solubility of water molecules in the membrane, it seems that the hydrophilic PVA membrane has a more effective interaction with water molecules in the presence of toluene, which may be due to the different effects of the molecules of these organic solvents on water molecules.

It is well established that the mutual solubilities of benzene-water are markedly larger than that of an alkane of similar size and an aromatic compound such as toluene or xylene. The mutual solubilities of some hydrocarbons with water are shown in Table 1. The relatively large mutual solubility of benzene with water compared with those of alkanes and aromatics is caused by the stronger solute-solvent Van der Waals interaction [18].

Table 1: Mutual solubilities of hydrocarbons and water at 25° C [19].

Compound	The solubility of hydrocarbon in water (ppm)	The solubility of water in hydrocarbon (ppm)
Benzene	1755.00	691
Toluene	573.00	543
o-Xylene	213.00	456
n-Hexane	12.40	90
n-Heptane	3.37	82

Therefore, the large mutual solubilities of water-benzene compared to water-toluene diminish the solubility of water molecules in the hydrophilic membrane, which results in lower water fluxes on the basis of the solution-diffusion mechanism. The increased water concentration in the permeate in both dehydration processes (Figure 2) indicates that water permeability (ratio of water to organic solvent flux) is increased by increasing feed temperature, as shown in Figure 4. In other words, the performance of the membrane is enhanced by increasing the feed temperature in water removal from both solvents. The closeness of the slopes of water permeability vs. temperature curves shows that water to solvent flux variations is close for both solvents at different temperatures.

Temperature is an important operating parameter in pervaporation because it affects both the sorption and diffusion rates. By increasing the temperature, the thermal motion of the polymer chains of the membrane increases, which increases the interspaces between the polymer chains. This can result in the enlargement of free volume inside the membrane, leading to easy permeation of the

constituents through the membrane. The vapor pressures of all the components in the feed mixture increase with increasing the feed temperature, but the vapor pressure at the permeate side is not affected. As a result, the driving force increases with increased feed temperature and hence the permeation flux increases as well [20].
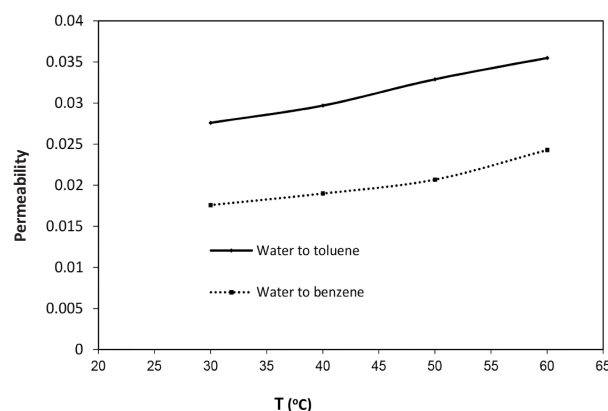

Figure 4: Water permeability in dehydration of benzene and toluene as a function of feed temperature (permeate pressure: 7 mmHg).

Increased water permeability at higher temperatures may be due to the increase in solubility, diffusivity or both. Furthermore, one-component permeability is dependent on the activation energy, according to Eq. (4):

$$J = J_0 \, exp(\frac{-E_p}{RT}) \tag{4}$$

where J_o is permeability constant, E_p represents activation energy and R and T are the feed temperature and gas constant, respectively [21]. Therefore, water has a higher permeation at higher temperatures compared with toluene and benzene due to its larger activation energy.

Figure 5 shows benzene and toluene fluxes vs. temperature. Both benzene and toluene fluxes increase with an increase in temperature.
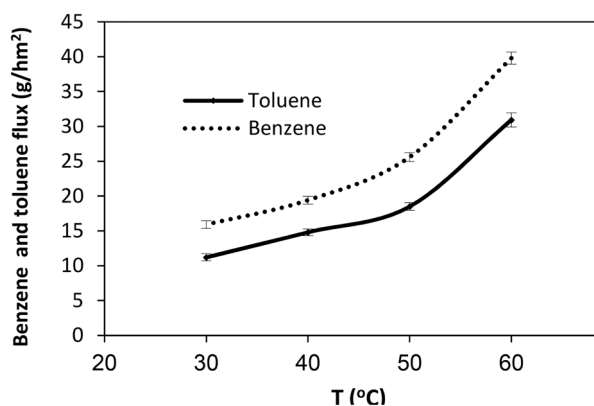
Figure 5: Benzene and toluene fluxes as a function of feed temperature (permeate pressure: 7 mmHg).

The difference between benzene and toluene fluxes is another reason for the different performances and selectivity of the membrane in the dehydration of these solvents. However, considering the hydrophilic character of the membrane and the small difference between the polarities and solubilities of toluene and benzene in the membrane, it seems that diffusion is the dominant factor in the flux differences of these two non-polar solvents. Diffusivity depends on the geometry of the membrane as well as its glassy rubber state. A small molecule will diffuse through a membrane more easily than a large one. Furthermore, diffusivity depends on the geometry of the penetrant. In other words, as the molecular size increases, the diffusion coefficient decreases. Dependency on size is determined by Stokes-Einstein equation presented in Eq. (5), which is the relation between frictional resistance and the radius of the diffusing component [22]:

$$f = 6\pi\eta r \qquad (5)$$

The diffusion coefficient is inversely proportional to the frictional resistance as:

$$D = \frac{KT}{f} \qquad (6)$$

According to Eqs. (5) and (6), the smaller size of the diffusing component causes frictional resistance and thus increases permeability coefficient.

The difference in the molecular size of benzene (0.59 nm) and toluene (0.68 nm) favors the permeability of the smaller molecule. In fact, the smaller benzene molecules can penetrate more easily than toluene molecules.

High benzene flux compared with toluene reduces membrane selectivity to water molecules, according to Eq. (2). Membrane performance is a function of water flux and selectivity to water molecules. The pervaporation separation index (PSI) was used to evaluate the overall PV performance [23]. This was calculated using Eq. (7):

$$PSI = J (\alpha-1) \qquad (7)$$

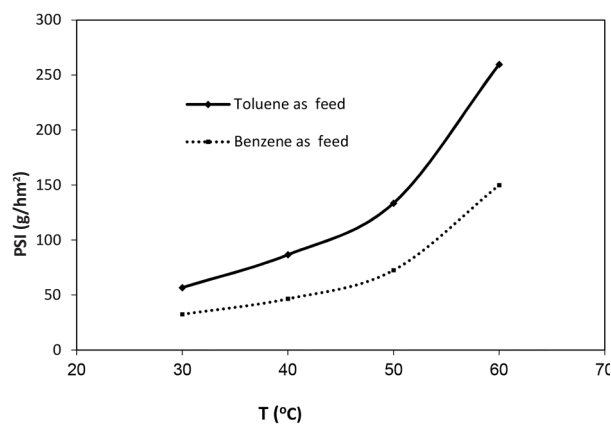where J and α are flux and selectivity, respectively.

Figure 6: PSI for dehydration of toluene and benzene as a function of feed temperature (permeate pressure: 7 mmHg).

PSI values in Figure 6 show that the hydrophilic PVA membrane performs better in toluene dehydration compared to benzene in the temperature range of 30-60 °C. Thus, the differences in molecular size and mutual solubilities of these solvents with water lead to different separation characteristics, which cause different performances of polyvinyl

alcohol hydrophilic membrane in the dehydration of benzene and toluene.

CONCLUSIONS

The higher concentration of water in the permeate in the dehydration of toluene by pervaporation indicates the more effective performance of PVA membrane in water removal from toluene compared to benzene, so that at 60 °C for toluene, PSI is 259.6 (g/hm²) while the corresponding value for benzene is 150 (g/hm²). In fact, the lower mutual solubility of toluene with water causes greater solubility of water molecules in the membrane, which results in more water permeability, based on the solution-diffusion mechanism. Furthermore, due to the higher diffusion coefficient, the smaller benzene molecules can diffuse more easily than toluene molecules, which causes higher benzene flux and lower concentration of water in the permeate. For example, at 60 °C in benzene dehydration, the water content in the permeate was 2.17 (wt. %) while the corresponding value in toluene dehydration was 3.43 (wt. %). However, the slopes of water permeability vs. temperature are close for both solvents at different temperatures.

On this basis, mutual solubility and molecular size considerably affect membrane performance. Moreover the data obtained in this work greatly help select the appropriate membrane for dehydration of aromatic compounds. However, the pervaporation process at low pressures is highly expensive. In addition obtaining supplementary data together with mass, energy and equipment cost calculation in order to optimize the separation conditions are necessary.

NOMENCLATURES

PV	: Pervaporation
PVA	: Polyvinyl Alcohol
PSI	: Pervaporation Separation Index

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