

Separation of alcohol-ester binary mixtures by pervaporation

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Abstract

In this study, the pervaporation behavior of azeotrope forming methanol-methyl acetate and ethanol-ethyl acetate binary mixtures at different compositions was investigated at 30 and 45 °C using PE-based films having different thickness, compositions and structures, and a PET film. Experimental fluxes and selectivities of the permeating components were determined and evaluated on the basis of the feed mixtures and membranes. In addition, sorption measurements were taken for pure permeating components to observe the interactions between the polymeric membrane and the feed component.

Introduction

Pervaporation is a rapidly developing clean separation technique, which has become popular for the past 15 years [1]. A liquid mixture is contacted with the upstream side of the membrane and the product permeating through the membrane is removed as a vapor at the downstream side with a low partial pressure. It can be used for the applications like dehydration of organic solvents or solvent mixtures, as alcohols, ethers, esters, ketones, etc.; extraction of organic solvents as esters, ethers, chlorinated hydrocarbons, aromatic compounds, etc. from aqueous solutions; recovery of aroma substances in the food industry [2-5].

In this study, azeotrope forming mixtures, methanol-methyl acetate and ethanol-ethyl acetate were aimed at separating by pervaporation. Due to their ease of availability, PE-based films with different compositions and structures were used in the separation of these binary mixtures. However, although selectivities were quite agreeable, low flux values obtained with PE-based films suggested the use of other membranes.

Experimental

Materials

Methanol, ethanol, methyl acetate and ethyl acetate used were Meck products of analytical

grade. Films produced from LDPE with the code of G03-5 were supplied by PETKIM Petrochemicals Inc. in Izmir. 20 % ionomer containing LDPE films and pure or 25% octene containing linear low density polyethylene (LLDPE) films were supplied by Koroza Inc. in Istanbul. Polyethylene terephthalate (PET) and PE+4 % EVA (ethylene vinyl alcohol) films was supplied by Saf plastik Inc. in Izmir. The thickness of the membranes used are given in the related tables.

Sorption set-up and procedure

Sorption experiments were performed with some of the membranes to determine the amount of single permeating component sorbed by the polymer film. The sorption set-up and procedure is given in literature [6,7]. The reproducibility in sorption experiments was within $\pm 5\%$.

Pervaporation set-up and procedure

Pervaporation experiments were performed with a stirred semi-batch glass set-up [6,7]. Vacuum was maintained at ≤ 7 mbar within ± 1 mbar by RZ 2 type Vacuubrand model vacuum pump. The experimental temperature was kept constant at $\pm 0.1^\circ\text{C}$ using a heating band and a variac, and maintained uniform by an adjustable stirrer. It was measured digitally by a probe mounted in the liquid feed mixture. The membrane rested on a perforated plate, which was cushioned by a nitrile rubber seal. The effective membrane area was 14,1 cm. Vapor

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permeate at the downstream side was collected alternatively in two liquid nitrogen traps. The detailed experimental procedure is given by Sentarli, et al [6] and Sain et al [7].

Analytical procedure

Compositions of liquid mixtures were determined by Chrompack 438 model GC equipped with a TCD detector and a packed Poropak Q column of 2 m length. The oven and detector temperatures were around 200 °C. Selectivities were calculated from the compositions of the permeating mixture. Fluxes were computed from the amount of permeate collected in the alternating traps. The reproducibilities of permeate compositions and fluxes were within $\pm 3\%$.

Results and discussion

Since pervaporation takes place by solution-diffusion mechanism, the importance of sorption in permeation of components through membranes has been stressed in literature [8]. The sorption data for pure methanol (MOH) and methyl acetate (MAc) pair, and pure ethanol (EOH) and ethyl acetate (EAc) pair are given respectively in Tables 1 and 2. As seen in these tables the membranes used sorb methyl acetate more than methanol and ethyl acetate more than ethanol. However, surprisingly higher sorption values were obtained with PET films. This can be attributed to higher solubility parameter of PET which is closer to the solubility parameters of the alcohols and esters used than PE [9].

Table 1.

Sorption data for pure methanol (MOH) and pure methyl acetate (MAc) using different membranes.

| Membrane | Thickness (μm) | Temperature ($^{\circ}\text{C}$) | Average Sorption (g solvent/100 g dry polymer) | |
|---------------------------------|-----------------------------|------------------------------------|--|-----------|
| | | | MOH | MAc |
| LDPE,G03-5 | 50 | 30 | 0.38 | 1.38 |
| LDPE,G03-5 | 50 | 45 | 0.40 | 1.59 |
| LDPE(ionomer based) PE+4%EVA | 75 60 | 45 30 | 0.79 0.22 | 2.81 3.69 |
| PE+4%EVA' | 60 | 45 | 0.63 | 3.70 |
| PET | 18 | 30 | 2.60 | 5.50 |
| PET | 18 | 45 | 2.71 | 5.42 |

Table 2.

Sorption data for pure ethanol (EOH) and pure ethyl acetate (EAc) using different membranes.

| Membrane | Thickness (μm) | Temperature ($^{\circ}\text{C}$) | Average Sorption (g solvent/100 g dry polymer) | |
|----------|-----------------------------|------------------------------------|--|------|
| | | | MOH | MAc |
| PE+4%EVA | 60 | 45 | 0.55 | 4.81 |
| PET | 18 | 45 | 2.45 | 5.15 |

Pervaporation data are given for pure methanol and methyl acetate in Table 3, and for various

mixtures of these components in Table 4. The selectivity is calculated from:

$$\text{Selectivity } (i/j) : \frac{\text{ratio of weicht \% 's of } i \text{ to } j \text{ in the permeate}}{\text{ratio of weicht \% 's of } i \text{ to } j \text{ in the feed}}$$

Tables 3 and 4 show that the flux increases and the selectivity decreases as the temperature increases, and the total flux decreases but the relevant selectivity increases as the composition of the more selective component (methyl acetate) decrease in

the feed. Pervaporation data at 45 °C are compared with VLE data from literature at 40 and 50 °C (10) in Figure 1. As seen in Figure1, all themembranes separate to a certain extent the azeotropic mixture of methanol and methyl acetate.

Table 3.

Pervaporation data in the form of mass fluxes (g/m²-h) for pure methanol (MOH) and methyl acetate (MAc) using different membranes.

| Membrane type; thickness | MAc | MOH | |
|---------------------------|-------|-------|-------|
| | 45 °C | 30 °C | 45 °C |
| PE+4%EVA; 55 µm | 252.8 | 13.9 | 22.8 |
| LDPEG03-5;32 µm | 343.U | - | 37.0 |
| LOPE (20% ionomer); 75 µm | 160.0 | - | 17.2 |
| LLDPE (25% octene); 20 µm | 983.0 | - | 50.9 |
| LLDPE (pure); 11 µm | 608.8 | - | 201.6 |
| PET;18 µm | - | 15.0 | 18.1 |

Table 4.

Pervaporation data for methanol-methyl acetate mixtures using different membranes (membrane thickness are given in Table 3).

| Membrane type | Feed temp. (°C) | MAc weight % in feed | MAc weight % in permeate | Total flux (g/m ² -h) | Selectivity (MAc/MOH) |
|---------------------|-----------------|----------------------|--------------------------|----------------------------------|-----------------------|
| PE+4% EVA | 45 | 92.0 | 94.0 | 231.1 | 1.36 |
| PE+4% EVA | 45 | 60.0 | 80.0 | 119.3 | 2.67 |
| LDPE (20 % ionomer) | - 45 | 80.0 | 88.8 | 79.1 | 1.98 |
| LLDPE (25 % octene) | 45 | 79.2 | 87.1 | 462.4 | 1.78 |
| LLDPE (25 % octene) | 45 | 60.2 | 82.0 | 382.4 | 3.01 |
| LLDPE (25 % octene) | 30 | 59.9 | 86.1 | 94.4 | 4.15 |
| LLDPE (pure) | 45 | 78.6 | 87.3 | 461.8 | 1.87 |
| LLDPE (pure) | 45 | 59.0 | 81.2 | 339.9 | 3.00 |
| LLDPE (pure) | 45 | 41.8 | 75.0 | 213.3 | 4.18 |
| LLDPE (pure) | 45 | 19.0 | 58.4 | 106.8 | 5.98 |

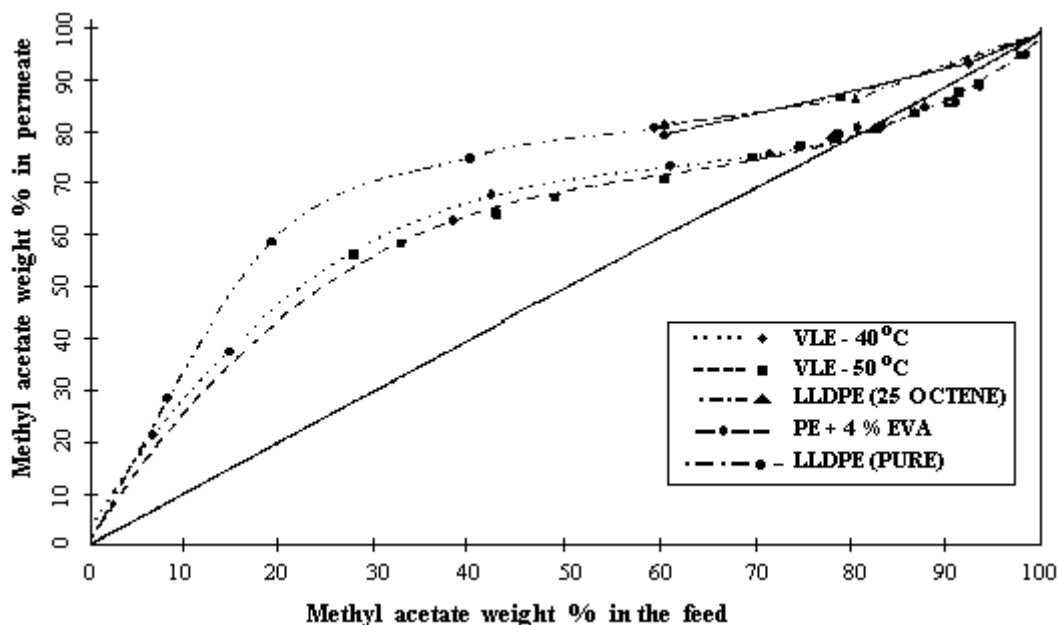


Fig. 1. Comparison of pervaporation data for methanol-methyl acetate binary VLE data from literature at 40 and 50 °C (10).

Pervaporation data are given for pure ethanol and ethyl acetate in Table 5, and for various mixtures of these components in Table 6. Although the sorption values obtained with

PET films for both ethanol and ethyl acetate are high, the total flux values for both the pure components and mixtures of them are low.

Table 5.

Pervaporation data in the form of mass fluxes ($\text{g}/\text{m}^2\text{-h}$) for pure ethanol (EOH) and ethyl acetate (EAc) using different membranes.

| Membrane type; thickness | EAc | EOH |
|---|---------------|--------------|
| | 45 °C | 45 °C |
| PE+4% EVA; 5.5 μm PET; 18 μm | 353 - 57.3 | 24.3 13.4 |

Table 6.

Pervaporation data for ethanol-ethyl acetate mixtures using different membranes (membrane thicknesses are given in Table 5).

| Membrane type | Feed temp. (°C) | EAc weight % in feed | EAc weight % in permeate | Total Flux ($\text{g}/\text{m}^2\text{-h}$) | Selectivity (EAc/EOH) |
|---------------|-----------------|----------------------|--------------------------|---|-----------------------|
| PE+4% EVA | 45 | 79.5 | 91.7 | 202.2 | 2.85 |
| PE+4% EVA | 45 | 60.0 | 86.2 | 145.4 | 4.17 |
| PE+4% EVA | 45 | 40.0 | 80.5 | 102.1 | 6.19 |
| PE+4% EVA | 45 | 19.0 | 70.0 | 53.2 | 9.92 |
| PE+4% EVA | 45 | 12.2 | 63.5 | 33.8 | 12.52 |
| PET | 45 | 80.0 | - | 21.2 | - |
| PET | 45 | 60.0 | - | 14.3 | - |

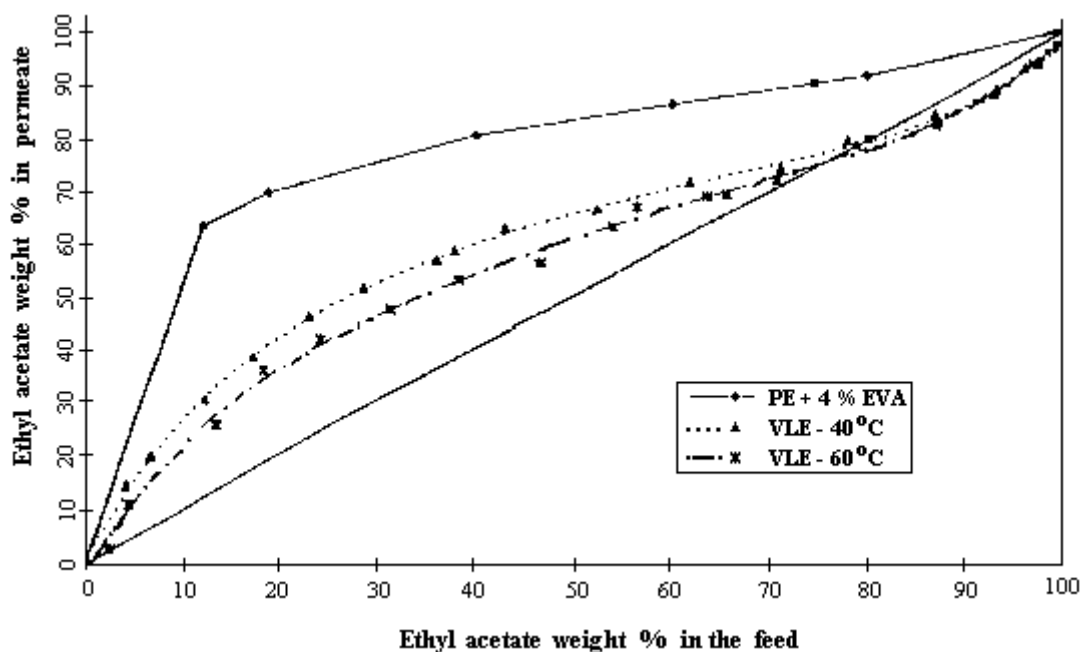


Fig. 2. Comparison of pervaporation data for ethanol-ethyl acetate binary VLE data from literature at 40 and 60 °C [10].

Pervaporation data using PE+4 % EVA membrane at 45 °C are compared with VLE data from literature at 40 and 60 °C [10] in Figure 2. As seen in Figure 2 PE+4 % EVA membrane separated the azeotropic mixture of ethanol and ethyl acetate quite reasonably.

Conclusions

PE based membranes can separate the azeotropic binary mixtures of methanol-methyl acetate and ethanol-ethyl acetate. However the fluxes are not high enough to justify their use in industrial applications. Although the sorption of pure ethanol, ethyl acetate, methanol and methyl acetate by PET films are much higher than other PE based films, the fluxes obtained through PET are so low that PET is unacceptable as a pervaporation membrane for the alcohol-ester binaries under study.

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