Pervaporative Membranes for Separation of Aroma Compounds from Aqueous Solutions

Anna Witek-Krowiak[1], Daria Podstawczyk[1] and Anna Dawiec[1]

[1]Wroclaw University of Technology, Department of Chemistry, Norwida 4/6, 50-373 Wroclaw, Poland

Abstract. In present investigation we have fabricated PDMS (polydimethylsiloxane) membranesby using spin coating technique for pervaporation of aroma compounds from aqueous solutions. Effect of zeolite FAU Y incorporation on membrane pervaporation performance was examined. The membrane pervaporation performance has been evaluated in terms of permeate flux and enrichment factor.The separation factors and yield of the permeation strongly depends on the membrane thickness. Modifications of the structure of PDMS, such as the incorporation of zeolite FAU Y to the polymer chain, resulting improvements in membrane separation properties.

Keywords: Pervaporation, Aroma, Membrane, Separation, PDMS, Zeolite

1. Introduction

Natural aroma compounds typically occur in low concentrations in fruits and vegetables. Therefore it is necessary to find the aroma recovery method, which ensures an adequate level of purity and sufficient quantity of the compound for industrial use. Conventional separation techniques such as solvent extraction or distillation are widely used in the industry. However, these methods have various limitations, particularly in relation to thermolabile compounds, permitting degradation and contamination of the product by the solvent.

Pervaporation can be alternative to the commonly used methods of extracting flavors and it has potential application in fruit juice industry. Some of the advantages of this membrane process, over conventional methods for aroma recovery, are that it can be operated at mild temperatures, it is based on physical separation mechanism, it does not require other solvents, and it has low energy consumption.

Pervaporation is a separation process based on a selective transport of some components from the multicomponent liquid mixture, through a dense membrane, associated with a partial evaporation of the selective component after permeation on the downstream side of the membrane. This phase change is possible by lowering the partial pressure of the permeate either by gas-sweeping. Separation is controlled by the differences of the solubility and diffusivity of each component in the nonporous pervaporative membrane. It is possible to separate substances on the basis of their physical properties such as hydrophobicity. Permeants dissolve in the membrane material and then diffuse through the membrane down in the concentration gradient direction. A separation is possible because of differences in solubility of each component in membrane material. Due to permeation rates, which are different for each component, one substance at low concentration in the feed stream can be highly enriched in permeate. Thus, the pervaporation is mainly regulated by the physicochemical structure of the membrane rather than the vapor–liquid equilibrium of the system [1], [2].

Polymeric membranes are the most commonly used materials since they are inexpensive, economically processible and at low operating cost. An improvement in permeation rate can be achieved by using asymmetric or composite membranes. Selection of the membrane-forming polymer is not random, but focused on the specific requirements of the structure of polymeric compound. Throughout good membrane selection, pervaporation can provide very good selectivity [3], [8].

The aim of this study is to use the spin coating technique to produce a PDMS membrane with an appropriate thickness and to evaluate the performance of spin-coated membranes using pervaporation of aroma compounds water solutions. Three aroma compounds, butyl acetate, ethanol and isopentanol, in different concentrations were selected. Also we have compared commercial membranes with this produced by spin coating and to examine the effect of zeolite Y incorporation on pervaporation performance and selectivity. The membrane pervaporation performance has been evaluated in terms of permeate flux and enrichment factor. Further, we have investigated the effect of membrane thickness and feed concentration on pervaporation of aqueous solutions of aroma compounds.

2. Materials and Methods

2.1. Materials

The applied commercial membranes were PERVAP-4060® (Sultzer, Germany) and Pervatech® (the Netherlands) hydrophobic membranes with an active layer made from α,ω-dihydroxypolydimethylsiloxane (PDMS). PDMS and crosslinking agent were supplied from Dow Corning. Ethanol, butyl acetate and isopentanol were purchased from POCH SA, zeolite FAU Y from Zeolyst International. The support layer membrane was polyvinylidene fluoride (PVDF) microfiltration membrane, obtained from MICRODYN NADIR.

2.2. Preparation of Pure PDMS Membrane

A PDMS clear solution was prepared by dissolving PDMS in hexane at room temperature with an agitation and mixing this solution with crosslinking agent (ratio 10:1). After bubble removal in a vacuum desiccator, 1ml of the polymer solution was spun on the PVDF microfiltration membrane supports in spin coater (Laurell Technologies, Netherlands). The coating rates was ranged from 2000 to 11000 rpm, which corresponds with the membrane thickness range of 8-69μm, the coating time was 120 s for all films. Then the membranes were dried at 60℃ for 2 hours to evaporate the solvent. The thickness was measured by a micrometer screw.

2.3. Preparation of the Zeolite-filled PDMS Membrane

PDMS and zeolite was mixed in the ratio 9:1 with the hexane as solvent. The solution was stirred in a beaker on a magnetic stirrer until a homogeneous suspension was obtained. The mixture was then cast on a PVDF microfiltration membrane with a knife, and spread with a roller. Membrane was left at room temperature for 24 h for soldification. The thickness was measured by a micrometer screw.

2.4. Sweeping Gas Pervaporation

Feed solutions for the experiments were aqueous solutions butyl acetate and isopentanol with concentrations 0.4-0.5% and 2-10% for ethyl alcohol. The temperature of the feed was kept constant at value 50℃ by the help of the controller of the thermostat (Medingen, Germany).

The pervaporation experiments were carried out by the apparatus developed by our laboratory. The feed solution was pumped by a pump purchased from KNF, from a feed tank to the pervaporation cell, which was a plate and frame module with an effective mass transfer area of 0,005m^2 (designed by our laboratory) and the retentate stream was recycled back to the feed tank. Permeate samples were collected in a reflux condenser cooled at a temperature of -5 ℃ by a cryostat (Julabo, Germany) and analysed every half or 1h or 2h, depending upon the amount of product obtained. Samples of the liquid feed mixture were also analysed in order to maintain constant concentration throughout the experiments. The downstream side was purged with a stream of inert gas. The concentrations of the feed solution and permeate were measured by gas chromatography (GC Varian 3800 with CP-8400 Autosampler, SpectraLab Scientific Inc., Canada). The permeation flux (*J*) and enrichment factor (*β*) were calculated from the following equations:

$$J = \frac{M}{t*A} \tag{1}$$

$$\beta = \frac{x_P}{x_F} \tag{2}$$

Where *M* is the weight of the permeate, *A* is the effective membrane area, *t* is the sampling time, x_P and

x_F are the weight fraction of component in the permeate and in the feed, respectively.

3. Results

3.1. Effect of Membrane Thickness

Seven different types of PDMS membranes with different thicknesses of active layers were used in pervaporation of ethanol/water mixture. The highest values of aroma stream and enrichment factor, which were 926,2 g/(m²•h) and 3,7 respectively, were obtained for commercial composite membrane Pervap 4060® (active layer thickness 2μm). The comparable results were obtained for the membrane formed by spin coating technique, with effective separation layer thickness of 6μm (Fig. 1.). Reducing the amount of permeate per unit time for the same area of all the membranes is due to the fact that increases the diffusion distance of molecules through the membrane, therefore the mass transport is slower.
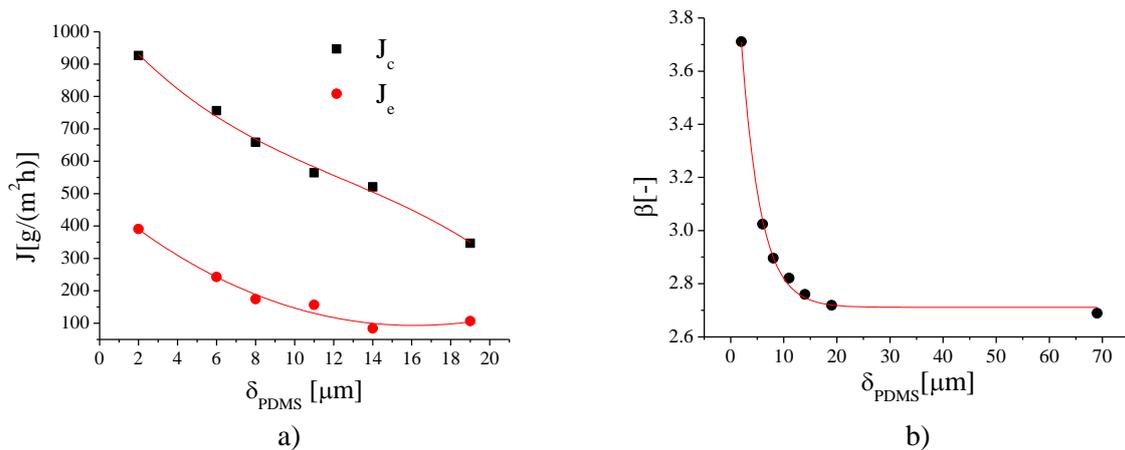

Fig. 1: Effect of membrane thickness on the a) permeate flux (total flux, J_c; ethanol flux, J_e), b) enrichment factor

3.2. Effect of Zeolite FAU Y Incorporation

For further investigation only five membranes (Pervap 4060 and Pervatech, membranes6 and 8μm, and zeolite filled PDMS membrane) were chosen.Streams of permeate and enrichment factors of isopentanol, ethanol and butyl acetate were compared (Fig. 2.). The most suitable membrane for the separation of the ester was the zeolite FAU Y filled composite membrane, while for isopentanol and ethanol, the highest values of aroma streams and enrichment factor was obtained on a commercial membrane Pervap 4060®.
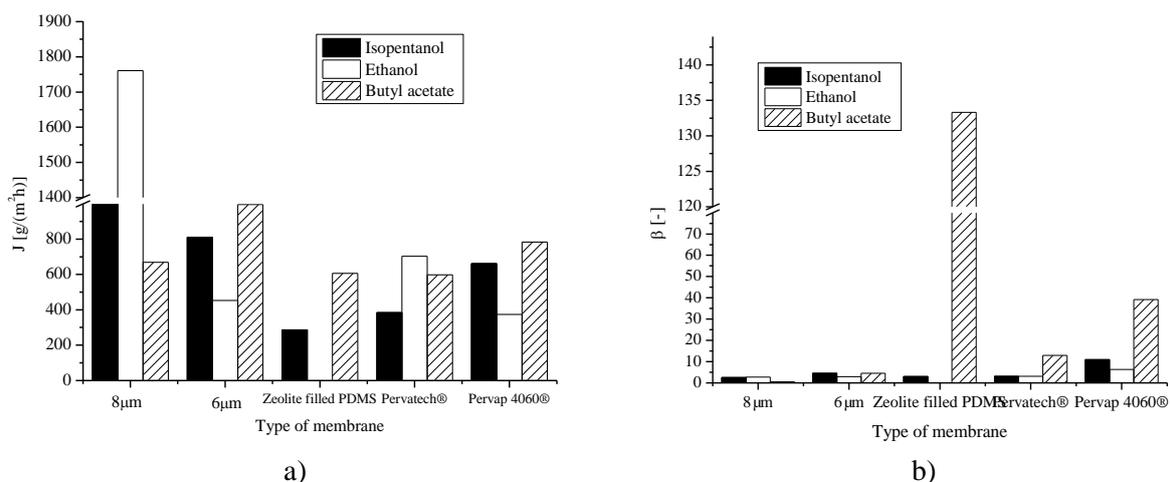

Fig. 2: Aroma (isopentanol, ethanol, butyl acetate)permeate flux and enrichment factor for selected membranes.

For isopentanol/water system, the zeolite filled membrane has the lowest flux and enrichment factor values. Quite opposite situation can be observed for an aqueous solution of butyl acetate, in this case the incorporation of the zeolite to the PDMS results an increase in aroma flux and a decrease in water stream,

while the enrichment factor was very high. These results can be explained by the fact that zeolite FAU Y is highly hydrophobic and could form some kind of channels for the ester molecules, causing an increase in membrane resistance to water. For the ethanol/water system, the amount of permeate was insufficient to investigate the weight fraction, and thus determine the enrichment factor.

4. Discussion

For the unfilled membranes the highest values of enrichment factor were obtained for commercial Pervap 4060® membrane for all feed solutions, which is consistent with expectations because this membrane has the lowest thickness. Prepared by spin-coating, membranes tend to decrease an aroma stream and enrichment factor with increasing hydrophobicity of the permeating compound, due to the size of particles separated.

The highest values of the degree of swelling were obtained for butyl acetate. It suggests that PDMS is ideal as a membrane for pervaporation of this compound. Polydimethylsiloxane membranes are highly selective for organic compounds, especially in the case of esters. Modifications of the structure of PDMS, such as the incorporation of zeolite FAU Y to the polymer chain, resulting improvements in membrane separation properties.

Present study has proven the importance of selective membranes for separation of aroma compounds by pervaporation. The aim of comparison of commercial membranes with those produced by spin coating was to find fast, easily available and economic methods for preparing polymeric membranes for pervaporation in laboratory scale. Spin coating is relatively fast technique, does not require additional reagents beyond the polymer and solvent, and ensures obtaining a polymer layer with an appropriate thickness. Simultaneously, the results obtained for such self-prepared membrane are satisfactory, comparable to those obtained for commercial membranes.

5. Conclusions

The study confirmed the validity of the use of polydimethylsiloxane membranes in the separation of aroma compounds from their aqueous solutions, but further studies on the modification of their structure should be made in order to further improve and scale up the pervaporation process, especially in searching for the appropriate membrane material.

6. Acknowledgements

7. References

[1] W. Kujawski. Application of pervaporation and vapor permeation in the environmental protection. *Pol. J. Environ. Stud*. 2000, 9: 13-26.

[2] J. Huang, J. Li, X. Zhan, C. Chen. A modified solution-diffusion model and its application in the pervaporation separation of alkane/thiophenes mixtures with PDMS membrane. *J. Appl. Polym. Sci*. 2008, 110: 3140–3148.

[3] H. O. E. Karlsson, G. Trägårdh. Pervaporation of dilute organic-waters mixtures. A literature review on modelling studies and applications to aroma compound recovery. *J. Membrane Sci.* 1993, 76: 121–146.

[4] A. Aroujalian, A. Raisi. Aroma compound recovery by hydrophobic pervaporation: the effect of membrane thickness and coupling phenomena. *Sep. Purif. Technol.* 2011, 82: 53–62.

[5] M. K. Djebbar, Q.T. Nguyen, R. Clement,, Y. Germain. Pervaporation of aqueous ester solutions through hydrophobic poly(ether-block-amide) copolymer membranes. *J. MembraneSci*. 1998, 146: 125-133.

[6] X. Zhan, J. Li, J. Huang, C. Chen. Enhanced Pervaporation Performance of Multi-layer PDMS/PVDF Composite Membrane for Ethanol Recovery from Aqueous Solution. *Appl. Biochem. Biotechnol*. 2010, 160: 632–642.

[7] A. Aroujalian, A. Raisi. Recovery of volatile aroma components from orange juice by pervaporation. *J. Membrane Sci.* 2007, 303: 154–161.

[8] A. Figoli et al. Bergamot essential oil extraction by pervaporation. *Desalination* 2006, 193: 160–165.