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Review

# Membranes for the dehydration of solvents by pervaporation

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ABSTRACT

This review aims at summarizing the main research carried out up to 2007 in hydrophilic pervaporation. Both polymeric and inorganic membranes are examined and the dehydration of alcohols such as ethanol and isopropyl alcohol covered in depth. When considering polymeric membranes, the research has been categorised into sections based upon the main polymer type used to achieve the separation. In the case of polymer blends, judgement has been used to group this accordingly. Inorganic membranes have been classified into two categories: inorganic, covering a broad range of inorganic materials and zeolitic, covering any inorganic membranes containing zeolitic material. The amalgamation of organic and inorganic material in the production of hybrid membranes is also reported.

Research performed in developing pervaporation membranes for the dehydration of other commonly used organics; acetic acid, tetrahydrofuran and acetone is then detailed and a summary of the current state of hydrophilic pervaporation is finally made.



## Contents



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## 1. Introduction

Industry today has to constantly review its production methods in order to remain competitive in the marketplace. This continuous improvement has led companies to invest in research into new technology to improve its production performance and reduce costs. Membrane separation processes have been seen to offer many advantages over existing separation processes such as "higher selectivity, lower energy consumption, moderate cost to performance ratio and compact and modular design" [1]. The Membrane Handbook [2] offers a good overview of the most commonly used membrane processes in industry today.

Pervaporation is one such type of membrane separation process with a wide range of uses such as solvent dehydration and separation of organic mixtures. It has significant advantages in azeotropic systems where traditional distillation is only able to recover pure solvents with the use of entrainers, which then must be removed using an additional separation step. Pervaporation can be used to break this azeotrope, as its mechanism of separation is very different to that of distillation. The Basic Principles of Membrane Technology [3] contains information on different membrane materials, fabrication techniques, module design and transport models for pervaporation and other membrane processes. In theory pervaporation can be used to separate any liquid mixtures but in practice, pervaporation tends to be used to separate azeotropic mixtures, close boiling-point mixtures, for the recovery of small quantities of impurities and for the enhancement of equilibrium reactions.

Pervaporation is seldom used by itself as a single process as it has to compete with reliable and better-understood processes such as distillation, liquid–liquid extraction, adsorption and stripping with existing infra-structure for such technologies available on many existing sites. However hybrid processes, combining pervaporation with one of these traditional separation techniques or with a chemical reactor are becoming increasingly common in industry where traditional techniques are insufficient and adding pervaporation allows performance targets to be met, superior performance and/or process optimisation.

A comprehensive review of polymeric membranes for pervaporation was recently made and published by Shao and Huang [4]. They investigated the potential pervaporation had for separating liquid mixtures in the areas of alcohol and solvent dehydration, organic(s) removal from water and organic/organic separations.

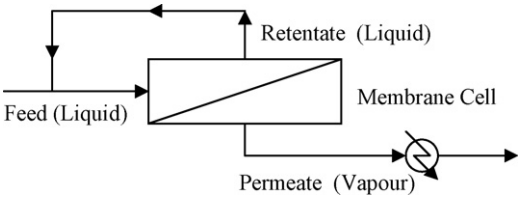


**Fig. 1.** Pervaporation membrane cell operation.

They also reported on the fundamentals of pervaporation transport in detail discussing modifications made to solution diffusion theory and discussion the importance of solvent coupling in diffusive transport and how this coupling can be accounted for. This review aims to complement the work of Shao and Huang taking a detailed look at hydrophilic pervaporation, identifying some of the key work performed with the various polymers and ceramics that have been used in developing pervaporation membranes for the dehydration of alcohols and other key organics. Table 1 contains some key data on the solvents covered in this review together with any binary azeotrope formed with water.

### 1.1. Pervaporation processes

#### 1.1.1. Operational characteristics

In pervaporation a liquid feed is passed over the membrane surface and one component is able to pass through the membrane preferentially. The feed to the membrane is usually at a temperature close to that of its saturation temperature and this combined with the underside of the membrane being held under vacuum causes the liquid passing across the membrane to vaporise. The vapour produced has a very different composition to that produced by simple distillation. The fraction of the feed that diffuses across the membrane is defined as the permeate, and the fraction that fails to pass through, the retentate. The permeate is then condensed which maintains the vapour concentration at the underside of the membrane low whilst the retentate is often recycled around to the feed tank to allow further separation to occur. It is often run as a batch operation with the run terminated once the required composition in the retentate has been achieved. This is illustrated in Fig. 1.

When selecting a membrane for a specific mixture there are two main parameters that need to be considered: first the mass

**Table 1**
Chemical properties and azeotropes with water of the solvents detailed in this review

| Chemical name | Formula | Molecular weight (g mol$^{-1}$) | Density (g cm$^{-3}$) | Boiling point (°C) | Vapour pressure @ 20 °C (hPa) | Azeotrope with water (wt% water) |
|---|---|---|---|---|---|---|
| Ethanol | $C_2H_5OH$ | 46.1 | 0.79 | 78 | 59.5 | 4 |
| Isopropanol | $C_3H_7OH$ | 60.1 | 0.78 | 82 | 43.2 | 12.6 |
| *n*-Propanol | $C_3H_7OH$ | 60.1 | 0.80 | 97 | 19.9 | 28.3 |
| 2-Butanol | $C_4H_9OH$ | 74.1 | 0.81 | 98 | 16.7 | 26.8 |
| *n*-Butanol | $C_4H_9OH$ | 74.1 | 0.81 | 118 | 5.3 | 42.5 |
| *t*-Butanol | $C_4H_9OH$ | 74.1 | 0.78 | 82 | 41 | 11.76 |
| Acetic acid | $C_2H_4O_2$ | 60.1 | 1.05 | 117 | 15.2 | Non-azeotrope |
| Tetrahydrofuran | $C_4H_8O$ | 72.1 | 0.89 | 66 | 190.7 | 5.3 |
| Acetone | $C_3H_6O$ | 58.1 | 0.79 | 56 | 245.3 | Non-azeotrope |

Chemical properties obtained from Sigma–Aldrich online MSDS sheets. Azeotropic data based on Azeotropic Data-III, in the Advances in Chemistry Series, American Chemical Society.