



Assessment of pervaporative separation of methyl acetate and methanol using organophilic membranes



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ABSTRACT

The separation performance efficiencies of polydimethylsiloxane (PDMS)-based (PERVAP™ 4060, PDMS 04-075, and PDMS 04-123) and polyoctylmethylsiloxane (POMS)-based (POMS 05-119) organophilic composite membranes were investigated, examining the amount of methyl acetate recovered from binary methyl acetate–methanol mixtures. The effects of feed composition (at 50 °C) and feed temperature (40 °C, 50 °C, and 60 °C) were investigated. Based on temperature variation tests, the enthalpies of evaporation for methyl acetate and methanol were estimated. Additionally, an empirical model was built on the basis of the solution-diffusion transport equation and extended to account for swelling characteristics of the membrane.

Whereas the membrane POMS 05-119 can be applied under the conditions described, particularly when the goal is to overcome the azeotropic barrier, separation performance of the PDMS-based membranes was inferior to the performance of a conventional flash distillation method.

1. Introduction

In non-aqueous solvent mixtures, numerous target alcohols form azeotropes with other organic compounds such as esters or ethers. Despite having a large commercial impact, pervaporative separation of organic mixtures has remained an undeveloped field of research (Smitha et al., 2004).

During pervaporation, a multicomponent, liquid feed stream is split into a liquid retentate and a vaporous permeate stream by selective dense membranes. As the driving force arises from the different chemical potentials of the feed and permeate streams, pervaporation is not limited by the vapour-liquid equilibrium of the mixture.

Mixtures of methanol (MeOH) and methyl acetate (MeOAc), for instance, are potential candidates for the application of pervaporative separation and were selected to study the separation performance of four organophilic membranes in this work. Methyl acetate forms a low boiling azeotrope when mixed with methanol at 53.5 °C (at 1.013 bar) consisting of 65 mol% methyl acetate and 35 mol% methanol (Gmehling et al., 1982). The efficiency of methyl acetate recovery from mixtures with methanol is not only crucial for methyl acetate production, but is also important in various transesterification reactions (e.g., the transesterification of methyl acetate with *n*-butanol for the production of *n*-butyl acetate (Steinigeweg and Gmehling, 2004), or for recycling residues during the polyvinyl alcohol production process (Vega Rodriguez et al., 2013). The production of methyl acetate via the

esterification of acetic acid with methanol is especially challenging because a second low boiling azeotrope is formed at 55.9 °C (at 1.013 bar) between methyl acetate (90 mol%) and the by-product water (10 mol%) (Gmehling et al., 1998). Furthermore, esterification reactions open up a new pathway for the separation of low-molecular weight carboxylic acids from aqueous effluents (Painer et al., 2015). Therefore, the development of pervaporation methods, when combined with reactive distillation methods via esterification with methanol, is a promising technological approach.

Several researchers (e.g., Steinigeweg and Gmehling, 2004; Sain et al., 1998; Brinkmann et al., 2008; Gorri et al., 2006; Abdallah et al., 2013; Genduso et al., 2015; Lux et al., 2015) have already demonstrated the high potential of pervaporative separation of methyl acetate–methanol mixtures using various hydrophilic polymer membranes. With these types of membranes, methanol is recovered via the permeate stream, whereas methyl acetate is retained in the retentate. However, few studies that have investigated the performance of organophilic polymeric membranes for recovery of methyl acetate from methyl acetate–methanol mixtures are available in the literature. Penkova et al. (2013) investigated the separation of reactive acetic acid–methanol–methyl acetate–water mixtures by pervaporation. They used poly-(2,6-dimethyl-1,4-phenylene oxide) (PPO) membranes and compared the separation performance of a homogeneous PPO membrane with that of a thin film composite membrane, which consists of a thin selective PPO layer on the surface of a fluoroplastic composite

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hydrophobic membrane (MFC) (Penkova et al., 2013). More research has been done on the separation of methanol from methanol–methyl *tert*-butyl ether (MTBE) mixtures by organophilic pervaporation. Smitha et al. (2004) gave a comprehensive review of pervaporation studies for methanol–methyl *tert*-butyl ether separation (Smitha et al., 2004). Other researchers mainly focused on ester or alcohol recovery from aqueous solutions (Toth and Mizsey, 2015; Mohammadi et al., 2005; Kujawski, 2000; Trifunovic, 2003).

Until now, extensive research has been performed to find suitable membrane materials for organophilic pervaporation. Silicone-based, polymeric, composite membranes have been found to exhibit good organophilicity (Mohammadi et al., 2005). In this study, polydimethylsiloxane (PDMS)- and polyoctylmethylsiloxane (POMS)-based membranes were used. PDMS consists of $-\text{O}-\text{Si}(\text{CH}_3)_2$ -groups and POMS, of units of $\text{O}-\text{Si}[(\text{CH}_2)_7\text{CH}_3](\text{CH}_3)$ -groups. Both chemical structures lend themselves to hydrophobic behaviour and low polarity (Lee et al., 2003; Trifunović and Trägårdh, 2006).

As the selective permeation of individual components through dense polymeric membranes is governed by the solution-diffusion properties of the components in the polymer, sorption has a dominant effect on the overall separation performance. The relative sorption of the permeating components depends on their relative solubility in the membrane. This can be explained by applying the solubility parameter theory. Hildebrand and Scott (1950) first defined the solubility parameter δ . For its determination, cohesive energy densities are used that are measures of the cohesive force holding molecules together in the liquid phase. The solubility parameter is useful for predicting the sorption, miscibility and swelling of a polymer in a solvent (Mandal, 2002; Lee et al., 2003), but only reflects the attractive forces of pure substances. In multicomponent mixtures, interactions may arise (Koenhen and Smolders, 1975). In general, pervaporation membranes are selected in such a manner as to selectively sorb the target component to be separated via the permeate stream. This component is ideally present in a low concentration (Mandal, 2002).

Table 1 summarizes the molar volume and solubility parameters of the two components, methanol and methyl acetate, as well as the solubility parameters of the active siloxane layers in the composite membranes (PDMS, POMS). Obviously, components with differing solubility parameters can be more easily separated by pervaporation than components that have similar size, solubility and polarity characteristics. To achieve a high level of affinity between the polymer and the permeant, the difference between the solubility parameters should be as small as possible (Mandal, 2002). Because methyl acetate ($\delta=19.9 \text{ MPa}^{1/2}$) and the active PDMS ($\delta=14.9 \text{ MPa}^{1/2}$) and POMS ($\delta=16.3 \text{ MPa}^{1/2}$) layers of the membranes have similar solubility parameters, we hypothesized that the membrane would display preferential sorption for methyl acetate as opposed to methanol. Methanol exhibits a much higher solubility parameter ($\delta=29.7 \text{ MPa}^{1/2}$). This difference in solubility parameters between methyl acetate and methanol is beneficial for pervaporative separation with reference to PDMS- and POMS-based membranes. Vopička et al. (2014) performed sorption studies of vapours and liquids in PDMS and specified methyl

Table 1

Molar volumes V_m and solubility parameters δ of methanol (MeOH) and methyl acetate (MeOAc) and solubility parameters δ of the active layers of the composite membranes (PDMS, POMS).

	V_m (cm ³ /mol)	δ (MPa ^{1/2}) ^a
PDMS	–	14.9 (Barton, 1990)
POMS	–	16.3 (Barton, 1990)
MeOH	40.7 (Mark, 1996)	29.7 (Smallwood, 1996)
MeOAc	79.7 (Mark, 1996)	19.9 (Smallwood, 1996)

^a The units of the solubility parameter δ can be expressed in (MPa^{1/2}) as the square root of a pressure or as the square root of the cohesive energy density (cal^{1/2} cm^{-3/2}). The conversion used was: 1 MPa^{1/2}=0.48888 cal^{1/2} cm^{-3/2}.

Table 2

Boiling point T_b under atmospheric conditions and saturation vapour pressure p^s at $T=50 \text{ °C}$ for methanol (MeOH) and methyl acetate (MeOAc) (Lide, 2003).

	T_b (at $p=1.013 \text{ bar}$) (°C)	p^s (at $T=50 \text{ °C}$) (bar)
MeOH	64.6	0.555
MeOAc	57	0.791

acetate as a mild solvent and methanol as a poor solvent (Vopička et al., 2014).

Another aspect favouring methyl acetate recovery via pervaporation arises from the higher saturation vapour pressure of methyl acetate as compared to methanol (Table 2). The higher saturation vapour pressure has a positive effect on the driving force of pervaporation, based on the difference in the partial pressure of a component between the feed and the permeate stream. Operation temperatures can be kept below the boiling point of methyl acetate (e.g., 50 °C).

Referring to these data, the methyl acetate separation efficiency from binary methyl acetate–methanol mixtures using organophilic membranes seems promising. Nonetheless, extensive experimental studies have not yet been conducted. Smitha et al. (2004) emphasized that membrane performance is still the key for judging the efficiency of pervaporation, whereas Wijmans (2003) highlighted that operating conditions are crucial in pervaporation. Excellent membranes may display poor performances when the operating conditions have not been properly set. Therefore, the effects of feed composition and feed temperature on the performance of the four organophilic composite membranes PERVAP™ 4060, PDMS 04–075, PDMS 04–123 and POMS 05–119 were studied in this work. Since the permeate flux and the separation factor depend on the operating conditions (Wijmans, 2003), the permeate flux was normalized with respect to the driving force, and the performances of the membranes were reported as permeances. Furthermore, the partial permeate flux of each component was described by applying an extended version of the solution-diffusion model, which considers the swelling behaviour of the polymeric membranes.

2. Materials and methods

2.1. Chemicals and membranes

Four flat-sheet, composite membranes with organophilic surface properties were applied for pervaporation. These were the polydimethylsiloxane based membranes PERVAP™ 4060 (provided by Sulzer Chemtech AG, Switzerland), PDMS 04–075 (provided by Helmholtz-Zentrum Geesthacht, Zentrum für Material- und Küstenforschung GmbH, Germany) and PDMS 04–123 (also provided by Helmholtz-Zentrum Geesthacht, Zentrum für Material- und Küstenforschung GmbH, Germany), and the polyoctylmethylsiloxane based membrane POMS 05–119 (Helmholtz-Zentrum Geesthacht, Zentrum für Material- und Küstenforschung GmbH, Germany).

The selective PDMS layer was supported by a polyacryl nitrile (PAN) layer on a substrate of non-woven, polyester material. Thickness of the PDMS layer of the membrane PERVAP™ 4060 was 2 μm , that of PDMS 04–075 was 5.5 μm and that of PDMS 04–123 was 1 μm . The membrane PDMS 04–075 was additionally cross-linked by irradiation which reduces its tendency to swell in solvents.

The selective POMS layer of the membrane POMS 05–119 was also supported by a PAN layer on a substrate of non-woven polyester material. The thickness of the selective POMS layer was 2.6 μm .

Reagent grade methyl acetate ($\geq 99\%$, Merck) and methanol ($\geq 99.9\%$, Roth) were used as supplied.

In order to guarantee standardized experimental operation, pre-conditioning of the membranes was crucial. Before usage, each membrane was swollen in a mixture of 50 wt% of methanol and

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