Sorption and pervaporation of methanol/water mixtures with poly(3-hydroxybutyrate) membranes

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ABSTRACT

In this contribution, poly(3-hydroxybutyrate) (PHB) membranes were evaluated in sorption and pervaporation experiments for methanol/water separation. Single component sorption tests showed that PHB membranes have higher affinity toward methanol than water: at 40 °C the sorption degree was 18.4 and 1.1%, respectively. This was in agreement with contact angle measurements, performed with both liquids, and Hansen solubility parameter. PHB sorption degree in the whole methanol/water composition range and three temperature levels were determined, showing an anomalous behavior (sigmoid like curves). A simple technique, named by us "Desorption by Dissolution", was developed to determine sorbed mixture composition. It basically consists on dissolving the polymer after sorption equilibrium in the mixture has been reached, to completely extract the mixture. Then, chromatographic analysis is used to determine solution composition. It does not require adapting equipment or using vacuum devices neither cold traps. When both components were present, methanol grams sorbed in the membrane were always lower than the mixture in which they were immersed, while water sorption was enhanced due to methanol presence. Very low standard deviation values were registered (<0.84) confirming the technique reliability. Single component fluxes and mass flux ratio in pervaporation increased with temperature: methanol flux was $3.5 \times 10^{-5}\,\mathrm{kg\,m^{-2}\,s^{-1}}$ at 25 °C, whereas at 50 °C exceeded $7 \times 10^{-5}\,\mathrm{kg\,m^{-2}\,s^{-1}}$; water flux increased from $1.8 \times 10^{-5}\,\mathrm{kg\,m^{-2}\,s^{-1}}$ at 30 °C to $2.2 \times 10^{-5}\,\mathrm{kg\,m^{-2}\,s^{-1}}$ at 50 °C. Since permeances decreased, the increase in fluxes with temperature can be attributed to the increase in vapor pressure driving forces. Mixture pervaporation results showed similar behavior, highlighting the fact that separation factor increased with temperature as well: 3.5 at 30 °C and 3.8 at 50 °C. Selectivities were higher than 12 for 10 wt% water/methanol + water mixtures. Results were discussed in terms of polymer crystallinity, solubility parameters, component size, activation energies and cluster formation.

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Keywords: Pervaporation; Sorbed mixture composition; Sorption selectivity; Methanol/water mixture; Permeance; Activation energy

1. Introduction

Pervaporation has been considered as an alternative energy-efficient method to separate azeotropic mixtures, close boiling point liquids, isomeric or heat sensitive components, and to remove low concentration pollutants from aqueous waste (Smitha et al., 2004). During pervaporation, separation takes place by preferential sorption and diffusion of the desired component through a dense membrane.

Alcohols dehydration is one of the most studied pervaporation separations systems. Particularly, ethanol/water and isopropanol/water mixtures have achieved a suitable development to be applied commercially. Large number of publications and patents can be found in literature related to ethanol/water (Chapman et al., 2008) and isopropanol/water (Kuila and Ray, 2013) separation, whereas the methanol/water is scarce (Pang et al., 2010) opening up an interesting research field.

Most membranes with reasonable selectivity to separate ethanol/water mixtures, reach very low selectivity when they are evaluated with methanol/water mixtures, mainly due to their small differences in molecular size and membrane affinities. Although this mixture does not form an azeotrope, this separation is costly to achieve by distillation because of the low relative volatility of methanol and water (Won et al., 2003), a challenge for researchers, precisely because of the similarity of the components forming the mixture.

The main uses of methanol are related to the manufacture of other chemicals and fuels. It is mainly used in the production of formaldehyde, acetic acid, methyl *tert*-butyl ether (MTBE) and as a basis for obtaining intermediate products to be used in the synthesis of resins, foams and plastics. It is considered the most promising fuel for fuel cells (Sridhar et al., 2005).

Table 1 summarizes the performance of several membranes for methanol–water separation under different pervaporation operating conditions, reported in research articles since 2003 to date.

The involved phenomena in pervaporation is described by the well-known sorption–diffusion model, in which selective sorption becomes a fundamental parameter to characterize a membrane. Regarding sorption experiments, when a polymer is contacted with a vapor or liquid mixture, mixture composition in the polymer under equilibrium conditions will generally differ from the contacting composition, mainly caused by a selective sorption phenomenon within the polymeric matrix. Relation of vapor or liquid composition with the corresponding polymer mixture sorbed values, is useful to study and predict polymer behavior for different applications such as membrane separation processes (Baker, 2004; Heintz et al., 1991; Mulder, 1991), film packaging (Barr et al., 2000), sensor development (Adhiri and Majumdar, 2004), among others.

The most widely used technique to determine sorbed mixture composition into a polymer matrix, consist of introducing the polymer film in the desired liquid mixture and when the sorption equilibrium is reached, film is removed, wiped carefully with tissue paper and immediately placed in a device for desorbing the liquid by vacuum and heat. Produced vapors are collected in another container, cooled with liquid nitrogen, and the composition is determined by gas chromatography or another technique. Most authors use this technique (Bhat and Pangarkar, 2000; Cunha et al., 2002; Kao et al., 2002; Luo et al., 2007; Ma et al., 2008; Niang and Luo, 2001; Peng et al., 2006; Wolinska-Grabczyk, 2006) and some others have done minor modifications, such as carrying out the desorption in the pervaporation system itself, instead of using an additional device (Kondolot Solak et al., 2008).

Despite being the most common technique, it has some drawbacks:

– Total desorption of the liquid sorbed by the membrane cannot be guaranteed. Some authors weigh the membrane along the desorption stage, ending the experiment when the membrane reaches its initial dry weight. This leads to considerable error due to successive stages of weighing and also causes long desorption times.
– To collect enough liquid volume, it is necessary to work with large membrane samples, that requires more time for sorption and desorption steps, and even to place the membrane in the desorption device. Consequently, it leads to

increasing component evaporation and accuracy loss, especially when working with very volatile substances.
– It is noteworthy that many authors report to weigh the membrane, before carrying out the desorption experiment, to establish the total sorption degree. So, in the whole process, the solvents can be evaporated from the membrane before desorption process begins. Under these conditions, is very likely that composition of the mixture in the membrane differs from the corresponding equilibrium value.

Recently, some new interesting alternative techniques to determine liquid mixture composition in polymeric films were reported. Kamaruddin and Koros (2000) studied methanol/MTBE mixtures sorption in a glassy polyimide. They extracted the organics from the polymer with a 5 wt% N,N-dimethyl acetamide (DMAc) water solution. Since DMAc is a swelling polyimide agent, desorption of organics from the glassy polymer must have been facilitated. Organic extract composition was analyzed with gas chromatography head-space analysis. Hauser et al. (1989) have reported the desorption of water containing organic mixtures from polyvinylalcohol, using carbon tetrachloride followed by desorbate analysis with infrared spectroscopy. Awkal et al. (2006) have reported a new technique based on in situ desorption in a ^{1}H NMR tube for determining the sorption selectivity of a series of new poly(urethane-imide)s and Clément et al. (2007) have designed a desorption apparatus which consist of a desorption mini-oven coupled with an on-line chromatograph.

In this contribution we present a simple technique, named by us as "Desorption by Dissolution", that does not require adapting equipment and there is no need of vacuum devices and liquid nitrogen. Moreover, it is suitable for analyzing polymers with low sorption degree and after sorption equilibrium is reached by the polymer, subsequent steps depend only on polymer dissolution time which is much easier to perform than desorption. With this technique it is possible to perform quick and reliable determination of membrane sorption selectivity thus providing valuable information for pervaporation process.

Sorption and pervaporation tests were performed with poly(3-hydroxybutyrate) (PHB) membranes and methanol/water mixtures. PHB is an intracellular polyester synthesized by certain bacteria as a carbon and energy storage compound. It was previously characterized (thermal behavior and crystallinity degree) and evaluated for methanol/MTBE separation by pervaporation by our research group with promising results (Villegas et al., 2011). Within these, highlight the fact that both flux and separation factor increase with feed mixture temperature. That is why we have decided to continue evaluating the performance in pervaporation of this membrane material for the separation of other mixtures of interest.

2. Experimental

2.1. Materials

Powder PHB ($m_w \sim 524.000\,\text{g mol}^{-1}$) was kindly provided by BIOCYCLE®, PHB Industrial S.A. (Brazil). Methanol was provided by Merck (Germany) and chloroform, by Cicarelli (Argentina). All chemicals were of analytical grade and used without further purification.