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Polyvinylidene fluoride dense membrane for the pervaporation of methyl acetate–methanol mixtures

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ABSTRACT

In the context of pervaporative separation of methyl acetate–methanol binary mixtures, polyvinylidene fluoride (PVDF) pervaporation membranes were prepared in order to selectively separate methyl acetate by pervaporation.

The PVDF membranes were compared to chlorinated polypropylene and polyvinyl alcohol dense membranes (developed for the same application) by pervaporation of a quaternary equimolar methyl acetate–methanol–*n*-butyl acetate–*n*-butanol reference feed. PVDF membranes resulted in a permeate richer in methyl acetate than the corresponding quaternary feed, and in a selectivity methyl acetate/methanol higher than one for the same mixture. Chlorinated polypropylene and polyvinyl alcohol membranes gave a permeate richer of both methanol and methyl acetate than the corresponding feed and were thus not applicable during the extensive study on the binary methyl acetate–methanol mixture.

These preliminary results performances were also assessed with the Hansen solubility parameters theory, which resulted inadequate for predicting the behavior of the two glassy-state and the rubbery-state (PVDF) polymeric membranes during pervaporation.

Thus, pervaporation of methyl acetate–methanol binary mixtures by PVDF membranes was studied experimentally using feed concentrations in the range 11–78 mol% methyl acetate, and temperatures in the range 30–44 °C, resulting in separation factors methyl acetate/methanol above 1 (up to 2.1 at 11 mol% methyl acetate in the feed), in the whole feed concentration range. High total fluxes up to 35 kg m⁻² h⁻¹ (at 78 mol% methyl acetate and 44 °C) were also observed.

Interestingly, when removing the contribution of the driving force to the separation, for concentrations below 60 mol% methyl acetate in the feed the membrane was selective for methanol, while for higher concentrations it was selective for methyl acetate (values up to 1.44).

This work shows that methyl acetate selective membranes (starting from the improvement of PVDF membranes) are realistic and can be employed in order to concentrate low content methyl acetate–methanol industrial waste streams.

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1. Introduction

The separation of a mixture of methyl acetate and methanol is an interesting and challenging issue, since these two components form an azeotrope. Industrially, an example is the methyl acetate–methanol mixture produced during polyvinyl alcohol (PVA) synthesis [1], as *saponification mother liquor* (the so called MM20 stream) [2,3]. This stream (~30 wt% methyl acetate in methanol, i.e., ~16 mol% methyl acetate at 40 °C) was sold in the past as solvent, but volatile organic compound legislation has drastically decreased this market [2] and it is now considered waste [3]. This means that

for the PVA industry it is of great interest to convert this stream to a more valuable compound. In the current process of conversion, methyl acetate is hydrolyzed through a strong acid catalyst into acetic acid and methanol. Dilute acetic acid is concentrated by azeotropic distillation [2]. Another possibility is transesterification of methyl acetate with *n*-butanol to methanol and *n*-butyl acetate. This transesterification reaction is a challenging reaction since the conversion is limited by the equilibrium [4]. Among other authors, who worked with various transesterification reaction/separation hybrid technologies [2,3,5,6], Luyben [7] described the design and control of a transesterification reaction/distillation coupled system fed with the MM80 stream (the azeotropic mixture of methyl acetate and methanol, i.e., about 81 wt% methyl acetate [about 65.3 mol%] at 53.5 °C and 1 atm). In this case a system of distillation columns permits to obtain two almost pure product streams of

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methanol and *n*-butyl acetate and re-circulate the two reagents to the reactor.

Before being converted to acetic acid or *n*-butyl acetate, the MM20 methyl acetate–methanol stream needs to be brought to higher concentrations in methyl acetate. The presence of the azeotrope suggests the employment of advanced distillation methods (in the literature the use of classic distillation in order to obtain the already mentioned MM80 composition or extractive distillation with water or ethylene glycol to obtain pure methyl acetate is reported [2]). Pervaporation, as a low energy consumption technology may be also considered for this purpose. In fact, the selectivity of a pervaporative separation depends on the different transport rates of compounds, which depend on their diffusivity and solubility in a dense membrane layer. Thus, the separation is not affected by the presence of an azeotrope [8–11]. In view of this, a single pervaporation step working at 1 atm needs of a membrane with separation factors higher or equal to 10 toward methyl acetate (when starting from the MM20 stream) in order to go just beyond the azeotrope (separation factors higher than 257 permits to obtain permeates of highly pure methyl acetate).

So far, the literature about the pervaporative separation of methyl acetate–methanol mixtures is limited. Some studies aimed at methanol selectivity (since methanol is a small and fast diffusing molecule) using in-house-prepared and commercial membranes: Gorri et al. [12] studied the commercial Sulzer Chemtech™ membrane Pervap 2255-30® obtaining separation factors methanol/methyl acetate ranging between about 4 and 7 with total fluxes ranging between 0.97 and 7.9 kg m⁻² h⁻¹ at 40 °C; Steinigeweg and Gmehling [6] employed the Sulzer Chemtech membranes Pervap 2255-40®, 2255-50® and 2255-60® at 45 °C, where the first and the second membrane types resulted in the best flux (an average of about 5.2 kg m⁻² h⁻¹) and the best separation factor for methanol (an average of about 4.4), respectively; Sain et al. [13] employed the commercial Cuprophan® membranes (supplied by AKZO™, Germany) obtaining a methanol separation factor of 4.7 and a flux of about 2.2 kg m⁻² h⁻¹ (on average) at 45 °C and fluxes ranging between 0.1 and about 3.7 kg m⁻² h⁻¹. Finally, Abdallah et al. [14] reported about their in-house prepared Nylon-6 membranes with outstanding properties (fluxes up to 80 kg m⁻² h⁻¹ and separation factors up to 344 at 40 °C). To date the membranes proposed by this last group of authors may be the best solution when pervaporation is considered as separation technology for this mixture. Nevertheless the study of the separation of methyl acetate–methanol mixtures by pervaporation is not complete. In fact, no methyl acetate selective membrane has yet been proposed. Only Penkova et al. [15] studied the separation of a reactive quaternary mixture composed of acetic acid, methanol, water and methyl acetate, using in-house prepared poly-(2,6-dimethyl-1,4-phenylene oxide) membranes, obtaining separation factors methyl acetate/all the rest of typically below 3.

According to the separation mechanism of pervaporation, in order to choose the best polymer to be selective for the components of a mixture, polymer–solvents affinity and components diffusivities inside the membrane have to be taken into account. In particular, when the membrane is made of a polymer in the rubbery-state (i.e., the working temperature of the material is higher than the glass-transition temperature, T_g), the affinity of the material to the component to be selectively permeated should be employed as selection parameter [16]. In fact, in the case of rubbery-state polymers the main contribution to the pervaporative separation is given by component solubilization at the membrane feed-side. To date the best methodology to assess the solubility of a solvent in a polymeric membrane material is the procedure proposed by Hansen [17]. In the Hansen Solubility Parameters (HSPs) theory, the dispersion interactions energy (derived from atomic forces), the polar cohesive energy and hydrogen bonding energy (δ_d , δ_p and δ_h , respectively) are considered as the main interaction energies between polymer and dissolved organics [18].

The HSPs method can be easily visualized in the energy density space (i.e., the space having as axis δ_d , δ_p and δ_h), where the distance between the solvent and center of the polymer solubility sphere reflects the affinity between polymer and solvent compounds [17,19].

The HSPs theory criterion was already applied (on a larger scale and with a high level of detail) by Buckley-Smith [19] during selection of membrane materials for pervaporation of a model solution containing linalool and linalyl acetate (major components of lavender essential oil), in ethanol. This work shows that when components with similar molecular size are pervaporated, the HSPs theory results to be a good membrane screening method. However Buckley-Smith remarked that diffusivity (not considered in HSPs), having a fundamental impact on components pervaporation, should be also taken into account during this screening step.

The three polymeric materials reported in this work were chosen among many materials since these materials have a good affinity toward methyl acetate on the base of the HSPs theory or on the basis of the experience gained in our laboratories (for what concerns the PVDF membrane). Hence, the polymeric membranes (in-house prepared on petri-dishes) were initially tested in order to assess the HSPs theory potential in selecting the appropriate material. The experimental tests of these membranes were pursued by pervaporation of a relevant alcohol–alcohol–ester–ester quaternary mixtures (i.e., the reaction medium mixture of the transesterification conversion of methyl acetate *n*-butyl acetate [2,4,6]), which was chosen since it contains two esters (methyl acetate is the component of interest) and two alcohols that differ by three carbon atoms (i.e., methanol, *n*-butanol and methyl acetate, *n*-butyl acetate); this means that the separation of methyl acetate from this mixture is rather challenging for the membrane since the presence of the other compounds may lead to unwanted plasticization–swelling and/or coupling phenomena [20]. The membrane showing the highest methyl acetate/methanol selectivity (values higher than one) was finally employed in the pervaporation of methyl acetate–methanol binary mixtures (main object of this work) throughout a wide feed concentration range.

2. Experimental

2.1. Materials

Chlorinated polypropylene (CIPP, Mw ~ 100,000) was purchased from Sigma Aldrich™. Polyvinylidene fluoride Solef 6020® was provided by Solvay™. Polyvinyl alcohol (PVA, MW 72000) was purchased from AppliChem™. N,N-Dimethylformamide (DMF), toluene ACS grade and dimethyl sulfoxide (DMSO) 99.9% ACS grade solvents were purchased from VWR International™. Nyssen Graphics™ 99.5% pure methanol, Alfa Aesar™ 99% pure methyl acetate, *n*-butanol AnalaR-Normapur® (VWR International) 99.9% pure and *n*-butyl acetate Chem-Lab™ (99+% pure), all without further purification, were blended to prepare all feed solutions.

2.2. Membranes synthesis

The three tested membranes were prepared by overnight stirring as follows: 10 wt% solution of CIPP in toluene, 10 wt% solution of PVA in DMSO and 10 wt% solution of PVDF in DMF. Subsequently, air bubbles were removed from the polymeric solution by applying vacuum for a maximum of 30 min. Each solution was then poured in a glass petri-dish and placed in a dynamic vacuum oven at 55 °C for at least 8 h.

The PVDF membranes to be used for the separation of the methyl acetate–methanol binary mixtures were prepared by casting the polymer with a 250 μm thick knife on a glass plate and drying under vacuum atmosphere at 55 °C for at least 8 h.

All prepared dense membranes were peeled off from the glass support by immersion in water.

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