

Nanofiltration properties of PTMSP in binary organic solvents mixtures

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Abstract. In this study, the stability and nanofiltration performance of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) in ethanol solutions of butylaldehyde, 1-decanal, 1-hexene, 1-decene was evaluated. It was found that PTMSP was insoluble in all aldehyde solutions, but it was soluble at olefin concentration of 80% or higher. Nanofiltration experiments demonstrate that binary mixtures of 1-decanal and ethanol viscosity are not the parameter affecting on membrane permeability and rejection of solute as well as swelling degree. In the case of decanol/ethanol solutions both solution viscosity and molar volume demonstrate the best fit of experimental data. It was shown that with the decrease of ethanol content in the feed, the rejection of anionic solute Remazol Brilliant Blue R (MW 626) increases from 94 up to 97%.

1. Introduction

Effective recovery of homogeneous catalysts from reaction mixture for its further recycling is a challenging task in homogeneous catalysis. For example, catalysts used in organic synthesis are based on expensive and toxic complexes of transition metals (Pt, Pd, Ru, Ph, etc.). Conventional separation approaches are based on energy-intensive distillation or extraction processes, which includes the phase transitions. The separation of the catalyst by such methods is quite often accompanied by its partial or complete deactivation. Organic solvent nanofiltration (OSN) is already well-known and still rapid growing area of membrane technology due to its great potential and advantages over the traditional separation methods like distillation or extraction [1-3]. In some cases, OSN can be considered as a unique separation process that could provide effective and almost quantitative recovering of target compounds in different areas, including chemical, petrochemical, and food industries. However, the major drawback towards rapid implementation of this technology is rather a limited number of membranes that possess sufficient stability in organic media, high permeability for selected solvents as well as high retention of target compounds. For successful and efficient implementation, the membranes for OSN process should have sufficient mechanical stability in organic solvents, demonstrate high retention values and transport of the organic solvent. One of the perspective membrane materials for OSN is the glassy polymers with intrinsic microporosity that naturally formed during the membrane casting as a result of rigid nature of polymer chains. For example, poly[1-(trimethylsilyl)-1-propyne] (PTMSP) has been already applied to fabricate high-performance OSN membranes due to its good mechanical properties [2-4]. This polymer is stable in the solvents like alcohols, ketones, and aldehydes. However, the recycling of homogeneous catalysts requires the



stability of the membrane material during the contact with not only the products but also the raw materials that are usually used for flushing of the retentate. By this means, if the membrane is supposed to be used in hydroformylation process, it should be stable in reaction mixtures contained aldehydes and olefins, respectively. Since the presence of co-solvents such as ethanol or acetone could improve the reaction rate of conversion of olefin to aldehyde [5], the goal of this work was the study of stability and nanofiltration performance of PTMSP membranes in decene-1/ethanol and decanal/ethanol mixtures.

2. Experimental part

2.1. Membrane preparation

PTMSP used in the work was synthesized on TaCl_5 catalyst with the cocatalyst $\text{Al}(\text{i-Bu})_3$, which provides a preponderance of the trans-structures of the polymer macromolecules [6]. To prepare the casting solution, polymer samples was dissolved in chloroform. Due to the high intrinsic viscosity for solutions of the PTMSP polymer concentration was 0.5 wt.%. Dense PTMSP films of a thickness of 30 ± 5 microns were obtained by casting PTMSP solution in chloroform with a polymer content 0.5 wt.% on cellophane, followed by slow drying at room temperature for 3-4 days.

To remove residual solvent obtained membrane was soaked for 2 days in 1-butanol, after which the sample was immersed in ethanol for at least 24 hours. After that, the membrane was washed sequentially in water-ethanol solutions with a gradual decrease of alcohol concentration and subsequent drying to constant weight. Immediately before filtration membrane was immersed in the corresponding solution for 1 hour.

2.2. Nanofiltration experiments

Nanofiltration experiments were performed with dead-end filtration cell. The cell was equipped with a magnetic stirring system to avoid concentration polarization. The active membrane area (S) was 10.7 cm^2 . Helium was chosen to create a pressure because of its low solubility in organic solvents in a wide range of pressures. Filtration experiments were carried out at transmembrane pressure 30 bar. The volume of the liquid was 50 cm^3 . During the experiment, 25 cm^3 of the solution was allowed to permeate through the membrane. The permeate flux (J) was determined by gravimetric method and calculated as follows:

$$J = \frac{m}{S \cdot \Delta t}, \quad (1)$$

where m – mass of permeate, Δt – time. Permeability coefficient (P) was calculated as follows:

$$P = \frac{J \cdot l}{\Delta p}, \quad (2)$$

where l – membrane thickness, Δp – applied pressure.

The composition of 1-Decene and 1-Decanal solutions in ethanol was measured via refractometer. Remazol brilliant blue R dye was chosen as a "model" of the catalyst because it has a molecular weight (MW 626) and it is easy to measure its concentration in solution. The concentration of dye was measured via a spectrophotometer.

2.3. Swelling degree and solubility tests

Polymer swelling degree (S_D) in the corresponding mixture was obtained by measuring a sample of polymer film thickness (h), and two perpendicular dimensions (d_1 and d_2) were measured. Sample with measured dimensions was soaked in corresponding liquid for 7 days. In swelling measures samples were $5 \times 5 \text{ cm}$ with thickness 50 microns. Swelling degree was calculated as follows (index 0 means value for dry sample):

$$S_D = \frac{h \cdot d_1 \cdot d_2 - h_0 \cdot d_{10} \cdot d_{20}}{h_0 \cdot d_{10} \cdot d_{20}} \quad (3)$$

Solubility tests were carried out in the same way. Small polymer film sample (1 cm²) was placed in corresponding liquid for 7 days. The sample was considered as insoluble if after 7 days it was possible to remove it from solution without damaging.

3. Results and discussion

3.1. PTMSP solubility

An important factor that must be considered in the filtration process is the membrane resistance to the filtered mixture. PTMSP-membranes stable in aldehydes and alcohols but soluble in olefins (see Table 1).

Table 1. PTMSP stability in binary ethanol solutions (“+” – stable, “-” – dissolved).

Solvent	Solvent content in ethanol, wt. %										
	0	10	20	30	40	50	60	70	80	90	100
Decanol	+	+	+	+	+	+	+	+	+	+	+
Butylaldehyde	+	+	+	+	+	+	+	+	+	+	+
1-Decanal	+	+	+	+	+	+	+	+	+	+	+
1-Hexene	+	+	+	+	+	+	+	+	+	-	-
1-Decene	+	+	+	+	+	+	+	+	+	-	-

In the hydroformylation process, reaction mixture to be separated might contain substrate (olefin), product (aldehyde) and solvent (ethanol). Therefore, in the beginning, the stability of PTMSP membranes was evaluated in the binary solutions of butylaldehyde, 1-decanal, 1-hexene or 1-decene in ethanol. For this purpose, PTMSP film samples were soaked in corresponding solutions for 7 days and then the membrane stability was visually analyzed. As can be seen from Table 1, PTMSP was insoluble in all aldehyde solutions, but PTMSP was soluble for olefin concentration of 80% or higher. Taking into account the fact that the reaction mixture in the large-scale hydroformylation processes can contain up to 85-90% of inert solvent, it can be concluded that PTMSP-based membranes show required solvent stability for this particular application.

3.2. Nanofiltration of binary solutions through PTMSP

Since catalyst should be separated from solution product filtration of 1-decanal solutions in Ethanol was carried out with PTMSP membranes (Figure 1).

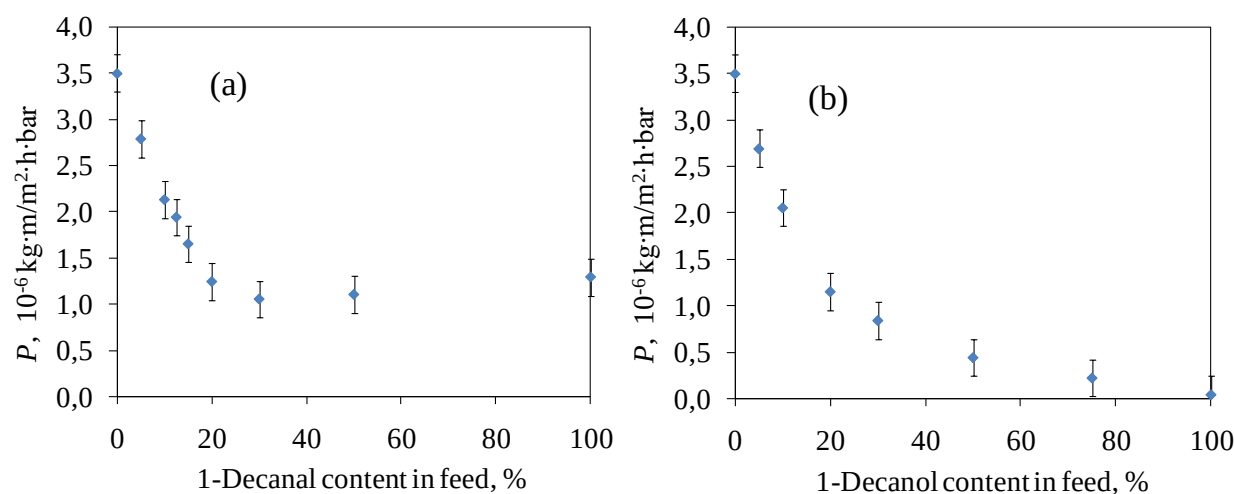


Figure 1. Permeability coefficient of 1-decanal (a) and decanol (b) solutions in ethanol through PTMSP membranes

As can be seen from Figure 1, PTMSP shows the highest permeability in ethanol and addition of 1-decanal up to 3- wt.% leads to about 3-folds reduction in liquid transport across the membrane. No significant changes in membrane permeability were observed with further increasing of 1-decanal content in the feed. In both cases of 1-decanal and decanol ethanolic solutions, no change of mixture composition occurred during the filtration. Therefore, it can be expected that the reaction mixture composition would remain the same as was reported previously for water-ethanol mixtures [7]. Such finding might be important in the case of solubility of homogeneous catalyst in the limited range of substrate-solvent or product-solvent mixture. In the case of decanol solutions, concentration monotonically decreased with increasing of decanol concentration in the whole range of concentrations. The permeability of decanol was 30 lower than for decanal. These results can be explained by the changes of solution viscosity (η) which increases in the following order: ethanol (1.19 mPa·s) < 1-decanal (17.9 mPa·s) < decanol (138 mPa·s).

Table 2. Correlation of PTMSP permeability

Parameter	Correlation (R^2)	
	Decanal/Ethanol	Decanol/Ethanol
$1/\eta$	0.0631	0.8899
S_D	-0.347	-0.539
S_D/η	-0.286	0.793
V_m	-1.753	-0.801
$1/V_m$	0.6274	0.6868
$1/\eta V_m$	0.4483	0.9913

However, the viscosity, as well as swelling degree (SD), was not the particular case for binary mixtures of 1-decanal and ethanol (see Table 2). In fact, maximum swelling degree (75%) takes place in 50/50 1-decanal/ethanol mixture but very low permeability and lower swelling degree for ethanol (61%) and 1-decanal (55%). The best fit was obtained in the case of reverse molar volume (V_m). A Larger molecule of 1-decanal moves slowly through PTMSP membrane and block transport channel for ethanol since no composition change take place.

In the case of decanol/ethanol solutions both solution viscosity and molar volume demonstrate the best fit of experimental data. It should be noted that viscosity itself correlates with molar volume, but

the only combination of two this parameters takes good correlation with experimental data. As well as for 1-decanal in the case of decanol solutions in ethanol swelling degree is not the parameter affecting on permeability since it monotonically increases with decanol concentration in contrast with permeability. More detailed explanation of permeability results obtained in this work is the object of further investigation.

3.3. Nanofiltration of ternary solutions through PTMSP

Ternary solutions containing binary solution mixture and the solute Remazol Brilliant Blue R (MW 626), 1-decanal/decanol and ethanol was used to determine membrane rejections. Remazol Brilliant Blue R concentration in solution was 10 mg/l. It was obtained that increasing of decanal content lead to a decrease of Remazol Brilliant Blue R rejection by PTMSP membrane (Figure 2).

The same result was obtained for decanol. In both cases, a minimum of rejection takes place at 5% concentration. As well as in case permeability swelling degree increases in investigated range of concentrations and does not affect by rejection. This result means that steric effect is not the main parameter for rejection of this dye by PTMSP. This result can be explained by specific interactions for the solvent(s)-solute-membrane system. As was shown before for rejection of different solutes from its ethanolic solution by PTMSP [8], there is a competition sorption of solvent and solute molecules into membrane material. Since the ethanol has lower affinity to PTMSP than more hydrophobic molecules of 1-decanal or 1-decanol, it can be expected that the sorption selectivity for the solvent over the anionic solute would increase with decrease ethanol content in the feed. Thus, an increase in sorption selectivity would also lead to an increase of overall selectivity of nanofiltration process.

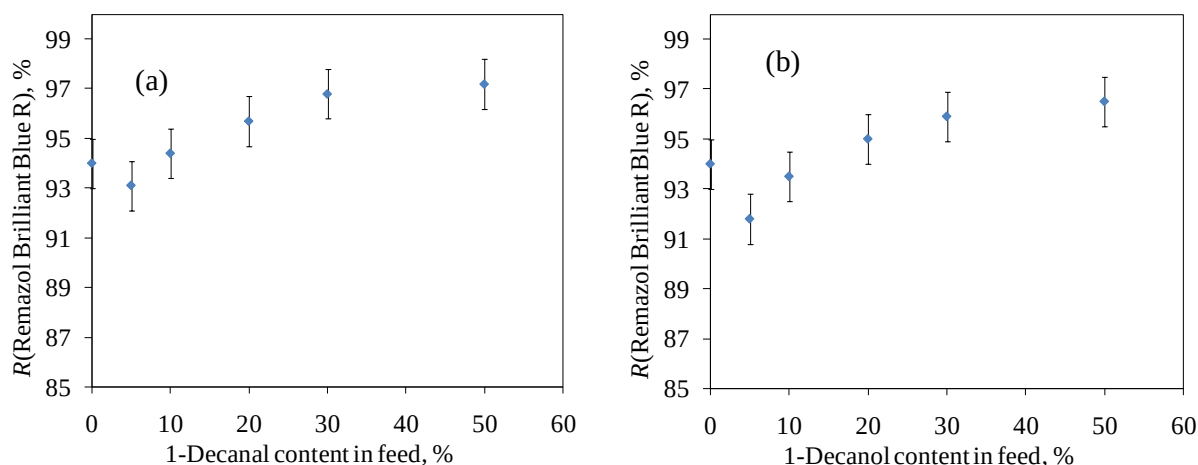


Figure 2. Rejection of Remazol Brilliant Blue R from 1-decanal (a) and 1-decanol (b) solution with ethanol by PTMSP membrane

4. Conclusions

In this study, the stability and nanofiltration performance of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) in ethanol solutions of butyraldehyde, 1-decanal, 1-hexene, 1-decene was evaluated. It was found that PTMSP was insoluble in all aldehyde solutions, but it was soluble at olefin concentration of 80% or higher. Nanofiltration experiments demonstrate that binary mixtures of 1-decanal and ethanol viscosity are not the parameter affecting on membrane permeability and rejection of solute as well as swelling degree. In the case of decanol/ethanol solutions both solution viscosity and molar volume demonstrate the best fit of experimental data. It was shown that with the decrease of ethanol content in the feed, the rejection of anionic solute Remazol Brilliant Blue R (MW 626) increases from 94 up to 97%.

Acknowledgments

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