



Application of negative retention in organic solvent nanofiltration for solutes fractionation



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ABSTRACT

For the first time, the utilization of negative retention in organic solvent nanofiltration (OSN) for solute fractionation was proposed and realized. Using membranes made of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) and ethanol as a solvent, this principle was successfully proved for two different pairs of dyes: (i) Orange II (anionic; 350 Da) and Solvent Blue 35 (neutral; 350 Da), (ii) Remazol Brilliant Blue R (anionic; 626 Da) and Oil Red O (neutral; 408 Da). The solutes ratio in the permeate after one step filtration with 80% of liquid recovery was achieved as follows (initial ratio in the feed – 1:1): 1:10 for Orange II to Solvent Blue 35 and 1:26 for Remazol Brilliant Blue R to Oil Red O. With compromising of liquid recovery, the solutes ratio in the permeate can be significantly improved; for example, 15% liquid recovery may provide the ratio in favor of neutral solute as 1:260 and 1:340, respectively. Pronounced difference in solutes retention was interpreted by membrane–solute interaction expressed in terms of equilibrium solute distribution coefficient K between the membrane and liquid and difference in solubility parameters δ . Low values of solute distribution coefficient K for Orange II and Remazol Brilliant Blue R (less than 1) revealed that both anionic dyes have a tendency to be concentrated in liquid phase resulting in high solute retention (more than 90%). Better rejection of Remazol Brilliant Blue R (1258 Å³) in contrast to Orange II (297 Å³) was explained by difference in solute size. High K values (more than 10) observed for Solvent Blue 35 and Oil Red O indicated that these two neutral solutes have a high affinity to membrane material and can be easily accommodated within interconnected free volume elements of PTMSP. Such solubility determined solute transport resulted in negative retention. Analysis of solubility parameters δ of components showed that neutral solutes have a stronger affinity to the membrane material rather than ethanol; meanwhile, PTMSP has a preferential affinity to solvent molecules over selected anionic dyes. These experimental observations allowed to conclude that the principle of one step solutes fractionation based on combination of negative and positive retention could be realized with PTMSP membranes for OSN applications.

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1. Introduction

Organic solvent nanofiltration (OSN) is a fast developing area of membrane separation that has many potentials for different applications such as homogeneous catalysts recycling, solvent replacement in multistage organic synthesis, recovery of organic solvents used in extraction processes in petrochemical, food, painting and pharmaceutical industries [1]. In this process dissolved solute molecules with a typical molecular weight of 200–2000 Da are separated from smaller molecules of organic solvent by selective rejection of the former one by the membrane. However, there is limited number of publications describing negative retention of

organic solutes in aqueous and non-aqueous nanofiltration with both polymeric and inorganic membranes [2–12]. It should be noted that the negative retention, in other words preferential transport of bigger molecule of solute over smaller molecule of organic solvent through the membrane, has a particular interest from fundamental point of view in understanding of affect of the solute-membrane interaction on nanofiltration performance of OSN membranes.

The negative retention can be realized in the case of greater affinity of solute molecules to membrane material rather than interaction of both components with organic solvent. It is worth to mention that the balance in solvent–solute–membrane interactions can be changed by replacement of one or two components. For example, replacement of polar solvent ethanol by non-polar solvent hexane resulted in noticeable drop of retention of

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carboxylic acids (228–340 Da) through hydrophilic reverse osmosis membrane made of cellulose acetate – from 60–85% down to –40%, respectively [3]. The negative retentions were observed while using isopropanol or methanol as solvent and n-alkanes or linear carboxylic acids as solutes, whereas positive retention was measured with polyethylene glycol as solute; in contrast, using toluene or n-hexane as solvent, all observed retentions were positive [10].

Interestingly, among the publications describing negative retention in OSN, there are very few studies reported considerably high retention of one solute (e.g. 80% and higher) and negative retention of another solute for the same organic solvent [5,7,8,10]. Interestingly, those results were obtained with the membrane made of high permeability polymers – glassy [5,7,8] or rubbery one [10]. For example, glassy polymers with intrinsic microporosity PTMSP, PMP and PIM-1 exhibit similarities in retention of three different dyes with the same molecular weight of 350 Da (solvent – ethanol): negative retention of neutral dye Solvent Blue 35 (down to –17%) and high retention of anionic dye Orange II (up to 96%) [7].

In addition to traditional solvent–solute separation, new process of different solutes fractionation is proposed in this work. If solute “A” is selectively rejected by the membrane, preferably with the retention of 90% and higher, while the solute “B” is concentrated in the permeate due to negative retention the solutes fractionation could be realized in one step dead-end filtration experiment. Fig. 1 illustrates solutes fractionation concept when the solution with two different solutes “A” and “B” is filtrated through OSN membrane. Since solutes “A” and “B” have positive and negative retention, therefore, the feed side can be enriched by solute “A” and, at the same time, depleted by solute “B” after the filtration. In contrast to already proposed different configurations of solute fractionating membrane cascades based on diafiltration or OSN units [13–15], the possible benefit of proposed concept is that required solute fractionation might be achieved via single filtration step.

This work is focused on demonstration of solutes fractionation principle based on negative retention in OSN. To this end, two different pair of dyes in ethanol solutions were used, and dense membranes made of poly[1-(trimethylsilyl)-1-propyne] (PTMSP) were selected. PTMSP is extremely high free volume fraction (about 25%) glassy polymer and it possesses the highest ethanol permeability coefficient among known membrane materials for OSN [7]. To the best of our knowledge, for the first time the utilization of negative retention in OSN for solutes fractionation was proposed and studied in this work.

2. Experimental part

2.1. Polymer synthesis

PTMSP was synthesized in toluene solution using TaCl_5 with cocatalyst triisobutylaluminum (TIBA) as the catalyst [16]. Polymerizations were carried out under the following conditions: $[\text{Monomer}]/[\text{Catalyst}] = 50$, $[\text{Cocatalyst}]/[\text{Catalyst}] = 0.3$, $[\text{Monomer}]_0 = 1 \text{ mol/l}$, $T = 25^\circ\text{C}$ ($M_w = 1,600,000$, $M_w/M_n = 2.9$, $[\eta]_{\text{toluene}}^{25} = 6.9 \text{ dl/g}$).

2.2. Membrane preparation

The dense membranes were cast from solution with polymer concentration of 0.5 wt.% (solvent: chloroform) onto commercial cellophane. Then the cast film was covered with a Petri dish and left for slow evaporation for several days, followed by drying in the oven at 40°C to a constant sample weight. Further treatment of all membranes was according to standard protocol of PTMSP membrane preparation [17].

2.3. Filtration study

The filtration experiments were carried out at room temperature and pressure of 20 bar in the set-up with dead-end filtration cells (active service area is about 20 cm^2) equipped with stirring system and described in detail elsewhere [7]. The filtration experiments were carried out in a continuous mode; the duration of each experiment was up to 70 h. For each experiment about 80% of feed solution was allowed to pass through the membrane. Technical grade ethanol was used as a solvent. Two ethanol solutions with different pairs of dyes were used – Solvent Blue 35 and Orange II (dye pair I), Oil Red O and Remazol Brilliant Blue R (dye pair II), respectively (see Table 1). The solutes concentration for the dye pair I was 7 mg/l for each dye (14 mg/l totally), for the dye pair II the corresponding value was higher and equal to 30 mg/l for each dye (60 mg/l totally) because of lower extinction coefficient k for Remazol Brilliant Blue R. The dye concentration in the feed and permeate was determined by spectroscopy at two different λ_{max} (see Table 2) experimentally obtained for each dye by using the following equation:

$$C_1 = \frac{A_{i1} \cdot k_{22} - A_{i2} \cdot k_{12}}{k_{22} \cdot k_{11} - k_{21} \cdot k_{12}}$$

$$C_2 = \frac{A_{i2} \cdot k_{11} - A_{i1} \cdot k_{21}}{k_{22} \cdot k_{11} - k_{21} \cdot k_{12}}$$

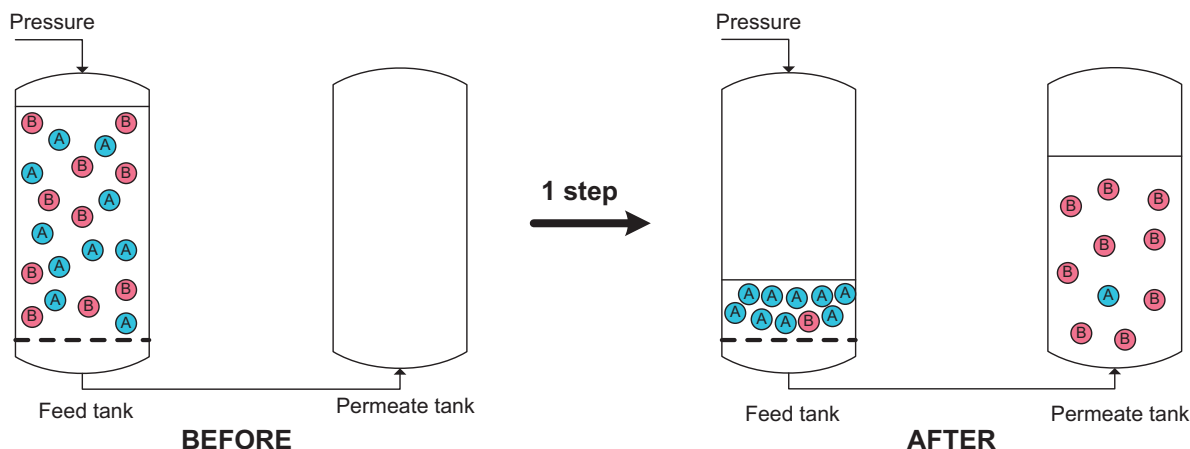


Fig. 1. Proposed principle of fractionation of solutes “A” and “B” with OSN.

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