Organic Solvent Nanofiltration with Cellulose Membranes

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Organic Solvent Nanofiltration (OSN) is a process which has the potential to replace or accompany conventional energy-intensive separation processes such as distillation and extraction in the chemical industry. While there are increasing number of research efforts and commercial units on OSN, the major limiting factor in wider use of this technology is considered to be the absence of membranes that can withstand aggressive organic solvents with predictable, reliable and stable performance over extended periods. In this study, we use cellulose as a novel membrane material for OSN applications. Insoluble in conventional molecular solvents due to its inter- and intramolecular hydrogen bonding capacity, cellulose is an ideal alternative for applications in such solvents.

Solutions of cellulose in the ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), and for some membranes acetone volatile cosolvent, were cast as 250 μm-thick films, and coagulated in water, thereby forming the membranes via phase inversion. Dyes were used as probe molecules to test membrane performance in ethanol and dimethyl sulfoxide (DMSO).

Table 1. Membrane fabrication conditions

Membrane code	Solution code	Casting solution composition (wt.%)			Solvent evaporation	Drying	BTCA crosslinking
		Cellulose	[EMIM]OAc	Acetone			
C12A	A	12	63	25	-	-	-
C12AE	A	12	63	25	+	-	-
C12AE-D	A	12	63	25	+	+	-
C12AE-D-X	A	12	63	25	+	+	+
C20	B	20	80	0	-	-	-
C20-D	B	20	80	0	-	+	-

The solutions used in membrane fabrication and post-treatment conditions are given in Table 1. Solvent evaporation was carried out under dry nitrogen flow to evaporate the volatile cosolvent acetone. Drying was carried out under nitrogen flow again at room temperature. Crosslinking was done with 1,2,3,4-butanetetracarboxylic acid.

Rejection of membranes prepared from solution A for Bromothymol Blue (BTB, neutral, $\tilde{V}_m$=251 cm^3/mol) increased with solvent evaporation and drying (Figure 1). Simultaneously the permeance decreased implying that the membranes got tighter. This was attributed to a higher cellulose concentration prior to coagulation for C12AE and pore collapse upon drying for C12AE-D. When the cellulose concentration in the casting solution was increased to 20%, the BTB rejection could be increased up to 94% (C20-D).

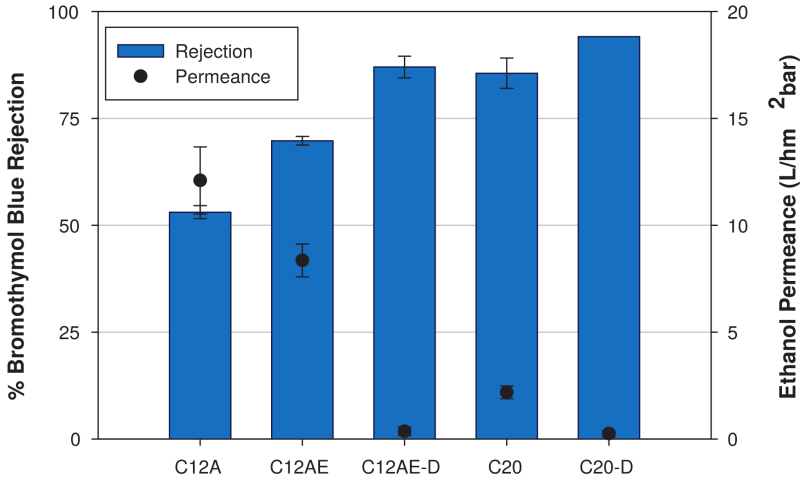


Figure 1. Bromothymol Blue rejection of membranes from the dye solution in ethanol and ethanol permeances.

C12AE-D and C12AE-D-X membranes showed over 70% rejection for BTB in ethanol and DMSO. Rejection of Rose Bengal (RB, anionic, $\tilde{V}_m$=241 cm^3/mol) was very low (10-20%) except for C12AE-D-X in DMSO, where it reached 93%, presumably due to unreacted carboxyl groups of BTCA on the membrane causing electrostatic repulsion between the membrane and the dye. Crystal Violet (CV, cationic, $\tilde{V}_m$=254 cm^3/mol) was retained to a moderate extent by C12AE-D while the rejection decreased upon crosslinking (Figure 2).

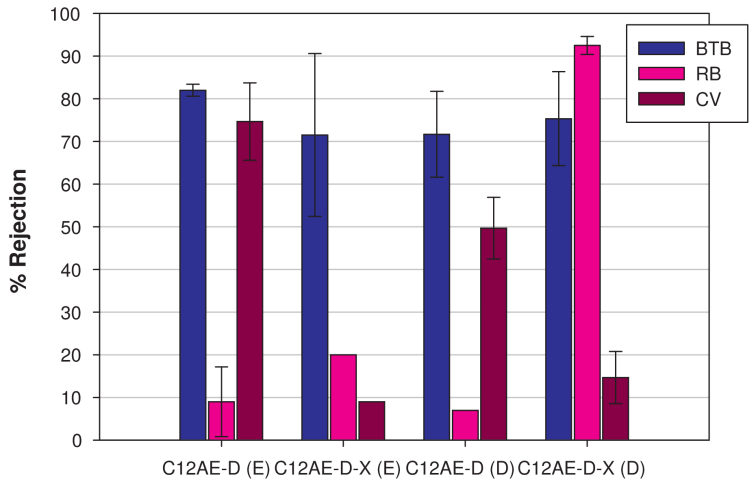


Figure 2. Rejection of Bromothymol Blue, Rose Bengal and Crystal Violet by dried (C12AE-D) and dried-and-crosslinked (C12AE-D-X) membranes.

Static dye sorption tests indicated that the changing rejection behaviour can be correlated to the extent of sorption in the membranes, where high sorption was accompanied by low rejections and vice versa, implying solute-membrane interactions play a dominant role in the separation performance of the membranes.