Grafting of cellulose acetate with ionic liquids for biofuel purification by a membrane process: Influence of the cation

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ABSTRACT

A new strategy was developed for grafting ionic liquids (ILs) onto cellulose acetate in order to avoid IL extraction and improve its performance for ethyl tert-butyl ether (ETBE) biofuel purification by the pervaporation membrane process. This work extended the scope of IL-containing membranes to the challenging separation of organic liquid mixtures, in which these ILs were soluble. The ILs contained the same bromide anion and different cations with increasing polar feature. The membrane properties were strongly improved by IL grafting. Their analysis in terms of structure-property relationships revealed the influence of the IL content, chemical structure and chemical physical parameters α, β, π^* in the Kamlet–Taft polarity scale. The ammonium IL led to the best normalized flux of $0.182 \, \text{kg/m}^2 \, \text{h}$ for a reference thickness of $5 \, \mu\text{m}$, a permeate ethanol content of 100% and an outstanding infinite separation factor for the azeotropic mixture EtOH/ETBE at $50 \, ^\circ\text{C}$.

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1. Introduction

Membrane separation processes are widely used worldwide for water treatment, gas and liquid separations. Compared to other separation processes such as distillation, adsorption and liquid–liquid extraction, membrane processes offer important energy savings, modularity and lower environmental impact (Baker, 2004; Drioli & Giorno, 2010; Hoek & Tarabara, 2013). In these processes, membrane optimization is essential for industrial success. In addition to being resistant to operating conditions, the membrane material should be both highly permeable and selective. Nevertheless, permeability and selectivity usually vary in opposite ways and the corresponding permeability/selectivity trade-off is a real challenge for membrane designers (Baker, 2004; Drioli & Giorno, 2010; Hoek & Tarabara, 2013; Robeson, 2008).

In this work, a membrane separation process is considered for purifying the ethyl tert-butyl (ETBE) biofuel, which is one of the major European biofuels. This ether is an oxygenated additive used in gasoline fuels to improve fuel combustion and air quality. Its main industrial synthesis process involves the reaction of isobutene

with bio-ethanol and leads to an azeotropic mixture EtOH/ETBE (20/80 wt%), whose current separation by a "ternary" distillation process is highly energy intensive (Wang et al., 2014; Weber de Menezes & Cataluna, 2008; Yee, Mohamed, & Tan, 2013). The pervaporation (PV) membrane process, alone or combined with simple distillation, could offer important energy savings for this separation (Chen, Eng, Glazer, & Wensley, 1988; Jonquieres, Arnal-Herault, & Babin, 2013; Streicher, 1997; Yee et al., 2013).

Nevertheless, ETBE purification by pervaporation is quite challenging and requires organoselective membranes capable of extracting ethanol from the targeted azeotrope (Jonquieres et al., 2013; Jonquieres, Clement, Lochon, Dresch, & Chrétien, 2002; Weber de Menezes and Cataluna, 2008; Yee et al., 2013). The relatively rare PV membranes reported for ETBE purification, i.e. cellulosic membranes, poly(vinyl pyrrolidone) blends and segmented copolymers, have been reviewed in the past few years (Billy et al., 2010; Wang et al., 2014; Zereshki, Figoli, Madaeni, Galiano, & Drioli, 2011). Cellulosic membranes have been mainly investigated for this separation. In particular, a cellulose acetate (CA) membrane was highly selective with a permeate ethanol content of 100% but its flux of $0.08 \, \text{kg/m}^2 \, \text{h}$ for a reference thickness of $5 \, \mu\text{m}$ was too low at $40 \, ^\circ\text{C}$ (Nguyen, Leger, Billard, & Lochon, 1997). Cellulosic esters blends enabled to vary the PV fluxes over a broad range 0.6–$3 \, \text{kg/m}^2 \, \text{h}$ with permeate ethanol mass fractions in the high

range 0.967–0.907 at 40 °C (Luo, Niang, & Schaetzel, 1997). Cellulosic semi-interpenetrated networks and graft copolymers have also been reported as promising ways for improving cellulosic membrane properties for ETBE purification (Billy et al., 2010; Luo, Niang, & Schaetzel, 1999; Nguyen, Clement, Noezar, & Lochon, 1998; Nguyen et al., 1997). In particular, CA grafting with short polymethacrylate grafts greatly improved membrane flux up to 0.87 kg/m^2 h while the permeate ethanol content (94%) remained high at 50 °C (Billy et al., 2010).

In other respects, ionic liquids (ILs) have been recognized as potential environmentally benign alternatives to classical volatile organic solvents due to their thermal stability, non-volatility, negligible vapor pressure and capacity to dissolve a large range of organic compounds (Rogers and Seddon, 2002; Wasserscheid & Welton, 2008). Beyond their use as "green solvents", ILs have also recently opened new perspectives in the development of materials for industrial separation applications (Chen, Rodríguez, & Rogers, 2012; Green & Long, 2009; Han & Row, 2010; Lozano et al., 2011; Lu, Yan, & Texter, 2009; Noble & Gin, 2011; Scovazzo et al., 2002). ILs have been reported for bio-products separations (Izak, Friess, & Sipek, 2010; Roosen, Müller, & Lasse, 2008), gas separations (Close, Farmer, Moganty, & Baltus, 2012; Hanioka et al., 2008; Hojniak et al., 2014; Lozano et al., 2011; Noble & Gin, 2011; Scovazzo, 2009) and, to a much less extent, liquid separation by PV (Cascon & Choudhari, 2013; Fadeev & Meagher, 2001; Heitmann et al., 2012; Izak et al., 2010; Izak, Ruth, Fei, Dyson, & Kragl, 2008; Matsumoto, Murakami, & Kondo, 2011; Plaza et al., 2013; Yahaya, Hamad, Bahamdan, Tammana, & Hamad, 2013).

A great ILs advantage for membrane separations is the variety of combinations for their cation and anion, which allows a good control of their physical chemical properties and a modulation of their polarity/hydrophobicity (Rogers & Seddon, 2002; Somers, Howlett, MacFarlane, & Forsyth, 2013; Wasserscheid & Welton, 2008; Yuan & Antonietti, 2011). Nevertheless, the separation of liquid mixtures by ILs-containing membranes is particularly challenging and has been reported rarely (Cascon & Choudhari, 2013; Fadeev & Meagher, 2001; Heitmann et al., 2012; Izak et al., 2008, 2010; Matsumoto et al., 2011; Plaza et al., 2013; Yahaya et al., 2013). With this respect, the selective recovery of butanol biofuels from aqueous solutions with *organophilic* IL-containing membranes has been mostly addressed (Cascon & Choudhari, 2013; Fadeev & Meagher, 2001; Heitmann et al., 2012; Izak et al., 2008, 2010; Mai, Kim, Ha, Shin, & Koo, 2013; Matsumoto et al., 2011; Plaza et al., 2013). The separation of other volatile organic compounds (ethanol, isopropyl alcohol, toluene etc.) by IL-containing membranes has been reported to a much less extent (Izak et al., 2010; Kohoutova et al., 2009; Takekoshi, Miyata, & Uragami, 2010). In the former works, the ILs introduction in PV membranes usually led to significant flux improvement while membrane selectivity was maintained or slightly reduced. The corresponding membranes were either supported liquid membranes (SLMs) or IL polymer "composites". Recently, the permanent IL immobilization in polydimethylsiloxane (PDMS) membranes by co-condensation of a triethoxysilane IL with hydroxyl terminated PDMS has also been reported for improving membrane stability during butanol recovery (Mai et al., 2013).

In this work, a new strategy for ILs grafting onto CA is proposed for improving its membrane properties for ETBE purification. We have already evidenced that quaternary ammonium ILs have great affinity for ethanol and are usually soluble in the azeotropic mixture EtOH/ETBE (Jonquieres, Awkal, Clément, & Lochon, 2009). Recently, 1-ethyl-3-methylimidazolium ethylsulfate IL has also been reported as an interesting extraction solvent for ETBE purification by liquid–liquid extraction and extractive distillation (Arce, Rodriguez, & Soto, 2007). By offering IL permanent immobilization, the original grafting strategy developed in this work avoided IL extraction during membrane separation and further extended the

scope of IL-containing membranes to the challenging separation of purely organic mixtures, in which these ILs are soluble.

To the best of our knowledge, the ILs grafting onto CA has not been reported yet and goes beyond the use of ILs as polysaccharide solvents or processing aids. However, copper-catalyzed click chemistry has been reported twice for grafting ILs onto cellulose (Gonsior and Ritter, 2011; Xu, Gao, & Kadla, 2013). Another recent work reported cellulose grafting by nucleophilic substitution of azido cellulose with carboxypropyl-trimethylammonium chloride (Bretschneider, Koschella, & Heinze, 2015). Compared to grafting by click chemistry, the original strategy developed in this work involved two steps only and avoided handling copper species always difficult to remove from the modified cellulosic materials.

Therefore, the first part of this work reports CA grafting with ILs containing the same bromide anion and different cations (imidazolium, pyridinium and ammonium) with increasing polar features. The bromide anion was chosen because of its hydrophilic character and the commercial availability of the corresponding chemical reactant for cellulose acetate modification. The chemical structure and morphology of the new membrane materials are characterized on the basis of complementary techniques (^{1}H NMR, DSC, SAXS).

The second part focuses on their sorption and PV properties for the separation of the azeotropic mixture EtOH/ETBE. The influence of the IL content and structure on the membrane properties is analyzed on the basis of structure-properties relationships, which reveal the key features of these systems for overcoming the common permeability/selectivity trade-off for ETBE purification.

2. Experimental

2.1. Materials

CA (CA, acetyl 39.7 wt%, M_W = 50,000 g/mol), 6-bromohexanoic acid (97%), 1-methylimidazole (99%), *N,N*-diethylmethylamine (97%), pyridine (99.8%), 4-dimethylaminopyridine (DMAP, ≥ 99%) were purchased from Sigma-Aldrich. ^{1}H NMR analysis confirmed the acetyl content of CA, corresponding to 2.46 of acetyl groups and 0.54 of hydroxyl groups per glycosidic ring. The degrees of substitution (DS) of the side groups were commonly defined as the number of side groups per glycosidic ring. 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl, >98%) was purchased from TCI Company. All reagents were used as received. All solvents, dichloromethane (DCM, ≥99.9%), tetrahydrofuran (THF, 99.7%), acetonitrile (≥99.9%), and dimethylformamide (DMF, ≥99.8%), were dried over molecular sieves before using. In order to prevent contamination by atmospheric moisture, all reagents and solvents were stored under nitrogen atmosphere.

2.2. Synthesis and characterization of CA grafted with different ILs

2.2.1. Synthesis of a bromo-CA derivative

In three necks round bottom reactor under argon flow, 15 g of CA (corresponding to 56.54 mmol of glycosidic rings and 30.53 mmol of hydroxyl groups) were dissolved in 300 mL of dry THF under vigorous stirring at room temperature. 150 mL of dry DCM, 6 g of bromohexanoic acid (30.76 mmol), and 0.373 g of DMAP (3.05 mmol) were added to the reaction mixture. The reaction mixture was cooled at 5 °C and 6.44 g of EDC.HCl (33.59 mmol) were added. The resulting mixture was stirred for 48 h at room temperature. The crude polymer was precipitated in 2 L of ethanol (96%), washed twice in ethanol, filtered and dried under vacuum at 60 °C overnight. The polymer was obtained as white solid fibers with a yield of 90% with a DS_{Br} of 0.5 according to ^{1}H NMR analysis.