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Oil-Water Separation using Membranes Manufactured from Cellulose / Ionic Liquid Solutions

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ABSTRACT

Membrane processes are currently essential for seawater desalination and their implementation in sustainable separations in the chemical industry is rapidly growing. The sustainability of the membrane manufacture itself has been however frequently questioned and needs to be improved. Ionic liquids are promising alternative solvent for membrane manufacture. We discuss general aspects of toxicity and recyclability compared to common organic solvents and take advantage of their unique capability of dissolution of polymers like cellulose, a natural and biodegradable polymer. Cellulose membranes were prepared from solutions in 1-ethyl-3-methylimidazolium acetate as flat-sheet and hollow fibers. The membranes performances were evaluated for oil and water separation, analyzing the influence of anionic, cationic and neutral surfactants added to emulsions with different oil content.

KEYWORDS: *Cellulose, membranes, ionic liquids*

INTRODUCTION

Reverse osmosis is the leading technology for water desalination in arid regions such as the Middle East. Membrane-based separation processes are more and more integrated into the chemical industry, promoting sustainability, productivity, and economic advantages. However, the membrane manufacture process itself needs to be more sustainable. Polymeric membranes are industrially prepared on large scale in continuous machines by a process consisting of steps of a polymer solution casting and immersion in a water bath. Reducing the emission volatile organic compounds (VOCs) during the manufacture and recycling the water bath would improve the membrane manufacture sustainability. VOCs, such as benzene, toluene, xylene, are carcinogens. Due to their negative impact on the environment and human health, the regulations of VOC-generating processes are now stricter, and indeed one of the most focused principles of green chemistry¹⁻² is the use of safer solvents and additives.

Table 1 shows a general solvent selection guidance, classified as preferred, usable, and undesirable, depending on their toxicities.³⁻⁵ In these classifications, the most common solvents for membrane fabrication, such as dimethyl formamide (DMF), N-methyl pyrrolidone (NMP), and dimethyl acetamide (DMAc), are categorized in the undesirable group, due to their toxicity. Their acute toxicity is compared in Table S1 (Supporting Information).

Table 1. Solvent selection guide.

Preferred	Usable	Undesirable
Water	Dimethylsulfoxide (DMSO)	Dichloromethane
1-Butanol	t-Butanol	Chloroform
2-Butanol	1-Propanol	1,2-Dichloroethane
Dimethyl carbonate	2-Propanol	Dimethyl formamide (DMF)
Ionic liquids	Acetone	N-Methyl pyrrolidone(NMP)
Supercritical CO ₂	Toluene	Pyridine
Fluorous media	Heptane	Dimethyl acetamide (DMAc)
Bio-sourced solvents	Tetrahydrofuran (THF)	Hexane

Sources (modified) from GSK and Pfizer's solvent selection guide³⁻⁴

The most common alternative solvents, explored in polymer science and engineering, are supercritical carbon dioxide (scCO₂), fluorous media, water, bio-sourced solvents, and ionic liquids. Advantages and disadvantages of these solvents are summarized in Table S2. Ionic liquids have no measurable volatile pressure and thus do not produce VOCs. From this point of view, they could be advantageous solvents for the membrane manufacture. Furthermore, their benefits and influence on the membrane properties were demonstrated by our group and others, as shown in Table 2. Ionic liquids are constituted by large ions, frequently having a low degree of symmetry. These factors lead to low lattice energy of

crystal formation and low melting point ⁶, being liquid at room temperature.⁷ The dominant interactions in ionic liquids are hydrogen bonding, π - π stacking, and electrostatic, which are less frequent or less intense in commonly used organic solvents.⁸ Some of the commonly combined cations and anions in ionic liquids ⁹ and their physical-chemical properties are illustrated in Figure S1 and Table S3. While ionic liquids are considered green due to their low VOC level, the impact on the aqueous environment has to be carefully considered, if they would be discarded as effluent. Some ionic liquids may be significantly toxic ¹⁰, but they can be tunable to become environmentally benign.¹¹ To choose the adequate ones, the tendency of the ionic liquid toxicity might be understood. The effect of the cationic and anionic compounds, the length of the alkyl chain in the cations, and the number of the alkyl chains, on their acute toxicity to plants, enzyme, flash water snails, microorganisms and fishes have been investigated by adding ionic liquids to water with small aqueous plants and animals.¹²⁻¹⁹ The toxicity increases as their hydrophobicity increase, due to a higher structural similarity to the lipid cell of microorganisms.^{13, 20} Imidazolium-based cations are less toxic than those of pyridinium, which are longer, and have a higher number of alkyl side chains. The anion selection also affects the toxicity. For example, with 1-butyl pyridinium or 1-butyl-3,5-dimethyl pyridinium cationic compounds, $N(CN_2)_2$ anions are more toxic than bromide. In summary, decreasing the hydrophobicity of ionic liquids, designing shorter hydrophobic groups or selecting hydrophilic cations and anions would help to have a less negative impact on the environment.

When considering using ionic liquids for instance in the production of membranes by phase inversion, by solution casting and immersion in water, the possibility of

recovering them would be important for environmental and economic reasons. Mai *et al.*²¹ reviewed various methods for ionic liquid recovery, as shown in Table S4. Distillation would be the simplest method to separate chemicals with low boiling temperature from ionic liquids. The ionic liquid recovery by membrane technology has been reported²², using commercial reverse osmosis (RO), nanofiltration (NF)²³, and pervaporation (PV) membranes, and electrodialysis (ED).²⁴

Besides the low VOC, the main advantage of ionic liquids is their capacity to dissolve polymers that otherwise require quite aggressive solvents. An example of polymers in this category is cellulose. Cellulose fibers and films have been long produced by the modification to cellulose xanthogenate, following the viscose process with heavy metals and H₂S as hazardous byproducts. The other options have been the cuprammonium process²⁵, also relatively aggressive for the environment, and the dissolution in methylmorpholine-N-oxide.²⁶ More recently, ionic liquids have been introduced as a solvent for cellulose. Since then, the potential of using nature cellulosic polymers has increased²⁷⁻³², and processes such as the biofuel production with the deconstruction of lignocellulosic biomass has become more efficient.³³⁻³⁵

The use of ionic liquids for the dissolution of other polymers and the membrane manufacture is still in an early stage. Table 2 summarizes recent examples of polymer dissolution and membrane fabrication reported by our group and others. These results demonstrate that the advantage of ionic liquids as a solvent transcend the environmental aspects and the capability of dissolution of highly insoluble systems. The membranes prepared with ionic liquids have a differentiated sponge-like morphology, and the performance in many cases overcome that of those prepared with organic solvents.

The preparation of cellulose membranes using ionic liquids was first reported by Li et al.³⁶ They used 1-allyl-3-methylimidazolium chloride. We first reported the preparation of flat-sheet cellulose membranes from solutions in 1-ethyl-3-methyl imidazolium acetate ([EMIM]OAc).³⁷ More recently cellulose membranes prepared with the same ionic liquid have been tested for organic solvent nanofiltration.³⁸ We demonstrated that the use of ionic liquids facilitates the dispersion of graphene oxide in polymeric membranes.³⁹ More recently cellulose/graphene membranes have been prepared from solutions in ionic liquids.⁴⁰ A cellulose solution in [EMIM]OAc was also used to modify electrospun fibers of polyvinylidene fluoride-co-hexafluoropropylene, enhancing the hydrophilicity and enabling the application for oil-water separation.⁴¹

We reported here the evaluation of flat-sheet cellulose membranes prepared by phase inversion, using casting solutions in ionic liquids, for application in oil-water separation. We prepare for the first time cellulose hollow fiber membranes from dope solutions in [EMIM]OAc.

Table 2. Summary of polymer dissolution in ionic liquids and membrane performance.

Polymer	Solvent	Solubility	Membrane structure, water permeance ($\text{L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$) /MWCO (kg mol^{-1})	References
Polyacrylonitrile (PAN)	[EMIM]OAc/ DMSO	> 12 wt% (25 °C)	^a Finger-like, 540 ± 30 (HF) / 54	[42]
	[EMIM]OAc	No (25 °C)	^a N/A	
Polyethersulfone (PES)	[EMIM]DEP	> 18 wt% (90 °C)	^a Sponge-like, 55 ± 5(FS) / 5.1, 45.8 (HF) / 1.4	[39, 43, 44]
	[MMIM]DMP	> 18 wt%	^a Sponge-like, 43 ± 3(FS) / 7.9	[44]
Polysulfone (PSf)	[EMIM]DEP	No (90 °C)	N/A	
	[MMIM]DMP	No (90 °C)	N/A	
Poly (ether imide sulfone)	[EMIM]SCN	> 24 wt% (90 °C)	^c Sponge-like, 90 ± 10 (FS) / 5.3	[45]
(EXTEM™, XH 1005)	[BMIM]SCN	> 24 wt% (90 °C)	^c N/A (too brittle)	[45]
	[EMIM]OAc	> 24 wt% (90 °C)	^c N/A (too brittle)	[45]
EXTEM™ (XH1015)	[EMIM]OAc	No (120 °C)	-	[46]
Cellulose acetate (CA)	[EMIM]OAc	> 12 wt% (60 °C)	^a Sponge-like, 130 (FS) / 77	[47]
	Ac/[EMIM]OAc	> 28 wt% (60 °C)	^a Sponge-like, 330 (FS) / 74	[47]
	[EMIM]SCN	> 12 wt% (50 °C)	^a Sponge-like, 90 (HF) / mean pore size 17.5 nm	[48]
	[BMIM]SCN	> 12 wt% (50 °C)	^c Sponge-like, 114.14 (FS) / mean pore size 39.16 nm	[49]
Cellulose	[EMIM]OAc	≥ 13.5 wt%	Composite membranes, 13.8 (FS) / 3	[37, 50]
	ionic liquids	various	-	[27, 28, 31, 51-54]
Chitin	ionic liquids	various	-	[31, 51]

1					
2					
3	^g Natural polymers	ionic liquids	various	-	[55, 56]
4					
5	Polystyrene- <i>b</i> -poly	THF/ DMF with	≥ 18 wt%	Spherical and hexagonal pores	[57]
6	(4-vinyl pyridine)	[B ₄ MPy]BF ₄ ,		([B ₄ MPy]BF ₄ , [B ₃ MPy]TFMS,	
7					
8	(PS- <i>b</i> -PV4P)	[B ₃ MPy]TFM,		[EMIM]BF ₄ , [B ₃ MIM]BF ₄ ,	
9					
10		[EMIM]BF ₄ ,[B ₃ MI		Lamella ([IM]TFSI and	
11					
12		M]BF ₄ , [IM]TFSI,		[HMIM]HSO ₄),	
13					
14		[HMIM]HSO ₄		1300, 1600, 1120,1800, 450,	
15				and 550 (FS), respectively /	
16					
17				N/A	
18					
19	Polybenzimidazole	[BMIM]Cl	≥ 10 wt% (140 °C)	-	[58]
20					
21	(PBI)	[BMIM]BF ₄	No (140 °C)	-	[58]
22					
23		[BMIM]OH	≥ 8 wt% (140 °C)	-	[58]
24					
25		[EMIM]OAc	≥ 20 wt% (120 °C)	^f Sponge-like with finger	[59]
26				voids, 141.3(FS) / 109	
27					
28	P84+ PBI	[EMIM]OAc	≥ 20 wt% (120 °C)	^f Sponge-like with finger	[46]
29				voids, 216 (FS) / 104	
30					
31	P84 co- polyimide	[EMIM]OAc	≥ 20 wt% (120 °C)	-	[46]
32					
33	polyamideimide	[EMIM]OAc	≥ 10 wt% (120 °C)	-	[46]
34					
35	(Torlon, 4000T)				
36					
37	Polyetherimide	[EMIM]OAc	No (120 °C)	-	[46]
38					
39	(Ultem, 1010)				
40					
41	Polyimide	[EMIM]OAc	No (120 °C)	-	[46]
42					
43	(Matrimid, 5218)				
44	*The concentration of polymers: ^a 12 wt%, ^b 16 wt%, ^c 24 wt%, ^d 7 wt%, ^e 10 wt% ^f 20 wt%, hollow fiber (HF), and flat				
45	sheet (FS), ^g Natural polymers: Wool keratin fibers, fibroin, sericin, etc.				
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Oily wastewater is one of the most abundant by-products of the food industry, chemical and petrochemical industry. For instance, for every barrel of recovered crude oil, 7 to 10 barrels of oily wastewater are produced, requiring proper management for effective oil separation. Oil in water systems can be categorized according to the oil droplets sizes. Floated or dispersed oil droplets larger than 10 μm can be easily mechanically removed. Water with oil droplets smaller than 10 μm are classified as oil-in-water (O/W) emulsions. Emulsified oil is difficult to remove by using common techniques such as physical, chemical and biological treatment. Conventional gravity separation techniques such as skimming, air flotation, coagulation, and flocculation methods are frequently used in the food industry, but can be ineffective in the treatment of micron/sub-micron oil droplets dispersed in water. Methods of de-emulsification or chemical addition not only require additional energy input but could sometimes enhance the pollution of an already vulnerable environment.⁶⁰ Oleophilic adsorbents can be considered a nontoxic tool for removing large and small oil droplets. Their drawbacks are cost and the need for frequent regeneration. Hydrocyclones are frequently used to de-sand and de-oil wastewater, combining centrifugal forces and gas flotation to separate water, oil and gas. Membranes are under consideration as a powerful technology for oil-water separation due to the tailored pore sizes in a range between 0.01 and 10 μm .⁶¹⁻⁶² The biggest challenge for membranes in the oil and gas industry is fouling. With that in mind, we carefully investigated the fouling resistance of the cellulose membranes prepared here from solutions in ionic liquids under different conditions.

MATERIALS AND METHODS

Materials. Avicel® PH-101 microcrystalline cellulose (MW=160,000–560,000 g mol⁻¹) was purchased from Fluka Analytical, produced by Wacker Chemie AG, Burghausen, Germany. Hydrochloride acid (HCl, 36.5–38.0%) and sodium chloride (99%) were purchased from Alfa Aesar. Tetrahydrofurane (THF, ≥99.5%, for synthesis) was purchased from ROTH® and used as received. Poly (ethylene glycol) (PEG) or poly(ethylene oxide) (PEO) of different molecular weights (0.2, 1.5, 3, 6, 10, 35, 100, 300 and 600 kg mol⁻¹) was purchased from Sigma Aldrich®, produced by BASF. The asymmetric porous support based on polysulfone (PSU) was prepared by phase inversion using continuously operating machine. Milli-Q® water (Millipore) with specific resistivity 18.2 MΩ cm at 26.1 °C was used for membrane preparation and testing. A crude oil sample was kindly provided by ARAMCO. Surfactants sodium dodecyl benzene sulfonate (CH₃(CH₂)₁₁C₆H₄SO₃Na) (SDBS), hexadecyltrimethylammonium bromide (N(CH₃)₃Br) (CTAB) and polysorbate 80 (Tween® 80) were purchased from Sigma Aldrich and used as received. 1-Ethyl-3-methyl imidazolium acetate ([EMIM]OAc) with purity equal or higher than 95% was supplied by Sigma.

Flat-sheet cellulose membranes preparation. Cellulose was dissolved in [EMIM]OAc, at 60 °C. The cellulose concentration was 2 and 5 wt %. The solutions were then cast at 23 °C, with a doctor blade adjusted to 150 μm gap, on a porous polysulfone asymmetric support. After casting, the membranes were immersed in deionized water and dried in air.

Hollow fiber membranes preparation. The cellulose hollow fiber membranes were prepared by phase inversion in a spinning machine, following the conditions in Table 3.

The cellulose was dried in vacuum oven at 70°C for 3 hours to eliminate any residual moisture. A 12 wt% solution in [EMIM] OAc was stirred for two days at 85-90°C and degassed before spinning.

Table 3. Conditions for the hollow fiber spinning

Parameters	Operating conditions
Dimensions of spinneret	0.9:0.6
Dope composition	12 % cellulose
Dope solution solvent	[EMIM]OAc
External coagulant	Tap water
Bore fluid	DI water
Bore fluid flow rate (mL/min)	4
Air gap (cm)	20
Dope solution temperature (°C)	90
Spinneret temperature (°C)	90
External coagulant temperature (°C)	25
Spinning pressure (bar)	3

Characterization of the hollow fibers. All permeation tests were carried out in a crossflow mode. A transmembrane pressure of 0.2 bar was applied, and the feed solution was introduced into the lumen of the hollow fiber so that the permeate radially flows from the inner to the outer side of the membrane. The feed solution volume were 200 mL; 5 mL permeate was first flown before collecting samples for the qualitative analysis. Poly(ethylene glycol) (PEG) solutions were prepared with a total concentration of 1g/L,

containing a mixture of PEG 400, 3k, 10k, 35kg/mol. Separated tests were performed with single PEG 3kg/mol solutions after the screening with the PEG mixture. Gel chromatography was used to measure the relative concentrations. The rejection was calculated by the equation $(R (\%) = 100 (1 - C_p/C_f))$. Cytochrome C, bovine albumin (BSA) and gamma globulin (IgG) were used as additional solutes for rejection characterization. To evaluate the rejection of the biomolecules, a Nanodrop UV-visible absorption analyzer was used. In the case of BSA and IgG the absorption peak was set at 280 nm, while for the cytochrome C it was set at 409 nm. The feed contained 100 ppm of IgG, BSA or cytochrome c prepared in phosphate-buffered saline solution (PBS).

Preparation of oil-in-water emulsion. Crude oil/water emulsions of 200, 500 and 1000 ppm oil concentrations were prepared by mixing the oil with 80 g/L of sodium chloride, one of three different surfactants, anionic (SDBS), cationic (CTAB) or neutral (Tween 80)[®], and 1 L of MilliQ water in a blender. Mixing at 20,000 rpm was repeated until a homogeneous emulsion was obtained. The surfactants were added in 1:10 ratio (surfactant:oil).

Characterization of flat-sheet cellulose membranes for oil-water separation.

For the oil-water separation experiment, we used a dead-end filtration set up. Membranes (14.6 cm active area) were placed in a stainless-steel cell and connected to a nitrogen gas cylinder. The transmembrane pressure was 5 bar for all experiments, unless otherwise stated. The permeate was collected and immediately analyzed. The stainless-steel cells were provided with an internal stirrer, allowing a continuous solution-mixing at 300 rpm during all experiments.

Fouling during oil-water filtration. The oil rejection and the fouling resistance of the cellulose membrane operating with the oil-in-water emulsion were measured in the following way. First, the permeance of pure water was measured. Secondly, the filtration of the oil-in-water emulsion was conducted. The difference in permeance between the pure water and the emulsion indicates the fouling rate. The stainless-steel cell was filled with 300 mL of oil-in-water emulsion, a minimum of 100 mL of permeant was collected and the remaining emulsion in the cell was analyzed as retentate. Without removing the membrane, the cell was rinsed with water, refilled with pure water and the permeance was measured again in order to obtain the recovery ratio. Finally, the oil-in-water emulsion permeance was measured as a function of time, to evaluate the flux decline trend. For further fouling confirmation, the membranes were taken out of the cell, rinsed with water and visually examined. Experiments were conducted with control membranes, without cellulose coating, and with the cellulose composite membranes. The feed, permeate and retentate were analyzed immediately after finalizing the experiment. The experiments were conducted with three different surfactants at 3 different pH values of neutral, acid and basic, respectively, using membranes prepared from 2 wt% and 5 wt% cellulose casting solutions in the ionic liquid. The pH adjustment for pH 4 and pH 11 for the oil-in-water emulsions was done with 1 M HCl and 0.1 M NaOH. The adjustment was performed using Fisher Scientific Accumet AB150 pHmeter.

Turbidity. The turbidity was measured using a 2100Q HACH portable turbidimeter that measures turbidity (in NTU units) of produced water feeds and permeates. The device is compliant with the USEPA Method 180.1.

Oil-in-water analysis. The oil concentration (ppm) in the feed and permeate was determined by spectrophotometry and gravimetry. The spectrophotometric analysis was mainly performed using a HD 1000 analyzer, based on fluorescence measurement. The calibration of the instrument with the crude oil used in the experiments was done before the experiment, by preparing 5 different concentrations and blank. 80 - 100 mL of emulsion were poured into the stainless steel non-transparent cell, the probe was immersed, and the cell was closed. The measurement was repeated at least three times. The cell and the probe were thoroughly washed with DI water and ethanol between measurements to remove any oil residue. For the experiments performed with hollow fiber membranes the oil contents in the feed, retentate and permeate were quantified by UV-visible spectrometry (NanoDrop 2000, Thermo Fisher Scientific). The gravimetric measurements were performed, by applying the total oil and grease method. Briefly, 80 mL of emulsion was added to the flask, followed by addition of HCl and 8 mL of tetrachloroethylene (tetrachloroethylene:emulsion added in 1:10 ratio). Afterward, the mixture was stirred, and the flask was left still until complete separation in two phases (water and oil) occurred. The oil phase was collected in a quartz cuvette and the concentration was measured in the spectrophotometer. The cuvette and flask were rinsed with tetrachloroethylene before the experiments to avoid any oil residue.

Streaming potential. Zeta potential and the emulsion droplet size were measured using a Malvern Zetasizer Nano ZS, based on dynamic and static light scattering and electrophoresis. A 0.5 mm² membrane sample was analyzed, varying the pH from 3 to 11, each measurement taking 30 minutes. The pH was adjusted. Besides the streaming potential of the membranes, the zeta potential of the emulsion droplets was measured with

the same instrument, using a disposable folded capillary cell. The experiment had three runs each repeating 100 times, and the average was then calculated. The particle size was measured using disposable 12 mm² polystyrene cuvettes.

RESULTS AND DISCUSSION

Membrane formation. Two membrane configurations were investigated in this work: flat-sheet and hollow fiber. The flat-sheet membrane was constituted by multilayers. An asymmetric porous polysulfone (PSU) membrane was prepared by non-solvent (water) induced phase separation. A PSU solution was cast on a polyester membrane and immersed in water, following a procedure commonly used in the industry. The porous dry support was then dip-coated using 2 and 5wt% cellulose solutions in the ionic liquid [EMIM] OAc. The multilayered membranes were immersed in water to extract the ionic liquid. The formed cellulose layer is a thin dense and selective coating with thicknesses of 0.4 μm and 0.9 μm , respectively, on the porous PSU membrane support. The support gives the mechanical stability to the membrane.

Flat-sheet membranes are used in many large-scale applications as spiral-wound or envelope-type modules. Hollow fiber membranes have the advantage of large surface area/volume ratios and the possibility of packing in even more compact systems. Therefore, we considered relevant to demonstrate that the cellulose/ionic liquid membranes could be manufactured as hollow fibers as well. The hollow fiber membranes prepared here, as discussed later, were self-standing and fully constituted by cellulose. For the manufacture, a much higher cellulose concentration (12 wt%), which provided the adequate viscosity required for the formation of a robust fiber.

Oil-water emulsions properties. Oily wastewater is produced in large-scale as a byproduct of the petrochemical industry and refineries, as well as other sectors such as the food industry. Membrane technology can be one of the solutions for this separation task. Fouling is, however, an important limitation. Cellulose membranes prepared from solutions in [EMIM]OAc were evaluated using a simulated feed constituted by an emulsion of crude oil, water, and 3 surfactants, added to reduce the droplets to sizes below 10 μm . The chosen surfactants were the anionic sodium dodecylbenzylsulfonate (SDBS), the cationic hexadecyltrimethylammonium bromide (CTAB), and the neutral Polysorbate® 80 (Tween® 80). The head of the anionic surfactant is a benzenesulfonate group. The head of the cationic one was a quaternary ammonium group and the neutral surfactant does not have a charged group. The droplet analysis revealed that the oil-in-water emulsion stabilized by the anionic surfactant has a size in the range of 0.7-2.4 μm , while those stabilized by cationic and non-ionic surfactants have a size in the range of 200-300 nm, and 200 nm, respectively, as shown in Table 4 at pH 4, 8 and 11. Table 4 also lists the zeta potential for each droplet system.

Table 4. Size and zeta potential of 200 ppm oil-in-water emulsion droplets, stabilized with different surfactants.

	pH 4	pH8	pH11
SDBS			
Droplet size/nm	2425 ± 759.0	1619 ± 76	759 ± 136
Zeta potential/mV	-34 ± 9	-36 ± 4	-62 ± 2
CTAB			
Droplet size/nm	218 ± 6	315 ± 72	231 ± 12
Zeta potential/mV	12.1 ± 0.3	-2 ± 1	-12 ± 4
Tween®			
Droplet size/nm	210 ± 3	227 ± 11	214 ± 5
Zeta potential/mV	-4.3 ± 0.2	-4.7 ± 0.6	-2 ± 1

The larger droplet sizes, detected with the anionic surfactant, reflect higher interface tension and a less stable emulsion when compared to the other two surfactants. Oil-water emulsions containing anionic surfactant were indeed the least stable ones, having oil visually separated from water within 3 days of preparation. Emulsions containing cationic surfactant were stable for 7 days, while emulsions containing non-ionic surfactant were stable for several weeks.

Charge effect on the cellulose membrane performance. The flat-sheet cellulose membranes were tested with emulsions in three pH values. The change of pH affects the membrane surface charge, as reflected by the zeta potential, and the emulsion itself. The membrane functional groups might protonate and deprotonate over the pH range, and so will the surfactant molecules in the emulsion, leading to different charge density values. The charge of the membrane and charge of the ions in the solution will cause either electrostatic repulsion or attraction, which will directly affect the performance of the membrane. The zeta potential of a membrane prepared by casting a 2 wt% cellulose solution in [EMIM]OAc on a PSU porous support is shown in Figure 1a. Figure 1c depicts the ions and counter-ions close to the membrane surface, forming the Stern layer of strongly bonded ions and the layer corresponding to the zeta potential measurement. At pH above 4.2 the membrane zeta potential is negative. Since this is a surface property, it should be independent of the cellulose layer thickness, and similar values are expected for membranes prepared with 5 wt% cellulose solutions.

The presence of different surfactants stabilizes the oil-in-water emulsion and also affects the charge of the oil droplets in different pH values, as depicted in Figure 1d. The zeta potential of oil droplets in emulsions stabilized by Tween[®] is practically neutral, while

the zeta potential of those stabilized by SDBS is negative in the whole investigated pH range. In the case of CTAB, the droplets acquire a positive charge at pH below around 7.5.

Oil-in-water emulsions with 200, 500 and 1000 ppm oil at pH values 4, 8 and 11 and 20 ppm of different surfactants were filtered through the cellulose membranes. Representative results are shown in Figure 2 for membranes obtained with 5 wt% cellulose solutions. At this pH, the membrane and oil droplets are negatively charged, or neutral in the case of those stabilized by Tween[®]. The highest permeances were obtained with SDBS, which leads to oil droplets with the most negative zeta potential. As can be seen from the permeate image in Figure 2d, a practically complete oil rejection is obtained, and only water permeates through the highly hydrophilic membrane. The quantification of the oil rejection is shown in Table 5. A permeate turbidity below 1 NTU is within the obligatory laws and restrictions of European standards and the US Environmental Protection Agency.

The filtration at pH 11 showed a similar trend. The results at pH 4 are slightly different, as shown in Figure 3. At this pH, the membrane zeta potential is slightly positive, and apparently the filtration of emulsions with CTAB is characterized by clearly higher permeance. This is due to the repulsion of the positively charged oil droplets by the now also positively charged membrane surface, which leads to lower fouling. This is particularly visible in the case of emulsions with low oil content. At high concentration, the effect of charge is not enough to minimize the permeance decrease with time.

Figure 1. (a) Zeta potential of a membrane prepared by casting a 2 wt% cellulose solution in [EMIM]OAc on a porous PSU support, as a function of pH; (b) zeta potential of oil droplets in an oil (200 ppm)-in-water emulsion containing 20 ppm surfactants (SDBS, CTAB or Tween®). Schemes illustrating the zeta (ζ) potential of the (c) membrane and (d) oil droplets in the oil-in-water emulsion containing CTAB at pH < 8.

Figure 2. Permeance through membranes prepared with 5 wt% cellulose solution, as a function of time, using as feed oil-in-water emulsions with 200, 500 and 1000 ppm oil and 20 to 100 ppm (ratio 1: 10 surfactant to oil) of different surfactants: (a) SDBS, (b) CTAB and (c) Tween[®] at pH 8. (d) Photograph of the 1000 ppm feed, and corresponding retentate and permeate.

Table 5. Filtration experiments using emulsions with different oil contents. The SDBS concentration was kept 1:10 surfactant to oil at pH 8. The flat-sheet membranes were prepared with 2 wt% cellulose solutions.

Oil concentration (ppm)				Permeate Turbidity (NTU)
Feed (nominal)	Feed	Retentate	Permeate	
200	204 ± 6	150 ± 5	non-detectable	0.3 ± 0.1
500	412 ± 104	397 ± 12	non-detectable	0.1 ± 0.0
1000	953 ±113	917 ± 97	non-detectable	0.1 ± 0.0

Figure 3. Permeance through membranes prepared with 5 wt% cellulose solution, as a function of time, using as feed oil-in-water emulsions with 200, 500 and 1000 ppm oil and 20 to 100 ppm (1:10 surfactant to oil) of different surfactants: (a) SDBS, (b) CTAB and (c) Tween[®] at pH 4.

Fouling. The flux decline observed in Figure 3 can be caused by fouling, concentration polarization, and by a membrane mechanical compaction under pressure in the dead-end cell. A complete flux recovery would be only possible without any contribution of a mechanical compaction. Figure 4 compares experiments performed with an uncoated

porous PSU membrane and those with a cellulose layer (0.4 μm thickness for 2 wt% and 0.9 μm for 5 wt% cellulose), regarding fouling and recovery of water permeance, after washing the membrane with pure water. Although PSU had higher initial water permeance, after filtering the oil-in-water emulsion, the water permeance recovery was almost zero. This leads to the conclusion that the PSU surface was irreversibly fouled by the oil droplets. The membrane with the thinnest cellulose coating (0.4 μm), obtained with 2 wt% cellulose solution, had a pure water permeance of $150 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$, which is about 60% of the value for the uncoated PSU membrane. When the oil-in-water emulsion was the feed, the permeance of the cellulose-coated membrane was much higher than for the uncoated PSU and the recovered water flux was around $90 \text{ Lm}^{-2}\text{h}^{-1}\text{bar}^{-1}$. The membrane coated with 5 wt% cellulose (larger thickness, around 0.9 μm) had a lower initial water permeance, when compared to PSU and the membrane coated with 2 wt% cellulose solution, but its permeance using the emulsion as feed was similar to that for the uncoated PSU membrane and the water flux recovery was more than 90 %. The filtration of emulsions containing CTAB and Tween[®] showed similar behavior.

Figure 4. Pure water permeance, permeance using the oil-in-water emulsion (200 ppm oil and 20 ppm SDBS) as simulated produced water and recovered water permeance, after cleaning the membrane only by washing with water, for flat-sheet (a) PSU and membranes prepared from (b) 5 wt% and (c) 2 wt% cellulose solutions, and for (d) the hollow fiber membrane. Experiments performed at pH 8.

Cellulose hollow fiber membranes. Cellulose hollow fibers were successfully prepared using a 12 wt% dope solution in [EMIM]OAc. The microscopic images in Figure 5 show the membrane morphology. Well-formed hollow fibers were obtained. As for the flat-sheet

cellulose layers, pores could not be detected by SEM microscopy, indicating that the hollow fiber membrane is relatively dense and the transport mechanism could be, at least in part, based on solution-diffusion. Only some structuration was observed in the cross-section of the membrane. Cellulose is highly hydrophilic. As in the case of flat-sheet membranes the transport of water is highly promoted. A pure water permeance of $50 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ was measured in a cross-flow set-up, operating with a transmembrane pressure of 0.2 bar with the feed flowing in the lumen of the fiber. This is a high permeation value, if we take into consideration that the membrane is non-porous and has a thickness larger than $100 \text{ }\mu\text{m}$, and therefore much larger than that of the selective cellulose layers of the flat-sheet membranes tested here. Experiments were performed with the cellulose hollow fiber membranes for the filtration of oil-in-water emulsions containing 200 ppm of crude oil and 20 ppm of SDBS in a cross-flow set-up (Figure 4d). The oil rejection was higher than 95%. The measured permeance was $25 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, confirming the excellent performance recorded for the flat-sheet membranes. The high oil rejection is mainly due to the preferential transport of water due to its affinity to the hydrophilic cellulose. Charge repulsion can play an additional role, as discussed for the flat-sheet membranes. Besides water and oil-in-water emulsion, the hollow fiber membranes were tested with aqueous solutions of a series of hydrophilic solutes, poly(ethylene glycol) (PEG) and proteins, to have a more comprehensive characterization and estimation of the membrane selectivity. The rejections of neutral but highly hydrophilic molecules, such as PEG with different molecular weights were 4 % of PEG 400 g/mol; 14 % of PEG 3 kg/mol; 63 % of PEG 10 kg/mol and 99 % of PEG 35 kg/mol. The larger PEG molecules have a more restricted diffusion through the membrane, even though their affinity to cellulose is still high. The

membrane rejected 20 % of cytochrome C (molecular weight 12 kg/mol, isoelectric point 9.6), 66 % of BSA (molecular weight 66 kg/mol, isoelectric point 5.4) and 91 % of bovine IgG (molecular weight 150 kg/mol, isoelectric point 7.2) at neutral pH. The zeta potential of cellulose above pH 4.2 is negative. Charge is probably not the main factor controlling the rejection of the proteins by the cellulose membrane. The high IgG rejection is governed by size. The relatively low rejection of BSA, compared with PEG 35 kg/mol, is probably due to a higher affinity to the cellulose.

Figure 5. (a) Scheme of a hollow fiber lab-scale spinning system and (b) scanning electron microscopy image of the fiber cross-section with different magnifications, as well as of the inner and outer surfaces.

CONCLUSION

Hydrophilic ionic liquids have been successfully used as greener solvents comparing to aprotic solvents such as DMF, DMAc, and NMP. Here we demonstrate the performance of cellulose membranes prepared from solutions in ionic liquid for oil-water separation under different conditions. The membranes are highly selective, allowing practically the complete removal of crude oil from oil-in-water emulsions. The membranes were subjected to several filtration tests, investigating the influences of the oil concentration, pH range and the addition of surfactants. By varying pH of the solution and charge of the emulsion droplets and the membrane charge and the fouling is affected. Emulsions with the negatively charged SDBS had the least flux decline and the highest permeance. The thinnest cellulose coating (2 wt% cellulose) provided high permeance, and high flux recovery, compared to the control polysulfone membrane. Finally, the preparation of cellulose hollow fibers has been demonstrated for the first time using dope solutions in [EMIM]OAc.

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Notes

The authors declare no competing financial interest.

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SUPPORTING INFORMATION

Table S1. Acute toxicity of common organic solvents.

Table S2. Advantages and disadvantages of alternative solvents

Table S3. Physical properties of selected ionic liquids

Table S4. Summary of methods used for recovery and recycling of ionic liquids

Figure S1. Most commonly used combinations of cations and anions in ionic liquids

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FOR TABLE OF CONTENTS USE ONLY

Cellulose membranes prepared by solution casting in ionic liquid with high water permeation and oil rejection.

Cellulose membrane with negative zeta potential

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