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Permeability of dilute ionic liquid solutions through a nanofiltration membrane – Effect of ionic liquid concentration, filtration pressure and temperature

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ABSTRACT

Nanofiltration is studied to separate glucose from dilute ionic liquid [emim][OAc]–water solutions. The aim of the research is to evaluate the effect of filtration pressure, temperature and ionic liquid (IL) concentration on the separation of ionic liquid and glucose. This kind of separation challenge can be formed in the regeneration of cellulose fibres in a wet spinning bath. The separation tests are done with an NF270 nanofiltration membrane. The tolerance of the NF membrane in ionic liquid is also estimated.

Effective osmotic pressures and viscosity were found to have a major role in the permeability of the membrane when filtration was done at dilute IL solutions. Temperature was found to have a significant effect on the flux due to reduced viscosity at higher temperatures. The flux was increased by about 50% when the temperature increased from 20 °C to 40 °C. The best possible separation factor values were achieved when the feed solution contained 1 wt% [emim][OAc] at 20 °C temperature and the filtration pressure was 6 bars. On the basis of the IL concentration and temperature test series, a good separation window for this kind of solution would be at permeate flux values from 50 L m^{-2} h^{-1} to 100 L m^{-2} h^{-1}. After a test series in concentrations of IL from 0.5 wt% to 10 wt%, the pure water permeability (PWP) was reduced by 23% from the original. The decline of PWP during the temperature tests series was 33%.
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1. Introduction

Since the beginning of this century, ionic liquids (ILs) have been studied intensively as dissolving agents for wood or cellulose. The research has focused lately especially on room temperature ionic liquids (RTILs), which are composed entirely of ions and are fluids below 100 °C. RTILs have advantageous properties, such as a low vapour pressure and low melting point. They are non-flammable and have high thermal stability as well as high ionic conductivity. Modern ILs contain an organic cation, which are often quarternised aromatic or aliphatic ammonium ions. Anions are organic or inorganic. Typical anions in ILs are hexafluorophosphate $[PF_6]^-$, tetrafluoroborate $[BF_4]^-$, alkyl sulphates $[RSO_4]^-$, alkyl sulfonates $[RSO_3]^-$, halides as chloride Cl^-, bromide Br^-, iodide I^- or nitrate $[NO_3]^-$ [1–4].

Chemical treatment of wood has been traditionally done by pulping processes in a large scale. Due to the well-known pulping processes and ready infrastructures, a new economically valuable process concept has to introduce some special properties [5]. Tailor-made ILs need to have some advantages in processing wood in a new way. Some of these benefits could be a high dissolution capacity for cellulose, specific dissolution (i.e. dissolves only one component of the whole wood), low melting point, good thermal stability, non-volatility, non-toxicity, chemical stability, or no cellulose structure degradation during processing, and easy cellulose regeneration from IL-solutions [6].

The recycling of ILs from process solutions is one of the key issues for the development of an economical process, because IL is usually the most expensive chemical in process solutions. When wood is dissolved in IL, cellulose can be recovered by precipitating it with the addition of an anti-solvent and then filtering it out from the solution [2]. After the separation of cellulose for value added products, the ILs need to be extracted, purified and recycled back to dissolve cellulose again in order to maintain an economical and sustainable process.

Although recent academic focus in this field has been on the dissolution of wood or cellulose in ILs, some studies have aimed at the purification of ILs and separation of the dissolved compounds from IL–water solutions. The recovery and purification of different ILs have been done at least by membrane filtrations

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[7–12], by adsorption on zeolites [13,14], by electrodialysis [15,16], and by ion exchange [17–19]. However, one conclusive and economic solution for recycling of ILs has not been presented in the literature.

Klein-Marcuschamer et al. [20] have done economic evaluation of IL usage as a pre-treatment chemical for biomass dissolution (biorefinery concept). They have made a list of barriers to overcome for it to be a profitable process. One of the most important factors is increasing the recycling rate of IL. Other two factors are reducing the IL cost and the IL load in the process. Nanofiltration (NF) could be one potential process or one part of a larger system for the purification of IL solutions. The recycling of ILs by NF has received rather little attention among researchers in the field, but a few studies have been published.

Abels et al. [7] studied the purification of 1,3-dimethylimidazolium dimethyl phosphate [mmim][DMP] from synthetic solutions containing saccharides. The model solution contained glucose (monosaccharide), cellobiose (disaccharide) and raffinose (trisaccharide) in an aqueous solution with the IL. They used both hydrophilic and hydrophobic NF membranes, and found that at high concentrations of IL, the permeate flux decreased for all the tested membranes due to the low permeability of the IL and therefore generated high effective osmotic pressure. Temperature changes seemed to have little effect on permeability, and even though they reduced solution viscosity, osmotic pressures still prohibited a higher permeation rate.

Abels et al. [7] also noticed that the rejection of saccharides decreased with a hydrophilic NF membrane when the concentration of IL increased in the feed solution. However, the rejection of saccharides was found to increase with a hydrophobic NF membrane when the concentration of IL increased in the solution. All the tested membranes showed some selectivity towards IL at low concentrations from 0 wt% to 40 wt%, but no selectivity from 40 wt% to 80 wt%, when the feed solution was a pure IL–water mixture. Finally, it was possible to purify the IL up to a purity of 80% in the tested conditions by using all three membranes.

The recovery of 1-n-butyl-3-methylpyridinium tetra fluoroborate from a lignocellulosic solution (coir fibre) was studied by Hazarika et al. [8] by using a self-made beta-cyclodextrin NF membrane and by using a commercial NF270 NF membrane [9]. After the dissolution of the coir fibre in IL, the cellulose was precipitated by adding water into the solution. After the separation of the cellulose, the supernatant was then filtered by both NF membranes. The rejection of the fraction was found to depend strongly on the pressure and concentration of the feed solution. It was possible to remove lignocellulose at rejection rates from 60% to 85%, depending on the concentration of the solution and the operating pressure. These studies showed that ILs could be retained by the membranes at more than 50%.

One possible application for NF is recycling and purification of fibre spinning bath wastewater containing ILs. Liu and Wang [10] studied the separation of 1-Allyl-3-methylimidazolium chloride [amim]Cl with a self-made hollow fibre composite NF membrane. The [amim]Cl-containing spinning bath wastewater was produced by an actual spinning mill. The tests showed that when the temperature increased, the viscosity of the solution decreased, the permeate flux increased, and the retention of [amim]Cl decreased. The spinning bath water was concentrated from $5.9\ g\ L^{-1}$ of IL to $28.1\ g\ L^{-1}$ (VRF was 33.3), and the recovery rate of IL was calculated to be 95.3%.

Fernándes et al. [11] have also studied the purification of spinning bath wastewater. They used both authentic and synthetic spinning bath waters. In addition, hydrophilic and hydrophobic ILs were studied. In the case of hydrophilic ILs, the authors recommend two-stage process; first the membrane retains most of the degradation by-products of cellulose, but not the IL. The second membrane must retain most of the IL in order to concentrate it before the next process step, such as evaporation. The evaporation process is needed due to the developing osmotic pressure difference that resists the concentrating of IL by more than approximately 20–25 vol% [7,12].

Wu et al. [21] have studied IL transport properties in the NF of IL–water solutions. In their study, a TFC® 3838 SR®3 membrane module was used in filtrations of 1-butyl-3-methylimidazolium tetra fluoroborate [bmim][BF_4] and 1-butyl-3-methylimidazolium bromide [bmim]Br ILs to evaluate the permeabilities of these ILs. Hydrodynamic permeability, rejection and solute permeability were determined on the basis of the measurement data. It was noticed that the rejection and flux for both ILs increased when the feed pressure was increased. Decrease in rejection of IL and permeate flux was observed when concentration of the ILs was increased in the feed. The maximum retention of [bmim]Br was found to be 67% and 60% for [bmim][BF_4].

The aim of the present research was to use a model solution that could be formed from the wet spinning bath of IL–cellulose dope when cellulose is precipitated to fibres [22]. This kind of a dilute ionic liquid solution can be found also in different process steps, for example the washing waters of IL-based processes (biorefinery). In addition, the aim was to gain more detailed understanding of the separation between the dilute (0.5–10 wt%) [emim][OAc] and small cellulose degradation products, such as glucose molecules, by NF. [emim][OAc] was chosen for this research, because it is a common and commercially available IL. The ionic liquid is hydrophilic, has low viscosity at room temperature, is non-volatile, and has good cellulose-dissolving properties. Glucose was chosen to mimic as a small organic component to be separated by NF, because it is formed during the wet spinning process of cellulose. The effects of pressure, temperature and IL concentration were studied. Viscosities of feed solutions were measured and effective osmotic pressures calculated from the concentration results. An estimation of membrane tolerance towards IL filtration is also presented.

2. Materials and methods

2.1. Membrane and chemicals

A polymeric NF270 membrane (DOW Filmtec™, USA) was used in the study. The membrane is a polyamide thin-film composite. A spiral membrane element was opened up and the membrane was used as flat sheets. The NF270 membrane element has the maximum pressure for 41 bars, and the maximum operation temperature is 45 °C according to the manufacturer. The manufacturer also gives the membrane an MWCO value from 200 Da to 400 Da, but in some studies it has been determined to be 257 ± 15 Da or 330 Da, depending on the measurement method and conditions [23,24]. The active layer of the NF270 membrane is described to be poly (piperazine-amide) [25].

The IL [emim][OAc] was purchased from BASF (Basionics™ BC 01, [143314-17-4], assay > 98%). The glucose was obtained from Sigma–Aldrich Co. (D-(+)-Glucose [50-99-7], assay > 99.5%). All the feed solutions were prepared into purified water obtained from an ELGA Labwater Centra-R120 water purification unit equipped with a deionization cartridge (ρ > 15 MΩ cm).

2.2. Cross-flow filtration equipment

In the cross-flow filtration equipment, the flow and pressure are generated by a Hydra-Cell™ diaphragm pump (model number: MO3XASGHHECA). A frequency converter was used to control the pumping speed. The jacketed feed tank ($V \approx 2.5$ L) is

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