

Factors Affecting the Nonsolvent-Induced Phase Separation of Cellulose from Ionic Liquid-Based Solutions

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Cite This: *ACS Omega* 2020, 5, 27314–27322



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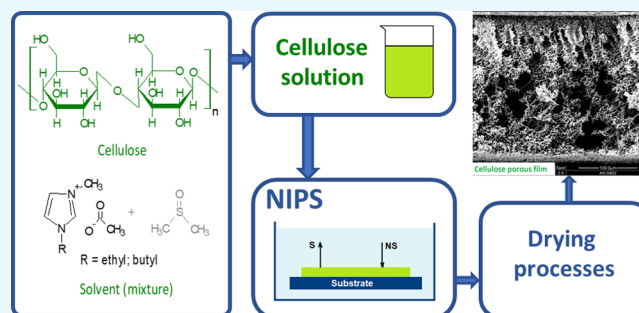


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ABSTRACT: In the present work, we report for the first time an in-depth study of the factors influencing porous cellulose film structure formation during the nonsolvent-induced phase separation (NIPS) process from biopolymer solutions in ionic liquid-based solvents. The length of the alkyl chain of the ionic liquid's cation, the solvent/co-solvent ratio, and the type of the cellulose precursor used were found to have great influence both on cellulose solution formation and properties and to the NIPS process with water acting as nonsolvent. In the undiluted form, both studied ionic liquids proved to dissolve almost equally well the cellulose; however, due to differences in viscosities of the formed biopolymer solutions and due to differences in miscibility with water of the two ionic liquids, the used ionic liquid had a strong influence on the film's porous structure formation. The use of increasing amounts of an aprotic co-solvent, here dimethylsulfoxide, improved biopolymer solubilization and also led to the formation of a more pronounced macroporous structure during the NIPS process. The cellulose type also affected the porous structure generation during the NIPS process: with the increase of the molecular weight of the precursor, the viscosity of the formed biopolymer solution increased and the tendency to generate macroporous structures decreased.



1. INTRODUCTION

Cellulose in a pure or functionalized form, or as a part of a composite, is one of the most important natural polymers due to good biocompatibility, biodegradability, and renewability. The classical use of cellulose as the main component of paper,¹ in separation membranes,^{2,3} in textiles,⁴ and in various artificial fibers has been more recently expanded to other applications like magneto-responsive composites,^{5,6} flame retardant materials,⁶ bio-imaging materials,⁷ and supported catalysts.^{6,8,9}

Normally, the processing of pure cellulose is relatively difficult due to the impossibility to melt it or to dissolve it into water or common organic solvents. This is the consequence of cellulose's closely packed, partially crystalline hierarchical structure, containing multiple inter- and intramolecular hydrogen bonds.¹⁰ The impossibility to solubilize cellulose in water and conventional other solvents due to its supra-molecular structure can be overcome by hydrogen bond-breaking activation steps and/or swelling. Therefore, cellulose has limited solubility in dimethylacetamide and *N*-methyl-2-pyrrolidone with the addition of lithium chloride. Lindman and collaborators on the other hand imply that cellulose is amphiphilic and that the hydrophobic interactions should be accounted for when trying to explain the solubility patterns of cellulose. They consider that the position of the polar and the less polar regions in cellulose strongly influence its solubility and that solubility would be facilitated in solvents that are also amphiphilic like *N*-methylmorpholine-*N*-oxide and ionic

liquids (IL).¹¹ The preparation of cellulose membranes is well established by three widespread methods, i.e., via the cellophane (xanthate), cuprophane, and cuenophane pathways; however, the carbon disulfide, copper sulphate, and cupric ethylene diamine used in these three methods are hazardous for human health.^{12,13} Lately, environmentally friendlier technologies based on the use of *N*-methylmorpholine-*N*-oxide have gained importance.¹⁴ Normally, during the cellulose "regeneration" process involving the dissolution and the re-precipitation, a change from the "cellulose I" to "cellulose II" crystalline structure takes place.¹⁵

In the last two decades, some specific room temperature ionic liquids (IL) started to gain importance as solvents for cellulose. Such alternative solvents are attractive due to their specific properties such as good chemical and thermal stability, low melting point when compared with other salts, low inflammability, and negligible vapor pressure. Their greatest advantage may be connected to the reduction or the lack of volatile compound emissions during their use.^{16–19} Some

Received: July 29, 2020

Accepted: September 24, 2020

Published: October 16, 2020



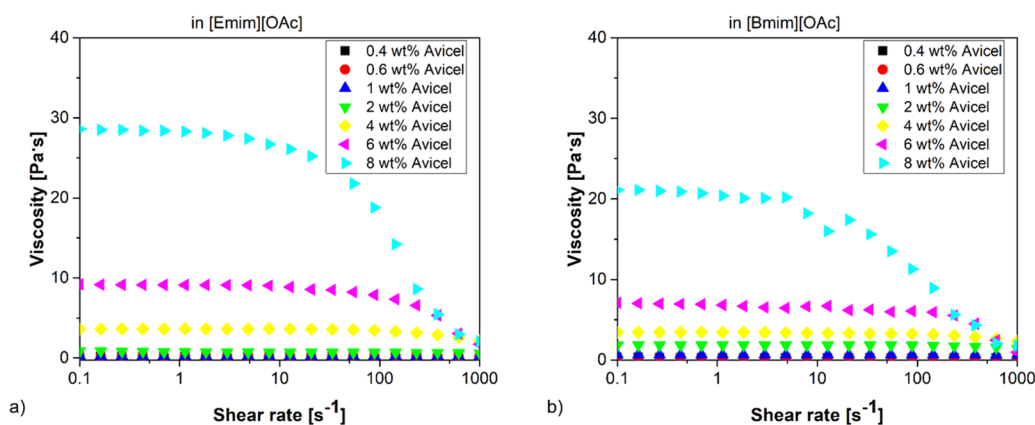


Figure 1. Viscosity versus shear rate for Avicel solutions in (a) [Emim][OAc] and (b) [Bmim][OAc].

factors influencing the cellulose regeneration from ionic liquids have been discussed recently by Da Silva and collaborators.²⁰ A summary of the ionic liquids, which are capable to dissolve cellulose, accompanied by the information about their maximal dissolving capacity and the optimal conditions at which the solutions were obtained was already published in 2009 by Pinkert and collaborators.²¹ Also, Abushammala and Mao reported recently a comprehensive outline of the most commonly used ionic liquids for dissolution of wood and cellulose accompanied by their physicochemical properties including their viscosity.²² Cellulose solutions in ionic liquids have also been used for membrane preparation, but these studies have not been dedicated to an in-depth investigation of all the factors influencing the membrane structure formation.^{23,24}

The most widespread methods for preparation of porous polymeric films and membranes are based on phase separation of polymers from their solutions. The phase separation may be induced thermally, by evaporation of a selective solvent, by uptake of nonsolvent vapor, or by immersion precipitation in a liquid nonsolvent.²⁵ In the last case, the liquid nonsolvent-induced phase separation (NIPS) process, the final pore morphology of the formed porous film/membrane strongly depends on the thermodynamic interactions between the involved components, the exchange rate between solvent and nonsolvent (modulated by the compositions of the polymer solution and of the coagulation bath), the solvent volatility, and the temperature.²⁶ From the kinetic point of view, the viscosity of the casting polymer solution has a very strong influence on the membrane formation process: the higher the viscosity of the polymer solution, the more delayed will be the exchange between solvent and nonsolvent during the process.²⁶

One of the most important problems in cellulose processing with ionic liquids, which is also very relevant during the membrane preparation by the NIPS process, is the high viscosity of the cellulose/ionic liquid solutions.²⁷ Therefore, the use of ionic liquid/co-solvent mixtures may in many cases be the optimal choice. The most appropriate co-solvents are polar aprotic organic solvents like dimethylsulfoxide (DMSO), *N,N*-dimethylacetamide (DMAc) and dimethylformamide,^{27–30} which are able to dissociate the anion and cation of the ionic liquid, improving the anion interaction with cellulose and facilitating its dissolution.²⁸ For a series of methylimidazolium acetate ionic liquids in the presence of DMSO as co-solvent, increasing the alkyl chain length in the

imidazolium cation from 1-ethyl to 1-butyl leads to the improvement of cellulose solubility. A further increase of the length of the alkyl chain to 1-hexyl or 1-octyl methylimidazolium acetate results in a decrease in cellulose solubility.³¹ For a series of ionic liquids composed of imidazolium cations and phosphate anions, in the presence of DMSO or DMF as co-solvents, with the increase in length of the alkyl chain, the viscosity of the ionic liquids increases and their ability to dissolve cellulose decreases.³² Cellulose-based solutions in ionic liquids have been successfully used for the preparation of membranes, thin flat sheet membranes supported on porous polysulfone, or as self-supported hollow fibers, and their performance was evaluated for the separation of oil from water in the presence of different surfactants.³³ Cellulose membranes were fabricated by the NIPS process from solutions in an ionic liquid solvent, with or without acetone as co-solvent.³⁴ Some of the membranes were obtained after a pre-evaporation step; others were obtained directly. Acetone was chosen as co-solvent due to its high volatility. Such membranes were tested for the separation of dyes of different charge.³⁴ Cellulose and cellulose acetate membranes prepared by NIPS from solutions in 1-ethyl-3-methylimidazolium acetate, in the presence and the absence of DMSO as co-solvent, were evaluated for the separation of dyes from water.³⁵

In the present work, we performed for the first time an in-depth study of the factors influencing the porous cellulose film structure formation during the NIPS process from biopolymer solutions in ionic liquid-based solvents. The main factors influencing the process analyzed here were the length of alkyl chain in the cation of the ionic liquid used (ethyl vs butyl), the ratio of an aprotic co-solvent used (in this case DMSO), and the type of cellulose used. We consider that knowing the complex influences of the abovementioned factors may allow the prediction and/or the design of a certain cellulose film structure and can help adjust the NIPS process according to the intended scope.

2. RESULTS AND DISCUSSION

2.1. Influence of the Ionic Liquid. For the preparation of solvent mixtures, two commercially available ionic liquids have been used: 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]) with the viscosity $\eta_{RT} = 298.3$ cP and the refractive index $n = 1.495$ and 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) with $\eta_{RT} = 130.3$ cP, $n = 1.501$. The water content of the ionic liquids, as determined by Karl Fischer titration, was $\sim 0.6\%$ for [Emim][OAc] and $\sim 1.1\%$ for

[Bmim][OAc]. As co-solvent, DMSO with $\eta_{20^\circ\text{C}} = 1.996$ cP and $n = 1.479$ was used due to its lower toxicity in comparison with other similar polar aprotic solvents. In the Supporting Information, Table S1, some of the properties of the used solvent mixtures are summarized. For a better understanding of differences in the viscosities of the different solutions, the mole ratios of water to hydroxyl groups on cellulose in the solutions are summarized in the Supporting Information, Table S2. One may observe that there is no excess of water in any solution but an excess of OH groups. The excess of OH groups is higher in the [Bmim][OAc]-based solutions. Even though some chloride-based methylimidazolium ionic liquids are known as good solvents for cellulose,³⁶ those were not selected for this study due to their high viscosity, which would make the film casting step extremely difficult.

Cellulose swells in both solvents before the complete dissolution leading to high viscosity biopolymer solutions. Figure 1 presents the viscosity dependence on the shear rate for the Avicel solutions with different concentrations in [Emim][OAc] (Figure 1a) and in [Bmim][OAc] (Figure 1b).

In both solvents, the complex viscosity of the biopolymer solutions increased with the increase of the biopolymer concentration. However, in the case of [Emim][OAc], this increase was more pronounced, suggesting a stronger entanglement of the cellulose chains in this solvent. The stronger entanglement of the cellulose chains in concentrated solutions in [Emim][OAc] was also confirmed by a higher value of the K parameter of the power law model, suggesting that [Bmim][OAc] is a slightly better solvent for Avicel cellulose than [Emim][OAc]. The cellulose solutions used for film preparations (8 wt %) showed in both solvents deviations from the Newtonian character as confirmed by the values of the n parameter of the power law model, which was below 1 (see Table 1).

Table 1. Power Law Equations for 8 wt % Avicel Solutions in [Emim][OAc] and [Bmim][OAc]

solvent [wt %]	K [Pas ⁿ]	n	power law equation
[Emim][OAc]	38.9	0.79	$\mu = 38.9 \cdot \gamma^{-0.21}$
[Bmim][OAc]	25.8	0.78	$\mu = 25.8 \cdot \gamma^{-0.22}$

Cloud point experiments were performed with dilute cellulose solutions in ionic liquids and ionic liquid/co-solvent mixtures. These experiments could not be performed at higher cellulose concentrations due to the high viscosity of the solutions. Figure 2 shows the influence of the length of the cation alkyl chain on the polymer solution stability against precipitation by water addition.

One may observe that for both ionic liquids, with the increase of the polymer concentration, the water content at the cloud point decreases. Apparently, the cellulose solutions in both pure ionic liquids have comparable stabilities against precipitation with water even though [Emim][OAc] has higher surface tension and higher density and is more hydrophilic than [Bmim][OAc].^{37,38} In reality, we must also take into consideration that the water content in the pure [Bmim][OAc] is about two times higher than the water content in the pure [Emim][OAc] (1.1% compared to 0.6%; see above).

Two main factors influence the solvent/nonsolvent exchange during the phase separation process with water: the miscibility of the ionic liquids with water and the viscosities of the biopolymer solutions. Both ionic liquids, [Emim][OAc] and

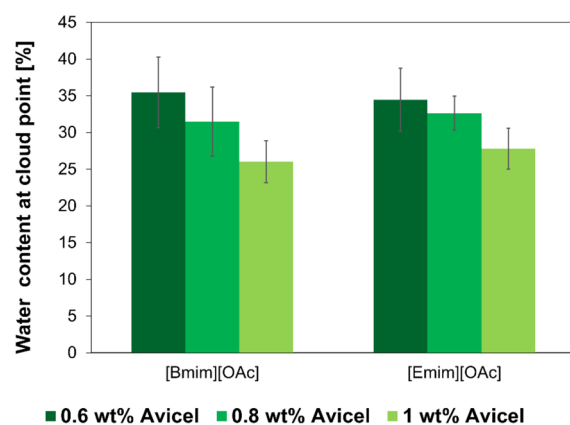


Figure 2. Dependence of the cloud point on the type of ionic liquid and cellulose concentration @ 25 °C.

[Bmim][OAc], are miscible with water, the miscibility of [Emim][OAc] being slightly better due to a smaller alkyl chain in the cation.³⁸ However, the viscosity of the Avicel solution in [Emim][OAc] is considerably higher than the viscosity of the corresponding solution in [Bmim][OAc] and therefore the transfer of water into the film and of the ionic liquid out of the film is much slower. This fact is consistent with the formation of a more compact film morphology when [Emim][OAc] was used as solvent (Figure 3).²⁶ The faster demixing in the case of

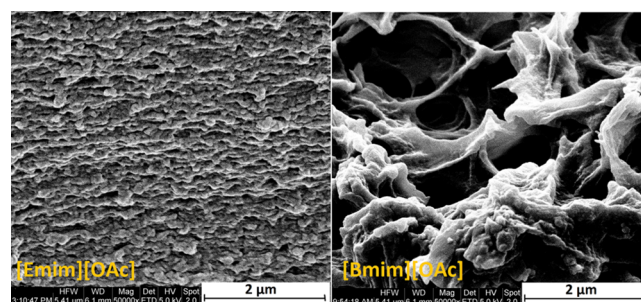


Figure 3. Influence of the ionic liquid on the porous film structure (cross section of 8 wt % Avicel-based films).

the [Bmim][OAc]-based biopolymer solution may also be connected with the higher water amount in the commercial [Bmim][OAc] ionic liquid (see above).³⁹

2.2. Influence of the Co-Solvent Ratio. The addition of a certain amount of an aprotic co-solvent (in this case DMSO) reduces the time necessary to dissolve the biopolymer⁴⁰ by breaking the ionic association between the anion and the cation in the ionic liquid and by improving the transport of the solvent between the polymer chains.²⁸ The DMSO fraction was varied between 0 and ~40 wt %. The higher the cellulose concentration in solution, the more entangled are the polymer chains, and therefore the more viscous is the polymer solution. Based on the entanglement degree of the macromolecular chains in solution, one can distinguish three cellulose concentration domains: 0–2 wt % as dilute solutions; 2–8 wt % as semi-dilute solutions, and >8 wt % as concentrated solutions. Accordingly, the specific viscosity of the polymer solutions increased with a different slope for each concentration domain (see also the Supporting Information, Figure S1). The presence of the three domains at the same cellulose concentration intervals regardless of the DMSO presence

suggests that the macro-conformation of the cellulose molecules is similar in the pure IL and in the IL:DMSO mixtures.

Figure 4 shows the viscosity versus shear rate dependence at 25 °C for 8 wt % cellulose solutions in [Bmim][OAc] with

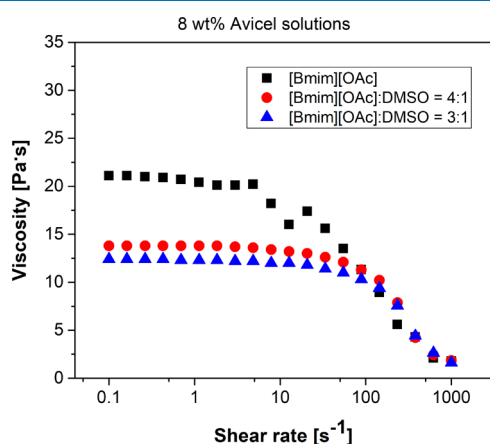


Figure 4. Viscosity versus shear rate for Avicel in [Bmim][OAc]-based solutions (8 wt % biopolymer, different co-solvent ratios).

different DMSO contents. All cellulose solutions present a shear thinning effect at high shear rates, suggesting an entanglement of the polymer chains in solution. The onset of shear thinning shifts to a higher shear rate with increasing DMSO fraction, in parallel with decreasing viscosity at low shear rate. By fitting of the experimental data with the power law model and by calculation of the model's parameters (Table 2), it could be observed that consistency coefficient K is

Table 2. Power Law Equations for Avicel in [Bmim][OAc]-Based Solutions (8 wt % Biopolymer, Different Co-Solvent Ratios)

solvent	K [Pa·s ^{n}]	n	power law equation
[Bmim][OAc]	25.8	0.78	$\mu = 25.8 \cdot \gamma^{-0.22}$
[Bmim][OAc]:DMSO = 4:1	15.6	0.87	$\mu = 15.6 \cdot \gamma^{-0.13}$
[Bmim][OAc]:DMSO = 3:1	13.7	0.88	$\mu = 13.7 \cdot \gamma^{-0.12}$

decreasing with the increase of the co-solvent ratio in the system, suggesting a lower entanglement of the biopolymer chains in solution in the presence of DMSO and by this, a better dissolution in this case. Also, the deviation from the Newtonian character of the concentrated cellulose solutions was considerably lower in the presence of DMSO as shown by the higher values of the liquidity index n .

Figure 5 presents the dependence of the cloud-point on the cellulose concentration and on the co-solvent ratio for Avicel solutions in [Bmim][OAc]-based solvents. Previous studies have shown that IL-aprotic co-solvent mixtures at ratios up to 1:1 enhance cellulose dissolution by 20–60% compared with pure ionic liquid.⁴¹ The stabilities against precipitation with water of the cellulose solutions are decreasing with the cellulose concentration in solution and also slightly decreasing with the increase of the co-solvent amount in solution (Figure 5).

The addition of DMSO as co-solvent on the one hand reduces the viscosity of the casting solution and due to the better transport, a faster exchange solvent/nonsolvent may be expected. On the other hand, as reflected in Figure 5, the

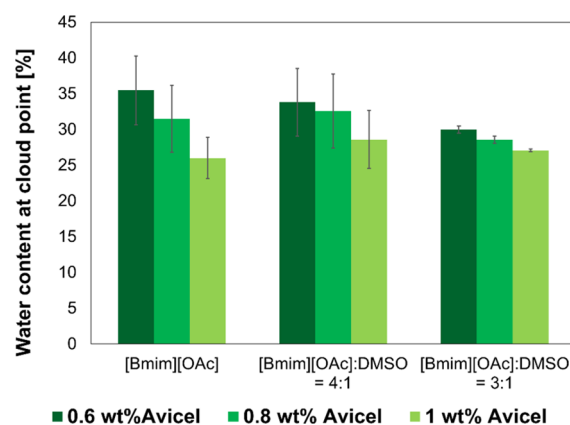


Figure 5. Dependence of the cloud point on the co-solvent fraction @ 25 °C.

stability against precipitation with water of the cellulose solutions is slightly diminished in the presence of a co-solvent. For Avicel cellulose, these two aspects are reflected in the formation of more porous films in the presence of the DMSO (Figure 6). This phenomenon is more pronounced when a cellulose precursor with a higher molecular weight like α -cellulose is used (see also the Supporting Information, Figure S2).

However, in all cases, the major gain in terms of casting solution processability indicates that the addition of DMSO fractions up to ~40% is largely beneficial to the whole porous film preparation process.

2.3. Influence of the Type of Cellulose. As expected, the higher the degree of polymerization, the more viscous were the formed polymer solutions for a given concentration; this can be clearly observed for the three types of cellulose evaluated in this study (Figure 7).

By fitting of the experimental data for the 8 wt % cellulose solutions in [Bmim][OAc]:DMSO = 3:1 with the power law model and by calculation of the respective parameters, it can be observed that the consistency coefficients for the MC and Avicel solutions are two orders of magnitude lower than the consistency coefficient of the α -cellulose solution (Table 3). A direct connection between the consistency coefficients and the molecular weight of the used precursor can be observed. The entanglement of the cellulose chains in solution is much more pronounced when a polymer with a very high polymerization degree (α -cellulose) is used.

The cellulose solutions obtained from all types of precursors are non-Newtonian fluids as their liquidity coefficients n are below 1, but the non-Newtonian character is much more pronounced for the α -cellulose containing solution (Table 3).

Figure 8 shows the influence of the cellulose type on the cellulose solution stability. One may observe that MC and Avicel cellulose, having the lower polymerization degree, yield slightly more stable polymer solutions. α -Cellulose with a higher polymerization degree yielded, as expected, less stable solutions for which slightly lower water fractions are required for precipitation.

The formation of the porous structure is strongly influenced by the polymerization degree of the polymer. One may clearly see that when cellulose with a high polymerization degree (in this case α -cellulose) is used under otherwise identical NIPS conditions, more compact films are formed (Figure 9). The main reason for this difference in the porous structure

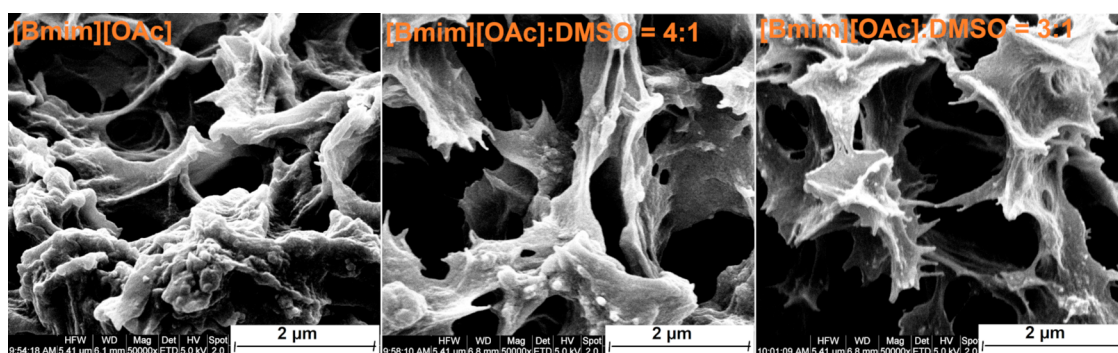


Figure 6. Influence of the co-solvent ratio on the porous film structure (cross section of 8 wt % Avicel-based films).

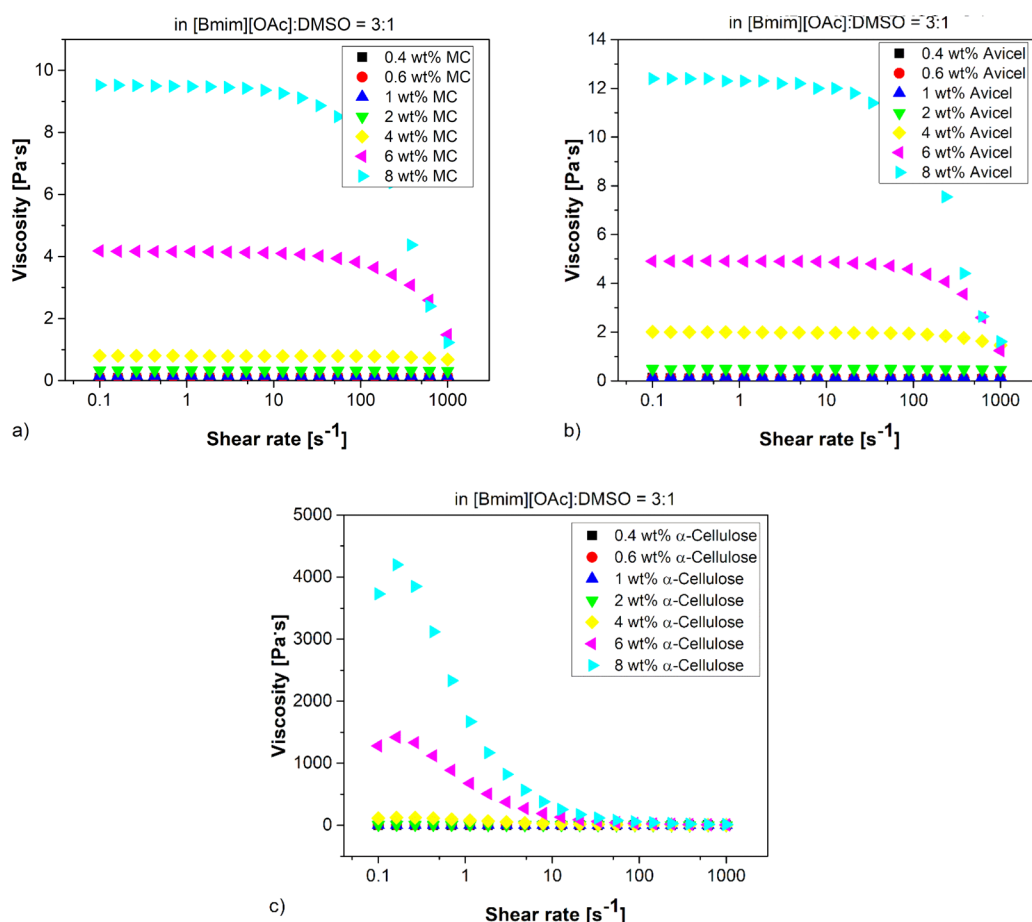


Figure 7. Viscosity versus shear rate for solutions in [Bmim][OAc]:DMSO = 3:1 of (a) MC, (b) Avicel, and (c) α -cellulose.

Table 3. Power Law Equations for Different Celluloses for 8 wt% Biopolymer Solutions in [Bmim][OAc]:DMSO = 3:1

cellulose type	K [Pa·s ^{n}]	n	power law equation
MC	10.2	0.9	$\mu = 10.2 \cdot \dot{\gamma}^{-0.1}$
Avicel	13.7	0.88	$\mu = 13.7 \cdot \dot{\gamma}^{-0.12}$
α -cellulose	1894.8	0.22	$\mu = 1894.8 \cdot \dot{\gamma}^{-0.78}$

formation is the much higher viscosity of the α -cellulose solution, which prevents a fast exchange between the solvent and nonsolvent.

One may consider that due to lower viscosity and, hence, better flow properties, the cellulose solutions prepared from polymers with lower degree of polymerization are more

adequate for processing as cast porous films or spun porous fibers.

The crystallinity of the three cellulose precursors as well as the one of the corresponding porous cellulose membranes was studied with help of XRD analyses (see also the Supporting Information Figure S3). All three commercial cellulose precursor powders (Avicel, MC, and α -cellulose) are consisting from nanocrystalline phases with crystallite sizes of approximately 4–5 nm. In the case of Avicel and MC celluloses, the types cellulose I & cellulose II, with a cellulose I:II ratio of \sim 80:20, have been detected (Figure 10a). The α -cellulose sample was constituted of pure cellulose I (Figure 10b). For both cellulose types, I and II, a crystallographic density of 1.8 g/cm³ was determined.⁴² One may expect that during the dissolution, the arrangement of the cellulose chains is

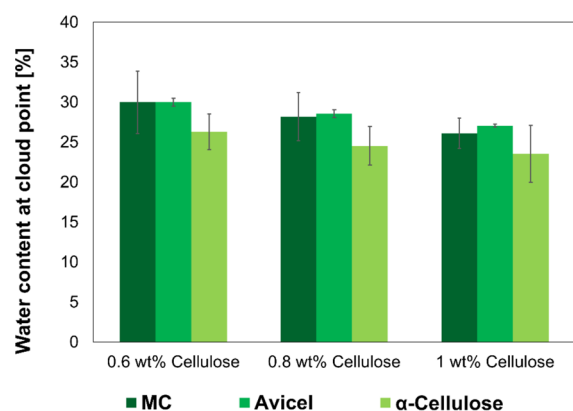


Figure 8. Dependence of the cloud point on the cellulose type @ 25 °C in [Bmim][OAc]:DMSO = 3:1

disrupted and by re-precipitation it is rearranged. Indeed, after the regeneration, only cellulose II phases with crystallite sizes of about 2 nm could be detected in all three porous films, suggesting that the regenerated materials were significantly more amorphous than their precursors. This can be related to the relatively fast phase separation process induced by immersion of the cellulose solution films in the aqueous coagulation bath. Details of all these analyses can be found in the Supporting Information (Figures S4–S6).

3. CONCLUSIONS

The obtained results suggest that, even though being very good solvents for cellulose solubilization, room temperature ionic liquids cannot directly be used as platform for the preparation of porous films and membranes by a film casting and phase separation process with water as nonsolvent. The high viscosities of the cellulose solutions obtained in pure ionic liquids would require the use of high temperatures during film casting and would lead to the formation of denser films when the phase separation process is performed at room temperature. The addition of a moderate fraction of a polar aprotic organic co-solvent, like DMSO, tremendously improved the cellulose solution processability and allowed the formation of porous films without having any negative impact to the casting solution preparation and the actual casting steps. The co-solvent addition in small amounts to the ionic liquids led to drastically reduced polymer solution viscosity without diminishing the overall solvent quality. In undiluted form, both studied ionic liquids proved to dissolve almost equally well the cellulose, a lower entanglement of the cellulose chains was observed when [Bmim][OAc] was used. However, due to differences in viscosities of the formed biopolymer solutions and due to differences in miscibility with water, the used ionic

liquid had a strong influence on the film's porous structure formation. As expected, using cellulose with a higher polymerization degree led to more viscous polymer solutions, which can be casted as films only at high temperature. Their high viscosity was also connected with a slower phase separation, which led to formation of compact films with low porosity. Knowing the complex influences of the above discussed factors, which affect both the cellulose solution formation and the nonsolvent-induced phase separation with water, allows the prediction and/or the design of cellulose films with pre-defined porous structure.

4. MATERIALS AND METHODS

4.1. Materials. For the preparation of cellulose solutions, three types of commercially available materials have been used: microcrystalline cellulose (MC) from Merck Millipore with a degree of polymerization (DP) \approx 210–230 (according to supplier specification); Avicel PH 101 (Avicel) from Sigma-Aldrich with DP \approx 180⁴³ and α -Cellulose from Sigma-Aldrich with DP \approx 780.⁴⁴ The room temperature ionic liquids 1-ethyl-3-methylimidazolium acetate ([Emim][OAc]) and 1-butyl-3-methylimidazolium acetate ([Bmim][OAc]), both in BASF quality (\geq 95%), have been purchased from Sigma-Aldrich. The ionic liquids and the cellulose materials are both hygroscopic. [Emim][OAc] and [Bmim][OAc] water content was \leq 1.1% according to supplier specification. Because in our previous works we had demonstrated that traces of water do not hinder cellulose solubilization and do not have a negative impact to the phase separation process,⁴⁵ all materials were used as received. Further on, we considered that this may also facilitate the up-scaling if desired. Dimethylsulfoxide (DMSO; analytical reagent, assay \geq 99.5%) from VWR International was used as co-solvent for cellulose dissolution. The precipitation of the porous films was performed in water purified with a Merck–Millipore purification system and having a resistivity of \sim 18.2 M Ω ·cm and a TOC value below 5 ppm.

4.2. Preparation of the Polymer Solutions. Cellulose solutions with different polymer concentrations (0.2, 0.4, 0.6, 0.8, 1, 2, 4, 6, 8, and 10 wt %) in solvent mixtures (pure ionic liquid or IL + DMSO) have been prepared as follows: the cellulose powder and the solvent mixture were inserted in a mortar and grinded together for several minutes until the cellulose was homogeneously dispersed in the solvent. The homogenous lump free paste was transferred to a snap-cap vial and heated for 5 h @ 70 °C until the dissolution of cellulose and a partial degassing of the formed solution were achieved. No further degassing under vacuum was performed in order to avoid the removal of the co-solvent.

4.3. Film Casting and Phase Separation Process. The polymer films were cast on glass substrates with the help of a motorized film applicator (model AB3400 from TQC), using a

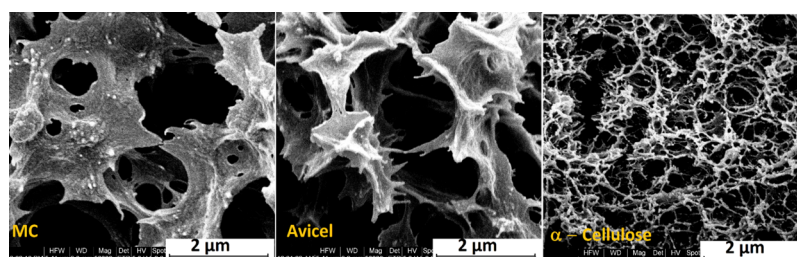


Figure 9. Influence of the cellulose type on the porous film structure (cross section of 8 wt % cellulose-based films).

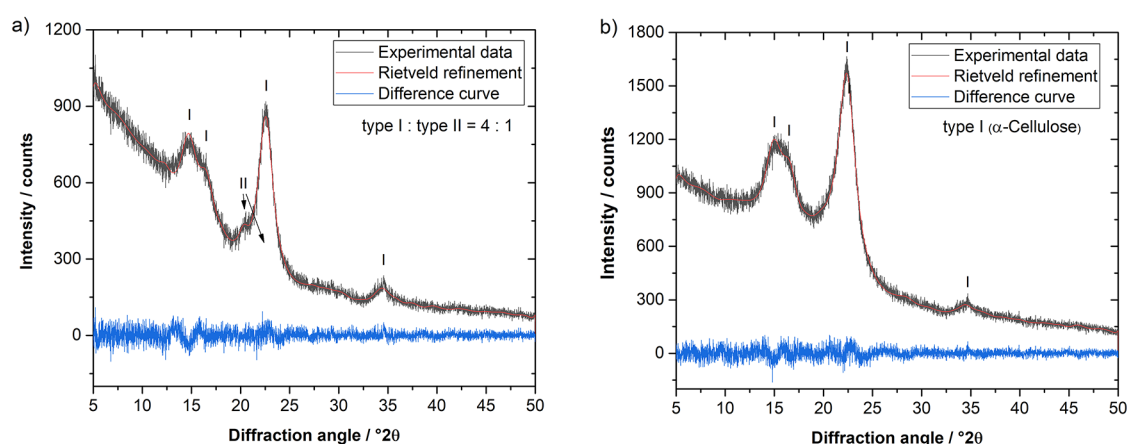


Figure 10. X-ray diffractograms with a representative Rietveld refinement of (a) Avicel with indicated both types I and II and (b) α -cellulose with only type I.

casting knife with a gap width of 300 μm and a speed of 20 mm/min. For the films prepared from MC and Avicel solutions, the casting could be performed at room temperature (RT). For preparation of the α -cellulose based films, the glass plate, the casting knife, and the polymer solution were all preheated to 70 $^{\circ}\text{C}$ before casting in order to ensure sufficient fluidity of the polymer solution. After cooling down to room temperature, the glass-supported casted liquid films were immersed in the coagulation bath consisting of purified water at RT and were left there for about 24 h in order to allow completion of phase separation and solvent exchange. Subsequently, the porous films were washed with fresh purified water and freeze-dried in an Alpha 1-2 freeze dryer from Christ for 4 h at 0.03 mbar and -56 $^{\circ}\text{C}$.

4.4. Characterization Methods. The rheology of the different cellulose solutions in ionic liquids and IL:DMSO mixtures was studied in rotation mode using an Anton Paar Physica MCR 301 rheometer with a plate and plate geometry and Peltier temperature control system. In order to eliminate any previous shear history and to allow the samples to establish their equilibrium structures, a steady pre-shear was applied at a shear rate of 1 s^{-1} for 60 s followed by a 120 s resting period. The measurements were performed with the hood of the Peltier system closed in order to minimize the influence of the laboratory environment. In the viscosity versus shear rate scans, the shear rate was varied between 0.1 and 1000 s^{-1} at room temperature.

For a better evaluation of the Newtonian versus non-Newtonian character of the biopolymer solutions, the viscosity versus shear rate data were fitted with the power law model⁴⁶ and the model parameters were calculated according with the following equation:

$$\mu = K \cdot \dot{\gamma}^{(n-1)} \quad (1)$$

Cloud point tests were performed by using the titration method. In a typical test, 3 g cellulose solution of known concentration in IL or an IL:DMSO mixture was inserted in a snap-cap vial. The exact amount of the polymer solution was obtained by weighing the vial on a microbalance A&D BM-22 before and after the polymer solution insertion. Small amounts of nonsolvent (water in this case) were then dropped to the polymer solution with the help of a syringe. During the whole course of titration, the polymer solution was well stirred and kept at RT (the temperature at which the phase separation was

performed). The composition at which a permanent turbidity was observed, the cloud point, was determined by weighing again the vial after water addition. For each sample, the measurements have been repeated several times and the presented results represent the averaged values.

Scanning electron micrographs of the porous films at different magnifications were taken with an FEI ESEM Quanta 400 FEG instrument. For the cross-section measurements, the samples were broken in liquid nitrogen. Samples were sputtered using an EMITECH Automatic Coater K550 with Au/Pd (80/20) at 0.1 mbar and 30 mA for about 30 s until a layer of 2–3 nm was obtained.

X-ray powder diffraction was performed with a Bruker D8 Advance diffractometer in Bragg–Brentano mode with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54$ \AA ; 40 kV and 40 mA). The cellulose samples (flat pieces fixed on Si single crystal sample holder) were investigated in the range of 5–90 $^{\circ}$ 2θ with a step size of 0.01 $^{\circ}$ 2θ and a counting time of 0.6 s. The data set CCDC 810597⁴⁷ for cellulose I beta from the Cambridge Crystallographic Data Centre (CCDC) database (CSD, Version 5.38⁴⁸) and atomic coordinates for cellulose II⁴⁹ were used for the interpretation of X-ray diffraction patterns and following Rietveld refinement with the TOPAS 5.0 program package from Bruker was performed. Here, the instrumental correction, as determined with a powder sample LaB₆ from NIST (National Institute of Standards and Technology) as standard reference material [SRM 660b; $a(\text{LaB}_6) = 4.15689$ \AA], was taken into account. By means of Rietveld refinement, the lattice parameters and phase ratio as well as the average crystallite size (using the Scherrer equation⁵⁰) and the crystallographic density for cellulose I and II were determined.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.0c03632>.

Properties (refractive index and viscosity) of IL-DMSO mixtures; specific viscosity vs Avicel cellulose concentration at different IL dilutions with DMSO @ 25 $^{\circ}\text{C}$; mole ratios of water to hydroxyl groups on cellulose in the solutions; influence of the co-solvent ratio on the porous film structure (cross-section of 6 wt% α -cellulose based films); XRD diffraction patterns for the three types of cellulose precursors and for the corresponding

porous cellulose films regenerated from 8 wt% polymer solutions in [Bmim][OAc]:DMSO = 3:1; crystallographic details for avicel and regenerated avicel membrane; crystallographic details for MC and regenerated MC membrane; and crystallographic details for α -cellulose and α -cellulose-regenerated membranes (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

The work was supported by the Deutsche Forschungsgemeinschaft (DFG), grant number WI 4325/2–1 and Deutsche Bundesstiftung Umwelt, fellowship 35001/705. We acknowledge support by the Open Access Publication Fund of the University of Duisburg-Essen.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the collaboration with Mr. Smail Boukercha (SEM characterization) at University of Duisburg-Essen. Thanks are also due to Mr. Ahmad Kayali, financed by the fellowship 35001/705 offered by Deutsche Bundesstiftung Umwelt (DBU), who did several cloud point experiments during his research stay at University Duisburg-Essen.

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DOI: 10.1021/acsomega.0c03632

URN: urn:nbn:de:hbz:465-20220223-153907-3

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