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Low energy recycling of ionic liquids via freeze crystallization during cellulose spinning

Yanrong Liu,^{a,b,c} Anne S. Meyer,^c Yi Nie,^a Suojia Zhang^{*a} and Kaj Thomsen^{*b}

A new method for recycling ionic liquids (ILs) from a cellulose spinning process is suggested. The method involves the combination of freeze crystallization and evaporation of H₂O from IL+H₂O mixtures to recycle the ILs. Processes with EmimAc and EmimDep were used as references to develop this IL recycling method. EmimAc+12.5 wt% H₂O and EmimDep+4 wt% H₂O were selected for a quantitative mass and energy analysis of the cellulose spinning and IL recycling process (the maximal initial H₂O levels in the ILs+H₂O mixtures for cellulose dissolution were determined experimentally). The energy requirement for the freeze crystallization+evaporation method was compared to evaporation only for recycling of EmimAc and EmimDep. To produce 1 kg dry cellulose fiber, 45.4 MJ and 62.6 MJ are required for recycling EmimAc and EmimDep respectively by the freeze crystallization+evaporation recycling method. Using evaporation only, 66.9 MJ is required for EmimAc recycling and 99.9 MJ for EmimDep recycling per kg cellulose fiber produced. Thus, to fabricate 1 kg dry cellulose fiber using freeze crystallization+evaporation rather than evaporation, 21.5 MJ can be saved for EmimAc and 37.3 MJ for EmimDep recycling. We also show that compared to a classical Lyocell fiber production method using N-methylmorpholine-N-oxide (NMMO) as solvent, use of ILs is energy saving in itself. Hence, significantly less H₂O is required in the cellulose spinning process with ILs than with NMMO, and in turn less H₂O has to be evaporated for the solvent recycling.

1. Introduction

The demand for textile fibers is increasing with the growth of the global population and the improvement of living standards. As commonly known, cellulose fibers, notably in the form of cotton, are crucially important for textile manufacturing all over the world. The classical industrial methods for producing cellulose fibers include the viscose process, the cuprammonium hydroxide process, and the NMMO process.¹ However, these processes have the drawbacks of being far from eco-friendly.²

Ionic Liquids (ILs) can be considered green solvents for cellulose dissolution, and certain ILs have been shown to function well as solvents for spinning of cellulose fibers.¹ Water is commonly used as an anti-solvent for coagulation of cellulose and for washing of the fibers to remove the IL after spinning. Hong et al.³ introduced an air-gap spinning process to spin cellulose fibers in EmimAc using distilled water as coagulation solvent. Sun et al.⁴ prepared the cellulose fiber with raw pulp in BmimCl based on dry-jet and wet-spun methods and washing of the BmimCl by tap water. Luo et al.⁵ and Zhu et al.⁶ investigated wet-spinning of electrically conductive cellulose fibers in AmimCl and EmimAc respectively using deionized water to remove the solvents. However, in none of these studies, recycling of ILs from IL+H₂O mixtures after the fiber spinning was investigated. Despite the merits of ILs compared to organic solvents, including non-flammability and low vapor pressure,⁷ their cost is still a key inhibitory factor for their application in the cellulose fiber industry. Therefore, it is urgent and necessary

to develop methods for IL recycling including feasible recovery of ILs from IL+H₂O systems in cellulose spinning processes.

Several IL recycling methods have been reported in the literature including membrane separation,⁸ evaporation,⁹ liquid-liquid extraction,¹⁰ centrifugal solvent-extraction,¹¹ and Supercritical CO₂ extraction.¹² Membrane separation usually results in low IL recovery due to the high viscosity of IL mixtures, which is a barrier for industrial implementation.¹³ Evaporation of H₂O from IL+H₂O mixtures has been used for recycling of the ILs, but this method is obviously energy consuming and the large energy requirement is a constraint for practical implementation. Liquid-liquid extraction by use of conventional organic solvents has also been suggested for recycling of ILs, but the use of organic solvents is not compatible with the “green” aspect of employing ILs.¹³

Based on our recent study determining the freezing points of a series of IL+H₂O mixtures,¹⁴ we hypothesized that freeze crystallization could be a feasible method for recovering ILs from dilute IL+H₂O solutions. Previous studies have shown that eutectic freeze crystallization is technically and economically feasible in cases where high product quality was required. Energy costs can be reduced by about 70% for certain systems by use of freeze crystallization compared to a three-stage evaporative crystallization.¹⁵ The present study was therefore undertaken to test the workability of this hypothesis in relation to minimizing energy use by employing freeze crystallization of H₂O in the separation and recycling of ILs during a cellulose spinning process. The study included 1. Cellulose solubility measurements for two selected ILs in mixtures with different water contents to identify the cellulose solubility in IL+H₂O mixtures. 2. Determination of the optimal initial water content from the cellulose solubility data. 3. Cellulose regeneration after spinning. 4. Prediction of the energy requirement for the IL recycling process. In addition, we included scanning electron microscopy (SEM) to assess the morphology of the cellulose fibers after spinning. Lastly, we compared the energy requirement of spinning using the ILs as solvents to the energy required in a classical cellulose spinning process employing NMMO as solvent.

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2. Computational details

The heat capacities (C_p) of ILs were obtained from published experimental values: EmimAc (298.15 K to 393.22 K)^{16,17} and EmimDep (298 K to 343 K)¹⁸. These values can also be found in the Ionic Liquids Database-IL Thermo (V2.0).¹⁹ A linear temperature dependency of heat capacity was calculated from these data for EmimAc and EmimDep as following: the slope, a , for the temperature dependency was calculated using equation 1. The heat capacities of EmimAc and EmimDep at the temperature T were calculated by equation 2. This equation was assumed to be valid at temperatures up to 393.15 K for EmimDep. The heat capacity of the cellulose, microcrystalline cellulose (MCC) was measured by Blokhin et al.²⁰. Their C_p data show an almost linear function of temperature in the temperature range relevant to our work. We used these data to fit parameters for MCC with equation 2. The specific enthalpy of EmimAc, EmimDep, and MCC at the temperature T was calculated with equation 3 using a reference temperature (T_{ref}) of 298.15 K.

$$a = \frac{C_{p,T_2} - C_{p,T_1}}{T_2 - T_1} \quad (1)$$

$$C_p = C_{p,298.15K} + a(T - 298.15) \quad (2)$$

$$H = \int_{T_{ref}}^T C_p dT \quad (3)$$

The specific enthalpy of water (liquid and vapor) was calculated using the NIST/ASME steam properties program (NIST standard reference database 10, version 3.0). For each step of the process (see later) the enthalpy of water vapor was calculated at the relevant temperature and pressure. A COSMO-RS evaluation of the water activity coefficient of the liquid solution leaving the evaporator at 393.15 K was used to predict the required pressure in the evaporator. The water activities (a_w) of the EmimAc+H₂O and EmimDep+H₂O mixtures were determined from the water mole fraction of these mixtures and the predicted water activity coefficient. In each case, this water activity was multiplied with the saturation pressure of water, 0.199 MPa at 393.15 K to get the required pressures of the evaporators. The specific enthalpies of water and water vapor at these conditions were calculated by the NIST/ASME steam properties program.

The heat capacity of liquid water cannot easily be measured below 273.15 K. The heat capacity of liquid water in the freezing step was therefore set as the approximate value of 4.2 kJ/(kg·K). The water enthalpy in the freezing step was calculated by equation 3 with a reference temperature of 273.16 K (The triple point temperature of water). The value used for the heat of fusion of ice in this study was 333.55 kJ/kg.²¹ The heat capacity of ice was cited from Arshad et al.,²² the value is 49.627 J/(mol·K), which corresponds to 2.76 kJ/(kg·K). Thus, the specific enthalpy of ice was calculated from equation 4. T_{ref} in equation 4 is the reference temperature for water enthalpy, 273.16 K.

$$H_{ice} = \int_{T_{ref}}^T 2.76 dT - 333.55 = 2.76(T - T_{ref}) - 333.55 \quad (4)$$

3. Results and discussion

3.1 MCC solubility in IL+H₂O mixture

By increasing the water content in mixtures with EmimAc and EmimDep, the MCC solubility decreases significantly (Table 1). At 12.5 wt% water in EmimAc, the solubility of MCC is 12 wt% at 363.15 K. At 4 wt% water in EmimDep the solubility of MCC is 8 wt% at 363.15 K. A sudden decrease in MCC solubility takes place when this threshold water content is exceeded (Figure 1). The data are in agreement with previous reports showing that water influences cellulose solubility in ILs.²³⁻²⁵ It was shown earlier that EmimAc with 15 wt % water can dissolve less than 1 wt% cellulose.²³ Olsson et al. reported that EmimAc is still an acceptable solvent for cellulose when mixed with certain amounts of water.²⁵ Thus, solutions of EmimAc with 12.5 wt% H₂O and solutions of EmimDep with 4 wt% H₂O can be used as initial solvents for MCC in a cellulose spinning process.

Table 1 MCC solubility in total mixtures at 363.15 K.

EmimAc (1)+H ₂ O (2)+MCC (3)		EmimDep (1)+H ₂ O (2)+MCC (3)	
w_2	w_3	w_2	w_3
0.005	0.27 ²⁶	0.0019	0.15 ²⁶
0.025	0.23	0.025	0.11
0.05	0.16	0.04	0.08
0.075	0.15	0.045	0.003
0.10	0.14		
0.125	0.12		
0.13	0.004		

w_2 : weight fraction of H₂O in solvent. w_3 : weight fraction of MCC in total mixture. The standard uncertainty of the weight fraction is 0.001.

Figure 1 Experimental values of MCC solubility plotted against H₂O weight fraction in solvent at 363.15 K.

3.2 EmimAc and EmimDep recycling processes

Figures 2 and 3 illustrate spinning processes using EmimAc and EmimDep as solvents and with recycling of IL. The initial

spinning solution derived from the measured solubility data are EmimAc (87.5 kg)+H₂O (12.5 kg)+MCC (13.6 kg) in Figure 2 and EmimDep (96 kg)+H₂O (4 kg)+MCC (8.7 kg) in Figure 3. By increasing the water content to 13 wt % in the case of EmimAc and to 4.5 wt % in the case of EmimDep, MCC will precipitate. However, the cellulose fiber (MCC) cannot be regenerated with these small amounts of excess water. In the spinning process, it was chosen to use an amount of deionized water corresponding to the mass of the spinning solution as coagulation bath in the regeneration process. After the cellulose fiber regeneration, the same quantity of washing water was used for washing EmimAc and EmimDep away from the wet fiber.

It was assumed that no cellulose was lost or recycled in the process. With a known amount of fiber, the water evaporated from the wet fiber could therefore be determined by the weight loss during the vacuum drying. According to the experiment, 48.0 kg water evaporated from the wet fibers in the EmimAc recycling process, and 48.2 kg in the EmimDep recycling process. The vacuum drying step took place at 353.15 K corresponding to a water saturation pressure of 0.0474 MPa. The experimental pressure was set to 0.015 MPa. Under these conditions, the fiber would be dried to a water activity, a_w of approximate 0.32. It is assumed that this water activity is a result of the interaction of water with IL rather than the interaction of water with fiber. According to COSMO-RS, a water activity of 0.32 is obtained for a solution with 0.68 mole fraction water in EmimAc. For EmimDep+H₂O the corresponding water mole fraction is 0.6. After drying, the mass of the dry fiber was 2.3 kg higher than the original mass of MCC in the EmimAc recycling process. In the EmimDep recycling process the same number was 3.6 kg. To obtain these water mole fractions, the final amounts of IL and water in the dry fiber product were determined to be 1.6 kg EmimAc+0.7 kg H₂O in the EmimAc process and 3.0 kg EmimDep+0.6 kg H₂O in the EmimDep process.

The EmimAc and EmimDep concentrations in the regenerated solvent (solution 1, Figures 2 and 3) and in the

washing water (solutions 2 and 3, Figures 2 and 3) were determined by electrical conductivity measurements. The EmimAc and EmimDep electrical conductivity standard curves are given in Figure 4. The measured electrical conductivities of solutions 1, 2, and 3 diluted 100 times are listed in Table 2. The concentrations and quantities of EmimAc and EmimDep in solutions 1, 2, and 3 were calculated from these calibration curves and are listed in Table 2. The amount of EmimAc recycled from these three solutions is 82.5 kg, corresponding to 94.2 % of the amount of IL used as solvent. For EmimDep 91 kg is recycled, corresponding to 94.8 % of the initial amount of EmimDep.

The amounts of IL and water remaining with the dry fiber was also determined from a mass balance assuming that the dry fiber corresponds to the initial amount of MCC. These values are given in Figures 2 and 3. These amounts are not in complete agreement with the amounts of IL recovered in solutions 1, 2, and 3 from Figures 2 and 3. The difference is partly caused by the uncertainty in calculating the water activity using COSMO-RS. This water activity was used for calculating the mole fraction of water in the solvent remaining with the dry fiber.

The mole fraction of water in the EmimAc+H₂O solution, Figure 2, box (d) is 0.944. In our previous study it was concluded that a solution with a water mole fraction below 0.708 is not suitable for recycling EmimAc by freeze crystallization of water.¹⁴ A water mole fraction of 0.708 corresponds to 85.9 kg EmimAc+44.0 kg H₂O. Thus, 260.6 kg water can theoretically be removed as ice from a solution of 85.9 kg EmimAc+304.6 kg H₂O. In order to further reduce the water content to 12.5 kg (Figure 2, box (g), 31.5 kg of water needs to be evaporated. Similarly for the EmimDep recycling process in Figure 3, the water mole fraction can be reduced from 0.957 to 0.682 by freezing of 254.1 kg water. Subsequently, 23.2 kg water has to be evaporated in the EmimDep recycling process. The amounts of components in each step of the EmimAc and EmimDep recycling processes are given in Figures 2 and 3.

Figure 2 EmimAc recycling in a cellulose spinning process. H_1 - H_8 are the enthalpies of the mixtures described in box (a) to box (h).

Figure 3 EmimDep recycling in a cellulose spinning process. H_1 - H_8 are the enthalpies of the mixtures described in box (a) to box (h).

Table 2 Electrical conductivity, quantity and recycling yield of EmimAc and EmimDep in solutions 1, 2 and 3.

EmimAc	Solution 1	solution 2	solution 3
Electrical conductivity (mS)*	1.50	0.498	0.203
EmimAc g/100 g (EmimAc+H ₂ O)	42.0	12.7	4.08
Quantity in solution (kg)	63.3	14.3	4.88
Recycling yield (wt%)	72.3	16.3	5.57
EmimDep	Solution 1	solution 2	solution 3
Electrical conductivity (mS)*	0.914	0.408	0.168
EmimDep g/100 g (EmimDep+H ₂ O)	47.2	20.3	7.50
Quantity in solution (kg)	56.7	25.2	9.13
Recycling yield (wt%)	59.1	26.2	9.51

*Electrical conductivity (mS). Values were measured after diluting solutions 1, 2, and 3 100 times.

Figure 4 EmimAc and EmimDep electrical conductivity standard curves. The standard uncertainty of the electrical conductivity is 0.07 mS.

3.3 Energy requirement for EmimAc and EmimDep recycling processes

Table 3 gives the values of the heat capacity parameters and the specific enthalpy of EmimAc, EmimDep, and MCC valid in temperature ranges relevant for Figures 2 and 3. Based on these values, the specific enthalpy of EmimAc and EmimDep in box (a), (b), (d), (f) and (g) in Figures 2 and 3 were calculated using equation 3. A reference temperature of 298.15 K was used for ILs and MCC. The enthalpies of EmimAc, EmimDep, and MCC in box (a) and (d) are therefore 0. Specific enthalpy values for water and ice relevant for the processes in Figures 2 and 3 are listed in Table 4.

Process diagrams for recycling processes for EmimAc (Figure 6) and EmimDep (Figure 7) using only evaporation are given in the electronic supplementary information. Key numbers for the

energy requirement of this process are given together with key numbers for the freeze crystallization+evaporation process in table 5.

The main energy requiring steps in the freeze crystallization+evaporation recycling processes in Figures 2 and 3 include the vacuum drying, the freeze crystallization, and the evaporation processes. For the cellulose spinning process using EmimAc as solvent, Figure 2, the energy consumption in the vacuum drying process is 123 MJ. The freeze crystallization process requires 212 MJ. The energy consumption of the evaporation process is 141 MJ. When EmimDep is used as solvent (Figure 3), the energy usage in the vacuum drying process is 124 MJ, the freezing process requires 190 MJ, and the evaporation process uses 105 MJ. The efficiency of a freezing process is typically 60%²⁷. The energy supplied to the freezing process in Figure 2 could therefore be as high as 354 MJ, and in Figure 3 the corresponding number could be 316 MJ. The total energy requirement for the vacuum drying process, the freezing process, and the evaporation process with EmimAc as solvent (Figure 2) is 618 MJ, which is equal to 45.4 MJ/kg cellulose fiber. The total energy requirement for EmimDep recycling in Figure 3 is 545 MJ corresponds to 62.6 MJ/kg cellulose fiber.

If recycling of EmimAc and EmimDep are performed by the evaporation method, the energy usage in the vacuum drying process is the same as calculated for the freeze crystallization+evaporation method. To remove water from the solvent by evaporation, the energy requirement is 787 MJ for EmimAc. For EmimDep the corresponding number is 745 MJ. Thus, the total energy usage for the EmimAc recycling process by evaporation is 910 MJ corresponding to 66.9 MJ/kg cellulose fiber. The EmimDep recycling process by evaporation requires 869 MJ corresponding to 99.9 MJ/kg cellulose fiber.

According to the energy balances, 21.5 MJ per kg cellulose fiber can be saved by using the combined freeze crystallization+evaporation process rather than evaporation only for recycling of EmimAc. The corresponding number is 37.3 MJ per kg cellulose fiber that can be saved if EmimDep is recycled using

freeze crystallization+evaporation. The energy balances therefore verify the hypothesis behind this work, namely that freeze crystallization+evaporation rather than evaporation for IL recycling will save a significant amount of energy.

In the EmimAc recycling process using freeze crystallization+evaporation (Figure 2), the total quantity of water used in the regeneration and washing steps is 340.8 kg. 260.6 kg water is recovered as ice and only 79.5 kg water is evaporated. The amount of cellulose fiber produced is 13.6 kg. To produce 1 kg cellulose fiber requires the evaporation of 5.8 kg water in the drying and the recycling process when using EmimAc as solvent. When using EmimDep as solvent (Figure 3), 8.2 kg water needs to be evaporated per kg fiber in the drying and recycling process. It is therefore clear that the energy requirement of the IL recycling process depends on the type of IL.

Cai et al²⁸ indicated that recycling of the amount of NMMO solvent required for producing 1 kg Lyocell fiber requires evaporation of 15-40 kg water. This amount only includes the recycling of solvent, not the drying of fiber. It therefore seems like using IL as solvent, and recovering the IL by freeze crystallization+evaporation will save a large amount of energy also compared to traditional cellulose processing.

Our previous work,¹⁴ shows that in the dilute region of aqueous solutions of ILs, ice starts forming when the solutions are cooled to their freezing points. A change in slope of the freezing point curve at increased concentration of IL indicates a change in solid phase which might be IL·nH₂O. Therefore, ILs with a potential to dissolve cellulose can be partly regenerated by freeze crystallization in the concentration range where pure ice is the stable solid phase.

Table 3 Values of heat capacity, temperature slope α , and specific enthalpy of EmimAc, EmimDep, and MCC in Figures 2 and 3.

Name	$C_{p,298.15K}$ kJ/(kg·K)	α kJ/(kg·K ²)	box (b) kJ/kg	box (f) kJ/kg	box (g) kJ/kg
EmimAc	1.89 ¹⁶	2.40×10 ⁻³	108	-194	190
EmimDep	1.74 ¹⁸	2.75×10 ⁻³	99.9	-159	178
MCC	1.20 ¹⁹	4.29×10 ⁻³	72.5		

α was calculated by equation 1. Specific enthalpies were calculated with equation 3. The specific enthalpies of EmimAc, EmimDep, and MCC in box (a) and (d) are 0.

Table 4 Specific enthalpy of water and ice relevant for Figures 2 and 3.

Process	H ₂ O (l) box (a) and (d) kJ/kg	H ₂ O (l) box (b) kJ/kg	H ₂ O (gas) box (c) kJ/kg	H ₂ O (l) box (f) kJ/kg	H ₂ O (l) box (g) kJ/kg	H ₂ O (gas) box (h) kJ/kg	H ₂ O (ice) box (e) kJ/kg
Figure 2	105	335	2649	-358	504	2724	-569
Figure 3	105	335	2649	-311	504	2725	-538

The specific enthalpy of water was calculated by NIST/ASME steam properties program. The water enthalpy in box (f) was calculated by equation 3. The ice enthalpy was calculated by equation 4.

Table 5 Energy requirements for recycling EmimAc and EmimDep using a freeze crystallization+evaporation process and a process in which all water is removed by evaporation.

Freeze crystallization+evaporation	Vacuum drying (MJ)	Freezing (MJ)	Evaporation (MJ)	Total (MJ)	Energy consumption per kg cellulose (MJ)
EmimAc	123	354*	141	618	45.4
EmimDep	124	316*	105	545	62.6
Evaporation	Vacuum drying (MJ)	Freezing (MJ)	Evaporation (MJ)	Total (MJ)	Energy consumption per kg cellulose (MJ)
EmimAc	123	—	787	910	66.9
EmimDep	124	—	745	869	99.9

*The freezing process is assumed to have an efficiency of 60 % while the vacuum drying and the evaporation processes are assumed to have efficiencies of 100%.

The total energy requirement for recycling EmimAc corresponds to producing 13.6 kg cellulose fiber. The total energy requirement for recycling EmimDep corresponds to producing 8.7 kg cellulose fiber.

3.4 The morphology and crystallinity analysis of regenerated MCC

The morphologies of the original MCC (dry) and regenerated MCC (dry) were observed by SEM (Figure 5). Figure 5 (a) shows the original MCC used in the experiment. Figure 5 (b) is MCC regenerated after dissolution in EmimAc with a water mole fraction of approximately 0.2 (EmimAc+5 wt% H₂O). Figure 5 (c) is MCC regenerated after dissolution in EmimAc with a water mole fraction of approximately 0.3 (EmimAc+7.5 wt% H₂O). Figure 5 (d) is MCC regenerated after dissolution in EmimDep with a water mole fraction of approximately 0.2 (EmimDep+2.5 wt% H₂O). With increasing water mole fraction in EmimAc+H₂O mixtures, the surface morphology of the regenerated MCC changes distinctly (Figure 5). With the same water mole fraction of approximately 0.2 in EmimAc (with 5 wt% H₂O) and in EmimDep (with 2.5 wt% H₂O) the surface morphologies of the regenerated MCC were also different. The SEM result indicates that the water content and the type of IL significantly affect the morphology and the properties of the fibers.

The X-ray diffraction (XRD) analysis is given in Figure 6. The original MCC displays a strong peak around $2\theta=22.8^\circ$, corresponding to the (002) crystal plane of cellulose, as well as a composite peak corresponding to the (101) and (10 $\bar{1}$) crystal planes at $2\theta=15^\circ$ and 15.5° approximately. The intensity of the (002) plane decreases dramatically for MCC treated with EmimAc+H₂O and EmimDep+H₂O. No distinct peak remains for the (101) and (10 $\bar{1}$) planes, which illustrates that the crystallinity of cellulose is greatly disrupted after the dissolution and regeneration from EmimAc+H₂O and EmimDep+H₂O. This disruption ability is diminished with the addition of water in EmimAc. These results are in agreement with the results obtained in the study by Doherty et al.²⁹

Figure 5 (a) Morphology of original MCC, (b) MCC regenerated from EmimAc with water mole fraction of 0.2 (5 wt% H₂O), (c) MCC regenerated from EmimAc with water mole fraction of 0.3 (7.5 wt% H₂O), (d) MCC regenerated from EmimDep with water mole fraction of 0.2 (2.5 wt% H₂O).

Figure 6 XRD of original MCC and regenerated MCCs.

4. Experimental

4.1 Chemical reagents

1-ethyl-3-methylimidazolium Acetate (EmimAc, 170.21 g/mol) and 1-ethyl-3-methylimidazolium Diethyl phosphate (EmimDep, 264.26 g/mol) which have the same cation and different anions were selected for this study. In our previous work it has been verified that these two ILs have a high capacity for cellulose dissolution.²⁶ EmimAc (99 wt%), was purchased from Shanghai Cheng Jie Chemical Co. LTD (Shanghai, China), and EmimDep was synthesized in one step. The synthetic method and the purity analysis of EmimDep was given in the supporting information of our previous work.²⁶ The structures of EmimDep was confirmed by its ¹H and ¹³C NMR spectra using a Bruker 600 spectrometer. Characteristic peaks and ¹H and ¹³C NMR data of EmimDep was shown in the supporting information of our previous work.¹⁴ Cellulose was microcrystalline cellulose (MCC) purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China).

4.2 Cellulose dissolution and IL recycling procedures

EmimAc and EmimDep were mixed with different amounts of water for assessing the solubility of MCC at 363.15 K. The MCC was dried at 353.15 K under vacuum for 48 h before use. An initial amount of MCC of approximately 0.05 g was added to the IL+H₂O mixtures (5 g) at the beginning. Subsequently, MCC was added stepwise in 0.05 g portions until the solubility limit was reached. When the MCC start solubility is less than 0.05 g, the stepwise added amount of MCC was changed to 0.005 g portions until the solubility limit was reached. An OLYMPUS BX 51 optical microscope was used to assess the dissolution of MCC in the different IL+H₂O mixtures. When MCC could be observed under the optical microscope without dissolving after 12 hours^{26,30,31} the solubility limit had been exceeded.

The recycling process was performed at laboratory scale, and then scaled-up proportional to the experimental amounts. The recycling process included the following steps: 1. Different amounts of MCC was dissolved in IL+H₂O mixtures at 363.15 K

to form the spinning solution. 2. The spinning solution was placed into a spinning equipment (Longer Pump, LSP01-1A) to make the cellulose fiber. A single hole spinneret needle was connected to a coagulation bath using deionized water as the regeneration solvent. After the cellulose regeneration, the cellulose fiber+IL+H₂O mixture was separated into wet cellulose fiber and aqueous IL solution. 3. The wet cellulose fiber was washed twice using deionized water to remove IL. 4. The amounts of IL in the solutions were determined by measuring the electrical conductivity. The three solutions were mixed and cooled to remove water as ice by freezing (prediction). Remaining water was evaporated to make the IL ready for recycling (prediction). 5. Finally, the wet fiber was dried in vacuum drying oven at the temperature of 353.15 K and the pressure of 0.015 MPa to remove water from it. The recycling procedures of EmimAc and EmimDep are illustrated in Figures 2 and 3.

In step 2 and 3, the electrical conductivities of the regenerated solvent and two batches of wash solutions were measured. A conductivity meter (Orion, 136S) with automatic data logging was used. Electrical conductivity calibration curves of aqueous EmimAc and EmimDep solutions were first determined. The amounts of EmimAc and EmimDep used for measuring the electrical conductivity calibration curve were approximately 0.05, 0.1, 0.2, 0.4, 0.6, 0.8 and 1 g per 100 g solution. The aqueous EmimAc and EmimDep solutions in step 2 and 3 were diluted 100 times in order to be within the concentration range of the calibration curves. The quantities of EmimAc and EmimDep in the regenerated solvent and in the washing solutions were determined according to these calibration curves. The electrical conductivity of each sample was measured more than 15 minutes until a consistent value was reached.

4.3 SEM and XRD analysis for regenerated MCC

The morphology of the original MCC and the selected regenerated MCCs obtained after using EmimAc+H₂O and EmimDep+H₂O as solvents were observed by SEM (JSM 6700F, Japan, 5.0 kV). The sample was sputtered with platinum for better observation using JEC-3000FC auto fine coater. The current and the sputtering time were set to 20 mA and 150 s respectively. XRD of the original MCC and of the regenerated MCC was employed to examine the crystalline structures of original MCC and regenerated MCC. Data were obtained using a Bruker D8 Focus instrument, and the X-ray tube was operated at 40 kV and 200 mA with 2 θ ranging from 5° to 30° at a scan speed of 0.05s⁻¹.

5. Conclusion

In this study, the solubility of MCC in two selected ILs (i.e. in IL+H₂O mixtures) as a function of water content was measured at 363.15 K. The MCC solubility decreases gradually as water is added and then suddenly reaches a solubility limit. The viscosity of the IL+H₂O mixtures were also taken into account, hence EmimAc with 12.5 wt% H₂O and EmimDep with 4 wt% H₂O were

chosen as solvents for cellulose spinning with IL recycling. The energy usage of two processes: freeze crystallization+evaporation versus evaporation of H₂O from ILs+H₂O mixtures was evaluated for recycling of the ILs. A higher initial amount of H₂O was used in practice for the cellulose solubilisation and spinning using EmimAc as compared to using EmimDep as solvent. Still, the higher solubility of cellulose (MCC) in EmimAc meant that less energy was required for freeze crystallization+evaporation of H₂O to recover and recycle the IL from EmimAc+H₂O mixtures than from EmimDep+H₂O mixtures (45.4 MJ vs 62.6 MJ per kg dry cellulose fiber). Using electrical conductivity measurement, it was verified that 94.2 wt% of EmimAc and 94.8 wt% of EmimDep could be recovered after cellulose spinning.

It was found that using freeze crystallization+evaporation for recycling of EmimAc and EmimDep, respectively, can save a significant amount of energy compared to a process where all water is removed by evaporation, namely 21.5 MJ for EmimAc and 37.3 MJ for EmimDep per kg dry cellulose produced. This new IL recycling method not only saves energy for IL recycling compared to evaporation, but is also much more energy efficient than conventional cellulose fiber production methods, such as the NMMO process. The freeze crystallization+evaporation method may also be applied to other processes requiring separation of IL+H₂O mixtures and thus potentially result in energy saving in multiple cellulose processing applications.

Conflicts of interest

There are no conflicts of interest to declare

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