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Phase diagram, solubility limit and hydrodynamic properties of cellulose in binary solvents with ionic liquid

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ABSTRACT

Cellulose solubility phase diagrams in two binary solvents based on 1-ethyl-3-methylimidazolium acetate (EmimAc) mixed with water and with dimethylsulfoxide (DMSO) were built. The minimal amount of EmimAc molecules needed to dissolve cellulose is 2.5–3 moles per anhydroglucose unit. This proportion allows calculation of the maximal cellulose concentration soluble in EmimAc–DMSO at any composition; in EmimAc it is around 25–27 wt%. Water forms hydrogen bonds with EmimAc and thus competes with cellulose for ionic liquid; the solubility of cellulose in EmimAc–water is much lower than that in EmimAc–DMSO. Hydrodynamic properties of cellulose in two solvent systems were compared. In EmimAc–DMSO cellulose intrinsic viscosity practically does not depend on DMSO content as predicted by the phase diagram. The intrinsic viscosity in EmimAc–water first increases with water content due to cellulose self-aggregation and then abruptly decreases due to coagulation.

1. Introduction

Ionic liquids (ILs) have been now accepted as very promising cellulose solvents, and the most studied are imidazolium-based ILs. They are non-volatile, have high dissolving capability and high thermal stability (as compared to other cellulose solvents and to cellulose itself). Making cellulose fibres and films (Cai, Zhang, Guo, Shao, & Hu, 2009; Kosan, Michels, & Meister, 2008; Zhang, Wu, Zhang, & He, 2005) and performing chemical derivatisation in the homogeneous conditions (Gericke, Liebert, & Heinze, 2009; Heinze, Schwikal, & Barthel, 2005) have been reported for 1-ethyl-3-methylimidazolium acetate (EmimAc), 1-butyl-3-methylimidazolium chloride (BmimCl) and 1-allyl-3-methylimidazolium chloride (AmimCl). ILs were used for making cellulose aerogels (Aaltonen & Jauhiainen, 2009; Sescousse, Gavillon, & Budtova, 2011; Tsioptsias, Stefopoulos, Kokkinomalis, Papadopoulou, & Panayiotou, 2008) and carbon nanotube reinforced fibres (Rahatekar et al., 2009; Zhang et al., 2007). ILs are also suggested in the biorefinery, for biomass pre-treatment, fractionation and making monomeric sugars for bio-fuel production (Bose, Armstrong, & Petrich, 2010; Brandt, Gräsvik, Hallett, & Welton, 2013; Stark, 2011). The mechanisms of cellulose dissolution in ILs (Remsing, Swatloski, Rogers, & Moyna, 2006; Zhang et al., 2010), molecular modelling of cellulose–IL interactions (Liu, Sale, Holmes, Simmons, & Singh, 2010) and the properties of cellulose–IL solutions (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Haward, Sharma, Butts, McKinley, & Rahatekar, 2012; Kuang, Zhao, Niu, Zhang, & Wang, 2008; Lovell et al., 2010) have been extensively studied during the past decade.

An important step in moving forward towards industrial use of ILs for cellulose processing is, aside IL recycling, the understanding of cellulose behaviour in the presence of "co-solvents" that are, in fact, cellulose non-solvents. Water is the most important one, being used for cellulose coagulation and also because of the high hydrophilicity of imidazolium-based ILs. Dimethylsulfoxide (DMSO) is the second most frequently used component mixed with ILs for performing cellulose derivatisation in the homogeneous conditions (Gericke, Liebert, Seoud, & Heinze, 2011) and also for making fibres via electrospinning (Härdelin et al., 2012; Quan, Kang, & Chin, 2009). The reasons for using DMSO are to decrease solvent viscosity and price and to vary surface tension. DMSO is fully miscible with EmimAc, BmimCl and AmimCl (Gericke et al., 2011) and seems not to perturb chemical reactions of cellulose modification (see, for example, Gericke, Liebert, et al., 2009; Gericke et al., 2011).

Despite that both fluids, water and DMSO, are cellulose non-solvents and are both fully miscible with imidazolium ILs, their "action" on cellulose and their interactions with ILs are very different. Using turbidimetry for cellulose–BmimCl–water mixture, it

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was shown that with 10 wt% water in BmimCl–water mixture it was possible to dissolve about 4 wt% of cellulose at 90 °C (Mazza, Catana, Vaca-Garcia, & Cecutti, 2008). By extrapolating their results to zero water concentration, authors concluded that maximal cellulose concentration in BmimCl is 8.75 g per 100 g of BmimCl at 95 °C. This prediction is somewhat in contradiction with 14% cellulose–BmimCl solutions used for spinning fibres (Kosan et al., 2008). Molecular dynamics study demonstrated that the addition of water changes the structural organization of EmimAc and "disrupts the interactions" between the IL and cellulose (Liu, Sale, Simmons, & Singh, 2011). It was demonstrated that 15 wt% of water in EmimAc–water mixture seems to be the limit for cotton linter dissolution in EmimAc–water, and this result was used for cellulose and xylan fractionation (Froschauer et al., 2013). Using light scattering, Kuzmina, Sashina, and Troshenkowa (2010) reported that cellulose solution suitable for "technical purposes" (i.e. spinning) can be obtained only with water content below 8 wt%. An interesting study of the role of solvent parameters on cellulose behaviour was recently reported (Hauru, Hummel, King, Kilpeläinen, & Sixta, 2012). It was shown that solvent net basicity determines the ability to dissolve cellulose (the study was performed for dilute cellulose solutions) and threshold parameters were obtained. The study of viscosity of dilute cellulose–EmimAc–water solutions revealed that the maximal water content in the mixture with EmimAc dissolving 1 wt%cellulose was 15 wt% (Le, Sescousse, & Budtova, 2011). Finally, it was found that mixing EmimAc and water is exothermal and neither macroscopic (density, viscosity) nor microscopic (NMR spectroscopy, relaxometry, diffusion) parameters obey ideal mixing law, indicating strong interactions between the components (Hall et al., 2012). All results cited above suggest that the presence of water disfavours cellulose–EmimAc interactions and thus strongly decreases cellulose solubility.

Contrary to water, DMSO seems to "help" cellulose dissolution in ILs: it decreases solvent and thus solution viscosity (Härdelin et al., 2012; Le et al., 2011; Lv et al., 2012; Quan et al., 2009) thus accelerating dissolution kinetics, does not change cellulose conformation and solvent thermodynamic quality (Lv et al., 2012) and enhances the interaction between anion and cellulose as shown by molecular dynamics simulations (Huo, Liu & Wang, 2013). It was reported that to dissolve 15 wt% cellulose, the maximum concentration of DMSO in the mixture with AmimCl is around 80 wt%; 2.5 wt% cellulose was dissolved in 10 wt% Emimac–90 wt% DMSO and fibres were successfully electrospun (Härdelin et al., 2012). The mechanisms of the interactions between imidazolium-based ILs and DMSO remain, however, unclear. Molecular dynamics simulations showed that while protic solvents, methanol and water, strongly interact with EmimAc anion (which explains the decrease in cellulose solubility), aprotic solvents, DMSO and DMF, "can partially break down the ionic association" (between anion and cation) and thus "produce more "free" $[CH_3COO]^-$ anions from anion−cation pairs" increasing cellulose solubility (Zhao, Liu, Wang, & Zhang, 2013). On the contrary, Remsing, Liu, Sereyev, and Moyna (2008) reported the "strengthening" of the interactions between imidazolium cation and anion in the presence of DMSO. Based on their findings they suggest that "this solvent has negligible effects on the dissolution of polysaccharides by $[C_4mim]Cl$." An experimental study of density, viscosity and ultrasonic sound velocity of some imidazolium-based ILs mixed with DMSO showed the deviation from ideal mixture behaviour which was dependent on alkyl chain length, but EmimAc was not studied (Govinda, Attri, Venkatesu & Venkateswarlu, 2013).

The comparison of two solvent systems, IL–water and IL–DMSO, shows that the concentrations of DMSO in the solvent mixture still keeping cellulose dissolved are much higher than the "allowed" concentrations of water. This raises an obvious question: what is the phase diagram of cellulose–IL–water and cellulose–IL–DMSO? The second question is what is the maximal cellulose concentration possible to dissolve in IL? Surprisingly, the answers to both questions are not known. Review articles give examples of various cellulose concentrations in solutions with ILs that are reported in literature but these values are not the dissolution limits (Mäki-Arvela, Anugwom, Virtanen, Sjöholm, & Mikkola, 2010; Pinkert, Marsh, Pang, & Staiger, 2009). An attempt to estimate the maximal cellulose concentration possible to dissolve in EmimAc was made by calculating the fractions of bound and free solvent from the measurement of ions diffusivity, probed by NMR, in cellulose–EmimAc solutions (Lovell et al., 2010). It was hypothesised that the maximum dissolvable cellulose concentration should be around 27 wt%. Most of experimental and modelling results show that ILs solvate carbohydrates through the formation of hydrogen bonds between the IL anion and hydroxyl groups of the sugar solutes (Liu et al., 2010; Rabideau, Agarwal, & Ismail, 2013; Remsing et al., 2006; Youngs et al., 2011; Zhang et al., 2010). Following BmimCl anion and cation relaxation times in solutions of glucose and cellobiose it was suggested that chloride ions interact in 1:1 ratio with carbohydrate hydroxyl protons (Remsing et al., 2006). Similar ratio, EmimAc:hydroxyl = 3:4 and 1:1, was reported in NMR spectroscopic studies of cellobiose solvation in EmimAc (Zhang et al., 2010). One may thus deduce that at least 3 moles of IL are needed to dissolve one anhydroglucose unit (AGU). Will this ratio hold true for IL–DMSO and IL–water mixture solvents?

The goal of this work is to build cellulose phase diagram in binary solvent mixtures, IL–water and IL–DMSO. We use a simple first-approximation approach consisting in the analysis of cellulose solutions with polarized and non-polarized light optical microscopy. Being rather rough, this approach gives the upper limit in cellulose maximum dissolvable concentration. By cumulating a large number of carefully performed experiments this approach allows building ternary phase diagrams. Cellulose intrinsic viscosity in both solvent systems is compared and analyzed in the view of the results obtained for ternary phase diagrams.

2. Experimental

2.1. Materials

Avicel PH-101 microcrystalline cellulose ("cellulose" in the following) with degree of polymerization DP = 180 as given by the manufacturer was purchased from Sigma Aldrich. The IL EmimAc was from BASF; the amount of water was below 0.5 wt% as obtained using Karl–Fischer method (Service Central d'Analyse du CNRS, Solaize, France). Distilled water and DMSO from Sigma Aldrich were used to prepare cellulose–EmimAc–co-solvent solutions.

2.2. Methods

2.2.1. Preparation of solutions

Cellulose was dried prior using at 80 °C under vacuum for 2 h.

(a) Cellulose–EmimAc–water solutions: first, EmimAc–water mixture was prepared by mixing the components in different proportions. Water concentration, C_{water} wt%, was calculated as follows:

$$C_{water}\ \text{wt\%} = \frac{100\% \times m_{water}}{m_{EmimAc} + m_{water}} \quad (1)$$

where m_i is the weight of the component. Cellulose was then added and stirred with a mechanical stirrer at 500 rpm and

80 °C for about 72 h. Polymer concentration was calculated as following

$$C_{\text{cell}} \quad \text{wt\%} = \frac{100\% \times m_{\text{cell}}}{m_{\text{cell}} + m_{\text{EmimAc}} + m_{\text{water}}} \tag{2}$$

(b) Cellulose–EmimAc–DMSO solutions: cellulose was first immersed in DMSO for a few hours. EmimAc was then added to make solvent composition varied from 10 to 98 wt% of DMSO (DMSO concentration calculated in the same way as water, see Eq. (1)) and cellulose concentration from 1 to 30 wt% (cellulose concentration was calculated according to Eq. (2) with m_{water} replaced by m_{DMSO}). Solutions were prepared under nitrogen by stirring at 500 rpm and 80 °C for about 72 h.

2.2.2. Optical microscopy

The observations of cellulose solutions were performed with Leica DM 4500P optical microscope in transmission mode. A droplet of solution was deposited on a glass slide and covered with a glass lamella. The solution was examined with polarized and non-polarized light at various magnifications. The experiments were performed at 20 °C.

2.2.3. Rheological measurements

Steady state viscosity was measured using Bohlin Gemini rheometer equipped with plate–plate geometry and a Peltier temperature control system. Low viscosity oil was used to protect solutions from water vapour absorption by IL. This precaution was demonstrated to be efficient and not perturbing solution flow (Gericke, Schlufter, et al., 2009). All measurements were performed at 20 °C.

3. Results and discussion

3.1. Viscosity of EmimAc–water and EmimAc–DMSO

In order to better understand polymer behaviour in a mixed solvent, the properties of each mixture were first evaluated. As far as EmimAc is fully miscible with water and with DMSO, the viscosity of EmimAc–water and EmimAc–DMSO was measured as a function of mixture composition. Experimental data were compared with viscosity values calculated according to the additive mixing rule. In the first approximation, the deviation of experimental results from the mixing rule should indicate special interactions between mixed components (McAllister, 1960; Powell, Roseveare, & Eyring, 1941).

To analyze the viscosity of EmimAc–DMSO and EmimAc–water mixtures as a function of mixture composition, steady state viscosity of mixtures was first measured. For all mixtures Newtonian flow was recorded for about two decades of shear rates (from 1–10 to 200–500 s^{-1}). The mean values of Newtonian viscosity at each composition were calculated and plotted vs DMSO and water molar fraction, F_{DMSO} and F_{water}, respectively (Fig. 1).

The addition of water or DMSO strongly decreases EmimAc viscosity, as expected. However, if comparing with the mixing rule, mixtures behave in a very different way. For EmimAc–DMSO (Fig. 1: open points – experiment and dashed line – mixing rule), mixture viscosity roughly obeys the mixing rule within the experimental errors. Thus we deduce, in the first approximation, that components simply coexist being mixed. For EmimAc–water, the experimental data are far from the mixing rule prediction. A detailed study of the properties of EmimAc–water mixture was performed recently (Hall et al., 2012): the change in ^{1}H chemical shift positions indicates that anion forms hydrogen bond with water molecules. The maximal deviations of experimental data (macroscopic: viscosity, density, mixing temperature and microscopic: NMR relaxometry and diffusion) from theoretical mixing rule were all found to occur at the composition of approximately 3

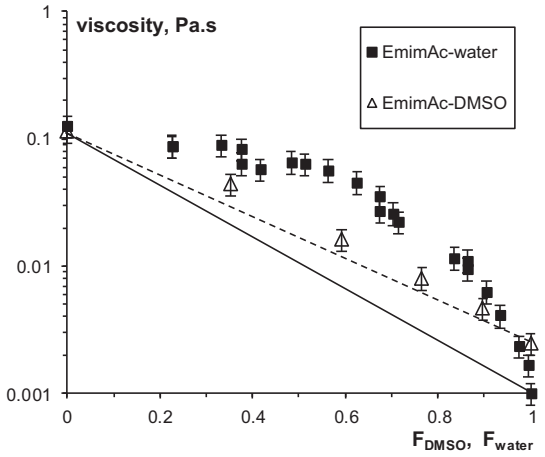

Fig. 1. Viscosity of EmimAc–water (dark points, data taken from (Hall et al., 2012)) and EmimAc–DMSO (open points) mixture as a function of water (F_{water}) or DMSO (F_{DMSO}) molar fraction. Solid line corresponds to the mixing rule for EmimAc–water and dashed line to EmimAc–DMSO. The errors are 15%.

water molecules per 1 EmimAc. What is important for building cellulose phase diagram in a binary solvent is that in EmimAc–water, the two solvent components are strongly interacting, whereas in EmimAc–DMSO, they do not. This difference will influence cellulose solubility and hydrodynamic properties in two solvent mixtures.

3.2. Phase diagram and the limit of cellulose dissolution in EmimAc–DMSO and EmimAc–water

Cellulose–EmimAc–DMSO and cellulose–EmimAc–water solutions were carefully analyzed with optical microscopy using polarized and non-polarized light in the view of the presence of non-dissolved cellulose. The magnification used was such that objects of the size of few microns were easily detectable. With this method, it is certainly not possible to judge if the dissolution occurred on the molecular level; however, a rough phase diagram can be built giving the upper limit of maximal cellulose concentration possible to dissolve in this or that solvent. The results are presented in Figs. 2 and 3 where cellulose wt% concentration in the system is plotted as a function of weight concentration of DMSO or water in the mixture EmimAc–DMSO or EmimAc–water, respectively. Open points correspond to completely transparent (in non-polarized light) or completely dark (in polarized light) solutions; crosses correspond to the cases when even a few small non-dissolved particles were detected.

The maximal dissolved cellulose concentration $C_{\text{cell max}}$ depends on DMSO or water concentration in the solvent, $W\%_{\text{DMSO}}$ or $W\%_{\text{water}}$: higher is non-solvent (DMSO or water) fraction in the mixture with EmimAc, lower is the maximal amount of cellulose that is possible to dissolve in the given solvent mixture. There is a significant difference in $C_{\text{cell max}}$ in EmimAc–DMSO and in EmimAc–water mixtures, compare Figs. 2 and 3: it is not possible to dissolve cellulose at $W\%_{\text{water}} > 20\%$ and, for example, $C_{\text{cell max}}$ at $W\%_{\text{DMSO}} = 10\%$ is five times higher than $C_{\text{cell max}}$ at the same water concentration.

In order to further analyze the experimental results obtained, we estimated the proportion between the maximal cellulose concentration dissolved at a given DMSO or water concentration in solvent mixture, as taken from Figs. 2 and 3, and the corresponding EmimAc concentration in the solution. The goal is to calculate the minimal amount of EmimAc needed to dissolve cellulose, or, in other words, the proportion between cellulose and potentially bound-to-cellulose EmimAc. For EmimAc–DMSO system, we assume that DMSO is not perturbing cellulose–EmimAc interactions, as suggested by Remsing et al. (2008). For EmimAc–water, two cases will

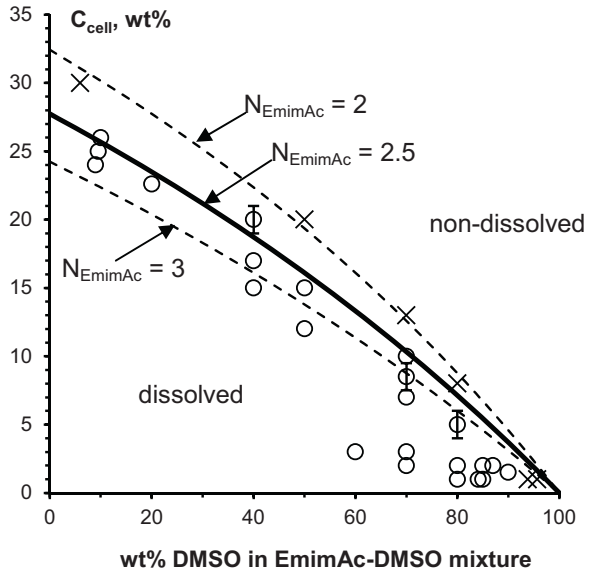

Fig. 2. Phase diagram for cellulose in EmimAc–DMSO. Solid line corresponds to the maximal cellulose concentration soluble in EmimAc–DMSO calculated supposing no interactions between EmimAc and DMSO and 1 AGU binding N_{EmimAc} = 2.5 mole of EmimAc; dashed lines correspond to AGU binding N_{EmimAc} = 3 and 2 moles of EmimAc.

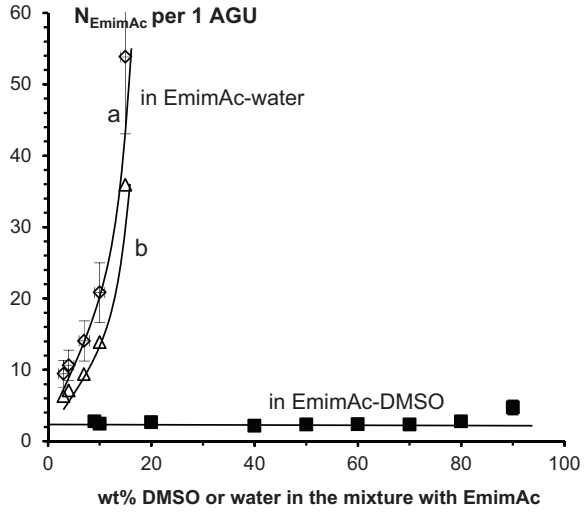

Fig. 4. Mole of EmimAc per AGU corresponding to the experimental maximal dissolved cellulose concentration in EmimAc–DMSO and EmimAc–water as a function of DMSO or water wt%, respectively. Two cases for EmimAc–water are shown: (a) supposing no interactions between EmimAc and water and (b) supposing 3 water molecules bound to 1 EmimAc. The error of 20% is shown for EmimAc–water (a) case. Solid lines are given to guide the eye.

be considered: (a) a somewhat non-realistic case of no interactions between the components and (b) 3 water molecules binding 1 EmimAc, as shown in Hall et al. (2012). The amount of EmimAc moles, N_{EmimAc}, per anhydroglucose unit, AGU, for both systems as a function of DMSO and water weight concentrations in solvent system is shown in Fig. 4. As far as optical microscopy is rather rough method for the exact determination of the limit of polymer solubility, the experimental error is high.

For EmimAc–DMSO mixture the proportion between cellulose and EmimAc is constant at any DMSO content and equal to about 2.5 mole of EmimAc per one AGU unit (Fig. 4). Quite an opposite result is obtained for cellulose dissolved EmimAc–water: higher is water content in the system, higher amount of EmimAc seems to be needed to dissolve cellulose. This result is an artefact because

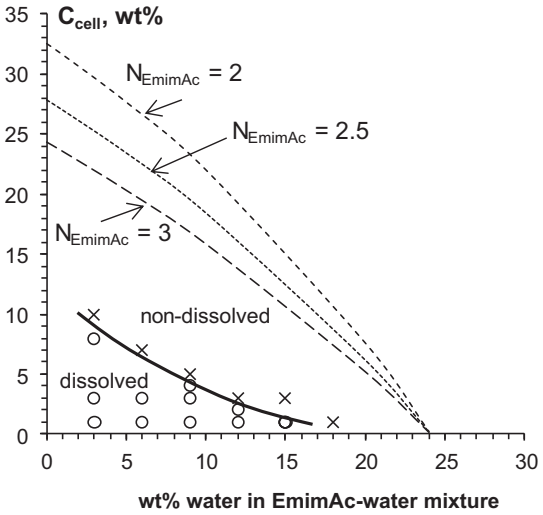

Fig. 3. Phase diagram for cellulose in EmimAc–water. Solid line is to guide the eye as an approximate maximal limit of cellulose concentration possible to dissolve in this solvent. Dashed lines correspond to the calculated limit of cellulose concentration supposing 3 water molecules binding 1 EmimAc and N EmimAc binding one AGU, with N_{EmimAc} = 2, 2.5 and 3.

both assumptions, (a) on the absence of interactions between EmimAc and water and (b) on the constant amount of water molecules bound to EmimAc (3–1), are not applicable. Fig. 1 confirms that two solvent systems are indeed very different.

Keeping in mind EmimAc/cellulose ratio obtained for EmimAc–DMSO mixture, N_{EmimAc} = 2.5 (Fig. 4), the theoretical maximal concentration of cellulose $C_{cell\ max}$ soluble in EmimAc–DMSO was calculated for three cases: N_{EmimAc} = 2, 2.5 and 3. The results are shown in Fig. 2: solid line for N_{EmimAc} = 2.5 and upper and lower dashed lines for N_{EmimAc} = 2 and 3, respectively. N_{EmimAc} = 2 obviously underestimates the amount of EmimAc needed to dissolve cellulose; the corresponding line crosses the region that contains visually non-dissolved cellulose. Taking into account the roughness of the method, we suggest that 1 AGU needs about 2.5–3 moles of EmimAc to be dissolved. It is logic to assume that each hydroxyl group on anhydroglucose unit needs to be bound to one IL molecule for cellulose to be dissolved. This means that maximal cellulose concentration possible to dissolve in EmimAc is around 25–27 wt%; the same values were predicted by $EMIM^+$ and Ac^- ions diffusing in cellulose–EmimAc solutions as probed by NMR (Lovell et al., 2010). These concentrations are difficult to reach in reality because of very high solution viscosity.

The same calculation of $C_{cell\ max}$ was performed for cellulose dissolved in EmimAc–water supposing that 3 water molecules bind 1 EmimAc and thus lower amount of ionic liquid is “available” to dissolve cellulose. The result is shown in Fig. 3 with dashed lines corresponding to N_{EmimAc} = 2, 2.5 and 3. All three cases fall far away in the region of non-dissolved cellulose, confirming again that a “simple” calculation of $C_{cell\ max}$ is not possible for this solvent system. If the special interactions between water and EmimAc should not exist, or at least the proportion between bound EmimAc and water should not depend on EmimAc–water composition, it could be possible to dissolve cellulose in the presence of much higher water content, as shows EmimAc–DMSO case. Cellulose and water are competing for EmimAc, with preferential interactions being between EmimAc and water, which leads to low maximal cellulose concentration possible to dissolve in EmimAc–water mixture.

Ternary phase diagrams for cellulose–EmimAc–DMSO and cellulose–EmimAc–water are summarized in Fig. 5. Shaded areas correspond to cellulose solubility region. The limit of cellulose

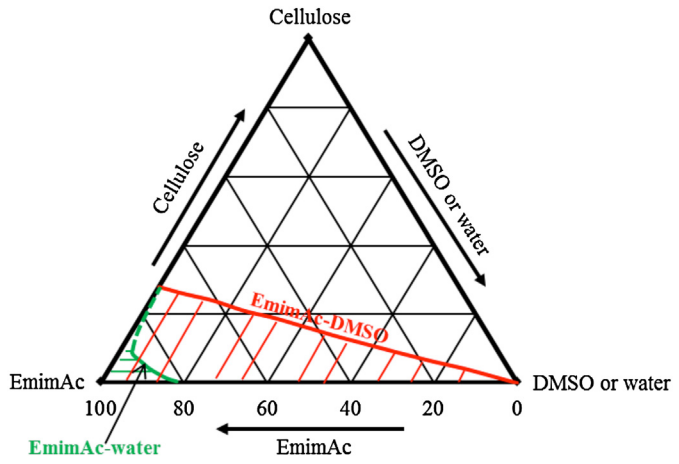

Fig. 5. Cellulose solubility phase diagram (shaded areas) in EmimAc–DMSO (line corresponds to 2.5 EmimAc molecules bound to 1 AGU) and in EmimAc–water (line corresponds to experimental results) with dashed line being a possible continuation of $C_{cell\ max}$ in EmimAc–water. Concentrations are in wt%.

solubility in EmimAc–DMSO correspond to $C_{cell\ max} = 2.5N_{EmimAc}$ and in EmimAc–water to the experimentally obtained data. The limit of cellulose solubility in EmimAc–water should meet 25–27 wt% cellulose in the absence of water, as shown by dashed line, but we do not have any experimental data for very low water contents. The experimental error in water concentration in this region is very high as far as both cellulose and especially ionic liquid are hydrophilic.

In order to prove the concept that ≈2.5 mole of EmimAc per AGU is needed to dissolve cellulose, provided that EmimAc is not interacting with DMSO, the following test experiment was performed. First, cellulose was dissolved in 1:1 (wt%/wt%) = EmimAc:DMSO mixture so that a 15 wt% cellulose solution was obtained. 15 wt% cellulose in EmimAc:DMSO = 1:1 mixture is very close to the dissolution limit which should be around 16.5 wt% supposing the proportion 2.5 mole of EMIMAc per one AGU works. This 15% cellulose solution was 5 times diluted by DMSO; as a result, cellulose concentration dropped to 5.5% and the concentration of DMSO became 83 wt%. The solution was transparent and stable in time. The same dilution was performed again leading to cellulose concentration 1.3 wt% and co-solvent concentration 96 wt% and solutions were still transparent and stable. It is thus possible to dilute cellulose–EmimAc solution with any DMSO amount without precipitating cellulose as far as the ratio EmimAc to AGU is kept higher than 2.5. This indirectly shows that DMSO is not perturbing cellulose–EmimAc interactions which is a very important result for cellulose processing or performing chemical reactions in homogeneous conditions in the view of adjusting solution viscosity. Indeed, Fig. 1 shows that the viscosity of EmimAc–DMSO can vary within almost two orders of magnitude.

Similar dilution tests were performed on cellulose–EmimAc–water system by diluting with water. As expected, cellulose coagulated.

3.3. Cellulose intrinsic viscosity in EmimAc–water and in EmimAc–DMSO

To demonstrate the difference in cellulose behaviour in EmimAc–water with EmimAc–DMSO on the molecular level, cellulose intrinsic viscosity in both solvent systems was evaluated at 20 °C. Polymer intrinsic viscosity [η] is an important characteristic of a dissolved polymer as it gives information about the size of the macromolecule and the thermodynamic quality of the solvent. The classical way to determine intrinsic viscosity is to use Huggins approach: solution is gradually diluted with the solvent in Ubbelohde capillary viscometer and $(\eta_{rel} - 1)/C$ is plotted versus polymer concentration C, where $\eta_{rel} = \eta_{sol}/\eta_{solv}$, η_{sol} and η_{solv} being solution and solvent viscosity, respectively, and polymer concentration C is expressed in mass per volume units. In order to recalculate cellulose concentration in g/cm^3, we used solvent (EmimAc + DMSO) density equal to 1.1 g/cm^3 as far as at 20 °C both components, EmimAc and DMSO, have this density. Intrinsic viscosity is deduced as a limiting value at infinite dilution, $C \to 0$. For cellulose–EmimAc–water solutions, data published in Le et al. (2011) will be used.

It is not possible to perform measurements in a capillary Ubbelohde viscometer because EmimAc is too viscous and too hygroscopic to be studied in contact with the air. We used the approach already taken in (Gericke, Schlufter, et al., 2009; Le et al., 2011; Sescousse, Le, Ries, & Budtova, 2010): first we measured steady state viscosity of rather dilute (below 2 wt%) cellulose–EmimAc–DMSO solutions at various cellulose concentrations and solvent compositions. For all cellulose–EmimAc–DMSO solutions studied a Newtonian plateau was recorded for at least one-two decades of shear rates. The same was reported for cellulose–imidazolium-based ionic liquids with and without co-solvent added (Gericke, Schlufter, et al., 2009; Haward et al., 2012; Härdelin et al., 2012; Lv et al., 2012; Sescousse et al., 2010), and thus we do not show flow data. Mean values of viscosity corresponding to Newtonian region were then calculated. We took Wolf approach developed to calculate the intrinsic viscosity (Eckelt et al., 2011; Wolf, 2007) as far as data presented in the classical Huggins plot were somewhat scattered (due to averaging of Newtonian viscosity) and do not allow an adequate [η] determination. Briefly, Wolf approach consists in the calculation of the limiting slope of $\ln(\eta_{rel})$ versus C which, according to phenomenological considerations, is identical to the intrinsic viscosity (Wolf, 2007). Being developed for polyelectrolyte solutions, this approach can also be successfully used for uncharged polymers. Indeed, both Huggins and Wolf approaches gave the same cellulose intrinsic viscosity values for cellulose dissolved in NMMO monohydrate (Eckelt et al., 2011); Wolf approach was also successfully used for determination of cellulose acetate and amylopectin intrinsic viscosities in EmimAc (Liu & Budtova, 2013; Rudaz & Budtova, 2013).

Cellulose intrinsic viscosity as a function of co-solvent weight fraction, water or DMSO, in EmimAc–co-solvent mixture is presented in Fig. 6. There is a remarkable difference in cellulose macromolecule behaviour in two solvent systems. In

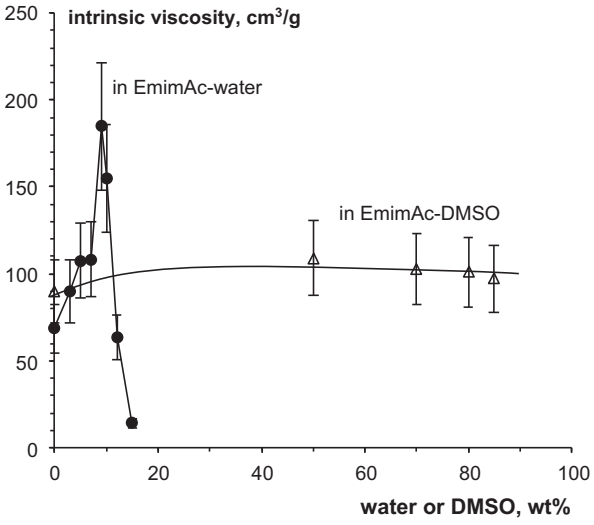

Fig. 6. Cellulose intrinsic viscosity as a function of water or DMSO weight fraction mixture with EmimAc, at 20 °C. Lines are given to guide the eye.

EmimAc–DMSO, cellulose intrinsic viscosity does not depend on DMSO content. As for EmimAc–water solvent, it was possible to measure cellulose intrinsic viscosity only in a very narrow range of water concentrations, from 0 to about 15 wt%. The reason is that starting solutions to be diluted were of about 1–1.5 wt% cellulose, and it is not possible to dissolve even 1 wt% cellulose in EmimAc–water mixtures containing more that 16–17 wt% of water (see Fig. 3). Cellulose intrinsic viscosity in EmimAc–water first strongly increases with the increase of water content reaching the maximal value roughly at 10 wt% of water in EmimAc–water mixture which corresponds to 1:1 = EmimAc:water molar composition. As far as water is strongly competing with cellulose for EmimAc, cellulose is self-aggregating and it is the size of aggregates that is "seen" by viscosity. The aggregation of cellulose in imidazolium-based ionic liquids mixed with water was recorded with light scattering: aggregate size increased with the increase of water content (Kuzmina et al., 2010). Within a certain narrow region of water content large cellulose aggregates are formed; they are precursors of coagulated cellulose before the phase separation occurs at higher water content. Further increase of water content leads to a sharp decrease of aggregates size; cellulose in EmimAc–water is close to a suspension and not a solution.

The results obtained on cellulose intrinsic viscosity in two solvent systems, EmimAc–water and EmimAc–DMSO, corroborate and complement cellulose solubility phase diagram in these solvents. The changes of hydrodynamic size of the macromolecule reflect subtle variations in the properties of dissolved polymer and are in-line with the overall phase diagram.

4. Conclusions

Cellulose phase diagrams and solubility limits in two solvent systems, EmimAc–water and EmimAc–DMSO, were determined using high-resolution optical microscopy with polarized and non-polarized light. Being rather rough and not allowing concluding on solution properties on the molecular level, this method allows comparison of cellulose dissolution in two solvent systems and the estimation of the moles of IL needed to dissolve one AGU. Cellulose hydrodynamic properties in both binary solvents were also analyzed and compared using steady-state viscosity data.

At least 2.5–3 molecules of EmimAc per AGU are needed to dissolve cellulose in EmimAc–DMSO mixture; this value does not depend on DMSO concentration in solvent mixture. As far as this proportion is respected, cellulose intrinsic viscosity does not depend on DMSO content and dilution of cellulose–EmimAc with DMSO is not coagulating cellulose. Cellulose phase diagram obtained in EmimAc–DMSO confirms the findings reported in literature on IL:AGU = 3:1 mole proportion obtained for other imidazolium-based ionic liquids. In overall, IL:AGU = 3:1 makes a "rule of thumb" allowing a simple prediction of cellulose solubility (or not) in IL:DMSO mixture of any composition which is very important for cellulose processing and chemical modifications if willing to modify solvent (and thus solution) viscosity without perturbing cellulose–IL interactions.

The maximum cellulose concentration possible to dissolve in EmimAc was deduced: it is 25–27 wt%. Practically speaking, these concentrations are difficult to reach because of very high viscosity and thus very slow dissolution kinetics which can be accelerated by heating which in turn may lead to cellulose degradation. Using EmimAc–DMSO mixture as cellulose solvent it is possible to decrease the viscosity by one order of magnitude (for example, for EmimAc:DMSO = 1:1 wt%:wt% mixture) still keeping cellulose dissolved at rather high concentrations (~15 wt%), as shows the phase diagram. This can be very attractive for using IL–DMSO mixture for spinning and casting cellulose solutions.

A remarkable difference between cellulose phase diagram in EmimAc–DMSO and EmimAc–water mixture was observed. The solubility limit in the latter solvent mixture is much lower as compared to EmimAc–DMSO and cannot be predicted by the same IL:AGU proportion. The addition of water higher than 10–15 wt% in cellulose–EmimAc solution leads to cellulose coagulation. The reason is strong interactions between the IL and water, as already reported in literature. Cellulose intrinsic viscosity in EmimAc–water first increases with water concentration due to cellulose self-aggregation. Further increase of water content leads to cellulose coagulation, as shows experimental phase diagram.

The results obtained demonstrate that the interactions between solvent components are of great importance for the understanding of cellulose phase diagram. We show that it is not possible to predict cellulose solubility in IL in the presence of water. On the contrary, DMSO seems not to perturb cellulose–IL interactions and allows determination of the amount of EmimAc molecules needed to dissolve one AGU. Cellulose dissolution limit in EmimAc is an important value for the further development of cellulose processing in ILs and using these solvent systems for chemical derivatisation.

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