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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:

$$C_{water}\ \ wt\% = \frac{100\% \times m_{water}}{m_{EmimAc} + m_{water}} \tag{1}$$

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