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Influence of water on the dissolution of cellulose in selected ionic liquids

Mathieu Mazza · Dan-Andrei Catana ·
Carlos Vaca-Garcia · Christine Cecutti

Abstract Cellulose (7% water) was thoroughly dispersed in various ionic liquids (IL) and the turbidity of the mixture was investigated to distinguish real dissolution from fine dispersion. The dissolving ability of 1-butyl-3-methylimidazolium chloride (BMIMCl known cellulose solvent) and 11 other commercial IL (not reported as cellulose solvents) was studied. From the latter, only 1,3-dimethylimidazolium dimethylphosphate (DMIMDMP) could dissolve cellulose. The influence of water content on the real dissolution of cellulose in these two IL was investigated. The maximum theoretical amount of dissolved anhydrous cellulose in the IL was determined by extrapolation methodology at different temperatures. For cellulose in BMIMCl, it was 8.75 g/100 g of IL at 95 °C. DMIMDMP could achieve real cellulose dissolution only in a practically anhydrous system (2.3 g/100 g of IL at 30 °C) but dissolution was physically limited by high viscosity.

Keywords Cellulose dissolution ·
Ionic liquids · Turbidimetric measurements

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Introduction

The cellulose-containing materials and their derivatives have been widely used in our society. In some physico-chemical processes, cellulose has to be dissolved. Solvents like LiCl/DMAc are used to perform reactions in homogeneous media (Vaca-Garcia et al. 1998; El Seoud and Heinze 2005) and solvents like NMMO and cuen have been used as non-derivatizing solvents for regeneration (Johnson 1985; Heinze 2005). For both applications, ionic liquids (IL) are currently attracting much attention because they are liquid at relatively low temperatures (<100 °C) and are described as chemically and thermally stable, non-flammable, and non-volatile. Their extremely low vapour pressure is the leading characteristic in processes where volatile organic compounds (VOC) must be avoided. As far as VOC emissions are concerned, IL are more environmentally friendly than traditional organic solvents (El Seoud et al. 2007).

Different studies have shown that cellulose can be dissolved in methylimidazolium salts, especially 1-butyl-3-methylimidazolium chloride (BMIMCl) (Swatloski et al. 2003, 2002) and 1-allyl-3-methylimidazolium chloride (AMIMCl) (Zhang et al. 2005), ammonium salt like benzyltrimethyl(tetradecyl)ammonium chloride (BDTACl) and pyridinium salt like 1-butyl-3-methylpyridinium chloride (BMPyCl) (El Seoud et al. 2007). In all these cases, the dissolution of the cellulose is also due to the action of the chloride anions, which interact with the hydroxyl groups of cellulose by disrupting the hydrogen

bonds in the biopolymer (Moulthrop et al. 2005). These interactions have been put in evidence by NMR in solutions of cellulose in BMIMCl at 5% at 90 °C (Moulthrop et al. 2005; Remsing et al. 2006). In other works, the maximum cellulose concentration in BMIMCl has been reported. Different values are reached depending on the temperature and on the heating device: 6 wt% at 80 °C (Schluffer et al. 2006), 10 wt% at 100 °C or up to 25 wt% if the dissolution is carried out using a microwave heating system (150 °C maximum) (Swatloski et al. 2002, 2003). Moreover, the solubility depends also on the origin of cellulose and its degree of polymerisation (Heinze et al. 2005; Barthel and Heinze 2006).

In all these studies, the assessment of dissolution was done by: static and dynamic light scattering methods (Chrapava et al. 2003), NMR (Moulthrop et al. 2005) and visual methods (Swatloski et al. 2002).

There is a possibility that confusion arises between real dissolution (complete solvation of the cellulose molecules) and fine dispersion of cellulose particles or even aggregates formation during or after dispersion in the solvent. In regeneration processes, it is important to reach total dissolution of cellulose in order to obtain a homogeneous product.

Thus, one of the aims of our study is to propose an alternative method to differentiate real dissolution of cellulose. Turbidimetry was selected as a simple technique.

A second aim of our study was to quantify the negative influence of water when dissolving cellulose in IL. Water can come from (i) the hygroscopicity of IL, (ii) the initial cellulose water content, and (iii) the process, in particular when precipitating the dissolved cellulose. Therefore this information can be exploited in different manners, for instance, the following questions can be answered: how much undried cellulose can one dissolve in a particular ionic liquid? In what extent the concentration of cellulose can be increased if cellulose is previously dried? What is the minimum quantity of added water to precipitate cellulose?

Materials and methods

Materials

Twelve commercial IL (Table 1) were purchased from Solvent Innovation (Köln, Germany) and Solvionic (Toulouse, France). They had a purity of

minimum 98% and were used as received. Sigma-Aldrich (France) furnished α -cellulose having a water content of 7% (determined by thermogravimetry and Karl Fischer methods) and was used without further drying in this study. Cellulose acetate (DS = 2.4) and tetrahydrofuran (THF, 99.5% purity) were purchased from Sigma-Aldrich (France). NaCl (99.5% purity) was purchased from Acros Organics (Belgium).

Turbidimetric measurements

Turbidity was measured with a nephelometer featuring a scattered light detector perpendicular to the light beam (Fig. 1). The correlation between transmitted and scattered light constitutes a precise evaluation parameter of the presence of non-dissolved particles in a solution as they are bigger than the wavelength of the incident light (860 nm). The units of turbidity from a calibrated nephelometer are called Nephelometric Turbidity Units (NTU). Calibration was done between 1 and 1,000 NTU. The latter corresponds to a milky opaque sample.

Dissolution of cellulose in ionic liquids

Turbidimetric clear glass vials containing a precise quantity of ionic liquid (around 15 mL) and a magnetic stirrer were placed into a heating oil bath. The use of a hot water bath was avoided to limit the water uptake by hygroscopy. Small precise amounts of cellulose (around 10 mg) powder were added discretely into the vials. In between each addition, at least 15 min were allowed for dissolution and turbidity was measured until a stable NTU value was reached. Tests were realised at 90 °C for BMIMCl and at 30 °C for the other IL, which are in liquid form at room temperature.

Influence of the water content

Initial solutions of cellulose in BMIMCl and 1,3-dimethylimidazolium dimethylphosphate (DMIMD MP) were prepared at 125 and 105 °C, respectively in order to evacuate the ambient moisture. Three different cellulose concentrations (0.5, 1, and 2 g in 100 g of IL) were used. The solutions were put into vials with a magnetic stirrer and placed in an oil bath at controlled temperature (85, 90 or 95 °C).

Table 1 Ionic liquids used in this study

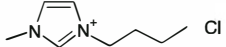
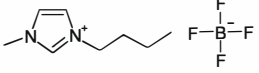
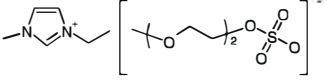
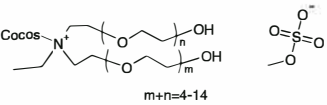
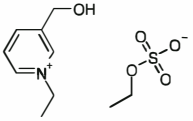
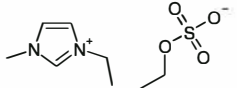
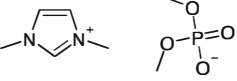
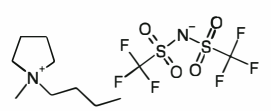
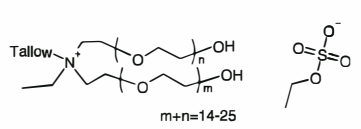
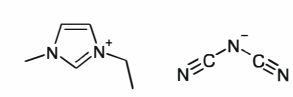
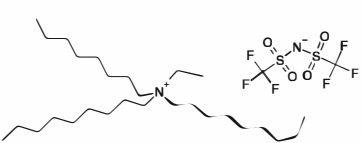
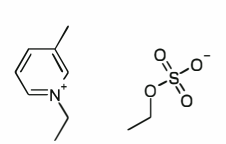
Reference on Fig. 3	Ionic liquid	CAS number	Formula	Melting point according to the supplier (°C)	Solvent cited in the literature or by the supplier
1	1-Butyl-3-methylimidazolium chloride BMIMCl	79917-90-1		66–68	Water, Ethanol
2	1-Butyl-3-methylimidazolium tetrafluoroborate BMIM BF ₄	174501-65-6		<–65	Water
3	1-Ethyl-3-methylimidazolium 2(2-methoxyethoxy) ethylsulfate	n.a.		<–65	Water
4	AMMOENG 100	n.a.		<–65	
5	1-Ethyl-3-hydroxymethylpyridinium ethylsulfate	n.a.		<–65	Water
6	1-Ethyl-3-methylimidazolium ethylsulfate	342573-75-5		<–65	Water
7	1,3-Dimethylimidazolium dimethylphosphate DMIMDMP	654058-04-5		<–65	Water

Table 1 continued

Reference on Fig. 3	Ionic liquid	CAS number	Formula	Melting point according to the supplier (°C)	Solvent cited in the literature or by the supplier
8	Butylmethylpyridinium bis(trifluoromethylsulfonyl)imide	223437-11-4		<-65	Water
9	AMMOENG 102	n.a.		10-15	
10	1-Ethyl-3-methylimidazolium dicyanamide	n.a.		<-65	Water
11	Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide	n.a.		<-65	Water
12	1-Ethyl-3-methylpyridinium ethylsulfate	n.a.		<-65	Water

n.a. not available

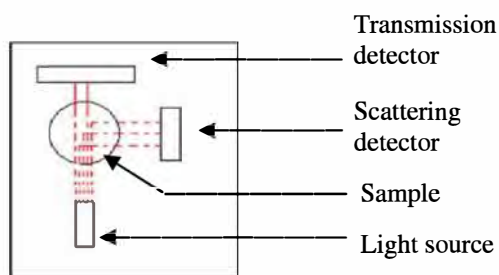


Fig. 1 Principle of a nephelometer

Small precise amounts of water (100 or 200 μL) were added discretely into the vials and turbidity was measured every 15 min until constant values. The water content in each vial is known precisely from the water content at the beginning (Karl Fischer titration) and the quantity of added water.

Results and discussion

Validation of the turbidimetric principle

Turbidity is the cloudiness of a fluid caused by particles in suspension. They will scatter a light beam passing through the sample. This property is considered as a significant consequence of solid particles in suspension. More light reaches the scattering detector if there are solid particles scattering the source beam. To some extent, how much light is scattered by a given amount of particles depends on the properties of the latter: shape, colour, and reflectivity. In our case, we will measure particles of a unique solute: cellulose. Comparisons can therefore be made.

Before testing the proposed method on cellulose, the principle of solubility evaluation by turbidimetry was validated using independently an ionic compound (NaCl) and a linear polymer (cellulose acetate) dissolved in water and tetrahydrofuran, respectively.

Turbidity is expected to keep reasonably constant as much as the solute is perfectly soluble. When the maximum solubility is reached, the newly added solute remains solid and turbidity is expected to increase sharply.

The predicted behaviour of turbidity was confirmed with the study of the dissolution of NaCl in water at 30 $^{\circ}\text{C}$ (Fig. 2). Turbidity was perfectly constant then increased sharply at concentrations higher than 38 g/100 g water. This result is

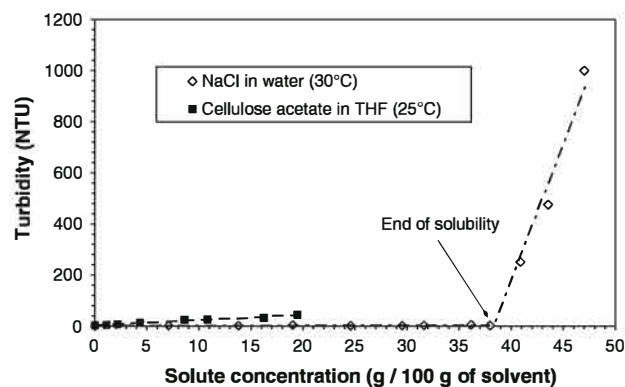


Fig. 2 Turbidity versus solute concentration: NaCl in water and cellulose diacetate in THF

consistent, though not the same, with the known solubility value: 36.1 g of NaCl in 100 cm^3 of water at 30 $^{\circ}\text{C}$ according to the Handbook of Chemistry and Physics, CRC citing (Apelblat and Korin 1998). Thus, the perfect dissolution of a salt in water does not increase the turbidity.

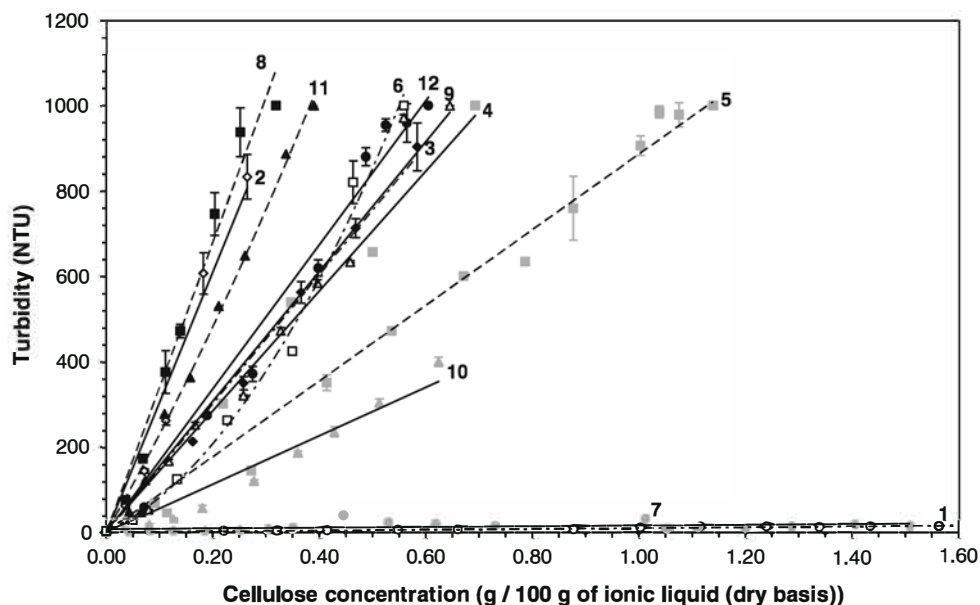
In the case of a polymer, the dissolution of cellulose acetate in THF (Fig. 2) gave a linear trend with a small slope, which can be considered almost constant with regard to the whole scale of turbidity (1–1,000 NTU). The end of solubility could not be reached because the solution became too viscous to be stirred preventing the homogenisation of the sample. Nevertheless, the main principle could be confirmed for ionic compounds and macromolecules.

Dissolution of cellulose in selected ionic liquids

All the commercial IL listed in Table 1 were tested to assess their ability to dissolve cellulose. Although undried cellulose was used in the experiments, the concentration values were reported on a dry basis.

Only two of the IL were able to dissolve cellulose: BMIMCl (number 1, already known: reference) and DMIMDMP (no. 7, not previously described as cellulose solvent). These two systems show practically flat lines in a plot of turbidity versus concentration (Fig. 3). The other 10 IL showed an immediate and constant linear rise of the turbidity when the cellulose concentration was increased. The turbidity values were significantly high to indicate the presence of solid particles even at the lowest concentrations. The rise in turbidity for a given increase in cellulose concentration was different

Fig. 3 Turbidity versus cellulose concentration for 12 ionic liquids. For legend, see Table 1



according to the ionic liquid. The slopes of the lines in Fig. 3 that correspond to the biphasic systems vary from 569 to 3,397 NTU/g cellulose. It is evident that the interactions between cellulose and IL are different and affect the light dispersing properties of the particles. Three groups of lines can be distinguished in Fig. 3 according to the slope values. It is interesting to observe that the IL that share the same type of anion belong to the same group: bis(trifluoromethylsulfonyl)imide for IL 8 and 11, alkylsulfate anions for IL 3, 4, 6, 9, and 12. The interactions affecting light scattering seem to be independent of the cation of the ionic liquid.

The maximum solubility of α -cellulose in BMIMCl and DMIMDMP was determined by addition of cellulose portions to the IL to put in evidence an abrupt change of turbidity (Fig. 4). The experiments were done at 90 °C for BMIMCl and 30 °C for

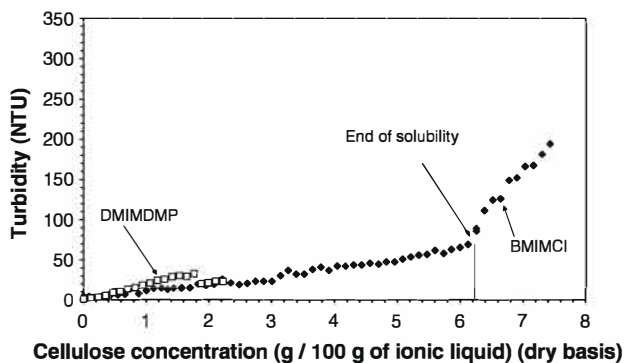


Fig. 4 Maximum solubility of cellulose in BMIMCl and DMIMDMP

DMIMDMP according to their melting points (Table 1).

The curve of the BMIMCl system showed a neat increase of slope at 6.2 g/100 g IL. This value is in agreement with the values reported by Swatloski et al. (11.1 g/100 g IL at 100 °C and 3.1 g/100 g IL at 70 °C).

In the DMIMDMP system, the end of cellulose solubilisation could not be detected by turbidimetry because the solution became too viscous to be stirred. This limit was reached at 2.3 g/100 g IL. Nonetheless, this value corresponds to the highest cellulose concentration that can be reached in this ionic liquid under the practical conditions.

Influence of the water content

Oven-dry cellulose was not used for this study. We decided to keep using the standard cellulose containing 7% water (moisture at equilibrium) to avoid the hornification phenomenon that can reduce severely its solubility. Results were, however, expressed on a dry basis.

In a system in which cellulose is perfectly dissolved, the addition of a non-solvent (in this case, water) perturbs the solvation of the biopolymer. Turbidity is expected to remain constant as far as cellulose is still soluble but when the maximum water content in the solution is reached, cellulose would precipitate and the turbidity is expected to increase sharply. After precipitation of all the cellulose molecules, the turbidity should keep constant.

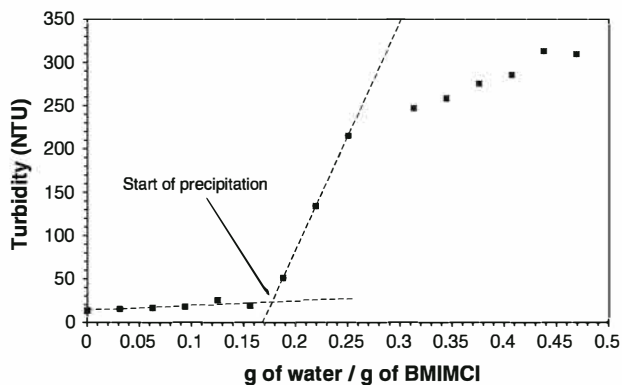


Fig. 5 Influence of water content in the turbidity of cellulose solutions. Example given for 1 g of cellulose in 100 g of BMIMCl at 95 °C. Maximum water content before precipitation was 0.1708 g of water/g of BMIMCl

The expected behaviour was verified in the case of the BMIMCl/cellulose solutions. An abrupt increase of the turbidity was observed at the beginning of precipitation. Turbidity starts to level off when little cellulose remains in solution and much cellulose passes in suspension (Fig. 5).

The start of the cellulose precipitation was determined by the tangent method. For an initial solution of 1 g cellulose/100 g BMIMCl, precipitation occurred at 0.1872 g water/g BMIMCl (Fig. 5). It is evident that this value, which represents the maximum water content in a homogeneous cellulose/IL system, depends on both the concentration of cellulose and the temperature. The values determined for different conditions are given in Table 2.

The relation between these values and the initial cellulose concentration at constant temperature showed a linear trend (Fig. 6). The intersection of the straight line with the Y-axis represents the maximum theoretical amount of cellulose that can be dissolved in BMIMCl at a given temperature when the water content in the solution is zero. At 95 °C, this value is 8.75 g/100 g of BMIMCl, i.e., 8.0 wt%. At 90 °C, the expected value decreases to

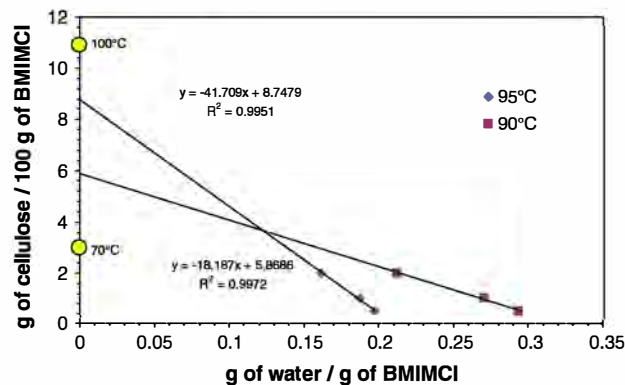


Fig. 6 Linear behaviour of cellulose in solution in BMIMCl as a function of maximum water content at constant temperature. Circles represent values from Swatloski et al. 2002

5.87 g/100 g IL, which is in agreement with the experimental result reported above (6.2 g/100 g IL). The small difference is justified by the uncertainty of the extrapolation.

The maximum solubility values for the reported by Swatloski et al. are also shown in Fig. 6 as points on the Y-axis. From our experimental and the reported values, we can plot the maximum solubility of cellulose in anhydrous conditions as a function of temperature (Fig. 7). The behaviour is not linear but follows a classic parabolic trend observed elsewhere for most solutes in classic solvents.

In the case of DMIMDMP at 95 °C, the turbidity increased immediately after the first addition of water to the cellulose solution. The increase was observed regardless of the cellulose concentration (0.5, 1, and 2 g of cellulose in 100 g of DMIMDMP). As more water was added in the solutions, the turbidity kept increasing (Fig. 8). It seems that perfect dissolution of cellulose in this ionic liquid is possible only in practically anhydrous conditions, as those used to trace Figs. 3 and 4. In addition, we verified that water and DMIMDMP form a miscible clear solution, as demonstrated by the flat line of Fig. 8. Therefore, the increasing behaviour of the turbidity is only due to

Table 2 Maximum water content (including cellulose moisture content) before precipitation for different cellulose concentrations in BMIMCl at different temperatures

Temperature (°C)	0.5 g of cellulose in 100 g of BMIMCl	1 g of cellulose in 100 g of BMIMCl	2 g of cellulose in 100 g of BMIMCl
95	0.1967	0.1872	0.1614
90	0.2934	0.2702	0.2120

Values given in g of water/g of BMIMCl

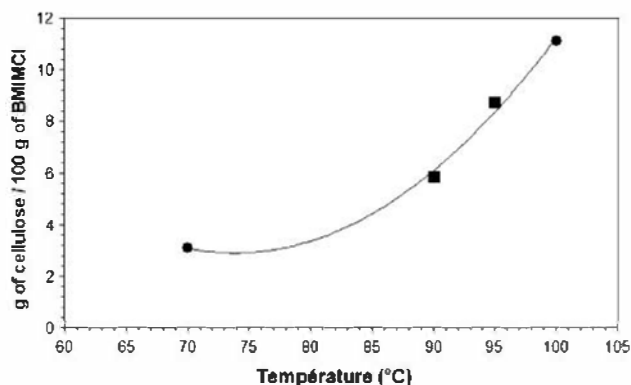


Fig. 7 Maximum theoretical solubility of cellulose in anhydrous conditions at different temperatures. Square-shaped points are experimental values. Circles are values obtained from Swatloski et al. (2002)

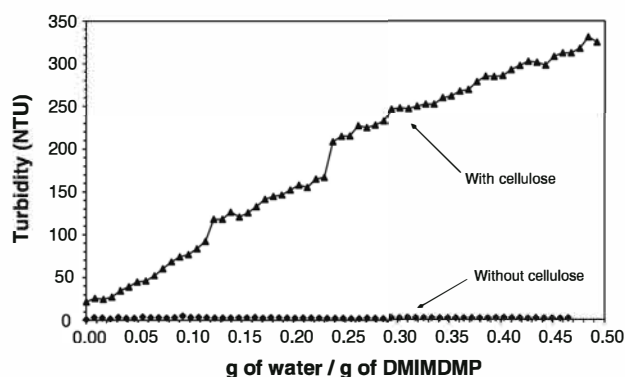


Fig. 8 Turbidity against water content for a solution of 0.5 g of cellulose in 100 g of DMIMDMP and for pure DMIMDMP

the precipitation of cellulose from the first addition of water in the case of DMIMDMP/cellulose solutions. No description of the cellulose dissolution mechanism was found in the literature that can help understand this behaviour. In contrast, these results may help in the future to understand the dissolution mechanism of this new ionic liquid.

Conclusion

It was demonstrated that turbidimetric measurements are a method allowing to distinguish real dissolution from fine suspension of cellulose in IL. Only one, among the selected new 11 IL tested, could dissolve cellulose (DMIMDMP).

The influence of water in the dissolution of cellulose was quantitatively evaluated. Cellulose could be dissolved in BMIMCl at different water

contents. The more water, the less concentration of cellulose in solution is obtained. The maximum theoretical amount of anhydrous cellulose in solution was 8.75 g/100 g of BMIMCl at 95 °C determined by extrapolation methodology. All the results are in agreement with those from literature.

Tests on DMIMDMP showed that the cellulose can be perfectly dissolved only if the system is practically anhydrous. The maximum obtained value was 2.3 g/100 g IL at 30 °C. More cellulose could be theoretically dissolved but the high viscosity of the solution avoided further dissolution. A small amount of water added to the system leads to the formation of cellulose aggregates.

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