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An investigation of lignocellulosic biopolymers solubility in Protic Ionic Liquids aqueous solutions

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Abstract

The use of Protic Ionic Liquids (PILs) to realize the pretreatment step of lignocellulosic biomass represents a promising technique, since they have been considered as green solvents for lignin dissolution and its extraction from biomass. In this study were evaluated the ability of six PILs and their aqueous solutions to dissolve Kraft lignin at the temperature of 323.15 K. This process was also evaluated within different periods of time (1, 2, 4, 8 and 24 hours), indicating that the saturation is reached within 8 hours to the majority of the systems studied. An optical microscope was used to analyze the lignin, xylose and cellulose dissolution process, separately, in tris(2-hydroxyethylammonium) lactate, which presented the highest ability to dissolve lignin among the PILs studied. This PIL was also used to assess the temperature effect, showing that lignin dissolution was increased when higher temperatures were applied.

Key words: *protic ionic liquids, solubility, lignocellulosic biomass.*

Introduction

Lignocellulosic biomass is composed by three major macromolecular components: cellulose (30-50%) hemicellulose (20-35%) and lignin (15-30%). For its exploitation, it is crucial to perform its fractionation and processing of its constituents, once each fraction of this resource can be used in a series of applications. Among its three major components, lignin is the least exploited one (Brandt et al., 2013). A promising alternative for delignification process is lignin dissolution with solvents, including Protic Ionic Liquids (PILs).

In this study, lignocellulosic biopolymers dissolution ability of six PILs (2-Hydroxyethylammonium uglycolate (HEAG), 2-Hydroxyethylammonium lactate (HEAL), 2-Hydroxytriethylammonium malonate (HEAMn), 2-Hydroxytriethylammonium malate (HEAM), bis(2-hydroxyethyl) ammonium lactate (BHEAL) and tris(2-hydroxyethyl) ammonium lactate (THEAL) and their aqueous solutions were evaluated. The techniques used were spectroscopy and polarized optical microscopy.

Results and Discussion

In this study, the following factors related to lignin solubility in PILs were analyzed: the anion and cation structure of PILs, the water content effect and the influence of time and temperature. The anion and cation structure and the water content effect can be observed in Figure 1, which presents the lignin solubility curves obtained at 323.15 K within 24 hours.

The curves presented in Figure 1 show that the increase of water content in the solution affects negatively the lignin solubility. In addition, it indicates that the anionic part of PIL plays a key role in lignin dissolution, while the cationic part plays a secondary role in this task. It was also observed that the presence of extra hydroxyl and carboxylic groups impaired the lignin solubility.

Regarding time influence, the experiments indicated that lignin solubility was enhanced with the increase of time, however the solubility data collected with 8 and 24 hours presented similar values, showing that the saturation is reached in about 8 hours to the majority of the systems evaluated.

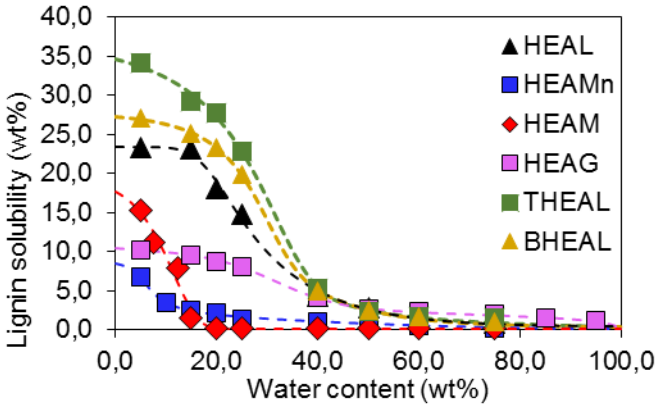

Figure 1. Kraft lignin solubility in PILs aqueous solutions at 323.15 K.

As can be seen, the THEAL was the best PIL among those tested to dissolve lignin. Therefore, this PIL was tested using the optical microscope equipped with a temperature controller. It was visually verified that this PIL do not dissolve cellulose, but can dissolve xylose and lignin. The THEAL was also chosen to investigate the temperature effect in its solubility. The results show that the temperature increase affects favorably the dissolution process.

Conclusions

This study conducted a comprehensive analysis about lignocellulosic biopolymers dissolution in alkanolammonium-based PILs and their aqueous solutions. It proved the capacity of applying these kind of solvents as media to dissolve mainly lignin.

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Brandt, A.; Gräsvik, J.; Hallett, J. P.; Welton, T. Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chemistry*, **2013**, v. 15, pp. 550-583.