

STUDY OF VISCOSITY OF CELLULOSE-IONIC LIQUID SOLUTIONS AT HIGH CONCENTRATIONS

¹Järvi, P., ²Granström, M., ¹King, A. W. T., ³Hietala, S., ⁴Olszewska A. M., ¹Kilpeläinen, I.,
⁵Argyropoulos, D. S.

¹ Laboratory of Organic Chemistry, University of Helsinki, Finland, P.O.BOX 55, FIN-00014
University of Helsinki

² BASF SE, GCI/R, M311 67056, Ludwigshafen, Germany

³ Laboratory of Polymer Chemistry, University of Helsinki, Finland, P.O.BOX 55, FIN-00014
University of Helsinki

⁴ Department of Forest Products Technology, Forest Products Surface Chemistry, Aalto
University, P. O. Box 16300, FIN-00075 Aalto

⁵ Organic Chemistry of Wood Components Laboratory, Department of Forest Biomaterials
North Carolina State University, NC 123321, USA

ABSTRACT

The rheological properties of homogenous solutions of microcrystalline cellulose (MCC) dissolved in two different ionic liquids (IL's), 1-allyl-3-methylimidazolium chloride ([amim]Cl) and 1,3-dimethylimidazolium dimethylphosphate ([mmim]Me₂PO₄), were investigated. More specifically, the solution shear viscosities were measured at different temperatures and high concentrations.

INTRODUCTION

Lignocellulosic materials are abundant in nature in the form of plants, trees and grasses. The main components of lignocellulosic materials (cellulose, hemicelluloses and lignin) are at present studied intensively as renewable feedstocks for new processes to create potentially biodegradable polymeric materials and chemicals. This is driven by the demand to find renewable replacements for fossil fuel-based materials out of environmental concerns.

Cellulose has been already widely used for numerous industrial applications, such as in the paper, textile, food and pharmaceutical industries. This already

extensive use has however been limited to heterogeneous modifications whereby cellulose is mostly surface modified due to the insolubility cellulose in traditional organic solvents and water. Dissolution and chemical modification has been previously only possible with refined cellulose solvent systems, such as NMMO, DMAc/LiCl, DMSO/TBAF¹⁻³ because of insoluble nature of cellulose to conventional solvents due to the regular hydrogen bond network.

It has been known for a while that certain IL's, consisting of organic cations and organic or inorganic anions, can dissolve lignocellulosic materials efficiently at mild temperatures up to rather high concentrations (~ 35 m-%).⁴⁻⁶ It has also been proven that cellulose can be chemically and physically modified in these solvents.⁷⁻⁸ The knowledge of the rheological properties of such solutions is essential for many laboratory to industrial scale cellulose modification processes.

In this study the rheological properties of homogenous solutions of microcrystalline cellulose dissolved in two different room temperature (RTIL's), 1-allyl-3-methylimidazolium chloride ([amim]Cl) and 1,3-dimethylimidazolium

dimethylphosphate ([mmim]Me₂PO₄), were investigated (Fig. 1).

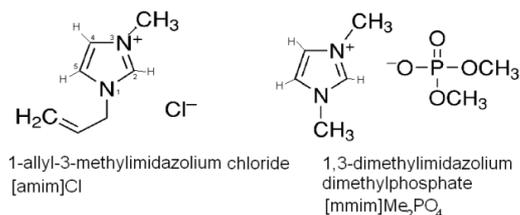


Figure 1. The structures of [amim]Cl and [mmim]Me₂PO₄.

EXPERIMENTAL

MCC was purchased from Aldrich and dried under vacuum at 50 °C before use. [amim]Cl and [mmim]Me₂PO₄ were synthesized and purified using the procedures described by Zhang et al.⁹ and Fukaya et al.¹⁰, respectively. The viscosity measurements were carried out using a TA Instruments AR2000 Stress controlled rheometer, equipped with a Peltier heated plate temperature control and a covered steel-plate geometry cell of a diameter of 20 mm. The steady state measurements were performed using shear rates varying from 1-1000 1/s.

RESULTS AND DISCUSSION

Viscosity of ionic liquids

It is widely known that IL's are considerably more viscous fluids than common molecular solvents and often the viscosity of an IL is highly dependent on temperature, which is a common feature for high viscosity material.¹¹⁻¹³ This behavior is also observed for [amim]Cl and [mmim]Me₂PO₄.

It was found that at 20 °C the viscosity of [amim]Cl is approximately ten times higher than that of [mmim]Me₂PO₄, having the value of 2.45 Pa*s. When the temperature is increased, the viscosity of [amim]Cl decreases much faster compared to [mmim]Me₂PO₄ and at 100 °C the viscosity of [amim]Cl is only two times higher than that of [mmim]Me₂PO₄. The viscosity of

IL's as a function of temperature is presented in the Fig. 2.

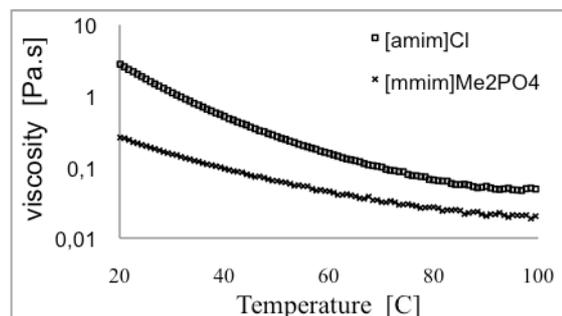


Figure 2. Viscosities of IL's as a function of temperature.

Usually solvents behave as Newtonian liquids, which mean that the viscosity is independent of the shear rate. This kind of behavior is also known for many IL's. For [amim]Cl however, Kuang et al.¹⁴ recently reported that this particular IL is not behaving as a conventional molecular solvent, but has long range density fluctuations or in other words, they form a dynamic network in the liquid state which causes the IL to behave as a shear thinning liquid. This kind of behavior was not observed in our study of pure [amim]Cl although it is well known that variation in impurities, such as water, can have significant effects on the physicochemical properties. In our studies, pure [amim]Cl as well as [mmim]Me₂PO₄ showed Newtonian behavior through a temperature range of 20-80 °C. However, the shear thinning behavior was seen in [amim]Cl-MCC solutions as they showed to be shear thinning at low temperatures and low concentrations, but at low concentrations, [mmim]Me₂PO₄-MCC-solutions are Newtonian at all temperatures.

Viscosity of MCC-IL solutions

The viscosities of the MCC-[amim]Cl and MCC-[mmim]Me₂PO₄ solutions were measured as a function of shear rate at different concentrations and temperatures. From the data it can be said that the zero

shear viscosities of MCC-[amim]Cl solutions (Fig. 3) over the range of cellulose concentrations are higher than the viscosities of the MCC-[mmim]Me₂PO₄ solutions at the same concentrations (Fig. 4).

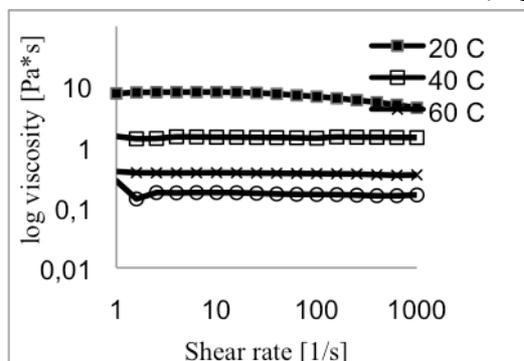


Figure 3. Viscosity of 1 m% MCC-[amim]Cl as a function of shear rate and temperature.

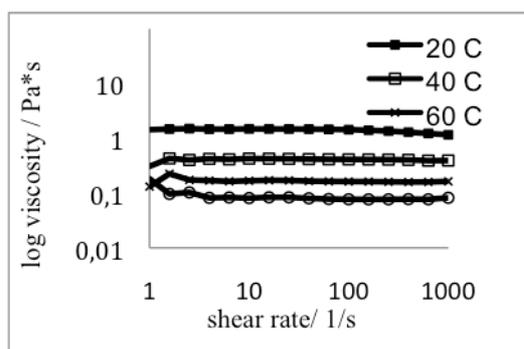


Figure 4. Viscosity of 1 m% MCC-[mmim]Me₂PO₄ solution as a function of shear rate and temperature.

Herein, it was also observed that the rheological behaviour of MCC-IL solutions is highly depended on temperature. Temperature has influence on both on the viscosity values of MCC-IL solutions and also on the solution behavior as a function of shear rate (Newtonian/ shear thinning).

When plotting the zero shear viscosities of the solutions against concentration, it can be seen that the viscosities are increased as the concentration is increased. This behavior shows linear dependence, with an increase in the slope with certain concentration, known as the critical concentration, as shown in Fig. 5 and 6 for MCC-[amim]Cl

and MCC-[mmim]Me₂PO₄ solutions, respectively. C* is independent on the temperature. The implications of this are that below the C*, the dissolved polymer coils do not interact and the concentration does not have that much influence on the viscosity. This is represented by a shallow gradient in this region compared to the gradient above C*. Above the C* the coils start to ‘feel’ each other (interact) and this is why the viscosity of the system increases sharply with concentration. To conclude, it can be said that the higher the concentration the higher is the viscosity of the system. The critical concentration (C*) for MCC-[amim]Cl was determined to be 2.33 m% and 2.63 m% for MCC-[mmim]Me₂PO₄.

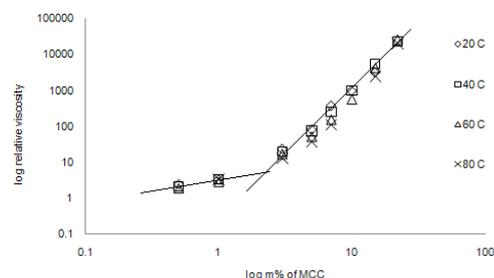


Figure 2. Relative viscosity of MCC[amim]Cl solutions plotted as a function of concentration.

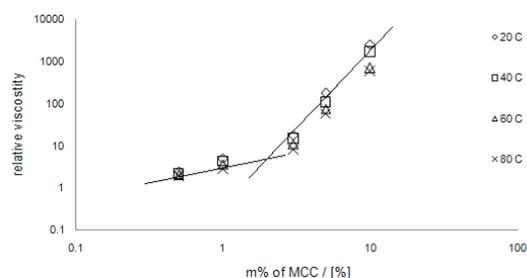


Figure 3. Relative viscosity of MCC-[mmim]Me₂PO₄ solutions plotted as a function of concentration.

Viscosities of MCC-[amim]Cl solutions

The viscosity behavior of MCC-[amim]Cl solutions as a function of shear rate is dependent on the concentration of the sample and temperature.

At low concentrations, below 2.33 m%, which is the concentration range below C* studied, the solutions behave as Newtonian liquids and the viscosity is not dependent on

the shear rate in the temperature range 60-80 °C. However, at 20-40 °C they are shear thinning, which can be due [amim]Cl, which shows shear thinning behavior at low temperatures in a pure state. These solutions are shear thinning at high concentrations, above the C^* and over the whole temperature range.

Viscosity of MCC-[mmim]Me₂PO₄

The viscosity behavior of MCC-[mmim]Me₂PO₄ solutions, as a function of shear rate, are dependent on the concentrations and temperatures. For low concentrations, below M_c 2.63 m% of MCC in IL, the solutions behave as Newtonian liquids and the viscosity is not dependent on the shear rate, in the temperature range 40-80 °C. However, at 20 °C they are shear thinning. At high concentrations, over the whole temperature range, these solutions are non-Newtonian and shear thinning.

CONCLUSIONS

The viscosities of MCC-[amim]Cl- and MCC-[mmim]Me₂PO₄-solutions are highly dependent on the temperature and concentration of the sample. The viscosity was found to decrease sharply when the temperature was increased, while it was found to increase drastically when the concentration was increased. At low concentrations, below the C^* values of 2.33 m% for MCC-[amim]Cl and 2.63 m% for MCC-[mmim]Me₂PO₄ and in the temperature range of 40-80 °C the samples behave like Newtonian liquids and their viscosities were found to be independent of shear rate. Above the critical concentration C^* , the entanglements of the polymer chains become more probable and the systems were found to behave like non-Newtonian shear thinning viscoelastic liquids.

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