

Comparison of rheological properties of kraft and microcrystalline cellulose dissolved in 1-butyl- 3-methylimidazolium chloride

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Abstract

Rheological behavior of kraft (KrC) and microcrystalline (MCC) cellulose dissolved in ionic liquid (IL) 1-butyl- 3-methylimidazolium chloride ([Bmim]Cl) were characterized using an advanced rheometer. Firstly, we studied experimentally the mass transport properties (viscosity and ionic conductivity) of [Bmim]Cl, [Bmim]Cl/DMAc and 0.25 wt% KrC/[Bmim]Cl/DMAc solutions at different concentration of DMAc at 25 °C. Then the shear rheology of cellulose/[Bmim]Cl solutions was studied in a range of concentrations (0.25-2 wt%) and temperatures (25-80 °C). As expected, DMAc dramatically decreases the viscosity and increases the conductivity of the solutions. The viscosity of kraft cellulose of high molecular weight was higher than that the microcrystalline cellulose of low molecular weight. All KrC/IL/DMAc and MCC/IL/DMAc solutions behave as non-Newtonian fluids. The viscosity of solutions increased with increase in solution concentration. The heightening of solution temperature lowers sharply the viscosity of the solution. The activation energy of KrC is higher than that of MCC.

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Received 11 June 2016,

Revised 26 Oct 2017,

Accepted 24 March 2018

Keywords: Cellulose; Ionic Liquid; Rheology; Viscosity-temperature; Shear viscosity.

1. Introduction

Cellulose is the most abundant natural material, but its limited solubility restricts its use in many applications. Cellulose derivatives have found applications in various fields [1, 2]. The structure of cellulose consists of both crystalline and amorphous regions, and this construction makes it difficult to be dissolved in several solvents. However, the three hydroxyl groups, inherent in each glucose residue of cellulose, result in strong hydrogen-bonding interactions and high crystallinity, thus making cellulose only dissolve in particular solvents such as DMSO/tetrabutylammonium fluoride [3] and N,N-dimethylacetamide (DMAc)/LiCl [4]. Nevertheless, these solvents are not without limitations: DMAc/LiCl, for instance, is volatile and DMSO/tetrabutylammonium fluoride is toxic. Alternatively, a new class of 'bio-friendly' solvents, ionic liquids (ILs), have recently grabbed much research attention due to their unique properties including non-volatility, non-flammability, thermal stability and ease of recycling [5-7]. Interest in room-temperature ionic liquids (ILs), considered as desirable green solvents for a wide range of separation and as reaction media for processes including catalysis, have significantly increased recently [8, 9]. Now, it has been reported that cellulose can be dissolved using room temperature ionic liquids such as 1-butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium chloride and 3-methyl-N-butyl-pyridinium chloride [10, 11]. Rheological properties of cellulose/ionic liquid solutions spanning from dilute to concentrated regimes have attracted much attention. Viscoelastic properties of cellulose in 1-allyl-3-methylimidazolium chloride (AmimCl) were studied with cellulose concentration below 3 wt% [12]. The shear rheological characterization of cellulose dissolved in ionic liquids (ILs) has received a lot of attention in recent years [13, 14]. Viscosity concentration dependences were reported for cellulose in two different kinds of IL, 1-ethyl-3-methylimidazolium acetate (EmimAc) and 1-butyl-3-methyl-imidazolium chloride ([Bmim]Cl) at various temperatures [15]. Both shear and elongation rheology of concentrated cellulose solutions was studied in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) at different temperatures [16]. The influences of co-solvent DMSO on ILs and cellulose/ILs were studied. Cellulose/IL/DMSO solutions behaved as Newtonian fluids at very low cellulose concentration, while the solution viscosity went up as the concentration increased, and exhibited a shear-thinning behavior at higher shear rates [17]. In this work, the influences of co-solvent DMAc on the viscosities of [Bmim]Cl and kraft cellulose (KrC)/[Bmim]Cl solution were first evaluated. The conductivity of [Bmim]Cl-DMAc mixtures and 0.25% KrC/[Bmim]Cl-DMAc were investigated at several temperatures, then the rheological properties of KrC/[Bmim]Cl solutions were systematically studied with a concentration range of 0,25-2 wt% at different temperatures (25 °C, 40 °C, 60 °C and 80 °C), and compared with those of microcrystalline cellulose MCC/[Bmim]Cl solutions. Finally, the activation energy for cellulose/[Bmim]Cl solutions as a function of concentration of the cellulose was calculated from the Arrhenius approximation.

2. Materials and methods

2.1. Materials

Bleached kraft cellulose with a degree of polymerization (DP) higher than 1000, provided by the company « Cellulose of Morocco », and commercialized microcrystalline cellulose of DP = 200 (Powder Aldrich Chemical), were used. The cellulose was dried for 6 h at 60 °C until constant weight before use. The IL 1-butyl-3-methyl-imidazolium chloride ([Bmim]Cl) was synthesized in laboratory [10]. N,N-dimethylacetamide (DMAc) was purchased from Aldrich Chemical.

2.2. Synthesis of 1-N-butyl-3-methylimidazolium chloride

The 1-méthylimidazole (8,21 g - 0,1 mol) and butane chloride (20 g - 0,2 mol) at a molar ratio 1:2 were added to a round-bottomed flask fitted with a reflux condenser for 48 h at 80 °C till the formation of a colorless viscous liquid.

The unreacted chemical reagents and other impurities, such as water, were removed by vacuum distillation, and the obtained product, (Bmim)Cl, was a viscous liquid.

2.3. Dissolution of cellulose in Ionic Liquid [Bmim]Cl

The ionic liquid (9.975 - 9.8 g) was preheated at 80 °C and then the cellulose 0.025 - 0.2 g (0.15-1.23 mmol) was added. This mixture was stirred with a magnetic stirrer at 80 °C for a maximum of 2 h. The solubility of cellulose in the ionic liquid was checked visually. The mixtures Cellulose-IL-DMAc and IL-DMAc with various concentrations of DMAc from 0% to 50% were prepared under continuous stirring for at least 15 min, and all solutions appeared transparent and homogenous when cooled to room temperature. These solutions were stored in a desiccator over P2O5 before measurement.

2.4. Characterization

The rheological behavior of cellulose/IL solutions were measured with a HAAK MARS advanced rheometer, equipped with cone-plate geometry (diameter: 35 mm, cone angle 1°). The temperature was controlled by a high power system that provided fast and precise adjustment of the temperature during heating and cooling stages. Then the measurements of the shear viscosity (η) were performed by applying an increasing shear stress ramp at a constant stress rate. All experiments were conducted at temperatures of 25 °C, 40 °C, 60 °C and 80 °C. The zero shear viscosity was determined by the ORIGIN 6.0 graphing software. The conductivity of [Bmim]Cl/DMAc and cellulose/[Bmim]Cl/DMAc solutions was measured by conductimeter type CD 810. The water absorption for [Bmim]Cl could not be avoided during the rheological measurements, but it could be neglected within one hour of experimental duration because of the reproducibility of time-temperature superposition [12]. In order to estimate the testing experimental error, the measurement of each solution was repeated twice. Errors were found to be within 4%.

3. Results and Discussions

3.1. Effect of DMAc on the viscosity of [Bmim]Cl and kraft cellulose/[Bmim]Cl

The influence of DMAc concentration on rheological properties of [Bmim]Cl and kraft cellulose/[Bmim]Cl solutions was evaluated. 0.25 wt% kraft cellulose/[Bmim]Cl/DMAc solutions with 0-50 wt% DMAc concentration were studied. Fig.1 illustrates the viscosities variation of [Bmim]Cl/DMAc mixture and KrC/[Bmim]Cl/DMAc solution as a function of molar fraction of DMAc (χ_{DMAc}) at 25 °C. It can be seen that the viscosity shear of [Bmim]Cl/DMAc and KrC/[Bmim]Cl/DMAc solutions decrease exponentially when the molar fraction of DMAc is increased. Through linear-fitting to the inset, the constant α of 0.14 was obtained for [Bmim]Cl/DMAc, indicating the viscosities of the mixtures can be excellently described by equation (1). Therefore, according to equation (1) and the constant α , the viscosities of BmimCl-DMAc mixtures can be predicted by the concentrations of the mixtures at 25 °C.

$$\eta = \eta_{\text{IL}} \exp \left[-\frac{\chi_{\text{DMAc}}}{\alpha} \right] \quad (1)$$

Where η_{IL} is the viscosity of pure IL, χ_{DMAc} is the molar fraction of DMAc, α is a IL dependent constant, is generally followed. Fig.2 shows the shear rate dependence of the shear viscosity of [Bmim]Cl/DMAc solutions with varying DMAc concentrations at 25 °C. All solutions exhibit shear-thinning behavior at DMAc concentrations below 20 %, it is well known that larger cations make [Bmim]Cl more viscous because of the increased intermolecular van der Waals interactions, in contrast, the [Bmim]Cl/DMAc solutions behave as Newtonian liquids in a concentration range 30-50 % of DMAc; this kind of behavior holds true also for many molecular solvents. In previous studies, it has been demonstrated that co-solvents such as DMSO, as well as the impurities, like chloride ion [Cl⁻] and water, can strongly affect the physical properties of ILs such as solvation, viscosity and polarity [17, 18]. The organic solvent DMAc,

providing stronger ion-solvent interactions with [Bmim]Cl, affect and reduce the viscosity of [Bmim]Cl solutions. All solutions of kraft and microcrystalline cellulose behave as non Newtonian liquids at different DMAc concentrations, which mean that the viscosity is dependent from the shear rate. Similar results were reported in the literature [17].

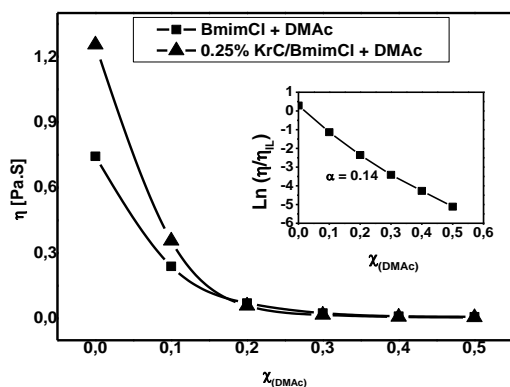


Fig. 1 Viscosity as a function of molar fraction of DMAc for [Bmim]Cl-DMAc mixture and 0.25 wt% kraft cellulose/[Bmim]Cl/DMAc solution at 25 °C

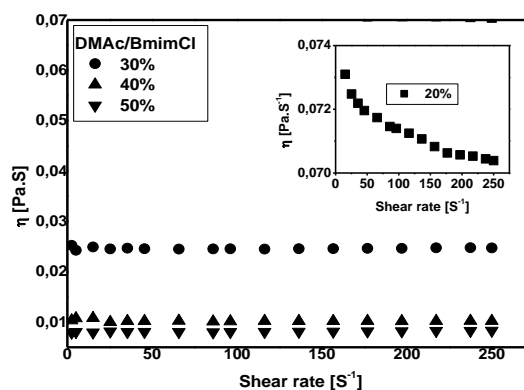


Fig. 2 Viscosity as a function of shear rate for [Bmim]Cl-DMAc mixture at different DMAc concentration at 25 °C

3.2. Effect of DMAc on the conductivity of [Bmim]Cl and kraft cellulose/[Bmim]Cl

Generally, IL conductivity is proportional to the number of charge carrier ions and their mobility of its cation because the diffusion coefficients of ILs cations are higher than anions [19]. For example, [Bmim]Cl and [Bmim]BF₄ shows conductivity value of 460 μS/cm and 1180 μS/cm respectively which is comparatively small [20, 21]. After anion exchanging, the conductivity could be increased. So, as compared to traditional organic solvents, IL has great advantages [22]. The ionic liquids are miscible with liquids of medium to high dielectric constant and immiscible with liquids with low dielectric constant [23, 24]. The effect of DMAc on the conductivity of [Bmim]Cl and KrC/[Bmim]Cl solution was studied over the temperature range 25 °C to 120 °C. Fig.3 shows the conductivity of [Bmim]Cl/DMAc and 0.25 % KrC/BmimC/DMAc as a function of molar fraction of DMAc. It can be seen that the mixing an IL and cellulose/IL solution with a co-solvent (DMAc) leads to a dramatically variation of conductivity of the medium. However, when the molar fraction of DMAc is increases the conductivity of IL and KrC/IL solution increases up to obtain a maximum value. This is due to the dissociation of ion pairs that is more efficient with organic solvent DMAc of high dielectric constante (37.8) and enhanced the transport parameters of the IL. The conductivity maximum was obtained at $\chi_{\text{DMAc}} \approx 0.83$ for [Bmim]Cl + DMAc is 5.25 mS/cm at T = 25 °C, while in the case of 0.25 % KrC/IL the maximum is at 5.8 mS/cm. One can observe that the conductivity of KrC/[Bmim]Cl is lower to that of [Bmim]Cl/DMAc at low molar fraction of DMAc (less than 0.2), and conversely when χ_{DMAc} is superior to 0.2. In addition, the influence of temperature on the conductivity of [Bmim]Cl, 0.25 % KrC/[Bmim]Cl and 0.25 % KrC/BmimCl/DMAc solutions with $\chi_{\text{DMAc}} \approx 0.2$ was investigated in the temperature range of 25-120 °C (Fig. 4). As it is expected, conductivity of [Bmim]Cl, [Bmim]Cl/DMAc and KrC/[Bmim]Cl/DMAc solutions increases with temperature, because mobility of ions also increases. Therefore, when starting from a pure IL, either addition of an organic solvent or increase in temperature induces significant modification of conductivity. It can be noticed that the conductivity of cellulose/IL is higher than that the pure [Bmim]Cl at the same temperature.

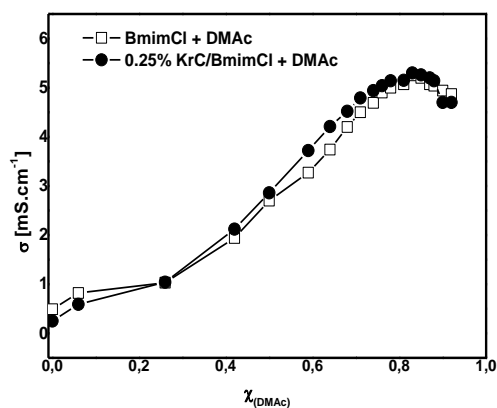


Fig. 3 Conductivity of BmimCl/DMAc mixture and 0.25% KrC/IL/DMAc solution vs. molar fraction of co-

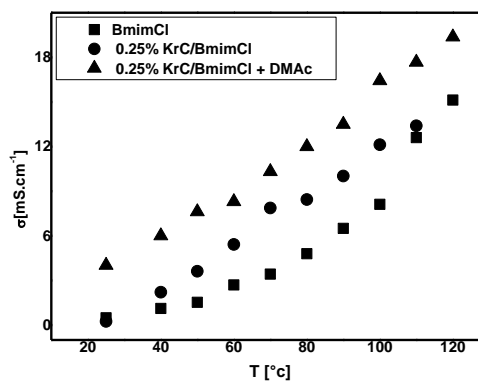


Fig. 4 Effect of temperature on conductivity of IL, 0.25% KrC/IL and 0.25% KrC/IL/DMAc ($\chi_{DMA} \approx$

3.3. Comparison of Rheological properties of KrC/[Bmim]Cl and MCC/[Bmim]Cl solutions

The viscosities of the KrC/[Bmim]Cl and MCC/[Bmim]Cl solutions were measured as a function of shear rate at different concentrations (0.25, 0.5, 1.0 and 2 wt%), and at different temperatures (25 °C, 40 °C, 60 °C and 80 °C). Fig. 5a depicts the viscosity profiles of KrC/IL and MCC/IL solutions at 25 °C at different concentrations. These data show that the viscosities of KrC/IL solutions are higher than the viscosities of the MCC/IL solutions, at the same concentrations and for the whole temperature range. The difference between the rheological behavior of kraft cellulose and microcrystalline cellulose is clarified further by the viscosity curves of KrC/IL and MCC/IL solutions at 25 °C and 40 °C, and with 0.25 wt% concentrations (Fig. 5b). The data in this figure make it clear that the viscosities of KrC/IL solutions, over the range of cellulose concentrations, are higher than the viscosities of the MCC/IL solutions at the same temperature. To summarize, the viscosity of KrC/IL is higher than that of MCC/IL solutions with the same concentration and at a constant temperature. One can speculate that this could be due to the difference in the degree of polymerization; the kraft cellulose generally has a higher molecular weight, and longer and greater entangled chains than microcrystalline cellulose. The chain length of the cellulose polymer varies depending on the cellulose source. For example, naturally-occurring vascular plant cellulose has a degree of polymerization (DP) higher than 10000. The value of DP is greatly dependent on the method of isolation [25]. The KrC/IL and MCC/IL solutions behave as non-Newtonian liquids and that the viscosity is dependent on the shear rate in the temperature range 25-80 °C. The viscosity behaviors of KrC/IL and MCC/IL solutions as a function of shear rate are dependent on the concentration and the temperature of the studied sample. As expected, the viscosity increases with increasing cellulose concentration due to the increase in the local intermolecular interactions between the polymer chains (entanglements) (Fig. 6). At studied shear rates, the disruption rate of the entanglements is balanced by the rate of the creation of new ones, resulting in constant viscosity (Newtonian behavior). Inversely, the disentanglement of the polymer coils in solution and the superiority of the rate disruption of interactions to that of the formation of new interactions lead to an alignment of the elongated polymer chains in the flow direction and consequently cause a fall in viscosity (shear-thinning behavior) [26].

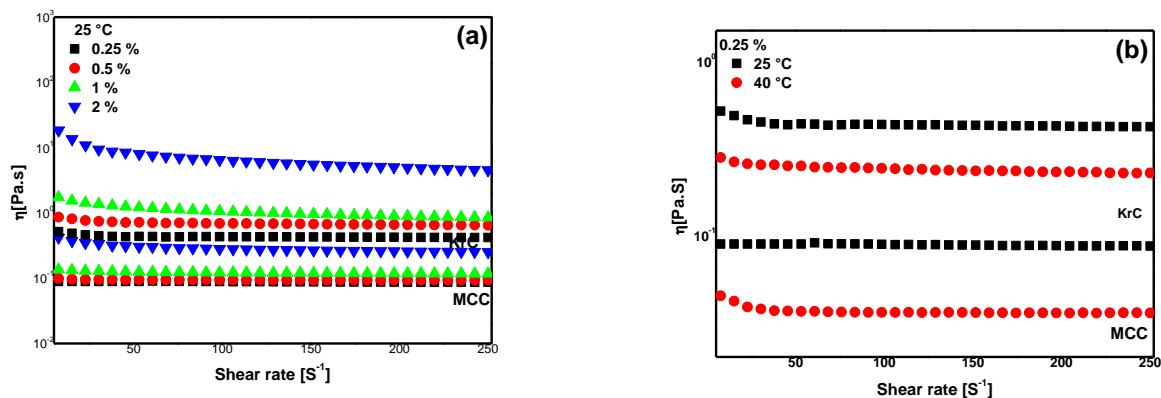


Fig. 5. Viscosity as a function of shear rate for KrC/IL and MCC/IL at different concentration (a) and at different temperature (b)

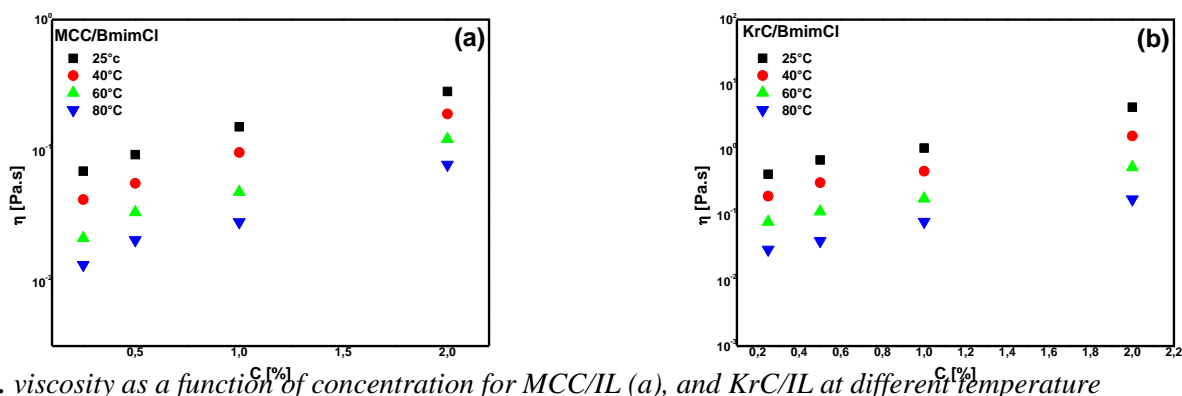


Fig. 6. viscosity as a function of concentration for MCC/IL (a), and KrC/IL at different temperature (b)

3.4. Rheological properties as a function of temperature

The effect of temperature on viscosity of KrC/[Bmim]Cl and MCC/[Bmim]Cl solutions is shown in Fig. 7. The viscosity-shear of solution significantly decreased with increment of temperature. It follows from this that the rheological behavior of cellulose/[Bmim]Cl solutions is highly dependent on temperature. For clarity sake, temperature-sweep measurements were carried out by applying zero-shear rates with values being picked within the plateau of constant Newtonian viscosity, depending on each constituent concentration, and by varying the temperature from 0 °C to 80 °C. All curves in the investigated concentration regime show that the behavior of the polymer solutions changed monotonically: the viscosity decreased when the temperature increased. The influence of temperature on the solution viscosity could be explained as follows: the viscous flow of polymer can be pictured as taking place by the movement of molecules or segments of molecules in jumps from one place in a lattice to a vacant hole [27]. The total "concentration hole" can be regarded as a space free of polymer, or "free volume" [28].

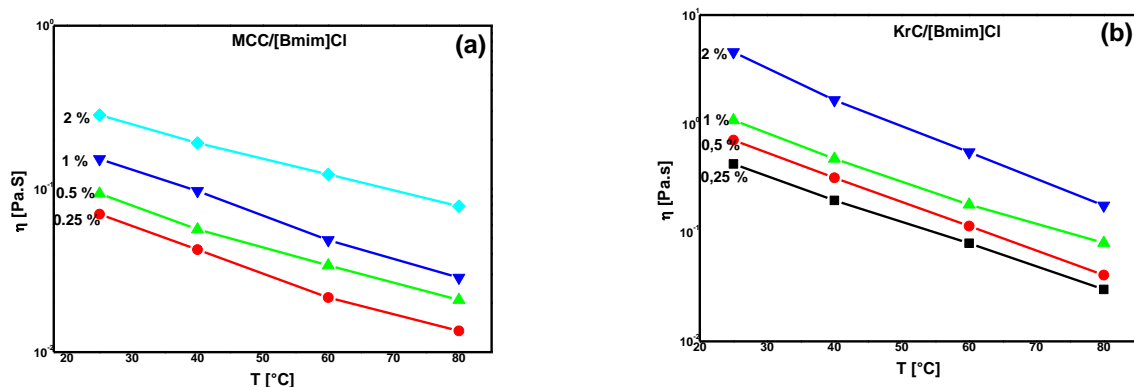


Fig. 7. Viscosity-shear as a function of temperature for MCC/[Bmim]Cl (a), and KrC/[Bmim]Cl (b)

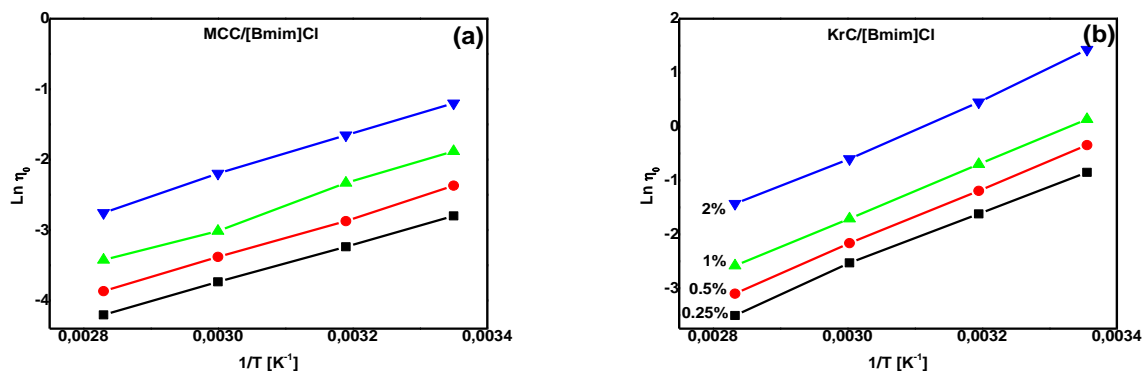


Fig. 8. Arrhenius plot for the zero shear viscosity of all solutions concentrations of MCC/[Bmim]Cl (a) and KrC/[Bmim]Cl (b)

Fig. 8 shows the relationship between the logarithm of a η_0 and the reciprocal of the absolute temperature, $1/T$, for KrC/[Bmim]Cl and MCC/[Bmim]Cl solutions at different cellulose concentrations. For a macromolecular material, the influence of temperature on steady rheological property can usually be illustrated by viscose activation energy (E_a), which can be calculated according to Arrhenius equation,

$$\eta_0(T) = \eta(\infty) \exp\left(\frac{E_a}{RT}\right)$$

Where η_0 is zero shear viscosity of the solvent at temperature T , $\eta(\infty)$ is a constant, T is temperature in K, and R the universal gas constant. The experimental dependences of $\ln(\eta_0)$ versus $1/T$ can be considered as linear (with a reasonable standard deviation of 0.992), from the slope of the linear fit of $\ln(\eta_0)$ versus $1/T$, the activation energy for each concentration of KrC/[Bmim]Cl and MCC/[Bmim]Cl solutions was calculated using the Arrhenius approach as shown in fig. 9. The activation energy increases with the increase of cellulose concentration, since intermolecular hydrogen bond interaction of hydroxyl groups on the cellulose molecules is strongly promoted. This trend is also reported by other groups on cellulose/ILs solutions [17]. The activation energy for MCC/[Bmim]Cl and KrC/[Bmim]Cl solutions varies respectively between 22.4-26.8 kJ/mol, and 42-45.4 kJ/mol. It is concluded that activation energy for kraft cellulose is higher than that of the microcrystalline cellulose at the same cellulose concentration.

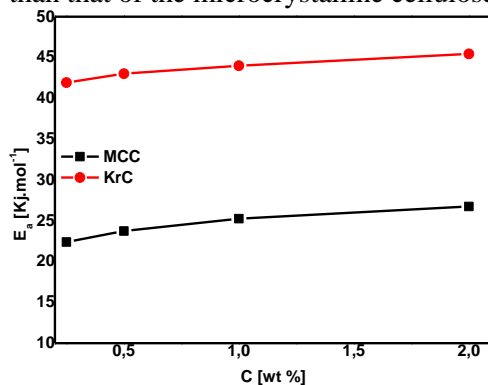


Fig. 9. Activation energy of kraft and microcrystalline cellulose as a function of concentration (C wt%)

4. Conclusion

In this study, the effect of DMAc on the shear viscosity and ionic conductivity of [Bmim]Cl and cellulose/[Bmim]Cl were examined firstly. The results obtained indicate that the DMAc organic solvent enhanced the mass transport of [Bmim]Cl (viscosity and ionic conductivity), for kraft cellulose/[Bmim]Cl/DMAc solutions, the viscosity decreased and the conductivity increases with the increasing of molar fraction of DMAc at 25 °C. The conductivity of [Bmim]Cl, 0.25% KrC/[Bmim]Cl and 0.25 % KrC/[Bmim]Cl/DMAc (χ_{DMAc}) increases sharply when temperature increased. Systematic studies were performed on the rheological properties of MCC/IL and KrC/IL solutions with a concentration range of 0.25-2 wt% and at different temperatures, using a rheometer. The viscosities of Kraft

cellulose/IL and MCC/IL solutions are highly dependent on the temperature and concentration of the sample. The viscosity was found to decrease sharply when the temperature increased, while it drastically increased with the concentration increase. The dependence on concentration and molecular weight shows that entanglements play an important role in the rheological behaviors of cellulose/[Bmim]Cl solutions. The viscosity of high molecular weight cellulose was higher than low molecular weight cellulose (MCC). All solutions, the entanglements of the polymer chains became more probable and the systems exhibited a shear-thinning behavior at shear rates in range 0,01-250 S⁻¹. The zero shear rate activation energy (E_a) of microcrystalline and kraft cellulose varied respectively between 22.3 - 27.8 kJ/mol, and 42 - 45.5 kJ/mol, as calculated from the Arrhenius equation. The E_a increases when the concentration increases. This study will hopefully lead to a better understanding of the interactions brought about by the dissolution of cellulose in [Bmim]Cl, thereby paving the way for the adoption and utilization of such systems in industrial applications.

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