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Rheological and hydrodynamic properties of cellulose acetate/ionic liquid solutions

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ABSTRACT

Rheological properties of cellulose acetate/1-ethyl-3-methylimidazolium acetate (EMIMAc) solutions are studied using shear dynamic and steady state rheology in a large range of polymer concentrations (from 0.1 to 10 wt.%) and temperatures (from 0 °C to 80 °C). Master plots for storage and loss moduli and for dynamic viscosity were built and shift parameters determined. Cellulose acetate/EMIMAc behaves as a classical polymer solution and obeys Cox–Merz law. Cellulose acetate intrinsic viscosity $[\eta]$ was determined as a function of temperature and compared with the literature data for cellulose acetates dissolved in other solvents and cellulose dissolved in EMIMAc. Cellulose acetate intrinsic viscosity turned out to be much less temperature sensitive than that of cellulose. Specific viscosity-C$[\eta]$ master plot was built: the slopes in log–log scale are 1.2 and 3.1 in dilute and semi-dilute regions, respectively. The activation energy as a function of concentration follows a power-law dependence.

1. Introduction

Cellulose-based polymers and materials have been known for more than one century; however, in our days they attract a lot of attention due to the demand in replacing synthetic polymers by biomass-based ones. The overall goals are to create new materials with targeted functional properties making polymer processing as "green" as possible.

Cellulose acetate (CA) is one of the most important cellulose esters used for numerous applications such as films, separation membranes, textiles, cigarette filters and coatings. One of the common ways of cellulose acetate processing is via dissolution followed by wet or dry casting; for example, membranes of various controlled porosity can be formed via phase inversion mechanism. At low degrees of substitution ($DS < 1$) cellulose acetate is soluble in aqueous solutions; at $DS > 1$ the solvents are inorganic systems such as acetone, chloroform, dichloromethane, methanol, formic acid, pyridine and *N*,*N*′-dimethylacetamide and their mixtures. Recently, imidazolium-based ionic liquids (ILs) were used for dissolving cellulose acetate. Room-temperature ionic liquids have very low vapor pressure, high thermal stability and polymer dissolution is very simple. These properties make ILs very attractive for processing of cellulose and cellulose derivatives. For example, 1-butyl-3-methylimidazolium thiocyanate ([BMIM]SCN) and 1-ethyl-3-methylimidazolium thiocyanate ([EMIM]SCN) were used for making flat sheet and hollow fiber cellulose acetate ultrafiltration membranes (Xing, Peng, & Chung, 2010; Xing, Peng, & Chung, 2011). It was shown that IL viscosity, being higher than those of the classical solvents, is one of the key factors affecting membrane formation and morphology. It is also important to note that it was possible to recover and reuse [BMIM]SCN for making cellulose acetate asymmetric membranes with characteristics similar to those obtained with the fresh solvent (Xing et al., 2010). Another imidazolium ionic liquid, 1-allyl-3-methylimidazolium chloride, was shown to have a strong plasticizing effect on cellulose acetate and can potentially be used for making new biomass-based polymer electrolytes (Ramesh, Shanti, & Morris, 2012).

For the processing to be successful, the understanding of the rheological properties of solutions as well as the molecular organization of the polymer in the solvent is required. The studies of the viscosity of CA/acetone or CA/*N*,*N*′-dimethylacetamide or CA/nitromethane solutions date back to the fifties of the last century (see, for example, Flory, Spurr, & Carpenter, 1958); the correlations between the molecular weight, intrinsic viscosity and sedimentation constant have been determined for cellulose acetate in various solvents and listed in handbooks. This is not the case for ionic liquids. While the rheological properties of cellulose/ionic solutions have already been extensively reported and discussed (Gericke, Schlufter, Liebert, Heinze, & Budtova, 2009; Kosan, Michels, & Meister, 2008; Kuang, Zhao, Niu, Zhang, & Wang,

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2008; Sescousse, Le, Ries, & Budtova, 2010), the understanding of the properties of cellulose acetate/ionic liquid solutions is rather limited because of fragmented studies. In Xing et al. (2010), the viscosity of CA/[BMIM]SCN solutions is measured as a function of polymer concentration but shown only for one shear rate; in Xing et al. (2011) steady state flow of CA/[EMIM]SCN is presented at various polymer concentrations but only at one temperature. Steady state and dynamic rheology of cellulose acetate/1-butyl-3-methylimidazolium chloride (BMIMCl) solutions are discussed in Wang et al. (2011); the activation energies were calculated for 8–15 wt.% CA concentrations (Wang et al., 2011); master plots for storage and loss moduli were built (Wang et al., 2011; Kosan, Dorn, Meister, & Heinze, 2010) and it was shown that Cox–Merz rule does not work, at 25 °C (Wang et al., 2011). The opened question for the latter finding is if solutions were at equilibrium as far as BMIMCl is solid at room temperature. To the best of our knowledge, the properties of CA/IL solutions in dilute concentration regime, which give such important hydrodynamic characteristics as intrinsic viscosity and overlap concentration, have never been reported.

The goal of our work was to perform an extended rheological study of cellulose acetate/IL solutions: we investigated shear dynamic and steady-state flow in semi-dilute state and polymer hydrodynamic properties in dilute state. The solvent chosen is 1-ethyl-3-methylimidazolium acetate (EMIMAc): it is a fluid in a large range of temperatures (crystallization/melting temperature is not known), non-corrosive and thermally stable up to 180 °C (Wendler, Todi, & Meister, 2012). We applied theories developed for polymer solutions and compared the results obtained with the literature data for cellulose acetates dissolved in other solvents and for cellulose/EMIMAc solutions.

2. Experimental methods

2.1. Materials

Cellulose acetate (CA) was from Sigma–Aldrich with molecular weight $M_n \sim 50\,000$ g/mol and between 39.2 and 40.2 wt.% of acetyl content, as given by the provider, which is equivalent to an average degree of substitution DS = 2.44. The ionic liquid, EMIMAc, was used as received from BASF (purity ≥90%).

2.2. Methods

2.2.1. Preparation of solutions

Cellulose acetate was dried at 50 °C under vacuum overnight prior to use. Solvent and polymer were mixed and stirred in a sealed reaction vessel at 70 °C for at least 24 h to ensure complete dissolution. Clear solutions were obtained. They were stored at room temperature and protected against moisture absorption. Concentrations are given in wt.% and recalculated, when needed, in g/mL, with the density of EMIMAc being 1.103 g/cm^3.

2.2.2. Rheology

Measurements of steady state and dynamic rheology of CA/EMIMAc solutions were performed on Bohlin Gemini rheometer equipped with cone-plate geometry (4° – 40 mm) and Peltier temperature control system. Shear rates were varied from 0.01 to 500 s^{-1} and temperatures from 0 °C to 80 °C. In dynamic mode frequency sweeps were performed at 5 Pa, corresponding to linear visco-elastic regime, in the same temperature range.

EMIMAc is highly hygroscopic and water significantly decreases its viscosity and may influence polymer/EMIMAc solution properties. To prevent moisture uptake, a thin film of low-viscosity silicon oil was placed around the borders of the measuring cell.

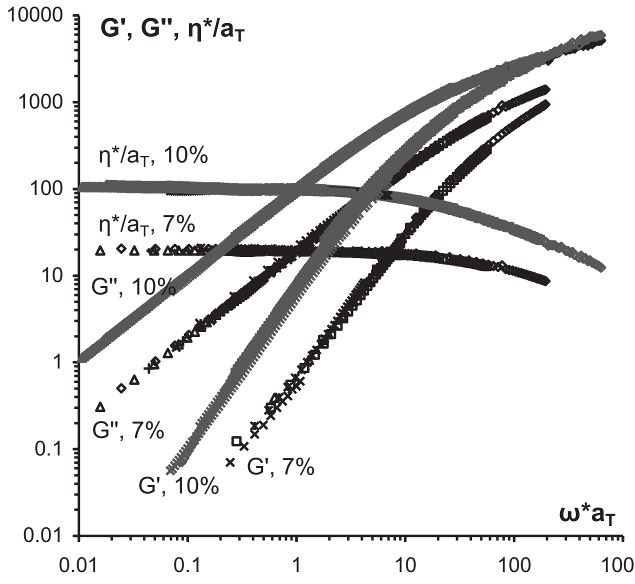

Fig. 1. Master plots of G', G'' and dynamic viscosity for 7 and 10 wt.% CA/EMIMAc solution for temperatures from 0 °C to 80 °C with 20 °C as reference.

3. Results and discussion

3.1. Dynamic and steady state rheology, Cox–Merz rule

Frequency scans of elastic $G'(\omega)$ and viscous $G''(\omega)$ moduli and dynamic viscosity $\eta^*(\omega)$ were performed for CA/EMIMAc solutions of various polymer concentrations at different temperatures. For each polymer concentration, time-temperature superposition principle was applied and master plots were built by shifting the experimental data by the corresponding a_T values. An example for 7 and 10 wt.% CA/EMIMAc solutions is given in Fig. 1; temperatures from 0 °C to 80 °C with a step of 10 °C are included in this plot and the reference temperature is 20 °C. a_T parameters used for building master plots for 5, 7 and 10 wt.% cellulose acetate solutions as a function of temperature are shown in Fig. 2.

Fig. 1 shows that cellulose acetate dissolved in EMIMAc behaves as a classical unentangled polymer solution with $G'' > G'$ over the entire frequency range studied (five decades) and with power law exponents $G' \sim \omega^x$ and $G'' \sim \omega^y$ at low frequencies being $x = 1.74$ and $y = 0.97$ for 10% solution; $x = 1.6$ and $y = 0.96$ for 7% solution and $x = 1.59$ and $y = 0.97$ for 5% solution (not shown in order not to overload the graph). The deviation from the theoretical exponents

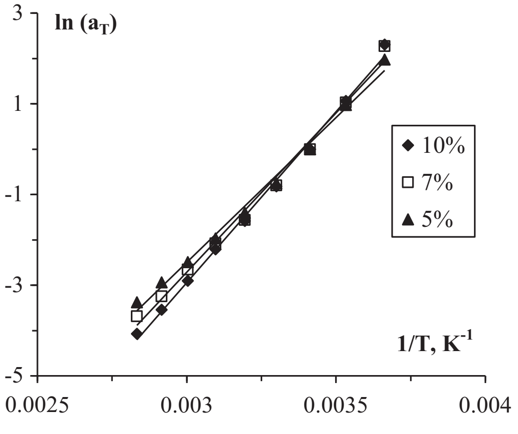

Fig. 2. a_T shift factor as a function of temperature for 5, 7 and 10 wt.% CA/EMIMAc solutions.

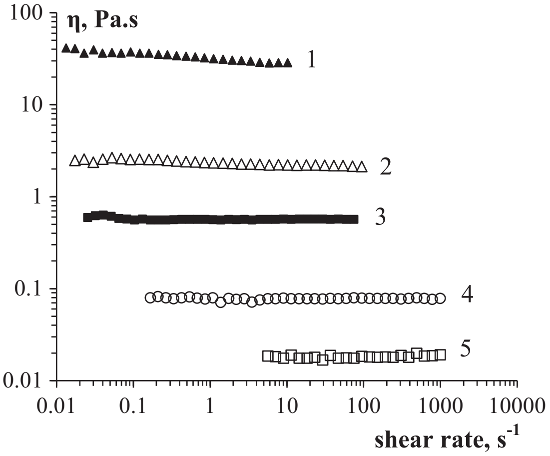

Fig. 3. Examples of flow curves for cellulose acetate–EMIMAc solutions of different concentrations and temperatures: 10% CA at 40 °C (1) and 80 °C (2); 0.5% CA at 10 °C (3), 40 °C (4) and 80 °C (5).

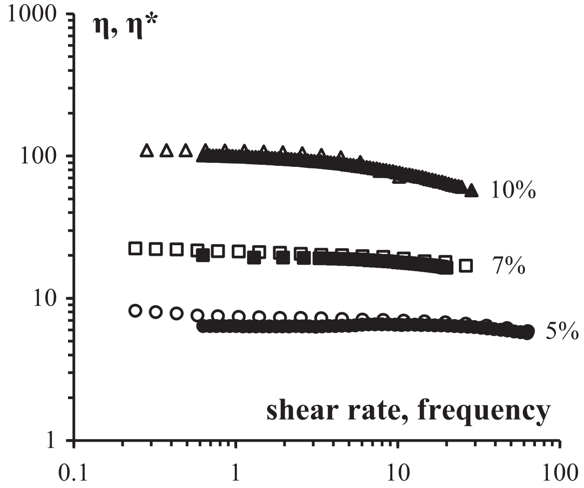

Fig. 4. Illustration of Cox–Merz rule for 5, 7 and 10 wt.% cellulose acetate–EMIMAc solutions at 20 °C, dark points correspond to dynamic viscosity and open points to steady state viscosity.

predicted by Maxwell approach describing visco-elastic response of a fluid, $x = 2$ and $y = 1$, is most probably related to polymer polydispersity.

Fig. 2 shows the shift factor, a_T, as a function of temperature, for three cellulose acetate concentrations, 5, 7 and 10%, all for the reference temperature of 20 °C. a_T allows a complete reconstruction of G', G'' and dynamic viscosity at any temperature and also a determination of the activation energy E_a. The latter is calculated using Arrhenius law:

$$a_T = \exp\left[\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] \tag{1}$$

where R is ideal gas constant, T is temperature in °K and T_{ref} the reference temperature. The slopes of $\ln(a_T)$ versus $1/T$ shown in Fig. 2 give the activation energy of 53 kJ mol^{-1} for 5 wt.%, 58 kJ mol^{-1} for 7 wt.% and 63 kJ mol^{-1} for 10 wt.%. These values will be compared later with the ones obtained from steady-state viscosity measurements.

Some examples of steady state flow curves of cellulose acetate/EMIMAc solutions for various concentrations and temperatures are given in Fig. 3. For all solutions, a Newtonian plateau was observed for at least one-two decades of shear rates. At high viscosities (corresponding to low temperatures and high concentrations) a beginning of shear thinning was observed. It is clear that the viscosity of cellulose acetate/EMIMAc solutions decreases with increasing temperature and decreasing concentration. This behavior has been already reported for cellulose/EMIMAc solutions (Gericke et al., 2009; Sescousse, Le, Ries, & Budtova, 2010). The mean values of viscosity at the Newtonian plateau at all concentrations and temperatures were calculated and used for further analysis.

It was interesting to check if cellulose acetate/EMIMAc solutions obey Cox–Merz rule, which is the case of "ordinary" polymer solutions. Frequency dependence of complex viscosity and shear rate dependence of steady-state viscosity are plotted for the same solutions in Fig. 4. Data sets corresponding to the same polymer concentration/temperature agree perfectly demonstrating that classical polymer theories can be applied to describe the properties of cellulose acetate/EMIMAc solutions.

The influence of cellulose acetate concentration C on solution viscosity η_0 (taken as a mean value from Newtonian region) at some selected temperatures is presented in Fig. 5; solvent viscosities ($C = 0$) are also included, data are shown in a semi-logarithmic scale. These data will serve a background for the calculation of the intrinsic viscosities and overlap concentrations.

3.2. Intrinsic viscosity and overlap concentration as a function of temperature

Polymer intrinsic viscosity $[\eta]$ is an important characteristic of a dissolved polymer as it gives information about the size of the macromolecule and the thermodynamic quality of the solvent. The "standard" method to determine intrinsic viscosity is to use Huggins approach: solution is gradually diluted with the solvent in Ubbelohde capillary viscometer and $(\eta_{rel} - 1)/C$ is plotted versus polymer concentration C, where $\eta_{rel} = \eta_{sol}/\eta_{solv}$, η_{sol} and η_{solv} being solution and solvent viscosity, respectively. Intrinsic viscosity is deduced as a limiting value at infinite dilution ($C \to 0$). Polymer concentration here is expressed in mass per volume units. We used solvent (EMIMAc) density equal to 1.1 g/cm^3 which is a mean value between 1.08 at 90 °C and 1.12 g/cm^3 at 20 °C (Sescousse et al., 2010). This small variation of density with temperature can be

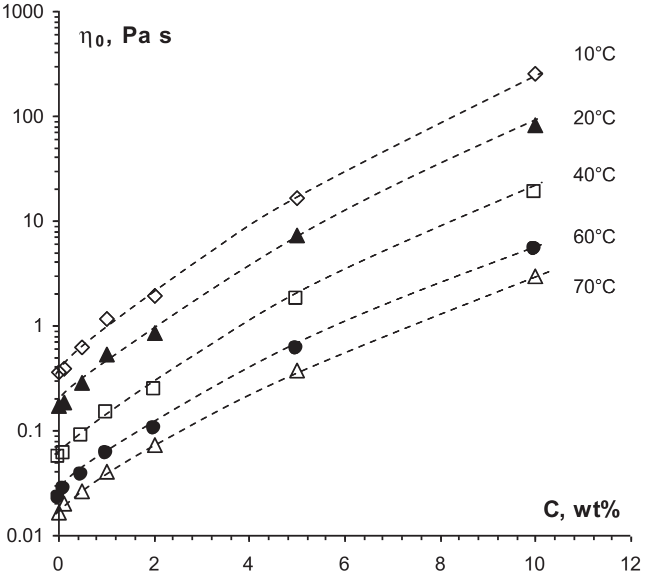

Fig. 5. Cellulose acetate/EMIMAc Newtonian viscosity as a function of polymer concentration at 10, 20, 40, 60 and 70 °C. Dashed lines are given to guide the eye.

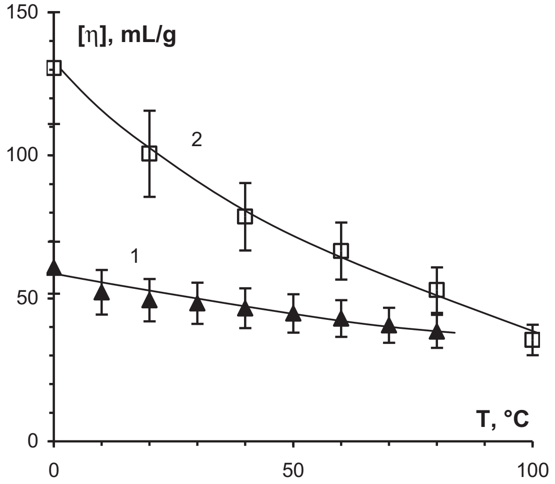

Fig. 6. Intrinsic viscosity as a function of temperature for cellulose acetate (1) and microcrystalline cellulose (2) (data taken from Gericke et al., 2009), both polymers are dissolved in EMIMAc. Lines are given to guide the eye.

neglected in the calculation of the intrinsic viscosity in the view of all other accumulated errors.

It was not possible to perform measurements in a capillary Ubbelohde viscometer because EMIMAc is too viscous and too hygroscopic to be studied in contact with the air. We used solution and solvent mean Newtonian viscosity values presented in Fig. 5. Wolf approach was applied to calculate the intrinsic viscosity (Wolf, 2007; Eckelt et al., 2011) as far as data presented in the classical Huggins plot were somewhat scattered (due to averaging of Newtonian viscosity) and do not allow an adequate $[\eta]$ determination. Briefly, Wolf approach consists in the calculation of the limiting slope of $\ln(\eta_{rel})$ versus C which, according to phenomenological considerations, is identical to the intrinsic viscosity (Wolf, 2007). Being developed for polyelectrolyte solutions, this approach can also be successfully used for uncharged polymers. Indeed, both Huggins and Wolf approaches gave the same cellulose intrinsic viscosity values for cellulose dissolved in NMMO monohydrate (Eckelt et al., 2011); Wolf approach was also used for determination of amylopectin intrinsic viscosity in EMIMAc (Liu & Budtova, in press). When possible, we calculated cellulose acetate intrinsic viscosity with both Huggins and Wolf approaches and got the same values.

Fig. 6 displays cellulose acetate intrinsic viscosity as a function of temperature. The same dependence for microcrystalline cellulose of DP = 300 dissolved in EMIMAc (Gericke et al., 2009) is also shown for comparison. $[\eta]$ decreases with increasing temperature for both polymers. This trend for cellulose esters had already been reported (see, for example, Flory et al., 1958; Suzuki, Miyazaki, & Kamide, 1980). The influence of temperature on the intrinsic viscosity was attributed to the change in the unperturbed chain dimension. The slopes of $\Delta(\ln[\eta])/\Delta T$ vary for cellulose acetate with DS = 2.86 and $M_\eta = 9 \times 10^4$ from $4.5 \times 10^{-3}\,°\mathrm{C}^{-1}$ when dissolved in *m*-cresol to $6.6 \times 10^{-3}\,°\mathrm{C}^{-1}$ in dimethylformamide (Flory et al., 1958); for cellulose acetate with DS = 2.46 and $M_w = 9.5 \times 10^4$ dissolved in acetone it was $6.9 \times 10^{-3}\,°\mathrm{C}^{-1}$ (Suzuki, Miyazaki, & Kamide, 1980). The slope $\Delta(\ln[\eta])/\Delta T$ obtained for cellulose acetate dissolved in EMIMAc is falling in the same interval as for the ones cited above: $5.9 \times 10^{-3}\,°\mathrm{C}^{-1}$. For microcrystalline cellulose dissolved in EMIMAc it is twice higher, $1.2 \times 10^{-2}\,°\mathrm{C}^{-1}$. Cellulose turned out to be much more temperature sensitive than cellulose acetate. At least two reasons explaining this result can be given. One is that cellulose starts to degrade at lower temperatures than cellulose acetate. The second is related to chain flexibility: in general, cellulose esters have higher Kuhn segment length than that of cellulose, they are thus less flexible and may less contract under temperature.

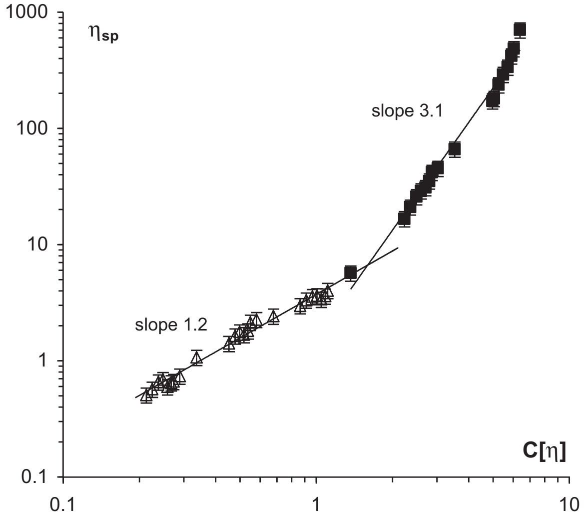

Fig. 7. Master plot of specific viscosity versus $C[\eta]$ for cellulose acetate–EMIMAc solutions for temperatures from 0 °C to 80 °C and concentrations from 0.1 to 10 wt.%.

Below 50 °C the values of cellulose acetate intrinsic viscosities are twice lower than the ones of microcrystalline cellulose dissolved in EMIMAc, despite the fact that both polymers are of a comparable molecular weight. A similar finding, i.e. the decrease of zero shear rate viscosity with the increase of the degree of acetylation, was reported for cellulose and cellulose acetate of the similar DP dissolved in BMIMCl (Kosan et al., 2010). It was interpreted by the fact that the increase of degree of acetylation decreases intra- and intermolecular interactions (via hydrogen bonding) between cellulose chains. We suggest that EMIMAc is thermodynamically a better solvent for cellulose than for cellulose acetate. To answer this intriguing question other experimental techniques and more experimental data are needed. The advantage of ionic liquids versus other cellulose solvents is that imidazolium ionic liquids allow dissolution of both cellulose and cellulose acetate and a direct comparison is possible.

Using the intrinsic viscosity obtained, a master plot of specific viscosity $\eta_{sp} = \eta_{rel} - 1$ as a function of $C[\eta]$ for all solution temperatures and concentrations studied was built (Fig. 7). All experimental points fall very well on one double-logarithmic plot. Fig. 7 shows that the slope in the dilute region is 1.2 (i.e. slightly greater than linear concentration-dependence of viscosity). The slope of 1.2–1.4 had already been reported for various polysaccharide solutions (see, for example, Morris, Cutler, Ross-Murphy, & Rees, 1981). In the semi-dilute region, the slope value is 3.1; at higher concentrations it seems to increase but more data are needed to provide a meaningful value. The change of the slope occurs at $C[\eta] \approx 1.4$–1.5.

The overlap concentration C^* divides dilute and semi-dilute concentration regions and is usually defined as the inverse of the intrinsic viscosity $C^* = 1/[\eta]$. According to Fig. 7 cellulose acetate overlap concentration should be roughly $C^* = 1.4/[\eta]$. C^* increases with temperature increase: it varies from ≈22 to 36 mg/mL (equivalent to 2.1–3.4 wt.%) for temperatures from 0 °C to 80 °C, respectively. For comparison, $C^* = 14$ mg/mL was obtained when cellulose acetate was dissolved in dimethylacetamide (neither polymer molecular weight nor exact temperature reported) (Hornig & Heinze, 2008). For cellulose acetate of DS = 2.86 and molecular weight of about 90 000 the overlap concentration varied for temperatures from 20° to 100 °C from 3 to 5 mg/mL in DMF, from 4 to 6 mg/mL in m-cresol and from 6 to 9 mg/mL for tetrachloroethane (Flory et al., 1958); for cellulose acetate of DS = 2.46 and $M_w = 9.4 \times 10^4$ C^* varies from 6 to 8 mg/mL in acetone for temperatures from 10 °C to 50 °C, respectively (Suzuki, Miyazaki, &

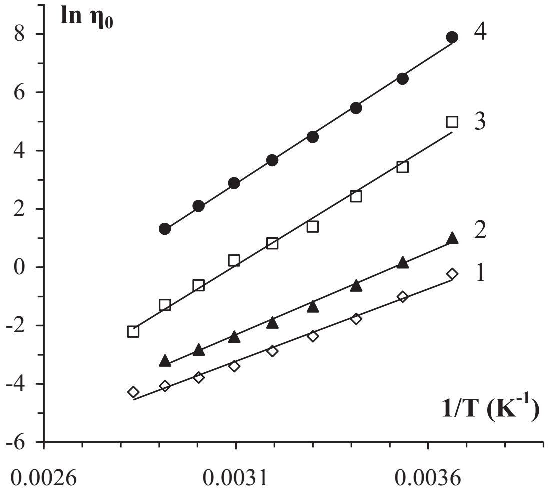

Fig. 8. Arrhenius plots for EMIMAc (1) and cellulose acetate/EMIMAc solutions: 1% (2), 7% (3) and 12% (4). Lines are linear approximations.

Kamide, 1980). In overall, cellulose diacetate overlap concentration values in EMIMAc are higher than those reported in other solvents indicating that m-cresol, tetrachloroethane, DMF and acetone are thermodynamically better solvents for cellulose acetate as compared with EMIMAc.

3.3. Activation energy

Temperature dependence of Newtonian steady state viscosity is usually analyzed with the Arrhenius approach, similar to Eq. (1): $\eta_0 = A\exp(E_a/RT)$ where A is an adjustable parameter. The activation energy is determined by the slope of $\ln(\eta_0)$ versus $1/T$ when the dependence is linear. Some examples of Arrhenius plots for cellulose acetate–EMIMAc solutions at different concentrations are given in Fig. 8. As already reported, $\ln(\eta)$ versus $1/T$ dependence for EMIMAc is slightly concave (Gericke et al., 2009; Sescousse et al., 2010) which comes from intrinsic properties of EMIMAc. The activation energy may thus depend on the temperature interval selected. Higher is cellulose acetate concentration, less pronounced is the deviation from the Arrhenius law. Since the temperature interval studied is the same for both solvent and polymer solution, we considered that in the first approximation Arrhenius approach can be applied to our data.

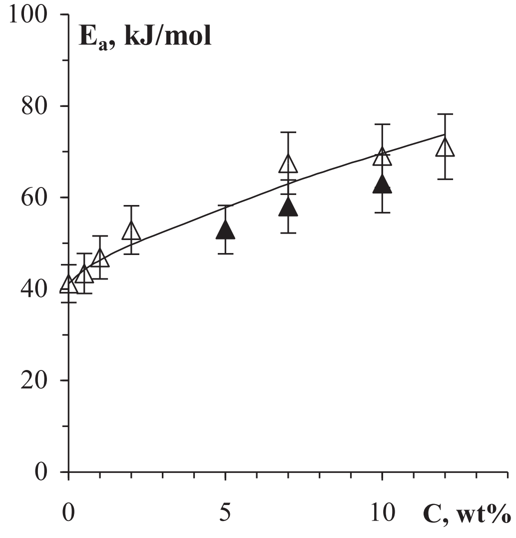

Fig. 9. Activation energy as a function of cellulose acetate concentration: points are experimental data (open from steady-state viscosity and dark from dynamic viscosity), line is power-law approximation according to Eq. (2).

Fig. 9 displays the activation energy, collected from dynamic and steady state viscosity, as a function of cellulose acetate concentration. It was shown that for microcrystalline cellulose-EMIMAc solutions the activation energy can be described as power-law concentration dependence (Sescousse et al., 2010):

$$E_a = E_a(0) + kC^m \tag{2}$$

where $E_a(0)$ is solvent activation energy and k and m are constants. The best fit gives $k = 5$ and $m = 0.75$ (solid line in Fig. 9). Activation energy values calculated from dynamic data (Fig. 2) are also shown: they are slightly lower but remain comparable with the ones calculated from steady-state viscosity. The values of the activation energy of viscous flow obtained are quite similar to the ones of microcrystalline cellulose/EMIMAc solutions (Gericke et al., 2009; Sescousse et al., 2010) and of cellulose acetate/BMIMCl solutions (Wang et al., 2011).

4. Conclusions

A comprehensive study of visco-elastic and flow properties of cellulose acetate/EMIMAc solutions was performed using dynamic and steady state rheology. It was demonstrated that cellulose acetate/EMIMAc behaves as non-entangled (below 10 wt.%) “ordinary” polymer solution and obeys Cox–Merz rule.

Cellulose acetate intrinsic viscosity in EMIMAc was determined as a function of temperature and compared with the intrinsic viscosity of microcrystalline cellulose in the same solvent. The hydrodynamic size of cellulose acetate macromolecule decreases with temperature increase which indicates the decrease of solvent thermodynamic quality. The negative temperature coefficient obtained is very similar to the one reported for cellulose acetates of similar DS and molecular weights dissolved in other solvents. Intrinsic viscosity decrease with temperature increase is much less pronounced for cellulose acetate dissolved in EMIMAc as compared with cellulose dissolved in EMIMAc, probably because of different chain rigidities. All data fall well on specific viscosity $-C[\eta]$ master plot showing slope of 1.2 in dilute region and 3.1 in semi-dilute. The overlap concentration of cellulose acetate in EMIMAc is higher than the one reported for diacetates of similar DS and molecular weights dissolved in other solvents; this indicates that EMIMAc thermodynamic quality is lower than that of classical inorganic fluids (DMF, tetrachloroethane and acetone).

The activation energy as a function of cellulose acetate concentration is described by power-law dependence. In overall, the rheological properties of cellulose acetate/EMIMAc solutions do not demonstrate any specific interactions between the polymer and the solvent (no gelation or formation of any special structures); they follow the trends already reported for cellulose acetates dissolved in other solvents and thus can be described by classical approaches. These findings will help the understanding and use of imidazolium-based ionic liquids for cellulose acetate processing.

Acknowledgements

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