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Viscosities of Acetate or Chloride-Based Ionic Liquids and Some of Their Mixtures with Water or Other Common Solvents

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For the temperature range (80 to 120) °C, viscosity data are reported for imidazolium-based ionic liquids 1-octyl-3-methylimidazolium chloride [Omim][Cl], 1-hexyl-3-methylimidazolium chloride [Hmim][Cl], 1-butyl-3-methylimidazolium chloride [Bmim][Cl], 1-ethyl-3-methylimidazolium chloride [Emim][Cl], 1-ethyl-3-methylimidazolium acetate [Emim][Ac], 1-butyl-3-methylimidazolium acetate [Bmim][Ac], and 1-butyl-3-methylimidazolium dicyanamide [Bmim] [N(CN)$_2$]. Acetate-based ionic liquids have considerably lower viscosities than the corresponding chloride-based ILs. At 25 °C, viscosity data are reported for binary mixtures of [Bmim][Ac] with diluents water, acetonitrile, dimethylformamide (DMF), and ethylene glycol. Even a small concentration of diluent very much reduces the viscosity of an ionic liquid.

Introduction

The utility of ionic liquids as “green and alternative” solvents has significantly expanded during the past few years. The high polarity of ionic liquids combined with their low vapor pressure, high thermal stability, and large liquidus range make them a promising class of solvents for a variety of chemical and biochemical applications.[1−5]

Much research has shown that ionic liquids (ILs) are good solvents for making biofuels.[6−10] Recent studies have shown that hydrophilic ILs such as 1-butyl-3-methylimidazolium chloride ([Bmim][Cl]), 1-allyl-3-methylimidazolium chloride ([Amim][Cl]), 1-ethyl-3-methyl-imidazolium acetate ([Emim][Ac]), and 1-methyl-3-methylimidazolium dimethyl phosphate ([Mmim][Me$_2$PO$_4$]) show promise for dissolving agricultural products.[8−10] For the enzymatic hydrolysis of cellulose, the preferred choice is ([Emim][Ac]), because it has a low melting point (<10 °C), is noncorrosive, and has a high hydrogen bonding−acceptor capability and a moderate viscosity.[11]

The viscosity of an ionic liquid influences the solubility of cellulose-containing natural products. Undesirable high viscosity impedes dissolution of biomass composites.[12−15]

Although the literature is rich in data concerning viscosities of neat ionic liquids,[16−19] there are only few published viscosity data for chloride or acetate-based ILs at higher temperatures.[23] Viscosity data for acetate and chloride-based ILs at higher temperatures (>100 °C) are needed because the dissolution of lignocellulosic biomass in these ILs is often carried out at higher temperatures. Further, literature data are scarce for mixtures of ionic liquids and common solvents, including water. Such data are useful, however, for process design where a cosolvent may be required to reduce the viscosity of an ionic liquid.

This work reports experimental viscosity data for [Emim][Cl], [Bmim][Cl], [Hmim][Cl], [Omim][Cl], [Emim][Ac], [Bmim][Ac], and [Bmim] [N(CN)$_2$] from (80 to 120) °C. At 25 °C, viscosity data are reported for binary mixtures of [Bmim][Ac] or [Emim][Ac] with water, acetonitrile, dimethyl formamide, and ethylene glycol.

Experimental Section

Materials and Procedure. Ionic liquids [Emim][Cl], [Bmim][Cl],[Hmim][Cl], and [Omim][Cl] were purchased from Merck, USA; [Emim][Ac], [Bmim][Ac], and [Bmim] [N(CN)$_2$] were obtained from Sigma-Aldrich (St Louis, MO). Mass fraction of impurities was less than 5 %. Acetonitrile, ethylene glycol, and dimethyl formamide (w > 99 %) were purchased from Fischer Scientific. Milli-Q double distilled water was used. Water contents were measured by the Karl Fischer method using a Mettler-Toledo coulometric titrator (Aquastar C2000).

Prior to viscosity measurements, all ionic liquids and diluents were dried in a vacuum oven (Fischer Scientific Isotemp 280) for more than 24 h at 110 °C under a partial vacuum of 3 ± 0.1 kPa. Dried samples were removed from the oven and immediately transferred to a desiccator filled with dry desiccant CaCl$_2$.

Binary systems were prepared gravimetrically using a high-precision balance (Mettler-Toledo) with uncertainty ±0.0001 g. During preparation, precaution was taken to minimize contamination by air moisture.

A Brookfield viscometer was used to measure viscosities. It is a rotational viscometer based on torque measurement. The “Searle”-system (not the chamber “Couette”-system) is used here. The spindle rotates. The torque is measured by the resistance of the fluid against the torque.

This viscometer is especially useful for ILs because it requires only a small sample and can be used for a wide range of temperatures. Viscosities can be measured from (0.0005 to 2) Pa•s. The sample chamber size is 6−8 v mL. The temperature was regulated with thermostats using either a water-circuit accessory with water as cooling and heating fluid or a high-temperature Thermosel heating cell. The temperature was measured by a sensor inside the chamber with accuracy ±0.1 °C. Measurements were made at low shear rates to ensure that ILs are Newtonian fluids. Measurements were repeated several (typically 3 to 5) times to ensure consistency and reproducibility. Viscosities reported here are expressed in Pa•s. Uncertainties are within ±2 % (0.0005 Pa•s).

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Table 1. Viscosities, η, of Dried Ionic Liquids at 25 °C[a]

	t_{fus}	η	
		Pa·s	
ionic liquid	°C	this work	literature
[Hmim][Cl]	5	ND	18.089(0.04)[23]
[Omim][Cl]	−5	ND	20.88 (0.05)[23]
[Emim][Ac]	−10	0.162 (0.012)	not available
[Bmim][Ac]	−7	0.485 (0.0085)	0.441 (0.015)[17]
[Bmim][N(CN)2]	−15	0.031 (0.012)	0.033 (0.012)[17]

[a] Mass fractions of water (w) are given in parentheses. ND is not determined because the viscosity is too high.

Table 2. Viscosities, η, of Seven Dry Ionic Liquids at t = (80, 100, and 120) °C

	η		
	Pa·s		
ionic liquid	t = 80 °C	t = 100 °C	t = 120 °C
[Emim][Cl]	0.065	0.027	0.013
[Bmim][Cl]	0.142	0.068	0.031
[Hmim][Cl]	0.293	0.087	0.043
[Omim][Cl]	0.375	0.161	0.081
[Emim][Ac]	0.017	0.009	0.005
[Bmim][Ac]	0.026	0.015	0.009
[Bmim][N(CN)$_2$]	0.011	0.006	0.004

Results and Discussion

Viscosities of Pure ILs. Table 1 shows viscosities of ILs measured at room temperature. For comparison, Table 1 also gives some viscosities from the literature. The viscosities measured here agree well with those previously published;[17−19,23] when water is present, the viscosity is reduced. Along with viscosities, Table 1 also reports water contents determined before and after viscosity measurements. There was no change in the mass fraction of water. Viscosities for [Hmim][Cl] and [Omim][Cl] at room temperature could not be determined because they exceed the measuring range of our viscometer.[23] However, we have measured their viscosities at higher temperatures.

The lower viscosities of [Emim][Ac] and [Bmim][Ac] are favorable for processing biomass. Several studies have shown that these ILs are good candidates for the dissolution of lignocellulosic biomass.[8−10] Chloride-based imidazolium ionic liquids also show promise as solvents for biomass processing but when compared to acetate-based ILs they have high viscosities at ordinary processing temperature. In addition, [Emim][Cl] and [Bmim][Cl] are solids at room temperature and highly hygroscopic. Because chloride anions interfere with enzymatic hydrolysis of cellulose, [Emim][Ac] and [Bmim][Ac] are better solvents for producing biofuels using cellulase enzymes.

Table 2 shows the measured viscosities of all seven ILs at different temperatures. Although ([Bmim][N(CN)$_2$]) does not dissolve appreciable amounts of biomass, it is able to dissolve carbohydrates such as fructose and glucose.[13−15]

Figures 1 and 2 show the effect of temperature on viscosities of chloride and acetate-based ILs .While viscosity (η) decreases with rising temperature, it increases with the length of the alkyl-chain on the cation. Changes in viscosity ($\Delta\eta$) with temperature follow the order of the alkyl-chain length. The viscosity of [Omim][Cl] drops from 0.375 Pa·s at 80 °C to 0.081 Pa·s at 120 °C ($\Delta\eta$ = 0.294). Over the same temperature range, the decrease in viscosity ($\Delta\eta$) for [Emim][Cl] is 0.052, significantly lower than that for [Omim][Cl].

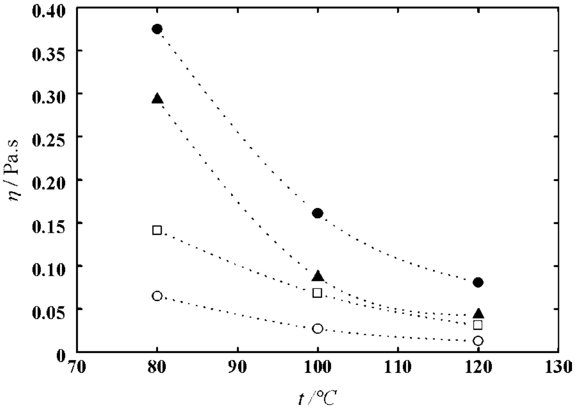

Figure 1. Viscosities of four chloride-based ionic liquids as a function of temperature. Viscosity falls with rising temperature but increases with alkyl-chain length on the cation. ○, [Emim][Cl]; □, [Bmim][Cl]; ▲, [Hmim] [Cl]; ●, [Omim][Cl]. Lines are only a guide to the eye.

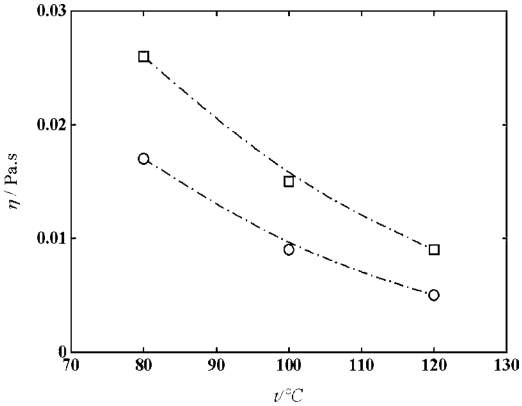

Figure 2. Viscosities of two acetate-based ionic liquids as a function of temperature. These viscosities are about 1 order of magnitude below those of corresponding chloride-based ionic liquids. ○, [Emim][Ac]; □, [Bmim][Ac]. Lines are only a guide to the eye.

Table 3. Decline of Viscosity, η, of [Emim][Ac] at 25 °C with Increasing Mass Fraction of Water w_w

	η
w_w	Pa·s
0.023	0.122
0.045	0.081
0.084	0.057
0.192	0.032
0.374	0.012
0.556	0.004
1.0	8.9×10^{-4}

The viscosities of two acetate-based ILs, [Emim] and [Bmim]-[Ac], are almost one order of magnitude below those of the corresponding chloride-based ILs. The decrease in viscosity for the acetate-based ILs from 80 to 120 °C is 0.017 for [Bmim][Ac] and 0.012 for [Emim][Ac] both lower than those for the corresponding chloride-based ILs.

Viscosities of Ionic Liquids Containing Water or some Other Diluent. Most ionic liquids have undesirable high viscosities. One possible way to lower their viscosities is by addition of water or some other diluent. Tables 3 and 4 and Figure 3 show that even a small concentration of water significantly lowers the viscosity. At a mass fraction w of water of 10 %, the viscosity decreases to nearly half that of the neat IL. Several authors have reported similar observations for other ionic liquids.[20−22]

Table 5 and Figure 4 show that, similar to the effect of water, the viscosity falls significantly at small concentration of diluent. Figure 5 combines the results shown in Figures 3 and 4. At the

Table 4. Decline of Viscosity, η, of [Bmim][Ac] at 25 °C with Increasing Mass Fraction of Water w_w

w_w	η / Pa·s
0.029	0.383
0.031	0.341
0.048	0.236
0.512	0.018
0.731	0.005
1.0	8.9×10^{-4}

same concentration, common diluents have a similar effect. The identity of a low-molecular weight diluent does not appreciably influence the decline in viscosity.

Conclusion

Viscosities of the seven ionic liquids [Emim][Cl], [Bmim][Cl], [Hmim][Cl], [Omim][Cl], [Emim][Ac], [Bmim][Ac] and [Bmim][N(CN)$_2$] were measured in the region 80−120 °*C*. High temperature reduces viscosity. Because the acetate-based ILs, [Emim][Ac] and [Bmim][Ac] have relatively low viscosities; they hold promise as solvents for pretreatment of lignocellulosic biomass prior to enzymatic hydrolysis.

For biomass conversion to fuels, viscosity plays a major role because high viscosity impedes the dissolution of biomass, sugars, or cellulose in ILs. To reduce viscosity without precipitating the solute, addition of a cosolvent may be useful.

Viscosity data at 25 °C show that for [Bmim][Ac] addition of a small amount of a diluent like water or some other common solvent reduces the viscosity to almost one-half that of the neat IL. Four common diluents have a qualitatively similar effect.

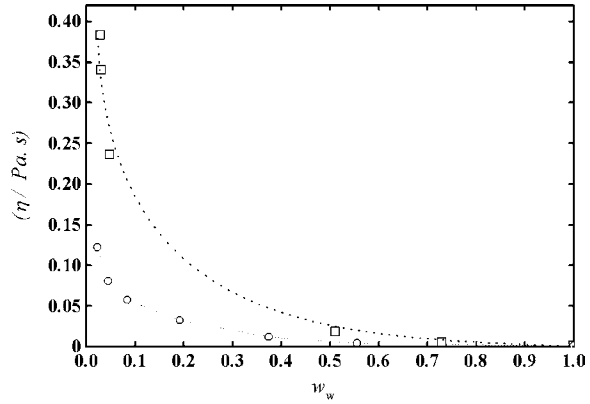

Figure 3. At 25 °C, the viscosities of [Emim][Ac] and [Bmim][Ac] decline significantly upon addition of water. w_w is the weight fraction of water. ○, [Emim][Ac]; □, [Bmim][Ac]. Lines are only a guide to the eye.

Table 5. Decline of Viscosity, η, of [Bmim][Ac] at 25 °C with Increasing Mass Fraction of w_d of Diluents

diluent	w_d	η / Pa·s
acetonitrile	0.089	0.148
	0.213	0.027
	0.389	0.005
	0.593	0.002
	1.0	3.4×10^{-4}
ethylene glycol	0.081	0.291
	0.248	0.102
	0.464	0.039
	0.678	0.026
	1.0	0.0161
dimethyl formamide	0.062	0.231
	0.191	0.054
	0.389	0.011
	0.606	0.004
	1.0	9.2×10^{-4}

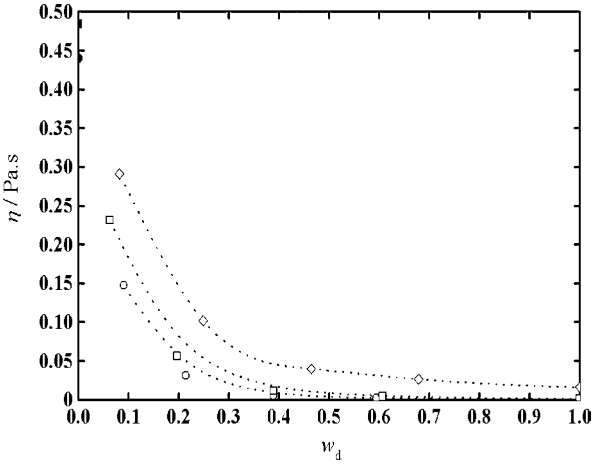

Figure 4. Decline of viscosity of [Bmim][Ac] upon addition of diluents acetonitrile, ethylene glycol or dimethylformamide at 25 °C. w_d is the weight fraction of diluent. ○, acetonitrile; □, dimethyl formamide; ◇, ethylene glycol; ●, refs 16 and 17; ■, this work. Lines are only a guide to the eye.

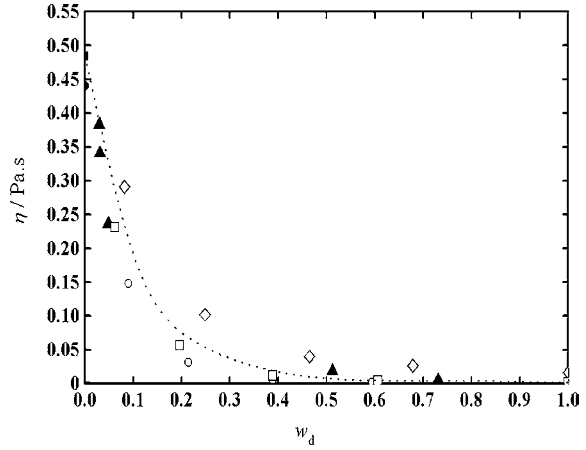

Figure 5. Decline of viscosity of [Bmim][Ac] upon addition of a diluent. At the same diluent concentration, all diluents have a similar effect. w_d is the weight fraction of diluent. ○, acetonitrile; □, dimethyl formamide; ◇, ethylene glycol; ●, refs 16 and 17; ■, this work. Lines are only a guide to the eye.

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