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## Effect of organic solvents on lowering the viscosity of 1-hexyl-3methylimidazolium chloride

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#### ABSTRACT

lonic liquids have been widely explored in making biofuels from biomass. Ionic liquid generally has high viscosity that would impede the dissolution of biomass. One of the possible ways is to use the organic solvent to lower the viscosity. In this work, experimental studies on the densities and viscosities of binary mixtures are conducted at atmospheric pressure (0.0967 MPa) in the temperature range from 303.15 K to 353.15 K. The mixtures are comprised by ionic liquid of 1-hexyl-3-methylimidazolium chloride and organic solvents of N,N-dimethylacetamide, N,N-dimethylformamide, dimethyl sulfoxide and pyridine. The excess properties are calculated to evaluate the interactions of ionic liquid with organic solvents. The Vogel-Fulcher-Tammann equation along with ideal Grunberg-Nissan equation is introduced to correlate the viscosity values. The results are used to quantitatively analyze the effects of organic solvents on lowering the viscosities of ionic liquid.

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#### 1. Introduction

Ionic liquids (ILs) have been widely studied in the past few years and are considered as the green solvents. Ionic liquids are composed of the inorganic or organic anions and organic cations. The ions can be re-organized and that makes ionic liquids designable. A large number of ionic liquids can be synthesized by combining various cations and anions to satisfy the properties for the special purpose and applications [1]. The tunable characteristics of ionic liquids make them more feasible to meet the requirements for industrial processes, and in general, they have favorable properties, e.g. low vapor pressure, large conductivity, high thermal stability, and large liquidus range, when compared to conventional solvents.

Rogers et al. firstly reported the work that ILs of 1-alkyl-3methylimidazolium chloride ( $[C_nmim][CI]$ , where *n* is the number of carbon in alkyl chain) can dissolve cellulose, and then more and more studies begin to focus on the use of ILs for the sustainable energy [2]. Especially, much research has reported that the acetateand chloride-based imidazolium ionic liquids, e.g. 1-butyl-3methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate, are recognized as the promising solvents for the biofuels manufacturing [3,4]. It is suggested that the ability of IL to dissolve cellulose is dependent on the capacity of IL anion to form

\* Corresponding author. E-mail address: wangxp@xjtu.edu.cn (X. Wang). hydrogen-bonding with the hydroxyl functional groups in the polymer [5].

However, there are disadvantages for the use of ILs in the biofuels manufacturing processes: high viscosity and limited miscibility with non-polar reagents or reaction products [5]. One possible way to solve the problems is to use the organic solvents as the additive or diluent [3]. Gericke et al. systematically studied the effects of 18 organic solvents on the ILs for the cellulose dissolution as well as the phase characteristic of the solutions [5]. In these 18 organic solvents, N,N-dimethylacetamide (DMA), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and pyridine (PYR), show great promise for solving the two major problems and advancing the dissolution of cellulose. Therefore, more and more publications have studied the mechanism of the organic solvents as the additive for making biofuels with ILs [6,7]. The studied results proposed that the organic solvent of DMSO does not remarkably affect the hydrogen-bonding formation as well as the interaction with glucose, and DMSO behaves continual improvement on solvation capabilities of the imidazolium ionic liquid [7]. However, little attention has been given to quantitatively study the influences of the organic solvents on thermophysical properties, e.g. density and viscosity, of the ILs, that are of utmost importance for the design of chemical and bio-chemical processes.

In this work, experimental study was conducted to investigate the effects of organic solvents as the additives to the thermophysical properties of chloride-based imidazolium ionic liquid, 1-hexyl-3-methylimidazolium chloride ( $[C_6mim][Cl]$ ), in the temperatures







from 303.15 K to 353.15 K at atmospheric pressure (0.0976 MPa). The excess properties are obtained to analyze the interactions of ionic liquid with organic solvents. The Vogel-Fulcher-Tammann (VFT) equation along with ideal Grunberg-Nissan equation is used to correlate the viscosity values.

#### 2. Experimental

#### 2.1. Materials

The descriptions for the organic solvents and the IL studied in this work are presented in Table 1. All of the organic solvents were purchased from Sigma-Aldrich (St Louis, MO). IL of  $[C_6mim][Cl]$  was obtained from Center for Green Chemistry and Catalysis (CGCC), Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS). The organic solvents were used without further purification.

#### 2.2. Procedure

The IL was dried by using the 3 A molecular sieves (Sigma-Aldrich, St Louis, MO). Before the use, 3 A sieves were soaked in acetone and methanol solution to eliminate the ions from the sieves. 3 A sieves were then put in a furnace at 473.15 K for overnight. A small volume of IL with 3 A sieves was dried in a vacuum oven with a pressure of  $2 \pm 0.1$  kPa at 353.15 K for more than 24 h.

The binary mixtures were prepared by using an analytical balance (Mettler-Toledo, AB204-N and ME204) with an uncertainty of 0.0001 g. The water contents in the pure substances and binary mixtures were determined by a Karl Fischer moisture titrator (Coulometric titration, MKC-710B, Kyoto Electronics Manufacturing Co., Ltd.) before and after the experimental measurements. A glove box filled with nitrogen was used during the sample preparation to eliminate the air moisture contamination. The water contents in the samples before and after the measurements were under 0.3% in mass.

#### 2.3. Density measurements

The densities of the pure substances and binary mixtures were determined by an Anton Paar digital vibrating U-tube densimeter (model DMA 5000 M). The uncertainty of the temperature in the apparatus was specified as 0.01 K and the repeatability for the densimeter provided by the manufacturer was regulated to  $1.0 \cdot 10^{-6}$  - g·cm<sup>-3</sup>. The relative standard uncertainty for the density was 0.001. The cell was well-washed by the water and acetone before and after the experimental measurement, and the densimeter was then calibrated by using the degassed and bidistilled water and dry air. During the experiment, the density was measured in triplicate.

#### 2.4. Viscosity measurements

The viscosities were measured with an Ubbelohde capillary viscometer (model 9721-R53, 9721-R56, 9721-R62, 9721-R71 and

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Descriptions	of the	substances	studied	in	this	work.

9721-R77) provided by Cannon Instrument Company (State College, PA, USA). The capillary viscometer was maintained in an oil bath controlled by the Lauda thermostat. The measurement was not conducted until the temperature was stable. The capillary was well-washed by the water and acetone before and after the experimental measurement, and the viscometer was then calibrated by viscosity standards provided by Cannon Instrument Company. The uncertainty of the temperature was within 0.01 K. The dynamic viscosity was obtained by multiplying the viscometer constant with the flow-time and density corresponding to the same temperature of the sample. The sample efflux time through the capillary viscometer was determined by an electronic stopwatch within 0.01 s. The relative expanded uncertainty of the viscosity in this study is less than 0.15 with the confidence level of 0.95. During the experiment, the sample viscosity was measured in triplicate.

#### 3. Results and discussions

#### 3.1. Experimental density data

The densities of pure organic solvents and IL are listed in Table 2 with the values reported in the literature [8,9,10,11,12,13,14,15]. The densities for the binary mixtures were measured at atmospheric pressure in the temperature range from 303.15 K to 353.15 K and the values obtained are presented in Tables 3–6. Among these four organic solvents, DMSO has the highest density value.

The density values were fitted as a function of temperature and calculated by the following equation:

$$\rho = a + b \cdot T + c \cdot T^2 \tag{1}$$

where  $\rho$  (g·cm<sup>-3</sup>) is the density; *a* (g·cm<sup>-3</sup>), *b* (g·cm<sup>-3</sup>·K<sup>-1</sup>) and *c* (g·cm<sup>-3</sup>·K<sup>-2</sup>) are the parameters fitted by the experimental data; *T* is the temperature in Kelvin.

The average absolute relative deviation (AARD) between the fitted values and the experimental data is obtained by:

$$AARD(\%) = \frac{100}{N} \sum_{i=1}^{N} \left| \frac{E_{cal,i} - E_{exp,i}}{E_{exp,i}} \right|$$
(2)

where *N* is the number of experimental points,  $E_{cal}$  and  $E_{exp}$  are the calculated and experimental data, respectively.

Density values of pure substances at 303.15 K and (0.0967 ± 0.002) MPa.

Substance	Density/g·cm <sup>-3</sup>				
	This work	Literature			
[C <sub>6</sub> mim][C1] DMA DMF DMSO PYR	1.03607 0.93185 0.93918 1.09029 0.97309	1.0351 [8], 1.0368 [9] 0.93169 [10], 0.93162 [11] 0.93900 [11], 0.93946 [12] 1.09041 [10], 1.09049 [13] 0.973228 [14], 0.972980 [15]			

The standard uncertainties (*u*) are u(T) = 0.01 K and  $u_r(\rho) = 0.001$ .

Substance	Abbreviation	CAS No.	Source	Initial Mass Fraction Purity	Purification Method	Water content in mass (%)
1-hexyl-3-methylimidazolium chloride N,N-dimethylacetamide N,N-dimethylformamide Dimethyl sulfoxide Pyridine	[C <sub>6</sub> mim][Cl] DMA DMF DMSO PYR	79917-90-1 127-19-5 68-12-2 67-68-5 110-86-1	CAS Sigma – Aldrich Sigma – Aldrich Sigma – Aldrich Sigma – Aldrich	≥0.98 ≥0.98 ≥0.99 ≥0.99 ≥0.99 ≥0.998	Drying None None None None	0.258 0.068 0.039 0.087 0.026

Table 2

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