Journal of Molecular Liquids 196 (2014) 314–318

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Study on the thermodynamic properties of ether-functionalized imidazolium-based ionic liquids

Ying Zhao [a,b], Jianying Wang [b], Haichao Jiang [b], Yongqi Hu [a,b,*]

[a] Chemical Engineering Institute, Tianjin University, Tianjin 30000, China
[b] College of Chemical and Pharmaceutical Engineering, Hebei University of Science and Technology, Shijiazhuang 050018, China

ARTICLE INFO

Article history:
Received 16 December 2013
Received in revised form 25 March 2014
Accepted 3 April 2014
Available online 18 April 2014

Keywords:
Ionic liquid
Density
Viscosity
Surface tension

ABSTRACT

Ether-functionalized imidazolium-based ionic liquids (EFIILs) exhibit extremely high SO_2 solubility. In this paper, a series of EFIILs were prepared, and their structures were confirmed by ^1H NMR. The thermodynamic properties of EFIILs, such as density, viscosity and surface tension, were measured from (298.15 to 343.15) K at atmospheric pressure. The molecular volume, coefficient of thermal expansion, standard entropy, surface entropy, and surface enthalpy were calculated from the experimental data. The results indicate that density, viscosity and surface tension of the specific EFIILs show linear decline as temperature rises, and decrease with the increase of ether chain length of the cation at the same temperature. The surface properties of EFIILs were also discussed systematically.

1. Introduction

Air pollution is an important issue which attracts a lot of attention in the world. As one of the main air pollutants, SO_2 is emitted from burning of fossil fuels, and it is harmful to the environment and the human health [1–3]. Hence, it is critical to control SO_2 emission from the industrial waste gas or fossil fuels combustion to minimize the total SO_2 emission load.

Room-temperature ionic liquids (RTILs) have been demonstrated to be a new type of SO_2 selective separation media. RTILs are non-volatile. SO_2 could be desorbed without loss of solvent [4,5]. Recently, many attempts have been made to explore functional ILs for SO_2 absorption through addition of functional groups as a part of the cation or anion [6]. Several researchers tried to synthesize a new type of ether-functionalized imidazolium-based ionic liquids (EFIILs) to absorb SO_2. Hong et al. [3] determined the SO_2 absorption capacity of EFIILs with a sulfonate anion, and reported that the absorption amount of SO_2 was at least 2 mol/mol IL at 298.15 K and atmospheric pressure. The SO_2 absorption capacity of EFIILs is enhanced with the increase of ether chain length of the cation, and this kind of ILs also exhibit efficient regeneration behavior.

The density, viscosity and surface tension of EFIILs are very important to their desulfurization performance. Although some of the applications have been studied, such as the desulfurization performance of EFIILs, their physicochemical properties are poorly understood. This information is very important as the thermodynamic properties of EFIILs are required not only for the development of correlation and prediction, but also for the product design and industrial process. Physical properties, especially, density, viscosity, and surface tension of EFIILs are closely related to their industrial processes of desulfurization [7–11].

The aim of this work is to measure the basic physicochemical properties of series of EFIILs over the temperature range from (293.15 to 343.15) K under atmospheric pressure. The EFIILs, namely 1-ethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ($[C_3O_1Mim][H_3CSO_3]$), 1-diethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ($[C_5O_2Mim][H_3CSO_3]$) and 1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ($[C_7O_3Mim][H_3CSO_3]$), have been synthesized and characterized. The density, viscosity and surface tension were measured. The volumetric and surface properties of EFIILs are also discussed systematically.

2. Experimental section

2.1. Materials and apparatus

2-Methoxyethanol (99%) was obtained from Tianjin Yongda Chemical Reagent Co., Ltd., China. Diethylene glycol monomethyl ether (99%) and triethylene glycol monomethyl ether (96%) were purchased from Tokyo Chemical Industry Co., Ltd., Japan. Methanesulfonyl chloride (99%) was obtained from Chengdu Gracian Chemical Technology Co., Ltd., China. N-methylimidazole (99%) was obtained from Shanhai Chengjie Chemical Co., Ltd., China. A complete specification of samples is listed in Table 1.

* Corresponding author at: Chemical Engineering Institute, Tianjin University, Tianjin 30000, China. Tel./fax: +86 311 81668302.
E-mail address: huyq2000@126.com (Y. Hu).

http://dx.doi.org/10.1016/j.molliq.2014.04.003
0167-7322/

Table 1
Sample table.

Chemical name	Source	Initial mass percent	Purification method
2-Methoxyethanol	Tianjin Yongda Chemical Reagent CO	99%	None
Diethylene glycol monomethyl ether	Tokyo Chemical Industry Co.	99%	None
Triethylene glycol monomethyl ether	Tokyo Chemical Industry Co.	96%	None
Methanesulfonyl chloride	Chengdu Gracian Chemical Technology Co.	99%	None
N-methylimidazole	Shanhai Chengjie Chemical Co.	99%	None

All the FT-IR spectra were conducted on FTS135 type Fourier transform infrared spectroscopy (FT-IR) instrument; ^{1}H NMR spectra were measured on a Bruker AVANCF 500 MHz spectrometer, using $CDCl_3$ as a solvent with TMS as the internal standard. The densities of all the ILs were measured using a densimeter (MYX-1). The viscosities of the liquids were determined using a viscosimeter Brookfield LVDV-II + Pro. Ultra Low Adapter (ULA) was used to increase accuracy. Measurements of surface tension of EFIILs were performed with a platinum ring with a DCAT21 (Data physics, Germany) digital tensiometer.

2.2. Synthesis of ether-functionalized imidazolium ionic liquids

All the ether-functionalized ILs, 1-ethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ([C_3O_1Mim][H_3CSO_3]), 1-diethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ([C_5O_2Mim][H_3CSO_3]) and 1-triethylene glycol monomethyl ether-3-methylimidazolium methanesulfonate ([C_7O_3Mim][H_3CSO_3]), were synthesized by a typical two-step process (see Fig. 1) as published in papers [3,12] by our research group.

[C_3O_1Mim]$^+$[H_3CSO_3]$^-$,
^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K) δ 9.61(bs, ^{1}H), 7.59 (bs, 1H), 7.51 (bs, 1H), 4.50 (t, *J* 5.0, 2H), 4.03 (s, 3H), 3.75 (t, *J* 5.0, 2H), 3.43 (s, 3H), 2.73 (s, 3H).
[C_5O_2Mim]$^+$[H_3CSO_3]$^-$,
^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K) δ 9.83 (bs, 1H), 7.59 (bs, 1H), 7.39 (bs, 1H), 4.54 (t, *J* 5.0, 2H), 4.03 (s,3H), 3.88 (t, *J* 5.0, 2H), 3.64 (m, 2H), 3.52(m, 2H), 3.37 (s, 3H), 2.79 (s, 3H).
[C_7O_3Mim]$^+$[H_3CSO_3]$^-$,
^{1}H NMR (500.0 MHz, $CDCl_3$, 298 K) δ 9.85 (bs, 1H), 7.64 (bs, 1H), 7.28 (bs, 1H), 4.54 (t, *J* 4.5, 2H), 4.08 (s,3H), 3.85 (t, *J* 4.5, 2H), 3.67–3.60 (m, 6H), 3.57–3.52(m,2H), 3.37 (s, 3H), 2.79 (s, 3H).

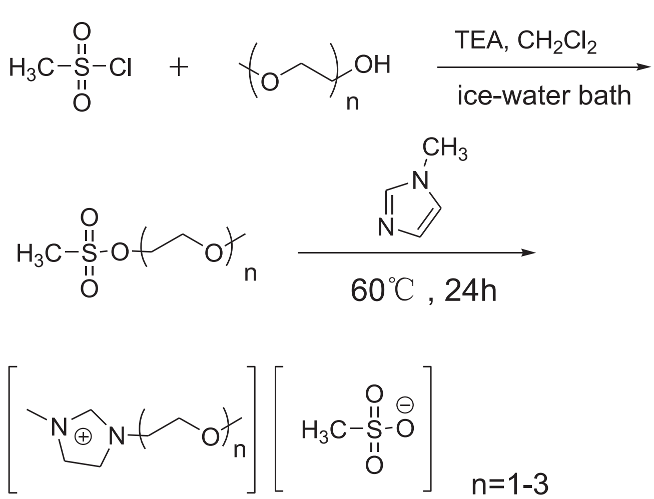

Fig. 1. Synthetic routes for ether-functionalized imidazolium-based ionic liquids.

2.3. Physicochemical properties measurements

The EFIILs are extremely hygroscopic. In order to reduce the content of water, all the ILs samples were dehydrated under vacuum at 80 °C for at least 48 h. After that, they were continue to be dehydrated and weighed every 15 min until a constant weight prior to the measurements. The water contents of the three ILs were lower than 0.1% using a Karl Fischer analysis. To avoid surface contamination and the absorption of water by the ILs, all the measurements were performed under nitrogen atmosphere. Circulating water from a thermostatically regulated bath was around the measuring cell to maintain the temperature with a temperature stability of ± 0.02 K [5].

The densities of the ILs [C_3O_1Mim][H_3CSO_3], [C_5O_2Mim][H_3CSO_3] and [C_7O_3Mim][H_3CSO_3] were measured by electron density meter with a precision of ± 0.0002 g·cm^3 of Shanghai FangRui instrument Co., Ltd. Experimental density values were measured over the temperature range from (293.15 to 343.15) K at atmospheric pressure and the results are presented in Table 2. The measurements were the average of the repeated experiments for three times and the average values were considered for further study [13].

The viscosities of the liquids were measured by a viscosimeter Brookfield LVDV-II + Pro with a precision of ± 0.01 mpa·s. Ultra Low Adapter (ULA) was used to increase accuracy. The measurement is from (293.15 to 343.15) K at atmospheric pressure and the results are presented in Table 6.

Measurements of surface tension of EFIILs were performed with a platinum ring with a DCAT21 (Dataphysics, Germany) digital tensiometer. The ring and vessel were thoroughly cleaned by immersion in a concentrated solution of nitric acid for several hours before experiments. Then it was rinsed with distilled water, carefully flamed in a Bunsen burner, washed again with distilled water and dried. The uncertainty of the measurements is ± 0.15 mN·m^{-1} [14].

3. Results and discussion

3.1. Appearance

The appearance of the series of EFIILs, [C_3O_1Mim][H_3CSO_3], [C_5O_2Mim][H_3CSO_3] and [C_7O_3Mim][H_3CSO_3], was shown in Fig. 2. The color of the ILs becomes light gradually.

Table 2
Density (ρ) of the ILs at different temperatures.

T/K	ρ[C_3O_1Mim][H_3CSO_3] (g/cm^3)	ρ[C_5O_2Mim][H_3CSO_3] (g/cm^3)	ρ[C_7O_3Mim][H_3CSO_3] (g/cm^3)
298.15	1.2338	1.2180	1.2014
303.15	1.2296	1.2123	1.1959
308.15	1.2239	1.2088	1.1922
313.15	1.2198	1.2035	1.1873
318.15	1.2151	1.1985	1.1829
323.15	1.2113	1.1943	1.1783
328.15	1.2068	1.1907	1.1748
333.15	1.2031	1.1870	1.1702
338.15	1.1991	1.1819	1.1647
343.15	1.1948	1.1775	1.1601

Standard uncertainties u are $u(T) = 0.01$ K, $u(\rho) = 0.0002$ g · cm^{-3}.