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Viscosities and Conductivities of [BMIM][Zn_xCl_y] (x = 1, 1.5, 2; y = 3, 4, 5) Ionic Liquids at Different Temperatures

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Functional ionic liquids *e.g.*, [BMIM]$ZnCl_3$, [BMIM]$Zn_{1.5}Cl_4$ and [BMIM]Zn_2Cl_5 were prepared by zinc chloride dissolved in [BMIM]Cl ionic liquids. Dynamic viscosity and conductivity data of ionic liquid were measured at temperature ranging from 323.15-353.15 K with an interval of 5 K. Dynamic viscosity increased with the rise of $ZnCl_2$ concentration and decreased with rise of temperature. The conductivity expressed an opposite results. The viscosity and conductivity at different temperature were well described by the Arrhenius equation and Vogel-Fulcher-Tammann (VFT) equation. All the correlation coefficients were above 0.98. The molar conductivity was calculated according to the conductivity and density data of ionic liquids. The relationship between the dynamic viscosity and the molar conductivity was discussed by Walden rule.

Keywords: Ionic liquids, Dynamic viscosity, Conductivity, Molar conductivity, Walden rule.

INTRODUCTION

Ionic liquids (ILs) are ascribed to their distinguished advantages such as chemical and thermal stability, wide liquid phase extent (-40 to 300ºC), non-detectable vapour pressure, high dissolvability, great conductibility and structure adjustment[1]. For example, ionic liquids does almost not produce steam at a high temperature and vacuum level because volatility of ionic liquids is close to zero. In addition, based on merits of ionic liquids, the applications of the ionic liquid are also growing rapidly in the fields *e.g.*, liquid-liquid extraction[2], chemical catalytic reaction[3], nano-particles preparation[4], environmental protection[5], electrochemistry, *etc*.

In recent years, metal chloride is dissolved in the ionic liquids to form a functional ionic liquid with catalytically activity[6,7]. Bica and Gaertner[8] used [BMIM]$FeCl_4$ ionic liquid as recyclable catalyst for aryl Grignard cross-coupling of alkyl halides. Qiao *et al.*[9] prepared [BMIM][$AlCl_4$] ionic liquid as catalyst for alkylation of benzene with 1-dodecene. Wang *et al.*[10] used [BMIM][$ZnCl_3$] ionic liquids as co-catalyst for coupling reaction of CO_2 with epoxides[10].

Dynamic viscosity and conductivity data of ionic liquid are of great importance especially in the area of the electrolytes. So, in order to develop the potential industrial applications of ionic liquid, basic physicochemical properties and their temperature dependence should be investigated. In this study, we synthesized three ionic liquids *i.e.*, [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$], [BMIM][Zn_2Cl_5]. These ionic liquids contained the same cation $[BMIM]^+$, but had different anion with $[Zn_xCl_y]^-$ (x = 1, 1.5, 2 and y = 3, 4, 5). The dynamic viscosity and conductivity data of ionic liquids were measured at temperature ranging from 323.15-353.15 K with an interval of 5 K. The viscosity and conductivity at different temperature were described by the Arrhenius equation and Vogel-Fulcher-Tammann (VFT) equation. The relationship between the dynamic viscosity and the molar conductivity was discussed by Walden rule.

EXPERIMENTAL

1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) ionic liquid was purchased from Linzhou Keneng Material Technology Co., LTD. Purity grade of [BMIM]Cl was above 99 % and it could be used after drying treatment. Zinc chloride was analytically pure and used after drying process.

Preparation of ionic liquids: [BMIM][$ZnCl_3$] ionic liquid was prepared by mixing 0.3 mol [BMIM]Cl and 0.3 mol $ZnCl_2$ at 90 ºC for 24 h. In the same way, [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5] were acquired by hybrid of 0.3 mol [BMIM]Cl and 0.45/0.6 mol $ZnCl_2$ at 90 ºC for 24 h.

Measurements of viscosity and conductivity: The conductivities of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and

[BMIM][Zn_2Cl_5] were measured by a Wayne-Kerr 6430B Autobalance Bridge fitted with a shanghai DJS-1 electrode and the temperature was controlled within ± 0.1 K using a HAAKEV26 temperature thermostat (Thermo Electron). In order to keep the ionic liquids dry, the experiment should carry out in a dry nitrogen atmosphere in the temperature range 323.15-353.15 K with an interval of 5 K. The viscosities of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5] were measured using an Ostwald viscometer. We used a thermostatic bath to control the temperature to get a stability of ± 0.1 K, which consumed 0.5 h to attain thermal equilibrium in the viscosity. Moreover, in order to prevent absorbing water from atmosphere, we should put the ionic liquids in a dry nitrogen atmosphere when measuring the viscosity.

RESULTS AND DISCUSSION

Conductivities of ionic liquids at different temperature: Fig. 1 showed conductivity of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5] at temperature from 323.15-353.15 K. It was clearly seen that conductivity of ionic liquids increased with the rise of temperature. The increase of zinc chloride amount could reduce the conductivity of ionic liquids. The kinematic velocity of ion was bigger at high temperature than the low. It was advantage for improving conductivity of ionic liquids. Comparison of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5], molecular weight of anionic part showed a increasing tendency at the same cationic part. The greater molecular weight of anion, the higher molecular volume it was. It was disadvantage for ion migration in a big molecular volume. Therefore, [BMIM][$ZnCl_3$] owned the higher conductivity than [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5]. The conductivity of [BMIM][$Zn_{1.5}Cl_4$] was higher than [BMIM][Zn_2Cl_5].

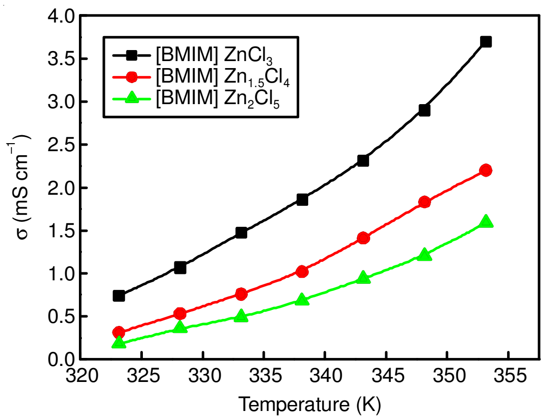

Fig. 1. Conductivity of ionic liquids at temperature from 323.15-353.15 K

According to the Arrhenius equation[11], the relationship between conductivity of ionic liquids and temperature was described as eqn. 1.

$$\ln \sigma = \ln \sigma_\infty - \frac{E_\sigma}{RT} \qquad (1)$$

Here, σ was the conductivity and σ_∞ expressed the empirical constant. E_σ noted for the activation energy for electrical conduction which indicated the energy needed for an ion to jump a free hole. The values of σ_∞, E_σ and R^2 (correlation coefficient) were listed in Table-1. From the Table-1, correlation coefficients (R^2) of three ionic liquids were above 0.99. The conductivity of ionic liquids was followed Arrhenius relationship. The E_σ and σ_∞ expressed an increasing tendency with rise of molecular weight of anionic part. In addition, the relationship was showed in Fig. 2.

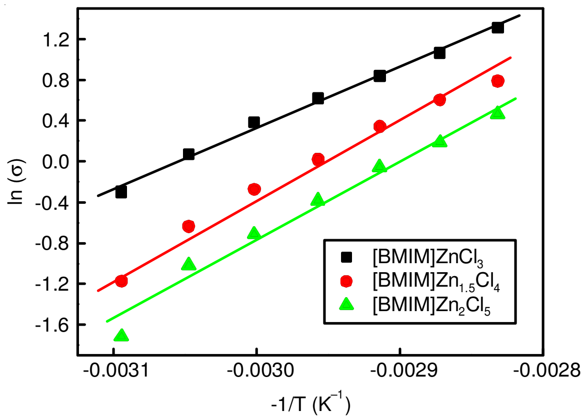

Fig. 2. Relationship between conductivity and temperature based on Arrhenius equation

According to the references[12,13], the conductivity of ionic liquids were followed by Vogel-Fulcher-Tammann (VFT) equation which was shown in eqn. 2.

$$\sigma = \sigma_0 \exp\frac{-B}{T - T_0} \qquad (2)$$

The σ_0, B and T_0 were the empirical constants. According to the VFT equation, the σ_0, B, T_0 and R^2 were calculated and listed in Table-1. VFT relationship was shown in Fig. 3. From the Table-1, it was seen clearly that R^2 calculated from VFT equation were greater than Arrhenius equation. All the R^2 were above 0.99 and VFT equation could greatly describe the relationship between conductivity and temperature of ionic liquids.

Viscosity of ionic liquids at different temperature: Fig. 4 showed the dynamic viscosity of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5] at temperature from 323.15-353.15 K. The viscosity of [BMIM][Zn_2Cl_5] was highest than [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][$ZnCl_3$]. The viscosity of [BMIM][$Zn_{1.5}Cl_4$] was highest than [BMIM][$ZnCl_3$]. For example, at 338.15 K, the viscosity values of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5]

TABLE-1
FITTED VALUES OF CONDUCTIVITY OF σ_∞, E_∞, σ_0, B, T_0 AND R_2 BASED ON ARRHENIUS EQUATION AND VFT EQUATION

Ionic liquids	Arrhenius equation			VFT equation			
	10^{-6} σ_∞ (mS cm^{-1})	E_σ (kJ mol^{-1})	R^2	σ_0 (mS cm^{-1})	B (K)	T_0 (K)	R^2
[BMIM]$ZnCl_3$	76.78	49.40	0.9969	214.0	441.7	245	0.9992
[BMIM]$Zn_{1.5}Cl_4$	2610	61.04	0.9925	44.40	228.4	277	0.9994
[BMIM]Zn_2Cl_5	7717	65.25	0.9901	24.90	196.0	283	0.9973

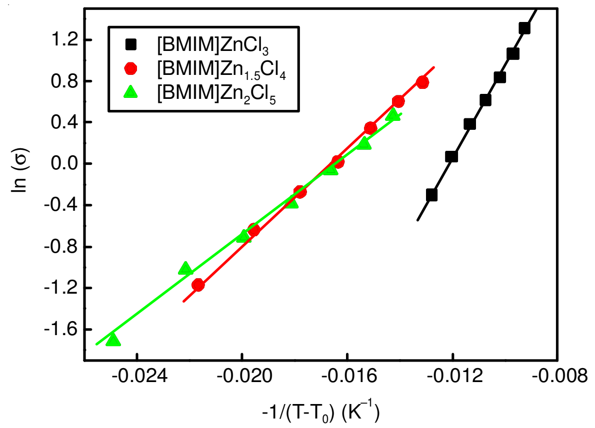

Fig. 3. Relationship between conductivity and temperature based on VFT equation

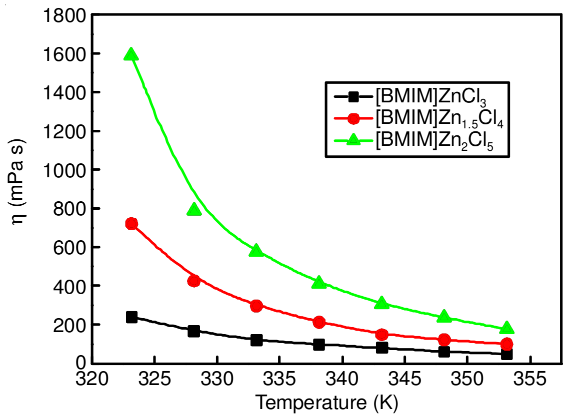

Fig. 4. Viscosity of ionic liquids at temperature from 323.15-353.15 K

were 99 mPa s, 213 and 412 mPa s, respectively. With the increase of temperature, viscosity of ionic liquids showed a trend of decline. For example, the viscosity of [BMIM][$ZnCl_3$] was 241 mPa s at 323.15 K. However, the viscosity of [BMIM][$ZnCl_3$] was only 47 mPa s at 353.15 K.

The relationship between dynamic viscosity and temperature could be described using Arrhenius equation which is shown in eqn. 3.

$$\ln \eta = \ln \eta_\infty + \frac{E_\eta}{RT} \tag{3}$$

Here, η_∞ was the empirical constant and E_η denoted the activation energy for viscous flow. Fig. 5 showed the relationship between viscosity of the logarithm and reciprocal of absolute temperature. From the Fig. 5, the lnç and 1/T were linear correlation. The fitting results were shown in Table-2. From the Table-2, values of E_η could be increased by rise of dissolution of zinc chloride.

The values of dynamic viscosity of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5] were also fitted by using the VFT equation that was commonly used for ionic liquids:

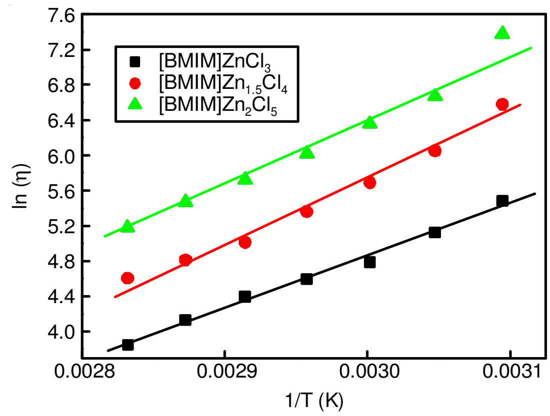

Fig. 5. Relationship between viscosity and temperature based on Arrhenius equation

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \tag{4}$$

Here, η_0, B, T_0 were the empirical constants. According to the VFT equation, values of dynamic viscosity and temperature could be described as Fig. 6. From the Fig. 6, viscosity of ionic liquids at different temperature was followed VFT equation very well. The fitting data was shown in Table-2. From the Table-2, the correlation coefficients which were calculated by VFT equation were superior to Arrhenius model.

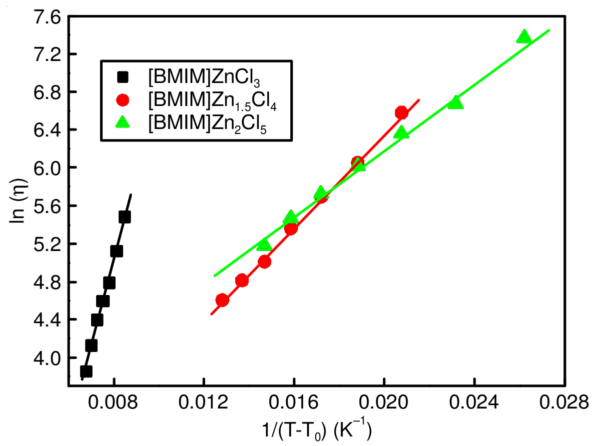

Fig. 6. Relationship between viscosity and temperature based on VFT equation

From above figure and table, we could obtain information that the high conductivity could be accompanied by the low viscosity without introducing some special conduction mechanism, such as ion hopping. The values of correlation coefficient resulting from VFT equation were 0.99 or better, which showed

TABLE-2
FITTED VALUES OF VISCOSITY OF σ_∞, E_σ, σ_0, B, T_0 AND R_2 BASED ON ARRHENIUS EQUATION AND VFT EQUATION

Ionic liquids	Arrhenius equation			VFT equation			
	10^6 η_∞ (mPa s)	E_η (kJ mol^{-1})	R^2	η_0 (mPa s)	B (K)	T_0 (K)	R^2
[BMIM]$ZnCl_3$	2.282	49.48	0.9964	0.1022	914.0	205	0.9972
[BMIM]$Zn_{1.5}Cl_4$	0.06397	62.82	0.9917	0.2423	247.8	275	0.9994
[BMIM]Zn_2Cl_5	0.03415	65.46	0.9885	0.07699	181.7	285	0.9971

TABLE-3
DENSITY OF THE IONIC LIQUIDS AT DIFFERENT TEMPERATURE

Ionic liquids	ρ (g cm^{-3})						
	323.15 K	328.15 K	333.15 K	338.15 K	343.15	348.15	353.15 K
[BMIM]$ZnCl_3$	1.38	1.38	1.37	1.37	1.37	1.36	1.36
[BMIM]$Zn_{1.5}Cl_4$	1.51	1.51	1.51	1.50	1.50	1.50	1.49
[BMIM]Zn_2Cl_5	1.61	1.60	1.60	1.60	1.60	1.59	1.59

TABLE-4
MOLAR CONDUCTIVITY OF IONIC LIQUIDS AT DIFFERENT TEMPERATURE

Ionic liquids	Λ (S cm^2 mol^{-1})						
	323.15 K	328.15 K	333.15 K	338.15 K	343.15	348.15	353.15 K
[BMIM]$ZnCl_3$	0.1665	0.2408	0.3332	0.4216	0.5235	0.6621	0.8447
[BMIM]$Zn_{1.5}Cl_4$	0.07763	0.1327	0.1903	0.2571	0.3555	0.4613	0.5583
[BMIM]Zn_2Cl_5	0.04992	0.1005	0.1367	0.1898	0.2623	0.3370	0.4465

TABLE-5
CALCULATED Λ_η VALUES OF IONIC LIQUIDS AT DIFFERENT TEMPERATURE

Ionic liquids	Λ_η (S cm^2 mol^{-1} mPa s)						
	323.15 K	328.15 K	333.15 K	338.15 K	343.15	348.15	353.15 K
[BMIM]$ZnCl_3$	40.1265	40.4544	39.984	41.7384	42.4035	41.0502	39.7009
[BMIM]$Zn_{1.5}Cl_4$	55.97123	56.3975	56.5191	54.7623	53.325	56.7399	55.83
[BMIM]Zn_2Cl_5	79.3728	79.194	78.7392	78.1976	80.0015	79.869	79.0305

that the VFT equation represented very well for the experimental dynamic viscosity and conductivity data.

Conductivity-viscosity relations: Molar conductivity (Λ) of [BMIM][$ZnCl_3$], [BMIM][$Zn_{1.5}Cl_4$] and [BMIM][Zn_2Cl_5] could be calculated from the experimental conductivity and density by the following equation:

$$\Lambda = \frac{\sigma M}{\rho} \quad (5)$$

M is the molar mass and ρ is the density of ionic liquids which was showed in the Table-3. According to the eqn. 5, the values of the molar conductivity (Λ) were also listed in Table-4.

According to the Walden rule[14], there was an equation to describe the relationship between molar conductivity and viscosity.

$$\Lambda_\eta = k(\text{constant t}) \quad (6)$$

We had calculated Λ_η values at different temperature and results were given in the Table-5. From the Table-5, Λ_η values at different temperature in the same ionic liquid were similar which was meant that ionic liquids followed Walden rule. The k of [BMIM][$ZnCl_3$]was 40.78 (S cm^2 mol^{-1}) (mPa s) which was calculated by average value of values at different temperature. The k of [BMIM][$Zn_{1.5}Cl_4$] was 55.70 (S cm^2 mol^{-1}) (mPa s) and [BMIM][Zn_2Cl_5] is 79.20 (S cm^2 mol^{-1}) (mPa s).

Conclusion

Functional ionic liquids *e.g.*, [BMIM]$ZnCl_3$, [BMIM]$Zn_{1.5}Cl_4$ and [BMIM]Zn_2Cl_5 were prepared by zinc chloride dissolved in [BMIM]Cl ionic liquids. Dynamic viscosity and conductivity data of ionic liquid were measured at temperature ranging from 323.15-353.15 K with an interval of 5 K. Dynamic viscosity increased with the increase of $ZnCl_2$ concentration and decreased with increase of temperature. The conductivity expressed an opposite results. The viscosity and conductivity at different temperature were well described by the Arrhenius equation and Vogel-Fulcher-Tammann (VFT) equation. All the correlation coefficients were above 0.98. The molar conductivity was calculated according to the conductivity and density data of ionic liquids. The relationship between the dynamic viscosity and the molar conductivity was discussed by Walden rule. Walden constants were 40.78 (S cm^2 mol^{-1}) (mPa s) for [BMIM][$ZnCl_3$], 55.70 (S cm^2 mol^{-1})(mPa s) for [BMIM][$Zn_{1.5}Cl_4$], 79.20 (S cm^2 mol^{-1})(mPa s) for [BMIM][Zn_2Cl_5] within the temperature range under consideration.

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