Hindawi
Journal of Chemistry
Volume 2017, Article ID 7428097, 5 pages
https://doi.org/10.1155/2017/7428097

*Research Article*

# Viscosities and Conductivities of [BMIM]Zn(Ac)$_x$Cl$_y$($x = 0, 1, 2, 3$; $y = 3, 2, 1, 0$) Ionic Liquids at Different Temperatures

**Hang Xu and Dandan Zhang**

*Chemical Engineering and Pharmaceutics School, Henan University of Science and Technology, Luoyang 471023, China*

Correspondence should be addressed to Hang Xu; xhinbj@126.com

Received 19 March 2017; Revised 21 April 2017; Accepted 21 May 2017; Published 7 June 2017

Academic Editor: Elena Gomez



Viscosity and conductivity data of [BMIM]Zn(Ac)$_x$Cl$_y$($x = 0, 1, 2, 3$; $y = 3, 2, 1, 0$) ionic liquids were detected at temperature ranging from 323.15 to 353.15 K with an interval of 5 K. The conductivities of different ionic liquids at the same temperature followed the trend [BMIM][ZnAcCl$_2$] > [BMIM][ZnAc$_2$Cl] > [BMIM][ZnCl$_3$] > [BMIM][ZnAc$_3$]. The viscosities of different ionic liquid abided by the order [BMIM][ZnCl$_3$] > [BMIM][ZnAcCl$_2$] > [BMIM][ZnAc$_2$Cl] > [BMIM][ZnAc$_3$]. Acetate ion could reduce the viscosity of ionic liquids. The relationship between viscosity/conductivity and temperature obeyed the Arrhenius equation and Vogel-Fulcher-Tammann (VFT) equation very well with above 0.99 correlation coefficients.

## 1. Introduction

Ionic liquid (IL) is a kind of liquid which is composed of ions under room temperature. Physical properties of ionic liquids are being odorless, being noncombustible, strong electrical conductivity, and very low vapor pressure which can be used as solvent in high vacuum system and reduce the problems of environmental pollution due to volatility [1]. Compared with traditional organic solvents and electrolytes, ionic liquid has a great ability to dissolve a large number of inorganic and organic substances and, sometimes, exhibits a double functional role of solvent and catalyst [2]. Ionic liquid can be used in the fields of chemical reaction solvent and catalytic reaction carrier. For example, Mehnert et al. [3] used [BMIM][PF$_6$] as chemical solvent for homogeneous hydroformylation catalysis. Bagheri et al. [4] prepared heteropolytungstate-ionic liquid as carrier which was supported on the surface of silica coated magnetite nanoparticles. Wang et al. [5] prepared ZnCl$_2$-[BMIM]Cl which was used in cocatalyzed coupling reaction of $CO_2$ with epoxides. Sun and Zhao [6] used [BMIM]Cl/[FeCl$_3$] ionic liquid as catalyst for alkylation of benzene with 1-octadecene. Liu et al. [7] studied using ionic liquid [BMIM][Ac] as a catalyst for methanolysis of polycarbonate.

In most cases, the physical properties of ionic liquid, especially conductivity and viscosity, have a great influence for chemical reaction process. In this study, four ionic liquids of [BMIM][ZnCl$_3$], [BMIM][ZnAcCl$_2$], [BMIM][ZnAc$_2$Cl], and [BMIM][ZnAc$_3$] were prepared and those viscosities and conductivities were measured at different temperatures. Arrhenius equation and Vogel-Fulcher-Tammann (VFT) were used to describe the relationship between the conductivity/viscosity and temperature.

## 2. Experimental

*2.1. Materials.* 1-Butyl-3-methylimidazolium chloride ([BMIM]Cl) and 1-butyl-3-methylimidazolium acetic acid ([BMIM]Ac) ionic liquids were purchased from Linzhou Keneng Material Technology Co., Ltd. Purity grades of [BMIM]Cl and [BMIM]Ac were above 99% and they could be used after drying treatment. Zinc chloride and Zinc acetate were analytically pure and used after drying process.

*2.2. Preparation of Ionic Liquids.* The ionic liquids had been prepared based on [8]. [BMIM][ZnCl$_3$] ionic liquid was prepared by mixing 0.3 mol [BMIM]Cl and 0.3 mol $ZnCl_2$ at 90°C for 24 h. [BMIM][ZnAcCl$_2$] ionic liquid was prepared by mixing 0.3 mol [BMIM]Ac and 0.3 mol $ZnCl_2$ at 90°C for 24 h. [BMIM][$ZnAc_2Cl$] ionic liquid was prepared by mixing 0.3 mol [BMIM]Cl and 0.3 mol $ZnAc_2$ at 90°C for 24 h. [BMIM][$ZnAc_3$] ionic liquid was prepared by mixing 0.3 mol [BMIM]Ac and 0.3 mol $ZnAc_2$ at 90°C for 24 h. All the samples should be dried in vacuum drying oven at 90°C for 24 h.

*2.3. Measurements of Conductivity and Viscosity.* The conductivities of [BMIM][$ZnCl_3$], [BMIM][$ZnAcCl_2$], [BMIM][$ZnAc_2Cl$], and [BMIM][$ZnAc_3$] 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 ILs dry, the experiment should be carried out in a dry nitrogen atmosphere in the temperature range 323.15 to 353.15 K with an interval of 5 K. The viscosities of [BMIM][$ZnCl_3$], [BMIM][$ZnAcCl_2$], [BMIM][$ZnAc_2Cl$], and [BMIM][$ZnAc_3$] 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 30 min to attain thermal equilibrium in the viscosity. Moreover, in order to prevent absorbing water from atmosphere, we should put the ILs in a dry nitrogen atmosphere when measuring the viscosity.

The water in the ionic liquid has a great influence on the data of conductivity and viscosity. So, moisture contents of ionic liquids were measured using a 851 Karl-Fischer Moisture Titrator (Metrohm). The results showed that the moisture contents of [BMIM][$ZnCl_3$], [BMIM][$ZnAcCl_2$], [BMIM][$ZnAc_2Cl$], and [BMIM][$ZnAc_3$] were 69.2 ppm, 83.5 ppm, 98.4 ppm, and 101.2 ppm, respectively. All the ionic liquids exhibited an extremely low moisture content in measuring process.

## 3. Results and Discussion

*3.1. Conductivities of ILs at Different Temperature.* The conductivities of [BMIM][$ZnAc_3$], [BMIM][$ZnAc_2Cl$], [BMIM][$ZnAcCl_2$], and [BMIM][$ZnCl_3$] ionic liquids are shown in Figure 1. From Figure 1, it is clearly seen that conductivities of ionic liquids increase with the rise of temperature. The conductivities of [BMIM][$ZnAc_3$] are 0.37 ms·cm$^{-1}$ at 323.15 K and 2.05 ms·cm$^{-1}$ at 353.15 K, respectively. The conductivities of [BMIM][$ZnAc_2Cl$] are 2.32 ms·cm$^{-1}$ at 328.15 K and 4.88 ms·cm$^{-1}$ at 348.15 K, respectively. The conductivities of [BMIM][$ZnAcCl_2$] are 3.36 ms·cm$^{-1}$ at 333.15 K and 4.86 ms·cm$^{-1}$ at 343.15 K, respectively. The conductivities of [BMIM][$ZnCl_3$] are 0.74 ms·cm$^{-1}$ at 323.15 K and 1.86 ms·cm$^{-1}$ at 338.15 K, respectively. With the rise of temperature, conductivities of ionic liquids have a great increase because the solvation degree and ion radius of ionic liquid are reduced. The ion motion is accelerated by the increase of temperature, which can also cause the improvement of the conductivity. Furthermore, the increase of temperature leads to the decrease of the solution viscosity and ions are easier to move. From Figure 1, the conductivities of different

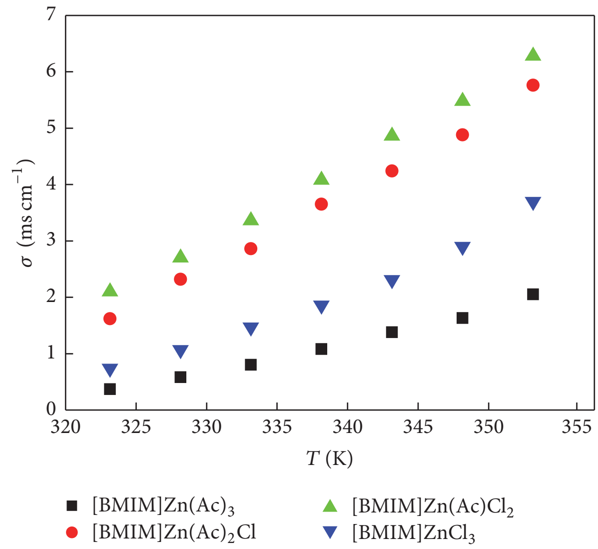



Figure 1: Conductivity of ILs at temperature from 323.15 K to 353.15 K.

ionic liquids at the same temperature followed the trend [BMIM][$ZnAcCl_2$] > [BMIM][$ZnAc_2Cl$] > [BMIM][$ZnCl_3$] > [BMIM][$ZnAc_3$]. For example, in 338.15 K, the conductivities of [BMIM][$ZnAc_3$], [BMIM][$ZnAc_2Cl$], [BMIM][$ZnAcCl_2$], and [BMIM][$ZnCl_3$] are 1.08 ms·cm$^{-1}$, 3.65 ms·cm$^{-1}$, 4.08 ms·cm$^{-1}$, and 1.86 ms·cm$^{-1}$, respectively. Compared with $[ZnAc_3]^-$, $[ZnCl_3]^-$ has the features of smaller ionic radius and lower mass which are advantage for ionic transportation. For another aspect, organic ion exhibits a weak ionization which is also bad for conductivity. So, conductivity of $[ZnAcCl_2]^-$ is better than $[ZnAc_2Cl]^-$. Contrary to $[ZnCl_3]^-$, the symmetry of $[ZnAc_2Cl]^-$ is low which is good for the ionic movement. The higher the symmetry in anion of ionic liquids, the lower the conductivity. The more the chlorine ion and the less the acetic acid, the greater the conductivity.

The relationship between conductivities of ionic liquid and temperature followed Arrhenius equation [9], which is described as

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

Here, $\sigma$ is the conductivity and $\sigma_{\infty}$ is the empirical constant. $E_{\sigma}$ notes for the activation energy. $T$ is the temperature and $R$ is 8.314 J·mol$^{-1}$·K$^{-1}$. According to the Arrhenius equation and experimental data, the relationship between conductivity and temperature is shown in Figure 2 and the calculated values of $\sigma_{\infty}$, $E_{\sigma}$, and $R^2$ (correlation coefficient) are listed in Table 1. From Table 1, correlation coefficients ($R^2$) of four ionic liquids are above 0.99. The conductivities of ionic liquids at different temperatures follow Arrhenius relationship very well. The [BMIM]Zn(Ac)$_3$ ionic liquid has the maximal $E_{\sigma}$ and $\sigma_{\infty}$ compared to the other three ionic liquids. The $E_{\sigma}$ values and $\sigma_{\infty}$ values follow the order of [BMIM]Zn(Ac)$_3$ > [BMIM]ZnCl$_3$ > [BMIM]Zn(Ac)$_2$Cl > [BMIM]Zn(Ac)Cl$_2$.

TABLE 1: Fitted values of conductivity of $\sigma_\infty$, $E_\sigma$, $\sigma_0$, $B$, $T_0$, and $R_2$ based on Arrhenius equation and VFT equation.

| ILs | Arrhenius equation | | | VFT equation | | | |
|---|---|---|---|---|---|---|---|
| | $10^{-6}\cdot\sigma_\infty$/mS·cm$^{-1}$ | $E_\sigma$/kJ·mol$^{-1}$ | $R^2$ | $\sigma_0$/mS·cm$^{-1}$ | B/K | $T_0$/K | $R^2$ |
| [BMIM]Zn(Ac)$_3$ | 137.5 | 52.70 | 0.9917 | 22.70 | 177.3 | 280 | 0.9996 |
| [BMIM]Zn(Ac)$_2$Cl | 3.197 | 38.68 | 0.9904 | 29.64 | 116.3 | 283 | 0.9990 |
| [BMIM]Zn(Ac)Cl$_2$ | 0.8267 | 34.47 | 0.9949 | 52.83 | 187.6 | 265 | 0.9998 |
| [BMIM]ZnCl$_3$ | 76.78 | 49.40 | 0.9969 | 214.0 | 441.7 | 245 | 0.9992 |

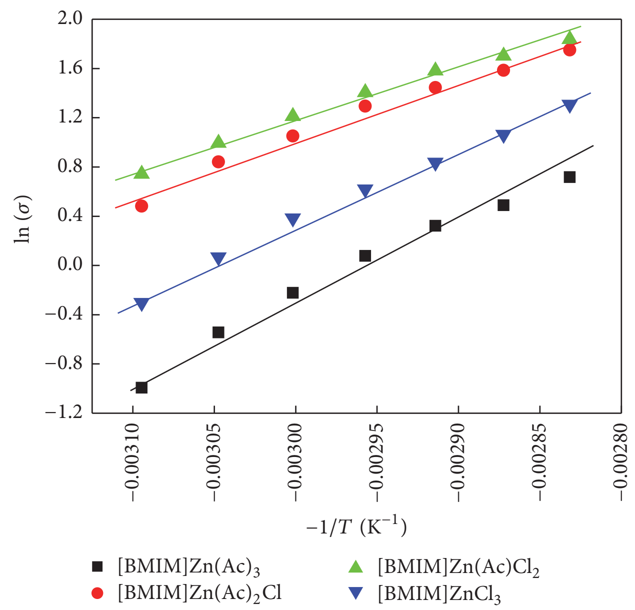



FIGURE 2: Relationship between conductivity and temperature based on Arrhenius equation.

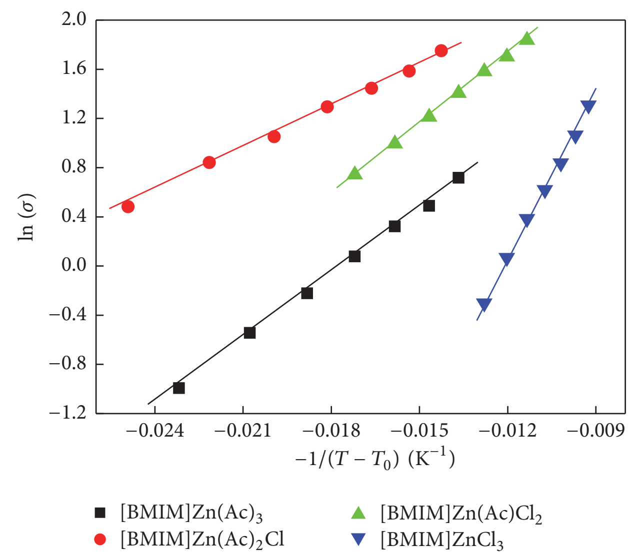



FIGURE 3: Relationship between conductivity and temperature based on VFT equation.

According to [10], the conductivity of ionic liquids also obeyed Vogel-Fulcher-Tammann (VFT) equation which is shown in

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

Here, $\sigma_0$, $B$, and $T_0$ are the empirical constants. According to the VFT equation, the relationship between conductivity and temperature is shown in Figure 3 and $\sigma_0$, $B$, $T_0$, and $R^2$ are calculated and listed in Table 1. From Table 1, it is clearly seen that all the $R^2$ values are above 0.99 which means VFT equation is better to describe the relationship between conductivity and temperature than Arrhenius equation. The biggest $\sigma_0$ and $B$ values are [BMIM]ZnCl$_3$ ionic liquid with 214.0 mS·cm$^{-1}$ and 441.7 K, respectively, compared to the other three ionic liquids. The smallest $T_0$ is [BMIM]ZnCl$_3$ ionic liquid with 245 K and the biggest is [BMIM]Zn(Ac)$_2$Cl with 283 K compared to others.

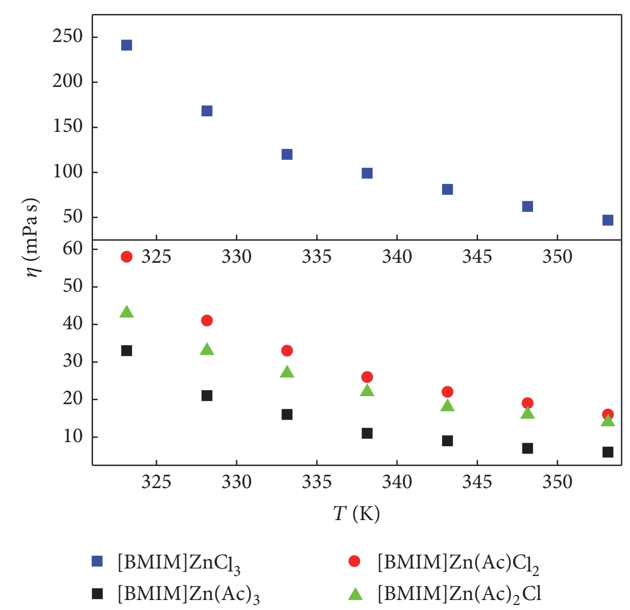



FIGURE 4: Viscosity of ILs at temperature from 323.15 K to 353.15 K.

*3.2. Viscosity of ILs at Different Temperature.* The viscosities of [BMIM][ZnAc$_3$], [BMIM][ZnAc$_2$Cl], [BMIM][ZnAcCl$_2$], and [BMIM][ZnCl$_3$] ionic liquids are shown in Figure 4. From Figure 4, it is clearly seen that viscosities of ionic liquids express a decrease in tendency with the rise of temperature. The reason is that high temperature is a disadvantage for the intermolecular association. In low temperature, high intermolecular association can improve the viscosity of ionic liquid. For example, the viscosities of [BMIM][ZnAc$_3$] are

Table 2: Fitted values of viscosity of $\sigma_\infty$, $E_\sigma$, $\sigma_0$, $B$, $T_0$, and $R_2$ based on Arrhenius equation and VFT equation.

| ILs | Arrhenius equation | | | VFT equation | | | |
|---|---|---|---|---|---|---|---|
| | $10^6 \cdot \eta_\infty$/mPa·s | $E_\eta$/kJ·mol$^{-1}$ | $R^2$ | $\eta_0$/mPa·s | B/K | $T_0$/K | $R^2$ |
| [BMIM]Zn(Ac)$_3$ | 0.06345 | 52.51 | 0.9922 | 0.3586 | 221.9 | 274 | 0.9989 |
| [BMIM]Zn(Ac)$_2$Cl | 75.29 | 34.73 | 0.9952 | 1.291 | 221.3 | 260 | 0.9994 |
| [BMIM]Zn(Ac)Cl$_2$ | 22.01 | 38.66 | 0.9927 | 2.442 | 142.7 | 278 | 0.9993 |
| [BMIM]ZnCl$_3$ | 2.282 | 49.48 | 0.9964 | 0.1022 | 914.0 | 205 | 0.9972 |

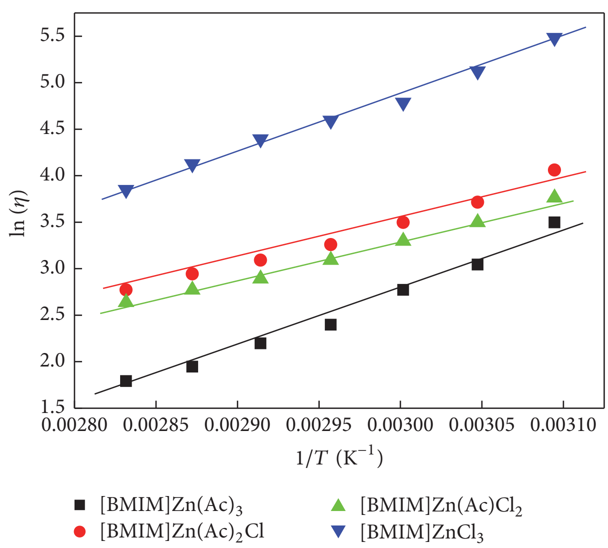



Figure 5: Relationship between viscosity and temperature based on Arrhenius equation.

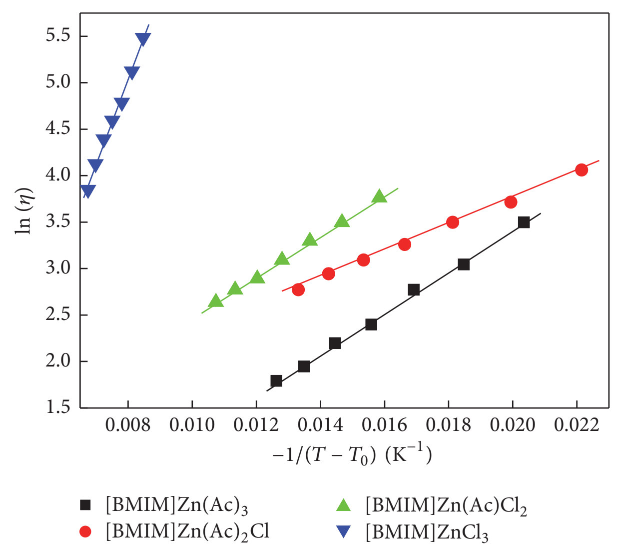



Figure 6: Relationship between viscosity and temperature based on VFT equation.

33 mPa·s at 323.15 K and 6 mPa·s at 353.15 K, respectively. The viscosities of [BMIM][ZnAc$_2$Cl] are 33 mPa·s at 328.15 K and 18 mPa·s at 348.15 K. The viscosities of [BMIM][ZnAcCl$_2$] are 58 mPa·s at 323.15 K and 22 mPa·s at 343.15 K. The viscosities of [BMIM][ZnCl$_3$] are 241 mPa·s at 323.15 K and 99 mPa·s at 338.15 K. The viscosities of [BMIM][ZnCl$_3$] are significantly higher than other ionic liquids. The viscosity order of four ionic liquids followed the tendency [BMIM][ZnCl$_3$] > [BMIM][ZnAcCl$_2$] > [BMIM][ZnAc$_2$Cl] > [BMIM][ZnAc$_3$]. Acetate ion can reduce the viscosity of ionic liquids. On the contrary, chloride ion can increase the viscosity of the ionic liquids.

According to [11], the Arrhenius equation exhibited in (3) can be used to describe the relationship between viscosity and temperature.

$$\ln \eta = \ln \eta_\infty + \frac{E_\eta}{RT}. \quad (3)$$

Here, $\eta_\infty$ is the empirical constant and $E_\eta$ denotes the activation energy for viscous flow. Figure 5 shows the relationship between viscosity of the logarithm and reciprocal of absolute temperature. From Figure 5, $\ln \eta$ and $1/T$ is linear correlation. The fitting result is shown in Table 2. From Table 2, the correlation coefficients are greater than 0.99 which indicated that Arrhenius formula is good enough to describe the relationship between viscosity and temperature of ionic liquids. The $E_\eta$ values of [BMIM]Zn(Ac)$_3$ and [BMIM]ZnCl$_3$ are 52.51 kJ·mol$^{-1}$ and 49.48 kJ·mol$^{-1}$, respectively. The $E_\eta$ values of [BMIM] Zn(Ac)$_2$Cl and [BMIM]Zn(Ac)Cl$_2$ are 34.73 kJ·mol$^{-1}$ and 38.66 kJ·mol$^{-1}$, respectively.

The viscosity values of four ionic liquids are also fitted by the VFT equation which is shown in

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

Here, $\eta_0$, $B$, $T_0$ are the empirical constants. According to the VFT equation, relationship between dynamic viscosity and temperature is shown in Figure 6. From Figure 6, viscosity of ionic liquids at different temperature followed VFT equation very well. The fitting data was shown in Table 2. From Table 2, the correlation coefficients which are calculated by VFT equation are superior to Arrhenius model.

## 4. Conclusions

Four ionic liquids of [BMIM][ZnCl$_3$], [BMIM][ZnAcCl$_2$], [BMIM][ZnAc$_2$Cl], and [BMIM][ZnAc$_3$] were prepared and those viscosity and conductivity data of ILs were detected at temperature ranging from 323.15 to 353.15 K with an interval of 5 K. The conductivity order at the same temperature followed the trend: [BMIM][$ZnAcCl_2$] > [BMIM][$ZnAc_2Cl$] > [BMIM][$ZnCl_3$] > [BMIM][$ZnAc_3$]. The higher the symmetry in anion of ionic liquid, the lower the conductivity. The more the chlorine ion and the less the acetic acid, the greater the conductivity. The viscosity order of four ionic liquids is as follows: [BMIM][$ZnCl_3$] > [BMIM][$ZnAcCl_2$] > [BMIM][$ZnAc_2Cl$] > [BMIM][$ZnAc_3$]. Acetate ion could reduce the viscosity of ionic liquids. On the contrary, chloride ion could increase the viscosity of the ionic liquids. The relationship between viscosity/conductivity and temperature obeyed the Arrhenius equation and Vogel-Fulcher-Tammann (VFT) equation very well with above 0.99 correlation coefficients. According to the $R^2$ values, VFT equation was superior to Arrhenius model.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Acknowledgments

This work is supported by the National Natural Science Foundation of China (no. 21006057), Nature Science Foundation of Henan Province (no. 162300410083), and Youth Teacher Support Program of Henan Provincial University (no. 2014GGJS-055).

## References

[1] A. R. Ferreira, L. A. Neves, J. C. Ribeiro et al., "Removal of thiols from model jet-fuel streams assisted by ionic liquid membrane extraction," *Chemical Engineering Journal*, vol. 256, pp. 144–154, 2014.

[2] W. Ochędzan-Siodłak and K. Dziubek, "Metallocenes and post-metallocenes immobilized on ionic liquid-modified silica as catalysts for polymerization of ethylene," *Applied Catalysis A: General*, vol. 484, pp. 134–141, 2014.

[3] C. P. Mehnert, R. A. Cook, N. C. Dispenziere, and M. Afeworki, "Supported ionic liquid catalysis—a new concept for homogeneous hydroformylation catalysis," *The Journal of the American Chemical Society*, vol. 124, no. 44, pp. 12932-12933, 2002.

[4] M. Bagheri, M. Masteri-Farahani, and M. Ghorbani, "Synthesis and characterization of heteropolytungstate-ionic liquid supported on the surface of silica coated magnetite nanoparticles," *Journal of Magnetism and Magnetic Materials*, vol. 327, pp. 58–63, 2013.

[5] F. Wang, C. Xu, Z. Li, C. Xia, and J. Chen, "Mechanism and origins of enantioselectivity for [BMIM]Cl ionic liquids and ZnCl2 co-catalyzed coupling reaction of $CO_2$ with epoxides," *Journal of Molecular Catalysis A: Chemical*, vol. 385, pp. 133–140, 2014.

[6] X. Sun and S. Zhao, "[bmim]Cl/[FeCl3] ionic liquid as catalyst for alkylation of benzene with 1-octadecene," *Chinese Journal of Chemical Engineering*, vol. 14, no. 3, pp. 289–293, 2006.

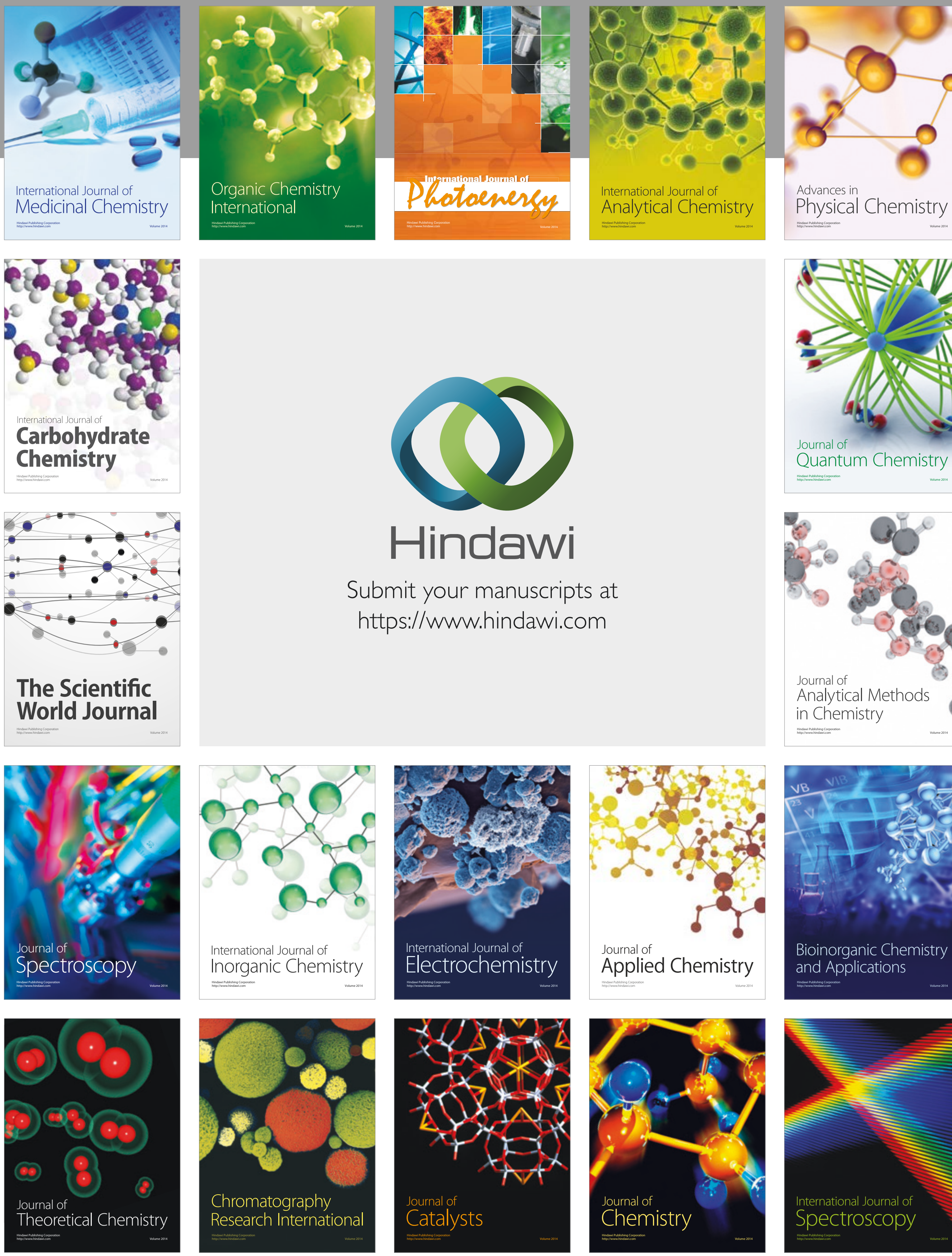
[7] F. Liu, L. Li, S. Yu, Z. Lv, and X. Ge, "Methanolysis of polycarbonate catalysed by ionic liquid [Bmim][Ac]," *Journal of Hazardous Materials*, vol. 189, no. 1-2, pp. 249–254, 2011.

[8] H. Xu, T. Yu, M. Li, and Z. Liang, "Viscosities and conductivities of [BMIM][ZnxCly] (x = 1, 1.5, 2; y = 3, 4, 5) ionic liquids at different temperatures," *Asian Journal of Chemistry*, vol. 27, no. 1, pp. 349–352, 2015.

[9] J. Restolho, A. P. Serro, J. L. Mata, and B. Saramago, "Viscosity and surface tension of 1-ethanol-3-methylimidazolium tetrafluoroborate and 1-methyl-3-octylimidazolium tetrafluoroborate over a wide temperature range," *Journal of Chemical and Engineering Data*, vol. 54, no. 3, pp. 950–955, 2009.

[10] H. Tokuda, K. Hayamizu, K. Ishii, M. A. B. H. Susan, and M. Watanabe, "Physicochemical properties and structures of room temperature ionic liquids. 2. Variation of alkyl chain length in imidazolium cation," *Journal of Physical Chemistry B*, vol. 109, no. 13, pp. 6103–6110, 2005.

[11] C. Schreiner, S. Zugmann, R. Hartl, and H. J. Gores, "Temperature dependence of viscosity and specific conductivity of fluoroborate-based ionic liquids in light of the fractional walden rule and angell's fragility concept," *Journal of Chemical and Engineering Data*, vol. 55, no. 10, pp. 4372–4377, 2010.


International Journal of Medicinal Chemistry
Organic Chemistry International
International Journal of Photoenergy
International Journal of Analytical Chemistry
Advances in Physical Chemistry
International Journal of Carbohydrate Chemistry
Journal of Quantum Chemistry
Hindawi
Submit your manuscripts at
https://www.hindawi.com
The Scientific World Journal
Journal of Analytical Methods in Chemistry
Journal of Spectroscopy
International Journal of Inorganic Chemistry
International Journal of Electrochemistry
Journal of Applied Chemistry
Bioinorganic Chemistry and Applications
Journal of Theoretical Chemistry
Chromatography Research International
Journal of Catalysts
Journal of Chemistry
International Journal of Spectroscopy