

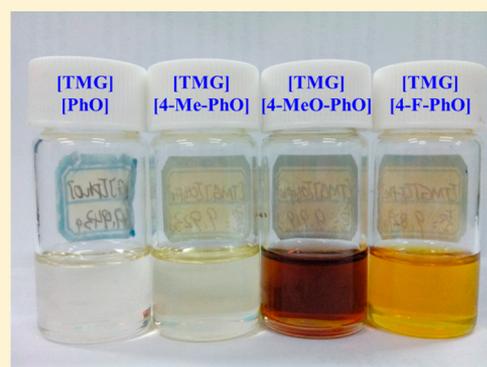
Low-Viscosity Tetramethylguanidinium-Based Ionic Liquids with Different Phenolate Anions: Synthesis, Characterization, and Physical Properties

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S Supporting Information

ABSTRACT: A new series of low-viscosity tetramethylguanidinium-based ionic liquids (ILs) with various substituted phenolate anions were prepared and characterized using nuclear magnetic resonance and Fourier transform infrared spectroscopy, elemental analysis, differential scanning calorimetry analysis, and thermogravimetry. Their densities, viscosities, refractive indices, and electrical conductivities were measured and correlated with thermodynamic and empirical equations in the temperature range of (298.15 to 343.15) K under ambient conditions. The effects of substituent groups in phenolate anions on these physical properties were then discussed on the basis of structure. Furthermore, the thermal expansion coefficient was calculated from the experimental values of density, and the correlation between the viscosity and the molar conductivity was proposed by the Walden rule. These ILs are classified as “poor ionic liquids” and have a poor temperature dependency of the thermal expansion coefficient.



INTRODUCTION

Ionic liquids (ILs) are a group of molten salts composed of relatively large organic cations and inorganic or organic anions, and they are often liquids at close to room temperature. In recent years, ILs have been attracting increasing attention because of their remarkable properties such as designable structure, low volatility, high thermal and chemical stability, and outstanding solubility.^{1–3} Thus, these features offer opportunities for the applications of ILs in many fields such as gas absorption, catalysis, liquid–liquid extraction, and biotransformation.^{3–6}

Nowadays, a large number of new task-specific ILs have been synthesized and reported for specific uses. However, one of the biggest difficulties in the applications of task-specific ILs is their highly viscous nature. High viscosity can lead to low diffusion coefficients and slow mass transfer, and prolong equilibrium times in many processes such as heat exchange, gas absorption, and liquid–liquid extraction. Thus, ILs of low viscosity are eagerly conceived and prepared through molecular design. In 2001, MacFarlane and co-workers first reported new families of low-viscosity dicyanamide-based ILs and found that 1-ethyl-3-methylimidazolium dicyanamide has the lowest viscosity of 21 mPa·s at room temperature.⁷ After that, Wu et al.⁸ designed and synthesized low-viscosity amino acids ILs with asymmetric tetraalkylammonium cations, and the equilibrium of CO₂ absorption in [N₂₂₂₄][L-Ala] could be reached within 30 min. Other kinds of imide-based, phenol-based, and ether-function-alized low-viscosity ILs had been also prepared and reported for the capture of CO₂ and SO₂, respectively.^{9–11}

Although there have been improvements of low-viscosity ILs, only a fraction of those ILs composed of several expensive anions such as [Tf₂N] and [N(CN)₂] are found to have low viscosities, and there are still few ILs whose viscosity is lower than 20 cP at room temperature.^{7,8,12} Therefore, the design and preparation of ILs with low cost and viscosity continue to be appealing and are highly conceived. In addition, it is believed that the physical properties of ILs such as density, viscosity, refractive index, and conductivity are very essential to most industrial processes involving ILs. Complete data sets are also required for the development of computational methods of molecular simulation.^{13,14} For the development of industrial processes, the basic physical data of ILs should be studied.

Herein, we designed and prepared diverse low-viscosity phenolic ILs via the neutralization of tetramethylguanidine with various phenols. The synthesized ILs were then characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, differential scanning calorimetry (DSC) analysis, and thermogravimetry. Several important physical properties such as density, viscosity, conductivity, and refractive index had been measured at the temperature ranging from (298.15 to 343.15) K under atmospheric condition. The effects of substituent groups in phenolate anions on their physical properties were also studied.

Received: July 7, 2014

Accepted: October 24, 2014

Published: November 5, 2014

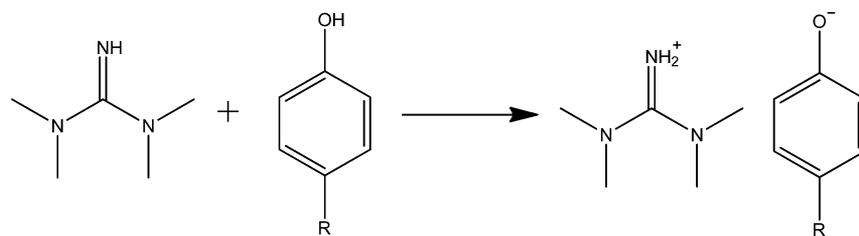


Figure 1. General route for the synthesis of phenolic ILs.

EXPERIMENTAL SECTION

Materials. Tetramethylguanidine (98 %), phenol (99.5 %), *p*-cresol (99 %), 4-methoxyphenol (99 %), and 4-fluorophenol were from Energy Chemical Reagent Co. Ltd. (Shanghai, China) and freshly distilled before use.

Synthesis of Phenolic ILs. Four phenolic ILs, [TMG]-[PhO], [TMG][4-Me-PhO], [TMG][4-MeO-PhO], and [TMG][4-F-PhO] (Figure 1), were prepared by the neutralization reactions of tetramethylguanidine with different substituted phenols. In a typical procedure, phenol (0.03 mol) was charged into a 10 mL flat-bottom flask. Then a stoichiometric amount of tetramethylguanidine (0.03 mol) was added and stirred vigorously for 4 h at room temperature to complete the reaction. After that, tetramethylguanidinium phenolate ([TMG][PhO]) was obtained in quantitative yield. The synthesis procedures of [TMG][4-Me-PhO], [TMG][4-MeO-PhO], and [TMG][4-F-PhO] were similar to that of [TMG]-[PhO]. Then the water contents were determined by Karl Fischer titration (Metrohm 756 KF coulometer), and the percentage of water was less than 0.1 % in each phenolic IL. Before measuring the values of density, viscosity, refractive index, and conductivity, all of the ILs samples were kept in vacuum oven at 50 °C to avoid contact from atmospheric air.

Characterization. ¹H and ¹³C NMR spectra were performed on a Bruker Avance 400 spectrometer. FT-IR spectra were recorded on a PerkinElmer Spectrum One spectrometer. Carbon, hydrogen, and nitrogen contents were analyzed using an elemental analyzer (EuroVector EA3000).

Thermal Decomposition and Glass Transition Temperature. The thermal stability of these four phenolic ILs was measured using a PerkinElmer Diamond TG/DTA thermogravimetric analyzer. Samples were heated from (25 to 350) °C in sealed aluminum pans in nitrogen. The heating rate was 10 °C/min. The accuracy of the measurement was better than ± 3 °C. The decomposition temperatures (*T_d*) were then calculated according to our previous work.¹⁵ Furthermore, the glass transition temperatures (*T_g*) of these four phenolic ILs were determined by the DSC curves (Netzsch DSC 200F3). The samples were heated in sealed aluminum pans under nitrogen atmosphere from (25 to 60) °C and then cooled to -60 °C and again heated to 60 °C at a scan rate of 10 °C/min.

Density and Viscosity Measurements. The densities and viscosities of phenolic ILs were measured with a Anton Paar densimeter (DMA4500) and cone-plate viscometer (Brookfield DV II+ Pro) in the temperature range of (298.15 to 343.15) K at atmospheric pressure. The temperature accuracy was controlled at ± 0.05 K. The precision of the density value was ± 0.001 g·cm⁻³. Before the measurements, the density apparatus was calibrated with double-distilled water and dry air.

The uncertainties of the viscometer were estimated to be ± 3 %, and the thermal equilibrium time was maintained about 30 min.

Refractive Index and Conductivity Measurements. Refractive indices were recorded with a Rudolph research analytical J357 refractometer with a measuring precision of ± 0.001 and a temperature accuracy of ± 0.05 K at temperatures from (298.15 to 343.15) K. Pure solvents with known refractive indices were applied to check and calibrate the apparatus before the measurements.¹² Conductivities were measured using a DJS-1C electrode attached in a conductivity meter (DDJS-308A, Shanghai Leici Co.). The conductivity accuracy was ± 3 %.

RESULTS AND DISCUSSION

The ¹H and ¹³C NMR spectral data, elemental analysis, and FT-IR spectra are shown in the Supporting Information (Figure S1). Thus, the structures identification and purity of the synthesized ILs are confirmed by all of the characterization results. The thermal gravimetric analysis (TGA) curves and DSC curves are also listed in the Supporting Information (Figures S2–S6). Then the *T_d* and *T_g* values obtained for these phenolic ILs are shown in Table 1. It is observed that the *T_d*

Table 1. Thermal Properties for Phenolic ILs

entry	ILs	<i>T_g</i> /°C	<i>T_d</i> /°C
1	[TMG][PhO]	-53.8	104
2	[TMG][4-Me-PhO]	-53.1	100
3	[TMG][4-MeO-PhO]	-52.6	115
4	[TMG][4-F-PhO]	-52.8	100

values are in the range of (100 to 115) °C and all of the *T_g* values are below -50 °C. This finding demonstrates that these phenolic ILs have a wide liquid range but show a relatively poor thermal stability. The effortless oxidation of phenolate anion and its derivatives at high temperature is considered to be the main cause of the weak thermal stability. Moreover, Yang et al.¹⁶ demonstrated that guanidinium-based ILs attaching bis(trifluoromethanesulfonyl)imide (Tf₂N) anions showed excellent thermal stability, which further validates that phenolic anions have a negative effect on thermal stability of guanidinium phenolic ILs.

The density data of four phenolic ILs are shown in Figure 2 and presented in Table 2. It is indicated that the densities of these ILs at 298.15 K are within (1.03468 to 1.10683), and the values are higher than those of the other phenolic ILs composed of [P₆₆₆₁₄] cation, which could be due to the high molecular volume of cation.¹⁰ It is also observed that the

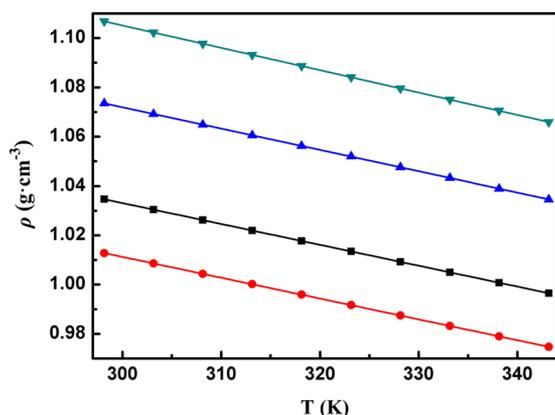


Figure 2. Densities ρ as a function of temperature: [TMG][PhO] (black boxes), [TMG][4-Me-PhO] (red solid circles), [TMG][4-MeO-PhO] (blue triangles), and [TMG][4-F-PhO] (green triangles).

densities decrease linearly with the increase of temperature, and the densities increase in the following sequence: [TMG][4-Me-PhO] < [TMG][PhO] < [TMG][4-MeO-PhO] < [TMG][4-F-PhO]. These results show that the improvement of the anion molecular weight does not correspondingly increase the density values for such ILs, and a similar phenomenon for other cholinium-based and imidazolium-based ILs was observed by Tao et al. and Ziyada and Wilfred.^{15,17} It is also interesting to find that different substituent groups in phenolate anions have a significant effect on the densities. [TMG][4-F-PhO] ILs shows the highest density value, even though the molecular mass of its anion is relative small. This might be ascribed to strong molecular force and hydrogen bonding in the presence of 4-fluorophenolate anion. The electron-withdrawing fluorine group shows more electronegativity compared to the other anions and then increases molecular agglomeration, leading to a higher density. This behavior is similar to the case of the replacement of H in CH_3 in $[\text{CH}_3\text{COO}]^-$ anion by an -OH or - NH_2 substituent group.¹⁸

Viscosity measurement was performed at temperatures from (298.15 to 343.15) K. The corresponding data are shown in Figure 3 and Table 3. It is seen that increasing the temperature causes an evident drop in the viscosity values of these phenolic ILs, and the structure of anions has a strong impact on the viscosity. [TMG][PhO] incorporating the smallest anion performs the lowest viscosity, whereas [TMG][4-MeO-PhO] shows higher viscosity due to the bulky volume of the anions.

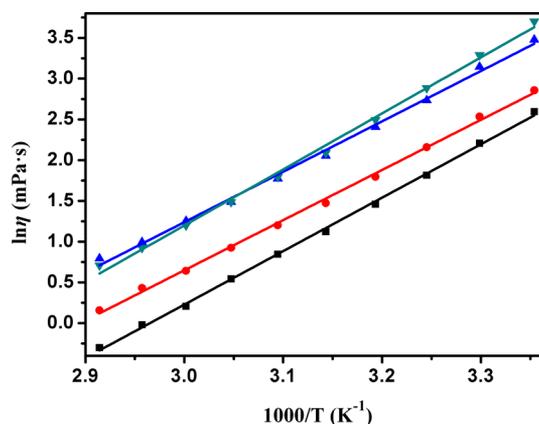


Figure 3. Viscosities η as a function of temperature: [TMG][PhO] (black boxes), [TMG][4-Me-PhO] (red solid circles), [TMG][4-F-PhO] (blue triangles), and [TMG][4-MeO-PhO] (green triangles).

This demonstrates that the anion with a larger size always leads to higher viscosity which is similar to those reported earlier by the literature.^{19,20} In addition, it is indicated that tetramethylguanidinium-based ILs incorporating various phenolate anions show very low viscosities in comparison to other phenolate-functionalized ILs. For example, the viscosities of [TMG][4-Me-PhO] and [TMG][4-MeO-PhO] are only (17.4 and 32.4) mPa·s, respectively. However, [P₆₆₆₁₄][4-Me-PhO] and [P₆₆₆₁₄][4-MeO-PhO] perform the viscosities of (392.7 and 253.4) mPa·s at room temperature, which originates from their relatively large cations.¹⁰

Table 4 presents the refractive index values for the investigated phenolic ILs, and the influence of temperature on refractive index is then shown in Figure 4. It is indicated that the refractive indices of these phenolic ILs at 298.15 K are within (1.5358 to 1.5206), and the values are corresponding to those of alkylimidazolium bromide ILs (1.5454 to 1.5027).²¹ It is also indicated that the increase of temperature makes an obvious reduction in the refractive indexes, and the order is [TMG][4-F-PhO] < [TMG][4-Me-PhO] < [TMG][4-MeO-PhO] < [TMG][PhO]. This implies that the order of the refractive indexes is not closely related to the order of anionic molecular weight. For example, [TMG][4-MeO-PhO] IL shows relatively high refractive index value, even though its anion has the largest molecular mass. This finding is matched well with the report by Seki et al.,²² in which refractive index

Table 2. Experimental Density Values, ρ , for Phenolic ILs as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}^a$

T/K	$\rho/(\text{g}\cdot\text{cm}^{-3})$			
	[TMG][PhO]	[TMG][4-Me-PhO]	[TMG][4-MeO-PhO]	[TMG][4-F-PhO]
298.15	1.03468	1.01279	1.07352	1.10683
303.15	1.03043	1.00857	1.06922	1.10229
308.15	1.02620	1.00436	1.06490	1.09774
313.15	1.02197	1.00015	1.06059	1.09319
318.15	1.01773	0.99593	1.05627	1.08866
323.15	1.01350	0.99171	1.05195	1.08412
328.15	1.00926	0.98747	1.04761	1.07958
333.15	1.00501	0.98322	1.04327	1.07504
338.15	1.00075	0.97896	1.03891	1.07050
343.15	0.99648	0.97468	1.03454	1.06594

^aStandard uncertainties u are $u(T) = 0.05 \text{ K}$, $u(p) = 10 \text{ kPa}$, and $u(\rho) = 0.001 \text{ g}\cdot\text{cm}^{-3}$.

Table 3. Experimental Viscosity Values, η , for Phenolic ILs as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}^a$

T/K	$\eta/(\text{mPa}\cdot\text{s})$			
	[TMG][PhO]	[TMG][4-Me-PhO]	[TMG][4-MeO-PhO]	[TMG][4-F-PhO]
298.15	13.40	17.40	32.40	40.50
303.15	9.09	12.60	23.20	26.80
308.15	6.14	8.66	15.40	17.90
313.15	4.30	6.02	11.10	12.10
318.15	3.07	4.36	7.80	8.10
323.15	2.33	3.32	5.89	6.02
328.15	1.72	2.52	4.42	4.42
333.15	1.23	1.90	3.50	3.32
338.15	0.98	1.54	2.70	2.52
343.15	0.74	1.17	2.21	2.03

^aStandard uncertainties u are $u(T) = 0.05 \text{ K}$, $u(p) = 10 \text{ kPa}$, and the relative standard uncertainty for viscosity $u_r(\eta) = 3\%$

Table 4. Experimental Refractive Index Values, n_D , for Phenolic ILs as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}^a$

T/K	n_D			
	[TMG][PhO]	[TMG][4-Me-PhO]	[TMG][4-MeO-PhO]	[TMG][4-F-PhO]
298.15	1.5358	1.5293	1.5334	1.5206
303.15	1.5332	1.5270	1.5309	1.5183
308.15	1.5305	1.5250	1.5282	1.5161
313.15	1.5282	1.5223	1.5255	1.5138
318.15	1.5258	1.5198	1.5230	1.5108
323.15	1.5230	1.5172	1.5205	1.5082
328.15	1.5202	1.5148	1.5180	1.5055
333.15	1.5178	1.5120	1.5153	1.5030
338.15	1.5150	1.5088	1.5126	1.5006
343.15	1.5122	1.5060	1.5102	1.4980

^aStandard uncertainties u are $u(T) = 0.05 \text{ K}$, $u(p) = 10 \text{ kPa}$, and $u(n_D) = 0.001$.

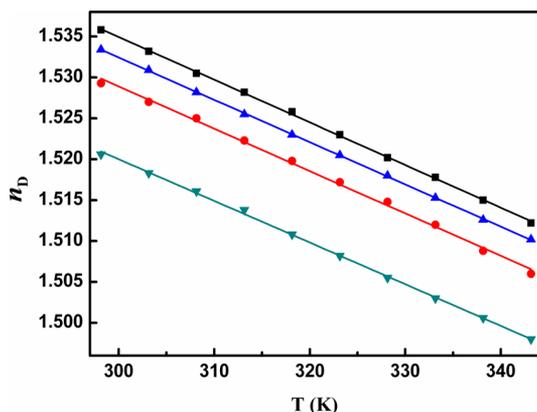


Figure 4. Refractive indices n_D as a function of temperature: [TMG][PhO] (black boxes), [TMG][4-Me-PhO] (red solid circles), [TMG][4-MeO-PhO] (blue triangles), and [TMG][4-F-PhO] (green triangles).

relies on the molecular polarizability of ion pairs per volume on the basis of the Lorentz–Lorenz equation.

The measured conductivities for these four ILs are listed in Table 5 and shown in Figure 5. It is observed that the conductivity values of these ILs are comparable to other series of guanidinium ILs composed of Tf_2N anions.¹⁶ The conductivity is found to increase with increasing temperature, whereas it decreases with a rise in the anion molecular size. For example, the conductivity of [TMG][PhO] increases to around 9 times from (298.15 to 343.15) K. The conductivity decreases from (240 to 140) $\mu\text{S}\cdot\text{cm}^{-1}$ at 298.15 K in the cases of

[TMG][PhO] and [TMG][4-MeO-PhO]. It has been pointed out that higher anion volume always facilitates an increase in the degree of ionic aggregation and thus leads to lower ionic mobility of the ILs.^{23,24} Therefore, the IL composed of a large anion contributes to a relatively low electrical conductivity.

The dependence of density (ρ), viscosity (η), refractive index (n_D), and conductivity (σ) for the present phenolic ILs on temperature can be described by the empirical equations.^{15,25,26}

$$\rho/(\text{g}\cdot\text{cm}^{-3}) = A_0 + A_1T \quad (1)$$

$$\ln \eta/(\text{mPa}\cdot\text{s}) = A_2 + A_3/T \quad (2)$$

$$n_D = A_4 + A_5T \quad (3)$$

$$\sigma/(\mu\text{S}\cdot\text{cm}^{-1}) = A_6 \exp\left(\frac{-A_7}{T - A_8}\right) \quad (4)$$

where T is the Kelvin temperature and $A_0, A_1, A_2, A_3, A_4, A_5, A_6, A_7,$ and A_8 are fitting parameters. These parameters are estimated using the least-squares method and are presented in Tables 6, 7, 8, and 9. Also the standard deviations (SD) are expressed as

$$\text{SD} = \sqrt{\sum_i^N (Z_{\text{exp}} - Z_{\text{cal}})^2 / N} \quad (5)$$

where Z_{exp} and Z_{cal} represent the experimental and calculated values and N is the number of experimental points. As seen from Tables 6 to 9, it is indicated that all of the correlation coefficients are over 0.99. The Arrhenius and Vogel–Tam-

Table 5. Experimental Conductivity Values, σ , for Phenolic ILs as a Function of Temperature at Pressure $p = 0.1 \text{ MPa}$ ^a

T/K	$\sigma/(\mu\text{S}\cdot\text{cm}^{-1})$			
	[TMG][PhO]	[TMG][4-Me-PhO]	[TMG][4-MeO-PhO]	[TMG][4-F-PhO]
298.15	240	151	140	159
303.15	333	217	191	240
308.15	457	296	255	335
313.15	626	385	329	473
318.15	787	507	428	627
323.15	964	623	526	792
328.15	1159	747	629	982
333.15	1380	878	735	1180
338.15	1606	1019	850	1408
343.15	1838	1173	961	1640

^aStandard uncertainties u are $u(T) = 0.05 \text{ K}$, $u(p) = 10 \text{ kPa}$, and $u(\sigma) = 3\%$.

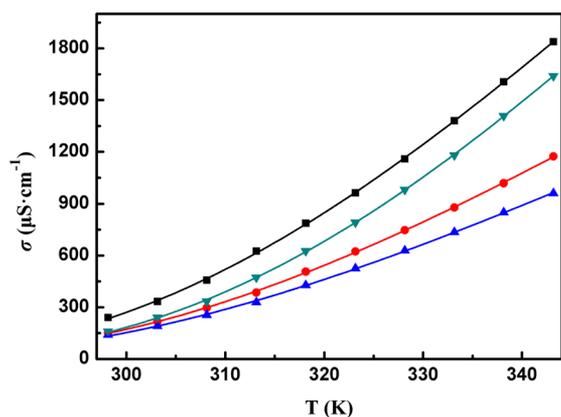


Figure 5. Conductivities σ as a function of temperature: [TMG]-[PhO] (black boxes), [TMG][4-Me-PhO] (red solid circles), [TMG][4-MeO-PhO] (blue triangles), and [TMG][4-F-PhO] (green triangles).

Table 6. Fitting Parameters of Density and Standard Deviations Calculated Using Equation 1

IL	A_0	$A_1 \cdot 10^4$	$SD \cdot 10^7$	R^2
[TMG][PhO]	1.28762	-8.48327	4.02198	1
[TMG][4-Me-PhO]	1.26516	-8.46327	7.88904	0.99999
[TMG][4-MeO-PhO]	1.33174	-8.65939	7.13609	0.99999
[TMG][4-F-PhO]	1.37766	-9.08376	1.55464	1

man-Fulcher (VTF) equations can describe the relationship of temperature with viscosity and conductivity very well.

The values of density at different temperatures are applied to calculate the thermal expansion coefficients (α_p) using the following equation:²⁷

$$\alpha_p = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p = -\frac{A_1}{A_0 + A_1 T} \quad (6)$$

where ρ , T , and α_p are density, absolute temperature, and thermal expansion coefficient, respectively. Table 10 shows that

Table 7. Fitting Parameters of Viscosity and Standard Deviations Calculated Using Equations 2

IL	A_2	A_3	SD	R^2
[TMG][PhO]	-19.43511	6554.44	0.07797	0.99873
[TMG][4-Me-PhO]	-17.81060	6152.98	0.09139	0.99802
[TMG][4-MeO-PhO]	-17.30556	6181.61	0.1239	0.99640
[TMG][4-F-PhO]	-19.42206	6873.52	0.13859	0.99635

Table 8. Fitting Parameters of Refractive Index and Standard Deviations Calculated Using Equation 3

IL	A_4	$A_5 \cdot 10^4$	$SD \cdot 10^6$	R^2
[TMG][PhO]	1.69134	-5.21333	4.09977	0.99944
[TMG][4-Me-PhO]	1.68426	-5.17818	9.29706	0.99711
[TMG][4-MeO-PhO]	1.68749	-5.16848	1.96199	0.99987
[TMG][4-F-PhO]	1.67285	-5.09455	5.39156	0.99899

the thermal expansion coefficients of phenolic ILs do not noticeably change in the temperature range of (298.15 to 343.15) K. The averaged relative deviation of α_p is less than 4%. This implies that these ILs almost have a temperature independency of the thermal expansion coefficient, $\alpha_p = (8.066 \times 10^{-4} \text{ to } 8.682 \times 10^{-4}) \text{ K}^{-1}$, and this behavior was compatible with the findings reported for ammonium- and imidazolium-based ILs.^{28,29}

The values of density and conductivity are used to calculate the molar conductivity using the following equation:

$$\Lambda = \sigma M / \rho \quad (7)$$

where Λ , M , and ρ represent molar conductivity, molar mass, and density, respectively. The molar conductivity data are then listed in Table 11. Furthermore, the relationship between the molar conductivity and viscosity can be described by Walden rule.^{30,31}

$$\Lambda \eta = W \quad (8)$$

where W represents a temperature-dependent constant and η is the dynamic viscosity. Figure 6 shows the Walden plots for these four phenolic ILs at different temperatures from (298.15 to 343.15) K. On the basis of the Walden rule, the ideal line of the aqueous KCl solutions at high dilution represents fully dissociated ionic solutions, which have ions of equal mobility. If the curves are remarkably over the ideal KCl line, this means an even faster transport of ions in view of the incomplete decoupling of ions in ILs. Under this condition, the ILs are considered as a "good ionic liquid". However, it is seen from Figure 6 that all of the curves of phenolic ILs reside below and

Table 9. Fitting Parameters of Conductivity Calculated Using Equation 4

IL	A_6	A_7	A_8	R^2
[TMG][PhO]	$2.74643 \cdot 10^4$	281.33286	239.10655	0.99982
[TMG][4-Me-PhO]	$1.59631 \cdot 10^4$	266.35135	241.21466	0.99979
[TMG][4-MeO-PhO]	$1.19918 \cdot 10^4$	257.56956	240.93913	0.99861
[TMG][4-F-PhO]	$3.25067 \cdot 10^4$	304.64163	241.15241	0.99991

Table 10. Thermal Expansion Coefficient Values, α_p , for Phenolic ILs as a Function of Temperature at Pressure $p = 0.1$ MPa

T/K	$\alpha_p \cdot 10^4 / (K^{-1})$			
	[TMG][PhO]	[TMG][4-Me-PhO]	[TMG][4-MeO-PhO]	[TMG][4-F-PhO]
298.15	8.1988	8.3561	8.0660	8.2070
303.15	8.2326	8.3911	8.0987	8.2408
308.15	8.2666	8.4265	8.1316	8.2749
313.15	8.3009	8.4621	8.1648	8.3093
318.15	8.3355	8.4981	8.1983	8.3440
323.15	8.3704	8.5344	8.2320	8.3789
328.15	8.4056	8.5709	8.2661	8.4142
333.15	8.4411	8.6078	8.3004	8.4497
338.15	8.4768	8.6450	8.3350	8.4856
343.15	8.5129	8.6826	8.3699	8.5217

Table 11. Molar Conductivity Values, Λ , for Phenolic ILs as a Function of Temperature at Pressure $p = 0.1$ MPa

T/K	$\Lambda / (mS \cdot cm^2 \cdot mol^{-1})$			
	[TMG][PhO]	[TMG][4-Me-PhO]	[TMG][4-MeO-PhO]	[TMG][4-F-PhO]
298.15	48.47876	33.24776	31.16849	32.60934
303.15	67.54171	47.97981	42.69374	49.42438
308.15	93.07445	65.72145	57.23073	69.27415
313.15	128.0214	85.84212	74.13892	98.21806
318.15	161.6175	113.5230	96.84266	130.7378
323.15	198.7923	140.0903	119.5057	165.8340
328.15	240.0085	168.6947	143.4990	206.4822
333.15	286.9822	199.1355	168.3792	249.1628
338.15	335.4024	232.1208	195.5415	298.5670
343.15	385.4990	268.3742	222.0107	349.2504

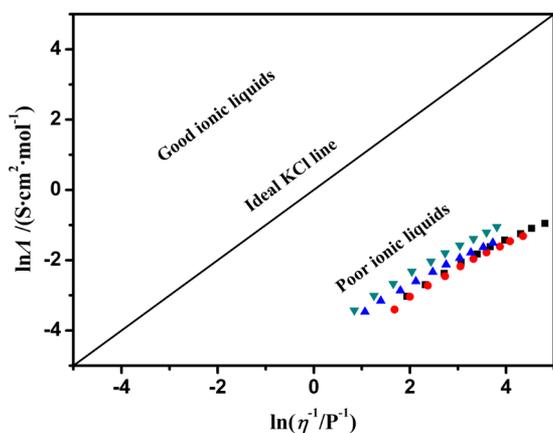


Figure 6. Walden plots for [TMG][PhO] (black boxes), [TMG][4-Me-PhO] (red solid circles), [TMG][4-MeO-PhO] (blue triangles), and [TMG][4-F-PhO] (green triangles). The solid straight line is the ideal line for a 0.01 M aqueous KCl solution.

far away from the ideal KCl line, indicating that these phenolic ILs must be defined as “poor ionic liquids”. This negative departure from the ideal KCl line may be due to the presence of an important fraction of ion pairs and/or aggregations, which results in the decreased conductivity at a certain viscosity.^{24,32}

Moreover, the lines are approaching straight lines, indicating that all of the phenolic ILs obey the Walden rule. Most of the reported ILs has also the same tendency.^{31–35}

CONCLUSION

A new series of low-viscosity tetramethylguanidinium-based ILs with different substituted phenolate anions were prepared, and the density, viscosity, refractive index and conductivity of these ILs were measured at temperatures from (298.15 to 343.15) K. The experimental results demonstrate that the density, viscosity, and refractive index decrease linearly with a rise in temperature, while the conductivity increases exponentially with the increase of temperature. Empirical equations were used to correlate the experimental data of physical properties, following in good agreement. In addition, the thermal expansion coefficients of phenolic ILs are found to be approximately independent of temperature. The Walden rule analysis demonstrates that these ILs comply with the Walden rule well, and they are classified as “poor ionic liquids”.

ASSOCIATED CONTENT

Supporting Information

Text describing additional experimental data and figures showing FT-IR spectra and TGA and DSC curves for the

TMG compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

This work was supported by the National Natural Science Foundations of China (Grant No. 21206063), the Science & Technology Programs of Jiangxi Provincial Department of Education (Grant No. GJJ14239), the Science & Technology Supporting Programs, the International Technological Cooperation Programs, and the Natural Science Foundations of Jiangxi Provincial Department of Science and Technology (Grant Nos. 20123BBE50081, 20132BDH80003, and 20122BAB203018), and the Sponsored Program for Cultivating Youths of Outstanding Ability in Jiangxi Normal University.

Notes

The authors declare no competing financial interest.

ABBREVIATIONS

[TMG][PhO] = tetramethylguanidinium phenolate

[TMG][4-Me-PhO] = tetramethylguanidinium methylphenolate

[TMG][4-MeO-PhO] = tetramethylguanidinium methoxyphenolate

[TMG][4-F-PhO] = tetramethylguanidinium fluorophenolate

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