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Evaluation of Thermophysical Properties of Imidazolium-Based Phenolate Ionic Liquids

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S Supporting Information

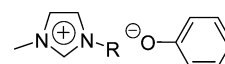
ABSTRACT: Thermophysical properties of imidazolium-based phenolate ionic liquids (ILs) were investigated over a wide temperature range. Different alkyl groups such as ethyl, butyl, hexyl, octyl, and decyl were tethered to the 1-methylimidazolium cation to study the effect of alkyl chain length on thermophysical properties such as density, viscosity, refractive index, heat capacity, and surface tension. The thermal stability of the phenolate ILs was investigated using thermogravimetric analysis. From the experimental values of density and surface tension, the molecular volume, standard molar entropy, lattice energy, surface entropy, and surface enthalpy of the ILs were calculated at 303.15 K.

INTRODUCTION

Ionic liquids (ILs) have been known for quite a long time, but in the last two decades there has been a significant increase in the application of ILs in the chemical industry as well as in academia. The commercialization of BASIL and DIFASOL processes has raised a global interest for industries around the world to work in the field of ILs.¹ ILs are molten salts composed of cations and anions.² The properties of ILs can be tuned by the careful choice of cations and anions. This tuning of properties makes ILs appropriate for a large number of applications. The cations of ILs are organic, and the anions can be either organic or inorganic. The structural modifications of cations and anions enables the production of almost 10⁶ ILs. This value is significantly higher than the small number of conventional solvents used in industrial applications.¹ These applications include separation processes, purification, catalysis, electrochemistry, solar cells, biomass dissolution, etc.^{3–10} Biomass dissolution can be done with ILs having anions with H-bond accepting nature.^{7,11–13} Binnemans and co-workers utilized the Lewis basicity of para substituted *tert*-butyl phenolate anion-based ILs (phenolate platform) for the development of a new route for the synthesis of hydrophilic ILs with very low halide content.¹⁴ They also utilized the phenolate platform for the synthesis of highly base stable quaternary ILs.¹⁵ It has been reported that ILs with phenolate anion are an effective medium for CO₂ capture applications.¹⁶ However, comprehensive study of the thermophysical properties of phenolate anion-based ILs is limited. In this work a detailed study of the thermophysical properties of phenolate-based ILs with the most commonly used imidazolium cation is presented. An overview of ILs used in this study is given in Figure 1.

EXPERIMENTAL SECTION

Materials and Methods. The chemicals used for the synthesis of ILs were purchased from Acros Organics (Geel Belgium) and Sigma-Aldrich (Bornem, Belgium). The synthesis



R = Ethyl, Butyl, Hexyl, Octyl, Decyl

Figure 1. Overview of the chemical structures and abbreviation of ILs used in this study.

of the ILs was carried out according to a reported procedure.¹⁷ However, rigorous purification and drying methods were applied to reduce the halide content and water content in the ILs compared to that of ILs in the previous report. The synthesized ILs were washed ten times with ethyl acetate (10 × 10 mL), and the ILs were dried in a vacuum line at 60 °C for 48 h. The water content and halide content of the ILs were reduced remarkably after the drying and purification. A Bruker Avance 500 spectrometer was used to record the ¹H and ¹³C NMR spectra. Water content of ILs was measured using a coulometric Karl Fischer titrator (Mettler Toledo, model DL39). The density and viscosity of the ILs was measured using the Anton Paar viscometer (model SVM3000) having a temperature uncertainty of $u(T) = \pm 0.01$ °C, viscosity uncertainty of $u(\mu) = \pm 0.32\%$, and uncertainty in the density calculations $u(\rho) = \pm 5 \times 10^{-6}$ g·cm⁻³. Surface tension was measured using the pendant drop method. The temperature range was from 293.15 to 353.15 K with uncertainty of $u(\sigma) = \pm 0.04$ mN·m⁻¹ and $u(T) = \pm 0.01$ K. An ATAGO programmable digital refractometer (RX-S000α) was used to measure the refractive indices of all the ILs. The temperature window was from 293.15 to 333.15 K. The uncertainty in measurement for this equipment is of the order of $\pm 4 \times 10^{-5}$, and the temperature accuracy is ± 0.05 K. Thermal decom-

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position temperature of the ILs was measured using a thermogravimetric analyzer (PerkinElmer, Pyris V-3.81). The heating rate was $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. The temperature accuracy is better than $\pm 1\text{ }^{\circ}\text{C}$. Melting point and heat capacity were measured using differential scanning calorimetry (DSC; PerkinElmer, model Pyris1). The sapphire method was used to calculate the specific heat capacity.¹⁸ The halide content of the ILs was measured using ion chromatogram (Metrohm, model 761 Compact IC). The details of these measurements can be found elsewhere.¹⁹

RESULTS AND DISCUSSION

Viscosity Measurement. An Anton Paar viscometer was used to perform the viscosity measurement in a temperature range from 293.15 K to 373.15 K. An increase in temperature decreased the viscosity. The viscosity versus temperature data are tabulated in Figures 2 and 3 and Table 1 in the Supporting

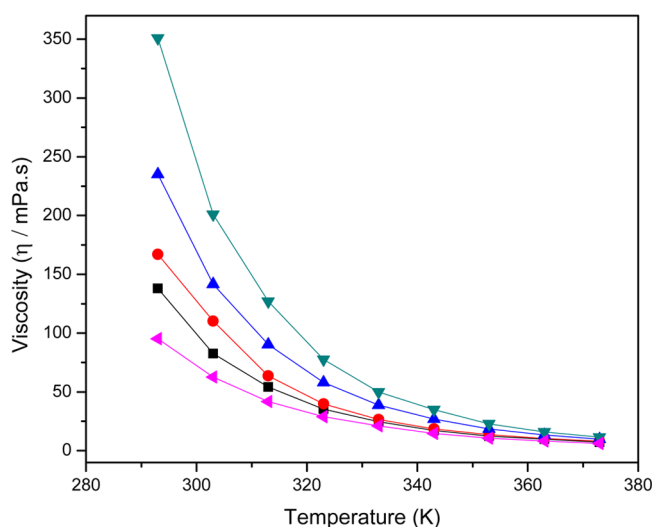


Figure 2. Experimental viscosity of ILs as a function of temperature: \blacktriangle , $[\text{C}_2\text{mim}][\text{Phe}]$; \blacksquare , $[\text{C}_4\text{mim}][\text{Phe}]$; \bullet , $[\text{C}_6\text{mim}][\text{Phe}]$; \blacktriangle , $[\text{C}_8\text{mim}][\text{Phe}]$; and \blacktriangledown , $[\text{C}_{10}\text{mim}][\text{Phe}]$.

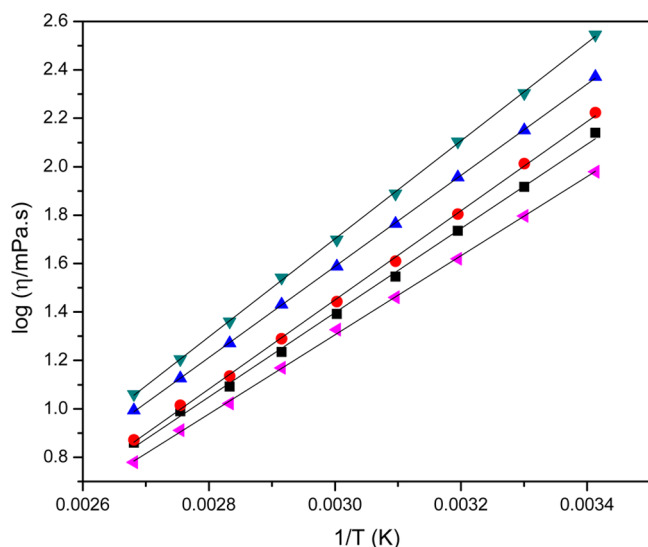


Figure 3. Plot of $\log(\eta)$ as a function of temperature: \blacktriangle , $[\text{C}_2\text{mim}][\text{Phe}]$; \blacksquare , $[\text{C}_4\text{mim}][\text{Phe}]$; \bullet , $[\text{C}_6\text{mim}][\text{Phe}]$; \blacktriangle , $[\text{C}_8\text{mim}][\text{Phe}]$; and \blacktriangledown , $[\text{C}_{10}\text{mim}][\text{Phe}]$.

Information. As can be seen in Figures 2 and 3, the alkyl spacer length has a strong impact on the viscosity of the phenolate-based ILs, and their viscosity is in the order $[\text{C}_{10}\text{mim}][\text{Phe}] > [\text{C}_8\text{mim}][\text{Phe}] > [\text{C}_6\text{mim}][\text{Phe}] > [\text{C}_4\text{mim}][\text{Phe}] > [\text{C}_2\text{mim}][\text{Phe}]$. The lowest viscosity was observed for phenolate ILs containing ethyl group as the side chain on imidazolium cation, and the highest viscosity was observed for $[\text{C}_{10}\text{mim}][\text{Phe}]$. Higher viscosity of the ILs with longer alkyl spacer length is due to the increased van der Waals interaction between the alkyl groups. Recently, Tao et al. reported tetramethylguanidinium (TMG)-based ILs with different phenolate anions with substituents such as methyl, methoxy, and fluorine groups at the para position of the phenol.²⁰ The viscosity of the TMG-based ILs is significantly lower than that of ILs reported in this study. The viscosity of tetramethylguanidinium phenolate, $[\text{TMG}][\text{Phe}]$, is 9.09 mPa·s at 303.15 K, whereas the least viscous imidazolium phenolate IL, $[\text{C}_2\text{mim}][\text{Phe}]$, has a viscosity value of 95.34 mPa·s at the same temperature. However, Tao et al. did not report the water content in the guanidinium-based phenolate ILs. It is well-known that water content in the ILs has a huge influence on their physical properties,²¹ especially on the viscosity. In addition, the ILs with guanidinium cations have low viscosity^{22,23} compared with that of other cationic cores. The viscosities of $[\text{C}_2\text{mim}][\text{TF}_2\text{N}]$, $[\text{C}_2\text{mim}][\text{BF}_4]$, and $[\text{C}_2\text{mim}][\text{PF}_6]$ were reported to be in the range of 34.0–40.1 mPa·s, 65.1–66.5 mPa·s, and 368.1–371. mPa·s, respectively, at 293.15 K, while the viscosity of $[\text{C}_2\text{mim}][\text{Phe}]$ is 95.34 mPa·s at similar temperature.^{24–26} The viscosity of $[\text{C}_4\text{mim}][\text{Phe}]$ is 138.07 mPa·s at 293.15 K, which is comparable to the viscosity of $[\text{C}_4\text{mim}][\text{BF}_4]$ (136.9–154.0 mPa·s).^{27–29} However, the viscosity of $[\text{C}_4\text{mim}][\text{PF}_6]$ (368–371 mPa·s at 293.15 K) is higher than that of $[\text{C}_4\text{mim}][\text{Phe}]$.^{27,30} On the other hand, the viscosity of $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ (52–63.9 mPa·s) is lower than that of $[\text{C}_4\text{mim}][\text{Phe}]$.^{24,31,32} The viscosity of $[\text{C}_6\text{mim}][\text{Phe}]$ is 167.07 mPa·s at 293.15 K, which is higher than that of $[\text{C}_6\text{mim}][\text{TF}_2\text{N}]$ (60.59–90.5 at 293.15).²⁴ $[\text{C}_6\text{mim}][\text{PF}_6]$ (680–690 mPa·s) and $[\text{C}_6\text{mim}][\text{BF}_4]$ (314–340 mPa·s) showed viscosity higher than that of $[\text{C}_6\text{mim}][\text{Phe}]$.^{27,30,33,34} The viscosity of $[\text{C}_8\text{mim}][\text{Phe}]$ is 235.12 mPa·s at 293.15 K, which is lower than the viscosity of $[\text{C}_8\text{mim}][\text{PF}_6]$ (804–866 mPa·s) and $[\text{C}_8\text{mim}][\text{BF}_4]$ (439–447.6 mPa·s) at similar conditions.^{27,30,34} However, the viscosity of $[\text{C}_8\text{mim}][\text{TF}_2\text{N}]$ (115.1–121.7 mPa·s) is lower than that of its $[\text{Phe}]^-$ analogue at similar experimental conditions.^{31,35,36} The viscosity of $[\text{C}_{10}\text{mim}][\text{BF}_4]$ (928 mPa·s at 293.15 K) is more than 450 mPa·s higher than that of $[\text{C}_{10}\text{mim}][\text{Phe}]$ (350.90 mPa·s).³⁰ $[\text{C}_{10}\text{mim}][\text{PF}_6]$ is solid at 293.15 K. As in previous ILs, $[\text{C}_{10}\text{mim}][\text{TF}_2\text{N}]$ (90–120.2 mPa·s) has a viscosity lower than that of $[\text{C}_{10}\text{mim}][\text{Phe}]$.

Density. The density of phenolate-based ILs was studied in a temperature window of 293.15–373.15 K. The temperature and alkyl spacer length has a strong influence on density. When the temperature increased, the density of ILs decreased, as shown in Figure 4 and Table 2 in Supporting Information. A similar trend was observed while increasing the alkyl spacer length of the cation. These results are in agreement with previously reported results of imidazolium-based ILs with other anionic species.³⁰ The density values of phenolate-based ILs is in the order $[\text{C}_2\text{mim}][\text{Phe}] > [\text{C}_4\text{mim}][\text{Phe}] > [\text{C}_6\text{mim}][\text{Phe}] > [\text{C}_8\text{mim}][\text{Phe}] > [\text{C}_{10}\text{mim}][\text{Phe}]$. The insufficient close packing of the cations is responsible for the decrease in density with an increase in chain length. The phenolate IL with ethyl

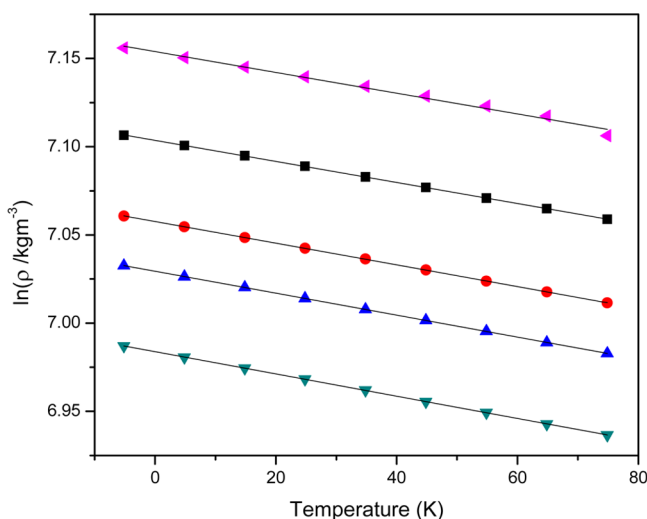


Figure 4. Density as a function of temperature: \blacktriangle , [C₂mim][Phe]; \blacksquare , [C₄mim][Phe]; \bullet , [C₆mim][Phe]; \blacktriangle , [C₈mim][Phe]; and \blacktriangledown , [C₁₀mim][Phe].

group has the highest density (1.2816 g·cm⁻³), and the lowest density of 1.0825 g·cm⁻³ was observed for [C₁₀mim][Phe]. The density of [TMG][Phe] (1.03468 g·cm⁻³ at 293.15 K) is lower than that of all the imidazolium-based phenolate ILs at similar conditions.²⁰ The [C_nmim] (*n* = 4–8) ILs with [Tf₂N]⁻ and [PF₆]⁻ anions have density higher than that of phenolate ILs. The density of [C₂mim][Tf₂N] is in the range of 1.5197–1.5260 g·cm⁻³, and [C₂mim][PF₆] is solid at 293.15 K.^{30,37,38} The density of [C₂mim][Phe] is 1.2816 g·cm⁻³ at similar conditions. [C₂mim][BF₄] (1.2479 g·cm⁻³) showed a density lower than that of their phenolate counterpart (1.2816 g·cm⁻³) at 293.15 K.³⁰ The densities of [C₄mim][Tf₂N] and [C₄mim][PF₆] are 1.4402–1.4427 g·cm⁻³ and 1.3698–1.3727 g·cm⁻³, respectively, at 293.15 K.^{30,38,39} In similar conditions, the density of [C₄mim][BF₄] was reported to be 1.1200–1.2077 g·cm⁻³,^{40–42} while the density of [C₄mim][Phe] is 1.2199 g·cm⁻³. When the alkyl spacer length increased to C6, the density of [C₆mim][Phe] (1.1652 g·cm⁻³) and the density of [C₆mim][BF₄] (1.1531 g·cm⁻³) became comparable at 293.15 K.³⁰ The densities of [C₆mim][PF₆] and [C₆mim][Tf₂N] are higher than that of their [Phe]⁻ anion analogues.^{30,37,43} The [BF₄]⁻ ILs with C8 and C10 carbon atoms also showed density data value comparable with that of [C₈mim][Phe] and [C₁₀mim][Phe].³⁰ The densities of [C₈mim][Tf₂N] and [C₁₀mim][Tf₂N] are higher than that of their [Phe]⁻ analogues.^{37,38,44} [C₈mim][PF₆] showed a density higher than that of [C₈mim][Phe], and [C₁₀mim][PF₆] is solid at 293.15 K, while [C₁₀mim][Phe] has density of 1.0825 g·cm⁻³ at 293.15 K.³⁰

Estimation of Volumetric Properties. The linear fitting of the experimental density values for the studied ILs were done by applying the following equation:

$$\ln\left[\frac{\rho}{\text{g}\cdot\text{cm}^{-3}}\right] = A_2 - A_3(T - 298.15)/K \quad (1)$$

where A_2 is a constant and $A_3 = \alpha/K = -(\partial \ln \rho / \partial (T - 298.15))_p$; α is the thermal expansion coefficient. The correlation coefficients and the standard deviation (SD) are shown in Table 3 in Supporting Information.

The parameters such as molecular volume (V_m), standard molar entropy (S^0), and lattice energy of the phenolate-based ILs are calculated according to eqs 2, 3, and 4, respectively. All these values are listed in Table 1. The V_m of ILs can also be predicted even before their synthesis with good accuracy by using quantum chemical calculations.^{45,46}

$$V_m = \frac{M}{N_A \rho} \quad (2)$$

$$S^0(303.15)/\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 1246.5(V_m/\text{nm}^3) + 29.5 \quad (3)$$

$$U_{\text{POT}}/\text{kJ}\cdot\text{mol}^{-1} = 1981.2(\rho/M)^{1/3} + 103.8 \quad (4)$$

where M is molecular weight and N_A is Avogadro's number.

As indicated in Table 1, an increase in the chain length increases the molecular volume of the ILs. The mean impact of a methylene ($-\text{CH}_2-$) group to the molar volume is 0.028 nm³, which is in agreement with that of *n*-alcohols (0.0280 nm³) and *n*-paraffins (0.0267 nm³).⁴⁷ The lattice energy values for the ILs [C₂mim][Phe], [C₄mim][Phe], [C₆mim][Phe], [C₈mim][Phe], and [C₁₀mim][Phe] are 364.52, 354.06, 336.21, 322.33, and 308.26 kJ·mol⁻¹, respectively, and is in close proximity to those of previously reported ILs.^{48–51} The studied ILs have lattice energy significantly lower than that of alkali halides.⁵² For instance, among alkali halides, CsI has the lowest lattice energy (613 kJ mol⁻¹), which is substantially higher than that of ILs.

Surface Tension. The surface tension values of the phenolate-based ILs were recorded in a temperature range from 293 to 353 K and are shown in Figure 5 and Table 4 in Supporting Information. The surface tension showed a linear relationship with temperature as in the case of density and viscosity. Among the synthesized ILs, [C₂mim][Phe] has the highest surface tension, while [C₁₀mim][Phe] showed the lowest surface tension. The surface tension decreased with the increase in the alkyl spacer length of the cation and followed the order [C₂mim][Phe] > [C₄mim][Phe] > [C₆mim][Phe] > [C₈mim][Phe] > [C₁₀mim][Phe]. The surface tension of phenolate ILs is lower than that of water (71.98 mN·m⁻¹) but higher than that of organic solvents such as methanol (22.07 mN·m⁻¹), acetone (23.5 mN·m⁻¹), and *n*-alkanes.^{53–55} The surface tension of [C₂mim][BF₄], [C₄mim][BF₄], and

Table 1. Calculated Values of Volume Properties of ILs at 303.15 K

| IL | P (kg·m ⁻³) | V_m (nm ³) | S^0 (J·K ⁻¹ ·mol ⁻¹) | U_{POT} (kJ·mol ⁻¹) |
|----------------------------|---------------------------|--------------------------|---|--|
| [C ₂ mim][Phe] | 1274.7 | 0.266 | 361.15 | 375.13 |
| [C ₄ mim][Phe] | 1212.7 | 0.318 | 425.97 | 354.06 |
| [C ₆ mim][Phe] | 1158.2 | 0.373 | 494.75 | 336.21 |
| [C ₈ mim][Phe] | 1125.9 | 0.425 | 559.68 | 322.33 |
| [C ₁₀ mim][Phe] | 1075.7 | 0.488 | 638.40 | 308.26 |

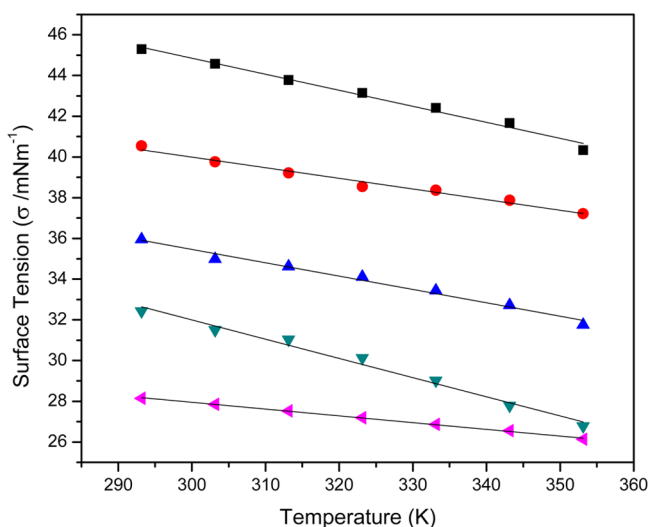


Figure 5. Surface tension as a function of temperature: ◼, [C₂mim][Phe]; ◼, [C₄mim][Phe]; ●, [C₆mim][Phe]; ▲, [C₈mim][Phe]; and ▼, [C₁₀mim][Phe].

[C₆mim][BF₄] is higher than that of [C_{*n*}mim][Phe] (*n* = 2, 4, 6), while the surface tension of [C₈mim][BF₄] and [C₁₀mim][BF₄] is lower than that of [C₈mim][Phe] and [C₁₀mim][Phe], respectively.^{56–61} Although, the surface tensions of [C₂mim][Tf₂N] (36.9 mN·m^{−1}), [C₄mim][Tf₂N] (33.6 mN·m^{−1}), and [C₈mim][Tf₂N] (31.9 mN·m^{−1}) are lower than their corresponding phenolate analogues, [C₁₀mim][Tf₂N] (32.1 mN·m^{−1}) showed a surface tension higher than that of [C₁₀mim][Phe] (28.15 mN·m^{−1}) at 293.15 K. The [C_{*n*}mim][PF₆] ILs with *n* = 4, 6, 8, and 10 showed a higher surface tension value than their corresponding [Phe][−] analogues at 293.15 K.^{57,58,62} The surface tension of [C₄mim][PF₆] is more than 3.5 mN·m^{−1} higher than that of [C₄mim][Phe].^{57,59,63,64} The surface tension of [C₆mim][PF₆] (39.0 at 293.15 K) is also higher than that of its corresponding phenolate analogue.^{57,59} The surface tension of [C₈mim][PF₆] is 36.1 σ/(mN·m^{−1}) at 293.15 K,³² whereas the surface tension of [C₈mim][Phe] is 32.43 σ/(mN·m^{−1}) at 293.15 K. The [C₁₀mim][PF₆] has a surface tension value of 31.2 mN·m^{−1} at 293.15, whereas the surface tension of [C₁₀mim][Phe] is 28.15 at similar conditions.^{57,61}

The linear fitting of the surface tension and the temperature are performed with the following equation:

$$\sigma/(\text{mN}\cdot\text{m}^{-1}) = A_4 - A_5 T \quad (5)$$

where σ represents surface tension and T is the temperature; A_4 and A_5 are fitting parameters. The values of these fitting parameters along with the standard deviation are given in Table 3 in Supporting Information. The surface tension values were used to estimate the surface entropy and surface enthalpy using eqs 6 and 7 at 303.15 K.

$$S_a = A_3 = -\left(\frac{\partial \sigma}{\partial T}\right)_p \quad (6)$$

$$E_s = A_2 = \sigma - \left(\frac{\partial \sigma}{\partial T}\right)_p \quad (7)$$

The resulting values are tabulated in Table 2. The [Phe]-based ILs showed remarkably lower surface entropy compared to that of organic solvents; nevertheless, the surface entropy

Table 2. Surface Thermodynamic Functions of Pure ILs at 303.15 K^a

| IL | $S_s (\times 10^3 \text{ mJ}\cdot\text{K}^{-1}\cdot\text{m}^{-2})$ | $E_s (\text{mJ}\cdot\text{m}^{-2})$ |
|----------------------------|--|-------------------------------------|
| [C ₂ mim][Phe] | 78.8 | 60.39 |
| [C ₄ mim][Phe] | 52.2 | 55.58 |
| [C ₆ mim][Phe] | 65.5 | 54.85 |
| [C ₈ mim][Phe] | 94.4 | 40.13 |
| [C ₁₀ mim][Phe] | 33.2 | 37.91 |

^aSurface entropy (S_s) and surface enthalpy (E_s).

values are in agreement with other classes of imidazolium-based ILs.⁶² This is because of the high surface orientation and more structured liquid phase in ILs. The surface enthalpy value of the ILs is very close to that of common organic solvents such as octane (51.1 mJ·m^{−2}) and benzene (67 mJ·m^{−2}), and the values decrease with an increase in the chain length, which is in agreement with previous observations.^{59,62} This may be because of the lower hydrogen bond interaction with the increase in chain length.

The critical temperature, T_c , is an important property in correlating equilibrium and transport properties of liquids.⁶⁵ The intrinsic nature of the ILs makes it difficult to get a reliable data for their critical temperature (T_c). To predict the critical temperature of ILs, Guggenheim⁶⁶ (eq 8) and Eötvös⁶⁷ (eq 9) empirical equations were used. The resulting values are shown in Table 3. The enthalpy of vaporization of ILs can be estimated using eq 10.

$$\sigma = E^{\sigma} \left(1 - \frac{T}{T_c^G}\right)^{11/9} \quad (8)$$

$$\sigma \left(\frac{M}{\rho}\right)^{2/3} = K(T_c^E - T) \quad (9)$$

$$\Delta_f^{\sigma} H_m^{\sigma} = 0.01121(\sigma V^{2/3} N_A^{1/3}) + 2.4 \quad (10)$$

where E^{σ} is the total surface energy of ILs, which equals the surface enthalpy because of the tiny volume difference due to thermal expansion at the temperatures that are not similar to the critical temperature, T_c^G ; σ is surface tension, M molecular weight, ρ density, K a constant, N_A Avogadro's number, and T the temperature at which the surface tension was measured.

The assumptions from Rebelo et al.⁶⁸ are used to calculate boiling temperature, T_b , of ILs according to $T_b \approx 0.6T_c$. The T_b values for the ILs are given in Table 3.

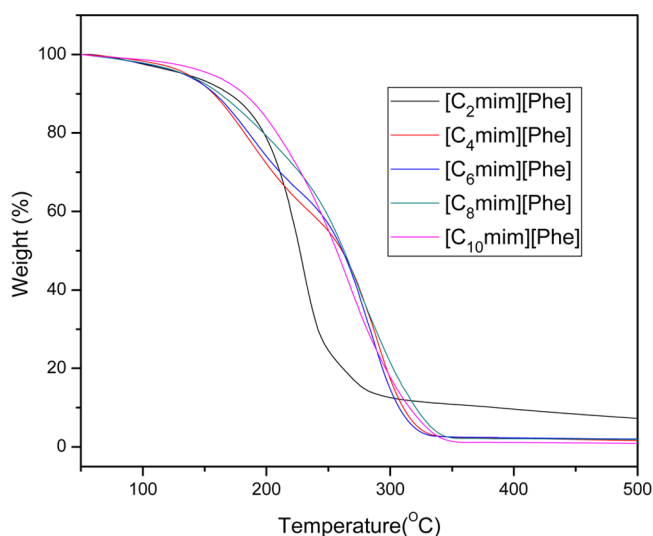
Thermal Decomposition. The thermal decomposition temperatures (T_d) and glass transition temperatures (T_g) of all ILs under study are shown in Table 4, and their TGA profiles are shown in Figure 6. All the phenolate-based ILs showed a thermal stability (>156 °C) at a scan rate of 10 °C·min^{−1} in aluminum pan under nitrogen atmosphere. The imidazolium-based phenolate ILs are more thermally stable than [TMG]-based phenolate ILs. For example, [C₂mim][Phe] is thermally stable up to 156 °C, which is about 50 °C higher than the value for [TMG][Phe].²⁰ The thermal stability of imidazolium ILs with weakly coordinating anions such as [Tf₂N][−], [BF₄][−], and [PF₆][−] is higher than that of phenolate ILs.^{27,42,69,70} For instance, the thermal decomposition temperatures of [C₄mim][BF₄], [C₄mim][PF₆], and [C₄mim][Tf₂N] are 361, 373, and 422 °C, respectively, which are remarkably higher than that of [C₄mim][Phe]. The lower thermal stability of the phenolate

Table 3. Critical Temperature (T_c), Normal Boiling Temperature (T_b), and Enthalpy of Vaporization ($\Delta_f^g H_m^\circ$) of ILs at 303.15 K

| IL | Guggenheim | | Eötvös | | $\Delta_f^g H_m^\circ$ (kJ·mol ⁻¹) |
|----------------------------|------------|-----------|-----------|-----------|--|
| | T_c (K) | T_b (K) | T_c (K) | T_b (K) | |
| [C ₂ mim][Phe] | 1377.31 | 826.39 | 950.48 | 570.29 | 131.09 |
| [C ₄ mim][Phe] | 1264.37 | 758.62 | 932.34 | 559.40 | 127.49 |
| [C ₆ mim][Phe] | 985.18 | 591.11 | 919.17 | 551.50 | 124.87 |
| [C ₈ mim][Phe] | 738.28 | 442.97 | 908.38 | 545.03 | 122.72 |
| [C ₁₀ mim][Phe] | 1358.96 | 815.38 | 889.81 | 533.88 | 119.03 |

Table 4. Thermal Decomposition Temperature (T_d), Glass Transition Temperature (T_g), Water Content, and Halide Content in ILs

| IL | T_d (°C) | T_g (°C) | water content (ppm) | halide (ppm) |
|----------------------------|------------|------------|---------------------|--------------|
| [C ₂ mim][Phe] | 156 | -53.14 | 161 | 110 |
| [C ₄ mim][Phe] | 158 | -52.13 | 170 | 102 |
| [C ₆ mim][Phe] | 162 | -63.80 | 153 | 93 |
| [C ₈ mim][Phe] | 168 | -66.35 | 149 | 90 |
| [C ₁₀ mim][Phe] | 180 | — | 161 | 97 |

Figure 6. TGA profile for synthesized ILs: [C₂mim][Phe], [C₄mim][Phe], [C₆mim][Phe], [C₈mim][Phe], and [C₁₀mim][Phe].

ILs is due to the alkaline nature of the phenolate anion. The glass transition temperature of the phenolate ILs is in the range of -52.13 °C to -66.35 °C. Glass transition temperature was not observed for [C₁₀mim][Phe] even after cooling to -150 °C. The glass transition temperatures of [TMG] phenolate ILs are comparable to those of imidazolium-based phenolate ILs. For instance, the glass transition temperature of [TMG][Phe] is -53.8 °C, while the glass transition temperature of [C₄mim][Phe] is -52.13 °C. [C₄mim][Tf₂N] has a lower glass transition temperature (-86 °C), while [C₄mim][BF₄]

(-50 °C) and [C₄mim][PF₆] (-58 °C) have glass transition temperatures comparable with that of [C₄mim][Phe].

Interstice Model for Ionic Liquids. The interstice model^{71,72} was developed for ILs to calculate the interstice volume, v , for ILs using an equation from classical statistical mechanics. This model was developed by abstracting the essence of the hole model for molten salts.⁷³ The model is based on four assumptions.^{49,74}

$$V = 0.6791(k_b T / \sigma)^{3/2} \quad (11)$$

The values of average volume of the interstices for all the synthesized ILs are given in Table 5.

The volume fractions of interstice, $\sum v/V$, are also given in Table 5. The values are between 12.80 to 16.20 and are in agreement with the substances which show a volume expansion of approximately 15% during the transformation from solids to liquids. The molar volume, V , can be described as the summation of the inherent volume, V_i , and the sum of the volumes of all interstices, $\sum v = 2N_A v$, i.e.

$$V = V_i + 2N_A v \quad (12)$$

The coefficient of thermal expansion, α , was calculated to validate the experimental values of α . This calculation was done by an assumption that expansion in an IL results only by the expansion of the interstice during the temperature change. The equation of α is derived from the interstice model and is given below.

$$\alpha = \left(\frac{1}{V} \right) \left(\frac{\partial V}{\partial T} \right)_p = \frac{3N_A v}{VT} \quad (13)$$

The calculated and experimental values of α for all the ILs under study are in good agreement. For example, the calculated and experimental values of α for [C₂mim][Phe] are 7.22 and 6.0, respectively (see Table 5). This indicates the usefulness of this model in the case of ILs.

Heat Capacity. The specific heat capacity as a function of temperature is presented in Figure 7 and Table 5 in Supporting Information. It was observed that the heat capacity of all the studied ILs increases slightly with an increase in temperature. Similar results were reported for other imidazolium-based ILs.¹⁸ The specific heat capacity for the phenolate-based ILs also increases with the increase in chain length, which is in agreement with previously reported imidazolium-based ILs.^{42,75}

Table 5. Values of Parameters of ILs for the Interstice Model at 303.15 K

| IL | v ($\times 10^{-24}$ cm ³) | $\sum v$ (cm ³) | $\sum v/V$ | α (calcd) ($\times 10^4$ K ⁻¹) | α (exptl) ($\times 10^4$ K ⁻¹) |
|----------------------------|---|-----------------------------|------------|--|--|
| [C ₂ mim][Phe] | 19.55 | 23.55 | 12.80 | 6.08 | 6 |
| [C ₄ mim][Phe] | 23.20 | 27.95 | 14.59 | 7.22 | 6 |
| [C ₆ mim][Phe] | 28.11 | 33.86 | 15.06 | 7.45 | 6 |
| [C ₈ mim][Phe] | 32.89 | 39.62 | 15.46 | 7.65 | 6 |
| [C ₁₀ mim][Phe] | 39.58 | 47.68 | 16.20 | 8.02 | 6 |

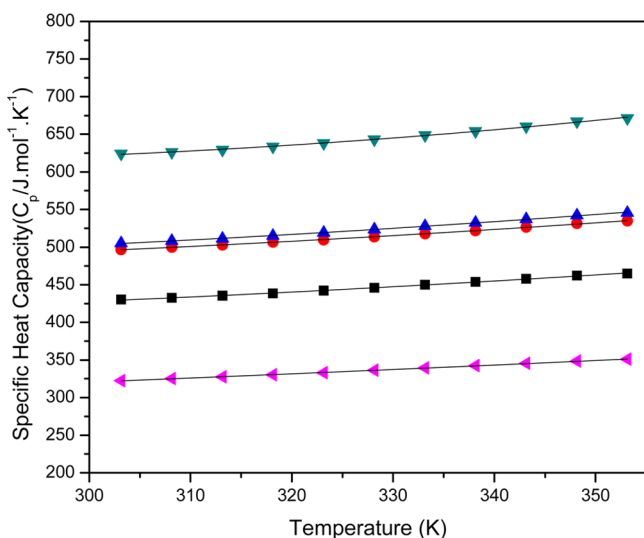


Figure 7. Specific heat capacity as a function of temperature: \blacktriangle , $[\text{C}_2\text{mim}][\text{Phe}]$; \blacksquare , $[\text{C}_4\text{mim}][\text{Phe}]$; \bullet , $[\text{C}_6\text{mim}][\text{Phe}]$; \blacktriangle , $[\text{C}_8\text{mim}][\text{Phe}]$; and \blacktriangledown , $[\text{C}_{10}\text{mim}][\text{Phe}]$.

$[\text{C}_{10}\text{mim}][\text{Phe}]$ showed a higher heat capacity compared with that of other phenolate ILs in this study because of the higher viscosity of $[\text{C}_{10}\text{mim}][\text{Phe}]$. The heat capacities of $[\text{C}_6\text{mim}][\text{Phe}]$ and $[\text{C}_8\text{mim}][\text{Phe}]$ are very similar, which is in agreement with previous reports regarding the imidazolium-based ILs with $[\text{TF}_2\text{N}]^-$ anions.⁴² The temperature-dependent values of the heat capacity is represented by a second-degree polynomial fit using the following equation:

$$C_p = B_0 + B_1T + B_2T^2 \quad (14)$$

where C_p is the heat capacity ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T is the temperature (K); B_0 , B_1 , and B_2 are fitting constants, and these values are given in Table 6 in Supporting Information.

Refractive Index. The refractive index data for the phenolate ILs is presented in Figure 8 and Table 7 in Supporting Information. An increase in chain length decreases the refractive index. The refractive index decreases in the order

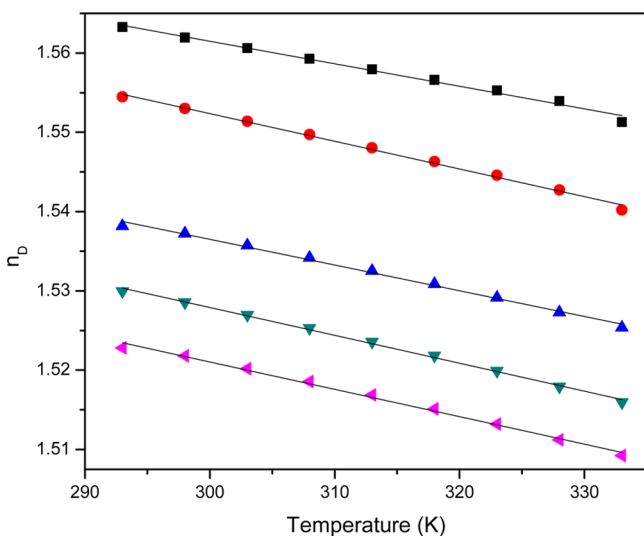


Figure 8. Refractive index as a function of temperature: \blacktriangle , $[\text{C}_2\text{mim}][\text{Phe}]$; \blacksquare , $[\text{C}_4\text{mim}][\text{Phe}]$; \bullet , $[\text{C}_6\text{mim}][\text{Phe}]$; \blacktriangle , $[\text{C}_8\text{mim}][\text{Phe}]$; and \blacktriangledown , $[\text{C}_{10}\text{mim}][\text{Phe}]$.

$[\text{C}_2\text{mim}][\text{Phe}] > [\text{C}_4\text{mim}][\text{Phe}] > [\text{C}_6\text{mim}][\text{Phe}] > [\text{C}_8\text{mim}][\text{Phe}] > [\text{C}_{10}\text{mim}][\text{Phe}]$. However, an increase in temperature causes a linear decrease in the refractive index of the synthesized ILs. There is no substantial difference between the refractive index of phenolate ILs with imidazolium and $[\text{TMG}]$ cation. For instance, the refractive index of $[\text{C}_6\text{mim}][\text{Phe}]$ is 1.5382 at 298.15 K, which is very close to the refractive index of 1.5358 for $[\text{TMG}][\text{Phe}]$ at similar conditions.²⁰ However, the refractive index of imidazolium ILs with other anions are significantly lower than that of their phenolate analogues.^{37,40,76,77} The refractive index of $[\text{C}_n\text{mim}][\text{TF}_2\text{N}]$ ($n = 2, 4, 6, 8, 10$) is in the range of 1.4235–1.4365 at 293.15 K, while the refractive index of phenolate ILs in this study showed refractive index of 1.5228–1.5633 at similar conditions.^{26,37,78} Refractive indices of $[\text{C}_4\text{mim}][\text{PF}_6]$ (1.41045), $[\text{C}_6\text{mim}][\text{PF}_6]$ (1.4184), and $[\text{C}_8\text{mim}][\text{PF}_6]$ (1.42452) are lower than that of their phenolate analogues.^{33,37,79}

The linear fitting of the refractive index (n_D) versus temperature are performed with eq 15. The values of the fitting parameters along with the values of R^2 and SD are given in Table 3 in Supporting Information.

$$n_D = A_6 + A_7T \quad (15)$$

CONCLUSION

The physicochemical properties of phenolate anion-based ILs containing imidazolium cation with varying alkyl chain length were investigated. The physical properties of these ILs such as density, viscosity, refractive index, and surface tension were measured in a broad temperature window, and all of them showed a linear relation with temperature. An attempt was made to study the effect of chain length on these properties as well. The density and surface tension of the ILs decreased with an increase in alkyl chain length. The heat capacity of the phenolate ILs increased slightly with temperature, while the refractive index decreased as the chain length increased. The density of these ILs was used to calculate the molar volume, standard entropy, thermal expansion coefficient, and lattice energy. Using the surface tension, surface properties such as surface entropy and surface enthalpies for the synthesized ILs were calculated. The critical temperature was estimated using Guggenheim and Eötvös equations. The synthesized ILs showed a good thermal stability up to 180 °C.

ASSOCIATED CONTENT

Supporting Information

Synthesis and characterization details of ILs; tables containing experimental viscosity (η), density (ρ), surface tension (σ), specific heat capacity (C_p), and refractive indices (n_D) as a function of temperature; and tables of fitting parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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