



Chemical Engineering Thermodynamics

Effect of alkyl chain length on the thermophysical properties of pyridinium carboxylates

Tazien Rashid¹, Chong Fai Kait², Thanabalan Murugesan^{1,*}¹ Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh 32610, Perak, Malaysia² Fundamental and Applied Sciences Department, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, Tronoh 32610, Perak, Malaysia

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ABSTRACT

In the present study, new series of pyridinium carboxylate protic ionic liquids (PILs) were synthesized by pairing pyridinium cation with carboxylate anion from C₁–C₃ forming pyridinium formate ([C₅H₆N⁺][HCOO[−]]), pyridinium acetate ([C₅H₆N⁺][CH₃COO[−]]) and pyridinium propionate ([C₅H₆N⁺][CH₃CH₂COO[−]]) respectively. The physical properties namely, density, viscosity, surface tension (298.15–343.15) K, and refractive index (293.15–323.15) K were measured. Thermal properties namely, glass transition temperature, molar heat capacity, and thermal decomposition temperatures were also determined. The thermal expansivity was calculated using the experimental density data. The effect of increasing the alkyl chain length on the thermophysical properties of the pyridinium carboxylate PILs has been evaluated. As expected the physical properties i.e. density, viscosity, surface tension and refractive index of the investigated pyridinium carboxylates decreased with increasing temperature. In general pyridinium carboxylate PILs possessed low viscosity, high thermal stability and excellent hydrogen bonding capability, and these properties lead them to outperform conventional solvents employed for lignin dissolution.

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1. Introduction

Effective lignocellulosic biomass exploitation has significantly enhanced over the past few years. Lignin is the second most abundant biorenewable resource in nature. Lignin is rich in aromatic groups and is a good source of potential products such as; phenol, carbon fiber, aromatic stock chemicals, and polymers. However, due to its complex molecular structure formed by inter- and intra-molecular hydrogen bonding, it remains difficult to dissolve in typical organic solvents. This confines the broader application of lignin due to which it is primarily burnt as a low grade fuel [1,2]. Due to its complex structure, it is difficult to develop a general technique to depolymerize lignin into desired aromatic feedstock and compounds. Furthermore, none of these challenges can be overcome unless efficient solvents can be synthesized/developed for effective dissolution/extraction of lignin [3].

Recently, ionic liquids (ILs) have gained much consideration as an auxiliary solvent for lignocellulosic biomass due to their distinctive features and extensive properties [4]. However, large scale industrial applications of ILs are still limited due to high production costs and complex synthesis routes with sophisticated purification steps required for their production [5,6]. Recently, protic ionic liquids (PILs) have appeared as attractive replacements for ILs due to their numerous

benefits over the conventional ILs [3,7–9]. The main advantage of PILs is that they can be synthesized in a one-step reaction and no further purification steps are involved [10]. Furthermore, they possess low viscosity, high thermal stability, enhanced hydrogen-bonding capability, less corrosive, and have high capacity for the dissolution of lignin [3].

Due to these advantages, PILs are considered for industrial applications in the recent few years, such as desulphurization of fuel [11], CO₂ capture [12], biomass processing [3,7] and in many acid–base-catalyzed organic reactions such as Knoevenagel condensation [13]. However, very little information is available on the elementary physical properties of this family of solvents, which are vital for the designing and scale up of any commercial process. In this work, pyridinium carboxylate PILs with three different alkyl chains i.e. ([C₅H₆N⁺][HCOO[−]]), ([C₅H₆N⁺][CH₃COO[−]]), ([C₅H₆N⁺][CH₃CH₂COO[−]]) were synthesized. Physical properties namely density, viscosity, refractive index and surface tension and thermal properties namely glass transition temperature and thermal decomposition temperature of these PILs have been estimated, for the better understanding of the PIL as solvents for further applications.

2. Materials and Methods

2.1. Chemicals

Pyridine (purity ≥99 wt%, Sigma Aldrich), formic acid, Acetic acid and Propionic acid (≥99 wt% purity, Sigma Aldrich), Karl Fischer

* Corresponding author.

E-mail addresses: murugesan@petronas.com.my, murugesan@utp.edu.my, tmgesan_57@yahoo.com (T. Murugesan).

titration calibration chemicals, Deuterated Dimethyl Sulphoxide (DMSO- d_6), and lignin (Kraft lignin-Indulin AT), were used as received. Deionized water was used for the experiments.

2.2. Synthesis of pyridinium carboxylates

Pyridinium carboxylates are produced when a proton transfer takes place from a carboxylic acid to pyridine [3]. For the present study PILs with three different alkyl chain lengths *i.e.* $[HCOO^-]$, $[CH_3COO^-]$ and $[CH_3CH_2COO^-]$ were synthesized. Initially pyridinium formate ($[C_5H_6N^+][HCOO^-]$) was prepared using a three necked round bottom flask containing pyridine. The flask was fitted with a dropping funnel for the addition of formic acid. The flask was placed in an ice water bath as the reaction is exothermic and the overall temperature was maintained below 20 °C. To ensure moisture free conditions in the flask dry nitrogen atmosphere was used. A magnetic stirrer was used to maintain the homogeneity of the reaction. Pyridine was stirred vigorously and then formic acid was added drop wise into the flask and left for overnight at room temperature. To remove the excess water present in the product, the samples were placed in the vacuum oven for 48 h at 70 °C. Laboratory parafilm was used to seal the oven dried solvent to avoid any moisture contaminations in the solvent. Following the similar procedure ($[C_5H_6N^+][CH_3COO^-]$) and ($[C_5H_6N^+][CH_3CH_2COO^-]$) were prepared. The characterization using ^1H NMR (DMSO- d_6 , 500 MHz), Karl Fischer water content for the ($[C_5H_6N^+][HCOO^-]$), ($[C_5H_6N^+][CH_3COO^-]$), ($[C_5H_6N^+][CH_3CH_2COO^-]$) revealed the subsequent results respectively; $\delta = 7.37(2H, d)$, $7.77(1H, t)$, $8.16(1H, s)$, $8.57(2H, t)$, $9.75(1H, s)$; water contents = $251 \mu L \cdot L^{-1}$; $\delta = 1.2(3H, s)$, $6.64(2H, m)$, $7.12(1H, t)$, $7.05(1H, t)$, $7.73(2H, d)$; water contents = $262 \mu L \cdot L^{-1}$; $\delta = 0.1445(3H, t)$, $1.35(2H, q)$, $6.47(2H, t)$, $6.85(1H, t)$, $7.57(2H, d)$; water contents = $247 \mu L \cdot L^{-1}$.

2.3. Physicochemical properties measurement

2.3.1. Density measurement

The vibrating tube digital density meter (Model DMA 4500 M, Anton Paar) with a stated measuring accuracy of $\pm 5 \times 10^{-4} g \cdot cm^{-3}$ was used to determine the density of the prepared pyridinium carboxylates over a temperature range of 298.15 to 343.15 K. The temperature was controlled using a solid-state thermostat with an accuracy of ± 0.01 K.

2.3.2. Viscosity measurement

The viscosity was measured using a rolling-ball viscosity meter (Anton-Paar, model Lovis-2000M/ME) with a stated measuring accuracy of 0.5%. The experimental data were measured within a temperatures range of 298.15 K to 343.15 K with an increment of 5 K. The temperature uncertainty of the equipment was ± 0.02 K.

Since the formic acid and pyridine are the precursors for the preparation of PILs, the accuracy of the instruments was validated/compared by measuring the density and viscosity of commercially available formic acid and pyridine, with those of literature.

2.3.3. Refractive index measurement

A fully automatic refractometer (ATAGO, model RX-5000 α) was used for the refractive index measurements with a stated measuring accuracy of $\pm 5 \times 10^{-5}$. The measurements were made at different temperatures from 293.15 K to 323.15 K with an increment of 5 K. An internal thermostat was used to control the temperature, and the uncertainty in the temperature measurements was ± 0.03 K.

2.3.4. Surface tension

A pendant drop surface analyzer (OCA 20, Dataphysics) with a stated accuracy of ± 0.03 K was used for surface tension measurements. The OCA 20 surface analyzer is equipped with a six fold power zoom lens camera for integrated fine focusing. Protic ionic liquids were taken from the sealed bottles using syringe with needle. The syringe was

then attached to the surface analyzer OCA 20. A drop was generated from the syringe and photographed by a CCD camera. The curvature of a liquid drop surface using the Young–Laplace equation was calculated using Dataphysics SCA 22 software. The measurements were made at different temperatures from 298.15 K to 343.15 K with an increment of 5 K. The expected uncertainty of the experiments is $0.2 mN \cdot m^{-1}$. All measurements for density, viscosity, refractive index and surface tension were made at atmospheric pressure and the stated values are the average of the replicate experiments.

2.3.5. Thermal decomposition temperature

A thermal gravimetric analyzer (Model Pyris V-3.81, Perkin-Elmer) was used to determine the thermal decomposition temperature “ T_d ” of the pyridinium carboxylates. Heating of the samples was carried out at a constant rate of $283 K \cdot min^{-1}$ within a temperature range of 323 K to 473 K, under N_2 gas blanket flowing at a constant rate of 20–25 $ml \cdot min^{-1}$.

2.3.6. Glass transition temperature

The glass transition temperature “ T_g ” of the present synthesized pyridinium carboxylates was determined by using a differential scanning calorimeter (DSC1, Mettler Toledo). A liquid nitrogen cooling system was used to create a nitrogen rich atmosphere. Samples were placed into the aluminum pans and were hermetically sealed. The sample was first cooled in the first cycle from 298 K to 123 K and in the second cycle the samples were allowed to heat from 123 K to 373 K at a constant rate of $283 K \cdot min^{-1}$. During the third cycle, samples were cooled back from 373 K to 123 K, and lastly heated back to 373 K at a constant rate of $283 K \cdot min^{-1}$, by following the established procedure. The second programmed reheating cycle was used to evaluate the “ T_g ” of the samples. The uncertainty in the temperature measurements was ± 0.2 K.

3. Results and Discussion

The measured physical properties data (density and viscosity) of commercially available formic acid and pyridine at three different temperatures (298.15, 303.15 and 308.15 K) are presented along with those of few literature (Table 1). Minor discrepancies in the present work and literature data could be attributed to the presence of trace

Table 1

Comparison of density (ρ) and viscosity (η) data of formic acid and pyridine used in the present work

T/K	$\rho/g \cdot cm^{-3}$			
	Formic acid		Pyridine	
	This work	Literature	This work	Literature
298.15	1.21339	1.21380 [14] 1.21135 [17] 1.21405 [19]	0.97793	0.9782 [15,16] 0.9790 [18] 0.9811 [20]
303.15	1.20699	1.20750 [14] 1.20507 [17]	0.97704	0.9780 [21] 0.9737 [18]
308.15	1.20091	1.20099 [22] 1.20120 [14]	0.96889	0.9692 [23]
T/K	$\eta/mPa \cdot s^{-1}$			
	Formic acid		Pyridine	
	This work	Literature	This work	Literature
298.15	1.58	1.599 [24] 1.607 [26] 1.51 [14]	0.88	0.885 [25] 0.899 [20]
303.15	1.48	1.474 [24] 1.36 [14] 1.437 [17]	0.81	0.820 [25] 0.8199 [18]
308.15	1.32	1.334 [24] 1.250 [14]	0.77	0.766 [25]

amount of water contents, volatile nature of the samples, temperature control, difference of equipment and techniques adopted by the researchers. However, this minor discrepancy can also be observed among various literature data reported previously for the same standards (Table 1).

3.1. Density

The values of the experimental densities of $([C_5H_6N^+][HCOO^-])$, $([C_5H_6N^+][CH_3COO^-])$, $([C_5H_6N^+][CH_3CH_2COO^-])$ over a temperature range of 298.15 to 343.15 K are listed in Table 2. As expected, the densities of all the present investigated PILs decreased linearly with increasing temperature which is consistent with the similar trends reported for 1-butyl-3-methylimidazolium carboxylate [27] and 1-alkyl-3-methylimidazolium hexafluorophosphate ionic liquids [28].

Table 2
Densities (ρ) of pyridinium carboxylates at different temperatures

T/K	$\rho/g \cdot cm^{-3}$		
	$[C_5H_6N^+][HCOO^-]$	$[C_5H_6N^+][CH_3COO^-]$	$[C_5H_6N^+][CH_3CH_2COO^-]$
298.15	1.03809	1.02062	1.00672
303.15	1.03323	1.01571	1.00190
308.15	1.02886	1.01080	0.99766
313.15	1.02359	1.00587	0.99199
318.15	1.01861	1.00091	0.98731
323.15	1.01371	0.99594	0.98241
328.15	1.00879	0.99094	0.97750
333.15	1.00384	0.98592	0.97255
338.15	0.99890	0.98087	0.96758
343.15	0.99389	0.97580	0.96260

The densities of the PILs decreased with increasing alkyl chain length in the anion containing carboxylic group (Table 2), which demonstrates that the anionic part has a significant role on the densities of PILs. With an increase in alkyl chain length, the packing efficiency of the molecules is lowered, resulting in an overall reduction in the density. This behavior is comparable to the similar behavior of ILs with different alkyl chain lengths in the anion [27,28]. The following empirical relation was used to correlate the density values of the present synthesized pyridinium carboxylates:

$$\rho = A_0 + A_1 T \quad (1)$$

where ρ is the density ($g \cdot cm^{-3}$), T is the temperature (K) and A_0 and A_1 are the correlation coefficients, and the estimated coefficients are presented in Table 3.

Table 3
Fitting parameters for Eq. (1)

Component	$A_0/g \cdot cm^{-3}$	$A_1 \times 10^4/g \cdot cm^{-3} \cdot K^{-1}$	$SD \times 10^4/g \cdot cm^{-3}$
$[C_5H_6N^+][HCOO^-]$	1.32991	−9.78811	1.59
$[C_5H_6N^+][CH_3COO^-]$	1.31542	−9.89183	2.88
$[C_5H_6N^+][CH_3CH_2COO^-]$	1.29806	−9.77194	1.35

The standard deviations were calculated using the following equation:

$$\sigma = \sqrt{\frac{\sum (X_{exp} - X_{cal})^2}{N_{DATA}}} \quad (2)$$

where, σ is the standard deviation, X_{exp} and X_{cal} are the experimental and calculated data and N_{DATA} is the total number of experiments performed. The molar volume provides more information about the

packing efficiency and the structure of a substance rather than density, hence the density values can be verified by another approximation method using molar volume [29]. The molar volume V_M of the present PILs was calculated using the experimental density data, and molar mass of PILs, as below:

$$V_M = M/\rho \quad (3)$$

The relation between the variation in molar ($V_M/cm^3 \cdot mol^{-1}$) of the PILs with temperature and number of carbon atoms " N_c " in the carboxylate anion is shown in Fig. 1.

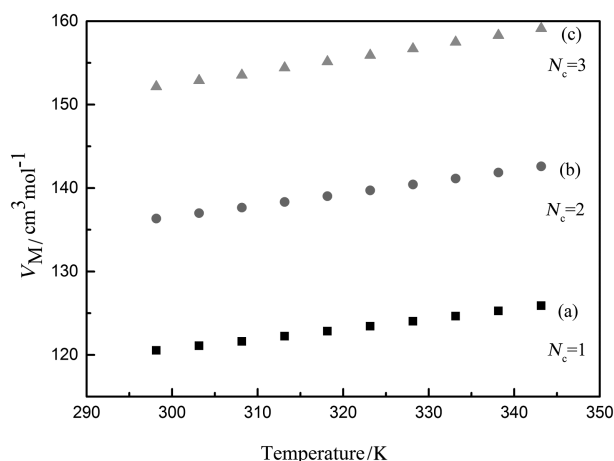


Fig. 1. Linear relationship between the molar volume and temperature of the pyridinium carboxylates: (a) $[C_5H_6N][HCOO^-]$, (b) $[C_5H_6N][CH_3COO^-]$, and (c) $[C_5H_6N][CH_3CH_2COO^-]$.

It can be seen that, for a selected cation $[C_5H_6N^+]$, there is an increase in molar volume of the pyridinium carboxylates with an increase in alkyl chain length in anion. The molar volume was found to increase in the order as: $[C_5H_6N^+][HCOO^-] < [C_5H_6N^+][CH_3COO^-] < [C_5H_6N^+][CH_3CH_2COO^-]$ (Fig. 1). Based on the present data (Fig. 1) the molar volume (V_M) and the number of carbon atoms (N_c) could be related as:

$$V_M = 15.80N_c + 104.73 \quad (4)$$

Eq. (4) shows that the molar volume increases by $15.80 \text{ cm}^3 \cdot \text{mol}^{-1}$ per addition of methylene group ($-\text{CH}_2-$) in the anion of the pyridinium carboxylates, and as a consequence, the volume occupied by the anion varies linearly with the number of carbons present in the anion. This result is in accordance with the reported values of $16 \text{ cm}^3 \cdot \text{mol}^{-1}$, $16.9 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $16.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ per addition of $-\text{CH}_2-$ in 1-butyl-3-methylimidazolium carboxylate ILs [27], *n*-alcohols [30] and *n*-paraffins [31] respectively.

An addition of methylene group ($-\text{CH}_2-$) to the present investigated pyridinium carboxylates contributes to an increase of molar volume and hence can be predicted easily. The thermodynamic considerations are essential to understand the thermal stability and nature of a substance (i.e. liquid, solid, molten salts and crystals) [32]. Standard entropy is one of the thermodynamic properties which is a measure of a system's unavailability to perform work, i.e. higher the entropy more is the system's disorder. According to Glasser [32] and Yang *et al.* [33] the standard entropy of the PILs was calculated by using the following relation;

$$S_0 \approx 1246.5 V + 29.5 \quad (5)$$

where $S_0/J \cdot K^{-1} \cdot \text{mol}^{-1}$ is the standard entropy and V/nm^3 is the molecular volume of the pyridinium carboxylates. The molecular

volume “ V ” is defined as the volume occupied by the sum of the ionic constituents (i.e. cation and anion) present in the solvent, which could be explained as:

$$V = V_M/N_A \quad (6)$$

where, N_A is Avogadro's number, ($N_A = 6.02245 \times 10^{23} \text{ mol}^{-1}$). A linear relation between the standard entropy (S_0) and the number of carbon atoms (N_c) is;

$$S_0 = 32.97N_c + 245.34 \quad (7)$$

From Eq. (7) it can be seen that the standard entropy of PILs increased linearly with an increase in number of carbon atoms in the alkyl chain of the pyridinium carboxylate anions. The estimated slope $32.97 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (Eq. (7)) is satisfactorily comparable with the reported value of $34.63 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for $[\text{C}_n\text{mim}][\text{BF}_4]$ [32], and $32.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for a comprehensive group of organic compounds [34]. An addition of methylene group in the alkyl chain of the anions results in an increase of $32.97 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ in the standard entropy of the pyridinium carboxylates. Pyridinium carboxylates with higher alkyl chain length are proven to be poor solvents for lignin dissolution [3].

The thermal expansivity or volume expansion coefficient is the reflection of the intermolecular forces and the free volume of solvents, i.e., greater thermal expansivity corresponds to greater free volume [28]. These intermolecular forces lead to a change in volume of a fluid with a change in temperature [35]. The measured density values at various temperatures were used to calculate the thermal expansivity of the pyridinium carboxylates.

$$\alpha_p = -\left(\frac{1}{\rho}\right)\left(\frac{\partial \rho}{\partial T}\right)_p = -\frac{(A_1)}{(A_0 + A_1 T)} \quad (8)$$

where, α_p is the thermal expansivity (K^{-1}), ρ is the density ($\text{g} \cdot \text{cm}^{-3}$), T is the temperature (K) and A_0 and A_1 are the fitting coefficients of Eq. (1) (Table 3). The thermal expansivity values of the pyridinium carboxylates can be calculated by using these coefficients. The thermal expansivity values are found to increase with increasing alkyl chain length at a given temperature. This higher thermal expansivity with increasing alkyl chain length is related to high conformational flexibility due to increased molar volume which may result in an increase in the translational dynamics of the pyridinium carboxylates [36].

3.2. Viscosity

The viscosities of the pyridinium carboxylates were measured at different temperatures from (298.15 to 343.15) K (Table 4). The viscosity considerably decreased with an increase in temperature for the present studied temperature range. The viscosity is referred as the measure of internal resistance of a fluid towards a shear stress. The decrease in viscosity at higher temperatures is due to the reduction in intensity of

intermolecular forces or internal forces present between the molecules. Similar trends were reported for protic alkanolammonium ILs [37].

The viscosities of the present pyridinium carboxylates are found to increase significantly with an increase in the alkyl chain length; this trend could be attributed to the reason that with an increase in alkyl chain length the intermolecular forces (H-bonding, π – π interaction, Coulombic forces) are increased, resulting in an increased charge delocalization and hence an increase in resistance to flow [37]. Thus the anionic part has an important role on the viscosities of these PILs. The viscosity values increased in the following order ($[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-] < [\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-] < [\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$). A possible explanation can be that, the van der Waals interactions tend to be stronger at increased alkyl chain length, which results as an increase in viscosity [38]. The experimental viscosities of the present synthesized pyridinium carboxylates are correlated by using the following logarithmic form of the Arrhenius equation [39]:

$$\ln \eta = \ln \eta_\infty + \frac{E_\eta}{RT} \quad (9)$$

where, η is the viscosity ($\text{mPa} \cdot \text{s}$), T is the temperature (K), R is the universal gas constant ($\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), η_∞ is the viscosity at infinite temperature ($\text{mPa} \cdot \text{s}$), E_η is the activation energy for viscous flow ($\text{kJ} \cdot \text{mol}^{-1}$). For viscous flow the activation energy is considered as the maximum possible energy obstructions that must be overcome by the molecules to move freely inside the fluid. The greater the activation energy, the more difficult it is for the ions to move freely, which may be due to the reasons such as; size of the ions, complicated arrangements or the stronger interfaces which are present among the molecules in the fluids. The activation energy (E_η) and the infinite temperature viscosities (η_∞) are the distinctive parameters and their values are obtained using the linear relation between $\ln \eta$ vs $1/T$ (Fig. 2) [40]. The calculated activation energies (E_η) and infinite temperature viscosities (η_∞) for the pyridinium carboxylates are presented in Table 5. The activation energy (E_η) increases with an increase in alkyl chain length which shows that the size and enlargement of the ions have an important role on the activation energy. From the standard deviation (SD) of the fit (≤ 0.007), it is clear that the

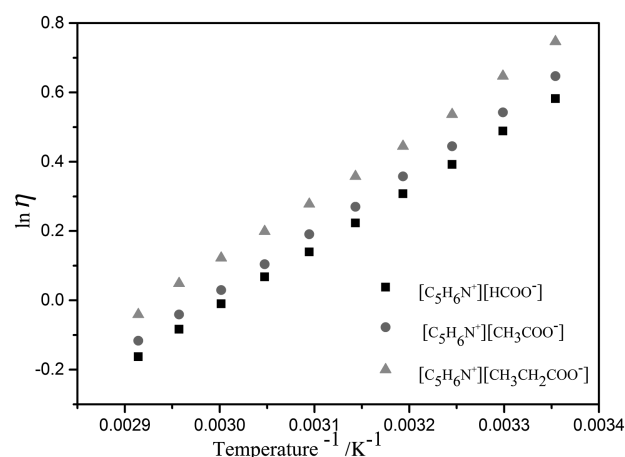


Fig. 2. The relationship of $\ln \eta$ and reciprocal of temperature of pyridinium carboxylate PILs.

Table 4
Viscosities of pyridinium carboxylates at different temperatures

T/K	$\eta/\text{mPa} \cdot \text{s}$		
	$[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$	$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$	$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$
298.15	1.79	1.91	2.11
303.15	1.63	1.72	1.91
308.15	1.48	1.56	1.71
313.15	1.36	1.43	1.56
318.15	1.25	1.31	1.43
323.15	1.15	1.21	1.32
328.15	1.07	1.11	1.22
333.15	0.99	1.03	1.13
338.15	0.92	0.96	1.05
343.15	0.85	0.89	0.96

Table 5
Estimated activation energies (E_η) and infinite temperature viscosities (η_∞) (Eq. (9))

Pyridinium carboxylates	$E_\eta/\text{kJ} \cdot \text{mol}^{-1}$	$\eta_\infty \times 10^2/\text{mPa} \cdot \text{s}$
$[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$	13.96	6.39
$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$	14.32	5.84
$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$	14.63	5.70

viscosity of the present synthesized pyridinium carboxylates is satisfactorily correlated using activation energy.

On the other hand, at infinite temperature the intermolecular interactions and forces are no longer effective and the infinite temperature viscosity (η_∞) is mostly ruled by the geometric symmetry of the ions [41]. In general, the infinite temperature viscosity (η_∞) of the pyridinium carboxylates decreases with increasing activation energy and similar trends were reported by Almeida *et al.* [41,26] and Okoturo and Vander Noot [42] which shows that the structural contribution of each ion to the dynamic viscosity cannot be ignored.

3.3. Refractive index

The refractive index is known as the speed of light in vacuum divided by the speed of light in the working medium. Generally, it is a measure of how light propagates through that medium, therefore, the more is the refractive index of a given solvent, the higher is the light refracted through it. The refractive index provides useful information about the electronic polarity of a molecule and can be used as a measure of relative hydrogen bond donating and accepting ability, which are useful to determine solubilities, partition constants, and reaction rates [29,43]. The refractive indices (n_D) for the pyridinium carboxylates were determined at various temperatures from 293.15 K to 323.15 K (Table 6). The results showed that the refractive index of the studied pyridinium carboxylates decreased linearly with an increase in temperature.

Table 6
Refractive indices (n_D) of PILs at different temperatures

T/K	n_D		
	$[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$	$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$	$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$
293.15	1.45342	1.46042	1.47632
298.15	1.45095	1.45816	1.47451
303.15	1.44860	1.45596	1.47229
308.15	1.44668	1.45323	1.47016
313.15	1.44424	1.45110	1.46782
318.15	1.44163	1.44864	1.46554
323.15	1.43957	1.44634	1.46352

The temperature dependency of experimental refractive indices is similar to that for the density and can be correlated using the following equation.

$$n_D = n_0 + n_1 T \quad (10)$$

where n_D is the refractive index, T is the temperature (K) and n_0 and n_1 are the coefficients, which were estimated by least-square analysis (Table 7).

Table 7
Fitting parameters for Eq. (10)

Pyridinium carboxylates	n_0	$n_1 \times 10^4$
$[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$	1.58843	−4.61024
$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$	1.59891	−4.72430
$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$	1.60373	−4.34119

The refractive indices increased linearly with an increase in alkyl chain length of anion at all the temperatures (Table 7), which might be due to the reason that at increased alkyl chain length, the electronic polarizability and dispersion forces between the molecules are increased, which causes the light to hit more molecules present in the solvent, and hence increase in refractive index, and similar findings were reported by Tariq *et al.* [28].

3.4. Surface tension

The measured surface tension values of pyridinium carboxylates are listed in Table 8. The surface tension decreases with an increase in alkyl chain length. This behavior could be attributed to the weakening of the Coulomb interactions, with increasing alkyl chain, as suggested by Zhou *et al.* [44].

Table 8
Surface tension of pyridinium carboxylates at different temperatures

T/K	$\gamma/\text{mN} \cdot \text{m}^{-1}$		
	$[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$	$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$	$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$
298.15	37.03	34.65	32.73
303.15	35.76	33.45	31.66
308.15	34.36	32.27	30.36
313.15	33.51	31.37	29.12
318.15	32.62	30.17	27.99
323.15	31.43	28.74	26.69
328.15	30.52	27.59	25.48
333.15	29.32	26.42	24.62
338.15	28.26	25.53	23.26
343.15	27.01	24.57	22.33

The van der Waals forces increase with increasing size of the molecules [4], which leads to the distribution and delocalization of the ionic charge and hence to a decrease in the hydrogen bond strength [4].

The surface tension is a measure of the most energetic interactions established between the anion and cation in a fluid such as; Coulombic interactions, hydrogen bonding and van der Waals forces which are further dependent on the alkyl chain length [4]. The longer alkyl chain leads to the intensification of attractive Lennard-Jones contribution [45,46]. The surface tension is less for compounds with longer alkyl chain, due to weak Coulombic forces [28,29].

3.5. Thermal decomposition temperature

Thermogravimetric analysis was performed for the investigated pyridinium carboxylates to estimate the thermal stability of the samples. The estimated “ T_{start} ” (start decomposition temperature) and “ T_d ” (final decomposition temperature) of all the studied samples are listed in Table 9, whereas their mass loss thermograms are shown in Fig. 3. Among all samples, $[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$ has the maximum decomposition temperature ($T_d = 113^\circ\text{C}$), indicating its high thermal stability. The acetate anion is less thermally stable compared to the formate and propionate anion. The DTGA of $[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$ could not be generated as the “ T_{start} ” and “ T_d ” of acetate anion were found to be very close which is attributed to its thermal instability. The anions containing odd number of carbon are more thermally stable than the anions with even number of carbons [47].

Table 9
Thermal decomposition temperature and glass transition temperature of pyridinium carboxylates

Pyridinium carboxylates	$T_{\text{start}}/^\circ\text{C}$	$T_d/^\circ\text{C}$	$T_g/^\circ\text{C}$
$[\text{C}_5\text{H}_6\text{N}^+][\text{HCOO}^-]$	57	113	−121.84
$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{COO}^-]$	51	59	−115.40
$[\text{C}_5\text{H}_6\text{N}^+][\text{CH}_3\text{CH}_2\text{COO}^-]$	52	110	−114.47

3.6. Glass transition temperature

The glass transition temperature “ T_g ” is an indicative of the cohesive energy of the solvent. The cohesive energy can be decreased by repulsive Pauli forces by the overlapping of the close electron shell, while it can be increased through the van der Waals forces and hydrogen-bonding

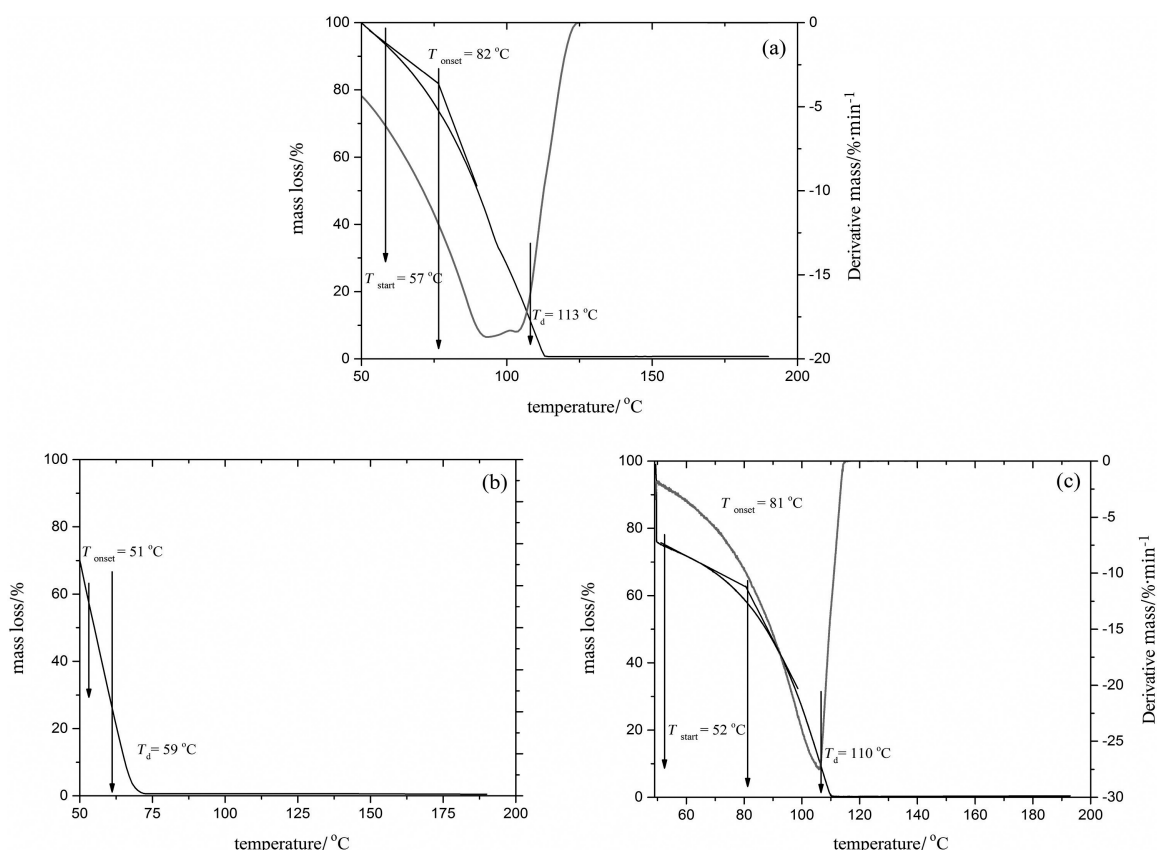


Fig. 3. Thermograms of pyridinium carboxylate PILs (a) $[C_5H_6N^+][HCOO^-]$, (b) $[C_5H_6N^+][CH_3COO^-]$ and (c) $[C_5H_6N^+][CH_3CH_2COO^-]$.

interactions. This can be achieved by the modification of the cationic and anionic components of the solvent. The viscosity and “ T_g ” values are significantly dependent on the type of anion [47,48]. Low “ T_g ” values are indicative of the solvent’s required physicochemical properties such as reduced viscosity [47]. The glass transition “ T_g ” of the pyridinium carboxylates was measured using DSC thermograms (Fig. 4). These solvents showed only glass transition and no melting points were observed [10].

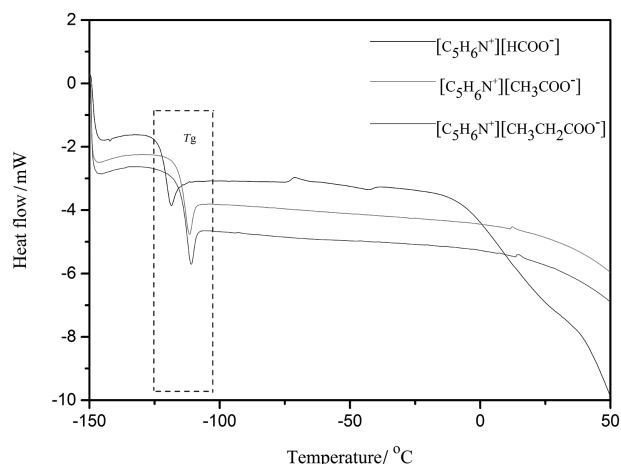


Fig. 4. DSC traces of pyridinium carboxylate PILs.

The glass transition temperatures of the present pyridinium carboxylates are listed in Table 9. The “ T_g ” values of the investigated

protic pyridinium carboxylates are similar to those of ammonium carboxylates reported in literature, where the stated “ T_g ” was in the range of $-114\text{ }^{\circ}\text{C}$ and $-44\text{ }^{\circ}\text{C}$ [10,49]. Based on the previous literature no “ T_g ” has been reported for the present synthesized carboxylates. A shorter alkyl chain exhibits a lower T_g value, and was found to increase slowly with increasing alkyl chain length due to the intensification of the van der Waals forces [50].

4. Conclusions

The thermophysical properties of a new series of pyridinium based PILs are established in detail. All properties are found to be an inverse function of temperature irrespective of the alkyl chain length. The densities and surface tension of the pyridinium carboxylates decrease with increasing alkyl chain length while an opposite trend was observed for the viscosity and refractive index. The molar volume was calculated using experimental density data and was found to be linearly dependent per addition of $-CH_2-$ group in the anion of pyridinium carboxylates. Pyridinium carboxylates possess low glass transition temperature which is desirable for the essential physicochemical properties of a solvent such as reduced viscosity. These basic thermophysical properties of pyridinium carboxylates could be helpful for their potential large scale application towards lignin extraction from biomass.

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