



The effects of temperature, alkyl chain length, and anion type on thermophysical properties of the imidazolium based amino acid ionic liquids

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ABSTRACT

The viscosity, surface tension, and density as well as molar volume and expansion coefficient of imidazolium based amino acid ionic liquids (AAILs) including alaninate ([ALA][−]), glycinate ([GLY][−]), glutamate ([GLU][−]), serinate ([SER][−]), and valinate ([VAL][−]) anions were investigated at the extended temperature until 373.15 K. Thermophysical as well as electronic properties were taken into account in order to explore the effect of alkyl chain length and anion on these properties. The results indicated that the interaction between ion pairs has a great effect on the properties; the strong interaction caused the higher viscosity and surface tension. The effect of temperature and alkyl chain length as well as anion type on the physicochemical properties was also studied. Raising the temperature resulted in a downward trend on the density, viscosity, and surface tension of all systems. In addition, the hypothetical critical temperatures of the AAILs were estimated making use of the Eötvös and Guggenheim equations. It was shown that the critical temperature decreases with alkyl chain length and its change depends on the ion pair interaction energy density and density of electronic chemical potential. The results of prediction critical temperatures of AAILs using surface tension data revealed that [EMIM][GLY] had the highest critical temperature due to its strongest ion pair interaction and stability and lower alkyl chain length in cation. Moreover, the anion charge density shows a straight correlation with interaction energy density that is in according with the stability of the ion pairs. Investigating viscosity as a transport property demonstrates that the lowest viscosity is observed for AAILs involving [GLY][−] anion that is described by high flexibility of the anion. Finally, the change in volume of AAILs is small as the temperature increases confirming AAILs as solvent do not expand much which explains their good solvent characteristics.

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1. Introduction

Compared to high temperature molten salts, ionic liquids (ILs) which are [1] known as “green” and “designer” solvents [2–4] have attracted considerable attention in recent years and their excellent properties [5,6] make ILs very promising in industry [7]. ILs contain large asymmetric organic cations coupled with relatively small organic or inorganic anions [4,8–10]. They were initially developed as suitable and attractive alternatives to the conventional organic solvents in chemical reactions [11–13] due to their unique properties such as negligible vapor pressure, relatively low melting temperatures (below 100 °C), nonflammability, environment friendly, wide electrochemical windows, very low volatility, excellent thermal and chemical stability, inherent polarity, high conductivity, and tunable solubility [4,8,14–20]. Some of these mentioned properties prevent the ILs from entering the environment through evaporation and producing air pollution [21].

Using the synthetic ILs can also cause problems, such as hydrolyzing some halogen-containing ILs in contact with water molecules and moisture [22], toxicity of precursors for preparing the aromatic cations-based ILs such as imidazolium and pyridinium [8,21,23,24], and high costs [25]. Most of the ILs are water soluble and therefore can damage the environment due to their low biodegradation and ecotoxicity [21, 25].

Physical and chemical properties of the ILs can be adjusted by changing or modifying the structure and nature of the cation or anion [26–28]. The amino acid ionic liquids (AAILs) are derived from natural amino acid ions [14,29–33] and are considered as an important class of ILs. They are biodegradable and environment-friendly [22,34]; the preparation process of these AAILs is economically desirable due to being simple and low-cost, and environmentally desirable due to being green [21,23]. The physio-chemical properties of AAILs are dependent on the properties of AAs. From the other side of view, amino acids are the structural units of protein [3,35]; these biomaterials can abundantly be found in nature [29,34,36]. In their structure, there are two functional groups of amino and carboxylic acid and are available as both cations and anions

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[27,36,37]. It has been found out that AAILs possess a high hydrogen bond (HB) basicity that is useful for dissolution of biomaterials, such as DNA, cellulose, and other carbohydrates. In addition, due to the functionality of amino acids, it is expected that AAILs provide a variety of applications, such as intermediates for peptide synthesis, chiral solvents, functional materials, and biodegradable ILs in the field of industrial and pharmaceutical chemistry [22,35]. For the investigation of the synthesis and the application of ILs in the field of catalysis, separation, cellulose dissolution, and electrochemistry, their thermophysical properties are very important for analysis [9,37,38].

The physicochemical properties of AAILs may be highly desirable due to their dependency on varying the length of the alkyl chain on the cation, varying the anion, and its size and charge. Density, surface tension, and viscosity as substantial thermophysical properties of the ILs have been studied widely. Based on the experimental data from these properties, one can obtain expansion coefficient, IL molar volume, as well as the surface thermodynamic functions i.e. surface excess entropy and surface excess enthalpy. Moreover, having adequate knowledge and information on thermophysical properties is important in efficient designing of industrial processes and new products based on ILs [39–43]. As Aparicio et al. [44] have mentioned, accurate knowledge on thermophysical properties is valuable. They have reviewed available data on imidazolium based ILs and compared their accuracies; their study does not include the AAILs as environmental friendly solvents, in general materials. Ghanem et al. [45] have synthesized four new AAILs based on 1-(2-hydroxyethyl-3-methylimidazolium) cation with AA anions including alaninate ([ALA][−]), glycinate ([GLY][−]), serinate ([SER][−]), and proline ([PRO][−]). They have measured thermophysical properties including density, viscosity, and surface tension; in addition, they have predicted physical properties, such as molecular volume. Their investigation demonstrates that these new AAILs can be considered eco-friendly. Fang et al. [46] have measured the density, surface tension, and refractive index for AAILs based on glutamate ([GLU][−]) in a specific temperature range. They have predicted a series of physicochemical properties of homologue components based on a semiempirical method in agreement with experimental values. Wei et al. [31] have measured the density, surface tension, and refractive index of the two AAILs based on [SER][−] anion in a temperature range. They have calculated on the basis of the experimental data, a series of the physicochemical properties i.e. thermal expansion coefficient (α_p), molecular volume (V_m), surface excess enthalpy (H^s), and the molar polarization (R_m). In their study, the relationship between each of the properties of the AAILs and temperature was discussed. They have concluded H^s , R_m , α_p , and V_m are approximately temperature-independent.

Mou and coworkers [47] have investigated 1-ethyl-3-methylimidazolium glycinate ([EMIM][GLY]) theoretically to understand the nature of the interactions between ion pairs in AAIL as well as the most stable geometries. Ghatee et al. [19] have predicted the critical temperature of a series of ILs and calculated anion-cation interaction energy by quantum mechanical density functional theory (DFT). They have also investigated the correlation of interaction energy with the predicted critical temperature and found that critical temperature is a function of cation and anion type. Mohajeri and Ashrafi [27] have studied the interactions between eight AA based anions and four imidazolium based cations by DFT and presented a systematic investigation of electronic structure and molecular interaction between the cation and anion. Wu and Zhang [48] have studied the gas-phase ion pairs of AAILs containing 1-ethyl-3-methylimidazolium and 20 natural amino acids at the B3LYP/6-311+G (d,p) level. Their focus was on the HB interaction though the electronic structure and ion pair interaction were also under consideration.

Qian et al. [49] have synthesized and studied AAILs experimentally and theoretically. Their results show that the viscosity of the AAILs decreases as the interaction energy enlarges. In addition, stronger the interaction energy leads to the lower the CO₂ absorption capacity. Herrera et al. [25] have studied four AAILs by molecular dynamics

(MD) simulation. To understand the effects of the anion structures on the properties of AAILs, Sirjoosingh et al. [50] have studied the molecular level structure, dynamics, and density of the 20 1-ethyl-3-methylimidazolium salts with MD at 298.15 K.

In spite of large number of theoretical and experimental studies on the ILs, the structural properties of AAILs were not investigated in details. It seems vital to obtain thermophysical properties and their relation with each other and find their dependency on the temperature, anion type, and alkyl chain length. In addition, searching a relationship between experimental and theoretical properties has not established previously. In line with these statements, the present study aims at (i) the available experimental density, viscosity, and surface tension data of 22 pure imidazolium based AAILs at $T = (293.15 \text{ to } 373.15) \text{ K}$ and atmospheric pressure were applied to calculate coefficients of thermal expansion, surface excess enthalpies, surface excess entropies, and critical temperatures. (ii) Furthermore, the influence of tuning the amino acid anion and length of cation of the different AAILs as well as temperature on thermophysical properties is explored. (iii) Anion as well as cation play a main role on the structural properties of AAILs; as a result, some electronic properties were computed by DFT computation and the stability of the AAIL will be studied. (iv) The charge and interaction energy densities were compared for the goal AAILs and their variation with anion type and alkyl chain length are taken into account. (v) Finally, it is aimed to establish a relation between these two different properties (classical and molecular characterizations). Interestingly, the variation of classical properties relies on the structural properties. Up to our knowledge, no publication in the existing literature covers all these aspects, let alone in one model, although they are of major practical interest; for some of these AAILs no previous computations were published on ion pair interaction energy and other electronic properties and no relation on surface tension as a function of viscosity.

2. Computational details

Conventional procedure of quantum mechanical DFT was performed to examine the interaction energy between the cation and anion (E_{int}), atomic charges, dipole moment, polarization, ion pair molar volume, ionization energy, vibrational frequencies, and electron affinity besides finding the electronic optimum structure. The Becke's three parameter hybrid method with the LYP (Lee-Yang-Parr) correlation functional (B3LYP) [51,52] was employed. We applied the Pople's style, one-electron basis set; as a result, the optimization for the final stable molecular structure was carried out at B3LYP/6-311++G** level of theory by using the Gaussian 03 package [53].

The Charges from Electrostatic Potentials using a Grid based method (CHELPG) developed by Chirlian and Francl [54] was applied to analyze electrostatic potentials (ESP) which a detailed assessment of ionic charges is given elsewhere [55]. The ESP represents a least-squares fit of charges to the calculated electrostatic potential outside the van der Waals surface for the molecule and is convenient for calculating intermolecular coulombic interactions of the types used in many force fields. In addition, they might best be thought of as a set of empirical quantities that are designed to reproduce long range interactions [56].

First ionization energy, I , and electron affinity, A , computed by DFT computation provide a linear correlation with electronic chemical potential as [57]:

$$\mu(\text{kJ/mol}) = -\frac{2625.50}{2} (I + A) \quad (1)$$

A systematic approach was used to compute E_{int} , which is defined as the difference between the energy of the pair of ionic system and the sum of the energies of the purely cationic and anionic species:

$$E_{\text{int}}(\text{kJ/mol}) = 2625.50 [E_{\text{AX}}(\text{au}) - E_{\text{A}^+}(\text{au}) - E_{\text{X}^-}(\text{au})] \quad (2)$$

where, for this purpose, each isolated IL and its corresponding cation and anion was optimized for the structure and energy at the B3LYP/6-311++G** level of theory as mentioned above. The calculation was performed on 22 isolated imidazolium based AAILs including [ALA]⁻, [GLY]⁻, [GLU]⁻, [SER]⁻, and valinate ([VAL]⁻) anions (Scheme 1).

To evaluate thermophysical properties, the following procedure was applied. In order to find the surface excess enthalpy, the values of surface tension versus temperature were under consideration as [58]:

$$\gamma = H^s - TS^s \quad (3)$$

where γ stands for surface tension, H^s for the surface excess enthalpy, and S^s for the surface excess entropy whose values are obtained from the temperature dependence of surface tension. Strictly speaking, the differentiation of γ with respect to T should be carried out at constant pressure.

According to Guggenheim [59], surface tension with increasing the temperature decreases that is described by a certain exponent and is universally applied to compounds of the same universality class, irrespective of their chemical nature. In addition to the scaling law, an empirical relation relates surface tension to the temperature as:

$$\gamma = a \left(1 - \frac{T}{T_c}\right)^{11/9} \quad (4)$$

where a is a substance-dependent constant.

One of the earliest and best-known empirical relations that involves the temperature dependence of surface tension is that of Eötvös:

$$\gamma \left(\frac{M}{\rho}\right)^{2/3} = k(T_c - T) \quad (5)$$

where k is a constant, ρ the liquid density, and M the molecular mass.

In this work, surface tension data were used to estimate the critical temperature of 20 AAILs, using Eqs. (4) and (5) comparing with estimation that surface tension vanishes at critical temperature from Eq. (3).

The thermal expansion coefficient which demonstrates the change of the liquid volume as the temperature changes is defined as:

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

and AAIL molecular volume obtained from the variation of density with temperature is defined as [18]:

$$V_m = \frac{M}{N_A \rho} \quad (7)$$

where N_A is the Avogadro's number. Notice that density changes with temperature linearly.

All the above calculations were carried out using temperature-dependent surface tension and density given from literature [5,9,17,31,32,38,46,60–63]. All the experimental data related to surface tension and density were collected for 22 imidazolium based AAILs including

[ALA]⁻, [GLY]⁻, [GLU]⁻, [SER]⁻, and [VAL]⁻ anions at different temperature ranges.

Viscosity is a physical transport property [1] which is related to the molecular structure [4] of ILs and intermolecular forces of fluids [64]. The experimental viscosity data of the AAILs are scarce and in the present work, we focused only on the data of 8 AAILs including [ALA]⁻, [GLY]⁻, and [SER]⁻ anions [9,17,65,66]. Noticeably, viscosity, η , depends on the temperature as an Arrhenius relation:

$$\eta = \eta_\infty \exp\left(\frac{E_\eta}{RT}\right) \quad (8)$$

where η_∞ and E_η are the parameters dependent on the structure and identity of the AAIL; R stands for the universal gas constant. E_η , the activation energy for viscous flow, and the viscosity at infinite temperature, η_∞ , were calculated from the slope and intercept respectively of the Arrhenius plot. The experimental viscosity data [17,67,68] of the studied AAILs were well fitted by the Arrhenius equation.

Ghatee et al. [69] have proposed a well-known equation on sharply varying viscosity with surface tension of ILs (below the critical temperature), due to temperature dependent of both properties:

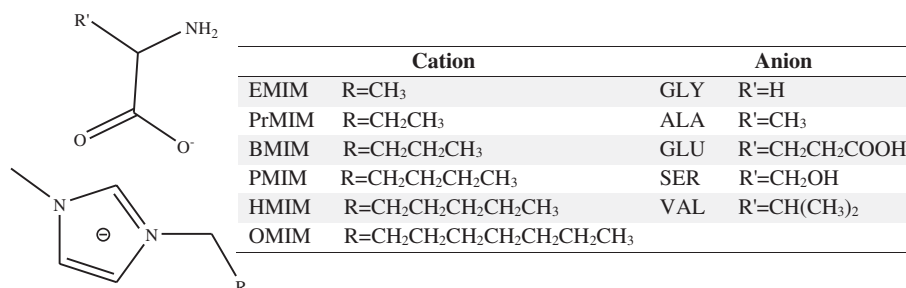
$$\ln \gamma = \ln C + D \left(\frac{1}{\eta}\right)^\phi \quad (9)$$

where $\ln C$ and D are substance dependent constants, independent of the thermodynamic state of the system, and ϕ is the universal exponent. For ILs, this exponent is equal to 0.30 to fit the imidazolium based ILs with simple anion content and in the case of AAILs we observe that $\phi = 0.20$.

3. Results and discussion

To explore the experimental dependency of $\ln \eta$ of AAILs with reciprocal temperature, the plots of $\ln \eta$ versus $1/T$ were under consideration in a broad range of temperature at atmospheric pressure. It was evaluated that the viscosity of all studied AAILs decreases by increasing temperature. Noticeably, the ion pair interaction of the AAILs follow the particular trend by temperature since the kinetic energy increases and governs on the potential energy and the movement will be more comfortable for the ions. In addition, both properties η_∞ and E_η change with cation change length and anion type and their values are presented in Table 1.

The results demonstrate that by increasing the length of alkyl chain, E_η/R changes inhomogeneously as well as η_∞ . In addition, the squared value of R (R^2) shows that the linear relation is conserved on all the studied systems and is greater than 0.9900. E_η is the energy barrier which must be overcome by the ion pairs to move past each other in the AAIL; besides, it can be correlated with structural information about the AAIL. The larger is E_η , the harder it is for the ion pairs to move past each other which might be due to either physical size or entanglement or more numerous or stronger interactions in the AAIL (and hence more order). At infinite temperature, interactions which contribute to viscosity at room temperature in AAILs are no longer effective and



Scheme 1. The structure of AAILs studied.

Table 1
 Predicated parameters of Eq. (8) for imidazolium based AAILs [17,67,68].

AAIL	$\ln \eta_{\infty}$	E_{η}/R	R^2
[EMIM][ALA]	-10.5992	4677.65	0.9951
[PrMIM][ALA]	-	-	-
[BMIM][ALA]	-	-	-
[PMIM][ALA]	-	-	-
[HMIM][ALA]	-	-	-
[OMIM][ALA]	-11.4039	5224.66	0.9954
[EMIM][GLY]	-8.9165	3875.31	0.9960
[PrMIM][GLY]	-	-	-
[BMIM][GLY]	-13.3618	5245.00	0.9925
[PMIM][GLY]	-	-	-
[HMIM][GLY]	-	-	-
[OMIM][GLY]	-10.6605	4898.99	0.9952
[PrMIM][GLU]	-	-	-
[BMIM][GLU]	-11.1302	4639.35	0.9983
[PMIM][GLU]	-	-	-
[HMIM][GLU]	-	-	-
[EMIM][SER]	-13.0853	5674.72	0.9941
[PrMIM][SER]	-	-	-
[BMIM][SER]	-	-	-
[OMIM][SER]	-14.0408	6390.90	0.9937
[EMIM][VAL]	-	-	-
[PrMIM][VAL]	-	-	-

the value of η_{∞} is governed purely by the geometric structure of the ions in the AAIL. Consequently, it may be representative of a structural contribution of the ions to the viscosity. In the literature, the values of E_{η} and η_{∞} [70] have been calculated for a few ILs but the structural implications of η_{∞} and E_{η} have not been fully realized for AAILs. However, the maximum values of viscosity are related to AAILs consisting [SER]⁻ anion; besides, the viscosity increases with increasing alkyl chain length which can be attributed to increasing the Van der Waals interaction force between the long alkyl chain lengths of imidazolium cation, hydrogen bonding of anions, and formula weight of the component ions [17,67,68]. The lowest viscosity values for this series of AAILs is observed for [GLY]⁻ anion that may be explained for the high flexibility of this anion.

As Gaciño et al. [28] have reported, a good lubricant is that whose viscosity varies as little as possible with temperature. In other words, the effectiveness of lubrication and energy losses do not vary with external factors concerning the temperature. As a result, it is expected that [EMIM][GLY] with the lowest value of E_{η} and the greatest value of $\ln \eta_{\infty}$ is the best lubricant.

Density as a physical property changes with temperature, anion, and cation. The experimental density data of 22 AAILs were chosen to evaluate isobaric expansion coefficient and molecular volume [5,9,17,31,32,38,46,60–63]. Fig. 1 illustrates the variation of density with temperature and length of alkyl in cation for the case of [C_nMIM][ALA].

It should be mentioned that for AAILs with the same anion, the density was calculated at the same temperature range. Illustrating the experimental results of density of AAILs with temperature displays that the density of all the AAILs decreases linearly with temperature. In addition, the density at a certain temperature, decreases with alkyl chain length due to the increase of dispersive interactions that has been observed for ILs previously [28,71]. The results represent that dependency in the case of density is mainly limited to the number of carbon atoms in the cation and is almost independent of the symmetry of the cation as the slope of the density versus temperature is approximately unchanged. According to the previous reports [17,67], comparing AAILs and ILs with the same cation verifies that the density of AAILs is lower than the density of ILs consisting perfluorinate anions and other inorganic anions which can be attributed to the size and local charge of anion and hydrogen bonding between anion and cation. From the other side of view, comparing AAILs with different phosphonium and

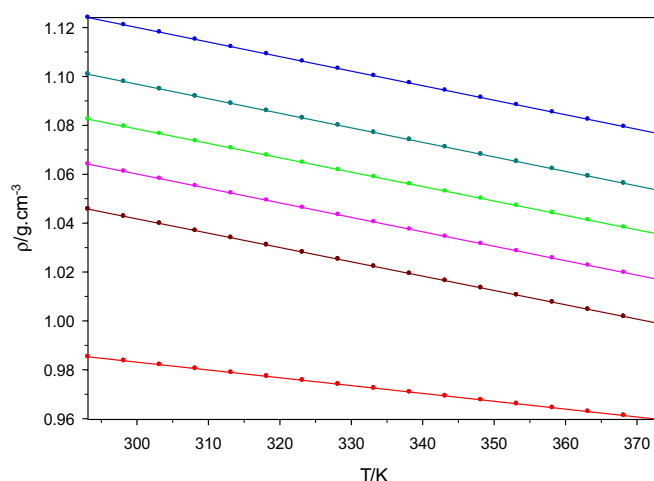


Fig. 1. The density variation versus temperature for imidazolium based AAILs consisting [ALA]⁻ anion [17,60]. Red, [OMIM][ALA]; dark red, [HMIM][ALA]; pink, [PMIM][ALA]; green, [BMIM][ALA]; dark green, [PrMIM][ALA]; and blue, [EMIM][ALA]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

imidazolium cations, the AAILs consisting imidazolium cation have higher density [67].

In the present study, the utmost value of density is related to imidazolium based AAILs consisting [GLU]⁻ anion. The above anion is the heaviest anion which is expected to possess weaker electrostatic interaction. High density of AAILs can be due to local large negative charge of anion with an asymmetric charge distribution, size of the anion, and inter- and intra-molecular hydrogen bonding between functional groups of [GLU]⁻ anion [18,67].

By investigating the density data of imidazolium based AAILs with different anions, we found the effect of alkyl chain length of cation and nature of anion on the density as well as temperature influence. For the AAILs with the same alkyl chain length, the density among the anions can be ranked as the following order:

For [EMIM]⁺ cation: [GLY]⁻ > [ALA]⁻ > [VAL]⁻

For [PrMIM]⁺ cation: [GLU]⁻ > [SER]⁻ > [GLY]⁻ > [ALA]⁻ > [VAL]⁻

For [BMIM]⁺ cation: [GLU]⁻ > [SER]⁻ > [GLY]⁻ > [ALA]⁻

For [PMIM]⁺ and [HMIM]⁺ cations: [GLU]⁻ > [GLY]⁻ > [ALA]⁻

For [OMIM]⁺ cation: [SER]⁻ > [GLY]⁻ > [ALA]⁻

Strictly speaking, the present order is in agreement with Herrera et al. [25] molecular dynamics simulation results for [EMIM]⁺ cation. It can be understood from the above order that the interaction energy between cation and anion in [GLU]⁻ is the weakest because of steric effect and anion size that will be under consideration in the next paragraphs. In addition, it is clear that the functional group and size of the anion play the main role on the density.

In order to evaluate the impact of molar mass on the density at 0 °C, ρ_0 , the studied AAILs were considered in the order of their molar mass. It was found that an increase in molar mass of AAILs causes a decrease in ρ_0 value.

The values of expansion coefficient of AAILs in the temperature range studied were also obtained from density variation with temperature, Eq. (6). This property shows the fractional change in density when temperature increases at constant pressure. The coefficient of determination for temperature dependence of expansion coefficient of the AAILs including [ALA]⁻, [GLY]⁻, [GLU]⁻, [SER]⁻, and [VAL]⁻ anions shows a linear dependency on temperature. Fig. 2 demonstrates the variation of α_p in the case of [C_nMIM][GLY] at the temperature range of 283.15 K to 373.15 K, as a typical sample.

Expansion coefficient of all AAILs increases with temperature. Furthermore, one can investigate the change of expansion coefficient at a certain temperature with alkyl chain length for the studied AAILs. Although the expansion coefficient of imidazolium based AAILs

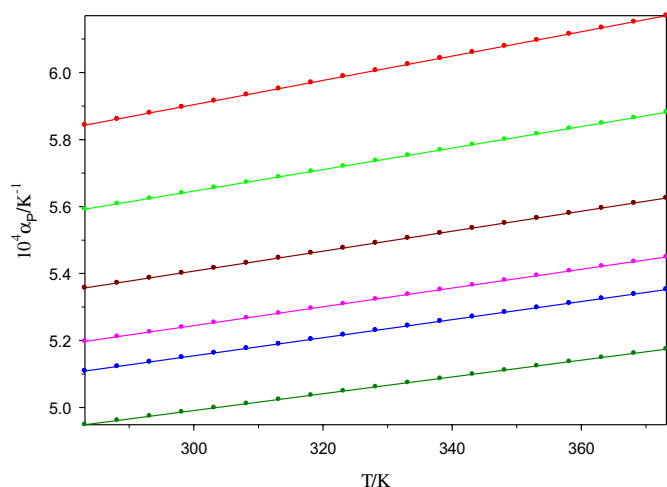


Fig. 2. The variation of thermal expansion coefficient against temperature for imidazolium based AAILs consisting [GLY][−] anion. Red, [OMIM][GLY]; dark red, [HMIM][GLY]; pink, [PMIM][GLY]; green, [BMIM][GLY]; dark green, [PrMIM][GLY]; and blue, [EMIM][GLY]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

[C₂₋₆MIM][ALA] increases with alkyl chain length, [OMIM][ALA] enjoys the lowest value of expansion coefficient. The Expansion coefficient values of imidazolium based AAILs consisting [GLY][−], [GLU][−], and [SER][−] anions at a certain temperature does not follow a particular trend with increasing alkyl chain length. The expansion coefficient values of [EMIM][VAL] and [PrMIM][VAL] imidazolium based AAILs at a certain temperature decrease with increasing alkyl chain length. In total, it can be concluded that the variation of isobaric expansion coefficient with alkyl chain length changes from anion to anion. As the results indicate, the change in volume of AAILs is small as the temperature changes which conforms the fact that these solvents do not expand much. Besides, the range of α_p for the target AAILs is between $2.5 \times 10^{-4} \text{ K}^{-1}$ and $6.25 \times 10^{-4} \text{ K}^{-1}$ compared to $7.0 \times 10^{-4} \text{ K}^{-1}$ to $11.0 \times 10^{-4} \text{ K}^{-1}$ for other solvents such as THF, NMP, phenetole, and DMF as well as imidazolium, pyridinium, pyrrolidinium, and

phosphonium based ILs [28,72,73]. Table 2 demonstrates the predicted parameters of α_p variation with temperature.

As the table shows, the variation of α_p with the temperature is not considerable; consequently, its slope and intercept are almost constant with alkyl chain length and anion type. The positive values of temperature dependence of α_p for AAILs can be related to their lower ion pair interaction as well as critical temperature in comparison with ILs. Since the ion pair interaction lessens by the temperature, the expansive coefficient may increase.

It is possible to examine AAIL molecular volume by using the experimental data of density. The values of molecular volume of AAILs at a certain temperature range were calculated using Eq. (7). It is well defined that molecular volume of all the considered AAILs increases linearly with alkyl chain length. Moreover, one can investigate the molecular volume variations at a certain alkyl chain length with the temperature for the AAILs including [ALA][−], [GLY][−], [GLU][−], [SER][−], and [VAL][−] anions that shows an increase as the temperature increases.

In general, interface among the fluids plays a vital role in most of the applications in pure and applied sciences concerning ILs and specifically AAILs. Consequently, the accurate data on interface properties, namely surface tension as a physical property [74], and the relationship of these properties with the molecular structure are vital necessities for choosing an improved AAIL for a specific purpose. In addition, surface tension is directly related to the liquid interfacial microstructure [74] and fluid intermolecular forces [64]. In fact, it is indirectly related with anion-cation interaction energy [19]. The experimental surface tension data of 20 AAILs have been taken from literature [5,17,31,32,38,46,60–63]. The values of these data for the AAILs with the same anion were calculated at the same temperature range. Surface tension dependency on temperature can be expressed by Eq. (3). The coefficient of determination for temperature dependence of surface tension of the AAILs including [ALA][−], [GLY][−], [GLU][−], [SER][−], and [VAL][−] anions are presented in Table 3.

The effect of the alkyl chain length and the anion size can be gathered by the current data. As the table shows, the anion size and complexity do not have a direct effect on the surface tension, H^s , and S^s while not only γ but also H^s decreases with alkyl chain length. Besides, H^s and S^s do not change substantially with alkyl chain length and their values are primarily ruled by the anion nature that constitutes a specific

Table 2

Predicted parameters of α_p variation with temperature for imidazolium based AAILs.

AAIL	$\alpha_0 \times 10^4 \text{ K}^{-1}$	$\frac{d\alpha}{dT} \times 10^7 \text{ K}^{-2}$	R ²
[EMIM][ALA]	5.2280	2.8700	0.9983
[PrMIM][ALA]	5.3353	2.9918	0.9987
[BMIM][ALA]	5.3755	3.0382	0.9986
[PMIM][ALA]	5.4971	3.1812	0.9984
[HMIM][ALA]	5.5416	3.2346	0.9981
[OMIM][ALA]	3.2257	1.0830	0.9992
[EMIM][GLY]	5.0819	2.7004	0.9998
[PrMIM][GLY]	4.9239	2.5047	0.9995
[BMIM][GLY]	5.5603	3.2083	1.0000
[PMIM][GLY]	5.1693	2.8040	0.9996
[HMIM][GLY]	5.3273	2.9825	0.9983
[OMIM][GLY]	5.8068	3.6282	1.0000
[PrMIM][GLU]	4.2575	1.8894	0.9998
[BMIM][GLU]	–	–	–
[PMIM][GLU]	4.4039	2.0345	0.9993
[HMIM][GLU]	4.3839	2.0151	0.9972
[EMIM][SER]	5.2921	2.9591	0.9999
[PrMIM][SER]	5.2443	2.8881	1.0000
[BMIM][SER]	5.4128	3.0817	1.0000
[OMIM][SER]	5.9101	3.7643	0.9999
[EMIM][VAL]	5.4284	3.0905	0.9995
[PrMIM][VAL]	5.1952	2.8248	0.9997

Table 3
Predicated parameters of Eq. (3) for imidazolium based AAILs studied.

AAIL	H^s (mJ·m ⁻²)	S^s (mJ·m ⁻² ·K ⁻¹)	R ²
[EMIM][ALA]	73.4738	0.0702	0.9839
[PrMIM][ALA]	70.9011	0.0702	0.9871
[BMIM][ALA]	68.4036	0.0698	0.9850
[PMIM][ALA]	67.1878	0.0715	0.9883
[HMIM][ALA]	64.5878	0.0715	0.9883
[OMIM][ALA]	44.6359	0.0556	0.9969
[EMIM][GLY]	57.2850	0.0270	0.9766
[PrMIM][GLY]	63.4490	0.0600	0.9968
[BMIM][GLY]	62.0970	0.0625	0.9941
[PMIM][GLY]	60.2021	0.0627	0.9957
[HMIM][GLY]	60.7351	0.0665	0.9977
[OMIM][GLY]	74.1525	0.1323	0.9997
[PrMIM][GLU]	151.1310	0.3030	0.9998
[BMIM][GLU]	–	–	–
[PMIM][GLU]	124.2360	0.2757	0.9997
[HMIM][GLU]	121.2360	0.2757	0.9997
[EMIM][SER]	–	–	–
[PrMIM][SER]	61.3389	0.0487	0.9973
[BMIM][SER]	59.5369	0.0473	0.9956
[OMIM][SER]	56.9342	0.0784	0.9819
[EMIM][VAL]	58.6138	0.0654	0.9991
[PrMIM][VAL]	60.6742	0.0757	0.9974

IL. The low surface excess entropy and surface excess enthalpy values of the studied AAILs except AAILs containing [GLU]⁻ anion may indicate, respectively, an enhancement of the degree of surface orientation and low interaction energy between ions as claimed by Altuwaïm et al. [72,75] for ILs compared to other solvents.

The figures of experimental results related to surface tension of AAILs with temperature, not shown, illustrate that the surface tension of all the AAILs decreases linearly with increasing temperature. Additionally, one can investigate the surface tension variations at a certain temperature with alkyl chain length for the target AAILs. The surface tension values of these AAILs at a certain temperature reduce with alkyl chain length that is in accordance with literature [76]. Similarly, the size of anion has a great effect on the surface tension and leads to decrease the surface tension. For the AAILs with the same alkyl chain length, the surface excess enthalpy values among the anions are ranked as following:

For [EMIM]⁺ cation: [ALA]⁻ > [VAL]⁻ > [GLY]⁻

For [PrMIM]⁺ cation: [GLU]⁻ > [ALA]⁻ > [GLY]⁻ > [SER]⁻ > [VAL]⁻

For [BMIM]⁺ cation: [ALA]⁻ > [GLY]⁻ > [SER]⁻

For [PMIM]⁺ and [HMIM]⁺ cations: [GLU]⁻ > [ALA]⁻ > [GLY]⁻

For [OMIM]⁺ cation: [GLY]⁻ > [SER]⁻ > [ALA]⁻

Notice that AAILs with [ALA]⁻ anion possess naturally higher values of surface excess enthalpy except [OMIM][ALA] that enjoys the lowest value corresponding to interaction energy density which will be discussed in the last paragraphs.

In order to evaluate the impact of molar mass on the surface tension at 273.15 K, the above AAILs were considered. It was found that the increase in surface excess enthalpy values of AAILs is not proportional to the molar mass. In other words, surface tension at 273.15 K is independent of molar mass of the anion and cation.

Fig. 3 depicts the isotherms of surface tension of AAILs versus molecular volume of AAIL [C_nMIM][ALA], as a typical sample.

As the figure illustrates, both surface tension and molecular volume change linearly with the temperature and by increasing the molecular volume, the surface tension decreases that is in good agreement with Almeida et al. [75] observation for ILs.

Critical and boiling temperatures are important relevant thermodynamic properties since they are used in many corresponding states correlations. There is a lack of values for both temperatures for most ILs because many of the ILs start to decompose as the temperature

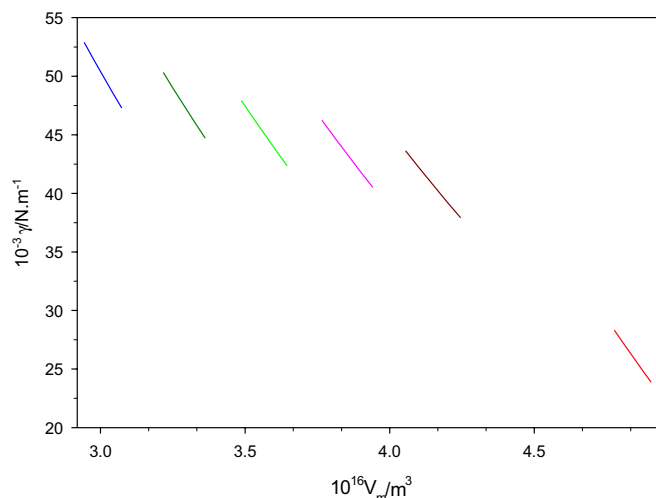


Fig. 3. The surface tension variation versus AAIL molecular volume for [C_nMIM][ALA]. Red, [OMIM][ALA]; dark red, [HMIM][ALA]; pink, [PMIM][ALA]; green, [BMIM][ALA]; dark green, [PrMIM][ALA]; and blue, [EMIM][ALA]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

approaches the boiling point. This makes it difficult to be experimentally determined and though it is achievable through empirical correlations. The experimental data for surface tension as a function of temperature can be used to predict the critical temperature for AAILs using the Guggenheim and Eötvös empirical equations (Eqs. (4) and (5)). Besides, critical temperature was estimated by considering that the liquid-vapor interface disappears at T_c by linear decrease of surface tension in spite of its fluctuations near the critical point; the results are reported in Table 4.

As one can see, the critical temperature estimated by considering $\gamma = 0$ at T_c is lower than those estimated directly by Eq. (4) and Eq. (5) because of considering linear change of surface tension near the critical temperature. Moreover, T_c of all the AAILs decreases by increasing alkyl chain length. Correspondingly, the prediction of T_c is useful to estimate the boiling point temperature (T_b) where T_b is approximately $0.6T_c$. In other words, the first estimation not only takes into account the influence of the critical region on the surface tension but also the effect of

Table 4
Predicted critical temperature for studied imidazolium based AAILs.

AAILs	T_c /K	Guggenheim- T_c /K	Eötvös- T_c /K
[EMIM][ALA]	1046.907	1208.447	1303.898
[PrMIM][ALA]	1010.249	1163.688	1244.353
[BMIM][ALA]	979.739	1126.352	1192.770
[PMIM][ALA]	940.288	1078.193	1130.626
[HMIM][ALA]	903.901	1033.717	1071.433
[OMIM][ALA]	802.443	908.876	857.514
[EMIM][GLY]	2123.830	2525.501	4872.136
[PrMIM][GLY]	1057.483	1224.663	1308.894
[BMIM][GLY]	992.829	1145.694	2071.118
[PMIM][GLY]	959.743	1102.211	1147.578
[HMIM][GLY]	912.685	1044.680	1076.906
[OMIM][GLY]	560.399	612.892	585.358
[PrMIM][GLU]	498.782	538.909	508.737
[BMIM][GLU]	–	–	–
[PMIM][GLU]	450.597	478.240	455.432
[HMIM][GLU]	439.716	464.926	443.716
[EMIM][SER]	–	–	–
[PrMIM][SER]	1260.387	1469.743	1740.464
[BMIM][SER]	1257.823	1466.635	1758.632
[OMIM][SER]	725.937	815.149	805.154
[EMIM][VAL]	896.334	1024.727	1055.557
[PrMIM][VAL]	801.357	909.198	902.346

pressure on the surface tension is ignored here. Interestingly, T_c increases as density of interaction energy becomes strong. From the other side of view, there is a direct relation between ion pair interaction and critical temperature; whenever, the interaction is strong the critical temperature is high.

Using the temperature dependence of the surface tension experimental data, the values of surface excess enthalpy of AAILs at a certain temperature range were also calculated. It was found that the surface excess enthalpy of all the AAILs is almost constant though the temperature increases while it lessens by alkyl chain length in the case of $[C_nMIM][ALA]$, $[C_nMIM][GLU]$, and $[C_nMIM][SER]$ without any order in the case of $[C_nMIM][GLY]$.

It has been proposed that since both viscosity and surface tension of fluids depend on temperature, intermolecular interaction, and the structure of liquids, these two properties are related by Eq. (9). This dependency was explored for AAILs for the first time and it was shown in Fig. 4.

As the figure illustrates, the variation of surface tension against fluidity depends on the ionic liquid anion and cation. The anion size as well as the alkyl chain length play key role on the values of intercept and slope, given in Table S1 of the Supplementary Data. In addition, there is a substantial relation between the order of Eq. (9) variation and T_c by increasing the chain length; Eq. (9) shows that both surface tension and fluidity variate that their change is in light with the T_c and anion charge density. On the other hand, the values of D in the AAILs with the same alkyl chain length change corresponding to the interaction energy and T_c .

There is a possibility of interaction between oxygen atoms of AA anions with several special sites over the ring of cation imidazolium of the AAILs. In the previously conducted studies [27,47], researchers have also found that the orientations of anions are mostly towards the three hydrogens of the imidazolium ring. Orientation towards H5 (hydrogen atom bonded to carbon of imidazolium ring which is between two nitrogen atoms of the ring, known as C2) positioned on C2 causes stronger interaction between the anion and cation. In order to investigate the structural properties of AAILs under study, possible conformers were optimized and the most stable one was accepted. In the present article, all the structures were optimized at B3LYP/6-311++G** level of theory in such a way that all the structural parameters of cations and anions as well as their relative position with respect to each other were free to be optimized. Therefore, the interaction among oxygen atoms of AA anions with H5 is investigated and the influence of alkyl side chain of the imidazolium ring and AA size on the nature of interaction are evaluated.

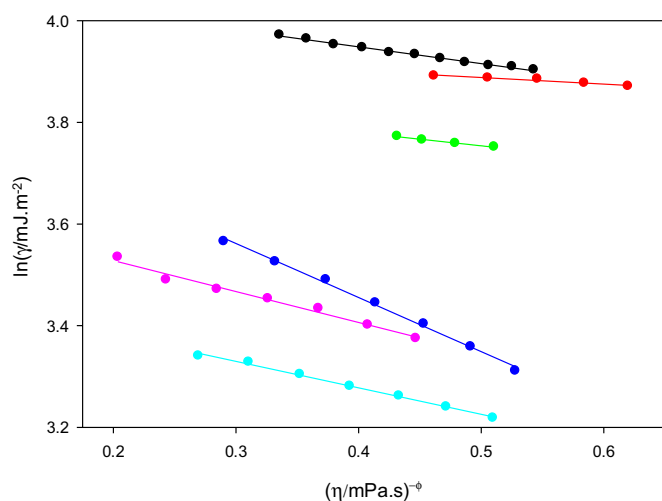


Fig. 4. Plots of Eq. (9) for imidazolium based AAILs. Black, [EMIM][ALA]; cyan, [OMIM][ALA]; red, [EMIM][GLY]; green, [BMIM][GLY]; blue, [OMIM][GLY]; and pink, [OMIM][SER]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The electronic properties involving electron affinity, EA, ionization energy, IE, ion pair molar volume, $V_{m,IP}$, molar polarization, R_m , dipole moment, μ , and ion pair interaction energies, E_{int} , were computed. The values of molecular properties vary based on cation size and anion type. Among molecular properties investigated in the present work, excluding polarization, other molecular properties of AAILs, does not follow a specific-uniformity ascending/descending trend with alkyl chain length. The results are presented in Table S2 of the Supplementary Data. For instance, the values of polarization of all AAILs studied in present work increase with increasing in alkyl chain length whereas the values of E_{int} does not follow a specific trend for all of the AAILs with alkyl chain length; E_{int} of AAILs including $[VAL]^-$, $[SER]^-$, and $[GLU]^-$ anions lessened by alkyl chain length. One can relate the variation of E_{int} value with anion size and steric effects. If the anion is more complex and bigger in size, the interaction energy is lower. See Fig. 5 for variation of E_{int} with anion type and alkyl chain length.

As one can find from Fig. 5, the interaction energy reduces with alkyl chain length of cation and is the weakest in the case of AAILs with $[GLU]^-$ anion. However, the highest values of dipole moment, polarization, ionization energy, and electron affinity are related to the AAILs consisting $[GLU]^-$ anion in spite of the lowest interaction between cation and anion pairs. For the lowest charge separation density in the case of $[C_nMIM][GLU]$ AAILs, it is expected that the ion pair interaction is the weakest. This trend of interaction energy variation with anion and alkyl chain length is in accordance with Wu and Zhang [48]. Their study at B3LYP/6-311+G(d,p) level of theory shows that, for 1-ethyl-3-methylimidazolium ($[EMIM]^+$) cation, the interaction energy of cation with $[GLY]^-$ is the strongest while E_{int} between $[EMIM]^+$ and $[GLU]^-$ is the weakest. Noticeably, the results confirm each other.

The variation of E_{int} in this series of AAILs studied can be explained by anionic charge and size. As a consequent, charge density of anion (ρ_{CA}) and interaction energy density ($\rho_{E_{int}}$) were computed and it was observed a direct relation with variation of ρ_{CA} with $\rho_{E_{int}}$. See Fig. 6 for more details.

As the figure demonstrates, the more charge density of anion, the stronger interaction between AAIL ion-pair. The interesting point is that the order of interaction energy between ion pair is in line with anion-cation intermolecular interaction energy resulted from simulation in the bulk [25].

It would be also nice to consider the relation of stability and interaction energy between the ion pairs. As it is expected, the density of electronic chemical potential and density of interaction for all the studied AAILs change in a linear fashion. Fig. 7 shows the linear dependency of ρ_{μ} against $\rho_{E_{int}}$.

The figure also describes these changes reasonably faithfully, yielding a more structural stability in the sense of stronger cation-anion interaction. The AAIL $[EMIM][GLY]$ with the highest value of anion cation interaction enjoys the most stability; however, $[HMIM][GLU]$

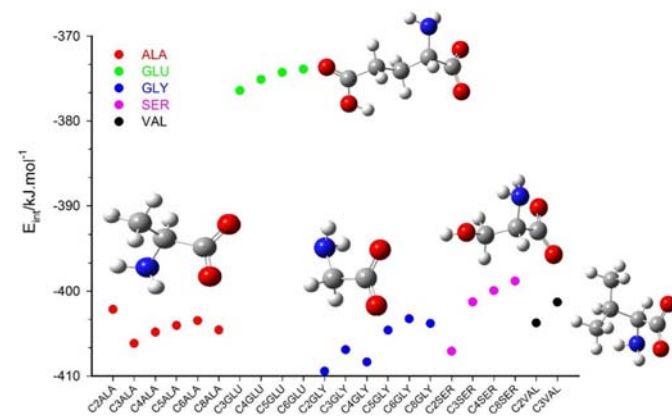


Fig. 5. The change of ion pair interaction with anion type.

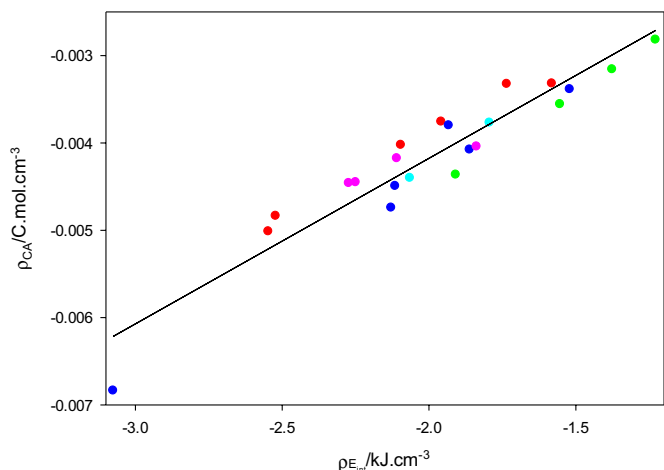


Fig. 6. The variation of ρ_{CA} versus $\rho_{E_{int}}$ for the aimed AAILs. The red stands for $[C_nMIM][ALA]$, green for $[C_nMIM][GLU]$, blue for $[C_nMIM][GLY]$, pink for $[C_nMIM][SER]$, and cyan for $[C_nMIM][VAL]$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

with the weakest ion pair interaction observes the lowest value of electronic chemical potential.

As stability of ILs can be studied using DFT method, the electron affinities and ionization energies are calculated from the electronic energy differences of reduced and oxidized species. The EA and IE values estimated for 22 ion pairs are presented in Fig. 8.

Based on the figure, it can be understood that stability decreases when moving right and upwards on the plot. The DFT method gives the most instability for AAILs including $[GLU]^-$ in according to the previous observations.

The last aim of the present study is to explore if there is any relation between the thermophysical and molecular properties of the imidazolium based AAILs including $[ALA]^-$, $[GLY]^-$, $[GLU]^-$, $[SER]^-$, and $[VAL]^-$ anions. The values of E_{int} AAILs decrease with alkyl chain length from ethyl to hexyl as density and surface tension values decrease in spite of increasing from hexyl to octyl though density and surface tension decrease.

Considering critical temperature, it can be undertaken that its variation is in line with ρ_{CA} and $\rho_{E_{int}}$. In other words, as it has been mentioned

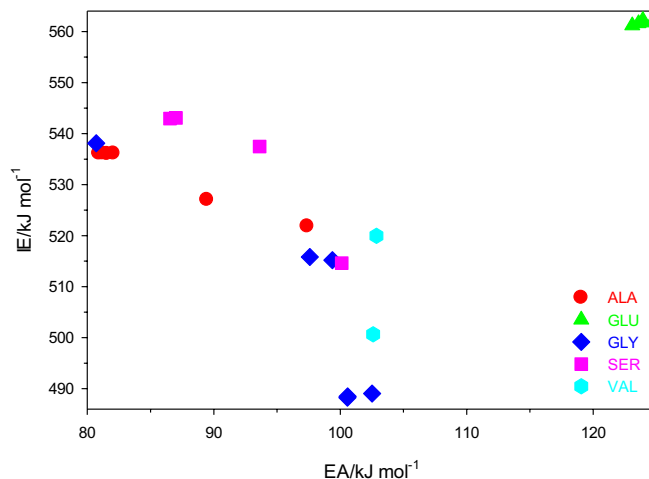


Fig. 8. The variation of IE versus EA. The red stands for $[C_nMIM][ALA]$, green for $[C_nMIM][GLU]$, blue for $[C_nMIM][GLY]$, pink for $[C_nMIM][SER]$, and cyan for $[C_nMIM][VAL]$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

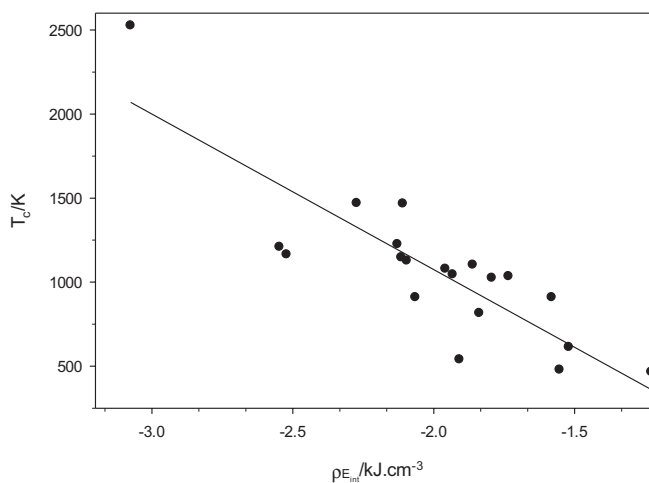


Fig. 9. The variation of T_c against $\rho_{E_{int}}$.

in the literature, the values of T_c are in direct correlation with electronic properties, Fig. 9.

4. Conclusions

The thermophysical properties of imidazolium based AAILs as a function of alkyl chain length of cation, anion type, and temperature were studied. There is a relatively well relation between thermophysical properties of viscosity, density, expansion coefficient, and surface tension with temperature; as a result, it may be possible to predict the critical temperature. In addition, the structure and geometry of anion and cation has an effect on the properties. The critical temperature of all the AAILs decreases with increasing alkyl chain length. The E_{int} values of AAILs including $[ALA]^-$, $[GLY]^-$, $[GLU]^-$, and $[SER]^-$ anions do not follow a uniformity ascending/descending trend with anion/cation while the density of interaction energy shows a linear relationship with the anion charge density and critical temperature. The ionic liquid molecular volume of all the AAILs increases with increasing the alkyl chain length and temperature. The coefficient expansion increases with temperature growth whereas the surface excess enthalpy of these AAILs is almost constant with increasing temperature and cation length. The present study demonstrates that the properties of AAILs change with the anion type and more experimental data are needed

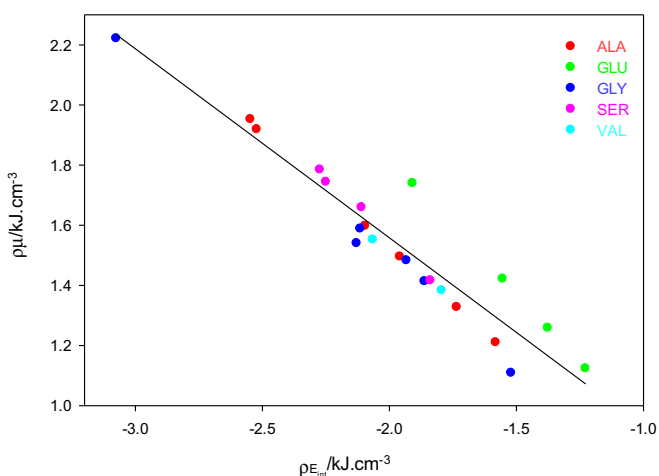


Fig. 7. The variation of ρ_{μ} versus $\rho_{E_{int}}$. The red stands for $[C_nMIM][ALA]$, green for $[C_nMIM][GLU]$, blue for $[C_nMIM][GLY]$, pink for $[C_nMIM][SER]$, and cyan for $[C_nMIM][VAL]$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to investigate the accurate relation between viscosity and surface tension. However, direct relationship between fluidity and surface tension with an exponent of 0.20 makes it possible to predict the transport properties by measuring the surface properties. Finally, the present study shows that the physical properties of the studied AAILs depend mainly on the nature of the anions, whereas the alkyl chain length has less effect.

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List of symbols

k	A constant in Eötvös empirical relation
D	A substance dependent constant
$\ln C$	A substance dependent constant
a	A substance-dependent constant in Guggenheim relation
E_{η}	Activation energy for viscous flow
N_A	Avogadro's number
ρ_{CA}	Charge density of anion
ρ	Density
μ	Dipole moment
EA	Electron affinity
E_{int}	Interaction energy between the cation and anion
$\rho_{E_{int}}$	Interaction energy density
E_{int}	Ion pair interaction energy
$V_{m,IP}$	Ion pair molar volume
IE	Ionization energy
R_m	Molar polarization
M	Molecular mass
V_m	Molecular volume
H^S	Surface excess enthalpy
S^S	Surface excess entropy
γ	Surface tension
T	Temperature
ρ_0	The density at 0 °C
R^2	The squared value of R
α_0	Thermal expansion coefficient at 0 °C
α_p	Thermal expansion coefficient
ϕ	Universal exponent
η_{∞}	Viscosity at infinite temperature
V	Volume

List of abbreviations

[BMIM] ⁺	1-butyl-3-methylimidazolium
[EMIM] ⁺	1-ethyl-3-methylimidazolium
[HMIM] ⁺	1-hexyl-3-methylimidazolium
[OMIM] ⁺	1-octyl-3-methylimidazolium
[PMIM] ⁺	1-pentyl-3-methylimidazolium
[PrMIM] ⁺	1-propyl-3-methylimidazolium
[ALA] ⁻	Alaninate
AA	Amino acid
CHELPG	Charges from electrostatic potentials
DFT	Density functional theory
DMF	Dimethylformamide
ESP	Electrostatic potentials
[GLU] ⁻	Glutamate
[GLY] ⁻	Glycinate
HB	Hydrogen bonding
IL	Ionic liquid
NMP	N-Methyl-2-pyrrolidone
[PRO] ⁻	Prolinate

[SER] ⁻	Serinate
THF	Tetrahydrofuran
[VAL] ⁻	Valinate

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2017.11.122>.

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