Heliyon 5 (2019) e01548

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.heliyon.com

Molecular interaction studies of binary systems comprising [C_2mim] [BF_4] with ethyl acetoacetate or benzaldehyde

Bakusele Kabane, Rajasekhar Chokkareddy, Gan G. Redhi *

Physical Chemistry Laboratories, Department of Chemistry, Durban University of Technology, Durban, 4000, South Africa

ARTICLE INFO

Keywords:
Physical chemistry

ABSTRACT

In this work, new data for the binary mixtures containing 1-ethyl-3-methylimidazolium tetrafluoroborate ([C_2mim] [BF_4]) ionic liquid (IL) with benzaldehyde or ethyl acetoacetate were investigated under atmospheric pressure (p = 0.1 MPa) and at temperatures (293.15–313.15) K. The binary mixtures were completely miscible at all proportions. Densities (ρ), viscosities (η) as well as speeds of sound (u) were conducted across the entire range of mole fraction ($x_i = 0$ to 1). The excess properties which include excess molar volumes (V_m^E), intermolecular free length (L_f), deviations in viscosity ($\Delta\eta$), isentropic compressibility(k_s), apparent molar isentropic compressibility (K_ϕ) as well as deviation in isentropic compressibility (Δk_s) were determined from the experimentally found results of speed of sound, viscosity and density. The obtained derived properties have been elucidated in terms of solute-solvent interactions taking place in the systems. The investigation of thermophysical properties of organic solvents with ionic liquids is essential as they decide the transformation of ionic liquids from small laboratory scale to large industrial applications. The obtained results are important and essential as they describe the molecular interactions, and can be used in constructing the structure-property correlation as well as molecular modelling that exist between [C_2mim] [BF_4] with benzaldehyde or ethyl acetoacetate. Redlich-Kister polynomial equation was used to fit the excess values and a good correlation was achieved.

1. Introduction

During recent years, ionic liquids (ILs) which are known to be the topic of interest in the science research community, focussing on acute examination as a new solution of designer solvents. Large organic cations are used to compose these types of solvents; they contain a diverse functionalized groups or alkyl substituents and organic or inorganic anions. One of the main reasons in support of the low melting temperatures of the ionic liquid are the asymmetric and large features [1,2]. Attributable to their ionic nature, nearly all of the ILs are known to present useful properties, which include non-flammability [3], insignificant vapour pressure [4], increased conductivity [5], and also their considerable ability to dissolve inorganic and organic material. These are liquids with feasible applications in several fields which include electrochemistry (solar panels, fuel cells, and batteries), chemistry (synthesis, catalysis, and polymerization), and biotechnology (bio--catalysis, protein purification) as well pharmaceutical industries. As a result, a clear understanding of their properties and behaviour with organic solvents is essential for a proper development of these applications [6,7].

According to the properties possessed by the ionic liquids, these liquids are environmentally friendly, but they can be pollutants as well if procedures used in handling these liquids are incorrect, because inappropriate handling may result in high possible soil and water contamination as a consequence of unexpected spills or incompetent waste water management [8]. If the ionic liquids contain any amount of water, this can extremely influence the ionic liquids phase equilibrium and thermodynamic properties [9,10]. As a result, in previous years, a notable number of studies have been focussing on examining thermodynamic and physical properties, which includes density and viscosity for the water saturated ionic liquids [11,12,13,14,15,16]. Imidazolium cations are the most measured class of ionic liquid and these ionic liquids have been utilised in many areas including catalysis, electrochemistry, synthesis as well as industrial applications [17,18,19,20,21]. Imidazolium based ionic liquids are also useful in the procedure for the removal of carbon dioxide from natural gas [22] as well as in extractive desulfurization of liquid fuels, principally with consideration of those sulphur compounds that are extremely complex to remove by ordinary hydrodesulfurization

* Corresponding author.
E-mail address: redhigg@dut.ac.za (G.G. Redhi).

https://doi.org/10.1016/j.heliyon.2019.e01548
Received 21 November 2018; Received in revised form 26 March 2019; Accepted 17 April 2019

(HDS) processes [23]. Recently, osmium oxide has been recycled by the use of 1-ethy-3-methylimidazolium tetrafluoroborate [C_2mim] [BF_4] [24]. In the capillary electrophoretic technique, this viscous liquid electrolyte is mostly utilised, in grape seed extract it is used for settling phenolic compounds. Normally, the level of toxicity of the imidazolium based liquids depends on the lower order n-alkyl chain which have low to average degree of potential damage, and in particular [C_2mim] [BF_4] is likely to cause serious harm when swallowed [25]. Examination of the intermolecular interaction aggregate response between the organic solvents and the ionic liquids becomes notable, as that type of interaction may produce positive results on mechanism and thermodynamic equilibrium of the reaction, as well the reaction rate of the reaction. In the family of aromatic aldehydes, benzaldehyde is one of the most industrially functional members in the group. Large numbers of industries have been using benzaldehyde as a raw material in organic synthesis, which also include perfumery chemicals [26]. A notable large amount of benzaldehyde is used in the production of other aldehydes, which include cinnamic, methylcinnamic and hexylcinnamic. In the process of many organic compounds, ethyl acetoacetate is mostly used as an intermediate. It is also utilised in the manufacturing of synthetic drugs and dyes. According to the literature search, no work was done on the investigation of excess properties between 1-ethyl-3-methylimidazolim tetrafluoroborate with benzaldehyde or ethyl acetoacetate mixtures. The systems comprising 1-ethyl-3-methylimidazolim tetrafluoroborate with benzaldehyde or ethyl acetoacetate are also useful for the design of many industrial and technological processes.

2. Experimental

2.1. Chemicals

The investigated ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) (Fig. 1) were supplied by Sigma Aldrich (South Africa), ethyl acetoacetate was supplied by Acros Organics New Jersey (USA) and benzaldehyde was supplied by Merck (South Africa) with stated purity of ≥99.5% (GC) for both chemicals and were used as received. The content of water of the ionic liquid used was removed by the use of vacuum treatment at 340 K under reduced pressure of 5×10^{-2} Pa. The content of water was examined by the use of Karl-Fischer auto titrator before commencement of the experimental work. The ionic liquid mass percent water content was found to be 340×10^{-6} % and the purity was ≥98% (determined by HPLC).

2.2. Method and apparatus

The binary mixtures were prepared in air tight stoppered glass vials by syringing exact amounts of pure compounds ([C_2mim] [BF_4] and ethyl acetoacetate or benzaldehyde). The weighed mass of each component was determined by the use of an OHAUS analytical mass balance with a precision of ±0.0001 g. Every safeguard was taken to minimise any type of contamination. A digital vibrating tube density meter and sound velocity analyser with automatic micro-viscometer (Anton Paar DSA 5000 M) with accuracy of $\pm 5 \times 10^{-6}$ g cm^3 in density, ± 0.5 m s^{-1} in sound velocity, ± 1 mPa s in viscosity and ±0.01 K in temperature was used to conduct the speed of sound, viscosity and density measurements for the prepared binary mixtures and pure compounds. The densimeter was calibrated as instructed by the supplier using standard solutions given by the supplier. For the density measurements, the principle employed by the instrument is a well-known oscillating U-tube, the DSA 5000 M is able to measure simultaneously the sound velocity between (1000–2000) m · s^{-1} and density over the range of (0–3 x10^3) kg · m^{-3} at temperatures between (273. 15 to 343.15) K, with a pressure difference ranging from (0–0.3) MPa and at low frequency of about 3 MHz. The approximate density and sound velocity uncertainty measurements were below $\pm 2 \times 10^{-5}$ g cm^{-3} for the density and ±0.8 m s^{-1} for sound velocity, and the temperature was maintained to ±0.02 K. For the derived properties (k_s, Δk_s and V_m^E), the estimated uncertainty was approximately $\pm 2 \times 10^{-8}$ Pa^{-1}, $\pm 0.7 \times 10^{-8}$ Pa^{-1} and ±0.006 cm^3 mol^{-1} correspondingly (see Tables 1 and 2).

3. Results and discussion

3.1. Measured properties

3.1.1. Density

The experimental density (ρ) for ([C_2mim] [BF_4] with benzaldehyde or ethyl acetoacetate) binary mixtures was conducted at (293.15–313.15) K, as a function of mole fraction (x) [C_2mim] [BF_4]. Fig. 2 shows the dependence of density with temperature for the pure ionic liquid. The results are displayed in Tables 3 and 4 as well as in Figs. 3 and 4 for the prepared miscible binary mixtures of [C_2mim] [BF_4] with benzaldehyde or ethyl acetoacetate. Looking at Figs. 3 and 4 of the binary mixtures, the density is directly proportional to the ionic liquid concentration, and it also decreases as the temperature increase at all intervals. Both Figs. 3 and 4 show a simple linear correlation with the mole fraction of ionic liquid.

Table 1
[C_2mim] [BF_4] ionic liquid, benzaldehyde and ethyl acetoacetate specifications.

Chemical Name	Supplier	Method used for purification	Initial Purity %	Analysis method
[C_2mim] [BF_4]	Sigma Aldrich	Vacuum drying and kept away from offensive wavelength	≥98	HPLC
Ethyl	Acros Organics	Used as received	≥99.5	GC
Acetoacetate Benzaldehyde	Merck	Used as received	≥99.5	GC

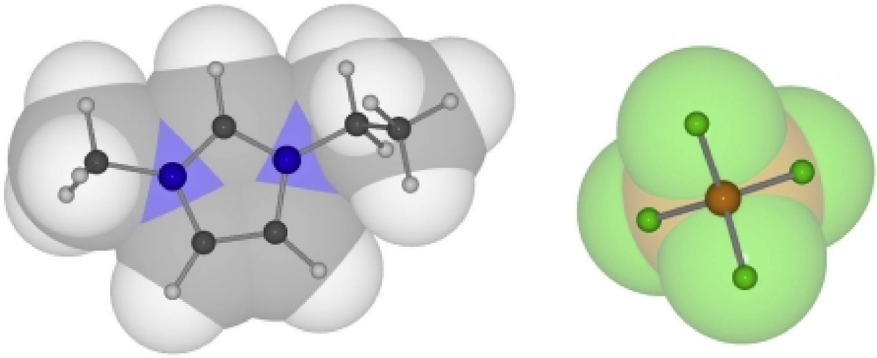

Fig. 1. Structure of the ionic liquid (1-ethyl-3-methylimidazolium tetrafluoroborate) used in this study.

Table 2
Densities, speed of sound and viscosity comparison between experimental and literature values of [C_2mim] [BF_4], benzaldehyde and ethyl acetoacetate.

Component	T/K	ρ/(g·cm^{-3})		u/(m· s^{-1})		η(mPa · s)	
		Exp.	Lit.	Exp.	Lit.	Exp.	Lit.
[C_2mim][BF_4]	293.15	1.2844	1.2830[a]	1634.1	1631.1[a]	49.32	45.29[c]
	298.15	1.2806	1.2887[b]	1628.6	1629.6[b]	41.01	37.19[c]
	303.15	1.2768	1.2761[a]	1610.3	1609.5[a]	34.71	31.36[c]
	308.15	1.2730	1.2824[b]	1605.2	1606.0[b]	28.80	25.56[c]
	313.15	1.2693	1.2685[a]	1587.1	1586.2[a]	22.63	21.54[c]
Ethyl acetoacetate	293.15	1.0283	1.029[d]	1350.9	1351.9[d]	1.82	
	298.15	1.0231	1.023[e]	1332.1	1332.9[f]	1.65	1.48[e]
	303.15	1.0179	1.015[e]	1313.1	1313.5[d]	1.51	1.34[e]
	308.15	1.0127	1.013[f]	1294.1	1294.6[d]	1.39	1.24[e]
	313.15	1.0074	1.008[g]	1275.3	1276.1[d]	1.29	
Benzaldehyde	293.15	1.0450	1.0455[h]	1477.2	1476.7[h]	1.57	1.56[i]
	298.15	1.0405	1.0410[h]	1458.9	1458.2[h]	1.45	1.43[i]
	303.15	1.0360	1.0365[h]	1440.6	1439.7[h]	1.34	1.32[i]
	308.15	1.0315	1.0320[h]	1422.3	1421.2[h]	1.25	1.22[i]
	313.15	1.0270	1.0272[h]	1404.0	1402.9[h]	1.16	1.13[i]

The standard uncertainties u are u (T) = ± 0.02 K, u (p) = ± 0.04 MPa, u (ρ) = ± 2 × 10^{-5}g.cm^{-3}, u (u) = ± 0.8 m s^{-1}, u (η) = 2 %.
[a] (Rao et al., 2017).
[b] (Vercher et al., 2015).
[c] (Zhang et al., 2004).
[d] (Amalendu et al., 2013).
[e] (Nayak et al., 2003).
[f] (Bermúdez-Salguero et al., 2011).
[g] (Gao et al., 2008).
[h] (Malek et al., 2012).
[i] (Ranjbar et al., 2009).

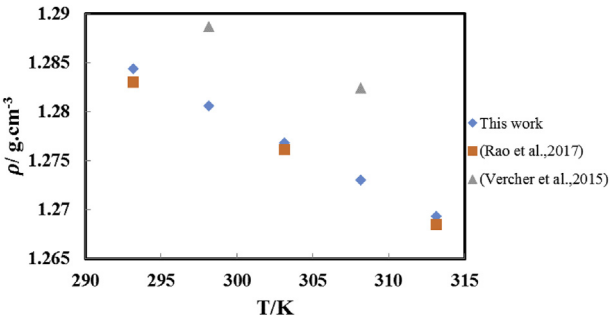

Fig. 2. Density (ρ) graph of the pure ionic liquid [C_2mim][BF_4] at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K compared to the literature values.

3.1.2. Speed of sound

This is a necessary and essential parameter that gives a clear sign about the density as well as viscosity, eg (the lower the speed of sound, the denser the medium). As much as it is not easy to give a clear detailed type of interaction occurring between the liquid mixtures, this parameter is functional, because it also describes the interactions occurring in the mixture which includes solvent-solvent, solvent-solute and solute-solute interactions between the liquid mixtures [27,28]. Speed of sound was measured simultaneously with the density at all investigated temperatures and mole fraction measurements, and the results are given in Tables 3 and 4 for the measured binary systems. Fig. 5 shows the dependence of speed of sound with temperature, and it is also evident that speed of sound is inversely proportional to the temperature. From Figs. 6 and 7, it is easily observed that the sound velocity increase as the concentration of [C_2mim] [BF_4] increases, and then decrease as the temperature increases.

3.1.3. Viscosity

Viscosity is one of the most commonly studied parameters which yield thermodynamic insight regarding to the activation energy for viscous flow. This is one of the highly sensitive parameters relating to the presence of impurities. Safety precautions were taken to consideration as to eliminate and avoid the adsorption of moisture during the experimental handling which may have a huge impact on the results. The viscosity results for the measurements of pure elements and both of the binary mixtures are specified in Table 5. The estimated uncertainty of measured viscosity values was estimated to be 2 %.

3.2. Calculated properties

3.2.1. Excess molar volumes

Eq. (1) below was used to determine excess molar volumes, which was computed from the experimentally determined densities of the binary mixtures and pure liquids at corresponding mole fractions and different temperatures (293.15–313.15) K respectively.

$$V_m^E = \sum_{i=1}^{2} x_i M_i \left(\rho^{-1} - \rho_i^{-1}\right) \quad (1)$$

From Eq. (1) above, x_i indicates the mole fraction, ρ and ρ_i represent the densities of the pure liquids and binary systems of ([C_2mim] [BF_4] + benzaldehyde or ethyl acetoacetate) respectively, M_1 and M_2 denotes the molar mass of the IL and molar mass of benzaldehyde or ethyl acetoacetate. The calculated results are summarised in Tables 3 and 4, and Figs. 8 and 9. Negative values were observed for the calculated excess molar volume across the entire mole fraction range and at all investigated temperatures for both of the studied mixtures. The negative data for the computed V_m^E increase as the temperatures increases. Such occurrence has been noticed for the binary systems containing ionic liquids [29]. By closely looking at the values given in Tables 3 and 4 of the binary mixtures, they clearly shows that [C_2mim] [BF_4] has a capacity to strongly interact with benzaldehyde or ethyl acetoacetate molecules, this effect might result from the dipolar interactions and hydrogen bonding [30,31,32]. The observed negative values simply indicate a well organised packing or attractive interactions occurred when the ionic liquid under investigation and benzaldehyde or ethyl acetoacetate molecules were assorted, resulting in volume contraction. The other factor that contributes towards negative values of V_m^E might rise from the unlike molecular interactions, which leads to the action of charge transfer and hydrogen bonding. Over the whole temperature range described in this present

Table 3

Densities (ρ), sound velocity (u), excess molar volume (V_m^E), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s), and intermolecular free length (L_f), of [C_2mim] [BF_4] + benzaldehyde binary systems at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and at p = 0.1 MPa.

x_1	ρ/g·cm^{-3}	u/m · s^{-1}	V_m^E/cm^3·mol^{-1}	$10^8 \cdot k_s$/Pa^{-1}	$10^8 \cdot \Delta k_s$/Pa^{-1}	L_f/(10^{-7} m)
293.15 K						
0	1.0450	1477.2	0	43.9	0	1.35
0.0182	1.0540	1485.5	-0.2323	43.0	-0.59	1.34
0.0416	1.0644	1493.6	-0.4516	42.1	-1.12	1.32
0.0803	1.0805	1505.0	-0.7295	40.9	-1.79	1.30
0.1062	1.0907	1511.9	-0.8893	40.1	-2.16	1.29
0.2053	1.1250	1535.4	-1.2567	37.7	-3.09	1.25
0.3051	1.1548	1555.7	-1.4321	35.8	-3.53	1.22
0.4059	1.1810	1573.6	-1.4648	34.2	-3.61	1.19
0.5056	1.2037	1589.2	-1.3885	32.9	-3.42	1.17
0.6051	1.2237	1602.6	-1.2250	31.8	-3.01	1.15
0.7056	1.2417	1614.5	-0.9925	30.9	-2.44	1.13
0.8054	1.2577	1624.7	-0.7025	30.1	-1.72	1.12
0.9060	1.2722	1633.5	-0.3638	29.5	-0.88	1.11
1	1.2844	1634.0	0	28.9	0	1.09
298.15 K						
0	1.0405	1458.9	0	45.2	0	1.38
0.0182	1.0495	1467.5	-0.2377	44.2	-0.62	1.37
0.0416	1.0600	1475.9	-0.4622	43.3	-1.19	1.35
0.0803	1.0761	1487.8	-0.7456	42.0	-1.91	1.33
0.1062	1.0863	1495.0	-0.9082	41.2	-2.30	1.32
0.2053	1.1208	1519.4	-1.2825	38.6	-3.28	1.28
0.3051	1.1507	1540.7	-1.4610	36.6	-3.75	1.24
0.4059	1.1769	1559.4	-1.4945	34.9	-3.83	1.22
0.5056	1.1997	1575.6	-1.4164	33.6	-3.63	1.19
0.6051	1.2197	1589.6	-1.2497	32.4	-3.20	1.17
0.7056	1.2378	1601.9	-1.0123	31.5	-2.58	1.15
0.8054	1.2538	1612.5	-0.7164	30.7	-1.82	1.14
0.9060	1.2684	1621.2	-0.3707	30.0	-0.92	1.13
1	1.2806	1628.6	0	29.4	0	1.12
303.15 K						
0	1.0360	1440.6	0	46.5	0	1.42
0.0182	1.0451	1449.5	-0.2439	45.5	-0.66	1.40
0.0416	1.0556	1458.2	-0.4731	44.6	-1.27	1.39
0.0803	1.0718	1470.4	-0.7622	43.2	-2.03	1.36
0.1062	1.0820	1477.9	-0.9279	42.3	-2.44	1.34
0.2053	1.1166	1503.2	-1.3093	39.6	-3.48	1.31
0.3051	1.1466	1525.4	-1.4911	37.5	-3.98	1.27
0.4059	1.1729	1544.9	-1.5244	35.7	-4.07	1.24
0.5056	1.1957	1561.9	-1.4442	34.3	-3.86	1.21
0.6051	1.2158	1576.4	-1.2746	33.1	-3.39	1.19
0.7056	1.2339	1589.3	-1.0328	32.1	-2.74	1.18
0.8054	1.2500	1600.3	-0.7307	31.2	-1.94	1.16
0.9060	1.2645	1609.3	-0.3782	30.5	-0.98	1.15
1	1.2768	1610.3	0	30.0	0	1.14
308.15 K						
0	1.0315	1422.3	0	47.9	0	1.45
0.0182	1.0406	1431.4	-0.2502	46.9	-0.71	1.43
0.0416	1.0512	1440.3	-0.4848	45.9	-1.35	1.42
0.0803	1.0675	1453.0	-0.7801	44.4	-2.25	1.39
0.1062	1.0777	1460.8	-0.9491	43.5	-2.59	1.38
0.2053	1.1124	1487.1	-1.3376	40.7	-3.69	1.34
0.3051	1.1425	1510.2	-1.5230	38.4	-4.23	1.29
0.4059	1.1689	1530.6	-1.5567	36.5	-4.33	1.27
0.5056	1.1917	1548.2	-1.4741	35.0	-4.10	1.24
0.6051	1.2119	1563.3	-1.3008	33.8	-3.61	1.22
0.7056	1.2300	1576.6	-1.0542	32.7	-2.91	1.20
0.8054	1.2461	1587.8	-0.7461	31.8	-2.05	1.19
0.9060	1.2607	1597.4	-0.3863	31.1	-1.04	1.18
1	1.2730	1605.2	0	30.5	0	1.16
313.15 K						
0	1.0270	1404.0	0	49.4	0	1.49
0.0182	1.0361	1413.4	-0.2567	48.3	-0.75	1.47
0.0416	1.0468	1422.6	-0.4968	47.2	-1.43	1.45
0.0803	1.0631	1435.7	-0.7984	45.6	-2.28	1.43
0.1062	1.0734	1443.7	-0.9705	44.7	-2.75	1.41
0.2053	1.1082	1471.0	-1.3670	41.7	-3.92	1.36
0.3051	1.1384	1495.1	-1.5560	39.3	-4.49	1.32
0.4059	1.1648	1516.3	-1.5901	37.3	-4.60	1.29
0.5056	1.1878	1534.7	-1.5056	35.7	-4.36	1.26
0.6051	1.2080	1550.3	-1.3273	34.4	-3.84	1.24
0.7056	1.2262	1563.9	-1.0749	33.3	-3.09	1.22
0.8054	1.2423	1575.6	-0.7613	32.4	-2.17	1.2

(*continued on next page*)

Table 3 (*continued*)

x_1	ρ/g·cm^{-3}	u/m · s^{-1}	V_m^E/cm^3·mol^{-1}	$10^8 \cdot k_s$/Pa^{-1}	$10^8 \cdot \Delta k_s$/Pa^{-1}	L_f/(10^{-7} m)
0.9060	1.2569	1585.6	-0.3939	31.6	-1.11	1.19
1	1.2692	1587.1	0	31.0	0	1.18

The standard uncertainties u are u (T) = ± 0.02 K, u (p) = ± 0.04 MPa, u (ρ) = ± 2 × 10^{-5}g.cm^{-3}, u (u) = ± 0.8 m s^{-1}, u (V_m^E) = ± 6.00 × 10^{-3} cm^3 mol^{-1}, u (Δk_s) = ± 0.7 × 10^{-8} Pa^{-1} and u (k_s) = ± 2 × 10^{-8} Pa^{-1}.

work, the change in $V_{m,\ min}^E$ ranges from (-1.4648 to -1.5901) cm^3· mol^{-1} and (-1.5955 to -1.8298) cm^3· mol^{-1} and occurs at $x_i = 0.4059$ and 0.4053 for benzaldehyde and ethyl acetoacetate respectively, which are not far off from the values reported by V. Srivivasa Rao et al. for binary mixtures of ([C$_2$mim] [BF$_4$] + aniline) [33].

3.2.2. Isentropic and deviation in isentropic compressibility

The word isentropic implies that as the sound waves passes into and out of a liquid, the temperature and pressure fluctuates inside of each microscopic volume but the entropy of the entire system remains unchanged. This statement holds true, especially when utilizing a low frequency generator (DSA 5000 M transducer that produces about 3 MHz frequencies) to measure speed of sound, velocity dispersion and absorption of waves occurs at high frequency more than 100 MHz, and is due to the connection of molecular processes with liquids [34]. $k_s$values were calculated with the use of the Newton Laplace Eq. (2).

$$k_s = \frac{1}{\rho u^2} \tag{2}$$

In Newton Laplace equation, ρ represents the densities and u denotes the speed of sound for the prepared binary systems. Δk_s values were derived with the use of Eq. (3) below.

$$\Delta k_s = k_s - \sum_i^2 \phi k_s, i \tag{3}$$

From the above equation, k_s and ϕ_i, are isentropic compressibilities and volume fractions of the pure liquids correspondingly. The computed values for k_s and Δk_s for the binary mixtures of ([C$_2$mim] [BF$_4$] + benzaldehyde or ethyl acetoacetate) at all investigated temperatures are presented in Tables 3 and 4. Based on the calculated results for k_s and Δk_s , it is clearly noticeable that the k_s values are inversely proportional to the mole fraction of the investigated IL at all temperatures; this effect arises from the increase in thermal agitation creating the soluble liquids more compressible [30,35]. Interactions that occurred in the binary mixtures contributed towards a decrease in free-space, and this effect contributes towards the negative Δk_s values [35]. The Δk_s negative values Figs. 10 and 11, shows that these miscible solutions are less compressible in comparison to the ideal mixtures. Due to the stronger interactions and closer approach of unlike molecules between benzaldehyde or ethyl acetoacetate and [C$_2$mim] [BF$_4$] binary mixtures, this leads in a decrease in compressibility of the mixtures, the observed effect is most likely. According to the volumetric studies, these observations are in good agreement. In addition, the Δk_s values across the mole fraction range of [C$_2$mim] [BF$_4$] are inversely proportional to the temperature. The$\Delta k_{s\ ,\ min}$ values obtained are -4.6 × 10^{-8} Pa^{-1} and -6.5 × 10^{-8} Pa^{-1} which occurs at $x_i = 0.4059$ and 0.4053, for ([C$_2$mim] [BF$_4$] + benzaldehyde or ethyl acetoacetate) respectively, at all temperatures.

3.2.3. Intermolecular free length

Intermolecular forces (IMFs) are the forces which mediate interaction among the molecules, including forces of repulsion or attraction which act between molecules as well as other types of neighbouring particles, to give an example of ions or atoms. Intermolecular free length (L_f), Eq. (4) is determined from Jacobson empirical relation and this helps to interpret the nature of intermolecular interaction [36].

$$L_f = k_j\,(k_s)^{1/2} \tag{4}$$

In the equation above, Jacobson's constant temperature dependent (93.875 + 0.375 T) · 10^{-8} is denoted by $k_j$and k_s denote the isentropic compressibilities. The intermolecular free length values for the calculated binary mixtures at different temperatures are given in Tables 3 and 4. Comparing the data of L_f for the pure [C$_2$mim] [BF$_4$] with those of benzaldehyde or ethyl acetoacetate, the values for the organic solvents are higher in comparison, but they are noticed to be inversely proportional to the concentration of [C$_2$mim] [BF$_4$] in the two mixtures. These conditions clearly specify the occurrence of the molecular interactions amongst the constituents of the investigated mixtures. Furthermore, the intermolecular free length is directly proportional to the temperature. The length between the surfaces of the two molecules which guide to a decrease in the sound velocity is caused by the progressive increase in the L_f. By closely inspecting Figs. 12 and 13 as well as Tables 3 and 4, it can be seen that the L_f and sound velocity are connected in an inverse manner. Intermolecular free length was utilized as to determine the properties that exist in the binary mixtures which consist of attractive and repulsive forces, and a simple linear correlation with the mole fraction of the ionic liquid was observed.

3.2.4. Apparent molar isentropic compressibility

Eq. (5) below was utilized to determine the apparent molar isentropic compressibility (K_ϕ) values.

$$K_\phi = \left[\frac{1000(\rho_0\ k_s - k_0\,\rho)}{m\,\rho\rho_0}\right] + \left[\frac{Mk}{\rho}\right] \tag{5}$$

where ρ_0 and ρ indicates densities of the pure solvent and binary mixtures correspondingly; molar mass of solute and molality of the solution are denoted by M and m, respectively, k_s and k_0 represents the isentropic compressibilities of the solution and solvent correspondingly. The data for $K_\phi$are also displayed in Table 6. It is observed that, if the solution is ideal, the K_ϕ of the solute is that of the pure component. The dissimilarities among these quantities contemplate the degree of molecular interactions such as solute-solvent and solute-solute interactions. Negative values in the system containing ethyl acetoacetate at low concentration of the ionic liquid were observed. This effect reflects that ethyl acetoacetate molecules are less compressible than in the high concentration of the ionic liquid. Hall et al and others [37,38], proposed the analysis of disagreement of lower values in regards of geometrical and structural compressibility. The geometrical compressibility is due to simultaneous compression of the molecules whereas structural compressibility is due from the breakdown of intermolecular bonds resulting in a decrease in the average intermolecular length. A slight change in K_ϕ of solute at all investigated temperatures against (m)$^{1/2}$ have been shown in Figs. 14 and 15.

3.2.5. Deviations in viscosity

Any deviation of physical properties of liquid mixtures, the dissimilarity among the viscosity of the ideal-mixture and viscosity of mixtures at the equivalent thermodynamic state (η^{id}) is explained as the deviation in viscosity ($\Delta\eta$). Eq. (6) below was used to determine the deviations in viscosity of liquid systems and results are displayed in Table 7.

$$\Delta\eta = \eta - \eta^{id} \tag{6}$$

Table 4

Densities (ρ), sound velocity (u), excess molar volume (V_m^E), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s), and intermolecular free length (L_f), of [C_2mim] [BF_4] + ethyl acetoacetate binary systems at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K and at p = 0.1 MPa.

x_1	ρ/g·cm^{-3}	u/m · s^{-1}	V_m^E/cm^3·mol^{-1}	$10^8 \cdot k_s$/Pa^{-1}	$10^8 \cdot \Delta k_s$/Pa^{-1}	L_f/(10^{-7} m)
293.15 K						
0	1.0283	1350.9	0	53.3	0	1.49
0.0167	1.0353	1360.1	-0.2245	52.2	-0.67	1.47
0.0455	1.0464	1373.1	-0.5028	50.7	-1.50	1.45
0.0885	1.0618	1390.2	-0.7814	48.7	-2.40	1.42
0.1056	1.0680	1396.8	-0.9108	48.0	-2.73	1.41
0.2055	1.1007	1432.9	-1.3241	44.2	-4.04	1.36
0.3057	1.1306	1467.3	-1.5349	41.1	-4.76	1.31
0.4053	1.1579	1499.5	-1.5955	38.4	-5.01	1.26
0.5053	1.1832	1529.7	-1.5319	36.1	-4.87	1.22
0.6054	1.2066	1557.3	-1.3649	34.2	-4.37	1.19
0.7055	1.2284	1581.9	-1.1112	32.5	-3.58	1.16
0.8058	1.2487	1604.1	-0.7843	31.1	-2.54	1.14
0.9053	1.2677	1623.6	-0.4137	29.9	-1.32	1.11
1	1.2844	1634.0	0	28.9	0	1.10
298.15 K						
0	1.0231	1332.1	0	55.1	0	1.53
0.0167	1.0302	1341.6	-0.2328	53.9	-0.72	1.51
0.0455	1.0414	1354.8	-0.5210	52.3	-1.61	1.49
0.0885	1.0569	1372.3	-0.8097	50.2	-2.57	1.46
0.1056	1.0631	1379.0	-0.9429	49.5	-2.92	1.45
0.2055	1.0960	1416.1	-1.3697	45.5	-4.31	1.39
0.3057	1.1260	1451.3	-1.5876	42.2	-5.08	1.34
0.4053	1.1535	1484.3	-1.6509	39.3	-5.34	1.29
0.5053	1.1790	1515.3	-1.5859	36.9	-5.19	1.25
0.6054	1.2025	1543.6	-1.4128	34.9	-4.66	1.21
0.7055	1.2244	1568.9	-1.1507	33.2	-3.81	1.18
0.8058	1.2448	1591.7	-0.8123	31.7	-2.71	1.16
0.9053	1.2638	1611.4	-0.4279	30.5	-1.39	1.13
1	1.2806	1628.6	0	29.4	0	1.12
303.15 K						
0	1.0179	1313.1	0	57.0	0	1.57
0.0167	1.0250	1322.8	-0.2419	55.8	-0.78	1.55
0.0455	1.0364	1336.3	-0.5403	54.0	-1.72	1.53
0.0885	1.0519	1354.2	-0.8398	51.8	-2.75	1.49
0.1056	1.0582	1361.1	-0.9764	51.0	-3.12	1.48
0.2055	1.0913	1398.9	-1.4180	46.8	-4.61	1.42
0.3057	1.1215	1435.1	-1.6431	43.3	-5.42	1.37
0.4053	1.1492	1468.9	-1.7081	40.3	-5.70	1.32
0.5053	1.1748	1500.8	-1.6399	37.8	-5.53	1.28
0.6054	1.1984	1529.8	-1.4605	35.7	-4.97	1.24
0.7055	1.2204	1555.8	-1.1901	33.9	-4.06	1.21
0.8058	1.2408	1579.1	-0.8409	32.3	-2.89	1.18
0.9053	1.2599	1599.4	-0.4429	31.0	-1.49	1.16
1	1.2768	1610.3	0	30.0	0	1.14
308.15 K						
0	1.0127	1294.1	0	59.0	0	1.61
0.0167	1.0199	1304.1	-0.2512	57.7	-0.83	1.59
0.0455	1.0313	1317.9	-0.5606	55.8	-1.84	1.56
0.0885	1.0470	1336.2	-0.8708	53.5	-2.94	1.53
0.1056	1.0533	1343.2	-1.0120	52.6	-3.34	1.52
0.2055	1.0866	1381.9	-1.4684	48.2	-4.92	1.45
0.3057	1.1171	1418.9	-1.7008	44.5	-5.79	1.40
0.4053	1.1448	1453.7	-1.7678	41.3	-6.09	1.35
0.5053	1.1706	1486.3	-1.6971	38.7	-5.90	1.30
0.6054	1.1943	1516.1	-1.5112	36.4	-5.30	1.26
0.7055	1.2164	1542.7	-1.2317	34.5	-4.33	1.23
0.8058	1.2369	1566.5	-0.8707	32.9	-3.07	1.20
0.9053	1.2561	1587.5	-0.4587	31.6	-1.59	1.18
1	1.2730	1605.2	0	30.5	0	1.16
313.15 K						
0	1.0074	1275.3	0	61.0	0	1.65
0.0167	1.0147	1285.5	-0.2611	59.6	-0.89	1.63
0.0455	1.0263	1299.6	-0.5816	57.7	-1.97	1.60
0.0885	1.0421	1318.2	-0.9035	55.2	-3.15	1.57
0.1056	1.0484	1325.4	-1.0485	54.3	-3.57	1.56
0.2055	1.0819	1365.1	-1.5202	49.6	-5.26	1.49
0.3057	1.1126	1402.9	-1.7607	45.7	-6.19	1.43
0.4053	1.1405	1438.5	-1.8298	42.4	-6.50	1.38
0.5053	1.1664	1472.0	-1.7565	39.6	-6.30	1.33
0.6054	1.1903	1502.6	-1.5640	37.2	-5.65	1.29
0.7055	1.2124	1529.8	-1.2740	35.2	-4.62	1.25
0.8058	1.2330	1554.1	-0.9007	33.6	-3.27	1.22

(*continued on next page*)

Table 4 (*continued*)

x_1	ρ/g·cm^{-3}	u/m · s^{-1}	V_m^E/cm^3·mol^{-1}	$10^8 \cdot k_s$/Pa^{-1}	$10^8 \cdot \Delta k_s$/Pa^{-1}	L_f/(10^{-7} m)
0.9053	1.2522	1575.6	-0.4745	32.2	-1.70	1.20
1	1.2692	1587.1	0	31.0	0	1.18

The standard uncertainties u are u (T) = ± 0.02 K, u (p) = ± 0.04 MPa, u (ρ) = ± 2 × 10^{-5}g.cm^{-3}, u (u) = ± 0.8 m s^{-1}, u (V_m^E) = ± 6.00 × 10^{-3} cm^3 mol^{-1}, u (Δk_s) = ± 0.7 × 10^{-8} Pa^{-1} and u (k_s) = ± 2 × 10^{-8} Pa^{-1}.

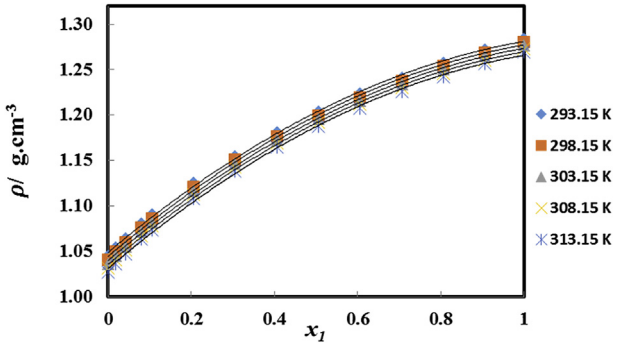

Fig. 3. Density of the binary mixtures of {[C_2mim][BF_4] (x_1) + benzaldehyde (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

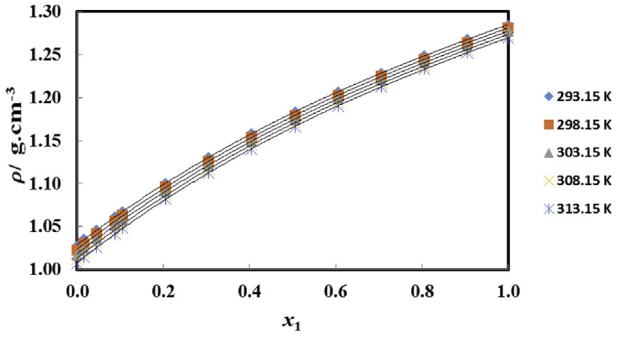

Fig. 4. Density of the binary mixtures of {[C_2mim][BF_4] (x_1) + ethyl acetoacetate (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

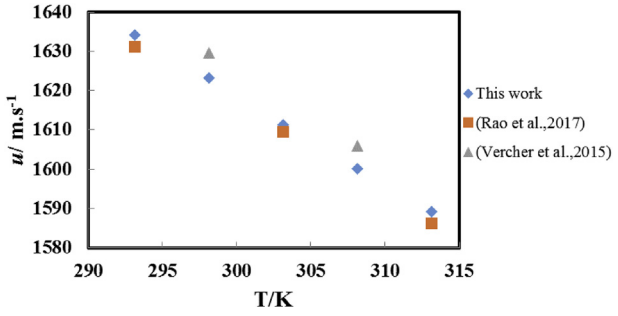

Fig. 5. Speed of sound (u) of IL against temperature ranges T = (293.15, 298.15, 303.15, 308.15 and 313.15) K compared to the literature values.

As much as there are many methods to determine η^{id}, the most commonly utilized procedure by the research groups is that determined on a mole fraction basis [39], Eq. (7).

$$\eta^{id} = x_1\eta_1^0 + x_2\eta_2^0 \quad (7)$$

In the equation above, η_1^0 represent viscosity of pure liquid *i*, at the mixture pressure and temperature. The deviation in viscosities values

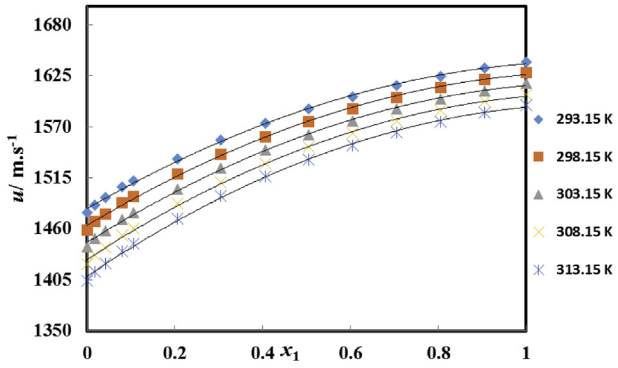

Fig. 6. Speed of sound (u) graph for the binary mixtures of {[C_2mim][BF_4] (x_1) + benzaldehyde (x_2) } at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

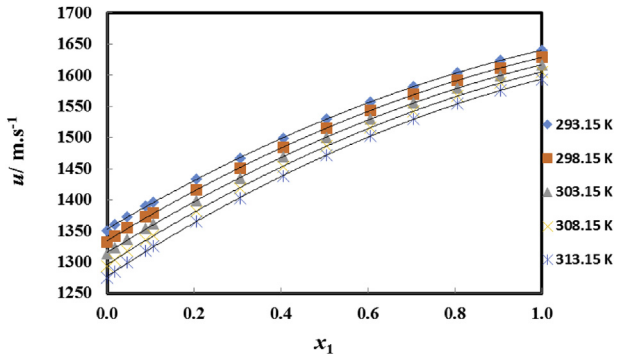

Fig. 7. Speed of sound (u) graph for the binary mixtures of {[C_2mim][BF_4] (x_1) + ethyl acetoacetate (x_2)} at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

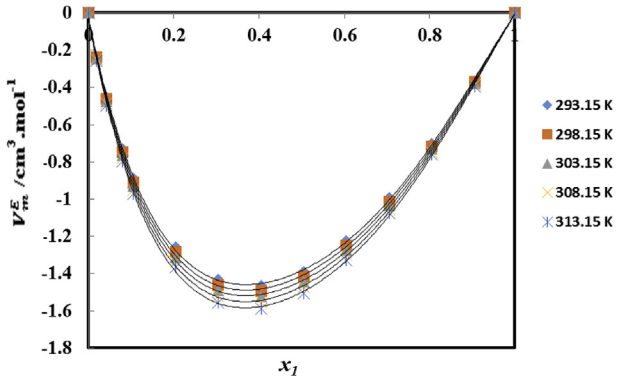

Fig. 8. Excess molar volume (V_m^E) of the miscible prepared mixtures of {[C_2mim][BF_4] (x_1) + benzaldehyde (x_2)} as a function of mole fraction of ionic liquid at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

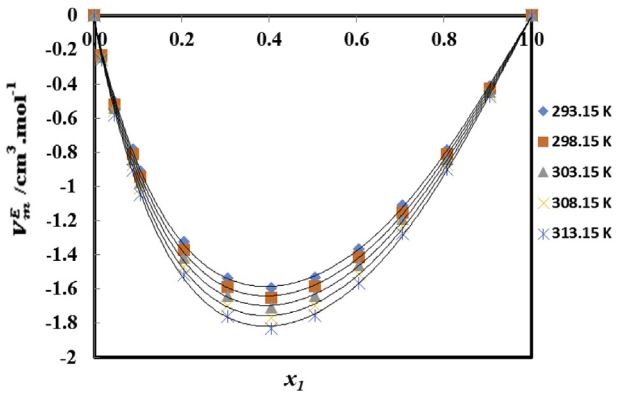

Fig. 9. Excess molar volume (V^E_m) of the miscible prepared mixtures of {[C_2mim][BF_4] (x_1) + ethyl acetoacetate (x_2)} as a function of mole fraction of ionic liquid, at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

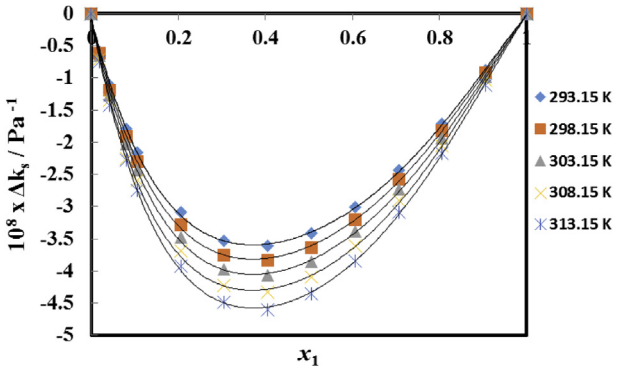

Fig. 10. Deviation in isentropic compressibility Δk_s, of the binary mixtures of {[C_2mim] [BF_4] (x_1) + benzaldehyde (x_2)} expressed in mole fraction of [C_2mim] [BF_4] at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

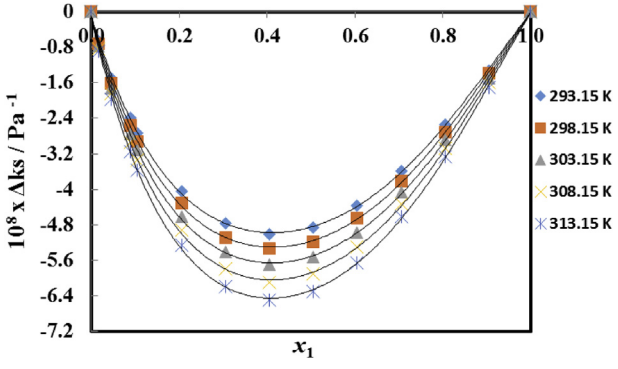

Fig. 11. Deviation in isentropic compressibility Δk_s, of the binary mixtures of {[C_2mim] [BF_4] (x_1) + ethyl acetoacetate (x_2)} expressed in mole fraction of [C_2mim] [BF_4] at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K. The plot was fitted by using the Redlich-Kister equation.

against mole fraction x_1 are plotted in Figs. 16 and 17 for both of the studied binary mixtures for all experimental temperatures. When benzaldehyde or ethyl acetoacetate is mixed with the investigated [C_2mim] [BF_4] ionic liquid, a sudden decrease in viscosities of the binary mixtures was observed, mainly at low temperatures. In the dilute solutions containing organic compounds in the IL, the decrease is specifically strong.

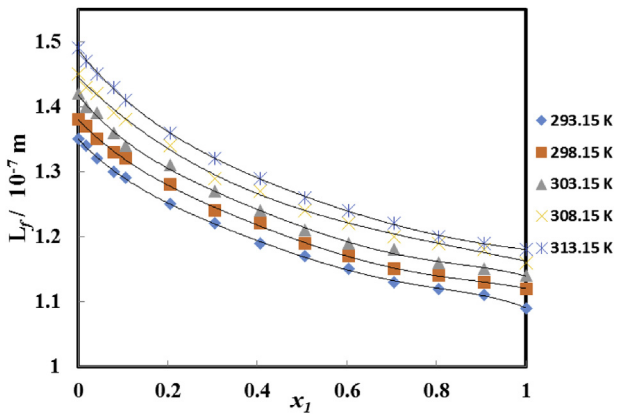

Fig. 12. Intermolecular free length L_f, of the binary mixtures of ([C_2mim][BF_4] + benzaldehyde) as a function of mole fraction of IL (x_1) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

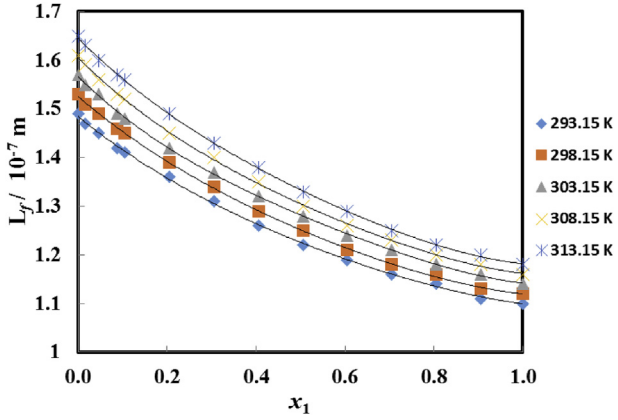

Fig. 13. Intermolecular free length L_f, of the binary mixtures of ([C_2mim][BF_4] + ethyl acetoacetate) given as a function of mole fraction of IL (x_1) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

Between [C_2mim] and tetrafluoroborate anions, the strong coulomb interactions is weakened when mixed with benzaldehyde or ethyl acetoacetate, which results in a greater mobility of the ions leading to a reduced viscosity of the binary mixtures. Negative deviation in viscosities is observed in all cases [39].

3.3. Correlation of the calculated properties

The values for the calculated thermophysical properties (intermolecular free length, deviation in isentropic compressibility, deviation in viscosity and excess molar volumes) for the binary mixtures of [C_2mim] [BF_4] with benzaldehyde or ethyl acetoacetate are presented in Tables 3, 4, and 7. Redlich-Kister polynomial Eq. (8) given below was used to fit these properties by the technique of non-linear least squares.

$$X = x_1 x_2 \sum_{i=1}^{k} A_i \, (1 - 2x_1)^{i-1} \tag{8}$$

From Eq. (8) above, x represents the excess molar volume or deviation in isentropic compressibility. The values of the fitting parameters A_i was determined by the least square method. Standard deviation and the results are given in Table 8. For the correlation, the given Eq. (9) below was utilized to calculate the standard deviation (σ).

Table 5
Viscosity η(mPa · s) for the binary mixtures of ([C_2mim] [BF_4] + ethyl acetoacetate or benzaldehyde) at T = (293.15–313.15) K and p = 0.1 MPa, as a function of mole fraction.

x_1	η(mPa · s)				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
[C_2mim] [BF_4] + Ethyl acetoacetate					
0	1.82	1.65	1.51	1.39	1.29
0.0167	1.99	1.81	1.65	1.51	1.39
0.0455	2.29	2.07	1.88	1.72	1.58
0.0885	2.77	2.49	2.25	2.05	1.88
0.1056	2.99	2.68	2.42	2.20	2.01
0.2055	4.43	3.93	3.52	3.18	2.88
0.3057	6.33	5.56	4.93	4.41	3.97
0.4053	8.78	7.66	6.73	5.97	5.33
0.5053	11.85	10.30	8.99	7.91	7.01
0.6054	15.75	13.63	11.80	10.31	9.08
0.7055	20.86	17.82	15.29	13.27	11.61
0.8058	26.98	23.01	19.53	16.86	14.64
0.9053	34.83	29.69	25.55	21.34	18.38
1	49.32	41.01	34.71	28.80	22.63
[C_2mim] [BF_4] + Benzaldehyde					
0	1.57	1.45	1.34	1.25	1.16
0.0182	1.77	1.62	1.49	1.38	1.29
0.0416	2.01	1.84	1.68	1.56	1.45
0.0803	2.47	2.24	2.05	1.88	1.73
0.1062	2.82	2.55	2.32	2.13	1.96
0.2053	4.49	3.99	3.58	3.24	2.95
0.3051	6.84	6.01	5.31	4.75	4.27
0.4059	10.01	8.70	7.61	6.72	5.98
0.5056	14.02	12.07	10.45	9.12	8.03
0.6051	19.00	16.17	13.84	11.98	10.47
0.7056	24.94	20.7	17.83	15.32	13.28
0.8054	30.99	25.68	22.18	18.92	16.33
0.9060	37.98	31.68	27.75	23.46	19.60
1	49.32	41.01	34.71	28.80	22.63

The standard uncertainties u are u (T) = ± 0.02 K, u (p) = ± 0.04 MPa and u (η) = 2.00 %.

Table 6
Apparent molar isentropic compressibility K_ϕ ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$) for the binary mixtures of ([C_2mim] [BF_4] + ethyl acetoacetate or benzaldehyde) at T = (293.15–313.15) K as a function of molality, m (mol Kg^{-1}).

m	K_ϕ ($m^3 \cdot mol^{-1} \cdot Pa^{-1}$)				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
[C_2mim] [BF_4] + Benzaldehyde					
0.1746	1.15	0.75	0.92	1.10	0.72
0.4088	1.82	1.75	1.92	1.86	1.56
0.8231	2.45	2.37	2.42	2.35	2.16
1.1201	2.59	2.58	2.57	2.57	2.48
2.4348	3.14	3.12	3.15	3.20	3.15
4.1370	3.48	3.48	3.53	3.55	3.56
6.4389	3.71	3.72	3.78	3.82	3.84
9.6378	3.89	3.94	3.99	4.04	4.08
14.4395	4.04	4.09	4.17	4.24	4.28
22.5817	4.17	4.24	4.31	4.38	4.45
39.0043	4.27	4.36	4.43	4.52	4.60
90.8327	4.38	4.46	4.55	4.64	4.72
[C_2mim] [BF_4] + Ethyl acetoacetate					
0.1306	-0.84	-1.40	-1.18	-1.71	-2.27
0.3661	0.35	0.01	-0.32	-0.64	-0.68
0.7459	1.08	0.88	0.69	0.51	0.33
0.9069	1.30	1.17	0.94	0.71	0.59
1.9873	2.07	2.01	1.89	1.78	1.68
3.3837	2.62	2.58	2.50	2.44	2.38
5.2367	3.00	2.97	2.95	2.90	2.89
7.8502	3.32	3.32	3.34	3.33	3.33
11.7897	3.62	3.64	3.67	3.68	3.70
18.4088	3.86	3.92	3.97	3.99	4.04
31.8798	4.09	4.15	4.21	4.27	4.35
73.4829	4.29	4.37	4.44	4.53	4.62

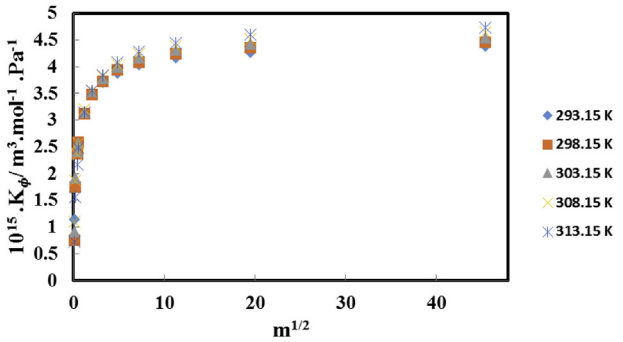

Fig. 14. Apparent molar isentropic compressibility K_ϕ, of binary mixtures ([C_2mim] [BF_4] + benzaldehyde) plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

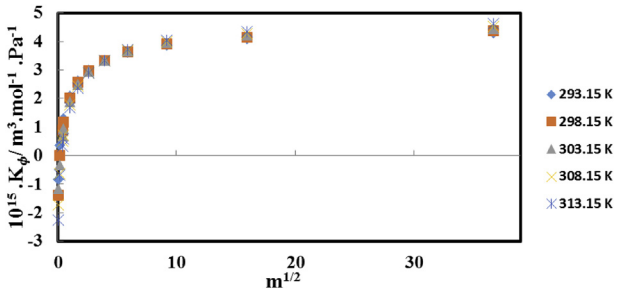

Fig. 15. Apparent molar isentropic compressibility K_ϕ, of binary mixtures ([C_2mim] [BF_4] + ethyl acetoacetate) plotted against $(m)^{1/2}$ at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

Table 7
Deviation in viscosity $\Delta\eta$ (mPa · s) for the binary mixtures of ([C_2mim] [BF_4] + ethyl acetoacetate or benzaldehyde) at T = (293.15–313.15) K and p = 0.1 MPa, as a function of mole fraction.

x_1	$\Delta\eta$ (mPa · s)				
	T = 293.15 K	T = 298.15 K	T = 303.15 K	T = 308.15 K	T = 313.15 K
[C_2mim] [BF_4] + Ethyl acetoacetate					
0	0	0	0	0	0
0.0167	-0.6175	-0.5028	-0.4238	-0.3414	-0.2515
0.0455	-1.6860	-1.3724	-1.1438	-0.9230	-0.6794
0.0885	-3.2528	-2.6474	-2.2011	-1.7693	-1.2992
0.1056	-3.8456	-3.1291	-2.5996	-2.0877	-1.5311
0.2055	-7.1485	-5.8074	-4.8138	-3.8497	-2.7931
0.3057	- 10.011	-8.1258	-6.7288	-5.3601	-3.8380
0.4053	-12.285	-9.9458	-8.2368	-6.5306	-4.6025
0.5053	-13.968	-11.236	-9.3038	-7.3375	-5.0589
0.6054	-14.822	-11.849	-9.8165	-7.6780	-5.1284
0.7055	-14.468	-11.597	-9.6423	-7.4633	-4.7367
0.8058	-13.113	-10.355	-8.7298	-6.6183	-3.8414
0.9053	-9.9928	-7.5938	-6.0174	-4.8705	-2.2278
1	0	0	0	0	0
[C_2mim] [BF_4] + Benzaldehyde					
0	0	0	0	0	0
0.0182	-0.6774	-0.5513	-0.4548	-0.3627	-0.2639
0.0416	-1.5504	-1.2577	-1.0417	-0.8314	-0.6062
0.0803	-2.9406	-2.3894	-1.9757	-1.5786	-1.1499
0.1062	-3.8241	-3.1034	-2.5648	-2.0472	-1.4857
0.2053	-6.8924	-5.5876	-4.6123	-3.6649	-2.6222
0.3051	-9.3047	-7.5060	-6.2057	-4.9029	-3.4365
0.4059	-10.9417	-8.8067	-7.2756	-5.7140	-3.8988
0.5056	-11.7001	-9.3809	-7.7649	-6.0536	-3.9797
0.6051	-11.4669	-9.2154	-7.6915	-5.9346	-3.6787
0.7056	-10.3215	-8.6617	-7.0557	-5.3687	-3.0283
0.8054	-9.0390	-7.6318	-6.0367	-4.5191	-2.1237
0.9060	-6.8518	-5.6113	-3.8233	-2.7498	-1.0121
1	0	0	0	0	0

The standard uncertainties u are u (T) = ± 0.02 K, u (p) = ± 0.04 MPa and u (η) = 2.00 %.

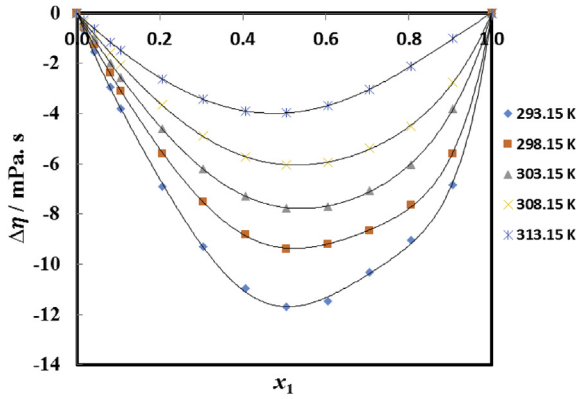

Fig. 16. Deviations in viscosity, $\Delta\eta$, of the binary mixtures of ([C_2mim][BF_4] + benzaldehyde) given as a function of mole fraction of IL (x_1) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

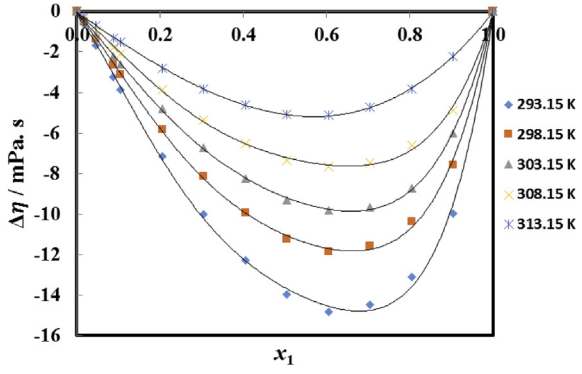

Fig. 17. Deviations in viscosity, $\Delta\eta$, of the binary mixtures of ([C_2mim][BF_4] + ethyl acetoacetate) given as a function of mole fraction of IL (x_1) at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

Table 8
Standard deviations σ, and coefficients A_i, achieved for the binary solution ([C_2mim] [BF_4] + Benzaldehyde or ethyl acetoacetate) at pressure p = 0.1 MPa and different temperatures for Redlich-Kister Eq. (8).

	T/K	A_0	A_1	A_2	A_3	σ
[Emim] [BF_4] + Benzaldehyde						
V^E_m/cm^3.mol	293.15	-5.524	-2.134	-1.985	-1.943	0.019
	298.15	-5.635	-2.174	-2.032	-2.007	0.020
	303.15	-5.747	-2.217	-2.090	-2.069	0.020
	308.15	-5.866	-2.265	-2.153	-2.13	0.021
	313.15	-5.988	-2.322	-2.208	-2.187	0.022
10^8. Δk_s/Pa^{-1}	293.15	-13.614	-5.287	-4.686	-4.775	0.052
	298.15	-14.454	-5.604	-4.909	-5.277	0.054
	303.15	-15.345	-5.952	-5.256	-5.556	0.060
	308.15	-16.297	-6.182	-5.724	-6.570	0.073
	313.15	-17.346	-6.720	-5.752	-6.273	0.075
L_f/(10^{-7} m)	293.15	3.952	-2.058	13.895	10.191	0.666
	298.15	4.025	-2.083	14.197	10.44	0.682
	303.15	4.1	-2.141	14.574	10.735	0.699
	308.15	4.189	-2.205	14.876	11.001	0.713
	313.15	4.259	-2.274	15.119	11.48	0.73
$\Delta\eta$ (mPa · s)	93.15	-2.362	-2.185	-2.098	-2.014	0.026
	298.15	-2.383	-2.218	-2.137	-2.109	0.028
	303.15	-2.402	-2.239	-2.209	-2.157	0.030
	308.15	-2.414	-2.279	-2.225	-2.195	0.031
	313.15	-2.435	-2.384	-2.301	-2.209	0.034
[Emim] [BF_4] + Ethyl acetoacetate						
V^E_m/cm^3.mol	293.15	-6.099	-2.055	-1.671	-1.762	0.022
	298.15	-6.312	-2.11	-1.731	-1.854	0.023
	303.15	-6.527	-2.188	-1.813	-1.923	0.024
	308.15	-6.754	-2.263	-1.894	-2.007	0.025
	313.15	-6.989	-2.343	-1.97	-2.101	0.027
10^8. Δk_s/Pa^{-1}	293.15	-19.369	-5.48	-4.272	-5.591	0.064
	298.15	-20.648	-5.81	-4.559	-6.253	0.069
	303.15	-22.012	-6.256	-4.954	-6.621	0.075
	308.15	-23.491	-6.745	-5.325	-7.075	0.081
	313.15	-25.069	-7.277	-5.764	-7.528	0.088
L_f/(10^{-7} m)	293.15	4.154	-1.871	14.495	11.1	0.716
	298.15	4.239	-1.899	14.836	11.477	0.734
	303.15	4.341	-1.959	15.152	11.769	0.753
	308.15	4.415	-1.966	15.513	12.073	0.770
	313.15	4.512	-2.003	15.850	12.493	0.788
$\Delta\eta$ (mPa · s)	293.15	-2.286	-2.238	-2.097	-2.018	0.025
	298.15	-2.426	-2.385	-2.179	-2.143	0.027
	303.15	-2.484	-2.430	-2.382	-2.274	0.029
	308.15	-2 507	-2.472	-2.396	-2.297	0.032
	313.15	-2.902	-2.598	-2.441	-2.371	0.035

$$\sigma(X) = \sum_{i=1}^{n} \left[\frac{X_{expt} - X_{calc}}{(N-k)} \right]^{1/2} \quad (9)$$

The number of experimental points is indicated by N and k denote the coefficient utilized in the Redlich-Kister equation. For all of the derived properties, the standard deviation showed low values at all studied temperatures. Based on these data, it can be seen that there is a good correlation with the experimental results.

4. Conclusions

In this study, new data for thermophysical properties measurements, which includes density, viscosity and speed of sound, have been determined as a function of temperature for [C_2mim] [BF_4], benzaldehyde, ethyl acetoacetate and their binary mixtures, and have been reported over the entire range of mole fractions (x_i = 0 to 1). From the experimentally found data of the measured speed of sound and density, the important and essential excess parameters such as excess molar volumes, isentropic compressibilities, deviation in isentropic compressibilities, apparent molar isentropic compressibility, and deviation in viscosity, intermolecular free length and apparent molar isentropic compressibility have been derived. Excess molar volume and deviation in isentropic compressibility were fitted with the use of the Redlich-Kister polynomial equation in order to test the correlation of derived parameters, and a great correlation for both mixtures was achieved. For the derived properties (excess molar volumes and deviation in isentropic compressibilities), negative differences were noticed for the investigated mixtures at all given temperatures, this effect suggests strong interactions that occurs in the binary mixtures of [C_2mim] [BF_4] with benzaldehyde or ethyl acetoacetate molecules. Large negative values of derived deviation in isentropic compressibilities and excess molar volumes have been observed in the binary mixtures containing ethyl acetoacetate, as well as ion dipole interactions as compared to the benzaldehyde mixtures. Negative deviations on viscosity across the temperatures and whole range of compositions were observed, and they are increasing, i.e. becomes less negative with increasing temperatures. Intermolecular free length has been discussed as well. The results obtained in this work are useful as they give insight into the possible molecular interactions that exists between the imidazolium based ionic liquids with benzaldehyde or ethyl acetoacetate mixtures.

Declarations

Author contribution statement

Gan Redhi: Conceived and designed the experiments; Wrote the paper.

Bakusele Kabane: Performed the experiments; Analyzed and interpreted the data.

Rajasekhar Chokkareddy: Contributed reagents, materials, analysis tools or data.

Funding statement

This work was supported by the Durban University of Technology and National Research Foundation (NRF) South Africa (Grant UID: 106653).

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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