Thermophysical and thermodynamic properties of binary liquid systems of [BMIM][MeSO$_4$] ionic liquid with carboxylic acids

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Thermophysical properties, namely, density (ρ) and speed of sound (u) of binary mixtures of 1-butyl-3-methylimidazolium methyl sulphate [BMIM][MeSO$_4$] ionic liquid (IL), with acetic acid or propionic acid have been measured in the mole fraction range from 0.1 to 1.0 at temperature ranging from 293.15 to 313.15 K at a 5 K interval, under atmospheric pressure of 101 kPa. From these measured values, the derived thermodynamic parameters, such as, isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s), excess molar volume (V_m^E) and intermolecular free length (L_f) have been calculated. It is observed that V_m^E and Δk_s decrease with increasing the temperature. Furthermore, these values are negative in the whole range of binary compositions. The measured data and variations in derived thermodynamic values suggest that significant interactions occur when the IL forms a binary mixture with carboxylic acids. These derived thermodynamic parameters (V_m^E, L_f and Δk_s) are correlated byusing the Redlich-Kister polynomial equation to generate binary factors and standard errors.

Keywords: Carboxylic acid, excess molar volume, intermolecular free length, isentropic compressibility, ionic liquids, thermophysical properties

For several decades, ionic liquids (ILs) have continuously engaged the interest of scientific and industrial communities, due to their appellations as "green" and "environment-friendly solvents"[1]. Essentially, ILs are organic molten salts in the combination of organic cations with organic or inorganic anions. They have a low boiling point below 100°C and are generally liquid at room temperature[2,3]. ILs have been considered to be worthy of intensive research since they are primarily exploited in an extensive range of industrial applications as substitutes for volatile organic solvents (VOS). ILs can be tailored to meet specific application purposes by targeting one or more of their useful properties, such as low vapour pressure[4,5], high chemical and thermal stability[6], low toxicity[7], good energy storage properties, low flammability[8], high ionic-conductivity[9,10] and large liquid range[9]. The ever-growing interest in ILs is a consequence of their remarkable properties which have attracted much attention of researchers who have exploited their usefulness in various industrial applications, such as nanotechnology[11], biotechnology[12], pharmaceuticals[13] and electrochemical[10]. Furthermore, ILs have also been used as plasticizers[14], lubricants[15], electrolytes[16], extraction of elements and recovery of dyes and heavy metals[17,18].

Notwithstanding the list of beneficial properties of ILs described above, there are some features for some ILs which act as obstacles to their use in industrial processes. One of the most significant obstacles is their high viscosity and basicity. Firstly, a solvent with high viscosity is difficult to handle in bulk quantities in industrial operations. Secondly, acids may be needed to reduce the pH of basic ILs (pH is more than 10 in nature for some ILs) in many practical applications. The high cost of acquiring large quantities of ILs coupled with the obstacles described above, emphasize the urgent need to investigate the suitability of diluents for ILs. This will help to expedite the use of diluted ILs as substitutes for VOS. For this propose, carboxylic acids have been utilised as diluents for imidazolium-based ILs[19-21].

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Carboxylic acids were used as solvents in the present study, on account of the strategic importance of this class of compounds, which have been used in a wide range of industrial applications, such as separations, manufacture of pharmaceuticals and as cleaning agents. Furthermore, carboxylic acids are also used in the manufacture of polyester resins, food preservatives, flavouring agents, as acidulants in beverages and in other chemical industrial processes[22,23]. Due to their important applications, it is of significance to understand the behaviour of their mixtures with ILs. This information will be helpful for the design and development of new equipment and efficient use of ILs in potential industrial applications[24].

A significant number of ILs, having diverse cations such as imidazolium, pyridinium, pyrrolidinium, and many others, have been investigated by researchers and have been successfully applied to different technological processes, such as liquid-liquid extraction[25], batteries[26,27], transistors, fuel cells[28,29] and electrochemical, as well as optical sensors[30]. Presently, ILs are being successfully exploited in pharmaceutical fields to study their biological activities with respect to their antimicrobial and cytotoxic properties[31], used in the extraction of biological components from active compounds[32] and as an intermediate in synthesizing pharmaceutically active compounds[33]. Some ILs, for example, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) and 1-propyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide ([PMIM][NTf$_2$]) have been used as inhibitors of microbial behaviour in soils due to their low toxicity towards complex organisms[34]. The chemical and 3D structure of 1-butyl-3-methylimidazolium methylsulphate ([BMIM][MeSO$_4$]) is given in Fig. 1.

To effectively explore the use of ILs in industries, it is essential to gain some valuable information about their thermophysical and thermodynamic properties of ILs that combine with other com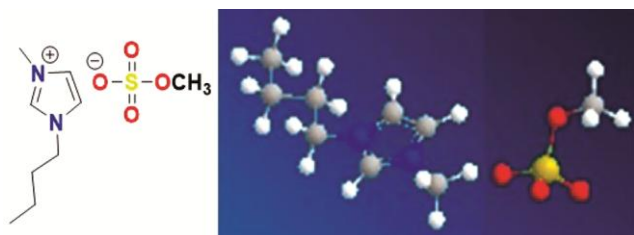pounds. Modifications of these unique properties have the potential to boost the worth of materials developed in industrial applications[35]. These properties may also be useful in investigating the molecular interactions which could occur in liquid mixtures, most importantly, wherever H-bonding occurs[36,37]. For an insight into the types of interactions which occur between ILs and diluents such as carboxylic acids, data on thermodynamic properties of these systems is essential. The thermodynamic properties of relevance are, excess molar volumes (V_m^E), isentropic compressibility (k_s) and deviations in isentropic compressibility (Δk_s). To derive these parameters are basic, but accurate, thermo-physical measurements are required. In this work, speed of sound and densities were employed for this purpose[38,39]. The results were used to calculate V_m^E, k_s, Δk_s. and L_f. The above data were then discussed in the light of their value in deducing the types of interactions which occur between the chosen IL and carboxylic acids.

Materials and Methods

Chemicals

Table S1[18-21] provides a summary of information on the chemicals used. Determination of moisture content of the IL was obtained by Columbic Karl-Fischer method and was found to have a value at 0.05%.

Apparatus and procedure

The masses of the components of the binary mixture were prepared obtained using a Mettler AJ100 mass balance with a precision of 0.0001 g. A glass syringe was used to transfer the components into a stoppered glass vial. The mixtures were well shaken to homogenize the solution. The uncertainty in the mole fraction of the samples was estimated to be in the range of ± 0.0002 g. Densities and speeds of sound were measured simultaneously for the pure liquids and their binary mixtures using a digital vibrating tube densitometer (Anton Paar DSA 5000 M) at various temperatures under atmospheric pressure (101 kPa). This equipment automatically controls the temperature as well as pressure to ± 0.01 K and 101 kPa, respectively. Details of the investigation techniques have been given elsewhere[40]. The uncertainty values in the speeds of sound and densities were not more than ± 1.0 m·s^{-1} and ± 2 × 10^{-5} g·cm^{-3}, respectively. Likewise, the estimated uncertainty for the derived thermodynamic properties such as V_m^E, Δk_s and L_f are ± 0.05 cm^3·mol^{-1}, ± 0.9 × 10^{-8} Pa^{-1} and ± 0.4 × 10^7 m, respectively.

Fig. 1 — The chemical and 3D structure of 1-butyl-3-methylimidazolium methylsulphate ([BMIM][MeSO$_4$]).

Results and Discussion

Densities and sound velocities of all chemicals used were measured and presented in Table S2, together with literature values for comparison purposes. Density (ρ) and speed of sound (u) were measured experimentally at temperatures ranging from 293.15 to 313.15 K under an atmospheric pressure of 101 kPa for pure IL, [BMIM][MeSO$_4$], acetic acid, propionic acid, and its binary combinations. The experimental data obtained for {[BMIM][MeSO$_4$] + acetic (1) or {[BMIM][MeSO$_4$] + propionic acid (2)} for their thermophysical properties are presented in Tables 1 and 2 and have been graphically represented in Figs. 2a, 2b, 4a, 4b, 5a and 5b. It can be seen from Table 1 that, there is an increase in the density with the increase

Table 1 — Density (ρ), excess molar volume (V_m^E), speed of sound (u), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s) and intermolecular free length (L_f) for the binary system of {[BMIM][MeSO$_4$] (x_1) + acetic acid (x_2)} at T = 293.15-313.15 K

x_1	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	u (m·s^{-1})	k_s ($10^8 \times$ Pa^{-1})	Δk_s ($10^8 \times$ Pa^{-1})	L_f (10^7 m)
			T = 293.15 K			
0.0000	1.0496	0.00	1159.3	70.89	0.00	1.7159
0.0302	1.0694	-0.19	1258.0	59.08	-10.55	1.5666
0.0637	1.0861	-0.26	1309.7	53.67	-14.58	1.4931
0.1006	1.1013	-0.31	1357.3	49.18	-17.45	1.4307
0.2004	1.1322	-0.39	1450.9	41.96	-20.66	1.3201
0.3008	1.1537	-0.42	1511.7	37.93	-20.54	1.2551
0.4008	1.1693	-0.42	1547.3	35.72	-18.62	1.2181
0.5008	1.1813	-0.40	1584.6	33.71	-16.50	1.1834
0.6018	1.1906	-0.36	1609.9	32.40	-13.64	1.1602
0.7006	1.1979	-0.30	1629.4	31.44	-10.53	1.1428
0.8017	1.2040	-0.22	1646.1	30.65	-7.14	1.1284
0.9034	1.2091	-0.13	1660.2	30.01	-3.59	1.1164
1.0000	1.2130	0.00	1668.5	29.61	0.00	1.1091
			T = 298.15 K			
0.0000	1.0440	0.00	1142.8	73.34	0.00	1.7615
0.0302	1.0644	-0.20	1242.3	60.88	-11.16	1.6048
0.0637	1.0817	-0.29	1294.5	55.17	-15.42	1.5277
0.1006	1.0974	-0.35	1342.6	50.55	-18.44	1.4624
0.2004	1.1291	-0.42	1436.9	42.90	-21.77	1.3472
0.3008	1.1511	-0.45	1498.2	38.70	-21.63	1.2796
0.4008	1.1671	-0.44	1534.0	36.41	-19.59	1.2411
0.5008	1.1794	-0.42	1571.6	34.33	-17.35	1.2051
0.6018	1.1890	-0.37	1597.2	32.97	-14.34	1.1810
0.7006	1.1965	-0.31	1616.8	31.97	-11.06	1.1630
0.8017	1.2029	-0.23	1633.5	31.16	-7.50	1.1481
0.9034	1.2081	-0.13	1647.7	30.49	-3.76	1.1357
1.0000	1.2121	0.00	1656.2	30.08	0.00	1.1280
			T = 303.15 K			
0.0000	1.0383	0.00	1126.3	75.92	0.00	1.8085
0.0302	1.0591	-0.21	1226.3	62.79	-11.77	1.6447
0.0637	1.0769	-0.32	1279.1	56.76	-16.28	1.5637
0.1006	1.0928	-0.38	1327.6	51.92	-19.44	1.4956
0.2004	1.1248	-0.46	1422.7	43.92	-22.92	1.3756
0.3008	1.1471	-0.48	1484.5	39.56	-22.73	1.3055
0.4008	1.1633	-0.47	1520.6	37.18	-20.59	1.2655
0.5008	1.1757	-0.45	1558.6	35.02	-18.22	1.2282
0.6018	1.1853	-0.39	1584.3	33.61	-15.05	1.2033
0.7006	1.1930	-0.32	1604.0	32.58	-11.60	1.1847

(*Contd.*)

Table 1 — Density (ρ), excess molar volume (V_m^E), speed of sound (u), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s) and intermolecular free length (L_f) for the binary system of {[BMIM][MeSO$_4$] (x_1) + acetic acid (x_2)} at T = 293.15-313.15 K   (*Contd.*)

x_1	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	u (m·s^{-1})	k_s ($10^8 \times$ Pa^{-1})	Δk_s ($10^8 \times$ Pa^{-1})	L_f (10^7 m)
			T = 303.15 K			
0.8017	1.1994	-0.24	1621.0	31.73	-7.87	1.1692
0.9034	1.2047	-0.13	1635.1	31.05	-3.95	1.1565
1.0000	1.2088	0.00	1643.8	30.62	0.00	1.1485
			T = 308.15 K			
0.0000	1.0327	0.00	1109.6	78.65	0.00	1.8574
0.0302	1.0539	-0.23	1210.4	64.77	-12.45	1.6855
0.0637	1.0721	-0.35	1263.7	58.41	-17.22	1.6006
0.1006	1.0882	-0.42	1312.6	53.33	-20.54	1.5295
0.2004	1.1206	-0.49	1408.6	44.98	-24.15	1.4046
0.3008	1.1431	-0.52	1470.8	40.44	-23.92	1.3318
0.4008	1.1595	-0.50	1507.3	37.96	-21.64	1.2904
0.5008	1.1720	-0.48	1545.6	35.72	-19.14	1.2516
0.6018	1.1818	-0.41	1571.6	34.26	-15.79	1.2258
0.7006	1.1895	-0.33	1591.4	33.20	-12.16	1.2066
0.8017	1.1960	-0.24	1608.5	32.32	-8.23	1.1906
0.9034	1.2014	-0.13	1622.8	31.61	-4.11	1.1775
1.0000	1.2055	0.00	1632.4	31.13	0.00	1.1685
			T = 313.15 K			
0.0000	1.0271	0.00	1094.9	81.22	0.00	1.9044
0.0302	1.0487	-0.25	1194.4	66.84	-12.89	1.7275
0.0637	1.0673	-0.38	1248.4	60.12	-17.94	1.6385
0.1006	1.0836	-0.45	1297.7	54.80	-21.44	1.5642
0.2004	1.1163	-0.52	1394.5	46.07	-25.22	1.4342
0.3008	1.1391	-0.55	1457.2	41.34	-24.97	1.3587
0.4008	1.1556	-0.54	1494.0	38.77	-22.59	1.3157
0.5008	1.1683	-0.51	1532.7	36.44	-19.96	1.2755
0.6018	1.1781	-0.43	1559.0	34.93	-16.47	1.2488
0.7006	1.1859	-0.35	1579.0	33.82	-12.67	1.2289
0.8017	1.1925	-0.26	1596.3	32.91	-8.57	1.2122
0.9034	1.1979	-0.14	1610.6	32.18	-4.26	1.1987
1.0000	1.2021	0.00	1621.2	31.65	0.00	1.1888

Standard uncertainties are ρ = ± 2 × 10^{-5} g·cm^{-3}, u = ± 1.0 m·s^{-1}, V_m^E = ± 0.05 cm^3 · mol^{-1}, Δk_s = ± 0.9 × 10^{-8} · Pa^{-1} and L_f = ± 0.4 × 10^7 m.

Table 2 — Density (ρ), excess molar volume (V_m^E), speed of sound (u), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s) and intermolecular free length (L_f) for the binary system of {[BMIM][MeSO$_4$] (**x_1**) + propionic acid (**x_2**)} at T = 293.15-313.15 K

x_1	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	u (m·s^{-1})	k_s ($10^8 \times$ Pa^{-1})	Δk_s ($10^8 \times$ Pa^{-1})	L_f (10^7 m)
			T = 293.15 K			
0.0000	0.9938	0.00	1166.4	73.97	0.00	1.7528
0.0332	1.0169	-0.32	1207.4	67.46	-5.04	1.6739
0.0693	1.0384	-0.58	1254.7	61.17	-9.72	1.5940
0.1009	1.0548	-0.76	1294.6	56.56	-12.93	1.5328
0.2007	1.0939	-0.94	1394.5	47.01	-18.05	1.3974
0.3004	1.1218	-0.91	1462.3	41.69	-18.95	1.3160
0.4005	1.1434	-0.81	1511.0	38.31	-17.90	1.2614
0.5005	1.1608	-0.71	1548.7	35.92	-15.85	1.2214
0.6014	1.1751	-0.58	1580.5	34.07	-13.23	1.1895

(*Contd.*)

Table 2 — Density (ρ), excess molar volume (V_m^E), speed of sound (u), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s) and intermolecular free length (L_f) for the binary system of {[BMIM][MeSO$_4$] (x_1) + propionic acid (x_2)} at T = 293.15-313.15 K   (*Contd.*)

x_1	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	u (m·s^{-1})	k_s ($10^8 \times$ Pa^{-1})	Δk_s ($10^8 \times$ Pa^{-1})	L_f (10^7 m)
			T = 293.15 K			
0.7012	1.1870	-0.45	1603.8	32.75	-10.12	1.1664
0.8022	1.1972	-0.31	1631.4	31.38	-7.00	1.1418
0.9024	1.2058	-0.17	1652.5	30.37	-3.57	1.1231
1.0000	1.2130	0.00	1668.5	29.61	0.00	1.1091
			T = 298.15 K			
0.0000	0.9884	0.00	1148.1	76.75	0.00	1.8019
0.0332	1.0121	-0.34	1189.8	69.80	-5.40	1.7184
0.0693	1.0343	-0.63	1238.1	63.08	-10.44	1.6335
0.1009	1.0509	-0.81	1278.6	58.20	-13.84	1.5692
0.2007	1.0906	-0.99	1379.7	48.17	-19.21	1.4275
0.3004	1.1190	-0.95	1448.2	42.61	-20.12	1.3426
0.4005	1.1411	-0.86	1497.4	39.09	-18.97	1.2859
0.5005	1.1589	-0.76	1535.5	36.60	-16.79	1.2443
0.6014	1.1735	-0.62	1567.6	34.68	-14.00	1.2113
0.7012	1.1856	-0.48	1591.1	33.32	-10.71	1.1872
0.8022	1.1961	-0.36	1618.8	31.91	-7.40	1.1618
0.9024	1.2049	-0.20	1640.0	30.86	-3.77	1.1426
1.0000	1.2121	0.00	1656.2	30.08	0.00	1.1280
			T = 303.15 K			
0.0000	0.9830	0.00	1129.7	79.71	0.00	1.8531
0.0332	1.0071	-0.36	1172.0	72.29	-5.79	1.7647
0.0693	1.0296	-0.67	1221.3	65.12	-11.19	1.6749
0.1009	1.0464	-0.86	1262.5	59.96	-14.80	1.6072
0.2007	1.0864	-1.05	1364.8	49.42	-20.44	1.4590
0.3004	1.1151	-1.01	1434.1	43.61	-21.35	1.3706
0.4005	1.1373	-0.92	1483.7	39.94	-20.11	1.3117
0.5005	1.1553	-0.81	1522.2	37.35	-17.78	1.2685
0.6014	1.1699	-0.66	1554.6	35.37	-14.82	1.2344
0.7012	1.1821	-0.51	1578.3	33.96	-11.33	1.2095
0.8022	1.1927	-0.37	1606.2	32.50	-7.83	1.1833
0.9024	1.2015	-0.20	1627.5	31.42	-3.98	1.1635
1.0000	1.2088	0.00	1643.8	30.62	0.00	1.1485
			T = 308.15 K			
0.0000	0.9776	0.00	1111.3	82.83	0.00	1.9060
0.0332	1.0021	-0.39	1154.4	74.88	-6.23	1.8123
0.0693	1.0249	-0.71	1204.5	67.25	-11.99	1.7175
0.1009	1.0419	-0.91	1246.4	61.79	-15.82	1.6462
0.2007	1.0823	-1.11	1349.9	50.70	-21.75	1.4913
0.3004	1.1112	-1.07	1419.9	44.64	-22.66	1.3992
0.4005	1.1336	-0.97	1470.1	40.82	-21.30	1.3380
0.5005	1.1517	-0.86	1509.0	38.13	-18.82	1.2932
0.6014	1.1664	-0.69	1541.7	36.07	-15.66	1.2579
0.7012	1.1786	-0.54	1565.6	34.61	-11.96	1.2322
0.8022	1.1893	-0.39	1593.7	33.11	-8.25	1.2050
0.9024	1.1982	-0.20	1615.2	31.99	-4.18	1.1846
1.0000	1.2055	0.00	1632.4	31.13	0.00	1.1685

(*Contd.*)

Table 2 — Density (ρ), excess molar volume (V_m^E), speed of sound (u), isentropic compressibility (k_s), deviation in isentropic compressibility (Δk_s) and intermolecular free length (L_f) for the binary system of {[BMIM][MeSO$_4$] ($\mathbf{x_1}$) + propionic acid ($\mathbf{x_2}$)} at T = 293.15-313.15 K   (*Contd.*)

x_1	ρ (g·cm^{-3})	V_m^E (cm^3·mol^{-1})	u (m·s^{-1})	k_s ($10^8 \times$ Pa^{-1})	Δk_s ($10^8 \times$ Pa^{-1})	L_f (10^7 m)
			T = 313.15 K			
0.0000	0.9723	0.00	1092.8	86.13	0.00	1.9610
0.0332	0.9971	-0.41	1136.9	77.60	-6.72	1.8614
0.0693	1.0202	-0.76	1187.8	69.47	-12.88	1.7613
0.1009	1.0374	-0.97	1230.3	63.69	-16.94	1.6863
0.2007	1.0782	-1.18	1335.1	52.03	-23.16	1.5242
0.3004	1.1073	-1.15	1405.9	45.69	-24.07	1.4283
0.4005	1.1299	-1.04	1456.7	41.71	-22.60	1.3647
0.5005	1.1481	-0.93	1496.0	38.92	-19.94	1.3183
0.6014	1.1629	-0.75	1528.9	36.79	-16.58	1.2817
0.7012	1.1752	-0.58	1553.1	35.28	-12.65	1.2551
0.8022	1.1859	-0.43	1581.4	33.72	-8.71	1.2270
0.9024	1.1948	-0.23	1603.0	32.57	-4.39	1.2060
1.0000	1.2021	0.00	1621.2	31.65	0.00	1.1888

Standard uncertainties are $\rho = \pm\ 2\ \times\ 10^{-5}$ g·cm^{-3}, u $= \pm\ 1.0$ m·s^{-1}, $V_m^E\ =\ \pm\ 0.05$ cm^3 · mol^{-1}, $\Delta k_s\ =\ \pm\ 0.9\ \times\ 10^{-8}$ Pa^{-1} and $L_f = \pm\ 0.4 \times 10^7$ m.

in [BMIM][MeSO$_4$] IL concentration in acetic or propionic acid solutions at the investigated temperatures. A perusal of Table 1 and 2 show that speeds of sound values decreased with the increase in temperature for both studied binary systems but, increased with increasing the concentration of IL. This is in line with the expectation that an increase in temperature would give more energy to the interacting molecules which cause them to move apart, whereas an increase in concentration would lead to the interacting molecules getting closer each other. Changes in speeds of sound values may thus serve as an indicator of the interaction strength due to solute-solute, solvent-solvent and solute-solvent interactions in binary solutions, as also noted by Roy et al.[41].

Excess molar volume

The excess molar volumes, V_m^E values for each concentration have been derived from the measured density data by using Eqn (1), given as follows:

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

Where x_1, x_2 are mole concentration, M_1, M_2 stand for molecular mass, ρ_1, ρ_2 represent the density of the [BMIM][MeSO$_4$] IL and acids, respectively, and ρ also denotes the density of the two-component solution. The V_m^E values of binary systems over the entire composition range at temperatures from T=293.15 to 313.15 K are given in Table 1 and 2. Typical graphical images of V_m^E plotted against the

mole concentrations of IL for both systems are shown in Figs. 2a and 2b, respectively. An analysis of Tables 1 and 2 reveals that V_m^E values were negative for both binary systems over the whole studied concentration at various temperature ranges. A similar trend in changes of V_m^E values was also observed by Deenadayalu et al.[42] for the binary systems of propionitrile with alcohols. The results for interactions of different, but similar types of ILs with acids, namely, binary mixtures of ILs [EMIM][MeSO$_4$] or [EMIM][EtSO$_4$] with acetic and propanoic acid, have been reported[21,43,44]. They provide a useful basis for assessing the results of the present study. Due to the greater fitting effect of carboxylic acid molecules in the interstices of IL, more negative excess properties were observed in this investigation at high mole fraction of carboxylic acid. As shown in Fig. 3, an example of crossed H-bonding occurred between the most acidic hydrogen which was at the C(2) position of imidazolium cation[43,44] and negative pole oxygen of carboxyl group of the carboxylic acid. The possibility of other H-bonding is also likely to occur between the oxygen of the anion of IL and hydrogens of -OH and -COOH groups. The ion-dipole interactions between [MeSO$_4$] anion of IL and positive pole carbon of carbonyl group of carboxylic acid may also contribute to negative excess properties (as shown in Fig. 3). In this case, imidazolium cation and anion act as H-bond donor and H-bond acceptor, respectively as shown in Fig. 3[21,45].
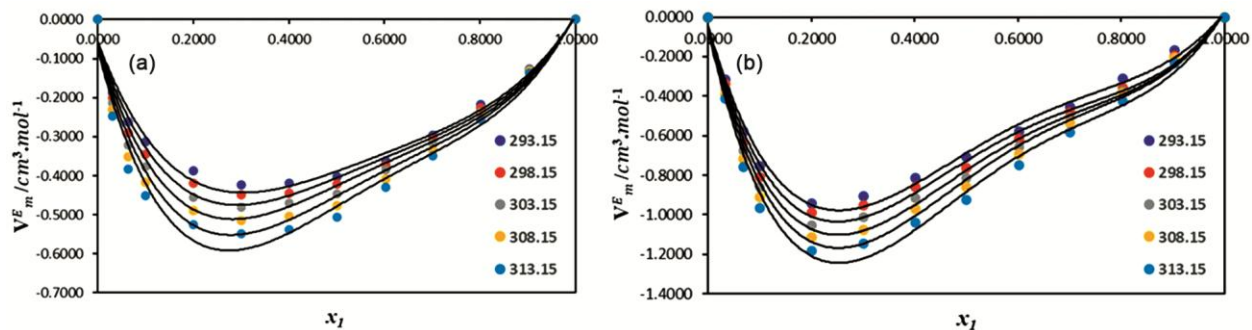
Fig. 2 — Excess molar volumes (V_m^E) for the mixture of (a){[BMIM][MeSO$_4$] (1) + acetic acid (2)} and (b) {[BMIM][MeSO$_4$] (1) +propionic acid (2)} as a function of the composition expressed in the mole fraction of [BMIM][MeSO$_4$] at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●).
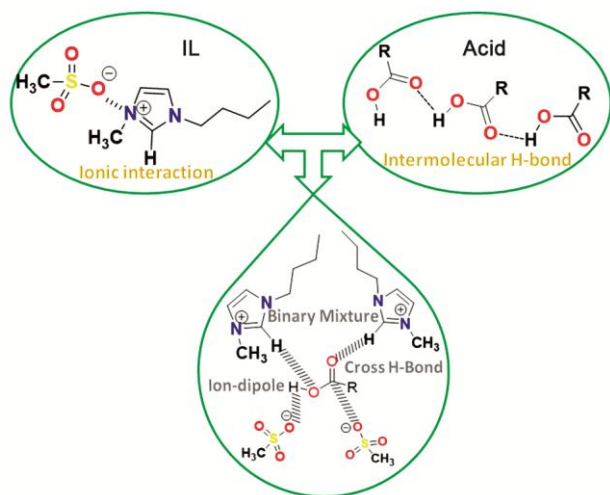

Fig. 3 — Presence of ion-dipole interactions and crossed H-bonding interactions between [BMIM][MeSO$_4$] and carboxylic acid. This image was inspired from reference[44].

Generally, the values of V_m^E for binary systems reveal the strength of intermolecular interaction between the components in mixtures. This could be an important pointer to the role of packing effects. However, additional factors such as the differences in size and shape of molecules may also contribute significantly[46], as exemplified by the results for the [BMIM][MeSO$_4$] interacting with series of alcohols[47]. The foregoing study points to the effect of chain length of molecular solvent interactions occurring between IL and alcohols in binary systems. Furthermore, the V_m^E valuesfor all binary systems of IL with alcohols are negative for all compositions at various temperatures. This implies that significant packing effects occurred on mixing of alcohols with [BMIM][MeSO$_4$] IL[38,47]. The order of interaction of a series of alcohols [BMIM][MeSO$_4$] with was as follows: methanol < ethanol < 1-propanol[47]. Literature reveals that interactions between alcohols and ILs increase with increasing the length of alkyl chain of both cations and anions of ILs. This is ascribed to differences in size and shape of ILs[48,49]. Table S3[50-53] summarises the results for some binary systems which were prepared using the same kind of imidazolium-based IL with various molecular solvents and acids. These studies yield information which could be used to elucidate the results of the present investigation. With regard to the effect of changes in the alkyl chain lengths of substituents in cations and anions, it was found that interactions decrease with the increase in alkyl chain length of the substituents in cation and anion of ILs, which was used to make binary mixtures of ILs with alcohols. Similarly, the mixing of acid and ILs also gives same effects, as shown by the result that propionic acid interacted more strongly with [EMIM][MeSO$_4$] IL than acetic acid[37]. Furthermore, the V_m^E values, for both studied systems, which were higher negative, suggest that an active filling effect operates in the binary solutions between [BMIM][MeSO$_4$] and acetic or propionic acids[54]. This process appears to result in a negative value of V_m^E[55]. The V_m^E minimal value (V_{mmin}^E) decreases with the increase in temperature for the both binary liquid systems. Also, the V_{mmin}^Evalue for the IL + acetic or propionic acid binary combinations is V_{mmin}^E = -0.5493 cm^3 for x$_1$ = 0.3008 and -1.1835cm^3 for x$_1$ = 0.2007, respectively at the investigated temperatures. V_m^E values for {[BMIM][MeSO$_4$] + propionic acid} are more negative than those of {[BMIM][MeSO$_4$] + acetic acid}. This implies that the interaction of [BMIM][MeSO$_4$] with propionic acid is stronger than that for [BMIM][MeSO$_4$] with acetic acid.

The same trend was inferred, from the more negative values of excess thermodynamic properties, by Ahluwalia et al.[56] and Lark and Banipal[57] for the

interactions of IL-acid binary mixtures. The former researchers proposed that the effect of interaction increases with increasing the alkyl chain length of carboxylic acid due to the positive inductive effect (+I) of longer alkyl chain[56]. The same phenomena could be occurring in our investigated system on following grounds: i) More positive inductive effect of ethyl group in propionic acid than methyl group in acetic acid; ii) Increasing electron density on the oxygen atom of carboxylic acid, and iii) Resulting energetically favoured cross H-bonding (Fig. 3). This supports the result that the V_m^E of IL + propionic acid is more negative than that of IL + acetic acid.

Isentropic compressibility and deviation in isentropic compressibility

Isentropic compressibility (k_s) is derived from the density and speed of sound via the Newton-Laplace Eqn (2) as shown below:

$$k_s = \rho^{-1}u^{-2} \qquad \qquad \dots (2)$$

Deviation in isentropic compressibility (Δk_s) has been derived from the following Eqn (3)

$$\Delta k_s = k_s - \sum_i^2 x_i k_{s,i} \qquad \qquad \dots (3)$$

Where k_s is the isentropic compressibility, while x_i and i are the molar concentration of the pure liquid and the two-component liquid combination, respectively.

The results obtained for isentropic compressibilities (k_s) and deviations in isentropic compressibilities (Δk_s), for the two-component liquid systems over the entire concentration range at the investigated temperatures, have been calculated and presented in Table 1 and 2. It can be seen from Table 1 and 2 that k_s value increases with the increase in temperature for the studied systems over the entire

composition range of two binary mixtures. This is attributed to the increase in the thermal agitation of solution which makes it more compressible[58]. The Δk_s becomes more negative because the free space between the molecules in the binary liquid mixtures was decreased by the interaction amongst the molecules in the liquid mixtures[18]. Figs 4a and 4b show the negative value of Δk_s over the whole concentration of {[BMIM][MeSO$_4$] + acetic acid (1) or propionic acid (2)} at all examined temperatures. The minimal value of $\Delta k_{s\,min}$ was -25.2171 × 10^8 Pa^{-1} and -24.0704 × 10^8 Pa^{-1} at the mole fraction of x = 0.2004 and 0.3004, respectively for both acetic and propionic acid binary systems. These values suggest that the IL interacts more strongly with propionic acid than with acetic acid. Furthermore, the results for the interactions of similar types of ILs with acids, namely, binary mixtures of [EMIM][MeSO$_4$] or [EMIM][EtSO$_4$] with acetic and propanoic acid, have been reported[21,59,60]. They provide a useful basis for assessing the results of the present study. Due to the greater fitting effect of carboxylic acid molecules in the interstices of IL, more negative excess properties were observed in this investigation at high mole fraction of carboxylic acid. Banprakash et al.[21] have attributed the relation between the negative value of Δk_s to stronger interaction between the molecules in [EMIM][MeSO$_4$] binary mixtures with solvents. In addition, the previous reports also denoted another significant effect which is also contributing significantly to molecular interactions, i.e inductive (+I) effect. This is ascribed to the presence of longer alkyl chain substituents of molecules in binary mixtures. This view has been supported by the work of Nain et al.[61] who investigated binary mixtures of an acrylate with a formamide or an acetamide and proposed that better packing of molecules increases with temperature.
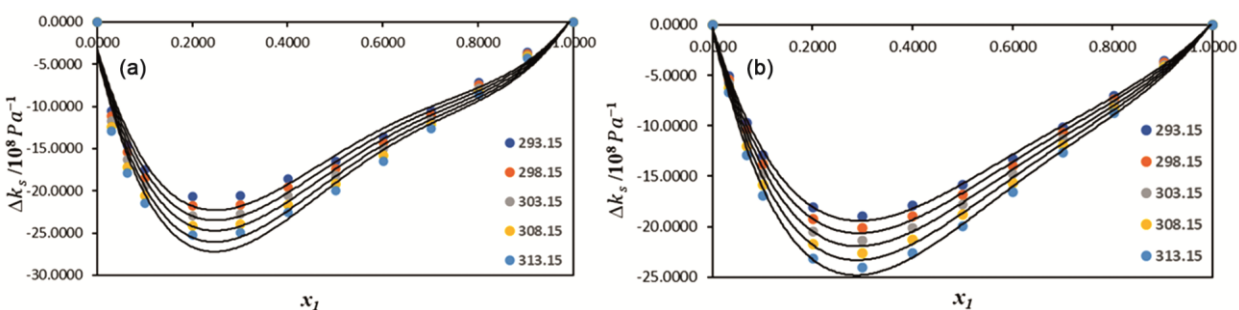

Fig. 4 — Deviation in isentropic compressibility (Δk_s) for the mixture of (a) {[BMIM][MeSO$_4$] (1) + acetic acid (2)} and (b) {[BMIM][MeSO$_4$] (1) + propionic acid (2)} as a function of the composition expressed in themole fraction of [BMIM][MeSO$_4$] at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●).

It is proposed that the binary mixture of {[BMIM][MeSO$_4$] + propionic acid} is more compressible than that of {[BMIM][MeSO$_4$] + acetic acid} and that this difference may be due to the extra alkyl group on propionic acid. The order of compressibility for the binary mixture is as follows: {[BMIM][MeSO$_4$] + propionic acid} > {[BMIM][MeSO$_4$] + acetic acid}. In the light of the results of previous studies and of the present one, it is proposed that negative values of thermodynamic properties are due to factors such as: i) H-bonding, ii) ion-dipole interactions and iii) geometrical fitting between the components of molecules[37]. It was also suggested[37] that the positive excess properties are favoured by: i) breaking up association of molecules, ii) physical effects comprised of non-specific interactions like dispersion forces which lead to weak interaction[37].

Intermolecular free length (L$_f$)

Intermolecular free length (L$_f$) is useful in determining the distance between the centre of two molecules in the two-component liquid combinations. Inter-molecular free length, L$_f$ can be estimated through using Jacobson's empirical relation which uses isentropic compressibility given by the Eqn (4) below:

$$L_f = k_c (k_s)^{1/2} \qquad \ldots(4)$$

Where k$_c$ denotes Jacobson's constant which is dependent on temperature and has a value of $(93.875 + 0.375 \, T) \, 10^{-8}$. Jacobson's empirical relation is acknowledged to be one of the useful means to compute the intermolecular free length via k$_s$[58]. The computed values of this parameter are presented in

Table 1 and 2 and have been graphically presented as well in Fig. 5a and 5b. The results reveal that an increase in the IL concentration results in a decrease in L$_f$ between interacting molecules of the binary combinations.

Correlation of derived properties

The obtained data of calculated deviation or excess properties of {[BMIM][MeSO$_4$] + acetic or propionic acid} two-component systems have been presented in Tables 1 and 2. The resultant parameters such as V$_m^E$, Δk$_s$ and L$_f$ were fitted to the Redlich-Kister model[62] according to the Eqn (5) expressed below:

$$X = x_1 x_2 \sum_{i=1}^{k} A_i (1-2x_1)^{i-1} \qquad \ldots(5)$$

where X denotes intermolecular free length (L$_f$), excess molar volumes (V$_m^E$), deviation in isentropic compressibility (Δk$_s$). The results of the fitted properties A$_i$ were acquired by means of a least-square method and summarised in Table 3, together with the equivalent average errors (σ) as given of Eqn (6) below:

$$\sigma(X) = \sum_{i=1}^{n} \left[\frac{X_{exp} - X_{calc}}{N-k} \right]^{1/2} \qquad \ldots(6)$$

where, k refers to the factor number and N represents the number of data points obtained from Redlich-Kister model. The values of V$_m^E$, Δk$_s$ and L$_f$ for Redlich-Kister model are given in Table 3. The standard deviation values, for the studied two-component systems, show lower values for V$_m^E$ and Δk$_s$ at various temperatures.
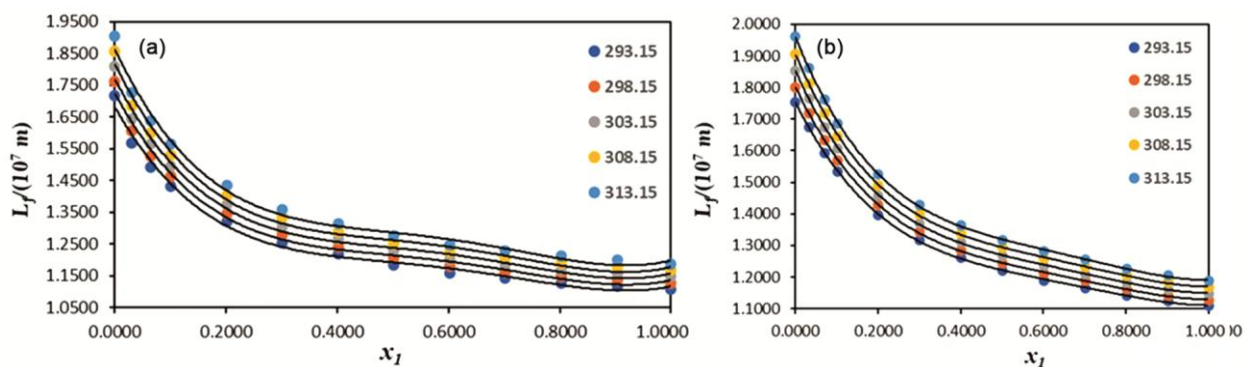

Fig. 5 — Intermolecular free length (L$_f$) for the mixture of (a) {[BMIM][MeSO$_4$] (1) + acetic acid (2)}; (b) {[BMIM][MeSO$_4$] (1) + propionic acid (2)} as a function of the composition expressed in the mole fraction of [BMIM][MeSO$_4$] at 293.15 K (●), 298.15 K (●), 303.15 K (●), 308.15 K (●) and 313.15 K (●).

Table 3 — Redlich-Kister fitting coefficients and standard deviation, σ, for the binary systems of {[BMIM][MeSO$_4$] (x$_1$) + acetic or propionic acid (x$_2$)} studied at T = 293.15, 298.15, 303.15, 308.15 and 313.15 K

	T (K)	A$_0$	A$_1$	A$_2$	A$_3$	σ
			{[BMIM][MeSO$_4$] (x$_1$) + acetic acid (x$_2$)}			
V$_m^E$ (cm^3·mol^{-1})	293.15	-1.548	-0.362	-1.327	-1.781	0.020
	298.15	-1.615	-0.438	-1.511	-1.962	0.021
	303.15	-1.696	-0.513	-1.69	-2.196	0.022
	308.15	-1.802	-0.578	-1.82	-2.485	0.024
	313.15	-1.908	-0.637	-1.982	-2.736	0.026
Δk$_s$ (10^8 × Pa^{-1})	293.15	-62.958	-37.894	-82.809	-106.787	0.999
	298.15	-66.154	-39.849	-87.703	-113.495	1.058
	303.15	-69.443	-41.871	-92.735	-120.198	1.118
	308.15	-72.905	-44.028	-98.104	-128.009	1.185
	313.15	-76.081	-46.287	-102.054	-132.957	1.213
L$_f$ (10^{7}m)	293.15	3.952	-2.185	14.993	12.068	0.597
	298.15	4.021	-2.238	15.315	12.411	0.611
	303.15	4.095	-2.294	15.653	12.766	0.626
	308.15	4.17	-2.351	15.999	13.129	0.642
	313.15	4.246	-2.41	16.351	13.507	0.657
			{[BMIM][MeSO$_4$] (x$_1$) + propionic acid (x$_2$)}			
V$_m^E$ (cm^3·mol^{-1})	293.15	-2.764	-2.285	-3.375	-2.695	0.010
	298.15	-2.918	-2.281	-3.816	-2.977	0.016
	303.15	-3.112	-2.445	-3.987	-3.196	0.017
	308.15	-3.299	-2.611	-4.134	-3.477	0.018
	313.15	-3.546	-2.732	-4.431	-3.614	0.019
Δk$_s$ (10^8 × Pa^{-1})	293.15	-63.104	-48.716	-42.563	-22.482	0.097
	298.15	-66.796	-51.621	-46.103	-25.555	0.106
	303.15	-70.698	-54.754	-49.873	-28.579	0.116
	308.15	-74.776	-58.111	-53.797	-32.254	0.125
	313.15	-79.173	-61.668	-58.229	-36.474	0.134
L$_f$ (10^{7}m)	293.15	4.08	-2.14	15.555	13.027	0.604
	298.15	4.152	-2.198	15.911	13.439	0.62
	303.15	4.228	-2.261	16.285	13.866	0.636
	308.15	4.305	-2.325	16.668	14.309	0.652
	313.15	4.384	-2.392	17.061	14.768	0.669

Conclusions

The data of densities and speeds of sound for binary solution of ionic liquid, [BMIM][MeSO$_4$], with acetic acid or propionic acid were determined at five different temperatures (293.15-313.15 K). The derived thermodynamic data such as V$_m^E$, k$_s$, Δk$_s$ and L$_f$ were evaluated from the measured densities and speeds of sound values. The excess molar volume (V$_m^E$) and deviation in isentropic compressibility (Δk$_s$), were found to be negative. This can be deduced that significant solute-solvent interactions occur in the binary solution of [BMIM][MeSO$_4$] with acetic or propionic acid. Theseinteractions could be attributed to the presence of strong compacting effect between the IL and acid molecules. This, in turn, may be due to the presence of H-bonding, dipole interactions and weak van der Waals interactions. These derived thermodynamic parameters (V$_m^E$, L$_f$ and Δk$_s$) were correlated using the Redlich-Kister polynomial equation to generate binary factors and standard errors.

Supplementary Data

The graphical images of density, speed of sound and table of thermophysical properties of acids and ionic liquids as well as table for comparable studies from literature have been included in supplementary data. Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_59A(08)1136-1147_SupplData.pdf.

Acknowledgement

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