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Intermolecular interactions in binary mixtures of phosphonium based ionic liquid and propanoic acid

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Thermophysical properties of binary systems containing trihexyltetradecylphosphonium chloride $[P^{+}_{14,6,6,6}]$ $[Cl^{-}]$ ionic liquid (IL) and propanoic acid (PA), have been investigated. Measurements of densities (ρ), and speeds of sound (u) have been made at p = 0.1 MPa and at varying temperatures ranging from 293.15 to 313.15 K. The computed excess properties which include excess molar volume (V_m^E), apparent molar volume (V_ϕ), intermolecular free length (L_f), isentropic compressibility (k_s), apparent molar isentropic compressibility (K_ϕ) and deviation in isentropic compressibility (Δk_s) have been computed from the experimental data of densities and speeds of sound. Based on the calculated derived properties, it is evident that the investigated IL and PA exhibit strong interactions across the entire mole fraction composition. Good correlation has been achieved with the Redlich-Kister equation.

Keywords: Solution chemistry, Ionic Liquids, Trihexyltetradecylphosphonium chloride, Propanoic acid, Density, Excess molar volumes, Speeds of sound

Any type of salt that melts without decomposing or vaporizing usually yields an ionic liquid (IL), which has been described as having numerous applications[1]. Investigation of thermophysical properties of pure ILs as well as their binary mixtures with organic solvents is important. The structural effects and intermolecular interactions of ILs with organic solvents have been reported widely[2-11]. The flexible physical properties of ILs make it easy to develop a novel IL, either by changing the type of alkyl side chain or introducing a new type of cation/anion of interest[5]. Detailed information of the thermophysical properties is essential for use of these non-volatile solvents for large scale industrial applications[12-15].

Phosphonium based ILs have gained extensive commercial accessibility over the past years. These promising liquids possess many advantages as they are thermally more stable[16], less toxic, readily available in bulk and are also inexpensive[17-18]. Due to the absence of the acidic proton, under nucleophilic and basic conditions, phosphonium based ILs are thermally more stable than their imidazolium counterparts[19]. Several applications for phosphonium based ILs include their utility as electrolytes in batteries, as solvents for extraction, corrosion prevention and as solvents for chemical synthesis[20-22].

However, investigations of physical properties of phosphonium based ILs in organic solvent mixtures are scarce. Phosphonium based ILs have a broad range of interesting properties[21], including electrochemical properties[22-24]. Some of the physical properties of pure $[P^{+}_{14,6,6,6}]$ $[Cl^{-}]$, such as density, viscosity[13], and surface tension[23] are reported. Recently, investigation of binary mixtures comprising methanol and dodecane, with the $[P^{+}_{14,6,6,6}]$ cation have been reported[24-27]. The nature of the solvent decides if it prefers to move towards the non-polar or polar domain of the ionic liquid[27]. The addition of solvents, results in the reduction of viscosity through interruption of the IL ion pair association[24,28]. Often, the addition of water may result in the change of the solution structure, which may also result in the formation of micellar structures[28].

The carboxylic acid groups are important, as they are effective in many industrial applications, which includes their use in the production of polyester resins, pharmaceutical products, cleaning agents and catalysts, for separation process etc. Mixtures of ionic liquids containing carboxylic acids are reported to have potential industrial applications[29-31].

In the present study, the excess solution properties of $[P^{+}_{14,6,6,6}]$ $[Cl^{-}]$ IL + PA binary systems were investigated across the mole fraction range. Propanoic acid is a polar solvent, and is thus expected to show strong interactions with the [$P^+_{14,6,6,6}$] [Cl^-].

Materials and Methods

The ionic liquid ([$P^+_{14,6,6,6}$] [Cl^-]) and propanoic acid were both supplied by Sigma Aldrich (South Africa), with a stated purity of ≥ 95% for [$P^+_{14,6,6,6}$] [Cl^-]; and ≥ 99.5% for PA. The supplied chemicals were degassed by the use of ultrasound and kept away from light, over 0.3 nm molecular sieves for several days prior to experimentation. The water content was determined by the use of Karl-Fischer auto titrator, before the commencement of experimental work. Both IL and PA, were found to contain small traces of water. Propanoic acid was found to contain 0.02%, whilst the IL contained 0.06% water. No further purification was performed before the analysis.

The binary mixtures were prepared by transferring the pure liquids using an air tight syringe into stoppered vials. The mass of each component was determined with an OHAUS analytical mass balance with precision of ±0.0001 g. A digital vibrating tube density and speed of sound analyser (Anton Paar DSA 5000 M) with an accuracy of about $\pm 5\times10^{-6}$ g cm^{-3} for density, 0.5 m s^{-1} for speed of sound and approximately 0.02 K for temperature, was used for the measurements of speeds of sound, and densities of pure liquids and binary systems. The speed of sound and density uncertainty measurements, were less than $\pm 2\times10^{-5}$ g cm^{-3} for density and ±0.8 m s^{-1} for speed of sound, and temperature was maintained at ±0.02 K. For the derived properties V_m^E, k_s and Δk_s, the estimated uncertainties were 0.004 cm^3 mol^{-1}, $\pm 2\times10^{-8}$ Pa^{-1} and $\pm 0.7\times10^{-8}$ Pa^{-1}, respectively.

Results and Discussion

Density

Density (ρ) of the binary mixtures and pure compounds was measured at atmospheric pressure and over the temperature range of (293.15−313.15) K. Results show that the densities are inversely proportional to the temperature at all intervals (Table 1 and Supplementary Data, Table S1) and in the binary mixtures, decrease as the concentration of the investigated IL increases (Fig. 1). This observed effect may arise from the weakening of [$P^+_{14,6,6,6}$] [Cl^-] and PA interactions, when the two components were mixed[14, 19, 32].

Speed of sound

The speed of sound is an essential and important parameter which gives a clear indication about the viscosity and density; the lower the speed of sound, the denser the medium. The parameter of speed of sound is useful, because it also describes the types of interactions occurring in the liquid mixtures which includes solvent-solvent, solvent-solute and solute-solute interactions[32-33]. Table 1 gives the speed of sound of the studied systems at all investigated temperatures and mole fractions. It can be seen that the speed of sound is inversely proportional to the temperature. Figure 2 shows the behaviour of speed of sound for the entire range of mole fraction. From Fig. 2, it is evident that the speed of sound increases as the concentration of [$P^+_{14,6,6,6}$] [Cl^-] increases, while it decreases as the temperature increases.

Excess molar volumes

The excess molar volumes were computed from the experimental densities of pure and binary systems at different temperatures (293.15, 298.15, 303.15, 308.15 and 313.15) K using Eq. (1),

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

where x_i represents the mole fractions, ρ and ρ_i denote the densities of the binary mixtures and pure liquids respectively, M_1 and M_2 denote the molar mass of IL and molar mass of PA respectively, where '1' refers to [$P^+_{14,6,6,6}$] [Cl^-] and '2' refers to propanoic acid. The calculated data for V_m^E are shown in Table 1 for the entire mole fraction range. From these data, it is clear that the investigated IL has a capacity to interact strongly with PA molecules, which may be due to dipolar interactions and hydrogen bonding[14,26]. The negative values for the calculated V_m^E of the binary systems of ([$P^+_{14,6,6,6}$] [Cl^-] + PA) suggest that there is more packing or more attractive interactions occurring between [$P^+_{14,6,6,6}$] [Cl^-] and PA, leading to a reduction in the volume. The other contributions towards the negative values for V_m^E may have resulted from the unlike molecular interactions due to van der Waals or dispersion forces. Furthermore, PA is a polar solvent, and the molecules are held together by hydrogen bonds and are thus expected to exhibit strong H-bonding interactions. This also implies that the anions show tight packing around the cation at all mole fractions; the cations are enclosed by the propanoic acid molecules. These types of interactions were also observed for the ([$P^+_{14,6,6,6}$] [Cl^-] + methanol) system[34]. Figure 3 shows that V_m^E values become more negative as the temperature increases. Across the entire temperature range presented in this work,

Table 1 — Densities (ρ), speed of sound (u), and excess molar volume (V_m^E) of [$P^+_{14, 6,6,6}$] [Cl^-] (1)+propanoic acid (2) binary systems at p = 0.1 MPa

x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	u (m s^{-1})	x_1	ρ (g cm^{-3})	V_m^E (cm^3 mol^{-1})	u (m s^{-1})
293.15 K				298.15 K			
0	0.9934	0	1165.32	0	0.9881	0	1146.65
0.0105	0.9876	-0.0612	1188.89	0.0105	0.9816	-0.0735	1170.64
0.0203	0.9810	-0.1071	1208.89	0.0203	0.9761	-0.1298	1190.94
0.0305	0.9756	-0.1415	1227.81	0.0305	0.9709	-0.1798	1210.12
0.0699	0.9591	-0.2230	1288.49	0.0699	0.9549	-0.2909	1271.56
0.1088	0.9476	-0.2838	1330	0.1088	0.9436	-0.3577	1313.53
0.2131	0.9298	-0.5559	1392.17	0.2131	0.9259	-0.6345	1376.32
0.3301	0.9187	-0.6701	1425.44	0.3301	0.9150	-0.7621	1409.38
0.4361	0.9116	-0.6075	1450.53	0.4361	0.9079	-0.6928	1433.97
0.5301	0.9069	-0.4833	1467.69	0.5301	0.9032	-0.5497	1450.92
0.6333	0.9031	-0.3557	1483.53	0.6333	0.8994	-0.4206	1470.57
0.7601	0.9001	-0.1895	1490.27	0.7601	0.8964	-0.2520	1475.73
1	0.8950	0	1515.13	1	0.8913	0	1495.30
303.15 K				308.15 K			
0	0.9826	0	1127.77	0	0.9772	0	1108.98
0.0105	0.9765	-0.077	1152.22	0.0105	0.9714	-0.0888	1133.91
0.0203	0.9712	-0.1360	1172.83	0.0203	0.9663	-0.1566	1154.81
0.0305	0.9662	-0.1772	1192.26	0.0305	0.9615	-0.2112	1174.48
0.0699	0.9507	-0.2984	1254.44	0.0699	0.9466	-0.3555	1237.41
0.1088	0.9398	-0.3716	1296.89	0.1088	0.9359	-0.4369	1280.33
0.2131	0.9229	-0.6828	1360.31	0.2131	0.9191	-0.7215	1344.41
0.3301	0.9122	-0.7983	1393.35	0.3301	0.9086	-0.8524	1377.45
0.4361	0.9053	-0.7300	1417.58	0.4361	0.9018	-0.7914	1401.38
0.5301	0.9007	-0.5970	1433.83	0.5301	0.8973	-0.6589	1417.16
0.6333	0.8970	-0.4576	1447.93	0.6333	0.8936	-0.5259	1430.76
0.7601	0.8940	-0.2819	1450.48	0.7601	0.8907	-0.3378	1439.79
1	0.8890	0	1476.21	1	0.8856	0	1457.47
315.15 K							
0	0.9718	0	1090.41	0.3301	0.9060	-0.9726	1361.73
0.0105	0.9663	-0.0939	1115.83	0.4361	0.8991	-0.8411	1385.39
0.0203	0.9615	-0.1649	1136.94	0.5301	0.8947	-0.7262	1400.83
0.0305	0.9569	-0.2217	1156.83	0.6333	0.8911	-0.5622	1414.06
0.0699	0.9424	-0.3693	1220.45	0.7601	0.8882	-0.3702	1422.67
0.1088	0.9326	-0.5184	1263.87	1	0.8832	0	1439.33
0.2131	0.9160	-0.7752	1328.62				

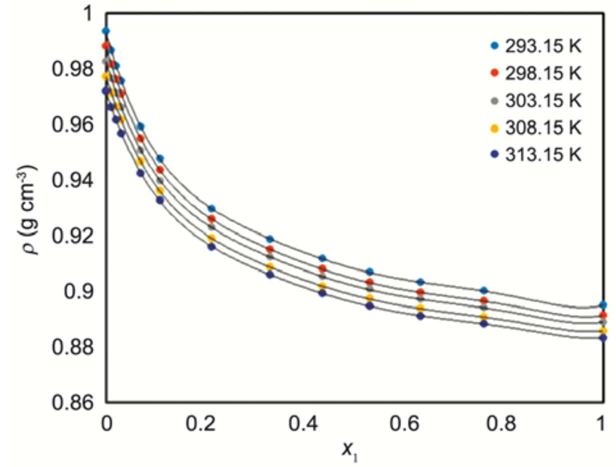

Fig. 1 — Plot of density of the binary mixtures of {[$P^+_{14, 6, 6, 6}$] [Cl^-] (x_1)+propanoic acid (x_2)} as a function of mole fraction at T = (293.15, 298.15, 303.15, 308.15 and 313.15) K.

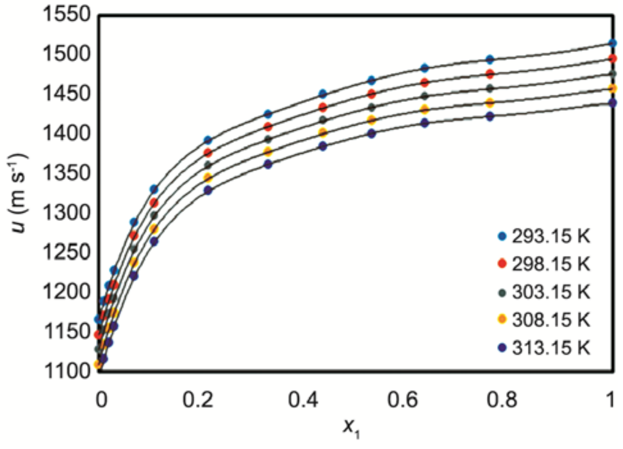

Fig. 2 — Plot of speed of sound (u) for the binary mixtures of {[$P^+_{14, 6, 6, 6}$] [Cl^-](x_1)+propanoic acid (x_2)} as a function of mole fraction of IL at varying temperatures.

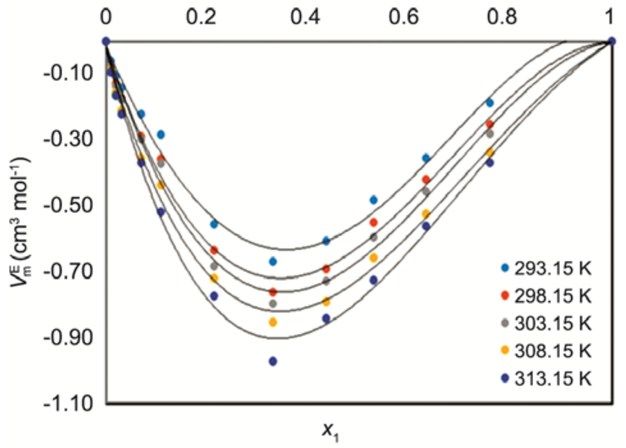

Fig. 3 — Plot of excess molar volume (V_m^E) of the {[P$^+_{14, 6, 6, 6}$] [Cl$^-$] (x_1)+propanoic acid (x_2)} of binary mixture as a function of mole fraction IL at varying temperatures [the plot was fitted by using the Redlich-Kister equation].

the change in $V^E_{m,min}$ ranges from –0.6701 to –0.9726 cm^3 mol^{-1}, and occurs at x_1 = 0.3301, which is not very different from the values reported by McAtee[26] for systems containing [P$^+_{14, 6, 6, 6}$] [Cl$^-$] + methanol.

Apparent molar volume

The density data was used to determine the values of apparent molar volume (V_ϕ) using Eq. (2) (Table 2).

$$V_\phi = \frac{M}{\rho} + \frac{1000}{m}\left(\frac{\rho_1 - \rho}{\rho_1 \rho}\right) \qquad \ldots(2)$$

In Eq. (2), molar mass of solute is represented by M, ρ and ρ_1 denote the densities of the solution and the solvent respectively while, molality of the mixture is represented by m. The derived apparent molar volume values are directly proportional to the temperature. This suggests a strong solute-solvent interaction as illustrated by the observed volume contraction[35]. At a low concentration of the ionic liquid, the ions are enclosed by the propanoic acid molecules which indicate the ion-solvent interaction and an increase in the molality of ionic liquid, increases the ion-ion interaction resulting in high V_ϕ values.

Isentropic compressibility and deviation in isentropic compressibility

Isentropic compressibility, $k_{s,}$ values were determined by the Newton Laplace Eq. (3),

$$k_s = \frac{1}{\rho u^2} \qquad \ldots(3)$$

where ρ denotes the density and u the speed of sound for the prepared mixtures. Deviations in isentropic compressibility (Δk_s) were determined by utilizing Eq. (4).

$$\Delta k_s = k_s - \sum_i^2 \phi k_{s,i} \qquad \ldots(4)$$

Here, k_s and ϕ are isentropic compressibilities and volume fractions of the pure liquids, respectively. The computed values for k_s and Δk_s for the binary systems of PA and [P$^+_{14, 6, 6, 6}$] [Cl$^-$] at all investigated temperatures are given in Table 2. It is evident that the k_s values are inversely proportional to the mole fraction of IL at all examined temperatures; this is due to the increase in thermal agitation allowing the miscible liquids to show increased compressibility[14,33]. Interactions in the binary mixtures lead to a decrease in free-space, and this effect contributes towards the negative values of Δk_s[36]. Furthermore, the negative values of Δk_s (Fig. 4) show that these miscible solutions are less compressible as compared to ideal mixtures.

This observed effect may be due to the closer approach of colliding molecules and significantly stronger interactions between [P$^+_{14, 6, 6, 6}$] [Cl$^-$] + PA mixtures resulting in a decrease in the compressibility of the mixtures. The obtained volumetric data is in good agreement with the theoretical values[14]. The Δk_s values across the mole fraction range of IL decreased with increasing temperature.

Apparent molar isentropic compressibility

The apparent molar isentropic compressibility (K_ϕ) values were determined using Eq. (5).

$$K_\phi = \left[\frac{1000(\rho_0 k_s - k_0 \rho)}{m \rho \rho_0}\right] + \left[\frac{M k_s}{\rho}\right] \qquad \ldots(5)$$

where ρ_0 and ρ indicate densities of the pure solvent and binary mixtures, respectively; m and M denote the molality of the solution and molar mass of solute, k_s and k_0 represent the isentropic compressibilities of the solution and solvent, respectively. From Table 2, it is clear that the K_ϕ values are directly proportional to the concentration of solute except for the molality of 13.53 mol kg^{-1} and 20.71 mol kg^{-1} at 298.15 K and 303.15 K, for the binary systems at all investigated temperatures. A similar trend was observed for the systems of methanol and methyl acetate at low molality, which occurred at 298.15 K and 303.15 K[35].

Table 2 — Molality (m), apparent molar volume (V_ϕ), intermolecular free length (L_f), isentropic compressibility (k_s), apparent molar isentropic compressibility (K_ϕ), and deviation in isentropic compressibility (Δk_s) of ([$P^+_{14,\ 6,6,6}$] [Cl^-](1) + propanoic acid(2)) binary systems at p = 0.1 MPa

x_1	m (mol kg^{-1})	$10^8 \times k_s$ (Pa^{-1})	$10^8 \times \Delta k_s$ (Pa^{-1})	V_ϕ (m^3 mol^{-1})	$10^7 \times L_f$ (m)	$10^{15} \times K_\phi$ (m^3 mol^{-1} Pa^{-1})
293.15 K						
0		74.13	0	0	1.755	0
0.0105	0.1438	71.70	-2.16	573.91	1.726	23.62
0.0203	0.2802	69.75	-3.89	574.71	1.702	24.37
0.0305	0.4217	67.99	-5.40	575.75	1.680	24.51
0.0699	1.0143	62.80	-9.55	577.00	1.615	25.00
0.1088	1.6377	59.66	-11.83	577.72	1.574	25.58
0.2131	3.4230	55.49	-14.02	578.63	1.518	26.63
0.3301	5.6535	53.57	-14.75	579.73	1.492	27.93
0.4361	9.0791	52.14	-13.39	579.75	1.472	28.13
0.5301	13.5314	51.49	-11.22	579.77	1.458	28.03
0.6333	20.7076	50.31	-9.76	579.89	1.466	28.02
0.7601	31.8278	50.18	-7.73	580.23	1.441	28.62
1		48.67	0	0	1.422	0
298.15 K						
0		76.98	0	0	1.804	0
0.0105	0.1438	74.34	-2.36	575.47	1.773	24.22
0.0203	0.2802	72.23	-4.23	576.16	1.747	24.47
0.0305	0.4217	70.33	-5.87	577.19	1.724	24.65
0.0699	1.0143	64.77	-10.34	578.49	1.655	25.29
0.1088	1.6377	61.42	-12.78	579.45	1.611	25.98
0.2131	3.4230	57.01	-15.09	580.67	1.552	27.20
0.3301	5.6535	55.02	-15.81	581.84	1.525	28.39
0.4361	9.0791	53.56	-14.33	581.85	1.504	28.83
0.5301	13.5314	52.59	-12.45	581.99	1.491	28.86
0.6333	20.7076	51.41	-10.75	582.19	1.474	28.75
0.7601	31.8278	51.29	-7.86	582.56	1.471	29.06
1		50.18	0	0	1.456	0
303.15 K						
0		80.01	0	0	1.856	0
0.0105	0.1438	77.14	-2.57	576.62	1.822	24.63
0.0203	0.2802	74.85	-4.61	577.37	1.795	24.69
0.0305	0.4217	72.81	-6.37	578.44	1.771	24.75
0.0699	1.0143	66.84	-11.19	579.89	1.696	25.55
0.1088	1.6377	63.26	-13.81	580.85	1.650	26.34
0.2131	3.4230	58.56	-16.26	581.92	1.588	27.35
0.3301	5.6535	56.47	-16.97	583.20	1.559	29.00
0.4361	9.0791	54.97	-15.36	583.23	1.538	29.63
0.5301	13.5314	54	-13.31	583.41	1.525	29.55
0.6333	20.7076	53.18	-1108	583.64	1.514	29.72
0.7601	31.8278	53.16	-7.91	584.02	1.513	29.97
1		51.62	0	0	1.491	0
308.15 K						
0		83.21	0	0	1.910	0
0.0105	0.1438	80.07	-2.82	577.76	1.874	24.84
0.0203	0.2802	77.59	-5.03	578.57	1.844	24.96
0.0305	0.4217	75.39	-6.95	579.68	1.818	25.04
0.0699	1.0143	68.99	-12.12	581.29	1.739	25.76
0.1088	1.6377	65.18	-14.19	582.47	1.691	26.70
0.2131	3.4230	60.19	-17.52	583.94	1.625	27.82

(*Contd.*)

Table 2 — Molality (m), apparent molar volume (V_ϕ), intermolecular free length (L_f), isentropic compressibility (k_s), apparent molar isentropic compressibility (K_ϕ), and deviation in isentropic compressibility (Δk_s) of ([$P^+_{14,\ 6,6,6}$] [Cl^-](1) + propanoic acid(2)) binary systems at p = 0.1 MPa (*Contd.*)

x_1	m (mol kg^{-1})	$10^8 \times k_s$ (Pa^{-1})	$10^8 \times \Delta k_s$ (Pa^{-1})	V_ϕ (m^3 mol^{-1})	$10^7 \times L_f$ (m)	$10^{15} \times K_\phi$ (m^3 mol^{-1} Pa^{-1})
			308.15 K (*Contd.*)			
0.3301	5.6535	58.01	-18.19	585.23	1.595	29.69
0.4361	9.0791	56.47	-16.45	585.29	1.574	30.39
0.5301	13.5314	55.49	-14.24	585.50	1.559	30.39
0.6333	20.7076	54.66	-11.84	585.74	1.548	30.61
0.7601	31.8278	54.16	-8.95	586.16	1.541	30.81
1		53.16	0	0	1.527	0
			313.15 K			
0		86.54	0	0	1.966	0
0.0105	0.1438	83.12	-3.09	578.87	1.926	24.96
0.0203	0.2802	80.46	-5.46	579.77	1.895	25.17
0.0305	0.4217	78.09	-7.52	580.93	1.867	25.36
0.0699	1.0143	71.24	-13.07	582.69	1.783	25.99
0.1088	1.6377	67.13	-16.10	583.31	1.731	26.96
0.2131	3.4230	61.85	-18.83	585.26	1.662	28.07
0.3301	5.6535	59.52	-19.52	586.42	1.630	30.29
0.4361	9.0791	57.95	-17.61	586.75	1.609	31.11
0.5301	13.5314	56.96	-15.22	586.96	1.592	31.18
0.6333	20.7076	56.16	-12.60	587.23	1.583	31.47
0.7601	31.8278	55.63	-9.53	587.71	1.576	31.70
1		54.65	0	0	1.562	0

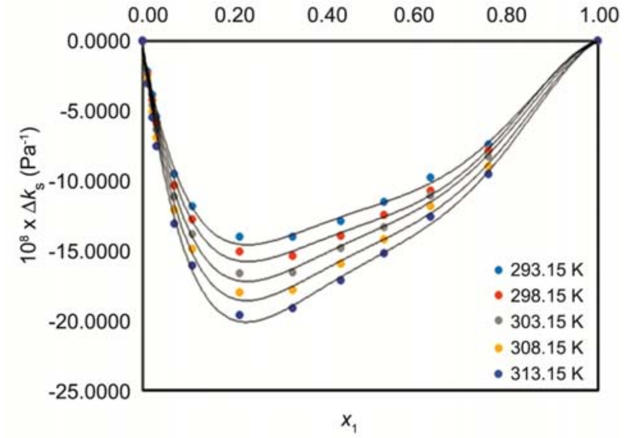

Fig. 4 — Plot of deviation in isentropic compressibility (Δk_s) of the binary mixtures of {[$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] (x_1)+propanoic acid(x_2)} as a function of mole fraction of IL at varying temperatures.

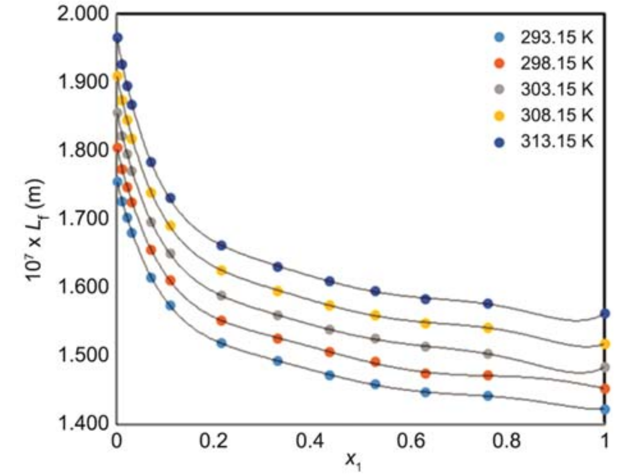

Fig. 5 — Plot of intermolecular free length (L_f) of the binary mixtures of {[$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] (x_1)+propanoic acid (x_2) given as a function of mole fraction of IL at varying temperatures.

Intermolecular free length

Intermolecular forces (IMFs) are the forces which mediate interaction between molecules, including forces of attraction or repulsion which act between the molecules and other types of neighbouring particles, e.g., atoms or ions. Intermolecular free length (L_f) values were computed from the Jacobson's empirical relation and isentropic compressibility given by Eq. (6).

$$L_f = k_j\ (k_s)^{1/2} \quad \ldots(6)$$

where k_j is the Jacobson's constant which is temperature dependent (93.875 + 0.375 T)×10^{-8} and k_s denotes isentropic compressibilities. The L_f values for the binary systems of [$P^+_{14,\ 6,\ 6,\ 6}$] [Cl^-] + PA is given in Table 2, across the investigated temperatures and entire mole fraction range, and the plot is given in Fig. 5. Intermolecular free length was mainly calculated to investigate the properties of liquids involving attractive and repulsive forces. The attractive forces between the molecules depend on the distance between their centres, while the distance between the surface of the molecules is indicative of the repulsive forces.

It is not easy to estimate the intermolecular length between the centres of attraction, since these centres are not aligned with structural centres of the solute and solvent molecules. Furthermore, the speed of sound variation in the liquid systems plays an important and essential role in examining the intermolecular free length. From Table 2 and Fig. 5, it is evident that the speed of sound and intermolecular free length are related inversely. Between two molecules, the considerable space or interval between the surfaces is determined by simply increasing the intermolecular free length, and additionally reducing the speed of sound. This is important for determining the nature of molecular interactions across the constituents in the liquid systems.

Correlation of the derived properties

The derived parameters (excess molar volume and deviation in isentropic compressibility) of the $[P^+_{14,6,6,6}]$ $[Cl^-]$ IL + PA system were fitted to Redlich-Kister equation. The fitting parameter A_i values were determined by the least square technique (See Supplementary Data, Table S2). The standard deviation (σ) for the excess molar volumes and deviation in isentropic compressibility, are very low at all investigated temperatures, indicating a good correlation with the experimental values.

Conclusions

Based on the computed values, the excess parameters of the completely miscible systems of $[P^+_{14,6,6,6}][Cl^-]$ + PA, were calculated from speeds of sound and densities to investigate the intermolecular interactions between the mixtures. Negative deviations from the ideal mixing behaviour were observed at all the investigated ionic liquid mole fractions and temperatures. The negative excess molar volumes indicate strong interactions between the IL and PA. Across the entire concentration range of IL, the computed excess molar volumes were negative, showing easy accommodation of PA in the voids of IL molecules with the minima between 0.3631 and 0.3374 mole fraction of IL. In the present study, the ions are enclosed only by the solvent and the positive and high apparent molar volume values indicate strong ion-solvent interaction. Also, the interaction becomes stronger as the temperature rises. The Redlich-Kister equation was used to fit all calculated excess property data. The results obtained in this work are useful for the interpretation of the nature of intermolecular interactions and the influence of temperature, for binary mixtures of $[P^+_{14,6,6,6}]$ $[Cl^-]$ IL with PA.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_57A(06)753-760_SupplData.pdf.

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