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Thermophysical properties of alkyl acetates in aqueous solutions of ionic liquid {1-butyl-3-methylimidazolium chloride} [bmim][Cl] at different temperatures

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Volumetric and acoustic methods have been used to study the interactions of alkyl acetates with the ionic liquid 1-butyl-3-methylimidazolium chloride [bmim][Cl] as a function of temperature. The density, ρ, and speed of sound, u, of methyl acetate, ethyl acetate and butyl acetate in aqueous 1-butyl-3-methylimidazolium chloride solutions have been measured in the temperature interval T = (288.15, 293.15, 298.15, 303.15 and 308.15) K and atmospheric pressure. In the present work, the apparent molar volumes (V_ϕ), limiting partial molar volumes (V^0_ϕ), transfer volumes at infinite dilution (ΔV^0_ϕ), adiabatic compressibility ($K_{\phi,s}$) limiting partial molar adiabatic compressibility ($K^0_{\phi,s}$) and the infinite dilution partial molar expansibilities (ϕ^0_E) along with Hepler's constant values, ($\partial^2 V^0_\phi/\partial T^2$) of alkyl acetates in aqueous ionic liquid solution at the measured temperatures, have been reported. The results have been interpreted in terms of intermolecular interactions capable of existing within the mixture containing ionic liquid and the ester molecules.

Keywords: Ionic liquid, Alkyl acetate, Apparent molar volume, Apparent molar adiabatic compressibility, Apparent molar expansivity

1 Introduction

The research on ionic liquids has gained momentum in the recent years. The high thermal stability[1], adjustable viscosity, non flammability[2], wide liquidus range[3], immeasurably low vapour pressure[4,5], high heat capacity, high conductivity, large electrochemical window[6] and special phase behaviour of ionic liquid thrust themselves into attention. These environmentally friendly solvents are a successful replacement with the abundantly used molecular solvents[7-13]. They also hand over the extra opportunity to judiciously select cations and anions which exert an efficient control over the properties of ionic liquid and the possible number to permutations and combinations of cations and anions account to a large indefinite number[14,15]. The meritorious qualities of ionic liquid make them eligible for a variety of applications in industrial areas. Various studies have been carried out upon the ionic liquids and their mixtures to understand their physical and thermodynamic properties[16-27]. However, a little is known about the physico-chemical behaviour of mixtures comprising of ionic liquids and ester[28-33]. That is why a step has been taken forward for the comprehensive coverage of data on the themodynamic properties of 1-butyl-3-methyl imidazolium chloride with alkyl acetates. The ultrasonic speed may be considered as a thermodynamic property, provided that a negligible amount of ultrasonic absorption of the acoustic waves of low frequency and low amplitude is observed; in which case, the ultrasonic absorption of the acoustic waves is negligible[34]. There is a negligible ultrasonic absorption of acoustic waves for the systems investigated in the presently studied systems. The results obtained through these measurements have been used to calculate different parameters, *i.e.,* apparent molar volume (V_ϕ), apparent molar adiabatic compressibility ($K_{\phi,s}$), partial molar volume (V^0_ϕ) and partial molar adiabatic compressibility ($K^0_{\phi,s}$) at infinite dilution. Then, these parameters are used to compute transfer parameters ΔV^0_ϕ and ΔK^0_ϕ, limiting apparent molar expansivity ϕ^0_E and values of the Hepler constant ($\partial^2 V^0_\phi/\partial T^2$) for alkyl acetates in aqueous ionic liquid solutions.

2 Experimental Details

1-Butyl-3-methylimidazolium chloride [bmim][Cl] with mass fraction > 0.98 was obtained from Sigma Aldrich, USA. Methyl acetate (MA) (Merck-Schuchardt, Germany, zur synthese GC > 0.99), ethyl acetate (EA) (S D Fine Chemicals Ltd, India, GC 0.995) and n-butyl acetate (BA) (SISCO Research

Laboratories Pvt Ltd, India, GC 0.99) have been used in this study. The ionic liquid, 1-butyl-3-methylimidazolium chloride was dried under high vacuum at 70°C overnight. The water content was reduced to less than 350 ppm which was indicated by the Karl-Fisher analysis of the samples. The ionic liquid was also characterized using ^{1}H NMR (Bruker 300 MHz) and IR (ABB MB3000) to make sure that there are no major impurities. All the organic solvents have been used after drying over 0.4 nm molecular sieves and under vacuum at ambient conditions. Degassed and double distilled water (specific conductance $<10^{-6}$ Scm^{-1}) was used for the preparation of the aqueous solutions. The details of the chemicals used in this study are provided in Table 1.

2.1 Density and Speed of Sound Measurements

All the solutions that have been used in the measurements were made afresh in triply distilled and degassed water (specific conductance $<10^{-6}$ Scm^{-1}) on A&D Co. limited electronic balance (Japan, model GR-202). Uncertainty in the solution concentration was estimated at ± 2 $\times10^{-5}$ mol·kg^{-1} in calculations. An automated vibrating tube densimeter (Anton Paar DSA 5000) has been used to measure density and speed of sound. A density check or an air/water adjustment was performed at 20°C with triply distilled, degassed water and with dry air at atmospheric pressure. The calibration of densimeter was done with triple distilled and degassed water in the experimental temperature range. Considering the sensitivity of density and speed of sound to temperature, it was controlled to ± 1 × 10^{-2} K by a built-in Peltier device. The sensitivity of the instrument corresponds to a precision in density and speed of sound measurements of 1 $\times10^{-3}$ kg·m^{-3} and 1 $\times10^{-2}$ ms^{-1}. In light of the full accuracies of all factors involved in the density readings, standard uncertainty of the density and speeds of sound are within ± 2 × 10^{-3} kg·m^{-3} and ± 3 × 10^{-2} m·s^{-1}, respectively. The measurements have been performed in triplicate to confirm the reproducibility of the results.

3 Results and Discussion

3.1 Apparent Molar Quantities

The experimental densities, ρ and speeds of sound, u at temperatures T = (288.15, 293.15, 298.15, 303.15, and 308.15) K of methyl acetate (MA), ethyl acetate (EA) and butyl acetate (BA) in binary aqueous solutions of 1-butyl-3-methyl imidazolium chloride [bmim][Cl] (ranging from pure water to 0.3068 mol·kg^{-1}) have been reported in Table 2. The apparent molar volume V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ have been calculated from the experimental densities and speeds of sound by the following Eqs.

$$V_\phi = M / \rho - \{1000(\rho - \rho_0) / m\rho\rho_0\} \quad \ldots(1)$$

$$K_{\phi,s} = M\kappa_S / \rho - \{1000(\kappa_{s,0}\rho - \kappa_s \rho_0) / m\rho\rho_0\} \quad \ldots(2)$$

$$\kappa_s = 1/(u^2\rho) \quad \ldots(3)$$

where m is the solution molality (mol·kg^{-1}) of solution (alkyl acetates + water), M is the molar mass of the solute (kg·mol^{-1}) ionic liquid and ρ_0, ρ, $\kappa_{s,0}$ and κ_s are the densities (kg·m^{-3}) and coefficient of adiabatic compressibility (Pa^{-1}) of solvent and solution, respectively. For determination of apparent molar volumes and apparent molar adiabatic compressibilities in ternary systems, that is, V_ϕ and $K_{\phi,s}$ for alkyl acetates, the mixed solvent (water + ionic liquid) consisted of fixed concentration (0.11-0.30 mol·kg^{-1}) of ionic liquid, while the concentration of the investigated alkyl acetates was varied between 0.05 and 0.92 mol·kg^{-1}. However, for butyl acetate V_ϕ and $K_{\phi,s}$ were measured only for 0.07 < m >0.54 due to difficulty and unfavourable interactions arising from different miscibilities of components. The resulting values of V_ϕ, and $K_{\phi,s}$ and molalities, m of alkyl acetates in fixed concentrations of IL at various temperatures are reported in Table 3. The values of V_ϕ for methyl acetate in 0.1106 mol·kg^{-1} aqueous

Table 1 — Specification of chemical samples

Chemical name	CAS No.	Provenance	Mass fraction purity
1-Butyl-3-methyl-imidazolium chloride	79917-90-1	Sigma-Aldrich, USA	> 0.98
Methyl acetate	79-20-9	Merck, Germany	> 0.99
Ethyl acetate	141-78-6	SD Fine Chem Ltd,,India	0.995
Butyl acetate	123-86-4	Sisco Research Lab Pvt. Ltd., India	0.99

Table 2 — Values of densities, ρ and speeds of sound, u of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures and atmospheric pressure

[a]m/mol·kg^{-1}	[b]$\rho\times10^{-3}$ / kg·m^{-3}					u / m·s^{-1}				
	T=288.15K	T=293.15K	T=298.15 K	T=303.15K	T=308.15K	T=288.15K	T=293.15K	T=298.15K	T=303.15K	T=308.15K
Methyl acetate + 0.0000 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999113	0.998227	0.997072	0.995677	0.994062	1466.69	1482.47	1496.62	1508.98	1519.62
0.0912	0.999379	0.998448	0.997256	0.995828	0.994133	1470.78	1486.10	1499.78	1511.70	1521.93
0.1795	0.999629	0.998652	0.997428	0.995967	0.994252	1475.08	1490.20	1503.50	1514.70	1524.35
0.2929	0.999938	0.998909	0.997641	0.996135	0.994392	1479.33	1493.42	1506.11	1517.08	1526.44
0.3492	1.000084	0.999031	0.997739	0.996221	0.994459	1476.53	1491.12	1504.17	1515.47	1525.14
0.4451	1.000324	0.999239	0.997902	0.996351	0.994566	1483.73	1497.40	1509.50	1519.94	1528.80
0.5460	1.000575	0.999442	0.998071	0.996488	0.994669	1491.95	1504.49	1515.53	1524.99	1532.94
0.6928	1.000921	0.999719	0.998306	0.996669	0.994804	1497.37	1509.12	1519.42	1528.22	1535.54
0.7952	1.001139	0.999916	0.998449	0.996788	0.994892	1500.59	1512.13	1522.06	1530.51	1537.55
0.9128	1.001388	1.000133	0.998629	0.996919	0.994986	1504.24	1514.88	1524.24	1532.15	1538.66
Methyl acetate + 0.1106 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999251	0.998358	0.997201	0.995800	0.994182	1468.25	1483.95	1498.00	1510.25	1520.80
0.0555	0.999405	0.998495	0.997318	0.995893	0.994260	1470.90	1486.64	1500.42	1512.36	1522.37
0.1176	0.999574	0.998646	0.997444	0.995994	0.994342	1474.17	1489.04	1502.42	1514.07	1524.05
0.1834	0.999750	0.998801	0.997575	0.996096	0.994425	1477.43	1492.31	1505.33	1516.51	1526.18
0.2938	1.000043	0.999055	0.997785	0.996260	0.994553	1482.97	1496.71	1509.02	1519.65	1528.70
0.3960	1.000306	0.999288	0.997971	0.996401	0.994658	1483.80	1497.85	1510.16	1520.63	1529.34
0.5177	1.000614	0.999552	0.998182	0.996558	0.994770	1488.32	1501.35	1512.97	1522.98	1531.44
0.6036	1.000821	0.999731	0.998321	0.996662	0.994837	1489.94	1502.83	1514.22	1524.01	1532.28
0.6994	1.001051	0.999921	0.998481	0.996770	0.994911	1499.13	1510.98	1521.18	1529.77	1537.19
0.8132	1.001321	1.000144	0.998661	0.996882	0.994985	1503.44	1514.24	1523.82	1531.96	1538.67
0.9153	1.001552	1.000338	0.998812	0.996990	0.995038	1506.73	1517.55	1526.74	1534.39	1540.37
Methyl acetate + 0.3068 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999561	0.998654	0.997482	0.996071	0.994443	1471.58	1487.11	1500.97	1513.06	1523.44
0.0747	0.999765	0.998835	0.997635	0.996199	0.994549	1475.83	1490.85	1504.27	1515.94	1525.94
0.1785	1.000032	0.999065	0.997828	0.996360	0.994682	1480.57	1495.03	1507.88	1519.00	1528.51
0.2898	1.000299	0.999287	0.998011	0.996514	0.994808	1485.21	1499.02	1511.29	1521.90	1530.93
0.3603	1.000461	0.999413	0.998118	0.996599	0.994880	1487.96	1501.42	1513.44	1523.64	1532.38
0.4694	1.000691	0.999591	0.998264	0.996721	0.994980	1492.72	1505.46	1516.71	1526.38	1534.54
0.5558	1.000861	0.999722	0.998361	0.996802	0.995040	1483.67	1497.59	1510.02	1520.74	1529.89
0.6832	1.001103	0.999887	0.998478	0.996895	0.995120	1487.33	1500.88	1512.89	1523.26	1532.05
0.7928	1.001281	0.999995	0.998571	0.996961	0.995170	1505.37	1516.54	1526.13	1534.17	1541.21
0.9081	1.001476	1.000102	0.998641	0.997002	0.995200	1493.41	1505.99	1517.16	1526.76	1534.86
Ethyl acetate + 0.0000 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999113	0.998227	0.997072	0.995677	0.994062	1466.69	1482.47	1496.62	1508.98	1519.62
0.0876	0.999162	0.998235	0.997038	0.995622	0.993992	1471.93	1487.13	1500.72	1512.55	1522.67
0.1597	0.999197	0.998239	0.997008	0.995574	0.993929	1476.00	1490.78	1503.95	1515.38	1525.15
0.2659	0.999251	0.998239	0.996962	0.995495	0.993831	1473.94	1488.96	1502.35	1514.01	1523.98
0.3963	0.999305	0.998239	0.996897	0.995395	0.993695	1480.85	1494.95	1507.51	1518.35	1527.58
0.4685	0.999332	0.998231	0.996869	0.995331	0.993616	1490.37	1503.25	1514.62	1524.38	1532.59
0.5572	0.999359	0.998227	0.996829	0.995249	0.993511	1494.47	1506.81	1517.62	1526.87	1534.63
0.6954	0.999408	0.998205	0.996749	0.995121	0.993332	1500.47	1511.91	1521.94	1530.43	1537.48

Contd —

Table 2 — Values of densities, ρ and speeds of sound, u of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures and atmospheric pressure — *Contd*

[a]m/mol·kg^{-1}	[b]$\rho\times10^{-3}$ / kg·m^{-3}					u / m·s^{-1}				
	T=288.15K	T=293.15K	T=298.15 K	T=303.15K	T=308.15K	T=288.15K	T=293.15K	T=298.15K	T=303.15K	T=308.15K
Ethyl acetate + 0.0000 mol·kg^{-1} [bmim][Cl]										
0.7958	0.999451	0.998196	0.996702	0.995014	0.993202	1504.03	1514.92	1524.44	1532.47	1539.08
0.9000	0.999472	0.998188	0.996641	0.994902	0.993039	1505.68	1516.32	1525.59	1533.39	1539.80
Ethyl acetate + 0.1106 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999251	0.998358	0.997201	0.995800	0.994182	1468.25	1483.95	1498.00	1510.25	1520.80
0.0754	0.999285	0.998362	0.997179	0.995749	0.994098	1473.01	1488.11	1501.65	1513.46	1523.57
0.1641	0.999319	0.998363	0.997148	0.995684	0.993996	1478.27	1493.13	1506.12	1517.27	1526.57
0.2693	0.999359	0.998363	0.997109	0.995602	0.993869	1482.27	1496.62	1509.15	1519.85	1529.00
0.3746	0.999394	0.998357	0.997059	0.995514	0.993738	1489.47	1502.84	1514.48	1524.32	1533.16
0.4775	0.999421	0.998348	0.997015	0.995421	0.993603	1495.03	1507.36	1518.20	1527.48	1535.26
0.5514	0.999443	0.998341	0.996979	0.995350	0.993505	1498.53	1510.30	1520.69	1529.55	1536.93
0.6797	0.999469	0.998334	0.996906	0.995211	0.993331	1500.91	1512.66	1522.79	1532.77	1539.57
0.7773	0.999490	0.998326	0.996845	0.995111	0.993189	1508.09	1518.38	1527.4	1534.99	1541.2
0.8922	0.999502	0.998315	0.996769	0.994976	0.993023	1510.78	1520.96	1529.59	1536.74	1542.77
Ethyl acetate + 0.3068 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999561	0.998654	0.997482	0.996071	0.994443	1471.58	1487.11	1500.97	1513.06	1523.44
0.0810	0.999611	0.998679	0.997479	0.996045	0.994401	1474.72	1489.85	1503.37	1515.14	1525.22
0.1611	0.999655	0.998697	0.997469	0.996011	0.994350	1475.75	1490.75	1504.16	1515.82	1525.81
0.2707	0.999711	0.998715	0.997445	0.995952	0.994266	1477.13	1492.00	1505.29	1516.84	1526.72
0.3811	0.999761	0.998721	0.997407	0.995875	0.994167	1492.32	1505.24	1516.65	1526.46	1534.72
0.4677	0.999801	0.998722	0.997371	0.995806	0.994081	1495.25	1507.76	1518.80	1528.26	1536.20
0.5555	0.999834	0.998719	0.997332	0.995722	0.993982	1502.66	1514.11	1524.16	1532.70	1539.79
0.7035	0.999882	0.998699	0.997231	0.995569	0.993789	1505.04	1516.14	1525.86	1534.08	1540.88
0.8139	0.999917	0.998665	0.997149	0.995441	0.993633	1508.68	1519.22	1528.41	1536.14	1542.48
0.8945	0.999949	0.998651	0.997113	0.995351	0.993521	1511.25	1521.38	1530.18	1537.55	1543.55
Butyl acetate + 0.0000 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999113	0.998227	0.997072	0.995677	0.994062	1466.69	1482.47	1496.62	1508.98	1519.62
0.0868	0.998959	0.998058	0.996885	0.995473	0.993839	1472.09	1487.32	1500.92	1512.56	1522.39
0.1730	0.998837	0.997922	0.996729	0.995305	0.993655	1472.33	1487.57	1501.04	1512.41	1522.21
0.2749	0.998731	0.997805	0.996591	0.995151	0.993484	1472.33	1487.76	1501.28	1512.95	1522.43
0.3980	0.998656	0.997709	0.996475	0.995015	0.993341	1472.58	1487.64	1501.03	1512.41	1522.21
0.4754	0.998639	0.997681	0.996429	0.994969	0.993289	1472.40	1486.58	1501.14	1512.56	1522.35
Butyl acetate + 0.1106 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999251	0.998358	0.997201	0.995800	0.994182	1468.25	1483.95	1498.00	1510.25	1520.80
0.0796	0.999124	0.998215	0.997050	0.995644	0.994019	1472.69	1487.93	1501.55	1513.40	1523.55
0.1735	0.999001	0.998079	0.996905	0.995493	0.993860	1473.24	1488.76	1502.33	1514.13	1523.85
0.2680	0.998905	0.99798	0.996790	0.995375	0.993736	1474.42	1489.02	1501.90	1513.78	1522.86
0.3870	0.998829	0.997889	0.996690	0.995268	0.993630	1473.90	1489.20	1502.61	1514.06	1523.10
0.4777	0.998795	0.997862	0.996650	0.995220	0.993585	1474.29	1489.16	1502.04	1513.32	1523.08
0.5417	0.998791	0.997851	0.996640	0.995205	0.993568	1473.89	1489.23	1502.65	1514.28	1523.36
Butyl acetate + 0.3068 mol·kg^{-1} [bmim][Cl]										
0.0000	0.999561	0.998654	0.997482	0.996071	0.994443	1471.58	1487.11	1500.97	1513.06	1523.44
0.0803	0.999491	0.998576	0.997398	0.995990	0.994362	1476.57	1491.81	1505.25	1516.85	1526.50
0.1134	0.999465	0.998547	0.997367	0.995959	0.994332	1477.12	1491.98	1505.27	1516.61	1526.18

Contd —

Table 2 — Values of densities, ρ and speeds of sound, u of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures and atmospheric pressure — *Contd*

[a]m/mol·kg^{-1}	[b]$\rho\times10^{-3}$ / kg·m^{-3}					u / m·s^{-1}				
	T=288.15K	T=293.15K	T=298.15 K	T=303.15K	T=308.15K	T=288.15K	T=293.15K	T=298.15K	T=303.15K	T=308.15K
					Butyl acetate + 0.3068 mol·kg^{-1} [bmim][Cl]					
0.2006	0.999408	0.998482	0.997295	0.995891	0.994265	1477.19	1492.10	1505.31	1516.43	1525.97
0.3131	0.999355	0.998421	0.997227	0.995823	0.994199	1477.02	1491.91	1505.21	1516.70	1526.29
0.3956	0.999335	0.998390	0.997190	0.995789	0.994169	1477.21	1492.10	1505.37	1516.53	1526.07
0.5056	0.999321	0.998365	0.997166	0.995766	0.994143	1477.67	1492.58	1505.52	1516.60	1526.14

[a]m is the molality of alkyl acetate; [b]Standard uncertainties σ (ρ) in densities measurements are $\pm 2\times10^{-3}$ kg·m^{-3} and σ (u) in speeds of sound measurements are $\pm 3\times10^{-1}$ m·s^{-1}. Standard uncertainties σ (T) in temperature measurements are ±0.01 K.

Table 3 — Values of apparent molar volumes V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures and atmospheric pressure

[a]m/mol·kg^{-1}	$V_\phi\times10^6$/ m^3·mol^{-1}					$K_{\phi,s}\times10^6$/ m^3·mol^{-1}·GPa^{-1}				
	T=288.15 K	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15 K	T=288.15 K	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15K
					Methyl acetate + water					
0.0912	71.21	71.78	72.28	72.75	73.10	-45.96	-45.03	-44.19	-43.43	-42.87
0.1795	71.24	71.82	72.30	72.78	73.13	-46.22	-45.29	-44.44	-43.68	-43.11
0.2929	71.27	71.84	72.32	72.82	73.18	-46.34	-45.40	-44.54	-43.78	-43.21
0.3492	71.30	71.86	72.35	72.82	73.20	-46.37	-45.42	-44.57	-43.81	-43.23
0.4451	71.34	71.87	72.38	72.85	73.23	-46.41	-45.46	-44.61	-43.84	-43.27
0.5460	71.36	71.90	72.40	72.87	73.27	-46.44	-45.49	-44.63	-43.87	-43.29
0.6928	71.40	71.95	72.43	72.91	73.32	-46.48	-45.52	-44.66	-43.89	-43.31
0.7952	71.45	71.97	72.47	72.93	73.35	-46.50	-45.54	-44.68	-43.90	-43.32
0.9128	71.48	71.98	72.48	72.96	73.39	-46.52	-45.56	-44.69	-43.92	-43.33
					Methyl acetate + 0.1106 mol·kg^{-1} [bmim][Cl]					
0.0555	71.35	71.73	72.19	72.72	73.12	-45.54	-44.61	-43.78	-43.03	-42.46
0.1176	71.37	71.74	72.21	72.74	73.16	-45.99	-45.05	-44.21	-43.45	-42.88
0.1834	71.38	71.76	72.23	72.77	73.18	-46.14	-45.20	-44.35	-43.59	-43.02
0.2938	71.38	71.78	72.27	72.80	73.24	-46.25	-45.30	-44.45	-43.69	-43.11
0.3960	71.39	71.79	72.29	72.84	73.29	-46.30	-45.35	-44.50	-43.73	-43.16
0.5177	71.40	71.81	72.33	72.88	73.35	-46.34	-45.39	-44.53	-43.76	-43.19
0.6036	71.42	71.83	72.36	72.91	73.39	-46.36	-45.41	-44.55	-43.78	-43.20
0.6994	71.43	71.85	72.37	72.94	73.43	-46.38	-45.43	-44.57	-43.80	-43.22
0.8132	71.43	71.88	72.39	72.99	73.48	-46.41	-45.45	-44.59	-43.81	-43.23
0.9153	71.45	71.89	72.41	73.01	73.52	-46.42	-45.47	-44.60	-43.82	-43.24
					Methyl acetate + 0.3068 mol·kg$^{=1}$ [bmim][Cl]					
0.0747	71.37	71.75	72.22	72.66	73.08	-45.57	-44.64	-43.80	-43.15	-42.48
0.1785	71.44	71.85	72.31	72.74	73.15	-45.95	-45.01	-44.16	-43.50	-42.83
0.2898	71.51	71.95	72.41	72.82	73.22	-46.06	-45.11	-44.26	-43.60	-42.93
0.3603	71.55	72.02	72.46	72.88	73.26	-46.10	-45.15	-44.29	-43.63	-42.96
0.4694	71.62	72.12	72.55	72.95	73.32	-46.14	-45.19	-44.33	-43.66	-42.99
0.5558	71.68	72.18	72.63	73.01	73.39	-46.16	-45.20	-44.35	-43.68	-43.01
0.6832	71.74	72.29	72.74	73.11	73.46	-46.18	-45.23	-44.37	-43.70	-43.03
0.7928	71.81	72.39	72.82	73.19	73.53	-46.20	-45.24	-44.38	-43.71	-43.04
0.9081	71.86	72.48	72.91	73.28	73.61	-46.22	-45.25	-44.39	-43.72	-43.05
					Ethyl acetate + water					
0.0876	87.62	88.17	88.75	89.12	89.43	-45.93	-45.00	-44.16	-43.40	-42.84
0.1597	87.65	88.19	88.77	89.14	89.47	-46.17	-45.24	-44.39	-43.63	-43.06
0.2659	87.65	88.22	88.79	89.18	89.51	-46.29	-45.35	-44.50	-43.74	-43.17
0.3963	87.68	88.23	88.82	89.22	89.58	-46.35	-45.41	-44.55	-43.79	-43.22
0.4685	87.70	88.25	88.81	89.25	89.61	-46.37	-45.42	-44.57	-43.80	-43.23
0.5572	87.72	88.26	88.82	89.29	89.66	-46.39	-45.44	-44.58	-43.82	-43.24

Contd —

Table 3 — Values of apparent molar volumes V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures and atmospheric pressure — *Contd*

[a]m/mol·kg^{-1}	$V_\phi \times 10^6$/ m^3·mol^{-1}					$K_{\phi,s} \times 10^6$/ m^3·mol^{-1}·GPa^{-1}				
	T=288.15 K	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15 K	T=288.15 K	T=293.15 K	T=298.15 K	T=303.15 K	T=308.15K
Ethyl acetate + water										
0.6954	87.73	88.30	88.86	89.33	89.73	-46.41	-45.46	-44.59	-43.83	-43.25
0.7958	87.73	88.30	88.86	89.37	89.78	-46.42	-45.46	-44.60	-43.83	-43.25
0.9000	87.75	88.31	88.88	89.41	89.85	-46.42	-45.47	-44.60	-43.83	-43.25
Ethyl acetate + 0.1106 mol·kg^{-1} [bmim][Cl]										
0.0754	87.72	88.20	88.65	89.15	89.73	-45.76	-44.83	-43.98	-43.23	-42.67
0.1641	87.75	88.22	88.68	89.19	89.76	-46.09	-45.15	-44.30	-43.54	-42.98
0.2693	87.76	88.23	88.70	89.22	89.80	-46.20	-45.26	-44.41	-43.65	-43.08
0.3746	87.78	88.25	88.74	89.26	89.83	-46.25	-45.31	-44.45	-43.69	-43.12
0.4775	87.80	88.27	88.76	89.30	89.87	-46.28	-45.33	-44.47	-43.71	-43.14
0.5514	87.81	88.28	88.77	89.33	89.89	-46.30	-45.35	-44.49	-43.72	-43.15
0.6797	87.83	88.29	88.81	89.39	89.93	-46.32	-45.36	-44.50	-43.73	-43.15
0.7773	87.84	88.30	88.84	89.42	89.97	-46.33	-45.37	-44.50	-43.74	-43.16
0.8922	87.87	88.30	88.87	89.47	90.01	-46.33	-45.37	-44.51	-43.74	-43.16
Ethyl acetate + 0.3068 mol·kg^{-1} [bmim][Cl]										
0.0810	87.52	87.92	88.37	88.77	89.12	-45.61	-44.64	-43.80	-43.14	-42.48
0.1611	87.55	87.96	88.41	88.83	89.18	-45.90	-44.97	-44.11	-43.46	-42.79
0.2707	87.58	87.99	88.47	88.90	89.26	-46.02	-45.07	-44.22	-43.56	-42.89
0.3811	87.60	88.04	88.53	88.98	89.34	-46.07	-45.12	-44.26	-43.60	-42.94
0.4677	87.61	88.07	88.57	89.04	89.40	-46.09	-45.15	-44.29	-43.63	-42.96
0.5555	87.63	88.10	88.61	89.11	89.46	-46.11	-45.16	-44.30	-43.64	-42.97
0.7035	87.66	88.16	88.71	89.21	89.58	-46.13	-45.17	-44.31	-43.65	-42.97
0.8139	87.68	88.21	88.77	89.28	89.65	-46.14	-45.18	-44.31	-43.65	-42.98
0.8945	87.68	88.23	88.77	89.32	89.70	-46.15	-45.19	-44.32	-43.65	-42.98
Butyl acetate + water										
0.0868	118.05	118.33	118.66	119.02	119.42	-45.92	-44.99	-44.15	-43.39	-42.83
0.1730	117.89	118.16	118.51	118.84	119.23	-46.18	-45.25	-44.40	-43.64	-43.07
0.2749	117.69	117.94	118.30	118.62	119.00	-46.28	-45.34	-44.49	-43.73	-43.16
0.3980	117.46	117.72	118.06	118.39	118.73	-46.33	-45.38	-44.53	-43.77	-43.20
0.4754	117.31	117.57	117.92	118.22	118.55	-46.34	-45.40	-44.55	-43.79	-43.21
Butyl acetate + 0.1106 mol·kg^{-1} [bmim][Cl]										
0.0796	117.85	118.16	118.39	118.61	118.88	-45.78	-44.85	-44.01	-43.26	-42.69
0.1735	117.71	117.99	118.22	118.44	118.71	-46.09	-45.16	-44.31	-43.55	-42.98
0.2680	117.58	117.80	118.06	118.27	118.54	-46.18	-45.24	-44.39	-43.63	-43.06
0.3870	117.38	117.61	117.86	118.07	118.31	-46.23	-45.29	-44.44	-43.68	-43.10
0.4777	117.25	117.44	117.70	117.92	118.14	-46.25	-45.31	-44.46	-43.70	-43.12
0.5417	117.15	117.34	117.58	117.81	118.03	-46.26	-45.32	-44.46	-43.71	-43.13
Butyl acetate + 0.3068 mol·kg^{-1} [bmim][Cl]										
0.0803	117.09	117.29	117.50	117.63	117.82	-45.60	-44.67	-43.83	-43.18	-42.51
0.1134	117.07	117.27	117.48	117.61	117.79	-45.77	-44.84	-43.99	-43.33	-42.67
0.2006	116.99	117.19	117.40	117.53	117.71	-45.94	-45.01	-44.16	-43.50	-42.83
0.3131	116.89	117.09	117.29	117.43	117.61	-46.02	-45.08	-44.23	-43.57	-42.90
0.3956	116.81	117.01	117.22	117.36	117.53	-46.05	-45.11	-44.26	-43.60	-42.93
0.5056	116.71	116.92	117.11	117.25	117.43	-46.08	-45.14	-44.28	-43.62	-42.95

[a] m is the molality of alkyl acetate

solution of [bmim][Cl] against molalities of methyl acetate are plotted in Fig. 1 at T = (288.15, 293.15, 298.15, 303.15 and 308.15) K. The plots of V_ϕ against concentration are linear in all cases. From the data, it is observed that V_ϕ values are positive and negative $K^0_{\phi,s}$ values have been obtained for the presently investigated mixtures at all temperatures. Further, a consistent increase has been observed for the V_ϕ values along with increase in temperature and concentration, which is prompted by ion-dipole

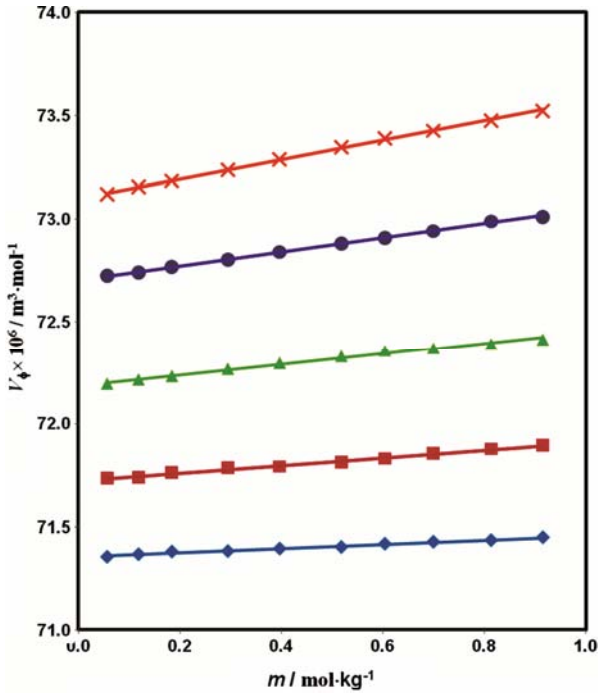

Fig. 1 — Plot of V_ϕ for methyl acetate in 0.1106 mol·kg^{-1} [bmim][Cl] at different temperatures against molalities m of methyl acetate: ◆, 288.15 K; ■, 293.15 K; ▲, 298.15 K; ●, 303.15 K; ✕, 308.15 K

interactions between cation of IL / ester and water molecules.

At any particular concentration of acetates, the values of V_ϕ with temperature follow the order: 288.15 K < 293.15 K < 298.15 K < 303.15 < 308.15 K for different aqueous solutions of [bmim][Cl]. The magnitude of $K_{\phi,s}$ values has been found to be decreasing with increase in the concentration of alkyl acetates. Hydrophilic-ionic interactions are playing a significant role in the mixture as it is clear from the negative value of $K_{\phi,s}$ as observed in Table 3, which is supported by the V_ϕ data of the systems under current investigation. The negative $K_{\phi,s}$ values show that water molecules around the solute are less compressible than around water molecules in the bulk which is on account of strong ion-dipole interactions between ions of IL/ester and water molecules. The strength of ion-dipole interactions between ions of IL/ester and water molecules increases as dielectric constants of alkyl acetates increases, that is, from methyl acetate to butyl acetate.

3.2 Apparent Molar Quantities at Infinite Dilution

The variation of apparent molar volumes V_ϕ and apparent molar adiabatic compressibility $K_{\phi,s}$ with the molal concentration can be adequately represented by the following relations:

$$V_\phi = V_\phi^0 + S_V m, \quad \ldots(4)$$

$$K_{\phi,s} = K_{\phi,s}^0 + S_k m \quad \ldots(5)$$

where V^0_ϕ and $K^0_{\phi,s}$ are the limiting values of apparent molar volume (equal to the infinite dilution partial molar volume) and apparent molar adiabatic compressibility (equal to the infinite dilution partial molar adiabatic compressibility), respectively. The S_v and S_k are the values of the experimental slopes which provide information regarding interactions present between solute molecules. The values of V^0_ϕ and S_V collectively with $K^0_{\phi,s}$ and S_k along with standard errors derived by least squares fitting of the V_ϕ and $K_{\phi,s}$ values to Eqs (4) and (5) have been reported in Table 4.

The partial molar properties at infinite dilution provide an approximation about solute-solvent interaction. It is observed from Table 3 that V^0_ϕ values of n-alkyl acetates in aqueous solutions of [bmim][Cl] are positive and the values increase with increase in [bmim][Cl] concentration which indicate towards greater ionic liquid-water interactions upon increasing concentration of [bmim][Cl]. The values also increase on increasing temperature pointing towards greater salvation of alkyl acetates in ionic liquid. The positive values of V^0_ϕ and negative values of $K^0_{\phi,s}$ strengthen and support the presence of ion-dipole interactions between cation of IL / ester and water molecules for the mixtures of acetates in aqueous [bmim][Cl] solutions at various temperatures. The temperature dependence of V^0_ϕ is shown in Fig. 2 in which values of V^0_ϕ are plotted for alkyl acetates in 0.1106 mol·kg^{-1} aqueous solution of [bmim][Cl] at different temperatures.

The ionic liquid–ionic liquid interactions override over ionic liquid-ester interactions which is clearly revealed by the sign (positive) and magnitude of S_V as it is an effective measure of solute-solute interactions in the system under investigation. The values of $K^0_{\phi,s}$ become less negative as the temperature is increased from 288.15 to 308.15 K and are found to be less negative than their corresponding values in water. The negative sign of $K^0_{\phi,s}$ indicates towards lesser compressibility of molecules in the vicinity of alkyl acetates than present in bulk phase. Also, with increase in temperature the $K^0_{\phi,s}$ values become less

Table 4 — Values of Limiting apparent molar volumes, V^0_ϕ, experimental slopes, $S_{v,}$ limiting apparent molar adiabatic compressibility $K^0_{\phi,s}$ and experimental slope S_K, of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures.

[a]m/mol·kg^{-1}	T / K	$V^0_\phi \times 10^6$/ m^3 mol^{-1}	$S_V \times 10^6$/m^3·kg mol$^{-3/2}$	$K^0_{\phi,s} \times 10^6$/m^3 mol^{-1}GPa^{-1}	$S_K \times 10^6$/kgm^{3}mol^{-2} GPa^{-1}
			Methyl acetate		
0.0000	288.15	71.18(±0.004)	0.33(±0.007)	-46.105(±0.066)	-0.53(±0.120)
	293.15	71.77(±0.006)	0.25(±0.010)	-45.171(±0.064)	-0.50(±0.116)
	298.15	72.25(±0.005)	0.26(±0.009)	-44.327(±0.063)	-0.48(±0.115)
	303.15	72.73(±0.004)	0.25(±0.007)	-43.571(±0.062)	-0.46(±0.114)
	308.15	73.07(± 0.004)	0.35(±0.007)	-43.010(±0.622)	-0.43(±0.114)
0.1106	288.15	71.35(±0.002)	0.10(±0.004)	-45.87(±0.102)	-0.74(±0.189)
	293.15	71.72(±0.003)	0.19(±0.006)	-44.94(±0.100)	-0.71(±0.186)
	298.15	72.19(±0.005)	0.26(±0.009)	-44.10(±0.098)	-0.68(±0.182)
	303.15	72.70(±0.002)	0.34(±0.004)	-43.35(±0.097)	-0.65(±0.180)
	308.15	73.10(±0.003)	0.47(±0.005)	-42.78(±0.096)	-0.63(±0.178)
0.3068	28815	71.33(±0.006)	0.59(±0.011)	-45.78(±0.085)	-0.59(±0.156)
	293.15	71.70(±0.006)	0.87(±0.011)	-44.85(±0.084)	-0.55(±0.154)
	298.15	72.16(±0.004)	0.83(±0.008)	-44.006(±0.083)	-0.53(±0.152)
	303.15	72.61(±0.003)	0.74(±0.006)	-43.35(±0.082)	-0.51(±0.149)
	308.15	73.04(±0.003)	0.63(±0.006)	-42.68(±0.080)	-0.50(±0.147)
			Ethyl acetate		
0.0000	288.15	87.62(±0.007)	0.155(±0.013)	-46.08(±0.066)	-0.47(±0.121)
	293.15	88.16(±0.006)	0.18(±0.010)	-45.15(±0.065)	-0.44(±0.119)
	298.15	88.75(±0.005)	0.15(±0.009)	-44.30(±0.064)	-0.42(±0.117)
	303.15	89.08(±0.003)	0.36(±0.005)	-43.55(±0.064)	-0.40(±0.116)
	308.15	89.38(±0.004)	0.50(±0.008)	-42.99(±0.063)	-0.38(±0.116)
0.1106	288.15	87.72(±0.004)	0.17(±0.007)	-45.95(±0.082)	-0.53(±0.151)
	293.15	88.20(±0.007)	0.13(±0.012)	-45.02(±0.080)	-0.50(±0.148)
	298.15	88.63(±0.004)	0.27(±0.007)	-44.18(±0.080)	-0.47(±0.146)
	303.15	89.12(±0.004)	0.38(±0.007)	-43.42(±0.078)	-0.45(±0.144)
	308.15	89.70(±0.002)	0.34(±0.003)	-42.86(±0.775)	-0.43(±0.143)
0.3068	288.15	87.53(±0.006)	0.19(±0.011)	-45.79(±0.074)	-0.49(±0.134)
	293.15	87.89(±0.004)	0.38(±0.007)	-44.84(±0.081)	-0.48(±0.147)
	298.15	88.33(±0.008)	0.52(±0.014)	-44.00(±0.079)	-0.45(±0.144)
	303.15	88.72(±0.005)	0.68(±0.009)	-43.34(±0.788)	-0.44(±0.143)
	308.15	89.06(±0.010)	0.72(±0.006)	-42.68(±0.078)	-0.43(±0.142)
			Butyl acetate		
0.0000	288.15	118.22(±0.001)	-1.90(±0.003)	-45.94(±0.090)	-0.97(±0.280)
	293.15	118.49(±0.009)	-1.93(±0.028)	-45.00(±0.087)	-0.95(±0.227)
	298.15	118.84(±0.009)	-1.94(±0.028)	-44.16(±0.086)	-0.92(±0.272)
	303.15	119.19(±0.007)	-2.03(±0.024)	-43.41(±0.085)	-0.90(±0.270)
	308.15	119.61(±0.002)	-2.23(±0.006)	-42.85(±0.084)	-0.89(±0.266)
0.1106	288.15	117.98(±0.004)	-1.53(±0.012)	-45.85(±0.09)	-0.89(±0.258)
	293.15	118.29(±0.010)	-1.76(±0.027)	-44.92(±0.091)	-0.86(±0.252)
	298.15	118.52(±0.004)	-1.73(±0.012)	-44.07(±0.089)	-0.84(±0.248)
	303.15	118.74(±0.005)	-1.72(±0.014)	-43.32(±0.088)	-0.83(±0.243)
	308.15	119.03(±0.002)	-1.85(±0.006)	-42.76(±0.087)	-0.80(±0.240)
0.3068	288.15	117.17(±0.004)	-0.90(±0.013)	-45.64(±0.077)	-1.01(±0.249)
	293.15	117.37(±0.003)	-0.89(±0.009)	-44.71(±0.075)	-0.99(±0.244)
	298.15	117.58(±0.004)	-0.92(±0.012)	-43.87(±0.073)	-0.96(±0.238)
	303.15	117.71(±0.005)	-0.89(±0.015)	-43.21(±0.072)	-0.95(±0.235)
	308.15	117.89(±0.002)	-0.91(±0.008)	-42.55(±0.072)	-0.93(±0.232)

[a]m is the molality of [bmim][Cl]

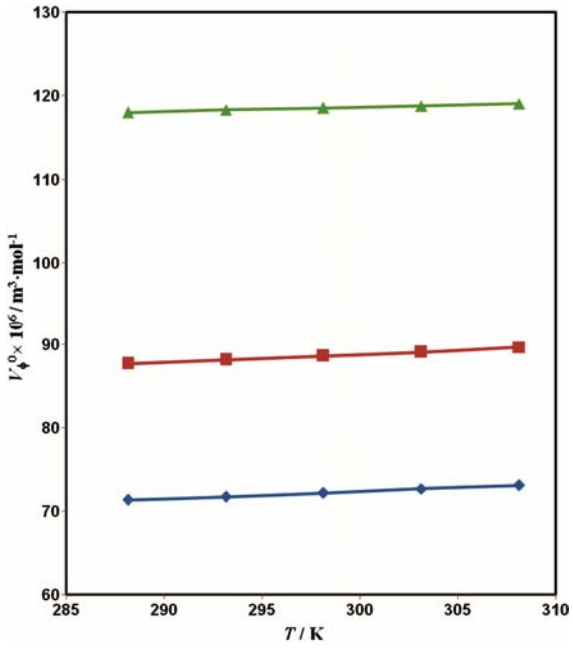

Fig. 2 — Plot of V_ϕ^0 for alkyl acetates in 0.1106 mol·kg^{-1} [bmim][Cl] at different temperatures: ●, MA; ■,EA; ▲, BA

negative which means decrease in electrostriction and some water molecules have been released to bulk. This creates volume shrinkage of the solvent. The dissociation of IL results into the ion pairs along with depletion of water molecules from ester. The release of water molecule into bulk by the hydration of ions results in strong interactions. Further, the V^0_ϕ values are suggested to result mainly from ion-dipole interactions between the organic molecules and cation of the IL as well as the accommodation of organic molecules in the interstices of IL networks. The overall values of V^0_ϕ are an indication of the intensity of ion-dipole interaction between the organic molecule/IL and water and the packing efficiency of the system[28]. Also, from NMR and dynamic[35-37] studies, it has been found that ILs undergo significant association or aggregation and liberate free ions from their aggregates on addition of molecular solutes. These free ions of IL are readily available to undergo interactions in the solution, which are ion-dipole interactions between the cations of [bmim][Cl] and the organic molecules.

3.3 Partial molar quantities of transfer

The partial molar volumes of transfer ΔV^0_ϕ and partial molar adiabatic compressibility of transfer $\Delta K^0_{\phi,s}$ from water to aqueous [bmim][Cl] have been calculated from following Eq.

$$\Delta Y^0_\phi = Y^0_\phi \text{ (in aqueous solute solution)} - Y^0_\phi \text{ (in water)} \quad \ldots(6)$$

where Y^0_ϕ denotes V^0_ϕ and $K^0_{\phi,s}$ and the corresponding values have been reported in Table 5.

In regard to the values of ΔV^0_ϕ, there is immeasurable contribution originating from solute–solute interactions and hence they provide information about solute–solvent interactions[38-40]. As per co-sphere overlap model[41], there are four types of interactions occurring between the alkyl acetates and [bmim][Cl]: (i) polar-ionic group interactions, (ii) polar-polar group interactions, (iii) polar-nonpolar group interactions, and (iv) nonpolar-nonpolar group interactions between ester + IL mixtures.

Table 5 reveals that the values of the transfer volume ΔV^0_ϕ of alkyl acetates are majorly negative but a few positive values have also been obtained at some concentrations that can be well interpreted in terms of solute-cosolute interactions. Taking the cosphere overlap model as a guideline; polar-nonpolar group interactions and nonpolar-nonpolar group interactions lead to negatives values of partial molar volume of transfer whereas polar-ionic group interactions and polar-polar group interactions lead to positive values of partial molar volumes of transfer. The negative values of ΔV^0_ϕ obtained in this case suggest that polar-nonpolar group interactions and nonpolar-nonpolar group interactions are dominant in ester + IL mixtures. The $\Delta K^0_{\phi,s}$ values are positive and slightly increase with increase in temperature and concentration of [bmim][Cl]. The values $K^0_{\phi,s}$ of the mixtures are sensitive to the total interaction between ionic liquid –ionic liquid or ionic liquid –water and any structure effect that could lead to the strengthening of ion-dipole interactions and/or the formation of a hydrogen bond, results in larger values of $\Delta K^0_{\phi,s}$.

3.4 Thermal expansion coefficients

The thermal expansion coefficient α was calculated as follows[42]:

$$\alpha = 1/V^0_\phi (\partial V^0_\phi / \partial T) \quad \ldots(7)$$

The use of coefficients of thermal expansion to interpret the solute–solvent interactions has been shown by Cabani *et al*[43]. The values of coefficients of thermal expansion at T = 298.15 K are reported in Table 6. The observance of Table 6 reveals that the

Table 5 — Partial molar volume of transfer, ΔV^0_ϕ and partial molar isentropic compressibility of transfer, $\Delta K^0_{\phi,s}$ of alkyl acetates in aqueous solutions of [bmim][Cl] at different temperatures.

[a]m/mol·kg^{-1}	T / K	$\Delta V^0_\phi \times 10^6$/ (m^3·mol^{-1})	$\Delta K^0_{\phi,s} \times 10^6$/ (m^3·mol^{-1}·GPa^{-1})
	Methyl acetate		
0.1106	288.15	0.17	0.233
	293.15	-0.05	0.229
	298.15	-0.07	0.228
	303.15	-0.03	0.225
	308.15	0.03	0.226
0.3068	288.15	0.15	0.323
	293.15	-0.07	0.320
	298.15	-0.09	0.321
	303.15	-0.13	0.222
	308.15	-0.04	0.325
	Ethyl acetate		
0.1106	288.15	0.10	0.125
	293.15	0.04	0.126
	298.15	-0.12	0.125
	303.15	0.04	0.126
	308.15	0.32	0.127
0.3068	288.15	-0.10	0.291
	293.15	-0.27	0.307
	298.15	-0.42	0.308
	303.15	-0.36	0.208
	308.15	-0.32	0.308
	Butyl acetate		
0.1106	288.15	-0.24	0.087
	293.15	-0.20	0.086
	298.15	-0.31	0.088
	303.15	-0.45	0.089
	308.15	-0.58	0.088
0.3068	288.15	-1.05	0.294
	293.15	-1.12	0.295
	298.15	-1.25	0.297
	303.15	-1.48	0.198
	308.15	-1.72	0.297

[a]m is the molality of [bmim][Cl]

values of α show an non-linear trend for all the alkyl acetates in aqueous [bmim][Cl] solutions which suggests that structural formula holds the accountability for the magnitude observed for α.

3.5 Limiting apparent molar expansivities

Limiting apparent molar expansivity ϕ^0_E has been estimated using the relation:

$$\phi^0_E = (\partial V^0_\phi / \partial T) \quad \ldots(8)$$

These calculated values are included in Table 6. The limiting apparent molar expansivity arises because of two major components[44].

Table 6 — Limiting apparent molar expansivity ϕ^0_E, coefficient of thermal expansion α, and temperature derivative of limiting apparent molar expansivity ($(\partial^2 V^0_\phi/\partial T^2)$) of alkyl acetates in aqueous solutions of [bmim][Cl] at T = 298.15 K

[a]m/mol·kg^{-1}	ϕ^0_E, $\times 10^6$ / (m^3.mol^{-1}.K^{-1})	$\alpha \times 10^3$/(K^{-1})	$(\partial^2 V^0_\phi/\partial T^2)$ / (m^3·mol^{-1})
	Methyl acetate		
0.0000	0.0948	0.291	-0.0029
0.1106	0.0895	0.290	0.0006
0.3068	0.0862	0.287	0.0006
	Ethyl acetate		
0.0000	0.0889	0.289	-0.0042
0.1106	0.0980	0.292	0.0015
0.3068	0.0781	0.290	-0.0006
	Butyl acetate		
0.0000	0.0698	0.266	0.0017
0.1106	0.0512	0.270	-0.0003
0.3068	0.0359	0.267	-0.0007

[a] m is the molality of [bmim][Cl]

$$\phi^0_E = \phi^0_E(\text{Elect}) + \phi^0_E(\text{Str}) \quad \ldots(9)$$

where ϕ^0_E (Elect) is the expansivity due to electrostriction changes (contribution of hydration around the solute) and ϕ^0_E (Str) is the expansivity which corresponds to changes in solvent structure. The lower temperature favours the structural component ϕ^0_E (Str) while the supremacy of the electrostriction component ϕ^0_E (Elect) is favoured at higher temperatures. Further, the temperature derivative of limiting apparent molar expansivity was calculated using the relation:

$$(\partial \phi^0_E / \partial T) = (\partial^2 V^0_\phi / \partial T^2) \quad \ldots(10)$$

The values of temperature derivative of partial molar expansivity ϕ^0_E as reported in Table 6 are positive for all mixtures. The possible probability of structural making or structural breaking effects of solute upon mixing the solvent is contingent[42,45] upon the sign of $(\partial^2 V^0_\phi/\partial T^2)$. The positive sign of $(\partial^2 V^0_\phi/\partial T^2)$ is representative of structure making solutes and negative for structure breaking solutes. Moreover, the negative values of $(\partial^2 V^0_\phi/\partial T^2)$ *i.e.* temperature coefficient of limiting apparent molar expansivity shows that the values of ϕ^0_E are low at lower temperature and the electrostriction component ϕ^0_E (Str) is a predominant factor in determining the solute–solvent interactions in the present study.

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