Supporting Information

Density, Speeds of Sound and Refractive Index of Pure and Binary Mixtures of Ionic Liquids Based on Imidazolium Cations and tetrafluoroborate Anion with Cyclohexylamine

Zubin Master, Naved I Malek*

Ionic Liquids Research Laboratory, Department of Chemistry, Sardar Vallabhbhai National Institute of Technology, Surat- 07, India

Table S1

Temperature dependence of B_i of Eq. 11 for excess molar volume V_m^E ($\times 10^6$ m^3 mol^{-1}), excess molar isentropic compressibilities $K_{s,m}^E$ ($dm^3TPa^{-1}mol^{-1}$), deviation in refractive index ($\Delta_\phi n_D$), along with standard deviation (σ) for $BmimBF_4$, $HmimBF_4$, $OmimBF_4$ with cyclohexylamine.

T(K)	B_1	B_2	B_3	B_4	σ
			$BmimBF_4$ + CyHxAm		
			V_m^E ($\times 10^6$ m^3/mol)		
293.15	-4.5739	-1.4257	0.0972	0.3536	0.0091
298.15	-4.7496	-1.3821	-0.7187	-0.1666	0.0840
303.15	-5.0401	-1.3323	-1.1838	-0.5102	0.1781
308.15	-5.4224	-1.5705	-1.6405	-0.4722	0.2951
313.15	-5.8162	-1.7012	-1.8529	-0.8076	0.4069
318.15	-6.3740	-1.8165	-1.4150	-0.5976	0.0296
323.15	-6.9010	-1.5523	-1.1093	-1.3451	0.0294
			$K_{s,m}^E$ (dm^3/TPa · mol)		

293.15	-6.2068	-3.3218	-0.4151	-1.5168	0.0202
298.15	-6.7475	-3.1284	-0.5969	-0.1788	0.0388
303.15	-7.1911	-2.8680	-1.7976	-0.5781	0.0383
308.15	-7.6972	-2.6074	-2.7064	-2.0305	0.0544
313.15	-8.5267	-2.9822	-3.2685	-2.8859	0.0490
318.15	-9.2669	-3.1787	-3.9055	-3.9686	0.0749
323.15	-10.0511	-3.1544	-4.1889	-5.4136	0.0731
		$\Delta_\phi n_D$			
293.15	-0.0121	-0.0042	0.0004		0.0001
298.15	-0.0124	-0.0044	-0.0006		0.0004
303.15	-0.0128	-0.0043	-0.0008		0.0005
308.15	-0.0131	-0.0042	-0.0012		0.0005
313.15	-0.0135	-0.0039	-0.0015		0.0005
318.15	-0.0137	-0.0033	-0.0024		0.0005
323.15	-0.0139	-0.0033	-0.0033		0.0005

HmimBF$_4$ + CyHxAm

V_m^E ($\times 10^6$ m^3/mol)

293.15	-4.0778	-4.0788	-0.2936	-0.3877	0.0107
298.15	-4.3346	-4.1398	-0.7626	-0.5310	0.0874
303.15	-4.4880	-4.0411	-0.9057	-1.1718	0.1336
308.15	-4.6654	-4.3810	-1.0922	-0.7053	0.1879
313.15	-4.9156	-4.3899	-1.0132	-0.9175	0.2482
318.15	-5.1538	-4.3593	-1.1307	-1.2150	0.0252
323.15	-5.3998	-4.6248	-1.1323	-0.9380	0.0213

$K_{s,m}^E$ (dm^3/TPa · mol)

293.15	-6.2907	-6.1700	0.8963	1.2716	0.0340
298.15	-6.5806	-5.7794	-0.1942	0.0187	0.0224
303.15	-6.9252	-5.7853	-0.6770	-0.1401	0.0101
308.15	-7.1856	-5.9542	-1.2975	0.0995	0.0341
313.15	-7.6409	-6.1524	-0.7424	0.7623	0.0306
318.15	-7.9834	-5.8915	-0.7285	0.1999	0.0107
323.15	-8.2678	-6.2057	-1.1918	0.6388	0.0216

$\Delta_{\phi} n_D$

293.15	-0.0136	-0.0016	-0.0045		0.0000
298.15	-0.0132	-0.0011	-0.0029		0.0002
303.15	-0.0123	0.0000	-0.0010		0.0001
308.15	-0.0116	-0.0003	0.0007		0.0001
313.15	-0.0109	-0.0002	0.0017		0.0001
318.15	-0.0101	-0.0006	0.0032		0.0002
323.15	-0.0094	-0.0006	0.0046		0.0003

OmimBF$_4$ + CyHxAm

$V_{\mathrm{m}}^{\mathrm{E}}$ ($\times 10^6$ m^3/mol)

293.15	-4.3992	-3.2401	-0.2379	-0.5302	0.0074
298.15	-4.6162	-3.3328	-0.7878	-0.3644	0.0815
303.15	-4.8222	-3.3476	-0.7900	-0.4554	0.1336
308.15	-5.0704	-3.4122	-1.0079	-0.3658	0.2076
313.15	-5.2674	-3.4485	-1.0619	-0.6888	0.2607
318.15	-5.4397	-3.2563	-0.9676	-1.2605	0.0249
323.15	-5.6035	-3.0801	-1.1269	-2.0184	0.0358

$K_{\mathrm{s,m}}^{\mathrm{E}}$ (dm3/TPa · mol)

293.15	-7.1242	-5.4079	-2.6045	-1.2252	0.0711
298.15	-7.9706	-5.7156	-1.8312	-0.9725	0.0392
303.15	-8.8703	-6.7137	-0.8988	0.6716	0.0329
308.15	-9.4896	-6.9673	-0.7968	0.5461	0.0381
313.15	-10.3374	-7.7512	-0.5427	0.7560	0.0289
318.15	-10.8724	-8.2632	-1.3314	0.9014	0.0357
323.15	-11.6808	-9.6746	-1.8172	2.0406	0.0581
		$\Delta_\phi n_D$			
293.15	-0.0140	-0.0043	-0.0037		0.0001
298.15	-0.0135	-0.0043	-0.0009		0.0005
303.15	-0.0130	-0.0037	0.0012		0.0004
308.15	-0.0124	-0.0042	0.0018		0.0004
313.15	-0.0118	-0.0038	0.0031		0.0004
318.15	-0.0114	-0.0040	0.0044		0.0004
323.15	-0.0109	-0.0047	0.0044		0.0004

TABLE S2

Dependence of Rao's molar sound functions R for the systems investigated at (293.15 - 323.15) K at atmospheric pressure P = 101.3 kPa.

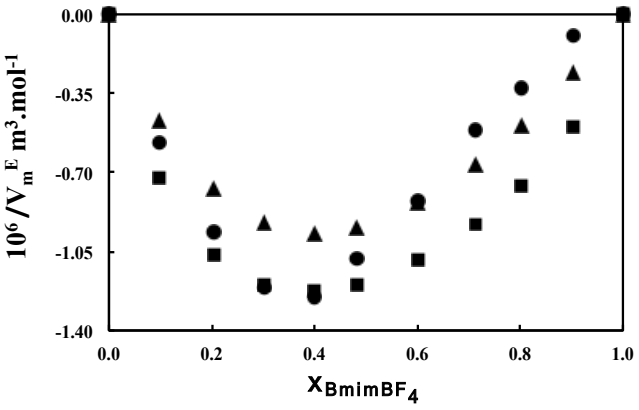
Mole Fraction	293.15 K	298.15 K	303.15 K	308.15 K	313.15 K	318.15 K	323.15 K
			$BmimBF_4$ + CyHxAm				
0.0000	1288.24	1288.43	1288.62	1288.83	1288.87	1288.90	1288.84
0.0982	1346.61	1344.18	1342.57	1340.93	1339.27	1338.02	1336.28
0.2032	1440.84	1437.34	1434.14	1431.10	1428.32	1425.53	1422.60
0.3010	1550.08	1546.18	1542.27	1538.15	1534.89	1530.04	1525.87
0.4012	1678.25	1673.54	1668.88	1664.14	1659.67	1654.98	1649.95
0.4828	1791.63	1786.47	1781.54	1776.40	1771.40	1766.13	1760.59
0.6016	1968.69	1962.95	1957.58	1951.83	1946.38	1940.63	1934.57
0.7124	2143.66	2137.58	2131.65	2125.53	2119.93	2113.94	2107.99
0.8012	2289.35	2283.86	2277.93	2271.62	2265.75	2259.27	2253.16
0.9024	2460.78	2454.76	2448.99	2442.37	2436.14	2429.97	2423.74
1.0000	2631.49	2624.94	2618.66	2611.89	2605.68	2599.57	2593.67
			$HmimBF_4$ + CyHxAm				
0.0000	1288.24	1288.43	1288.62	1288.83	1288.87	1288.90	1288.84
0.0970	1376.64	1374.99	1373.32	1371.77	1369.80	1367.77	1366.07
0.1808	1479.55	1476.56	1473.69	1471.13	1467.83	1464.70	1461.86
0.2945	1643.38	1639.26	1635.23	1631.23	1626.75	1622.27	1617.85
0.3960	1806.23	1801.09	1796.16	1791.09	1785.88	1780.30	1775.25
0.5009	1985.66	1979.67	1974.14	1968.13	1962.21	1956.17	1950.40
0.6048	2171.64	2165.36	2158.89	2152.69	2145.93	2139.23	2132.83
0.7029	2353.04	2346.15	2339.31	2332.68	2325.64	2318.52	2311.65
0.8008	2538.71	2531.45	2524.18	2517.11	2509.62	2502.31	2495.07
0.8991	2729.31	2721.61	2714.04	2706.51	2698.85	2691.16	2683.78
1.0000	2929.21	2920.94	2912.81	2904.81	2896.91	2889.06	2881.28
			$OmimBF_4$ + CyHxAm				
0.0000	1288.24	1288.43	1288.62	1288.83	1288.87	1288.90	1288.84
0.1076	1426.51	1424.23	1422.25	1420.24	1418.21	1416.40	1414.28
0.2030	1579.46	1576.36	1573.27	1570.18	1566.97	1564.00	1561.00

0.3072	1767.43	1763.18	1758.95	1754.31	1750.09	1745.61	1741.57
0.4001	1947.22	1941.72	1936.69	1931.21	1926.03	1920.67	1915.68
0.4920	2131.85	2125.98	2120.16	2113.84	2107.93	2101.79	2095.61
0.6078	2372.64	2365.77	2358.96	2352.15	2345.09	2337.76	2330.58
0.7023	2574.31	2566.64	2558.76	2550.94	2543.37	2535.55	2527.66
0.7996	2785.04	2776.51	2767.84	2759.39	2751.18	2743.14	2735.22
0.8963	2997.80	2988.39	2979.26	2970.25	2961.43	2952.70	2944.06
1.0000	3228.19	3218.29	3208.50	3198.98	3189.73	3180.35	3171.24

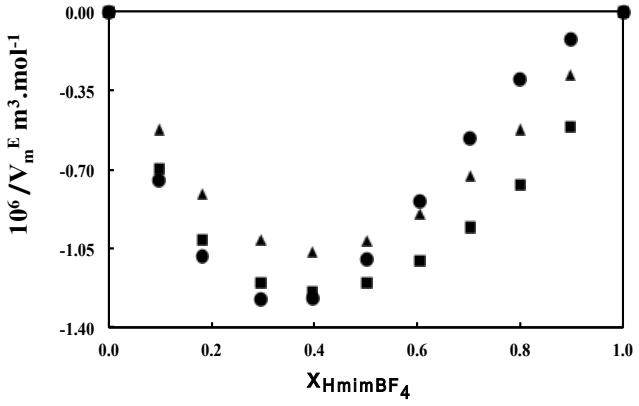
TABLE S3

Dependence of excess molar volume for the systems investigated ($BmimBF_4$+ CyHxAm, $HmimBF_4$+ CyHxAm and $OmimBF_4$+ CyHxAm) at 298.15 K at atmospheric pressure P= 101.3 kPa.

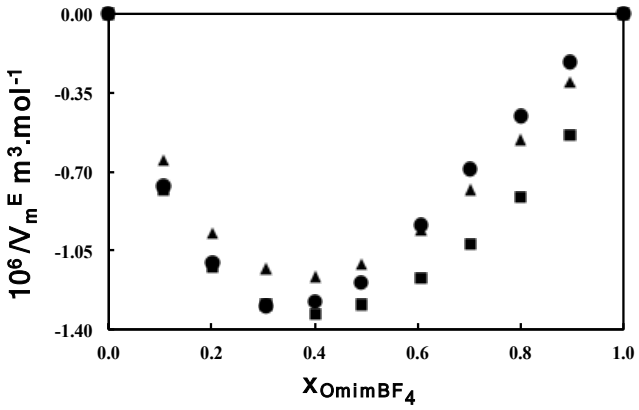
$X_{BmimBF4}$	V_m^E	$X_{HmimBF4}$	V_m^E	$X_{OmimBF4}$	V_m^E
0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.0982	-0.5684	0.0970	-0.7474	0.1076	-0.7650
0.2032	-0.9502	0.1808	-1.0812	0.2030	-1.1006
0.3010	-1.1278	0.2945	-1.2758	0.3072	-1.2935
0.4012	-1.2169	0.3960	-1.2716	0.4001	-1.2747
0.4828	-1.2144	0.5009	-1.0955	0.4920	-1.1915
0.6016	-1.0739	0.6048	-0.8445	0.6078	-0.9384
0.7124	-0.8711	0.7029	-0.5663	0.7023	-0.6880
0.8012	-0.6597	0.8008	-0.3011	0.7996	-0.4512
0.9024	-0.3545	0.8991	-0.1197	0.8963	-0.2152
1.0000	0.0000	1.0000	0.0000	1.0000	0.0000



[A]



[B]



[C]

Figure S1 Comparison of excess molar volumes (V_m^E) for (a) $BmimBF_4$ (b) $HmimBF_4$ and (c) $OmimBF_4$ + CyHxAm at 298.15 K (■) ERAS and (▲) PFPT model.

The Prigogine-Flory-Patterson Theory (PFPT)

We have used Prigogine-Flory-Patterson (PFP) statistical theory to predict the excess molar volume of the studied systems. In PFP theory, V_m^E is divided in to three different contributions; the free volume (V_m^E(fv)), the characteristic pressure ((V_m^E (ip)) and the energy of interaction V_m^E(int). The expression to predict V_m^E through PFP theory is:

$$\frac{V_m^E}{x_1V_1^* + x_2V_2^*} = \frac{V_m^E(fv)}{x_1V_1^* + x_2V_2^*} + \frac{V_m^E(ip)}{x_1V_1^* + x_2V_2^*} + \frac{V_m^E(\text{int})}{x_1V_1^* + x_2V_2^*}$$

$$= -\frac{(\tilde{V}_1 - \tilde{V}_2)^2[(14/9)\tilde{V}^{-1/3} - 1]\Psi_1\Psi_2}{[(4/3)\tilde{V}^{-1/3} - 1]\tilde{V}} + \frac{(\tilde{V}_1 - \tilde{V}_2)(P_1^* - P_2^*)\Psi_1\Psi_2}{P_2^*\Psi_1 + P_1^*\Psi_2} + \frac{(\tilde{V}^{1/3} - 1)\tilde{V}^{2/3}\psi_1\theta_2 X_{12}}{[(4/3)\tilde{V}^{-1/3} - 1]P_1^*}$$

Here x_i, P_i^*, V_i^*, $\tilde{V}_i$, θ_i, and Ψ_I are the mole fraction, characteristic pressure, characteristic volume, reduced volume, segment fraction and contact energy fraction of component *i*, respectively. χ_{12} is the Flory's contact interaction parameter.