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Acoustic and Refractive Behaviour of the Binary Mixture of 1-Butyl-3-methylimidazolium Tetrafluoroborate with 1-Alkanol at 298.15 to 313.15 K

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Abstract: Densities, refractive indices and speeds of sound and their excess properties for 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim] [BF4] with 1-pentanol over the entire range of mole fraction are reported at temperatures ranging from 298.15 K to 313.15 K and atmospheric pressure. Isentropic and excess isentropic compressibility for ionic liquids with 1–alcohols were calculated from the experimental results. The excess values are fitted to the Redlich−Kister polynomial equation to estimate the binary coefficients and standard error between the experimental and calculated values. The measured speeds of sound were compared to the values obtained from Schaaffs' collision factor theory, Jacobson's intermolecular free length theory of solutions and Nomoto's relation. In addition, the experimentally obtained refractive indices were compared to the calculated values using Lorentz-Lorenz, Dale-Gladstone and Eykman mixing rules. The theoretical results obtained from these relations fairly agrees within the experimental precision. Further, the molecular interactions involved in IL binary mixture system were studied.

Keywords: Density, Refractive index, Speed of sound, Ionic liquids, 1–alkanols, Binary mixtures

1. Introduction

Ionic liquids (ILs) have recently emerged as environment friendly solvents for their use in the industrial manufacture of chemicals. In the past decade, ILs have been increasingly used for diverse applications such as organic synthesis, catalysis, electrochemical devices, and solvent extraction of a variety of compounds [1–4]. The interest in ILs was initiated because of their advantageous physico−chemical properties. ILs are composed of cations and anions having a low melting point. The physico−chemical properties of the ILs can be tuned by changing the cation or the anion. Thus, novel solvents can be formed and can be used for a specific application which cannot be done with the use of conventional organic solvents. The information regarding the thermo-physical properties of pure ILs as well as their mixtures with other compounds is essential for the design and development of equipment for commercial applications.[Bmim][BF4] is most efficient in the removal of di-benzothiophene (DBT) containing liquid fuels [5]. Pentanol is used as co-solvent in the petroleum industry to increase the selectivity and solvent power for extracting aromatic hydrocarbons.

Similar study has been carried out by us [6-8] and many other workers for non ionic liquids, particularly hydro carbons, cyclic compound, to validate these theoretical models and also the solvent - solvent interactions present in liquid mixture.

The present work is aimed at studying the molecular interactions in the binary mixture of the IL 1-butyl-3-methylimidazolium tetrafluoroborate [Bmim][BF4] with 1-Alconol. Isentropic and excess isentropic compressibility's for ionic liquids with 1–alconols were calculated from the experimental results. Excess and deviation properties were further correlated using the Redlich-Kister polynomial eqation [9]. The measured speeds of sound were compared to the values obtained from Schaaffs' collision factor theory (CFT)[10], Jacobson's intermolecular free length theory(FLT)[11-12] of solutions and Nomoto's relation (NR) [13]. In addition, the experimentally obtained refractive indices were compared to the calculated values using Lorentz-Lorenz [14], Dale-Gladstone [15] and Eykman mixing rules [16]. Experimental values and excess thermodynamic properties of IL systems allow researchers to draw information on

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The corresponding excess molar volume and excess isentropic compressibility and coefficients of thermal expansion were calculated. Furthermore, the Redlich and Kister (R–K) polynomial was used to obtain the coefficients and to estimate the standard deviations for the calculated excess and deviation properties. Moreover, the effect of the alkyl chain in ILs, chain length of 1–alkanol and the temperature on the excess and deviation properties are investigated.

2. Experimental

2.1 Materials

[Bmim][BF4] (mass fraction, 0.99) is procured from Merck, Germany, and is used without further purification. 1-Pentanol (mass fraction 0.97) is procured from Sigma-Aldrich, USA, and is purified by the fractional distillation method under reduced pressure. The water content is checked by conductometric titration with platinum electrode. The purity of the chemicals was ascertained by comparing the experimental values of density, refractive index and speed of sound, at temperatures T = (298.15 to 313.15) K with the literature value [17-18].

2.2 Apparatus and Procedure

The binary mixture is prepared by weighing appropriate amounts of pure liquids on a digital electronic balance model Shimadzuax-200 with an uncertainty of ± $1 \cdot 10^{-4}$kg. Before each series of experiments, we calibrated the instrument at atmospheric pressure with doubly distilled water. The average uncertainty in the composition of the mixtures was estimated to be less than ±0.0001.A crystal controlled variable path ultrasonic interferometer supplied by M/s Mittal enterprises (model-05F), New Delhi (India), operating at a frequency of 2 MHz was used in the ultrasonic measurements. The reported uncertainty is less than ± 3% which is the highest uncertainty found from all the data points. Refractive index was measured by Abbe refractometer (Agato 3T, Japan). Refractive index data were accurate to ±0.0001units. The purity of chemicals used was confirmed by comparing the densities and ultrasonic speeds with those reported in the literature as shown in Table 1.The uncertainty in the density measurement was within ± 0.7 kg.m^{-3} (about 0.06%).The densities of the pure components and their mixtures were measured with the bi-capillary pyknometer. The liquid mixtures were prepared by mass in an air tight stopped bottle using an electronic balance model Shimadzuax-200 accurate to within ±0.1 mg. Isentropic compressibility, k_s, were calculated from the relation,

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

Where ρ is the density and u is the ultrasonic velocity.

3. Results and calculations

The experimental density, speed of sound, and refractive index values for binary systems of 1-butyl-3-methylimidazolium tetrafluoroborate with 1–pentanol are reported at T = (298.15 to 313.15) K and atmospheric pressure are listed in Table 2. The excess volume, V^{E} and excess isentropic compressibility values k_s^E were calculated from the relation as

$$V^E = \sum_{i=1}^{n} \frac{x_1 M_1}{\rho} - \sum_{i=1}^{n} \frac{x_1 M_1}{\rho} \quad \text{and} \quad k_s^E = k_s - k_s^{idl} \tag{2}$$

Where, $$k_s^{idl} = k_s x_1 + k_s x_2 \tag{3}$$

and volume fractions, ∅ were calculated from the relation;

$$\emptyset = \frac{x_i V_I}{(\sum_{i=1}^{n} x_i V_i)} \tag{4}$$

The dependency of V^{E} on composition is shown in figure 1 where all V^{E} values are negative for the systems under study and this is due to the interstitial accommodation of ILs into alkanols structure [5]. The negative V^{E} trend reflects the formation of hydrogen bonded hetero associations and the dissociation of alkanol structure as the chain length increases. This is conformed from the previously reported studies [2,3,5]. In addition as expected, V^{E} becomes less negative as the temperature increases for ILs with 1–propanol. The excess isentropic compressibility values k_s^E were calculated from relations by Benson *et al.* [20] where κ_s^{id} is the isentropic compressibility of the ideal solution, κ_s is the isentropic compressibility and it is calculated using the Laplace–Newton $V = 1/u^2\rho$ where the relation is judged to be valid and therefore the speed of sound may be regarded as a thermodynamic quantity. The excess isentropic compressibility are negative for the system

under study and exhibited a similar trend as the excess volume (see figure 2) while κ^E becomes more negative as the temperature increases as shown in Table 2. Which suggest the dominance of interstitial of accommodation of the components effect over the dissociation effect. The calculated excess properties were fitted to the Redlich-Kister (R–K) polynomial equation ,Schaaff's Collision Factor Theory (CFT), Jacobson's Free Length Theory (FLT) and Nomoto's relation (NR) [9-13] were used to predict the speed of sound (u_m) for 1-Butyl-3-methyl imidazolium Tetrafluoroborate + 1-Pentanol binary systems. The critical temperatures for the pure ILs were predicted using available data [20] since they are needed for CFT,

$$u = u_\infty \sum_{i=1}^{n} \frac{(x_i s_i)(\sum_{i=1}^{n} x_i B_i)}{V} \tag{5}$$

Where u_∞ = 1600 m·s^{-1}, S_i and B_i are the space filling factor and the actual volume of the molecule per mole of pure component *i* in the mixture. Jacobson's Free Length Theory (FLT) can be expressed as;

$$u = \frac{K}{L_f \rho^{1/2}} \tag{6}$$

Where *K* is the Jacobson's constant and $L_{f,m}$ is the intermolecular free length of the binary mixture and Nomoto's relation as;

$$u = \left[\frac{\sum_{i=1}^{n} x_i u_i}{\sum_{i=1}^{n} x_i V_i}\right] 3 \tag{7}$$

In addition, Lorentz-Lorenz (L–L), Dale-Gladstone (D–G) and Eykman (Eyk) mixing rules [14-16] were used to predict refractive indices for studied system. They are given as;

$$\frac{n^2-1}{n^2+2} = \sum_{i=1}^{n} \emptyset \left[\frac{n^2-1}{n^2+2}\right]$$
$$n - 1 = \sum_{i=1}^{n} [\emptyset_i (n-1)]$$
$$\frac{n^2-1}{n^2+0.4} = \sum_{i=1}^{n} \emptyset_i \left[\frac{n^2-1}{n^2+0.4}\right] \tag{8}$$

The comparison shows that Nomoto's relation for predicting speed of sound is the best among the relations used in the case of 1-Butyl-3- methylimidazolium Tetrafluoroborate + 1-Pentanol while both Nomoto's and Schaaff's Collision Factor Theory are also comparable. As for the refractive index mixing rules, all rules used showed good agreement with the experimental data for the system under study.

4. Conclusions

Density, speed of sound and refractive index and their excess or deviation properties of ILs with 1–pentanol binary mixtures have been reported at different temperatures and atmospheric pressure. Although ILs show stronger hydrogen bonding with 1–pentanol than conventional solvents. Prediction of the speed of sound can be obtained using Nomoto's relation and Schaaff's Collision Factor Theory while refractive index can be predicted using Lorentz-Lorenz, Dale-Gladstone and Eykman mixing rules for systems containing ionic liquids. In addition, The calculations showed a systematic dependence of excess and deviation properties on the chain length and on temperature for all investigated mixtures.

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References

[1]. Shekaari H. and Sedighehnaz S.M., Volumetric properties of ionic liquid 1,3-dimethyl imidazolium methyl sulfate + molecular solvents at *T* =(298.15–328.15) K, *Fluid Phase Equilib.* 291 (2010) 201–207.

[2]. Wang J-Y., Zhao F-Y., Liu Y. M., Wang X-L. and Hu Y-Q., Thermo physical properties of pure 1-ethyl-3-methy limidazolium methyl sulphate and its binary mixtures with alcohols, *Fluid Phase Equilib. 305* (2011) 114–120.

[3]. Requejo P. F., Gonzalez E. J., Macedo E. A. and Dominguez A. J., Effect of the temperature on the physical properties of the pure ionic liquid 1-ethyl-3-methylimidazolium methyl sulfate and characterization of its binary mixtures with alcohols, *Chem. Thermodyn*. *74* (2014) 193-200.

[4]. Pereiro A. B. and Rodiguez A., Thermodynamic Properties of Ionic Liquids in Organic Solvents from (293.15 to 303.15) K, *J. Chem. Eng. Data 52* (2007) 600–608.

[5]. Domanska U., Pobudkowska A. and Wisniewska A., Solubility and Excess Molar Properties of 1,3-Dimethylimidazolium Methylsulfate, or 1-Butyl-3-Methylimidazolium Methylsulfate, or 1-Butyl-3-

Methylimidazolium Octylsulfate Ionic Liquids with n-Alkanes and Alcohols: Analysis in Terms of the PFP and FBT Models1, *J. Solution Chem. 35* (2006) 311- 334.

[6]. Shukla R.K., Gangwar V.S. and Singh S.K., Effect of Molecular Structure of Lubricating Oil on Sound Velocity and Bulk Modulus, , *J.Pure Appl. Ultrason,40 (4)* (2018)111-115.

[7]. Shukla Rajeev Kumar., Gangwar V.S., and Pundhir Vivek Kumar., Density and speed of sound of binary liquid systems in temperature range 288.15 to 318.15 K, , *J.Pure Appl. Ultrason, 39* (2017) 18-22.

[8]. Shukla R.K., Gupta G.K., Pramanik S.K., Sharma A.K. and Balwant Singh., Comparative Study of Speed of Sound and Isentropic Compressibility of Chlorobenzene + Benzene Binary Mixture from Various Models at Temperature Range 298.15 to 313.15 K, *J.Pure Appl. Ultrason, 35* (2013)80-86.

[9]. Redlich O. and Kister A. T., Algebraic Representation of Thermodynamic Properties and the Classification of Solutions, *Ind. Eng. Chem.* 40 (1948) 345-348.

[10]. Schaffs W., Molecular Acoustics / Molekularakustik *Springer-Verlag, Berlin* 1963, (Chapters. XI and XII).

[11]. Jacobson B., Intermolecular Free Length in the Liquid State. Adiabatic and Isothermal Compressibilities, *Acta. Chem. Scand. 8* (1952) 1485-1498.

[12]. Jacobson B., Ultrasonic Velocity in Liquids and Liquid Mixtures, *J. Chem. Phys. 20* (1952) 927-928.

[13]. [13] Nomoto O., Empirical Formula for Sound Velocity in Liquid Mixtures, *J. Phys. Soc. 13* (1958) 1528-1532. *J. Phys. Soc. Jpn*. 13, (1958) 1528-1532.

[14]. Lorentz L. and Lorenz, L.V., Ueber die Refraktion Konstante, *Wied. Ann. 11* (1880) 70–75.

[15]. Gladstone J. H. and Dale T. P., Researches on the Refraction and Dispersion and sensitiveness of Liquid, *Philos. Trans. 153* (1863) 317-343.

[16]. Eykman J. F., Reel. Trao. Recherches réfractométriques (suite), *Chim Pays-Bas. 14* (1895) 185-188.

[17]. Timmermans J., *Physico- Chemical Constants of Pure Organic Compounds*, 8th Ed., Elsevier Pub. Corp. Inc., New York (1950).

[18]. Riddick J.A., Bunger W.S. and Sakano T., *Organic Solvents, Physical Properties and Methods of Purification*, 4th ed, John wiley and Sons Press., New York (1986).

[19]. Letcher T. M., Domanska U. and Mwenesongole E., The excess molar volumes and enthalpies of (*N*-methyl-2-pyrrolidinone + an alcohol) at*T* = 298.15 K and the application of the ERAS theory, *Fluid Phase Equilib. 149* (1998) 323– 337.

[20]. Benson G. C. and Kiyohara O., Evaluation of excess isentropic compressibilities and isochoric heat capacities, *J. Chem. Thermodyn. 11* (1979) 1061-1064.

[21]. AlTuwaim M. S., Alkhaldi K. H. A. E., Al–Jimaz A. S. and Mohammad A. A., Temperature dependence of physicochemical properties of imidazolium-, pyroldinium-, and phosphonium-based ionic liquids , *J. Chem. Eng. Data. 59* (2014) 1955–1963.

Table 1 Comparison of Experimental Density (ρ_{exp}), Refractive Index (n_{exp}) and Speed of Sound (u_{exp}) of Pure Components with Literature (lit) Values at Temperatures from T = (298.15 to 313.15) K

Components	***T/K***	***ρ/kg·m^{-3}***		***n***		***u/m·sec^{-1}***	
		ρ_{exp}	ρ_{lit}	n_{exp}	n_{lit}	u_{exp}	u_{lit}
1-butyl-3-methylimidazoliumtetrafluoroborate	298.15	1198.78	1200.57 [b]	1.42058	1.4197 [e]	1565.09	1565.1
	303.15	1195.18	1196.98	1.41913	1.4181	1553.15	1552.6
	308.15	1191.60	1194.2	1.41764	1.4166	1541.35	1540.3
	313.15	1188.04	1189.86	1.41621	1.4155	1529.69	1528.3
1-pentanol	298.15	811.00	81099	1.408	1.40784	1276	1275.4
	303.15	807.00	80711	1.407	1.4065	1259	1262
	308.15	803.00	8036	1.406	1.4047	1242	1245
	313.15	800.00	7999	1.404	1.40178	1226	1228

Table 2 Experimental Density (ρ_{exp}), Refractive Index (n_{exp}), and Speed of Sound (u_{exp}) and values obtained from theoretical models ($u_{Sch,}$ $u_{Nom,}$ u_{Jacob} and $n_{L\text{-}L,}$ $n_{D\text{-}G,}$ n_{Eykman}) and Isentropic Compressibility (k_s) of Binary Liquid Mixtures of 1-Butyl-3- methylimidazolium Tetrafluoroborate + 1-Pentanol T = (298.15 to 313.15) K

x_1	ρ_{exp}/kg·m^{-3}	n_{exp}	u_{exp}/m·sec^{-1}	u_{Sch}/m·sec^{-}	u_{Nom}/m·sec^{-}	u_{Jacob}/m·sec^{-}	$n_{L\text{-}L}$	$n_{D\text{-}G}$	n_{Eykman}	k_s TPa^{-1}
					298.15K					
0.1045	889.12	1.4083	1287.2	1307.6	1267.2	1297.1	1.4080	1.4074	1.4087	395.47
.2036	903.24	1.4093	1312.5	1332.2	1291.2	1304.1	1.4089	1.4082	1.4093	382.74
.3044	951.23	1.4117	1350.2	1370.2	1331.4	1321.5	1.4113	1.4093	1.4099	372.48
.4062	978.12	1.4127	1386.2	1401.5	1361.5	1341.2	1.4126	1.4099	1.4113	364.36
.4946	1004.5	1.4143	1420.5	1440.2	1401.2	1358.5	1.4141	1.4121	1.4127	358.83
.6071	1021.34	1.4151	1425.2	1461.2	1411.4	1401.2	1.4149	1.4132	1.4139	353.01
.6973	1056.15	1.4163	1465.7	1467.5	1481.2	1445.5	1.4151	1.4136	1.4146	349.19
.7830	1098.23	1.4189	1501.2	1488.8	1500.1	1496.2	1.4182	1.4156	1.4171	345.71
.9106	1102.13	1.4202	1557.2	1525.4	1537.5	1522.1	1.4191	1.4172	1.4183	342.15
					303.15K					
0.1045	882.12	1.4081	1296.1	1301.2	1271.5	1290.2	1.4076	1.4074	1.4084	406.17
.2036	893.12	1.4089	1333.4	1357.4	1297.1	1330.3	1.4083	1.4079	1.4088	392.47
.3044	947.12	1.4111	1371.2	1381.2	1335.4	1362.3	1.4094	1.4083	1.4089	381.43
.4062	974.13	1.4122	1400.6	1421.5	1389.7	1381.5	1.4099	1.4091	1.4107	372.67
.4946	1000.50	1.4131	1406.5	1431.2	1400.2	1396.7	1.4111	1.4101	1.4113	366.80
.6071	1018.60	1.4146	1437.2	1451.4	1411.5	1407.5	1.4136	1.4117	1.4123	360.47
.6973	1051.04	1.4158	1472.5	1492.5	1461.3	1467.9	1.4148	1.4132	1.4137	356.20
.7830	1093.15	1.4173	1501.2	1521.8	1489.3	1491.2	1.4167	1.4146	1.4172	352.62
.9106	1098.21	1.4182	1536.3	1539.3	1517.8	1527.7	1.4178	1.4163	1.4177	348.60
					308.15K					
0.1045	872.20	1.4078	1270.2	1296.5	1251.4	1281.3	1.4074	1.4073	1.4082	417.36
.2036	890.12	1.4086	1306.4	1322.4	1283.2	1336.4	1.4089	1.4082	1.4088	402.64
.3044	936.04	1.4096	1341.2	1366.5	1317.5	1342.2	1.4091	1.4099	1.4097	390.76
.4062	971.02	1.4111	1370.2	1390.2	1347.4	1367.5	1.4078	1.4107	1.4120	381.33
.4946	997.30	1.4118	1391.6	1413.7	1368.2	1376.4	1.4112	1.4111	1.4109	374.84
.6071	1011.41	1.4131	1421.6	1441.5	1392.2	1393.2	1.4123	1.4129	1.4121	368.10
.6973	1034.12	1.4137	1452.8	1468.5	1411.3	1417.3	1.4129	1.4130	1.4133	363.45
.7830	1046.17	1.4140	1489.2	1489.2	1427.5	1421.2	1.4138	1.4131	1.4144	359.34
.9106	1088.04	1.4162	1521.2	1521.2	1459.4	1489.4	1.4154	1.4152	1.4172	355.04
					313.15K					
0.1045	861.12	1.4074	1276.1	1276.1	1236.4	1276.2	1.4074	1.4070	1.4080	4 28.90
.2036	889.16	1.4082	1310.2	1310.2	1270.2	1286.4	1.4079	1.4076	1.4088	413.10
.3044	932.12	1.4091	1347.5	1347.5	1301.4	1301.2	1.4092	1.4081	1.4093	400.33
.4062	969.13	1.4098	1372.3	1372.3	1327.2	1333.4	1.4096	1.4099	1.4112	390.18
.4946	994.02	1.4101	1394.2	1394.2	1347.5	1351.5	1.4101	1.4107	1.4117	383.16
.6071	995.14	1.4111	1420.4	1420.4	1381.9	1389.2	1.4117	1.4123	1.4123	375.88
.6973	1006.12	1.4123	1451.4	1451.4	1411.2	1411.3	1.4117	1.4134	1.4136	370.85
.7830	1036.11	1.4132	1496.5	1496.5	1449.5	1437.2	1.4130	1.4133	1.4141	366.50
.9106	1083.12	1.4141	1530.2	1530.2	1489.3	1491.4	1.4142	1.4149	1.4162	361.70

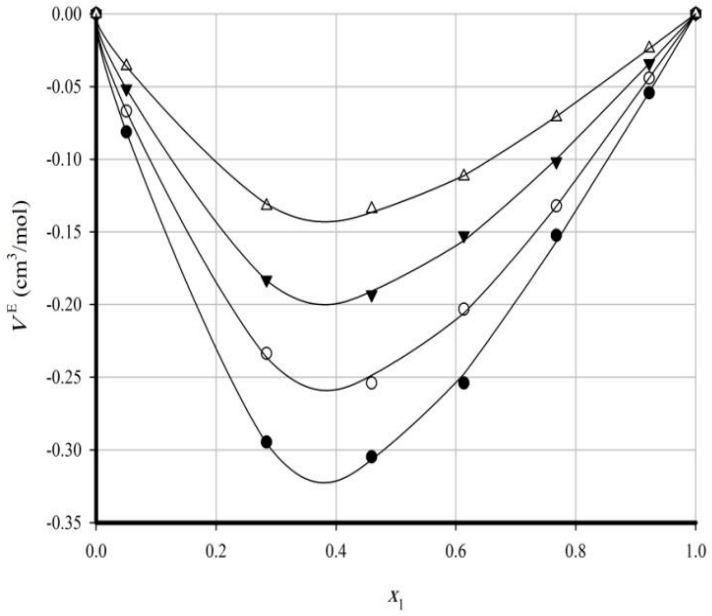

Fig. 1 Excess molar volumes, V^E, as a function of x_1 for {x [Bmim][BF4] + (1 − x) 1-pentanol} binary mixtures, at T = 298K (●),303K (○), 308K (▼) and 313K (Δ).

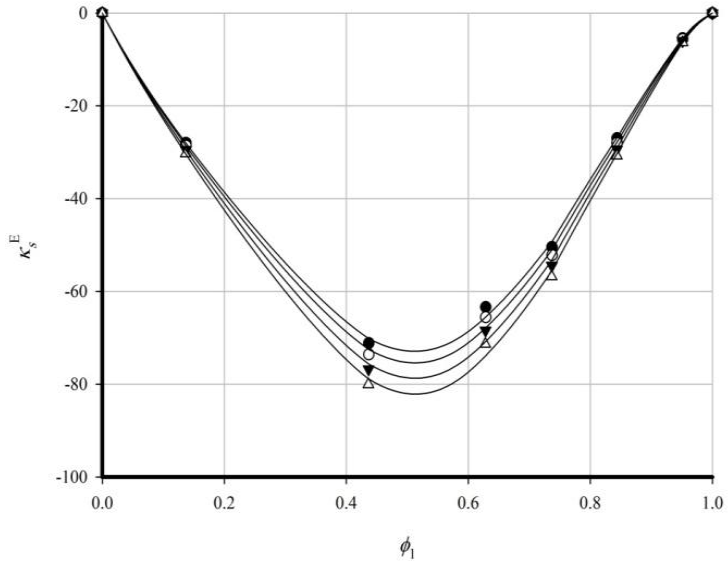

Fig. 2 Excess isentropic compressibility, k_s^E, as a function of □$_1$for {x [Bmim][BF4] + (1 − x) 1-pentanol }binary mixtures, at T = 298K (●),303K (○), 308K (▼), 313K (Δ).

