Non-ideal behaviour of a room temperature ionic liquid in an alkoxyethanol or poly ethers at $T = (298.15$ to $318.15)$ K

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Abstract

Non-ideal behaviour of 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$] in ethylene glycol monomethyl ether; CH$_3$OCH$_2$CH$_2$OH (EGMME), ethylene glycol dimethyl ether; CH$_3$OCH$_2$CH$_2$OCH$_3$ (EGDME) and diethylene glycol dimethyl ether; CH$_3$(OCH$_2$CH$_2$)$_2$OCH$_3$ (DEGDME) have been investigated over the whole composition range at $T = (298.15$ to $318.15)$ K. To gain insight into the mixing behaviour, results of density measurements were used to estimate excess molar volumes, V_m^E, apparent molar volumes, $V_{\phi,i}$, partial molar volumes, $\overline{V}_{m,i}$, excess partial molar volumes, $\overline{V}_{m,i}^E$, and their limiting values at infinite dilution, $V_{\phi,i}^\infty$, $\overline{V}_{m,i}^\infty$, and $\overline{V}_{m,i}^{E,\infty}$, respectively. Volumetric results have been analyzed in the light of Prigogine–Flory–Patterson (PFP) statistical mechanical theory. Measurements of refractive indices n were also performed for all the binary mixtures over whole composition range at $T = 298.15$ K. Deviations in refractive indices $\Delta_\phi n$ and the deviation of molar refraction Δ_{xR} have been calculated from experimental data. Refractive indices results have been correlated with volumetric results and have been interpreted in terms of molecular interactions. Excess properties are fitted to the Redlich–Kister polynomial equation to obtain the binary coefficients and the standard errors.
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1. Introduction

Ionic liquids (IL) [1] are attracting great interest as 'greener' alternatives to conventional organic solvents because of their wide thermal liquid range and negligibly low vapour pressures [2]. Physicochemical properties and behavior of ILs with respect to their miscibility with other solvents or substrates can be tuned either by changing the chemical nature of the cation or that of the anion. They have been used for a variety of applications, ranging from novel reaction media for organic synthesis, chemical processing, (liquid + liquid) separations, (vapor + liquid) equilibria, batteries, and fuel cells investigations [3–6].

Homogeneous mixtures of IL with organic solvents have immense potential as substitutes for conventional binary mixtures for the design of any technological processes. Although the characterization of ILs as solvents, or reaction media, has been established for a large number of systems, detailed knowledge on the thermodynamic behaviour of the mixtures of ionic liquids with organic solvents is very limited.

1-Butyl-3-methylimidazolium hexafluorophosphate [bmim][PF$_6$] is one of the most commonly investigated room temperature ionic liquid. Its thermo-physical properties [7–10], (solid + liquid) and (liquid + liquid) equilibria in aqueous or non-aqueous solvents [11–13], solubility in hydrocarbons [14] and thermodynamic mixing properties with some molecular organic solvents [15–21] have been reported. In this paper, we present the density and refractive index measurements for the binary mixtures of [bmim][PF$_6$] with ethylene glycol monomethyl ether

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(EGMME), ethylene glycol dimethyl ether (EGDME) and diethylene glycol dimethyl ether (DEGDME) over the whole composition range at constant temperatures. The chosen solvents are amphiphilic compounds and have been systematically studied over the past few years with aqueous and non-aqueous solvents in our laboratory as well as at other places [22–32]. The present work is mainly devoted to the study of the changes arising from the polar head group, *i.e.* substitution of a methyl group for a hydroxyl hydrogen and that of addition of a –OC$_2$H$_4$-group in the amphiphilic compound. The primary objective of this work is to characterize molecular interactions and to provide some quantitative insight concerning the experimental volumetric and refractive behavior of the binary mixtures of alkoxyethanol or poly ethers in an ionic liquid.

2. Experimental

2.1. Materials

Air and moisture stable IL; 1-butyl-3-methylimidazolium hexafluorophosphate (>98.0 mol%), was purchased from Sigma–Aldrich. Because the trace amounts of water in ILs can have a dramatic effect on physical properties [33], IL was dried and degassed under vacuum at 60 °C for 2–3 days to get rid of moisture. Karl–Fisher analysis of the samples indicated that the water content was reduced to 0.01 mass%. Synthesis grade ethylene glycol monomethyl ether (>99.5 mol%), ethylene glycol dimethyl ether (>99 mol%), diethylene glycol dimethyl ether (>99 mol%), were obtained from Merck-Schuchardt, and were used without further purification. Purity of the compounds was also checked by comparing density and refractive index val-

ues with the literature values at 298.15 K in table 1 [8,15,22–30,34–36]. All samples were kept in tightly sealed dark bottles to minimize the absorption of atmospheric moisture and CO$_2$, and dried over 0.4 nm molecular sieves before use. Before measurement, all liquids were partially degassed under vacuum. Binary mixtures were prepared by mass, using an analytical balance with a precision of ±0.0001 g (Denver Instrument APX-200). All the binary mixtures were homogeneous in the experimental temperature range. Homogeneity was ensured by measuring UV absorbance at different time intervals as well as through the visual appearance of the samples. The mole fraction of each mixture was obtained with an accuracy of 1×10^{-4} from the measured masses of the components. All molar quantities are based on the relative atomic mass table of 1985 issued by IUPAC in 2001 [37].

2.2. Density measurements

The density of the pure liquids and their binary mixtures were measured with an Anton Paar (Model DMA 4500) vibrating-tube densimeter with a resolution of 5×10^{-5} g·cm^{-3}. The densimeter was calibrated with doubly distilled, degassed water, and with dry air at atmospheric pressure. The temperature of the apparatus was controlled to within ±0.01 K by a built-in Peltier device that corresponds to an uncertainty in density of ±0.0002%. The overall uncertainty in comparison with literature data for the calibrating liquids and in the averaged density measurements of the binary mixtures is judged to be less than 0.02%. Measurements using the mixtures and the corresponding pure components were quite consistent with an estimated reproducibility of 2×10^{-4} g·cm^{-3}.

TABLE 1
Observed and literature values of densities ρ, isobaric thermal expansivities α_p, molar isobaric heat capacities $C_{p,m}$, and refractive indices n at $T = 298.15$ K

Compound	ρ/(kg·m^{-3})		α_p/(k·K^{-1})	$C_{p,m}$/(J·K^{-1}·mol^{-1})	n	
	Observed	Literature			Observed	Literature
[bmim][PF$_6$]	1367.88	1366.657[a] 1367.3[b] 1367.45[c] 1367.88[d]	0.622[e]	397.57[f]	1.4089	1.40937[b]
EGMME	960.05	960.02[g]	0.956[h]	174.25[i]	1.4004	1.40046[j]
EGDME	864.47	862.62[k]	1.277[l]	193.3[m]	1.3790	1.37730[n]
DEGDME	939.10	938.73[l]	1.055[i]	279.58[l]	1.4058	1.4058[m]

[a] Reference [15].
[b] Reference [16].
[c] Reference [17].
[d] Reference [18].
[e] Reference [31].
[f] Reference [8].
[g] Reference [25].
[h] Reference [26].
[i] Reference [27].
[j] Reference [28].
[k] Reference [29].
[l] Reference [30].
[m] Reference [35].
[n] Reference [36].

Reproducibility of the results was confirmed by performing the measurements in triplicate. Experimental uncertainty in the estimated excess molar volume is approximately $\pm 2 \times 10^{-3} \, \text{cm}^3 \cdot \text{mol}^{-1}$. The uncertainty estimates do not include the effects of certain minor impurities that may be present in the 1-butyl-3-methylimidazolium hexafluorophosphate.

2.3. Refractive index measurements

Refractive indices were measured using a Mettler-Toledo (Model RE-40D) refractrometer having a high resolution optical sensor. Measurements were made with a resolution and limit of error $\pm 1 \times 10^{-4}$. The temperature of the apparatus was controlled to within ± 0.1 K by a built-in Peltier device. Dried and degassed samples kept in desiccators were directly injected through a syringe in the measuring cell. Reproducibility of the results was confirmed by performing at least three experiments for each sample.

3. Results and discussion

3.1. Volumetric behaviour

Measured density values as a function of composition at $T = (298.15$ to $318.15)$ K are presented in table 2. Density values were used to estimate excess molar volume using the relation

$$V_m^E = V_m - V_M^{id} = \frac{(x_1 M_1 + x_2 M_2)}{\rho} - \left[\frac{x_1 M_1}{\rho_1^*} + \frac{x_2 M_2}{\rho_2^*} \right], \quad (1)$$

where V_m and V_m^{id} are the real and ideal molar volumes of the solutions; ρ, ρ_1^* and ρ_2^* are the density of mixture, component 1 and component 2 of the mixture; M_1, M_2 and x_1, x_2 are the molar masses and mole fractions of component 1 and component 2, respectively. Composition dependence of V_m^E were correlated using a Redlich–Kister type polynomial equation

$$F(x) = x_1 x_2 \sum_{i=0}^{n} A_i (2x_1 - 1)^i. \quad (2)$$

The coefficients A_i of equation (2) were calculated by the method of least squares. The values obtained for the coefficients A_i along with the standard deviations σ are reported in table 3. Comparison of excess molar volumes for different binary mixtures ([bmim][PF$_6$] + EGMME or EGDME or DEGDME) as a function of composition at $T = 298.15$ K is shown in figure 1. Excess molar volumes are negative in organic solvent rich region and positive in ionic liquid region for the mixtures [bmim][PF$_6$] + EGMME and [bmim][PF$_6$] + DEGDME while completely negative for the mixture [bmim][PF$_6$] + EGDME. There is an increase in the magnitudes of the excess molar volumes with the substitution of a methyl group for hydroxyl hydrogen. Not so clear-out appears the variation of V_m^E

TABLE 2
Experimental densities ρ for the binary mixture at different temperatures

x_1	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\rho/(\text{g} \cdot \text{cm}^{-3})$	$\rho/(\text{g} \cdot \text{cm}^{-3})$
	$T = 298.15$ K	$T = 308.15$ K	$T = 318.15$ K
	[bmim][PF$_6$] + EGMME		
0.0000	0.96005	0.95081	0.94145
0.0037	0.96455	0.96253	0.94596
0.0078	0.96943	0.96734	0.95088
0.0120	0.97436	0.97219	0.95582
0.0354	1.00013	0.99766	0.98170
0.0801	1.04278	1.03997	1.02448
0.1468	1.09424	1.09112	1.07609
0.2542	1.15735	1.15341	1.13953
0.3960	1.21908	1.21360	1.20172
0.6104	1.28464	1.27788	1.26748
0.8127	1.32813	1.32065	1.31110
0.8961	1.34477	1.33668	1.32790
0.9345	1.35285	1.34449	1.33600
0.9749	1.36190	1.35335	1.34499
1.0000	1.36788	1.35933	1.35087
	[bmim][PF$_6$] + EGDME		
0.0000	0.86447	0.85347	0.84227
0.0125	0.87928	0.86836	0.85725
0.0416	0.91209	0.90137	0.89047
0.1055	0.97653	0.96623	0.95579
0.1219	0.99151	0.98131	0.97100
0.2474	1.08914	1.07957	1.06997
0.3744	1.16422	1.15509	1.14598
0.4937	1.21989	1.21103	1.20222
0.7092	1.29636	1.28772	1.27925
0.9329	1.35378	1.34527	1.33685
1.0000	1.36788	1.35933	1.35087
	[bmim][PF6] + DEGDME		
0.0000	0.93910	0.92960	0.91930
0.0039	0.94216	0.93257	0.92234
0.0076	0.94503	0.93537	0.92520
0.0127	0.94897	0.93922	0.92913
0.0304	0.96227	0.95230	0.94243
0.0505	0.97674	0.96673	0.95703
0.1003	1.01023	1.00046	0.99093
0.1617	1.04781	1.03853	1.02898
0.2070	1.07360	1.06459	1.05502
0.3024	1.12455	1.11544	1.10604
0.4018	1.17396	1.16458	1.15565
0.5023	1.21947	1.21050	1.20205
0.5623	1.24360	1.23527	1.22697
0.7197	1.29224	1.28605	1.27769
0.9477	1.34516	1.33693	1.32847
0.9842	1.35924	1.35131	1.34285
0.9952	1.36536	1.35687	1.34847
1.0000	1.36788	1.35933	1.35087

with the addition of a –OC$_2$H$_4$-group in the molecule of EGDME. However, there is a crossover in the magnitude of V_m^E for the mixtures of [bmim][PF$_6$] + EGDME and [bmim][PF$_6$] + DEGDME in the central region of the curve. It is interesting to compare the volumetric behaviour of an alkoxyethanol or polyethers in water [29] or methanol [24,28,38] to the behaviour in [bmim][PF$_6$]. The overall magnitude of V_m^E of binary mixtures of investigated an alkoxyethanol or poly ethers with [bmim][PF$_6$], or water or methanol is in the order [bmim][PF$_6$] > water > methanol.

TABLE 3
Parameters of equation (1) with standard deviations σ of $V_m^E/(\text{cm}^3 \cdot \text{mol}^{-1})$ at different temperatures

T/K	A_0	A_1	A_2	A_3	A_4	σ
			[bmim][PF$_6$] + EGMME			
298.15	0.5722	4.8326	0.8244	8.4357		0.0203
308.15	0.4170	4.9719	0.6853	8.4503		0.0030
318.15	0.2498	5.1444	0.5789	8.4003		0.0282
			[bmim][PF$_6$] + EGDME			
298.15	−11.6593	6.5406	−4.2977	1.6419		0.0006
308.15	−12.4838	6.9996	−4.6084	1.6610		0.0022
318.15	−13.4110	7.4327	−4.9536	1.7784		0.0015
			[bmim][PF$_6$] + DEGDME			
298.15	−14.5917	−3.4546	10.5665	34.7160	10.4204	0.0312
308.15	−15.0097	−5.3946	3.7434	35.2616	18.9685	0.0055
318.15	−15.9839	−5.8674	5.2429	37.3647	16.6026	0.0078
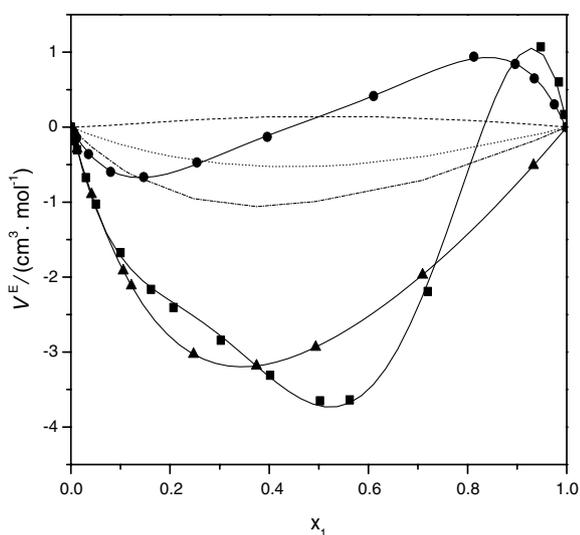
FIGURE 1. V_m^E for binary mixtures of [bmim][PF$_6$] + EGMME (●); + EGDME (▲); DEGDME (■) at 298.15 K. Curves (—, EGMME; -...-, EGDME: ......, DEGDME) were drawn using PFP theory.
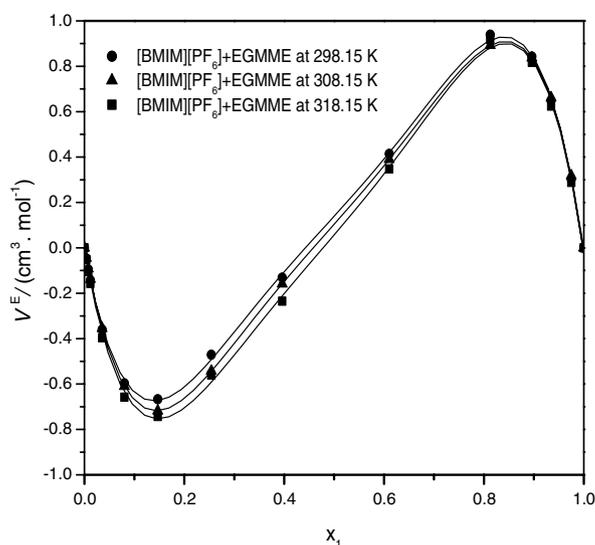
FIGURE 2. V_m^E for binary mixtures of [bmim][PF$_6$] + EGMME at (298.15, 308.15, and 318.15) K.

Temperature dependence of V_m^E for all the three binary mixtures over whole composition range is shown in figures 2–4. Magnitude of V_m^E increases with the rise of temperature in all the binary mixtures.

The volume of mixing that accompanies the addition of [bmim][PF$_6$] to ether is the result of different effects which can be divided into physical, chemical, and geometrical contributions. Physical interactions involve mainly dispersion forces, giving a positive contribution to V_m^E. Chemical or specific interactions result from disruption of the ether structure through breaking of hydrogen bonds, as well as weakening of the interactions between like molecules and enhancement of unlike interactions mainly ion–dipole interactions between [bmim] cation and ether dipoles, or complex forming interactions, i.e. due to formation of liquid clathrates or quasi-clathrates. Geometrical or structural effects, arising from interstitial accommodation due to
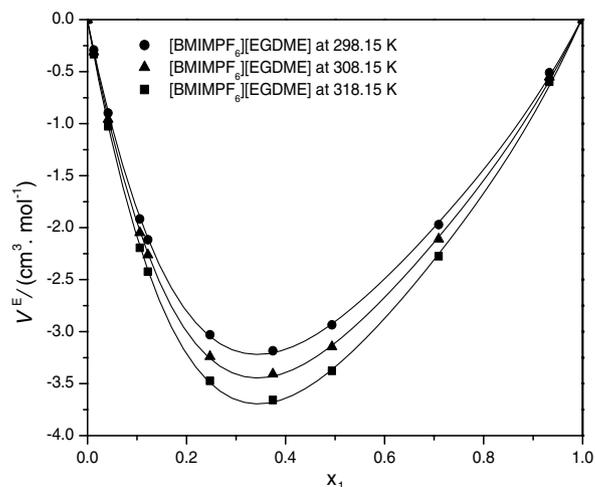
FIGURE 3. V_m^E for binary mixtures of [bmim][PF$_6$] + EGDME at (298.15, 308.15, and 318.15) K.
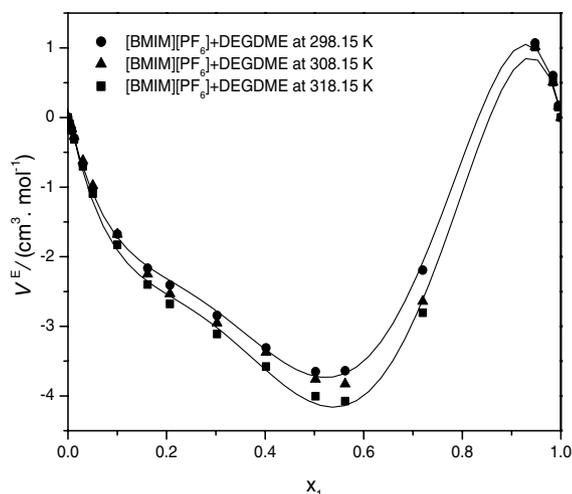
FIGURE 4. V_m^E for binary mixtures of [bmim][PF$_6$] + DEGDME at (298.15, 308.15, and 318.15) K.

differences in the molar volumes of liquid components and hence contribute negative terms to V_m^E.

3.2. Prigogine–Flory–Patterson theory

The Prigogine–Flory–Patterson (PFP) theory [39–41] has been commonly employed to analyze excess thermodynamic functions. This theory has been useful in interpreting the results of measurements of the excess properties of a number of binary systems formed by molecular species that differ in size and shape . Although in the development of the theory, hydrogen bonds and interactions of strong electrostatic nature are specifically excluded, a purely empirical application of the Flory formalism can still provide an interesting correlation between the excess volumes of more complex mixtures. In fact, and despite the ionic character of the IL systems, the use of Flory-type theories has proven successful in predicting and modeling both the excess properties and fluid-phase behavior of IL-containing mixtures [42–45]. PFP theory considered a molecule to be made of up of equal segments (isometric portions), the effective number being r. Each segment has a intermolecular contact sites capable of interacting with neighboring sites. According to PFP theory, V_m^E is divided into an interactional contribution, a free volume contribution and a P^* contribution. The expression for V_m^E which separates the three contributions is given as

$$\frac{V_m^E}{(x_1 V_1^* + x_2 V_2^*)} = \frac{(\tilde{v}^{1/3} - 1)\tilde{v}^{2\backslash 3}}{[(4/3)\tilde{v}^{1/3} - 1]}\psi_1\theta_2\left[\frac{\chi_{12}}{\tilde{v}}\right] \quad \text{(interactional)} -$$
$$\frac{(\tilde{v}_1 - \tilde{v}_2)^2[(14/9)\tilde{v}^{1/3} - 1]}{[(4/3)\tilde{v}^{1/3} - 1]}\psi_1\psi_2 \quad (\tilde{v} \text{ curvature}) +$$
$$\frac{(\tilde{v}_1 - \tilde{v}_2)^2 - (P_1^* - P_2^*)}{P_1^*\psi_2 + P_2^*\psi_1}\psi_1\psi_2 \quad (P^*\text{effect})$$

(3)

where ψ represents the contact energy fraction, given by:

$$\psi_1 = 1 - \psi_2 = \frac{\varphi_1 P_1^*}{\varphi_1 P_1^* + \varphi_2 P_2^*}.$$

(4)

Here x is the mole fraction, P^* and V^* are the characteristic pressure and molar volume, respectively, $\tilde{v}$ is a reduced volume, θ and ϕ are segment and site fractions, respectively, and χ_{12} is the so-called cross interaction parameter. The 1 and 2 subscripts refer to the two pure components, whereas quantities without a subscript refer to the mixture.

The values of the parameters for the pure liquid components and the mixture are obtained using the Flory theory [41]. The parameters for the pure liquid components derived using Flory's expression are listed in table 4. The cross interaction parameter χ_{12} required for the calculation of V_m^E using PFP theory was derived from values of excess molar volumes at equimolar composition for each mixture. A detailed account of calculation procedure of various parameters required for the calculation of V_m^E using PFP theory is given in supplementary information. The calculated equimolar values of the three contributions together with χ_{12} parameter are summarized in table 5. Study of table 5 reveals that both the P^* contribution and the free volume effects are negative for all the mixtures, whereas interactional contribution is positive for EGMME.

Cross-interaction parameter χ_{12} when negative for EGDME and DEGDME systems, suggests a relatively

TABLE 5
Calculated values of the contributions to the excess molar volume at equimolar composition from the Prigogine–Flory–Patterson theory at $T = 298.15$ K

Compound	$\chi_{12}/(\text{J} \cdot \text{cm}^{-3})$	Calculated contribution		
		Interaction	Free volume	P^* effect
EGMME	41.36	0.524	−0.186	−0.189
EGDME	−1.395	−0.192	−0.776	−0.208
DEGDME	−2.217	−0.322	−0.470	−0.143

TABLE 4
Characteristic parameters of pure components at $T = 298.15$ K

Compound	$\kappa_T/(\text{T} \cdot \text{Pa}^{-1})$	$\tilde{v}$	$V/(\text{cm}^3 \cdot \text{mol}^{-1})$	$V^*/(\text{cm}^3 \cdot \text{mol}^{-1})$	$T^*/(\text{K})$	$P^*/(\text{J} \cdot \text{cm}^{-3})$
[bmim][PF$_6$]	411.75[a]	1.1647	207.7539	178.370	7001	611
EGMME	800.00[b]	1.2386	79.2667	63.996	5364	547
EGDME	1116.51[c]	1.3019	104.2489	80.076	4611	578
DEGDME	819.42[c]	1.2589	142.8820	113.50	5081	608

[a] Reference [31].
[b] Reference [28].
[c] Reference [29].

strong inter-molecular specific interactions (ion–dipole or van der Waals) with [bmim][PF$_6$]. However, when it is positive, as for EGMME, it is expected that the specific interactions decreases. The free volume becomes less negative as the difference between the reduced volumes of two components in the mixture decreases and thereby interstitial accommodation becomes less significant, resulting in decrease of V_m^E, as in case of EGMME system. The P^* effect which depend on the relative cohesive energy of the expanded and less expanded component is negative for all the systems and hence makes a negative contribution to the for all the mixtures. Theoretical values of calculated using PFP theory are also plotted in figure 1 along with the experimental V_m^E values. The behaviour is only qualitatively similar for the mixtures of IL with EGDME and DEGDME and does not explain the behaviour with EGMME where V_m^E changes from negative to positive at higher mole fractions. Quantitatively the V_m^E values calculated using PFP theory is not completely satisfactory with the experimental results.

3.3. Apparent and partial molar volumes

The apparent molar volumes of the [bmim][PF$_6$] in organic solvents were derived from the relation

$$V_{\phi,1} = \frac{M_2(1-x_1)(\rho_2^* - \rho)}{x_1\rho\rho_2^*} + \frac{M_1}{\rho}. \quad (5)$$

Variation of apparent molar volumes of [bmim][PF$_6$] as a function of composition is shown in figure 5. Since apparent molar properties do not clearly separate the contributions of both components of the mixture, we directed our attention to more structurally informative properties such as excess partial molar volumes. The excess partial molar volumes, $\overline{V}_{m,1}^E = \overline{V}_{m,1} - V_{m,1}$ and $\overline{V}_{m,2}^E = \overline{V}_{m,2} - V_{m,2}$, can be calculated from V_m^E. The partial molar volumes of the [bmim][PF$_6$] was evaluated [46,47] over the whole composition range using the relation
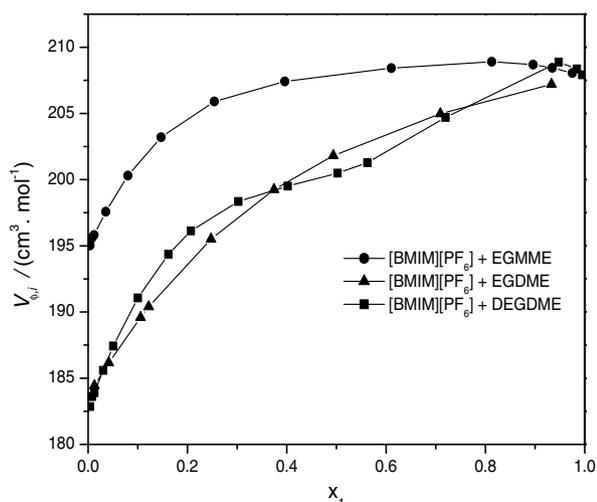

FIGURE 5. $V_{\phi,i}$ for binary mixtures of [bmim][PF$_6$] + EGMME (●); + EGDME (▲); DEGDME (■) at 298.15 K.

$$\overline{V}_{m,1} = V_{m,1} + \left(\frac{V_m^E}{x_1}\right) + x_1(1-x_1)\left[\frac{\partial(V_m^E/x_1)}{\partial x_1}\right]_{P,T}. \quad (6)$$

The results of excess partial molar volume of [bmim][PF$_6$] in organic solvents are shown in figure 6. Apparent molar volumes and excess partial molar volumes of [bmim][PF$_6$] show similar behaviour over the whole composition range. The sharp decrease in $V_{\phi,1}$ and $\overline{V}_{m,1}^E$ at low mole fraction would imply more structure or clustering in the organic liquid rich environment. In the thermodynamic analysis of liquid mixtures, values of the limiting properties at infinite dilution are particularly significant. The limiting values estimated for apparent and partial molar volumes of [bmim][PF$_6$] are reported in table 6 and are in the order EGMME > EGDME > DEGDME. Excess partial molar volumes at infinite dilution are also listed in table 6. Negative $\overline{V}_{m,i}^{E,\infty}$ values were obtained for all the mixtures reflecting that the solute–solvent interactions are stronger than the intermolecular interactions between the pure components and follow the order EGMME < EGDME < DEGDME.

3.4. Refractive index and molar refraction

Refractive indices n for all the binary mixtures as function of composition over the whole mole fraction range and at $T = 298.15$ K are reported in table 7. Since deviation of n from ideality $\Delta_\phi n$ correlates well with V_m^E and physically
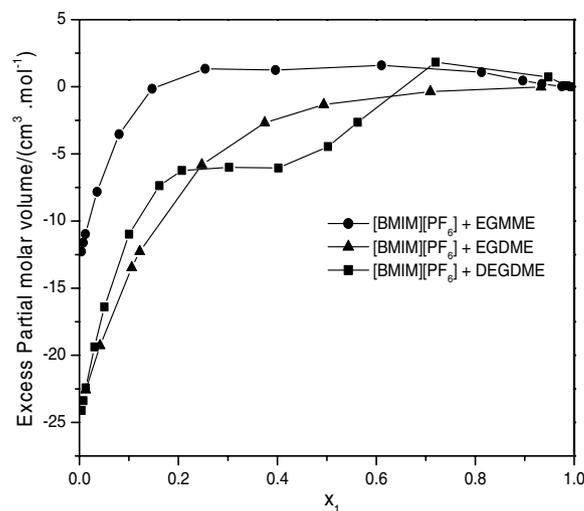
FIGURE 6. $\overline{V}_{m,i}^E$ for binary mixtures of [bmim][PF$_6$] + EGMME (●); + EGDME (▲); DEGDME (■) at 298.15 K.

TABLE 6
Apparent, partial and excess partial molar volume of [bmim][PF$_6$] at infinite dilution in mono or poly ethers at $T = 298.15$ K

Compound	$V_{\phi,i}^\infty/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\overline{V}_{m,i}^\infty/(\text{cm}^3 \cdot \text{mol}^{-1})$	$\overline{V}_{m,i}^{E,\infty}/(\text{cm}^3 \cdot \text{mol}^{-1})$
EGMME	194.83	194.94	−12.81
EGDME	183.66	183.63	−24.13
DEGDME	182.64	182.61	−25.14

TABLE 7
Refractive indices n for binary mixtures at $T = 298.15$ K

x_1	n	x_1	n	x_1	n
[bmim][PF$_6$] + EGMME		[bmim][PF$_6$] + EGDME]		[bmim][PF$_6$] + DEGDME	
0.0000	1.4004	0.0000	1.3790	0.0000	1.4058
0.0037	1.4006	0.0041	1.3781	0.0039	1.4063
0.0078	1.4010	0.0125	1.3798	0.0076	1.4065
0.0120	1.4013	0.0416	1.3859	0.0127	1.407
0.0354	1.4030	0.1055	1.3926	0.0304	1.4081
0.0801	1.4050	0.1219	1.3941	0.0505	1.4092
0.1468	1.4065	0.2474	1.4009	0.1003	1.4113
0.2542	1.4078	0.3744	1.4043	0.1617	1.4141
0.3960	1.4083	0.4937	1.4062	0.2070	1.4149
0.6104	1.4086	0.7092	1.4076	0.3024	1.4148
0.8127	1.4086	0.9329	1.4087	0.4018	1.4142
0.8961	1.4089	1.0000	1.4089	0.5023	1.4138
0.9345	1.4090			0.5623	1.4123
0.9749	1.4090			0.7197	1.4098
1.0000	1.4089			0.9477	1.4094
				0.9842	1.4089
				1.0000	1.4058

FIGURE 7. $\Delta_\phi n$ for binary mixtures of [bmim][PF$_6$] + EGMME ($\bullet$); + EGDME ($\blacktriangle$); DEGDME ($\blacksquare$) at 298.15 K.

interpretable as the deviation of reduced free volume from ideality when calculated on volume fraction basis [48] as

$$\Delta_\phi n = n - \phi_1 n_1 - \phi_2 n_2, \tag{7}$$

where ϕ_1 and ϕ_2 are the volume fractions of component 1 and 2, respectively. $\Delta_\phi n$ values were correlated using equation 2 and the binary coefficients along with the standard deviations are given in table 8. Values for all the binary mixtures are plotted in figure 7 as a function of volume fraction over the whole composition region. It is worth pointing out that the wide validity of the rule that $\Delta_\phi n$ is negatively correlated with V_m^E is true for the binary mixtures of mono or poly ethers with [bmim][PF$_6$]. Magnitude of $\Delta_\phi n$ is in the order EGMME < DEGDME < EGDME and the maxima appear to shift towards the higher volume fraction region with the substitution of a methyl group for a hydroxyl hydrogen in the ether molecule.

The hard core volume of real mixtures is assumed to be additive on a mole fraction basis by a number of models e.g. Flory theory [41], therefore, deviation of molar refraction R (which is considered as hard core volume) from ideality was calculated on mole fraction basis using the relation

$$\Delta_x R = R - x_1 R_1 - x_2 R_2. \tag{8}$$

Here, molar refraction R is defined by: $R = V_m (n^2 - 1)/(n^2 + 2)$, and all the symbols have their usual meaning. $\Delta_x R$ Values were correlated using equation 2 and the binary coefficients along with the standard deviations are given in table 8. Shown in figure 8, are negative for all the mixtures and the magnitude is in the order EGMME < DEGDME < EGDME.

FIGURE 8. $\Delta_x R$ for binary mixtures of [bmim][PF$_6$] + EGMME ($\bullet$); + EGDME ($\blacktriangle$); DEGDME ($\blacksquare$) at 298.15 K.

TABLE 8
Parameters of equation (1) with standard deviations σ at $T = 298.15$ K

Compound	A_0	A_1	A_2	A_3	A_4	σ
			$\Delta_\phi n$			
EGMME	0.0129	−0.0089	0.0030			0.0001
EGDME	0.0388	−0.0193	−0.0004			0.0008
DEGDME	0.0296	−0.133	0.0093			0.0001
			$\Delta_x R/(cm^3 \cdot mol^{-1})$			
EGMME	−11.2063	10.2264	−1.7087	10.5753	−5.8080	0.0114
EGDME	−34.4190	19.7506	−11.6047	8.1338	−4.1977	0.0109
DEGDME	−32.4620	6.2822	5.7162	28.9328	4.1771	0.0256

4. Conclusions

[bmim][PF$_6$] is completely miscible over the whole composition range in the alkoxyethanol or poly ethers investigated in this report. Departure from ideality is significant for all the mixtures and increases with the replacement of hydroxyl hydrogen with that of a methyl group in the ether molecule. Temperature dependence of volumetric properties shows only a small change in magnitude. Limiting volumetric properties at infinite dilution indicate structuring of IL and interstitial accommodation of molecules in low mole fraction region. Refractive behaviour correlates well with that of volumetric behaviour. Prigogine–Flory–Patterson (PFP) theory does not explain the volumetric behavior of investigated mixtures completely satisfactorily.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2007.06.002.

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