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Densities of 1-Butyl-3-methylimidazolium Hexafluorophosphate + Poly(ethylene glycol) in the Temperature Range (283.15 to 363.15) K

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ABSTRACT: Densities of 1-butyl-3-methylimidazolium hexafluorophosphate ($[\mathrm{bmim}][\mathrm{PF}_6]$) + poly(ethylene glycol) [PEG] mixtures prepared with PEGs of average molecular weight 400 (PEG400), number-average molecular weight M_n 570 to 630 (PEG600), and number-average molecular weight M_n 950 to 1050 (PEG1000), respectively, have been measured over the entire composition regime in the temperature range (283.15 to 363.15) K at 10 K intervals using a density meter based on electromagnetically induced oscillations of a U-shaped glass tube and an in-built Peltier thermostat. The density of ($[\mathrm{bmim}][\mathrm{PF}_6]$ + [PEG]) mixtures at each composition for all three PEGs is found to decrease linearly with increasing temperature. The excess molar volumes (V^E) of all the three ($[\mathrm{bmim}][\mathrm{PF}_6]$ + PEG) mixtures were observed to be negative at all temperatures and were correlated to the mole fraction of $[\mathrm{bmim}][\mathrm{PF}_6]$, $X_{[\mathrm{bmim}][\mathrm{PF}_6]}$, in the mixture by Redlich−Kister-type equations. Importantly, the absolute values of V^E for ($[\mathrm{bmim}][\mathrm{PF}_6]$ + PEG) mixtures appear to increase slightly with increasing temperature. These observations are attributed to the presence of complex interactions within the ($[\mathrm{bmim}][\mathrm{PF}_6]$ + PEG) mixtures. Specifically, they are proposed to have their origin in extensive intermolecular H-bonding involving the C2 hydrogen of $[\mathrm{bmim}^+]$ and termini −OH as well as the ethoxy −O− of PEG within ($[\mathrm{bmim}][\mathrm{PF}_6]$ + PEG) mixtures.

INTRODUCTION

Due to their unique physicochemical properties and negligible vapor pressure, room-temperature ionic liquids (ILs) are attracting enormous interest from the scientific community as potential solvents to replace volatile organic compounds (VOCs). Among various alternatives to these VOCs,[1−7] these ILs along with poly(ethylene glycols) [PEGs] have found immense industrial importance.[7] Solvent systems composed of (IL + PEG) provide exciting "hybrid green" systems that may afford interesting and favorably modified physicochemical properties enhancing the potential of both ILs and PEGs in many chemical applications.[8,9] Though the physicochemical properties of ILs and PEGs are proposed to be tunable by altering cation/anion combinations in ILs and by varying the average molar mass of PEGs, respectively, nearly not enough modification in key physicochemical properties can be achieved by doing so. Consequently, cosolvent-modified PEG and IL systems are becoming a topic of active research, where "green" cosolvents, such as water, ethanol, supercritical CO_2, etc., have obvious importance. (IL + PEG) mixtures rather than neat ILs and neat PEGs may provide substantially improved physicochemical properties for many industrial applications. The most striking property of both IL and PEG that renders them the most attention is perhaps their extremely low vapor pressure, which has been employed widely in chemistry and related disciplines.[10−24]

Despite various investigations of these relatively benign media, information on physical properties of (IL + PEG) mixtures is still incomplete and limited. Among key physicochemical properties, density has enormous importance as far as various industrial applications are concerned. Only few publications report density as a function of temperature for any kind of (IL + PEG) mixtures. We are aware of only very few publications showing temperature-dependent densities of (IL + PEG) mixtures. In one of such studies, densities of the mixture of PEG (M_w = 200, 300, 400) and polyethyleneimine with ILs $[\mathrm{bmim}][\mathrm{BF}_4]$ and $[\mathrm{bmim}][\mathrm{PF}_6]$ in the temperature range (303 to 338) K are reported.[25] However, in this work, temperature as well as

Table 1. Comparison of Experimental Densities (ρ) of Neat PEG400, PEG600, and $[\mathrm{bmim}][\mathrm{PF}_6]$ with the Literature Values at Different Temperatures

	$\rho/\mathrm{g \cdot cm^{-3}}$					
	PEG400		PEG600		$[\mathrm{bmim}][\mathrm{PF}_6]$	
T/K	exp.	lit.	exp.	lit.	exp.	lit.
283.15	1.1348	1.1351[a]				
293.15	1.1262	1.1265[a]				
303.15	1.1178	1.1181[a] 1.1180[b]	1.1184	1.1186[a]	1.3626	1.3624[d]
313.15	1.1094	1.1098[a] 1.1097[b] 1.1102[c]	1.1100	1.1102[a]	1.3541	1.3542[d]
323.15	1.1012	1.1015[a] 1.1017[b] 1.1020[c]	1.1017	1.1019[a]		
333.15	1.0959	1.0962[a]	1.0964	1.0965[a]		
343.15	1.0898	1.0901[a]	1.0903	1.0904[a]		
353.15	1.0830	1.0833[a]	1.0835	1.0836[a]		
363.15	1.0755	1.0758[a]	1.0760	1.0761[a]		

[a] Ref 43. [b] Ref 44. [c] Ref 45. [d] Ref 46.

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Table 2. Densities (ρ/g·cm^{-3}) of the Mixture of 1-Butyl-3-methylimidazolium Hexafluorophosphate ([bmim][PF_6]) (1) + Poly(ethylene Glycol) [PEG] (2) from T = (283.15 to 363.15) K as a Function of Mass Fraction (w_1) of [bmim][PF_6]

	T/K								
w_1	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15
[bmim][PF_6] + PEG400									
0.0000	1.1348	1.1262	1.1178	1.1094	1.1012	1.0959	1.0898	1.0830	1.0755
0.0732	1.1537	1.1450	1.1367	1.1284	1.1202	1.1148	1.1086	1.1017	1.0941
0.1508	1.1728	1.1641	1.1557	1.1474	1.1392	1.1337	1.1274	1.1204	1.1126
0.2336	1.1928	1.1841	1.1757	1.1673	1.1591	1.1535	1.1471	1.1400	1.1321
0.3214	1.2138	1.2051	1.1966	1.1882	1.1780	1.1742	1.1677	1.1604	1.1524
0.4153	1.2358	1.2271	1.2185	1.2101	1.2019	1.1960	1.1894	1.1820	1.1738
0.5160	1.2595	1.2508	1.2422	1.2338	1.2256	1.2196	1.2128	1.2053	1.1969
0.6238	1.2851	1.2764	1.2678	1.2594	1.2512	1.2451	1.2382	1.2305	1.2220
0.7397	1.3132	1.3045	1.2959	1.2874	1.2792	1.2730	1.2659	1.2580	1.2493
0.8647	1.3447	1.3360	1.3273	1.3188	1.3105	1.3042	1.2969	1.2889	1.2799
1.0000	1.3802	1.3720	1.3626	1.3541	1.3457	1.3391	1.3317	1.3234	1.3142
[bmim][PF_6] + PEG600									
0.0000	solid	solid	1.1184	1.1100	1.1017	1.0964	1.0903	1.0835	1.0760
0.0504	solid	1.1402	1.1317	1.1234	1.1151	1.1097	1.1036	1.0967	1.0891
0.1061	solid	1.1544	1.1459	1.1375	1.1293	1.1238	1.1176	1.1106	1.1030
0.1688	solid	1.1700	1.1614	1.1531	1.1449	1.1393	1.1330	1.1259	1.1181
0.2400	solid	1.1872	1.1787	1.1703	1.1621	1.1564	1.1500	1.1429	1.1350
0.3215	1.2154	1.2068	1.1982	1.1898	1.1815	1.1758	1.1693	1.1620	1.1539
0.4154	1.2380	1.2290	1.2204	1.2120	1.2037	1.1978	1.1912	1.1838	1.1756
0.5248	1.2633	1.2547	1.2462	1.2377	1.2295	1.2235	1.2167	1.2091	1.2008
0.6546	1.2937	1.2852	1.2766	1.2681	1.2598	1.2537	1.2467	1.2390	1.2304
0.8084	1.3313	1.3227	1.3141	1.3056	1.2973	1.2910	1.2838	1.2758	1.2670
1.0000	1.3802	1.3720	1.3626	1.3541	1.3457	1.3391	1.3317	1.3234	1.3142
[bmim][PF_6] + PEG1000									
0.0000	solid	solid	solid	1.1095	1.1010	1.0957	1.0896	1.0828	1.0753
0.0306	solid	solid	solid	1.1179	1.1102	1.1048	1.0987	1.0918	1.0842
0.0663	solid	solid	solid	1.1274	1.1197	1.1143	1.1081	1.1012	1.0936
0.1088	solid	solid	solid	1.3673	1.1303	1.1248	1.1186	1.1116	1.1039
0.1593	solid	solid	solid	1.1507	1.1442	1.1386	1.1323	1.1252	1.1174
0.2213	solid	solid	solid	1.1665	1.1588	1.1532	1.1468	1.1396	1.1317
0.2990	solid	solid	1.1937	1.1854	1.1778	1.1720	1.1656	1.1583	1.1503
0.3987	solid	solid	1.2178	1.2095	1.2010	1.1952	1.1886	1.1812	1.1730
0.5319	solid	1.2576	1.2490	1.2408	1.2323	1.2263	1.2195	1.2119	1.2035
0.7189	1.3103	1.3019	1.2933	1.2851	1.2766	1.2704	1.2633	1.2554	1.2468
1.0000	1.3802	1.3720	1.3626	1.3541	1.3457	1.3391	1.3317	1.3234	1.3142

composition range are rather restricted. In another study, the Pandey group reported temperature-dependent densities of ([bmim][PF_6] + PEG200) mixtures.[26] As far as temperature-dependent densities of neat ILs are concerned, a noteworthy attempt was made by Brennecke et al. to provide information on thermophysical properties of imidazolium-based ILs at different temperature and pressure.[27,28] Another recent contribution toward temperature-dependent density measurement of ILs 1-alkyl-3-methylimidazolium iodides was from Ghatee et al. in which the densities of ILs were reported in the temperature range (298 to 393) K.[29] Pal and co-workers have reported excess thermodynamic properties of binary mixtures of [bmim][PF_6] with alkoxyalkanols.[30] Recently, Sanmamed et al. have proposed an experimental methodology for precise determination of densities of room-temperature ILs as a function of temperature and pressure.[31] Singh and Kumar reported the volumetric behavior of [bmim][PF_6] with ethylene glycol derivatives.[32] Although various groups have studied thermodynamic properties of mixtures of [bmim][PF_6] with some organic solvents,[33−37] systematic investigation of [bmim][PF_6] with PEGs is rare and considered necessary to be explored due to the important features associated with ILs and PEGs.

Here, we report the densities of ([bmim][PF_6] + PEG) mixtures prepared using PEGs of average molecular weight 400 (PEG400), number-average molecular weight M_n 570 to 630 (PEG600), and number-average molecular weight M_n 950 to 1050 (PEG1000) over the entire composition range in the temperature range (283.15 to 363.15) K at 10 K intervals. Our choice of IL is governed by the fact that [bmim][PF_6] is perhaps the most investigated IL to date as evident from the chemical literature of the past decade and a half. Further, IL [bmim][PF_6] has a melting point of 9 °C,[38] which allows the measurements of densities at 10 °C (283.15 K) as the samples are in the liquid state. Lastly, IL [bmim][PF_6], as opposed to another common and popular IL [bmim][BF_4], is recently reported to have good hydrolytic stability.[39−42] This may result in increased potential applications of this IL in industrial settings. We have selected PEG400, PEG600, and PEG1000 mainly due to the fact that, except for PEG600 and PEG1000 and their mixtures with IL [bmim][PF_6] at very few temperatures, our mixtures remain liquid at most of the temperatures in the temperature range (283.15 to 363.15) K. Further, enough variation in polymer chain length is achieved in going from PEG400 to PEG1000. To measure the densities of ([bmim][PF_6] + PEG) mixtures, we have used a density meter which is based on electromagnetically induced oscillations of a U-shaped glass tube having a built-in Peltier thermostat controller. The standard deviations associated with the density measurement are ≤0.00005 $g\cdot cm^{-3}$.

EXPERIMENTAL SECTION

Materials. PEGs of average molecular weight 400 (PEG400), number-average molecular weight M_n 570 to 630 (PEG600), and number-average molecular weight M_n 950 to 1050 (PEG1000) were obtained in the highest purity from Sigma-Aldrich and stored under dried conditions. IL [bmim][PF_6] was obtained from Merck (Ultrapure, halide content <10 ppm, water content <10 ppm) and was stored under dry argon.

Method. The ([bmim][PF_6] + PEG) mixtures were prepared by mass using an Adventurer Ohaus AR2130 balance having a precision of ± 0.1 mg. PEG1000 is solid at ambient conditions with a melting point of ∼38 °C. Therefore, the solutions for PEG1000 were prepared by melting it in a water bath at ∼60 °C and then mixing it with appropriate aliquots of [bmim][PF_6]. This system was allowed to equilibrate to the desired temperature before any data acquisition. Densities of the ([bmim][PF_6] + PEG) mixtures were measured using a Mettler Toledo, DE45 delta range density meter. The measurements were performed at 10 degree intervals in the temperature range (283.15 to 363.15) K. The density measurement with the above-mentioned density meter was based on electromagnetically induced oscillations of a U-shaped glass tube. Table 1 presents a comparison of densities of pure components measured with our instrumentation with those available in the literature.[43−46] It is clear that the two values are in good agreement. All data analyses were performed using Microsoft Excel and SigmaPlot v10 software.

RESULTS AND DISCUSSION

Experimentally observed densities of ([bmim][PF_6] + PEG) mixtures as a function of temperature are reported in Table 2. The temperature dependence of experimentally obtained densities is found to follow the simple linear equation

$$\rho = \rho_0 + aT \qquad (1)$$

where ρ ($g\cdot cm^{-3}$) is the density of the ([bmim][PF_6] + PEG) mixture. The values of ρ_0 and the coefficient a along with their standard deviations are listed in Table 3. Measured densities of ([bmim][PF_6] + PEG) mixtures along with the fit to eq 1 as solid lines are presented in Figure 1. It is clear from the recovered values of r^2 listed in Table 3 as well as from a careful examination of Figure 1 that the densities of ([bmim][PF_6] + PEG) mixtures simply decrease linearly with a temperature increase in the range (283.15 to 363.15) K. It is worth mentioning that the dependence of the densities of aqueous PEG mixtures on temperature is mostly quadratic in nature.[43]

Table 3. Results of the Regression Analysis of Density ($\rho/g\cdot cm^{-3}$) versus Temperature (T/K) Data According to the Equation $\rho/(g\cdot cm^{-3}) = \rho_0/(g\cdot cm^{-3}) + a(T/K)$ for 1-Butyl-3-methylimidazolium Hexafluorophosphate ([bmim][PF_6]) (1) + Poly(Ethylene glycol) [PEG] (2) in the Temperature Range (283.15 to 363.15) K[a]

w_1	$\rho_0/g\cdot cm^{-3}$	$a\cdot 10^{-4}$	r^2
	([bmim][PF_6] + PEG400)		
0.0000	1.339 (± 0.006)	−7.267 (± 0.195)	0.9950
0.0732	1.359 (± 0.006)	−7.303 (± 0.182)	0.9957
0.1508	1.380 (± 0.006)	−7.374 (± 0.176)	0.9960
0.2336	1.402 (± 0.006)	−7.441 (± 0.170)	0.9964
0.3214	1.425 (± 0.005)	−7.518 (± 0.163)	0.9967
0.4153	1.449 (± 0.005)	−7.594 (± 0.155)	0.9971
0.5159	1.475 (± 0.005)	−7.660 (± 0.145)	0.9975
0.6238	1.503 (± 0.004)	−7.736 (± 0.135)	0.9979
0.7397	1.533 (± 0.004)	−7.823 (± 0.125)	0.9982
0.8647	1.568 (± 0.004)	−7.932 (± 0.118)	0.9985
1.0000	1.609 (± 0.004)	−8.104 (± 0.115)	0.9986
	([bmim][PF_6] + PEG600)		
0.0000	1.325 (± 0.006)	−6.843 (± 0.195)	0.9959
0.0504	1.347 (± 0.006)	−7.115 (± 0.192)	0.9957
0.1061	1.363 (± 0.006)	−7.157 (± 0.184)	0.9961
0.1688	1.380 (± 0.006)	−7.215 (± 0.179)	0.9963
0.2400	1.399 (± 0.006)	−7.285 (± 0.172)	0.9967
0.3215	1.427 (± 0.005)	−7.534 (± 0.163)	0.9967
0.4154	1.451 (± 0.005)	−7.603 (± 0.154)	0.9972
0.5248	1.479 (± 0.005)	−7.671 (± 0.141)	0.9977
0.6546	1.512 (± 0.004)	−7.768 (± 0.129)	0.9981
0.8084	1.554 (± 0.004)	−7.884 (± 0.118)	0.9984
1.0000	1.609 (± 0.004)	−8.104 (± 0.115)	0.9986
	([bmim][PF_6] + PEG1000)		
0.0000	1.316 (± 0.006)	−6.609 (± 0.190)	0.9967
0.0306	1.323 (± 0.006)	−6.560 (± 0.169)	0.9974
0.0663	1.334 (± 0.006)	−6.603 (± 0.169)	0.9974
0.1088	1.340 (± 0.006)	−6.475 (± 0.179)	0.9970
0.1593	1.357 (± 0.006)	−6.561 (± 0.181)	0.9970
0.2213	1.379 (± 0.006)	−6.790 (± 0.170)	0.9975
0.2990	1.406 (± 0.005)	−7.029 (± 0.148)	0.9978
0.3987	1.437 (± 0.005)	−7.267 (± 0.158)	0.9976
0.5319	1.478 (± 0.005)	−7.546 (± 0.142)	0.9979
0.7189	1.530 (± 0.004)	−7.800 (± 0.115)	0.9985
1.0000	1.609 (± 0.004)	−8.104 (± 0.115)	0.9986

[a] Standard deviations are given as ± in parentheses.

To afford the extent of molecular-level interactions within ([bmim][PF_6] + PEG) mixtures, we estimated excess molar volume (V^E) from the experimental density data using the relationship

$$V^E = \frac{(X_1M_1 + X_2M_2)}{\rho} - \left(\frac{X_1M_1}{\rho_1} + \frac{X_2M_2}{\rho_2}\right) \qquad (2)$$

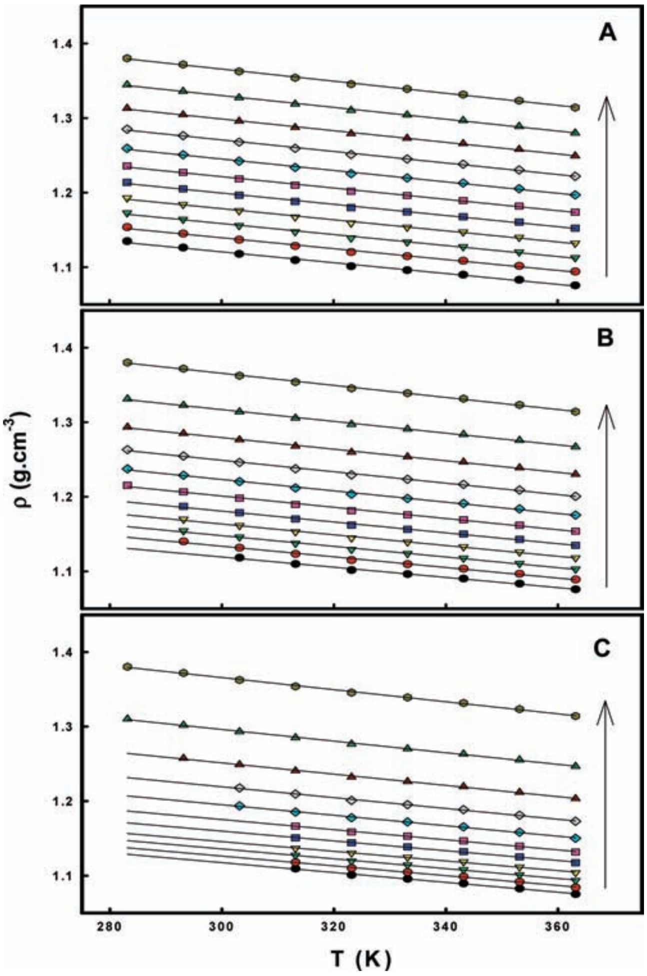

Figure 1. Variation of density with temperature for [bmim][PF$_6$] (1) + poly(ethylene glycol) [PEG] (2) mixtures: ([bmim][PF$_6$] + PEG400) (panel A), ([bmim][PF$_6$] + PEG600) (panel B), ([bmim][PF$_6$] + PEG1000) (panel C). The solid lines represent a fit to the equation $\rho = \rho_0 + aT$. Parameters ρ_0 and a along with the goodness-of-fit in terms of r^2 are reported in Table 3. Arrows show an increase in the amount of [bmim][PF$_6$] in the mixture.

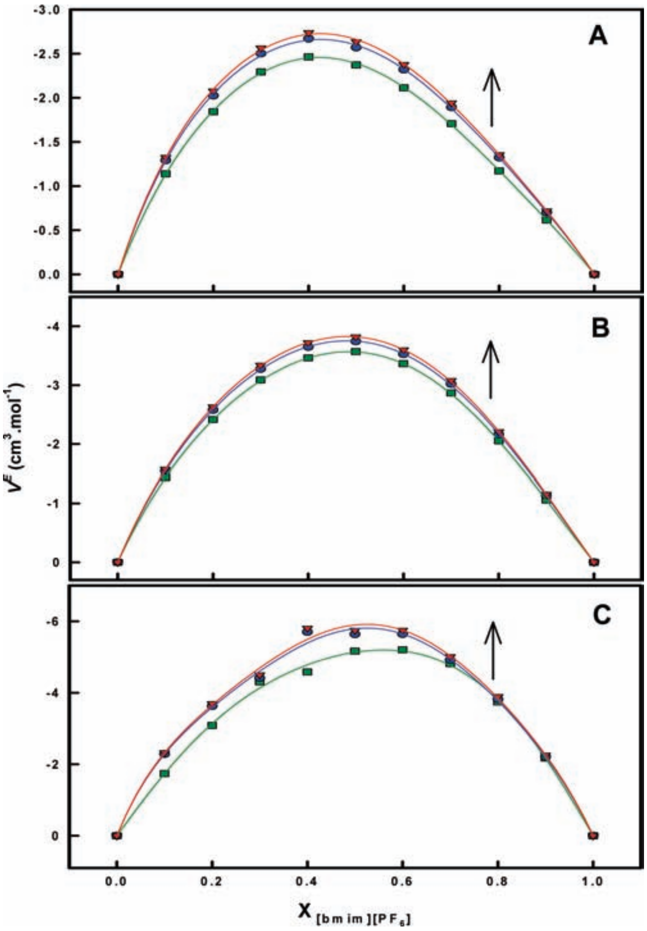

Figure 2. Variation of excess molar volume (V^E/cm^3·mol^{-1}) with mole fraction of [bmim][PF$_6$] for ([bmim][PF$_6$] + PEG400) (panel A) as the temperature is increased (green ■, 283.15 K; blue ●, 323.15 K; red ▼, 363.15 K), for ([bmim][PF$_6$] + PEG600) (panel B) as the temperature is increased (green ■, 303.15 K; blue ●, 333.15 K; red ▼, 363.15 K), and for ([bmim][PF$_6$] + PEG1000) (panel C) as the temperature is increased (green ■, 313.15 K; blue ●, 333.15 K; red ▼, 363.15 K). Arrows show increase in temperature. Solid curves show fits according to the Redlich−Kister equation [eq 3] with parameters (A_j) reported in Table 4.

Here, X_1 and X_2 refer to the mole fractions of [bmim][PF$_6$] and PEG, respectively, in the mixture, and ρ_1 and ρ_2 refer to the densities of neat [bmim][PF$_6$] and neat PEG, respectively, at the given temperature. M_1 and M_2 are molar mass and average molar mass of [bmim][PF$_6$] and PEG, respectively (M_2 is taken as 400, 600, and 1000 for PEG400, PEG600, and PEG1000, respectively). In Figure 2, the excess molar volumes (V^E) of ([bmim][PF$_6$] + PEG) mixtures at selected temperature are presented as a function of [bmim][PF$_6$] mole fraction ($X_{[\text{bmim}][\text{PF}_6]}$). A careful examination of Figure 2 reveals that V^E are negative and are quite significant at each temperature throughout the entire composition range for all ([bmim][PF$_6$] + PEG) mixtures. Surprisingly, the absolute values of V^E for all ([bmim][PF$_6$] + PEG) mixtures appear to increase slightly with increasing temperature indicating deviation from ideal behavior to become more pronounced as the temperature is increased. Furthermore, the V^E have their maximum values close to the equimolar mixture composition for all three ([bmim][PF$_6$] + PEG) mixtures [maximum V^E at $X_{[\text{bmim}][\text{PF}_6]}$ ∼0.4, ∼0.5, and ∼0.5 for ([bmim][PF$_6$] + PEG400), ([bmim][PF$_6$] + PEG600), and ([bmim][PF$_6$] + PEG1000), respectively].

The negative V^E usually indicates contraction in volumes upon mixing. The C2 hydrogen of the 1,3-dialkylimidazolium cation is the major contributor to the hydrogen bond donating (HBD) acidity of [bmim][PF$_6$],[47−50] and termini OHs, and to some extent, ethoxy −O−, afford substantial hydrogen bond accepting (HBA) basicity to PEGs.[51] It is suggested that the presence of extensive intermolecular H-bonding between the C2 hydrogen of [bmim$^+$] and termini −OH as well as ethoxy −O− of PEG within ([bmim][PF$_6$] + PEG) mixtures could be responsible for the high negative values of excess molar volumes.[8] Hydrogen bonding between PF$_6^-$ and termini hydrogens of PEG may also contribute toward this. This hypothesis is further substantiated by the fact that, at a given temperature, the absolute value of V^E for the ([bmim][PF$_6$] + PEG) mixture increases with increasing PEG average molecular weight as a longer PEG polymer chain would contain more oxyethylene units thus affording more HBA sites. More HBA sites, in turn, may result in increased H-bonding

Table 4. Fit Parameters (A_j) and Correlation Coefficient (r^2) in the Redlich−Kister Equation [Equation 3] of Excess Molar Volume (V^E) for [bmim][PF_6] (1) + PEG (2) Mixtures

T/K	A_0	A_1	A_2	A_3	A_4	r^2
			[bmim][PF_6] + PEG400			
283.15	−9.5587	3.4394	0.8987	0.2828	−1.8108	0.9992
293.15	−9.5844	3.4468	0.7924	1.2248	−1.1264	0.9993
303.15	−9.9376	3.3961	0.6126	0.7251	−1.9712	0.9992
313.15	−10.1238	3.4275	0.4598	0.9695	−1.9614	0.9991
323.15	−10.3869	3.3787	0.4225	1.0792	−2.2888	0.9985
333.15	−10.4332	3.4009	0.3731	1.0609	−2.1962	0.9987
343.15	−10.4913	3.4311	0.4544	1.0228	−2.3201	0.9986
353.15	−10.5579	3.4677	0.4455	0.9550	−2.3576	0.9987
363.15	−10.6463	3.4582	0.4434	1.1282	−2.3454	0.9986
			[bmim][PF_6] + PEG600			
303.15	−14.2853	0.8974	0.9979	2.7010	−0.4918	0.9996
313.15	−14.5540	1.0009	0.7890	2.8505	−0.5140	0.9992
323.15	−14.9104	1.1627	0.4722	2.6868	−0.3940	0.9988
333.15	−14.9917	1.1675	0.5355	2.6751	−0.4739	0.9988
343.15	−15.0836	1.1923	0.5349	2.6700	−0.4583	0.9986
353.15	−15.1617	1.1412	0.5814	2.7450	−0.5200	0.9988
363.15	−15.2879	1.1686	0.5403	2.7241	−0.4480	0.9991
			[bmim][PF_6] + PEG1000			
313.15	−20.5381	−4.0800	−4.9155	1.7625	4.9115	0.9418
323.15	−23.0450	−2.7202	4.5477	4.8564	−11.4859	0.7606
333.15	−23.1693	−2.8303	4.6110	5.1629	−11.7561	0.7636
343.15	−23.2890	−2.8272	4.5596	5.1686	−11.7286	0.7633
353.15	−23.4498	−2.8475	4.6750	5.1668	−11.8743	0.7614
363.15	−23.5955	−2.8530	4.6030	5.1129	−11.7737	0.7638

between $bmim^+$ and PEG giving rise to further contraction in volume. This is in line with recently reported "hyperpolarity" found within mixtures of IL [bmim][PF_6] + tetraethylene glycol (TEG)[52] and within mixtures composed of ([bmim][PF_6] + PEGs) with PEG200, PEG400, PEG600, and PEG1500, respectively.[8,9] The interactions within the mixture are affected by the temperature and the composition of the mixture. In liquid mixtures, the absolute value of the molar excess volume usually decreases with increasing temperature in systems where interactions are present. However, for ([bmim][PF_6] + PEG) mixtures, a slight increase in the absolute value of V^E as the temperature is increased from (283.15 to 363.15) K is observed. This could be attributed to the inherent complexity of the ([bmim][PF_6] + PEG) mixtures as far as interactions within the system are concerned. As mentioned earlier, the H-bonding interactions between the unlike components (i.e., between cation/anion of ILs and HBA/HBD sites of PEG) within the mixtures along with interstitial accommodation of $bmim^+$ and/or PF_6^- within the H-bonded PEG network would result in volume contraction and thus the negative V^E for our systems. The further contraction in the mixture volume upon heating could be tentatively attributed to the weakening of the H-bond among PEG molecules and/or among [bmim][PF_6] moieties with subsequent strengthening of the H-bonding between PEG and [bmim][PF_6]. This may result in increased absolute value of V^E with increasing temperature of the mixture. Further investigations in our laboratory are currently underway to understand the reasons for this observation.

The excess molar volumes were fitted to the Redlich−Kister type polynomial expressions.[53] According to the combined nearly ideal binary solvent/Redlich−Kister (CNIBS/R-K) model, the V^E in a binary solvent mixture at a constant temperature can be expressed as

$$V^E = X_1X_2 \sum_{j=0}^{k} A_j(X_1 - X_2)^j \tag{3}$$

where A_j and j are the equation coefficients and the degree of the polynomial expansion, respectively. The numerical values of j can be varied to find an accurate mathematical representation of the experimental data. Regression analysis was performed to fit the polynomials [i.e., eq 3] to our experimental data, and the results of the fit are reported in Table 4. It is convenient to use a cross-validation method which is a practical and reliable method to test the predictive significance when only little data are available.[54] The solid lines connecting each of the V^E in Figure 2 at all proportions are obtained from the CNIBS/R-K model fit (with $j = 4$) as reported in Table 4 which also suggests a fair-to-good correlation between the predicted and the experimentally obtained values. It is observed from the r^2 values that the fits are satisfactory for ([bmim][PF_6] + PEG400) and ([bmim][PF_6] + PEG600) mixtures, whereas it is not that good for ([bmim][PF_6] + PEG1000) mixtures at all temperatures.

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