

Density, Excess Molar Volume, and Viscosity for the Methyl Methacrylate + 1-Butyl-3-methylimidazolium Hexafluorophosphate Ionic Liquid Binary System at Atmospheric Pressure

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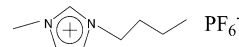
Densities and viscosities for the methyl methacrylate (MMA) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]) ionic liquid binary system, over the whole concentration range in the temperature range from (283.15 to 353.15) K, were measured by using an Anton Paar DMA 5000 densimeter and an Anton Paar AMVn Measuring Assembly, respectively. The excess molar volumes V^E were calculated by using the measured experimental densities and correlated by the Redlich–Kister type equation. The correlation results are in good agreement with the experimental data, and optimal fitting parameters are present. All the V^E values within the scope of research are negative and become more and more negative with increasing temperature.

Introduction

In recent years, room temperature ionic liquids (RTILs) composed of an organic cation and organic or inorganic anion have attracted the attention of a growing number of scientists and engineers for their potential applications as greener “designer solvents”. 1-Butyl-3-methylimidazolium hexafluorophosphate ionic liquid ([BMIM][PF₆], its structure shown in Scheme 1) is one of the most important traditional ionic liquids and has been widely used in the fields of separation, catalysis, and synthesis, etc.^{1–3} Additionally, RTILs have recently attracted more and more concern as media for polymerization. Conventional or controlled radical polymerization of methyl methacrylate (MMA) has been carried out in various RTILs. Zhang et al.¹ first reported the nitroxide-mediated free radical polymerizations of styrene and MMA in [BMIM][PF₆], and Hawker's group used them to mediate free radical polymerizations of styrene and MMA which were carried out in the same ILs under various conditions. Haddleton et al.² reported the first example of transition metal mediated living-radical polymerization of MMA in a RTIL and found that the rate of polymerization was enhanced compared to that in other polar or coordinating solvents.

In spite of the importance of ILs and their interesting applications, accurate values for many of their fundamental physical and chemical properties are either scarce or even absent. Although it is important for the design of technological process, the detailed knowledge on thermodynamic and transport properties of the mixture of ionic liquids with other molecular solvents is very limited. Specifically, experimental data of density and viscosity of a binary mixture are important not only to design chemical industry separation processes and transport equipment but also to predict the properties and characteristics of ILs from the theoretical point of view. It is essential to design the process

Scheme 1. Molecular Structure of 1-Butyl-3-methylimidazolium Hexafluorophosphate



involving ionic liquids on an industrial scale.^{3–5} To our best knowledge, no experimental density and viscosity data for the MMA and [BMIM][PF₆] binary system have been reported in the literature, though the polymerization of MMA in [BMIM][PF₆] has been reported.

In our previous work, the density and viscosity measurements on the MMA and methanol binary system over the whole composition range were reported.⁶ In this work, the densities and viscosities for MMA (1) + [BMIM][PF₆] (2) binary mixtures have been measured over the entire composition from (283.15 to 353.15) K, from which the excess molar volumes V^E have been calculated and correlated by the Redlich–Kister polynomial equation. Optimal fitting parameters are presented, and the effect of MMA concentration on the association behavior of the [BMIM][PF₆] is also investigated.

Experimental Section

Materials. Methyl methacrylate (MMA) with > 99.0 % mass fraction was obtained from Yili Fine Chemical Co. Ltd., Beijing, China. The purity of MMA was detected by gas chromatography, and it was used without further purification. [BMIM][PF₆] with 284.18 g·mol⁻¹ molar mass, > 99.0 % mass fraction, and < 0.1 % water mass fraction (supplied data) was obtained from Henan Lihua Pharmaceutical Co. Ltd. [BMIM][PF₆] ionic liquid was dried under vacuum at 70 °C for at least 48 h before use. Below 100 ppm, water contents in the experimental samples were analyzed by Karl Fisher titration (751 GPD Titrimo, Metrohm, Switzerland). During the experimental process, the purity of the solvents was monitored by comparison of density measurements with the literature data.

Apparatus and Procedure. The binary mixtures were prepared by filling glass vials with [BMIM][PF₆] and MMA, and

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Table 1. Densities ρ and Viscosities η of MMA and [BMIM][PF₆] at Different Temperatures

comps	T/K	$\rho/(\text{g}\cdot\text{cm}^{-3})$			$\eta/(\text{mPa}\cdot\text{s})$		
		exptl	lit.	Er %	exptl	lit.	Er %
[BMIM][PF ₆]	283.15	1.380337	1.3803 ²¹	0.0027	802.1	755 ²¹	6.2384
	288.15	1.376063	1.3760 ²¹	0.0046	552.6	521 ²¹	6.0653
						524.4 ³⁵	5.3776
	293.15	1.371797	1.37156 ²²	0.0173	389.8	369 ²¹	5.6369
			1.3717 ²¹	0.0007		382 ³⁴	2.0419
			1.370 ³⁴	0.1312		366.7 ³⁵	6.2994
	298.15	1.367531	1.366657 ²³	0.0639	282.2	273 ²¹	3.3700
			1.36595 ²⁴	0.1157		281 ³³	0.4270
			1.36722 ¹⁴	0.0227		269.0 ³⁵	4.9071
			1.3674 ²¹	0.0009			
	303.15	1.363277	1.36240 ²³	0.0644	209.2	202 ²¹	3.5644
			1.36286 ¹⁴	0.0306		199.7 ³⁵	4.7571
			1.36319 ²¹	0.0006			
	308.15	1.359191	1.35856 ¹⁴	0.0464	159.1	158.4 ²¹	0.4419
			1.35876 ²²	0.0317		153.9 ³⁵	3.3788
	313.15	1.355087	1.35430 ¹⁴	0.0581	123.4	120 ²¹	2.8333
			1.3550 ²¹	0.0006		120.7 ³⁵	2.2369
			1.35419 ²³	0.0662		119 ³⁴	3.6975
			1.354 ³⁴	0.0803			
	318.15	1.350980	1.35032 ²²	0.0489	97.78		
	323.15	1.346874	1.34598 ¹⁴	0.0664	78.77	74.9 ²¹	5.1669
			1.3468 ²¹	0.0005			
	328.15	1.342781			61.34		
	333.15	1.338696	1.3386 ²²	0.0072	50.38	49.5 ²¹	1.7778
			1.337 ³⁴	0.1268		52.5 ³⁴	-4.0381
	343.15	1.330560	1.33045 ²¹	0.0083	35.25	34.7 ²¹	1.5850
	353.15	1.322473	1.32238 ²¹	0.0070	25.77	25.5 ²¹	1.0588
			1.321 ³⁴	0.1115		25.7 ³⁴	0.2724
MMA	283.15	0.954802			0.6808		
	288.15	0.949097			0.6337		
	293.15	0.943365			0.5899		
	298.15	0.937615	0.93780 ²⁵	-0.0197	0.5540	0.584 ²⁹	-5.1370
			0.93763 ²⁶	-0.0001			
			0.93766 ²⁷	-0.0005			
	303.15	0.931837	0.93174 ²⁶	0.0104	0.5248		
			0.93174 ²⁸	0.0104			
	308.15	0.926032	0.92574 ²⁶	0.0315	0.4956	0.492 ²⁹	0.7317
			0.9257 ²⁸	0.0359			
	313.15	0.920185	0.92026 ²⁶	-0.0081	0.4719		
	318.15	0.914317			0.4497		
	323.15	0.908405			0.4294		
	328.15	0.902468			0.4100		
	333.15	0.896479			0.3938		
	343.15	0.884418			0.3636		
	353.15	0.872129			0.3398		

vials were closed with screw caps ensuring a secure seal and to prevent humidity. The mixtures of the various compositions were freshly prepared and taken from the vial with the syringe and then were put into an apparatus immediately to prevent the mixtures from atmospheric moisture. Density and viscosity were measured at the same time using the same samples to reduce the experimental error.

The detailed experimental apparatus and measuring procedure have been described in our previous work.⁶ Density was measured by an Anton Paar DMA 5000 high-precision vibrating tube densimeter with an accuracy of $\pm 1 \cdot 10^{-6} \text{ g}\cdot\text{cm}^{-3}$, which was calibrated with ultrapure water and dry air, and the uncertainty in density measurements was $\pm 5 \cdot 10^{-6} \text{ g}\cdot\text{cm}^{-3}$. The highest temperature accuracy ($\pm 0.001 \text{ K}$) is controlled traceably to national standards by two integrated Pt 100 platinum thermometers. Viscosity was measured by an Anton Paar AMVn Automated Microviscometer (reproducibility $< 0.5 \%$, repeatability $< 0.1 \%$).⁷ Various combinations of capillary/ball with different diameters (1.6 mm, 1.8 mm, 3.0 mm, 4.0 mm, etc.) can be selected allowing us to measure viscosities from (0.3 to 2500) mPa·s. Calibration was carried out using ultrapure water

or viscosity standard oils (No.H117) (Anton Paar Co). The temperature is controlled by a built-in precise Peltier thermostat within $\pm 0.01 \text{ K}$. The experimental data of pure components and compared with the literature data were given in Table 1. The overall average relative error (Er) of density and viscosity measurements for [BMIM][PF₆] and MMA is less than 0.036 % and 2.612 %, respectively. The results show that our experimental data are in good agreement with literature data.

Results and Discussion

Experimental density ρ and viscosity η results of the MMA (1) + [BMIM][PF₆] (2) binary system were reported in Table 2, in which MMA mole fraction (x_1) was a function over the temperature range (283.15 to 353.15) K. Excess molar volumes V^E were calculated from the experimental results by the following equation

$$V^E = \frac{x_1 M_1 + x_2 M_2}{\rho_M} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \quad (1)$$

where x_i , ρ_i , and M_i are the mole fraction, density, and molar masses of the pure component i , respectively, the subscript M

Table 2. Experimental Densities ρ , Viscosities η , and Excess Molar Volumes V^E of MMA (1) + [BMIM][PF₆] (2)

x_1	$T/K = 283.15$	$T/K = 288.15$	$T/K = 293.15$	$T/K = 298.15$	$T/K = 303.15$	$T/K = 308.15$	$T/K = 313.15$	$T/K = 318.15$	$T/K = 323.15$	$T/K = 328.15$	$T/K = 333.15$	$T/K = 343.15$	$T/K = 353.15$
	$\rho/(\text{g}\cdot\text{cm}^{-3})$												
0.0986	1.360727	1.356381	1.352041	1.347842	1.343673	1.339494	1.335321	1.331153	1.326996	1.322846	1.318711	1.310465	1.302231
0.2094	1.335266	1.330982	1.326717	1.322446	1.318175	1.313914	1.309659	1.305410	1.301169	1.296917	1.292662	1.284513	1.275985
0.3073	1.310417	1.306048	1.301685	1.297323	1.292970	1.288620	1.284277	1.279937	1.275582	1.271138	1.267356	1.259315	1.250714
0.4053	1.282194	1.277721	1.273259	1.268808	1.264369	1.259943	1.255531	1.251130	1.246737	1.242359	1.237992	1.229290	1.220625
0.4977	1.250448	1.245869	1.241301	1.236747	1.232201	1.227671	1.223150	1.218637	1.214134	1.209647	1.205167	1.196230	1.187324
0.5993	1.211208	1.206490	1.201584	1.197089	1.192403	1.187726	1.183054	1.178390	1.173733	1.169083	1.164441	1.155167	1.145906
0.7009	1.164351	1.159456	1.154070	1.149686	1.144808	1.139934	1.135064	1.130194	1.125325	1.120457	1.115589	1.105843	1.096084
0.8003	1.109097	1.103970	1.098448	1.093722	1.088593	1.083459	1.078316	1.073169	1.068012	1.062848	1.057670	1.047287	1.036871
0.9007	1.042117	1.036709	1.031096	1.025867	1.020427	1.014968	1.009493	1.003999	0.998489	0.992980	0.987485	0.976413	0.965130
	$\eta/(\text{mPa}\cdot\text{s})$												
0.0986	434.9	308.3	224.9	168.1	128.5	100.5	80.38	62.98	51.32	42.36	35.43	25.61	19.25
0.2094	218.0	161.2	122.3	94.88	75.44	58.33	47.27	38.91	32.45	27.39	23.38	17.56	13.65
0.3073	118.6	91.29	71.80	55.22	44.49	36.45	30.27	25.48	21.70	18.69	16.24	12.57	10.01
0.4053	64.04	50.28	40.30	32.87	27.22	22.86	19.43	16.70	14.51	12.71	11.22	8.922	7.259
0.4977	34.64	28.16	23.27	19.54	16.62	14.29	12.43	10.90	9.640	8.584	7.691	6.278	5.224
0.5993	17.78	14.99	12.81	11.07	9.662	8.505	7.550	6.745	6.066	5.498	4.991	4.187	3.579
0.7009	8.859	7.717	6.781	6.014	5.374	4.838	4.379	3.990	3.653	3.362	3.111	2.708	2.415
0.8003	3.909	3.485	3.136	2.836	2.583	2.369	2.175	2.007	1.868	1.743	1.629	1.432	1.272
0.9007	1.719	1.575	1.450	1.342	1.247	1.165	1.092	1.026	0.9687	0.9201	0.9150	0.8545	0.7810
	$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$												
0.0986	-0.4099	-0.4220	-0.4345	-0.4682	-0.4443	-0.5192	-0.5371	-0.5568	-0.5790	-0.6013	-0.6259	-0.6767	-0.7277
0.2094	-0.7624	-0.8078	-0.8565	-0.9057	-0.9014	-0.9874	-1.0245	-1.0642	-1.1071	-1.1485	-1.1908	-1.3304	-1.4189
0.3073	-1.1353	-1.1909	-1.2486	-1.3083	-1.3231	-1.4170	-1.4694	-1.5247	-1.5807	-1.6252	-1.7659	-1.9863	-2.1382
0.4053	-1.4802	-1.5437	-1.6106	-1.6813	-1.7149	-1.8187	-1.8892	-1.9642	-2.0441	-2.1281	-2.2174	-2.4083	-2.6212
0.4977	-1.5972	-1.6661	-1.7389	-1.8162	-1.8628	-1.9702	-2.0504	-2.1352	-2.2259	-2.3214	-2.4229	-2.6391	-2.8815
0.5993	-1.7840	-1.8566	-1.9097	-2.0153	-2.0739	-2.1817	-2.2691	-2.3613	-2.4599	-2.5629	-2.6730	-2.9071	-3.1699
0.7009	-1.8045	-1.8749	-1.8916	-2.0284	-2.0910	-2.1913	-2.2782	-2.3692	-2.4665	-2.5679	-2.6762	-2.9061	-3.1654
0.8003	-1.6199	-1.6789	-1.6968	-1.8083	-1.8644	-1.9464	-2.0201	-2.0975	-2.1800	-2.2660	-2.3576	-2.5527	-2.7772
0.9007	-1.2784	-1.3169	-1.3363	-1.4014	-1.4401	-1.4917	-1.5407	-1.5912	-1.6460	-1.7051	-1.7733	-1.9144	-2.0632

Table 3. Coefficients of the Redlich–Kister Equation for V^E of the MMA (1) + [BMIM][PF₆] (2) System

properties	T/K	A_0	A_1	A_2	A_3	A_4	A_5	σ
$V^E/(\text{cm}^3 \cdot \text{mol}^{-1})$	283.15	-6.6366	-3.4870	-0.3126	-2.8169	-5.9969	-1.7083	0.0413
	288.15	-6.9106	-3.6104	-0.5462	-2.4584	-5.6662	-2.4074	0.0409
	293.15	-7.1819	-3.4340	-0.0111	-2.0718	-6.3390	-3.5686	0.0358
	298.15	-7.5117	-3.8814	-0.8667	-1.9475	-5.4966	-3.1821	0.0408
	303.15	-7.7011	-4.1592	-0.8606	-1.9492	-5.2487	-3.5617	0.0411
	308.15	-8.1358	-4.2126	-0.9165	-1.9435	-5.8163	-3.0416	0.0420
	313.15	-8.4604	-4.4153	-0.9290	-1.9321	-5.9161	-3.0872	0.0427
	318.15	-8.8038	-4.6218	-0.9353	-1.9483	-6.0275	-3.0751	0.0433
	323.15	-9.1707	-4.8644	-0.9026	-1.8754	-6.2403	-3.1413	0.0411
	328.15	-9.5567	-5.1771	-0.6715	-1.7114	-6.7985	-3.2377	0.0457
	333.15	-9.9799	-5.0244	-1.2047	-2.9163	-6.0258	-2.5313	0.0501
	343.15	-10.8471	-5.2943	-2.2804	-2.1481	-4.7568	-4.6319	0.0569
	353.15	-11.8358	-5.8191	-1.9766	-3.1960	-5.5168	-3.3728	0.0597

represents mixture properties. The data of excess molar volume were also presented in Table 2 and were correlated by the Redlich–Kister polynomial equation⁸

$$V^E = x_1 x_2 \sum_{k=0}^5 A_k (x_1 - x_2)^k \quad (2)$$

where the coefficients of A_k are adjustable parameters which were obtained by fitting the equations to the experimental values with a least-squares method.

The correlated results for excess molar volumes, including the values of the parameters A_k together with the standard deviation σ , were given in Table 3, in which the tabulated standard deviation σ was defined as follows

$$\sigma = \left[\frac{\sum (V_{\text{exptl}}^E - V_{\text{calcd}}^E)^2}{n - p} \right]^{1/2} \quad (3)$$

where n is the number of data points and p is the number of coefficients. The subscripts, exptl and calcd, denoted the experimental and the calculated value, respectively.^{9–12} The relative deviation between the experimental and calculated value of all data point was less than 0.04.

As seen from Table 3, the experimentally derived excess molar volumes were correlated satisfactorily by the Redlich–Kister equation. The excess molar volume V^E of mixtures versus the mole fraction of MMA from (283.15 to 353.15) K was plotted in Figure 1. It shows that the excess molar volumes V^E

are asymmetric and negative for all of these systems studied over the entire composition range, that a minimum in V^E is reached with mole fraction of MMA near $x_1 = 0.7$, and that the absolute values of the excess volume V^E increase with increasing temperature. A similar phenomenon has been observed for [BMIM][PF₆] + benzyl alcohol and [BMIM][PF₆] + benzaldehyde systems by Zhong et al.¹³ and for acetonitrile + [BMIM][PF₆] systems by Huo et al.¹⁴ The negative excess molar volumes indicated that a more efficient packing and/or attractive interaction occurred when the [BMIM][PF₆] and MMA were mixed.

However, Holbrey and Seddon¹⁵ found that ionic liquids (including [BMIM][PF₆] and [BMIM][BF₄]) exhibited liquid clathrate formation in trichloromethane with a ratio of ionic liquid/CHCl₃ (1:3). Rogers and co-workers¹⁶ reported the formation of liquid clathrates with various ratios in (ionic liquid + aromatic) mixtures. Wang et al.¹⁷ and Zhong et al.¹³ suggested that quasiclathrates were probably formed in the mixtures of [BMIM][PF₆] + organic components. They addressed the issue that at least an unusual structure appeared in the vicinity of this particular composition of the mixtures ($x = 0.3$).^{18–20} The quasiclathrates are probably also formed in the mixtures of [BMIM][PF₆] + MMA studied, and a minimum in V^E is reached with the mole fraction of [BMIM][PF₆] near 0.3.^{30–32}

Conclusions

New experimental data of density and viscosity for the mixture of MMA + [BMIM][PF₆] were measured over the entire range of compositions at atmospheric pressure from (283.15 to 353.15) K, from which the excess molar volumes V^E were calculated and the Redlich–Kister polynomial equation was applied successfully for the correlation of the excess molar volumes. The estimated coefficients and standard deviation values were also presented. It was found that density and viscosity for pure components or mixtures decreased with increasing temperature, and viscosity was more sensitive than density to temperature or composition change. It was found that all of these calculated quantities were negative, and the Redlich–Kister fitting curves were asymmetric.

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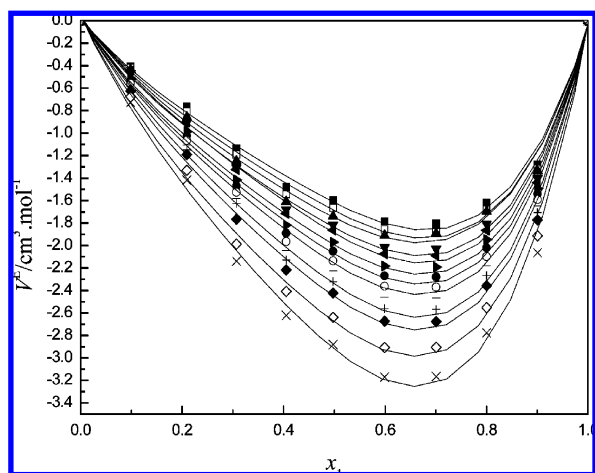


Figure 1. Excess molar volume V^E vs mole fraction x of methyl methacrylate for MMA (1) + [BMIM][PF₆] (2). ■, 283.15 K; □, 288.15 K; ▲, 293.15 K; ▼, 298.15 K; solid triangle pointing left, 303.15 K; solid triangle pointing right, 308.15 K; ●, 313.15 K; ○, 318.15 K; +, 323.15 K; ×, 328.15 K; ◆, 333.15 K; ◇, 343.15 K; ×, 353.15 K. The symbols represent experimental values, and the solid curves represent the values calculated from eq 2.

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