Densities, Refractive Indices, and Viscosities of the Ionic Liquids 1-Methyl-3-octylimidazolium Tetrafluoroborate and 1-Methyl-3-butylimidazolium Perchlorate and Their Binary Mixtures with Ethanol at Several Temperatures

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Densities, refractive indices, and viscosities were determined for two ionic liquids, 1-methyl-3-octylimidazolium tetrafluoroborate and 1- methyl-3-butylimidazolium perchlorate, and for their mixtures with ethanol at atmospheric pressure and temperatures from (278.15 to 363.15) K. The results for the pure components were correlated successfully by empirical equations. Excess molar volume, viscosity deviation, and refractive index deviation were calculated and correlated by the Redlich–Kister polynomial equation. As the numbers of parameters for Redlich–Kister polynomial equations are large, a model with one parameter was proposed to calculate densities, viscosities, and refractive indices of binary mixtures. On the basis of the proposed model, the physical properties of binary solutions are calculated from pure component physical properties, their mole fractions, and an adjustable parameter, which is determined by fitting of the experimental data. The results of the model represent reasonable accuracy for physical properties of binary systems.

Introduction

Room temperature ionic liquids (ILs) are a new class of substances that remain in the liquid state in a wide range of temperatures. Because of their unique properties such as low vapor pressure, good thermal and chemical stability, and excellent solubility for organic and inorganic compounds, they have attracted much interest in recent years. Due to the negligible vapor pressure of ILs, these substances are referred to as green solvents and can be used in environmental applications. In order to apply ILs in different processes and reactions, it is necessary to know their fundamental physical properties. A number of researchers have studied some of properties of ILs such as density or viscosity. However, the accurate values for many of these properties are scarce or absent. The presence of water or alcohol in ionic liquids has a large effect on physical properties.[1–3] There are a number of papers, which have studied the physical properties of binary systems of ionic liquids.[4–7] The binary data for physical properties of ILs may help to find out suitable ILs in specific applications such as liquid–liquid extraction. Recently, the physical properties of ionic liquids in ternary systems of methanol and water have been also investigated by Deenadayalu et al.[8]

In this paper, we report densities, viscosities, and refractive indices for two types of ionic liquids, one based on an imidazolium containing cation, namely, 1-methyl-3-octylimidazolium tetrafluoroborate ([Omim][BF_4]) and another one, 1-methyl-3-butylimidazolium perchlorate ([Bmim][ClO_4]), and their binary mixtures with ethanol at different temperatures. Because of the unique properties of perchlorate ions[9] such as high electronegativity, high solubility in nonaqueous solvents, and good chemical stability, it is worthwhile to measure the physical properties of ([Bmim][ClO_4] with ethanol. To our knowledge, there is not experimental data about this ionic liquid existing in the literature. Fischer et al.[10] used this ionic liquid for Diels–Alder cycloaddition reaction between methyl acrylate and cyclopentadiene.

The literature survey reveals that a number of data on the physical properties of pure [Omim][BF_4] are available,[11–14] but there is no data for its binary with ethanol. Gu and Brennecke[11] reported some experimental data for the density of [Omim][BF_4] at different pressures and temperatures. Harris et al.[12] reported a number of data for density and viscosity of pure [Omim][BF_4] at different temperatures. Recently, Coutinho et al.[13] have measured the density of [Omim][BF_4] at various pressures. Sanmamed[14] and his co-workers have measured the viscosity and density of [Omim][BF_4]. The binary mixture of [Omim][BF_4] with butanol and pentanol were studied by Heintz et al.[15]

In the present work, densities, viscosities, and refractive indices of mixtures [Omim][BF_4] or [Bmim][ClO_4] with ethanol are measured in temperature range of (283 to 353) K. The excess molar volume and viscosity and refractive index deviations are correlated by a Redlich–Kister type equation.[16] As the Redlich–Kister equation is independent of temperature, and the numbers of parameters are high for each system, a new model is proposed. In this model, the physical properties of a binary system are calculated based on the pure component physical properties and an adjustable parameter, which is determined by fitting of experimental data.

Experimental Section

Chemicals. Ethanol with purity of higher than 99 % and [Omim][BF_4] (assay ≥ 98 %, water ≤ 1 %, chloride ion ≤ 0.1 %, CAS No. 244193-52-0) were purchased from Merck. [Bmim][ClO_4] was prepared from 1-butyl-3-methylimidazolium chloride in our laboratory. 1-Butyl-3-methylimidazolium chloride was prepared according to the literature.[17] A 91.6 g (0.52 mol) portion of finely powdered 1-butyl-3-methylimidazolium chloride was mixed with 0.52 mol of lithium perchlorate in 200 mL of distilled water. The reaction mixture was stirred at room temperature for 2 h affording a heterogeneous mixture. The

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10.1021/je700521t CCC: $40.75 © 2008 American Chemical Society
Published on Web 02/27/2008

Table 1. Density ρ, Viscosity η, and Refractive Index n_D of [Omim][BF_4] at Several Temperatures

T	ρ	η	
K	g·cm^{-3}	mPa·s	n_D
283.15	1.1249	1036.98	1.4363
288.15	1.1214	718.75	1.4350
293.15	1.1179	462.90	1.4336
298.15	1.1144	334.17	1.4322
303.15	1.1109	246.18	1.4310
308.15	1.1075	191.95	1.4288
313.15	1.1041	147.92	1.4271
318.15	1.1007	116.38	1.4260
323.15	1.0973	91.95	1.4250
328.15	1.0939	74.79	1.4235
333.15	1.0906	60.95	1.4222
338.15	1.0872	50.88	1.4210
343.15	1.0839	42.06	1.4195
348.15	1.0805	35.78	1.4180
353.15	1.0772	30.11	1.4167
358.15	1.0738	25.87	1.4155
363.15	1.0705	21.57	1.4142

Table 2. Density ρ, Viscosity η, and Refractive Index n_D of [Bmim][ClO_4] at Several Temperatures

T	ρ	η	
K	g·cm^{-3}	mPa·s	n_D
283.15	1.2635	466.36	1.4763
288.15	1.2599	330.8	1.4751
293.15	1.2562	241.56	1.4740
298.15	1.2527	180.26	1.4725
303.15	1.2492	137.85	1.4712
308.15	1.2457	107.28	1.4696
313.15	1.2422	85.75	1.4685
318.15	1.2388	69.52	1.4667
323.15	1.2353	57.22	1.4655
328.15	1.2319	47.78	1.4642
333.15	1.2284	39.9	1.4627
338.15	1.2250	34.14	1.4615
343.15	1.2216	29.49	1.4602
348.15	1.2182	25.74	1.4590
353.15	1.2148	22.64	1.4577

Table 3. Comparison of Experimental Density Data ρ and Viscosity η with Literature Values[12] for pure [Omim][BF_4] at Different Temperatures

T	ρ/g·cm^{-3}			η/mPa·s		
K	exp	lit.	100Δ	exp	lit.	100Δ
278.15	1.1285	1.1175	0.98			
283.15	1.1249	1.1140	0.98	1036.98	982	5.60
288.15	1.1214	1.1106	0.97	718.75	673	6.80
293.15	1.1179	1.1071	0.98	462.90	473	−2.14
298.15	1.1145	1.1037	0.98	334.17	341	−2.00
303.15	1.1110	1.1002	0.98	246.18	251	−1.92
308.15	1.1075	1.0968	0.98	191.95	188.2	1.99
313.15	1.1041	1.0934	0.98	147.92	144.1	2.65
323.15	1.0973	1.0866	0.98	91.95	88.8	3.55
333.15	1.0906	1.0798	1.00	60.95	57.8	5.45
343.15	1.0839	1.0732	1.00	42.06	39.4	6.75

organic phase was washed with water in order to remove the chloride ion. To the remaining suspension were added 100 mL of dichloromethane and 35 g of anhydrous magnesium sulfate. The suspension was filtered after 1 h, and the volatile materials were removed under reduced pressure (0.1 bar) at 303.15 K for 2 h to afford 0.48 mol, 91 %, of 1-butyl-3-methylimidazolium perchlorate as a light yellow, viscous liquid. ^{1}H NMR (500 MHz, Acetone-d_6): δ 0.94 (t, J = 7.3 Hz, 3H), 1.34–1.43 (m, 2H), 1.89–1.95 (m, 2H), 4.04 (s, 3H), 4.35 (t, J = 7.3 Hz, 2H), 7.69 (s, 1H), 7.75 (s, 1H); 8.99 (s, 1H). ^{13}C NMR (125 MHz, Acetone-d_6): δ 13.2, 19.5, 32.2, 36.2, 49.7, 122.9, 124.3, 137.1.

Both ionic liquids were kept in bottles under an inert gas. As the physical properties of ionic liquids are sensitive to impurities and water content, the ionic liquids were dried and degassed for 24 h at 343.15 K under vacuum. The water content was determined by using a 684 Carl Fischer coulometer. The water contents for [Omim][BF_4] and [Bmim][ClO_4] were found to be ($2.4 \cdot 10^{-5}$and $2.167 \cdot 10^{-3}$) mass fraction, respectively.

Apparatus and Procedure. Densities were measured using an Anton Paar DMA-5000 digital densitometer. The repeatability and uncertainty in experimental measurement have been found to be lower than $\pm\ 1 \cdot 10^{-5}$ and $\pm\ 2 \cdot 10^{-5}$, respectively. The refractive indices were determined using a Kruss Abbe refractometer model AR3D, and the temperatures were controlled using a thermostat bath with ± 0.1 K accuracy. The uncertainty was below than ± 0.2 K for the thermostat bath. The calibration of the refractometer was checked by pure liquids with known refractive indices. The experimental uncertainty for refractive index was $\pm\ 2 \cdot 10^{-4}$. Kinematic viscosities were measured using an Anton Paar automated micro viscometer (AMVn), which measures viscosities based on the falling ball principle. The sample was introduced into a glass capillary with a steel ball, and viscosity was determined from the falling time of the steel ball. A built-in Pt100 thermometer ensures temperature control within ± 0.1 K. The experimental uncertainty was lower than ± 2 mPa·s for the viscosity range of (500 to 1200) mPa·s and ± 0.2 mPa·s for the viscosities lower than 500 mPa·s.

The samples were prepared by weighing the appropriate amount of pure ionic liquid and ethanol into stoppered bottles. The mass of sample was determined using a laboratory balance with the precision of $\pm\ 10^{-4}$ g. the experimental uncertainty for mass was $\pm\ 2 \cdot 10^{-4}$.

Table 4. Adjustable Parameters of Equation 2 and Root Mean Square Deviation (rmsd) for the Density and Refractive Index of Different Components

component	physical properties	a	b	rmsd
[Bmim][ClO_4]	ρ/g·cm^{-3}	1.4604	$-6.96 \cdot 10^{-4}$	$1.56 \cdot 10^{-4}$
[Bmim][ClO_4]	n_D	1.5534	$-2.72 \cdot 10^{-4}$	$1.99 \cdot 10^{-4}$
[Omim][BF_4]	ρ/g·cm^{-3}	1.3168	$-6.79 \cdot 10^{-4}$	$2.00 \cdot 10^{-4}$
[Omim][BF_4]	n_D	1.5152	$-2.79 \cdot 10^{-4}$	$2.25 \cdot 10^{-4}$
ethanol	ρ/g·cm^{-3}	1.0423	$-8.64 \cdot 10^{-4}$	$3.71 \cdot 10^{-4}$
ethanol[18]	n_D	1.4766	$-4.00 \cdot 10^{-4}$	

Results and Discussion

Pure Components. The densities, viscosities, and refractive indices of [Omim][BF_4] and [Bmim][ClO_4] were measured experimentally from (283.15 to 363.15) K and reported in Tables 1 and 2. The experimental data for density and viscosity were compared with the experimental data reported by Harris et al.[12] for pure [Omim][BF_4] at different temperatures, in Table 3.

The difference is defined as:

$$\Delta = (z_{exp} - z_{lit.})/z_{exp} \quad (1)$$

where z_{exp} and z_{lit} are the experimental values of density or viscosity in the present work and in the literature, respectively.

As seen in this Table, the data for densities, in which the same apparatus was used, represent small differences. On the other hand, differences in values of viscosities are higher. This might be because of the different apparatus used in the present work and that by Harris et al. and also the difference in water contents and other impurities in the applied ILs in these works.

The values of density ρ and refractive index n_D can be fitted by least-squares method using the following linear equation:

$$z = a + b(T/\mathrm{K}) \quad (2)$$

where z is ρ or n_D; T is the absolute temperature; and a and b are adjustable parameters.

Table 5. Adjustable Parameters of Equation 4 and Root Mean Square Deviation (rmsd) for the Viscosity of Different Components

component	physical properties	a	b	c	d	rmsd
[Bmim][ClO_4]	log η	−53.3690	$7.9142 \cdot 10^3$	$1.3027 \cdot 10^{-1}$	$-1.0978 \cdot 10^{-4}$	0.0016
[Omim][BF_4]	log η	−78.2789	$1.0760 \cdot 10^4$	$2.0700 \cdot 10^{-1}$	$-1.9100 \cdot 10^{-4}$	0.0123
ethanol[18]	log η	−6.4406	$1.1176 \cdot 10^3$	$1.3721 \cdot 10^{-2}$	$-1.5465 \cdot 10^{-5}$	

Table 6. Density ρ, Viscosity η, and Refractive Index n_D of the Binary Mixture of Ethanol (1) + [Omim][BF_4] (2) at Several Temperatures

x_1	T/K	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	Δn_D	x_1	T/K	ρ/g·cm^{-3}	η/mPa·s	n_D	V^E/cm^3·mol^{-1}	$\Delta\eta$/mPa·s	Δn_D
0.081	283.15	1.1229	718.47	1.4335	−0.941	−234.32	0.0031	0.511	283.15	1.0647	51.57	1.4265	−0.461	−456.23	0.0275
0.081	288.15	1.1194	507.18	1.4323	−0.952	−119.81	0.0033	0.511	288.15	1.0613	41.43	1.4250	−0.513	−292.89	0.0276
0.081	293.15	1.1159	366.59	1.4310	−0.966	−56.27	0.0034	0.511	293.15	1.0578	35.28	1.4237	−0.551	−190.33	0.0280
0.081	298.15	1.1124	268.93	1.4295	−0.971	−35.42	0.0034	0.511	298.15	1.0542	28.87	1.4230	−0.555	−133.62	0.0291
0.081	303.15	1.1089	203.35	1.4284	−0.989	−21.62	0.0036	0.511	303.15	1.0506	23.94	1.4208	−0.611	−96.25	0.0285
0.081	308.15	1.1055	156.29	1.4268	−1.017	−14.73	0.0040	0.511	308.15	1.0469	20.13	1.4195	−0.627	−71.31	0.0292
0.081	313.15	1.1022	123.27	1.4255	−1.038	−8.01	0.0042	0.511	313.15	1.0432	17.09	1.4180	−0.618	−53.16	0.0294
0.081	318.15	1.0988	97.69	1.4240	−1.057	−4.80	0.0042	0.511	318.15	1.0393	14.67	1.4168	−0.608	−40.23	0.0300
0.081	323.15	1.0954	79.43	1.4225	−1.073	−1.85	0.0038	0.511	323.15	1.0349	12.72	1.4150	−0.508	−30.86	0.0297
0.081	328.15	1.0921	65.03	1.4213	−1.090	−0.83	0.0042	0.511	328.15	1.0303	11.10	1.4137	−0.382	−24.25	0.0301
0.081	333.15	1.0887	54.15	1.4205	−1.108	0.53	0.0047	0.511	333.15	1.0287	9.77	1.4125	−0.686	−19.04	0.0306
0.081	338.15	1.0854	45.46	1.4190	−1.126	1.08	0.0045	0.511	338.15	1.0252	8.65	1.4118	−0.728	−15.22	0.0315
0.081	343.15	1.0821	39.03	1.4175	−1.145	1.85	0.0045	0.511	343.15	1.0213	7.74	1.4110	−0.705	−12.28	0.0325
0.161	283.15	1.1180	492.73	1.4315	−1.361	−377.52	0.0069	0.612	283.15	1.0397	27.12	1.4225	−0.244	−341.92	0.0333
0.161	288.15	1.1145	354.89	1.4305	−1.377	−217.81	0.0074	0.612	288.15	1.0360	22.05	1.4212	−0.257	−221.01	0.0337
0.161	293.15	1.1110	261.54	1.4292	−1.393	−124.73	0.0076	0.612	293.15	1.0322	18.24	1.4200	−0.271	−145.87	0.0343
0.161	298.15	1.1075	194.74	1.4280	−1.396	−83.30	0.0079	0.612	298.15	1.0284	15.35	1.4185	−0.249	−102.90	0.0346
0.161	303.15	1.1040	150.36	1.4270	−1.442	−55.17	0.0082	0.612	303.15	1.0247	12.98	1.4172	−0.302	−74.54	0.0350
0.161	308.15	1.1007	117.36	1.4255	−1.483	−38.90	0.0087	0.612	308.15	1.0209	11.16	1.4160	−0.319	−55.46	0.0358
0.161	313.15	1.0973	93.20	1.4240	−1.505	−26.76	0.0088	0.612	313.15	1.0172	9.61	1.4143	−0.316	−41.61	0.0359
0.161	318.15	1.0939	75.37	1.4225	−1.531	−18.29	0.0088	0.612	318.15	1.0134	8.39	1.4130	−0.340	−31.67	0.0364
0.161	323.15	1.0905	61.66	1.4210	−1.552	−12.62	0.0085	0.612	323.15	1.0097	7.39	1.4115	−0.349	−24.43	0.0366
0.161	328.15	1.0871	51.12	1.4200	−1.575	−9.09	0.0091	0.612	328.15	1.0059	6.55	1.4100	−0.363	−19.29	0.0369
0.161	333.15	1.0837	42.99	1.4188	−1.597	−6.02	0.0093	0.612	333.15	1.0022	5.80	1.4085	−0.372	−15.28	0.0372
0.161	338.15	1.0803	36.47	1.4173	−1.620	−4.11	0.0091	0.612	338.15	0.9985	5.18	1.4078	−0.382	−12.30	0.0382
0.161	343.15	1.0770	31.51	1.4160	−1.653	−2.49	0.0094	0.612	343.15	0.9947	4.70	1.4065	−0.394	−9.97	0.0387
0.315	283.15	1.0987	167.49	1.4300	−0.879	−543.29	0.0167	0.753	283.15	0.9913	12.45	1.4132	−0.137	−212.65	0.0341
0.315	288.15	1.0952	127.69	1.4288	−0.914	−340.13	0.0170	0.753	288.15	0.9875	10.36	1.4125	−0.154	−138.03	0.0352
0.315	293.15	1.0918	98.92	1.4273	−0.949	−216.66	0.0171	0.753	293.15	0.9836	8.79	1.4110	−0.169	−91.51	0.0356
0.315	298.15	1.0883	78.63	1.4260	−0.959	−148.56	0.0174	0.753	298.15	0.9797	7.53	1.4098	−0.140	−64.83	0.0363
0.315	303.15	1.0848	63.33	1.4245	−1.009	−104.66	0.0173	0.753	303.15	0.9757	6.51	1.4085	−0.195	−47.12	0.0368
0.315	308.15	1.0813	51.59	1.4230	−1.042	−76.15	0.0178	0.753	308.15	0.9718	5.66	1.4072	−0.204	−35.22	0.0375
0.315	313.15	1.0778	42.48	1.4219	−1.057	−55.61	0.0184	0.753	313.15	0.9680	4.96	1.4070	−0.208	−26.52	0.0392
0.315	318.15	1.0743	35.84	1.4205	−1.084	−40.77	0.0186	0.753	318.15	0.9641	4.38	1.4065	−0.237	−20.28	0.0406
0.315	323.15	1.0709	30.38	1.4190	−1.105	−30.40	0.0185	0.753	323.15	0.9602	3.89	1.4055	−0.256	−15.74	0.0414
0.315	328.15	1.0674	26.04	1.4178	−1.129	−23.23	0.0189	0.753	328.15	0.9564	3.50	1.4045	−0.275	−12.47	0.0423
0.315	333.15	1.0640	22.54	1.4160	−1.149	−17.59	0.0186	0.753	333.15	0.9525	3.17	1.4040	−0.283	−9.88	0.0436
0.315	338.15	1.0605	19.73	1.4145	−1.171	−13.50	0.0186	0.753	338.15	0.9486	2.89	1.4033	−0.296	−7.96	0.0448
0.315	343.15	1.0571	17.42	1.4132	−1.199	−10.42	0.0190	0.753	343.15	0.9447	2.65	1.4020	−0.300	−6.48	0.0453

These parameters for both ionic liquid and ethanol[18] are reported in Table 4. In this table, the root-mean-square deviations (rmsds) are reported for each property by the following equation:

$$\mathrm{rmsd} = \left[\frac{\sum_i^n (z_{\mathrm{exp}} - z_{\mathrm{cal}})^2}{n}\right]^{1/2} \tag{3}$$

where z_{exp} and z_{cal} are the values of experimental and calculated properties, respectively, and n is the number of data.

The viscosities values were fitted using the equation, which was proposed by Yaws et al.:[18]

$$\log(\eta/\mathrm{mPa{\cdot}s}) = a + \frac{b}{(T/\mathrm{K})} + c(T/\mathrm{K}) + d(T/\mathrm{K})^2 \tag{4}$$

where a, b, c, and d are adjustable parameters and can be calculated by correlating the experimental data for viscosity. The adjustable parameters for both ionic liquid and ethanol[18] are reported in Table 5.

Binary Systems. Densities, refractive indices, and viscosities of binary mixtures of ethanol (1) + [Omim][BF_4] (2) and ethanol (1) + [Bmim][ClO_4] (2) at different temperatures are given in Tables 6 and 7, respectively. It is worthwhile to mention that at high mole fractions of ethanol ($x_1 > 0.5$) and temperatures lower than 293 K, the binary mixture of ethanol + [Bmim][ClO_4] is separated into two phases. For this reason, the experimental data in the mentioned concentration and temperature ranges could not be obtained.

The excess molar volume, viscosity deviation, and refractive index deviation were calculated from experimental data according to the following equations:

$$V^E = \sum_{i=1}^{N} x_i M_i \left(\frac{1}{\rho} - \frac{1}{\rho_i}\right) \tag{5}$$

$$\Delta\eta = \eta - \sum_{i=1}^{N} x_i \eta_i \tag{6}$$

Table 7. Density ρ, Viscosity η, and Refractive Index n_D of the Binary Mixture of Ethanol (1) + [Bmim][ClO_4] (2) at Several Temperatures

	T	ρ	η		V^E	$\Delta\eta$	
x_1	K	g·cm^{-3}	mPa·s	n_D	cm^3·mol^{-1}	mPa·s	Δn_D
0.100	283.15	1.2493	255.52	1.4750	−0.154	−164.35	0.0100
0.100	288.15	1.2457	188.52	1.4738	−0.159	−109.32	0.0101
0.100	293.15	1.2421	142.20	1.4725	−0.182	−75.31	0.0100
0.100	298.15	1.2386	109.99	1.4710	−0.198	−52.35	0.0100
0.100	303.15	1.2351	86.43	1.4697	−0.211	−37.72	0.0101
0.100	308.15	1.2317	69.74	1.4685	−0.222	−26.90	0.0105
0.100	313.15	1.2282	56.98	1.4670	−0.230	−20.27	0.0102
0.100	318.15	1.2247	46.98	1.4655	−0.245	−15.66	0.0105
0.100	323.15	1.2213	39.45	1.4645	−0.261	−12.11	0.0108
0.100	328.15	1.2178	33.69	1.4630	−0.274	−9.37	0.0107
0.100	333.15	1.2144	28.86	1.4615	−0.284	−7.10	0.0107
0.100	338.15	1.2110	24.94	1.4603	−0.294	−5.83	0.0108
0.100	343.15	1.2075	21.69	1.4590	−0.304	−4.90	0.0109
0.165	283.15	1.2394	181.83	1.4725	−0.320	−207.81	0.0148
0.165	288.15	1.2357	136.86	1.4715	−0.323	−139.56	0.0152
0.165	293.15	1.2319	105.92	1.4700	−0.317	−95.97	0.0149
0.165	298.15	1.2280	83.35	1.4687	−0.285	−67.33	0.0152
0.165	303.15	1.2241	66.48	1.4673	−0.259	−48.78	0.0152
0.165	308.15	1.2203	54.25	1.4660	−0.219	−35.47	0.0156
0.165	313.15	1.2162	44.76	1.4648	−0.146	−26.97	0.0156
0.165	318.15	1.2112	37.20	1.4637	0.046	−20.96	0.0164
0.165	323.15	1.2072	31.56	1.4620	0.094	−16.33	0.0160
0.165	328.15	1.2010	27.02	1.4608	0.474	−12.98	0.0162
0.165	333.15	1.1987	23.50	1.4595	0.292	−9.91	0.0165
0.165	338.15	1.1954	20.45	1.4580	0.270	−8.14	0.0163
0.165	343.15	1.1903	18.12	1.4565	0.496	−6.59	0.0162
0.291	283.15	1.2166	87.42	1.4680	−0.616	−243.64	0.0246
0.291	288.15	1.2128	68.04	1.4667	−0.628	−166.87	0.0247
0.291	293.15	1.2089	54.90	1.4655	−0.619	−116.70	0.0249
0.291	298.15	1.2050	44.84	1.4640	−0.586	−83.26	0.0250
0.291	303.15	1.1998	36.75	1.4627	−0.421	−61.26	0.0252
0.291	308.15	1.1958	30.63	1.4615	−0.385	−45.68	0.0257
0.291	313.15	1.1931	26.13	1.4600	−0.503	−34.90	0.0256
0.291	318.15	1.1889	22.14	1.4587	−0.450	−27.36	0.0262
0.291	323.15	1.1847	19.51	1.4570	−0.385	−21.25	0.0259
0.291	328.15	1.1801	17.16	1.4560	−0.275	−16.90	0.0264
0.291	333.15	1.1752	15.43	1.4545	−0.109	−13.03	0.0265
0.291	338.15	1.1693	13.79	1.4532	0.190	−10.57	0.0267
0.291	343.15	1.1594		1.4518	1.024		0.0268
0.401	283.15	1.1920	50.26	1.4625	−0.868	−229.65	0.0315
0.401	288.15	1.1883	40.89	1.4612	−0.901	−157.77	0.0317
0.401	293.15	1.1846	33.49	1.4595	−0.928	−111.67	0.0315
0.401	298.15	1.1809	27.92	1.4580	−0.933	−80.47	0.0317
0.401	303.15	1.1772	23.38	1.4568	−0.977	−59.57	0.0321
0.401	308.15	1.1736	20.06	1.4555	−0.999	−44.55	0.0325
0.401	313.15	1.1699	17.38	1.4540	−1.015	−34.30	0.0325
0.479	283.15	1.1736	35.48	1.4590	−1.313	−208.16	0.0368
0.479	288.15	1.1698	29.17	1.4575	−1.347	−143.79	0.0369
0.479	293.15	1.1661	24.41	1.4563	−1.378	−101.99	0.0372
0.479	298.15	1.1622	20.67	1.4550	−1.371	−73.75	0.0377
0.479	303.15	1.1583	17.56	1.4535	−1.403	−54.72	0.0378
0.592	293.15	1.1296	12.98		−1.719	−86.27	
0.592	298.15	1.1258	11.13		−1.730	−63.04	
0.592	303.15	1.1220	9.60		−1.796	−47.22	
0.592	308.15	1.1175	8.48		−1.756	−35.81	
0.592	313.15	1.1148	7.43		−1.886	−28.03	
0.637	293.15	1.1104	11.66		−1.692	−76.77	
0.637	298.15	1.1046	10.06		−1.511	−56.05	
0.637	303.15	1.1027	8.71		−1.767	−41.95	
0.637	308.15	1.1006	7.52		−1.967	−31.98	
0.637	313.15	1.0967	6.66		−1.990	−24.99	
0.790	293.15	1.0226	5.38		−1.412	−46.27	
0.790	298.15	1.0187	4.62		−1.412	−34.07	
0.790	303.15	1.0148	4.03		−1.501	−25.69	
0.790	308.15	1.011	3.74		−1.539	−19.49	
0.790	313.15	1.007	3.46		−1.558	−15.19	
0.860	293.15	0.9605	4.96		−0.772	−29.87	
0.860	298.15	0.9567	4.22		−0.766	−21.92	
0.860	303.15	0.9527	3.59		−0.852	−16.54	
0.860	308.15	0.9487	3.16		−0.884	−12.62	
0.860	313.15	0.9446	2.80		−0.894	−9.90	

$$\Delta n_D = n_D - \sum_{i=1}^{N} x_i n_{D,i} \tag{7}$$

where ρ and ρ_i are the densities of the mixture and pure components, respectively; x_i represents the mole fraction of the i component; M_i is the molecular weight of the i component; η and η_i are the viscosities of the mixture and pure components, respectively, and n_D and $n_{D,i}$ are the refractive indices of the mixture and pure components, respectively.

The excess molar volume, viscosity deviation, and refractive index deviation were fitted for each temperature by a Redlich–Kister equation:

$$\Delta Q_{ij} = x_i x_j \sum_{P=0}^{M} B_P (x_i - x_j)^P \tag{8}$$

where ΔQ_{ij} is the excess property, x is the mole fraction, B_P is the fitting parameter, and M is the degree of the polynomial expansion. A third order polynomial was found to be optimum for properties of the ethanol (1) + [Omim][BF_4] (2) binary system. The fitting parameters are given in Table 8. Figure 1 shows the comparison of the experimental excess molar volume with those obtained from the Redlich–Kister polynomial equation for a binary mixture of ethanol (1) + [Omim][BF_4] (2) at different temperatures. In this figure, the excess molar volume represents a minimum around $x_1 = 0.20$, and this minimum shifts upward with an increase in temperature. The values of viscosity deviation as well as a Redlich–Kister fit are plotted in Figure 2.

The excess properties of the ethanol (1) + [Bmim][ClO_4] (2) binary system are fitted by the Redlich−Kister equation using a fourth-order polynomial, and fitting parameters are reported in Table 9.

As it can be seen from the data of Tables 8 and 9, and also from Figures 1 and 2, the Redlich–Kister polynomial equation can fit the molar excess volume, viscosity deviation, and

Table 8. Fitted Parameters of Equation 8 and Root Mean Square Deviation (rmsd) for Ethanol (1) + [Omim][BF_4] (2)

	B_0	B_1	B_2	B_3	rmsd
		T = 283.15			
V^E/cm^3·mol^{-1}	−1.7208	3.6638	−6.7374	6.8188	0.0493
$\Delta\eta$/mPa·s	−1885.43	1561.62	−445.38	−846.97	6.7020
Δn_D	0.1073	0.0929	0.0453	0.0383	1.52E−04
		T = 293.15			
V^E/cm^3·mol^{-1}	−2.0008	3.9595	−6.5745	6.4506	0.0527
$\Delta\eta$/mPa·s	−798.24	672.96	36.89	−986.55	2.8421
Δn_D	0.1096	0.0976	0.0572	0.0408	1.02E−04
		T = 303.15			
V^E/cm^3·mol^{-1}	−2.2141	4.2123	−6.6269	6.2185	0.0570
$\Delta\eta$/mPa·s	−403.13	306.91	74.71	−534.77	1.4561
Δn_D	0.1110	0.1007	0.0679	0.0447	8.92E−05
		T = 313.15			
V^E/cm^3·mol^{-1}	−2.2680	4.4164	−7.1676	6.3242	0.0546
$\Delta\eta$/mPa·s	−222.86	157.00	66.87	−328.39	0.8919
Δn_D	0.1154	0.1023	0.0854	0.0625	2.58E−04
		T = 323.15			
V^E/cm^3·mol^{-1}	−2.0922	4.6268	−8.9985	5.0364	0.0376
$\Delta\eta$/mPa·s	−129.18	79.13	59.34	−208.05	0.5632
Δn_D	0.1148	0.1058	0.1104	0.0949	2.38E−04
		T = 333.15			
V^E/cm^3·mol^{-1}	−2.5271	4.6047	−7.9798	6.1438	0.0552
$\Delta\eta$/mPa·s	−79.65	40.98	49.82	−136.70	0.3917
Δn_D	0.1161	0.1161	0.1331	0.0836	5.26E−04
		T = 343.15			
V^E/cm^3·mol^{-1}	−2.6235	4.8101	−8.3803	6.0921	0.0538
$\Delta\eta$/mPa·s	−51.33	21.33	42.92	−98.55	0.3183
Δn_D	0.1222	0.1220	0.1284	0.0912	6.58E−04

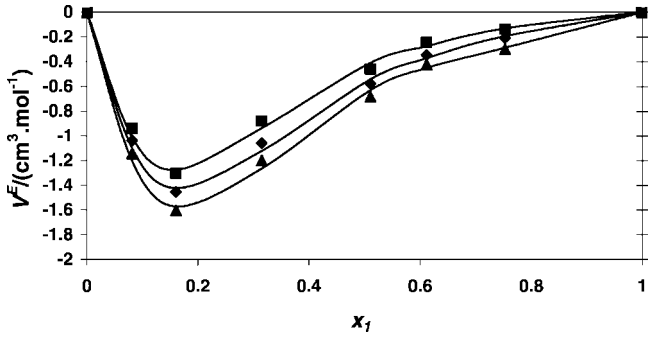

Figure 1. Excess molar volume V^E for the system of ethanol (1) + [OMIM][BF_4] (2) at different temperatures: ■, 283.15 K; ♦, 313.15 K; ▲, 343.15 K. The solid lines represent the corresponding correlation by the Redlich–Kister equation.

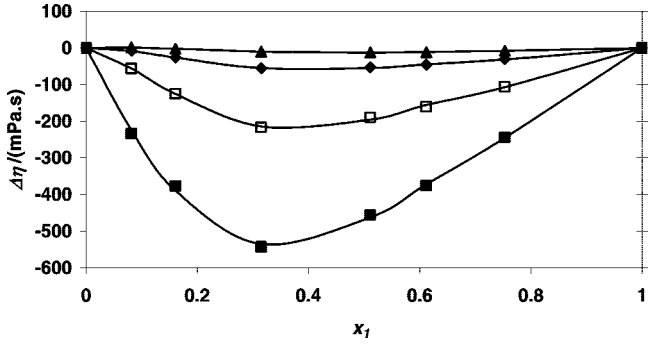

Figure 2. Viscosity deviation $\Delta\eta$ for the system of ethanol (1) + [OMIM][BF_4] (2) at different temperatures: ■, 283.15 K; □,293.15 K; ♦, 313.15 K; ▲, 343.15 K. The solid lines represent the corresponding correlation by the Redlich–Kister equation.

Table 9. Fitted Parameters of Equation 8 and Root Mean Square Deviation (rmsd) for Ethanol (1) + [Bmim][ClO_4] (2)

	B_0	B_1	B_2	B_3	B_4	rmsd
			T = 293.15			
V^E/cm^3·mol^{-1}	−5.5580	−8.0495	−1.7640	9.4641	7.5172	0.0436
$\Delta\eta$/mPa·s	−400.01	282.65	−190.73	119.11	2.53	1.1103
			T = 298.15			
V^E/cm^3·mol^{-1}	−5.5095	−7.2975	0.6016	7.5571	2.5712	0.0780
$\Delta\eta$/mPa·s	−290.36	194.27	−120.17	82.52	−8.91	0.7887
			T = 303.15			
V^E/cm^3·mol^{-1}	−5.8460	−9.3500	2.5718	10.4231	−0.7969	0.0477
$\Delta\eta$/mPa·s	−215.98	139.20	−86.72	54.81	4.62	0.6594
			T = 308.15			
V^E/cm^3·mol^{-1}	−5.8316	−10.4481	0.9198	12.2574	2.2785	0.0495
$\Delta\eta$/mPa·s	−164.54	102.62	−49.40	27.76	−0.16	0.4383
			T = 313.15			
V^E/cm^3·mol^{-1}	−6.1481	−10.2604	0.9541	11.7145	3.5574	0.0371
$\Delta\eta$/mPa·s	−127.78	75.37	−32.64	22.14	−2.13	0.3171

refractive index deviation well. However, these equations have too many parameters for the systems in the present study. Moreover, they do not represent any dependency to the temperature. For this reason, an alternative equation is fitted to the experimental data of densities, refractive indices, and viscosities for the binary mixtures as follow:

$$z = x_1 z_1 + (1 - x_1) z_2 + A x_1 \qquad (9)$$

where z is log η, ρ or n_D of the mixture, z_1 and z_2 are log η, ρ, or n_D of the pure ethanol and ionic liquid, respectively, and can be calculated using eqs 2 or 3, x_1 is the mole fraction of ethanol, and A is an adjustable parameter which is determined by fitting the experimental data. Since the equations for calculation of pure components properties are temperature-dependent, it can be concluded that parameter A depends implicitly to the temperature. The parameter A in eq 9 can be referred to as an index for deviation from ideality.

Table 10. Adjustable Parameter of Equation 9 and Root Mean Square Deviation (rmsd) for the Density, Refractive Index, and Viscosity of the Binary Mixture Ethanol (1) + [Bmim][ClO_4] and Ethanol (1) + [Omim][BF_4] (2)

	A	rmsd
ethanol (1) + [Bmim][ClO_4] (2)		
ρ/g·cm^{-3}	0.2108	0.0287
n_D	0.0840	0.0019
log(η/mPa·s)	0.2563	0.0291
ethanol (1)+ [Omim][BF_4] (2)		
ρ/g·cm^{-3}	0.1848	0.0165
n_D	0.0537	0.0024
log(η/mPa·s)	0.2936	0.0229

The adjustable parameter of eq 9 and root-mean-square deviation for each property are reported in Table 10. As Table 10 shows, this correlation can fit the experimental data in different temperatures and mole fractions of ethanol. The root-mean-square deviations for each of the binary system are acceptable. The comparison of the experimental data with the calculated ones for density of ethanol (1) + [Bmim][ClO_4] or [Omim][BF_4] (2) at different mole fractions of ethanol are plotted in Figure 3. As the figure shows, the model can correlate the experimental data for density of the mixture with good accuracy. Figure 4 shows the deviation of calculated values with the experimental refractive indices for the binary mixtures of the mentioned systems. The agreements of the experimental data with calculated ones are very good.

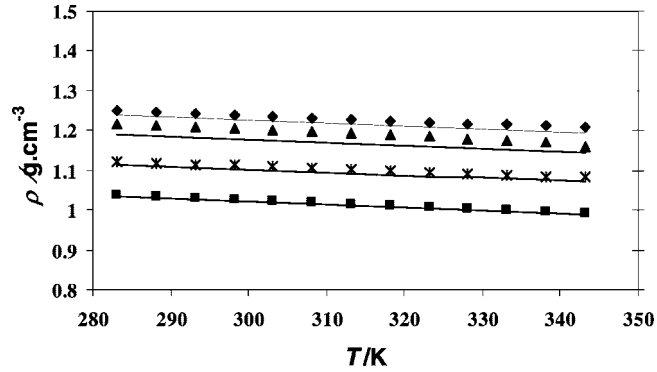

Figure 3. Comparison of experimental value and fitted model of density for the binary mixture of ethanol (1) + [Bmim][ClO_4] (2) at mole fraction ♦, x_1 = 0.1; ▲, x_1 = 0.291 and the binary mixture of ethanol (1)+ [Omim][BF_4] (2) at mole fraction ■, x_1 = 0.645; *, x_1 = 0.0831. The solid lines represent the corresponding correlation.

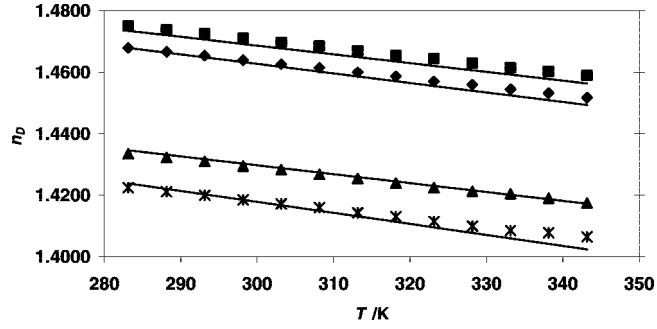

Figure 4. Comparison of experimental value and fitted model of refractive indices for the binary mixture of ethanol (1) + [Bmim][ClO_4] (2) at mole fraction ♦, x_1 = 0.1; ▲, x_1 = 0.291 and the binary mixture of ethanol (1)+ [OMIM][BF_4] (2) at mole fraction *, x_1 = 0.645; ■, x_1 = 0.0831. The solid lines represent the corresponding correlation.

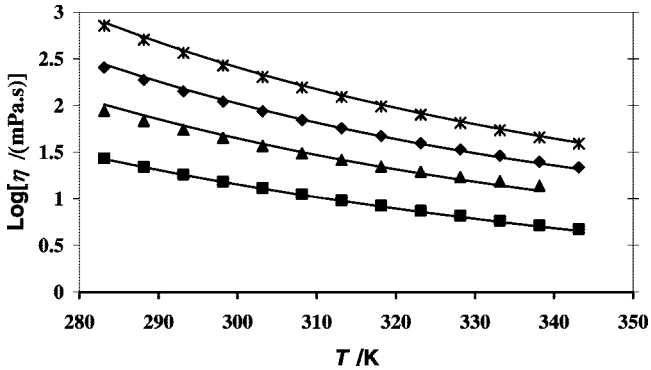

Figure 5. Comparison of experimental value and fitted model of viscosities for the binary mixture of ethanol (1) + [Bmim][ClO_4] (2) at mole fraction ♦, $x_1 = 0.1$; ▲, $x_1 = 0.291$ and the binary mixture of ethanol (1) + [Omim][BF_4] (2) at mole fraction ■, $x_1 = 0.645$; *, $x_1 = 0.0831$. The solid lines represent the corresponding correlation.

The comparisons of the viscosity experimental data with the calculated values from the model are shown in Figure 5.

The results of the model show that the physical properties of binary mixtures of ionic liquids can be calculated by using the data for the pure components with reasonable accuracy.

Conclusions

The experimental data for densities, refractive indices, and viscosities of pure ionic liquids of [Bmim][ClO_4] and [Omim][BF_4] at different temperatures were presented in this research. The densities and refractive indices decrease linearly with increase in temperature, but the variations in viscosities show a nonlinear form. The experimental values for density, refractive index, and viscosity were fitted, and the adjustable parameters were calculated. The results of fitting for pure systems showed good agreement with the experimental data.

Densities, refractive indices, and viscosities for binary mixtures of ethanol (1) + [Omim][BF_4] (2), and ethanol (1) + [Bmim][ClO_4] (2) at different temperatures and compositions were determined. The excess molar volume, viscosity deviation, and refractive index deviation were calculated and fitted by a Redlich–Kister equation. Since the numbers of parameters in this equation are high, the experimental data for the binary mixtures were fitted alternatively by a new equation. By using this equation, the binary mixture properties can be calculated based on the properties of pure components, their mole fractions, and an adjustable parameter, which determines the nonideality.

Literature Cited

(1) Carmichael, A. J.; Seddon, K. R. Polarity Study of Some 1-Alkyl-3-methylimidazolium Ambient-Temperature Ionic Liquids with the Solvatochromic dye, Nile Red. *J. Phys. Org. Chem.* **2000**, *13*, 591–595.

(2) Law, G.; Watson, P. R. Surface Orientation in Ionic Liquids. *Chem. Phys. Lett.* **2001**, *345*, 1–4.

(3) Seddon, K. R.; Stark, A.; Torres, M. J. Influence of Chloride, Water and Organic Solvents on the Physical Properties of Ionic Liquids. *Pure Appl. Chem.* **2000**, *72*, 2275–2287.

(4) Rodriguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145–2155.

(5) Gonzalez, E. J.; Alonso, L.; Dominguez, A. Physical Properties of Binary Mixtures of the Ionic Liquid 1-Methyl-3-octylimidazolium Chloride with Methanol, Ethanol, and 1-Propanol at $T =$ (298.15, 313.15, and 328.15) K and at $P = 0.1$ MPa. *J. Chem. Eng. Data* **2006**, *51*, 1446–1452.

(6) Gomez, E.; Gonzalez, B.; Calvar, N.; Tojo, E.; Dominguez, A. Physical Properties of Pure 1-Ethyl-3-methylimidazolium Ethylsulfate and its Binary Mixtures with Ethanol and Water at Several Temperatures. *J. Chem. Eng. Data* **2006**, *51*, 2096–2102.

(7) Gonzalez, E. J.; Gonzalez, B.; Calvar, N.; Dominguez, A. Physical Properties of Binary Mixtures of the Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate with Several Alcohols at $T =$ (298.15, 313.15, and 328.15) K and Atmospheric Pressure. *J. Chem. Eng. Data* **2007**, *52*, 1641–1648.

(8) Deenadayalu, N.; Kumar, S.; Bhujrajh, P. Liquid Densities and Excess Molar Volumes for (Ionic liquids + Methanol + Water) Ternary System at Atmospheric Pressure and at Various Temperatures. *J. Chem. Thermodyn.* **2007**, *39*, 1318–1324.

(9) Bartoli, G.; Locatelli, M.; Melchiorre, P.; Sambri, L. Taking up the Cudgels for Perchlorates: Uses and Applications in Organic Reaction under Mild Conditions. *Eur. J. Org. Chem.* **2007**, *13*, 2037–2049.

(10) Fischer, T.; Sethi, A.; Welton, T.; Woolf, J. Diels-Alder Reactions in Room-temperature Ionic Liquids. *Tetrahedron Lett.* **1999**, *40*, 793–796.

(11) Gu, Z.; Brennecke, J. F. Volume Expansivities and Isothermal Compressibilities of Imidazolium and Pyridinium-based Ionic Liquids. *J. Chem. Eng. Data* **2002**, *47*, 339–345.

(12) Harris, K. R.; Kanakubo, M.; Woolf, L. A. Temperature and Pressure Dependence of the Viscosity of the Ionic Liquids 1-Methyl-3-octylimidazolium hexafluorophosphate and 1-Methyl-3-octylimidazolium Tetrafluoroborate. *J. Chem. Eng. Data* **2006**, *51*, 1161–1167.

(13) Gardas, R. L.; Freire, M. G.; Carvalho, P. J.; Marrucho, I. M.; Fonseca, I. M. A.; Ferreira, A.G. M.; Coutinho, J. A. P. High-pressure Densities and Derived Thermodynamic Properties of Imidazolium-based Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 80–88.

(14) Sanmamed, Y. A.; Gonzalez-Salgado, D.; Troncoso, J.; Cerdeirina, C. A.; Romani, L. Viscosity-induced Errors in the Density Determination of Room Temperature Ionic Liquids using Vibrating Tube Densitometry. *Fluid Phase Equilib.* **2007**, *252*, 96–102.

(15) Heintz, A.; Klasen, D.; Lehmann, J. K.; Wertz, C. Excess Molar Volumes and Liquid–Liquid Equilibria of the Ionic Liquid 1-Methyl-3-octyl-imidazolium tetrafluoroborate Mixed with Butan-1-ol and Pentan-1-ol. *J. Solution Chem.* **2005**, *34*, 1135–1144.

(16) Redilch, O.; Kister, A. T. Thermodynamics of Nonelectrolyte Solutions, Algebraic Representation of Thermodynamic Properties and the Classification of Solutions. *Ing. Eng. Chem.* **1948**, *40*, 345–348.

(17) Dupont, J.; Consorti, C. S.; Suarez, P. A. Z.; Souza, R. F. *Organic Syntheses*; Wiley: Sidney, 2004; Coll. 10.

(18) Yaws, C. L. *Chemical Properties Handbook*; McGraw-Hill: New York, 1999.

Received for review September 11, 2007. Accepted January 23, 2008.

JE700521T