

Densities, Viscosities, and Refractive Properties of the Binary Mixtures of the Amino Acid Ionic Liquid [bmim][Ala] with Methanol or Benzylalcohol at $T = (298.15 \text{ to } 313.15) \text{ K}$

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ABSTRACT: Densities, viscosities, and refractive indices were determined for two ionic liquid (IL) mixtures formed by 1-butyl-3-methylimidazolium alanine acid salt ([bmim][Ala]) with methanol or benzylalcohol, respectively, over the mole fraction range from (0.1 to 0.9) and at temperatures from (298.15 to 313.15) K at intervals of 5 K and atmospheric pressure. Excess molar volumes, viscosity deviations, and refractive index deviations have been calculated from the experimental data and fitted to a Redlich–Kister polynomial function. The results have been interpreted in terms of ion–dipole interactions and structural factors of the IL and alcohol molecular liquids.

1. INTRODUCTION

Mixing different organic liquids gives rise to solutions that generally do not behave ideally. The thermodynamic and transport properties of liquids and liquid mixtures¹ are used to study the molecular interactions between the various components of the mixture and also to understand engineering applications concerning heat transfer, mass transfer, and fluid flow. Properties such as density, viscosity, and refractive index of binary liquid mixtures over the whole concentration range are useful for a full understanding of their thermodynamic and transport properties and are important to arrive at an understanding theoretically and practically.

A number of researchers have studied some of properties of ionic liquids (ILs) such as density or viscosity. The presence of water or alcohol in ILs has a large effect on physical properties.^{2–4} There are a number of papers concerning the thermodynamics properties of binary systems of ILs.^{5–7} A few successful samples have been reported; amino acid ILs are candidates to act as a platform for functional pure amino acid ILs in large quantities at low cost. Despite their importance and interest, detailed knowledge of the physicochemical properties of ILs has not been studied systematically. Particularly, properties of the mixtures of ILs with organic molecular liquids that are paramount for the design of many technological processes are very limited. In a previous article,⁸ we reported experimental thermodynamic properties for binary mixtures 1-butyl-3-methylimidazolium glutamic acid salt ([bmim][Glu]) or 1-butyl-3-methylimidazolium glycine acid salt ([bmim][Gly]), respectively, with benzylalcohol. The present article continues this work, reporting values of densities, viscosities, and refractive indices, of binary mixtures binary 1-butyl-3-methylimidazolium alanine acid salt ([bmim][Ala]) with methanol or benzylalcohol, respectively, at (298.15 to 313.15) K and at atmospheric pressure. From these experimental results, excess molar volume, viscosity, and refractive index deviations from the ideal behavior were calculated.

2. EXPERIMENTAL SECTION

Chemicals. The ILs [bmim][Ala] were prepared and purified by using the procedures described by Fukumoto⁹ (see Figure 1).

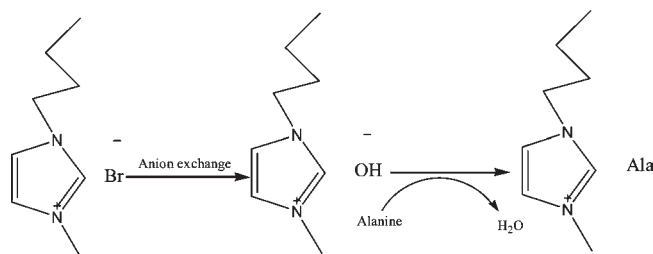


Figure 1. Preparation of the amino acid IL [bmim][Gly] by the neutralization method: 1, [bmim][Br]; 2, [bmim][OH]; 3, ([bmim][Ala]).

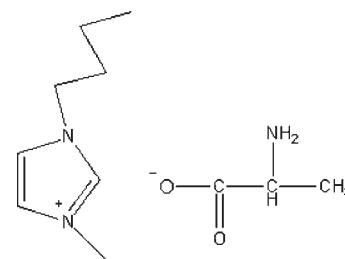


Figure 2. Molecular structure of the IL [bmim][Ala].

In the process above, the ILs were washed several times with dichloromethane and anhydrous ether to decrease the bromine content. It was determined that no precipitation of AgBr occurred by the addition of AgNO₃ to the wash liquid. To reduce the water content and volatile compounds (methylimidazole, dichloromethane, and anhydrous ether) to negligible values, vacuum (< 1.0 kPa) and moderate temperature to 353 K were applied to the [bmim][Ala] samples for several days, always immediately prior to their use.

The samples were analyzed by Karl Fisher titration (ZSD-2 type) and showed a mass % of water lower than $1 \cdot 10^{-4}$ for [bmim][Ala].

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Table 1. Densities ρ , Refractive Indices n_D of the Pure Components, and Comparison with the Literature Values

component	T/K	$\rho/\text{g}\cdot\text{cm}^{-3}$		$\eta/\text{mPa}\cdot\text{s}$		n_D	
		exptl	lit.	exptl	lit.	exptl	lit.
[bmim][Ala]	298.15	1.0802	1.0794 ¹⁰	78.295		1.5184	
	303.15	1.0765	1.764 ¹⁰	59.772		1.5168	
	308.15	1.0742	1.739 ¹⁰	47.028		1.5153	
	313.15	1.0711	1.707 ¹⁰	37.946		1.5135	
methanol	298.15	0.7864	0.7866 ¹¹	0.532	0.5470 ¹⁵	1.3266	1.32653 ¹⁷
	303.15	0.7822	0.7819 ¹²	0.515	0.5100 ¹⁵	1.3243	1.3241 ¹⁸
	308.15	0.7767	0.7771 ¹³	0.465	0.4840 ¹⁶	1.3224	1.32223 ¹⁸
	313.15	0.7729	0.7726 ¹⁴	0.441	0.4470 ¹⁵	1.3208	1.32018 ¹⁸
benzylalcohol	298.15	1.04164	1.0415 ¹⁹	5.550	5.160 ²²	1.5371	1.5378 ²¹
			1.0416 ²⁰				
	303.15	1.03742	1.0376 ¹⁹	4.675	4.670 ²²	1.5349	1.5354 ²¹
	308.15	1.03384	1.0339 ¹⁹	4.010	4.004 ²²	1.5323	1.5318 ²¹
			1.0330 ²⁰				
	313.15	1.03043	1.0306 ¹⁹	3.522	3.520 ²²	1.5301	

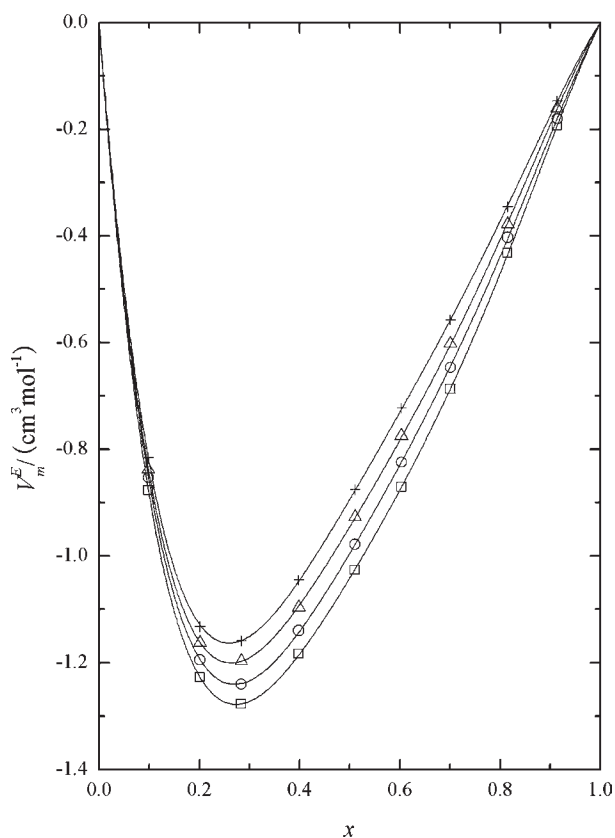


Figure 3. Excess molar volume vs mole fraction for $\{x_1[\text{bmim}][\text{Ala}] + (1 - x_1)\text{methanol}\}$ mixtures; \square , $T = 298.15\text{ K}$; \circ , $T = 303.15\text{ K}$; \triangle , $T = 308.15\text{ K}$; $+$, $T = 313.15\text{ K}$.

The bromine contents were measured by titration with AgNO_3 , and the obtained values were below the detection limit ($< 200\text{ ppm}$). The structure of IL was identified by $^1\text{H NMR}$ (AVANCE III 400 MHz digital NMR spectrometer) and in good agreement with the literature,¹⁰ A detailed formula is shown in Figure 2. From the

Table 2. Densities, Refractive Indices, Excess Molar Volumes, Viscosity Deviations, and Refractive Index Deviations for Binary Mixtures at Temperatures from (298.15 to 313.15) K and Atmospheric Pressure

x_1	ρ		η		V_m^E		Δn	
	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	n_D	$\text{mPa}\cdot\text{s}$	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$	$100\Delta n_D$	
$x([\text{bmim}][\text{Ala}] + (1 - x)\text{Methanol})$								
$T = 298.15\text{ K}$								
0.0986	0.90631	1.824	1.3952	-0.8769	-6.3589	4.9688		
0.2015	0.96855	2.979	1.4380	-1.2276	-13.2094	7.2779		
0.2837	0.99811	4.892	1.4595	-1.2771	-17.6900	7.8488		
0.3985	1.02498	8.963	1.4787	-1.1731	-22.5478	7.5642		
0.5105	1.04262	15.196	1.4914	-1.0264	-25.0263	6.6861		
0.6035	1.05347	22.228	1.4994	-0.8708	-25.2275	5.7082		
0.7011	1.06238	31.135	1.5058	-0.6875	-23.9121	4.4756		
0.8152	1.07044	45.030	1.5111	-0.4327	-18.8909	2.8113		
0.9139	1.07600	60.328	1.5147	-0.1934	-11.2699	1.2814		
$T = 303.15\text{ K}$								
0.0986	0.90165	1.753	1.3926	-0.8531	-4.6029	4.9315		
0.2015	0.96393	2.760	1.4350	-1.1947	-9.6949	7.1891		
0.2837	0.99359	3.714	1.4564	-1.2402	-13.6121	7.7444		
0.3985	1.02056	6.403	1.4755	-1.1399	-17.7261	7.4505		
0.5105	1.03831	10.727	1.4883	-0.9782	-20.0391	6.5681		
0.6035	1.04927	16.008	1.4964	-0.8243	-20.2690	5.5893		
0.7011	1.05830	22.635	1.5029	-0.6467	-19.4248	4.3621		
0.8152	1.06650	32.906	1.5087	-0.4028	-15.9159	2.7455		
0.9139	1.07220	45.018	1.5126	-0.1803	-9.6521	1.2387		
$T = 308.15\text{ K}$								
0.0986	0.89659	1.829	1.3901	-0.8381	-3.2257	4.8705		
0.2015	0.95934	2.349	1.4323	-1.1631	-7.4988	7.1029		
0.2837	0.98932	3.429	1.4533	-1.1968	-10.2457	7.6185		
0.3985	1.01681	5.513	1.4723	-1.0967	-13.5078	7.3075		
0.5105	1.03485	9.168	1.4850	-0.9267	-15.0675	6.4188		
0.6035	1.04607	13.402	1.4930	-0.7752	-15.1640	5.4219		
0.7011	1.05534	18.285	1.5000	-0.6024	-14.8256	4.2402		
0.8152	1.06385	26.268	1.5059	-0.3785	-12.1546	2.6288		
0.9139	1.06971	35.298	1.5105	-0.1608	-7.7206	1.1828		
$T = 313.15\text{ K}$								
0.0986	0.89246	1.340	1.3881	-0.8162	-2.7975	4.8289		
0.2015	0.95528	2.113	1.4297	-1.1322	-5.8849	7.0025		
0.2837	0.98535	2.792	1.4502	-1.1595	-8.2893	7.4686		
0.3985	1.01289	5.197	1.4692	-1.0452	-10.1896	7.1586		
0.5105	1.03110	8.300	1.4817	-0.8757	-11.2874	6.2522		
0.6035	1.04242	11.913	1.4898	-0.7235	-11.1622	5.2737		
0.7011	1.05182	15.870	1.4970	-0.5574	-10.8657	4.1065		
0.8152	1.06049	21.918	1.5034	-0.3451	-9.0969	2.5539		
0.9139	1.06651	29.177	1.5082	-0.1467	-5.5399	1.1316		
$x_1([\text{bmim}][\text{Ala}] + (1 - x_1)\text{Benzylalcohol})$								
$T = 298.15\text{ K}$								
0.1012	1.05286	6.989	1.5355	-0.4407	-5.9226	0.0248		
0.1939	1.05980	8.647	1.5340	-0.6477	-11.0113	0.0495		
0.3103	1.06602	11.904	1.5320	-0.7687	-16.2191	0.0695		
0.3971	1.06957	14.699	1.5304	-0.8032	-19.7384	0.0765		

Table 2. Continued

x_1	ρ		η		V_m^E		$\Delta\eta$	
	$\text{g}\cdot\text{cm}^{-3}$	$\text{mPa}\cdot\text{s}$	n_D	$\text{cm}^3\cdot\text{mol}^{-1}$	$\text{mPa}\cdot\text{s}$	$100\Delta n_D$		
0.4864	1.07240	18.754	1.5287	-0.7841	-22.1793	0.0724		
0.6015	1.07514	26.240	1.5264	-0.6928	-23.0662	0.0591		
0.6945	1.07658	34.416	1.5245	-0.5375	-21.6551	0.0425		
0.8015	1.07773	46.723	1.5223	-0.3029	-17.1320	0.0218		
0.9026	1.07872	61.327	1.5203	-0.0865	-9.8824	0.0087		
$T = 303.15\text{ K}$								
0.1012	1.04856	5.691	1.5333	-0.4253	-4.5601	0.0238		
0.1939	1.05561	6.738	1.5319	-0.6371	-8.6233	0.0469		
0.3103	1.06188	9.274	1.5300	-0.7537	-12.4979	0.0685		
0.3971	1.06549	11.463	1.5285	-0.7884	-15.0914	0.0738		
0.4864	1.06842	14.625	1.5268	-0.7765	-16.8496	0.0697		
0.6015	1.07116	20.505	1.5246	-0.6756	-17.3110	0.0565		
0.6945	1.07271	26.616	1.5227	-0.5291	-16.3241	0.0393		
0.8015	1.07395	35.941	1.5206	-0.3015	-12.8942	0.0216		
0.9026	1.07498	46.957	1.5186	-0.0842	-7.4491	0.0072		
$T = 308.15\text{ K}$								
0.1012	1.04509	4.951	1.5308	-0.4152	-3.4126	0.0237		
0.1939	1.05225	5.953	1.5295	-0.6189	-6.4001	0.0451		
0.3103	1.05875	7.695	1.5277	-0.7389	-9.6633	0.0663		
0.3971	1.06251	9.977	1.5263	-0.7763	-11.1150	0.0704		
0.4864	1.06553	12.613	1.5247	-0.7591	-12.3207	0.0683		
0.6015	1.06843	17.359	1.5226	-0.6624	-12.5267	0.0522		
0.6945	1.07011	22.129	1.5209	-0.5203	-11.7566	0.0378		
0.8015	1.07146	29.006	1.5189	-0.2954	-9.4826	0.0201		
0.9026	1.07258	36.886	1.5170	-0.0801	-5.9523	0.0068		
$T = 313.15\text{ K}$								
0.1012	1.04162	4.280	1.5286	-0.4056	-2.7255	0.0225		
0.1939	1.04877	5.515	1.5273	-0.6023	-4.6834	0.0438		
0.3103	1.05535	7.175	1.5256	-0.7256	-7.0288	0.0637		
0.3971	1.05907	8.904	1.5242	-0.7535	-8.2874	0.0684		
0.4864	1.06218	11.023	1.5227	-0.7442	-9.2433	0.0647		
0.6015	1.06520	15.009	1.5206	-0.6576	-9.2189	0.0505		
0.6945	1.06687	18.654	1.5189	-0.5098	-8.7755	0.0357		
0.8015	1.06831	24.471	1.5170	-0.2947	-6.6417	0.0182		
0.9026	1.06952	30.691	1.5152	-0.0902	-3.9021	0.0056		

NMR, the total peak integral in the ^1H NMR spectrum was found to correspond for all ILs to a nominal purity higher than 99 %.

Methanol and benzylalcohol (analytical reagent grade, mass fraction > 0.99), used in the experiments, was purchased from Shanghai Chemical Factory. It was further purified by fractional distillation until constancy of the boiling point and density for successive fractions. To check the purity of the substances, gas chromatography was used to check the purity of methanol. Gas chromatographic studies showed no evidence of appreciable impurities in reagents. The density, viscosity, and refractive index of [bmim][Ala], methanol, and benzylalcohol were determined at $T = (298.15 \text{ to } 313.15)\text{ K}$ and compared with the literature values^{10–22} as listed in Table 1; the agreement is good. Gas chromatographic studies showed no evidence of appreciable impurities in reagents.

Apparatus and Procedure. Binary mixtures were prepared by mass in airtight glass bottles. The mass measurements were

Table 3. Parameters and Standard Deviations, σ , of Equation 4 for Binary Mixtures at Different Temperatures

	a_0	a_1	a_2	a_3	σ
$x_1([\text{bmim}][\text{Ala}] + (1 - x_1)\text{Methanol})$					
$T = 298.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-4.1660	-3.1093	-3.1439	-2.2806	0.0015
$\Delta\eta/\text{mPa}\cdot\text{s}$	-99.3055	26.7298	-10.3759	25.0436	0.1266
$100\Delta n_D$	27.1474	18.6683	14.1285	9.0284	0.0087
$T = 303.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.9813	-3.1601	-3.0921	-2.1119	0.0022
$\Delta\eta/\text{mPa}\cdot\text{s}$	-78.7805	26.8652	-10.5953	24.7293	0.1386
$100\Delta n_D$	26.6471	18.5903	14.1532	9.2242	0.0084
$T = 308.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.7821	-3.1231	-3.0957	-2.2252	0.0028
$\Delta\eta/\text{mPa}\cdot\text{s}$	-59.4589	17.3164	-9.8022	30.1766	0.1573
$100\Delta n_D$	26.0393	18.7440	14.0195	9.0448	0.0089
$T = 313.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.5766	-3.1904	-3.0832	-2.0685	0.0023
$\Delta\eta/\text{mPa}\cdot\text{s}$	-44.6727	10.7663	-8.6499	19.7040	0.1287
$100\Delta n_D$	25.3774	18.5237	14.2009	9.5229	0.0100
$x_1([\text{bmim}][\text{Ala}] + (1 - x_1)\text{Benzylalcohol})$					
$T = 298.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.1211	-1.0689	0.2957	-2.0858	0.0025
$\Delta\eta/\text{mPa}\cdot\text{s}$	-89.349	34.1955	0.9893	-7.5862	0.1054
$100\Delta n_D$	0.2871	0.1870	-0.1594	-0.1214	0.0008
$T = 303.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.0764	-1.0649	0.3556	-1.9542	0.0033
$\Delta\eta/\text{mPa}\cdot\text{s}$	-67.838	23.1829	0.3736	-2.8229	0.1133
Δn_D	0.2774	0.1835	-0.1642	-0.1143	0.0006
$T = 308.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-3.0206	-1.0210	0.3955	-1.9512	0.0032
$\Delta\eta/\text{mPa}\cdot\text{s}$	-49.2897	11.8289	-4.5362	10.6876	0.1051
$100\Delta n_D$	0.2648	0.1813	-0.1510	-0.1088	0.0009
$T = 313.15\text{ K}$					
$V_m^E/\text{cm}^3\cdot\text{mol}^{-1}$	-2.9529	-0.9894	0.3036	-1.7917	0.0028
$\Delta\eta/\text{mPa}\cdot\text{s}$	-36.7325	10.8221	-0.0012	-2.8065	0.1309
$100\Delta n_D$	0.2550	0.1805	-0.1549	-0.1059	0.0004

performed on a precise analytical balance (model: FA2014, SPSIC, China) with an accuracy of $1\cdot 10^{-5}\text{ g}$. The required properties were measured on the same day of the mixture. Caution was taken to prevent evaporation, and the overall experimental uncertainty in the mole fraction composition is estimated to be less than $\pm 1\cdot 10^{-4}$. The conversion to molar quantities was based on the relative atomic mass table of 2006 issued by the International Union of Pure and Applied Chemistry (IUPAC).²³

Densities, ρ , of the pure compounds and their mixtures were determined with an Anton Paar DMA4500 vibrating tube densimeter automatically thermostatted within $\pm 0.01\text{ K}$. The densimeter was calibrated with deionized double-distilled water, heptane, octane, isooctane, cyclohexane, and benzene, using ρ values from the literature.^{24,25} After each series of measurements, the densimeter should be washed by two kinds of lotions and dried.

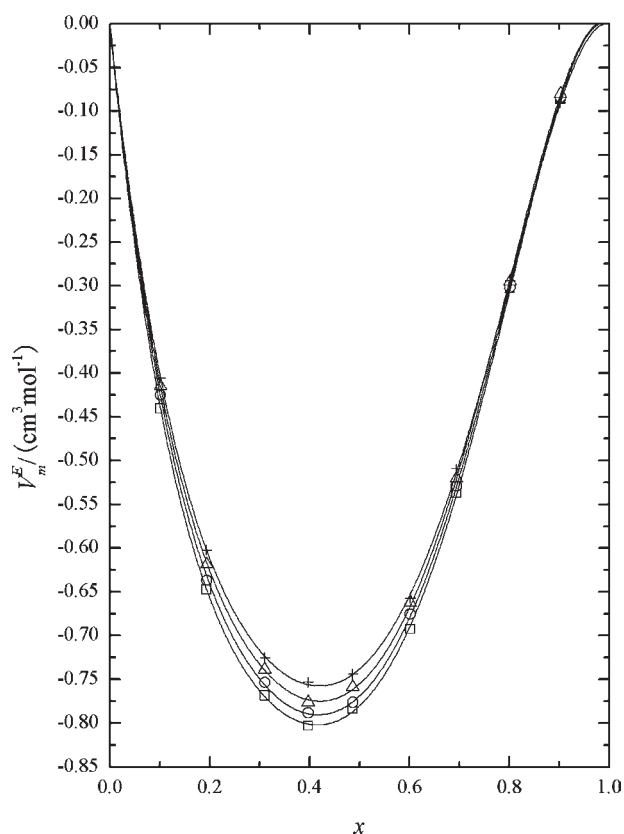


Figure 4. Excess molar volume vs mole fraction for $\{x_1[\text{bmim}][\text{Ala}] + (1 - x_1) \text{benzylalcohol}\}$ mixtures: \square , $T = 298.15 \text{ K}$; \circ , $T = 303.15 \text{ K}$; \triangle , $T = 308.15 \text{ K}$; $+$, $T = 313.15 \text{ K}$.

The experimental technique was checked by determining V_m^E of the standard mixtures: (cyclohexane + benzene) at the temperatures 293.15 K. Our results agree well with published values.²⁶ The uncertainty of our density data was estimated to be $\pm 5 \cdot 10^{-4} \text{ g} \cdot \text{cm}^{-3}$. The accuracy in V_m^E is believed to be less than $\pm (0.01 |V_{\text{max}}^E| + 0.005) \text{ cm}^3 \cdot \text{mol}^{-1}$, where $|V_{\text{max}}^E|$ denotes the maximum experimental value of the excess molar volume with respect to the mole fraction.

The viscosity was measured by an Anton Paar AMVn automated microviscosimeter (reproducibility $< 0.5 \%$, repeatability $< 0.1 \%$), which uses the rolling-ball principle. 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 $\pm 0.01 \text{ K}$. Triplicate measurements of flow times were reproducible within $\pm 0.02 \text{ s}$. The uncertainty of the viscosity measurement was estimated to be less than $\pm 0.1 \text{ mPa} \cdot \text{s}$.

Refractive indices of the mixtures at the sodium D-line were determined with an Abbe refractometer equipped with a circulating water bath permitting the sample to be maintained at constant temperature to within $\pm 0.01 \text{ K}$. The instrument was calibrated by measuring the refractive index of deionized water. The sample support was rinsed with acetone and dried with a paper towel. The uncertainty in refractive index measurements was found to be $5 \cdot 10^{-4}$.

The properties were measured three times for every sample, and the results were average values.

3. RESULTS AND DISCUSSION

The experimental values of the density, viscosity, and refractive index for binary mixtures at different temperatures and at

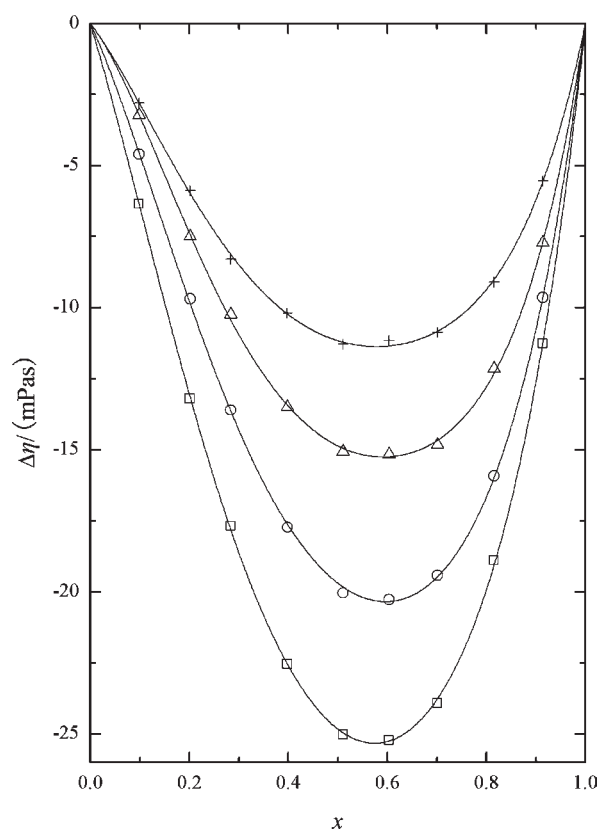


Figure 5. Viscosity deviations $\Delta\eta$ vs mole fraction for $\{x_1[\text{bmim}][\text{Ala}] + (1 - x_1) \text{methanol}\}$ mixtures: \square , $T = 298.15 \text{ K}$; \circ , $T = 303.15 \text{ K}$; \triangle , $T = 308.15 \text{ K}$; $+$, $T = 313.15 \text{ K}$.

atmospheric pressure are listed in Table 2. Excess molar volumes were calculated from our experimental data according to the following equation:

$$V_m^E = x_1 M_1 (1/\rho - 1/\rho_1) + x_2 M_2 (1/\rho - 1/\rho_2) \quad (1)$$

where x_1 and x_2 are the mole fractions of components 1 and 2, ρ_1 and ρ_2 are the densities of pure components 1 and 2, ρ is the density of the mixture, and M_1 and M_2 are the molecular weights of components 1 and 2.

The viscosity deviations were calculated from the following relation:

$$\Delta\eta = \eta - (x_1 \eta_1 + x_2 \eta_2) \quad (2)$$

where η is the viscosity of binary mixtures and η_1 and η_2 are the viscosities of components 1 and 2, respectively.

The refractive index deviations, Δn_D , at various temperatures from the linear additive values of the mole fractions were calculated by means of eq 3:

$$\Delta n_D = n_D - (x_1 n_{D1} + x_2 n_{D2}) \quad (3)$$

where n_D is the refractive index of the mixture and n_{D1} and n_{D2} are the refractive indices of components 1 and 2, respectively.

The values of V_m^E , $\Delta\eta$, and Δn_D of the studied binary mixtures, at all measured temperatures, are given in Table 2. The significant digits were determined taking into account each experimental error.

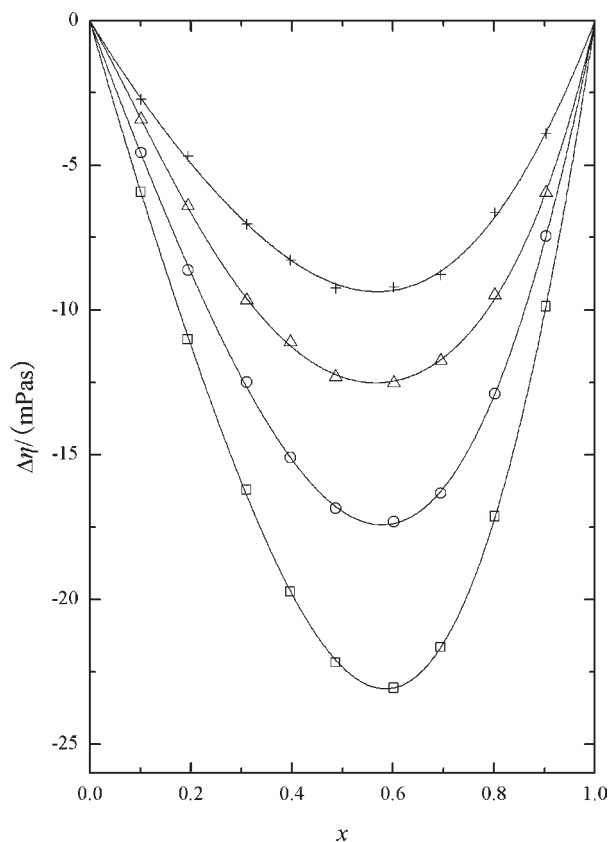


Figure 6. Viscosity deviations $\Delta\eta$ vs mole fraction for $\{x_1[\text{bmim}][\text{Ala}] + (1 - x_1) \text{benzylalcohol}\}$ mixtures: \square , $T = 298.15 \text{ K}$; \circ , $T = 303.15 \text{ K}$; \triangle , $T = 308.15 \text{ K}$; $+$, $T = 313.15 \text{ K}$.

The excess molar volume and refractive index deviations were fitted by means of a Redlich–Kister type equation²⁷ of the form:

$$Y^E = x_1(1 - x_1) \sum_{j=0}^{j=n} a_j(1 - 2x_1)^j \quad (4)$$

where Y^E represents either V_m^E , $\Delta\eta$, or Δn_D , a_j are adjustable parameters, and x_1 is the mole fraction of ($[\text{bmim}][\text{Ala}]$). The number of coefficients used for each property was determined as the minimum number needed to adequately represent the data. The standard deviation, σ , between the experimental and calculated values was defined as:

$$\sigma = \left[\sum (Y_{\text{exptl}}^E - Y_{\text{calcd}}^E)^2 / (N - p) \right]^{1/2} \quad (5)$$

where N and p are the number of direct experimental values and parameters, respectively. The values of the parameters a_j together with the standard deviation σ for each property Y^E are given in Table 3.

Excess molar volume, V_m^E , viscosity deviations, $\Delta\eta$, and refractive index deviations, Δn_D , are graphically represented in Figures 3 to 8, respectively. No data have been encountered in the literature for comparison. These plots show that the refractive index deviations are always positive, while the excess molar volumes and the viscosity deviations are mostly negative over the whole studied concentration and temperature ranges.

As can be seen in Figures 3 and 4, the V_m^E values for binary mixtures of $[\text{bmim}][\text{Ala}]$ with methanol or benzylalcohol are negative over the whole composition range, following the sequence:

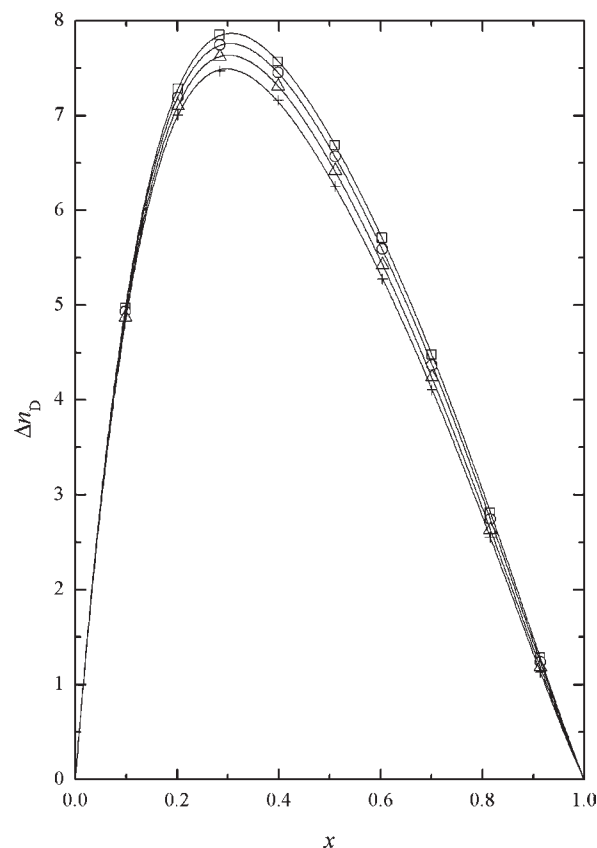


Figure 7. Refractive index deviations Δn_D vs mole fraction for $\{x_1[\text{bmim}][\text{Ala}] + (1 - x_1) \text{methanol}\}$ mixtures: \square , $T = 298.15 \text{ K}$; \circ , $T = 303.15 \text{ K}$; \triangle , $T = 308.15 \text{ K}$; $+$, $T = 313.15 \text{ K}$.

benzylalcohol > methanol, and decrease slightly with temperature. The figures are asymmetrical, and in the mole fraction of 0.3 there occurs a minimum for both of the two systems.

Excess molar volumes, which are a measure of the deviations of the actual property from the property if the system behaves ideally, give information on molecular interactions between the component molecules of the mixture and are influenced by effects such as differences in shape and size of the component molecules, reorientation of the component molecules in the mixture, and intermolecular interactions.^{28,29} It is known that V_m^E is the result of several opposing effects. Interactions between like molecules lead to increased V_m^E values, while negative contributions to V_m^E arise from interactions between unlike molecules, or structural effects as changes in free volume, or interstitial accommodation. For the investigated systems, the negative V_m^E values determined here may be due to interactions between unlike molecules. Comparing V_m^E values of ($[\text{bmim}][\text{Ala}] + \text{methanol}$) and ($[\text{bmim}][\text{Ala}] + \text{benzylalcohol}$), the V_m^E of the mixture containing methanol is smaller than that of containing benzylalcohol. This may be interpreted assuming a more efficient packing occurred for methanol than benzylalcohol. The similar phenomenon has been observed for ($[\text{bmim}][\text{BF}_4] + \text{benzaldehyde}$) by Qi et al.³⁰

The viscosity deviation represents deviations from a rectilinear dependence of viscosity on mole fraction. It can be observed from Figures 5 and 6 that $\Delta\eta$ values are all negative over the whole composition range for ($[\text{bmim}][\text{Ala}] + \text{methanol}$) and ($[\text{bmim}][\text{Ala}] + \text{benzylalcohol}$) and increase sharply with

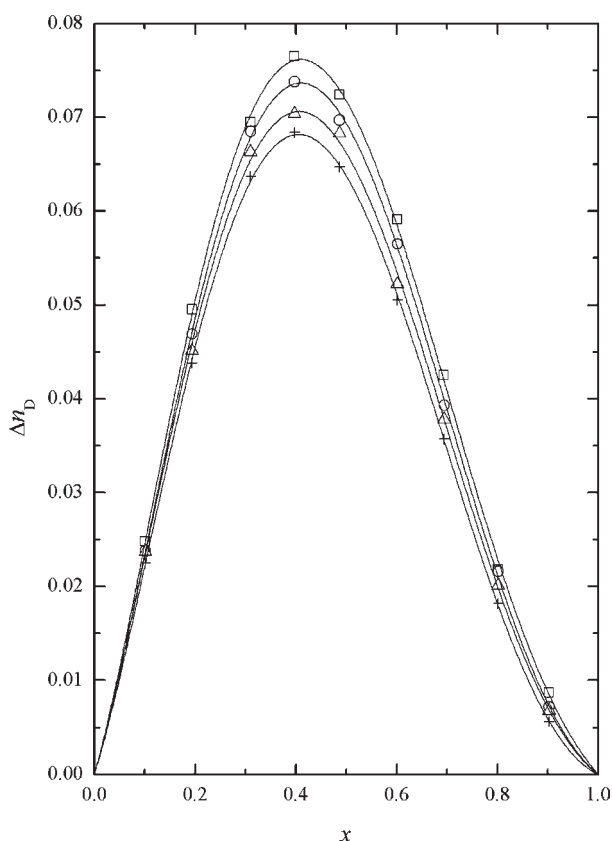


Figure 8. Refractive index deviations Δn_D vs mole fraction for $\{x_1[\text{bmim}][\text{Ala}] + (1 - x_1) \text{benzylalcohol}\}$ mixtures: \square , $T = 298.15$ K; \circ , $T = 303.15$ K; \triangle , $T = 308.15$ K; $+$, $T = 313.15$ K.

temperature. A minimum in $\Delta\eta$ is reached with the mole fraction of this IL near to 0.6 for these two systems.

The deviation of refractive indices Δn_D is positive over the whole composition range, with the maxima lying nearly at $x_1 \approx 0.4$. Figures 7 and 8 show the deviation of refractive indices Δn_D at various temperatures of the mixture of $[\text{bmim}][\text{Ala}]$ with methanol and benzylalcohol; the values increase as the temperature increases. Comparing benzylalcohol and methanol, the refractive indices of $[\text{bmim}][\text{Ala}]$ and benzylalcohol have a similarity, and the deviations of refractive indices Δn_D of $\{[\text{bmim}][\text{Ala}] + \text{benzylalcohol}\}$ are smaller than that of $\{[\text{bmim}][\text{Ala}] + \text{methanol}\}$. It means that the difference of the refractive indices between two components influence to the deviation of refractive indices Δn_D .

Comparing the minima of the excess volume, viscosity, and refractive index for each mixture, we can find that they do not coincide. The minimum of the excess molar volume is at the mole fraction of $x \approx 0.3$, while the minimum for the excess viscosity is at $x_1 \approx 0.6$, and the maximum of the excess refractive index is at $x_1 \approx 0.4$. The reason may be the structural factor of the two alcohols.

4. CONCLUSION

In the present work, the densities, viscosities, and refractive indices of two binary systems ($[\text{bmim}][\text{Ala}] + \text{methanol}$) and ($[\text{bmim}][\text{Ala}] + \text{benzylalcohol}$) have been measured experimentally over a range of temperature from (298.15 to 313.15) K and at atmospheric pressure. Excess molar volumes (V_m^E), viscosity deviations ($\Delta\eta$), and refractive index deviations (Δn_D) have

been obtained from the experiment and fitted by the fourth-order Redlich–Kister equation. The excess molar volumes and viscosity deviations were totally negative and increase with the temperature increase, and viscosity was more sensitive than V_m^E to temperature. The calculated refractive index deviations, Δn_D , for the two mixtures are all positive at all temperatures and increase when temperature increases from (298.15 to 313.15) K.

The present results add useful data on amino acid ILs to the growing database on IL properties, a database that is essential for the many applications of these liquids currently under exploration.

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