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Experimental Measurements, Correlation, and Prediction Models to Study 1-Ethyl-3-methylimidazolium Tetrafluoroborate Ionic Liquid Ternary Mixtures

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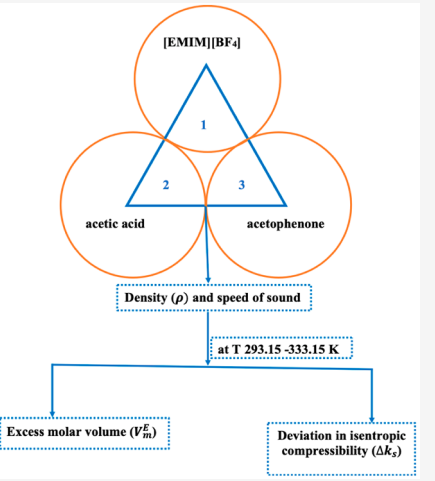
ABSTRACT: Volumetric and acoustic properties were obtained using density, ρ_{123}, and speed of sound, u_{123}, experimental values for ternary systems of {[EMIM][BF_4] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_1) and {[EMIM][BF_4] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_2) at T = (293.15−333.15) K and 0.1 MPa. The observed V^E_{m123} and Δk_{s123} data of the studied ternary mixtures were modeled with a total of 63 evaluated models, which resulted from a sum of each of nine predictive terms (no estimated parameters) with each of seven correlative terms (estimated parameters). The entire model is a correlative model, and if all of the parameters of the correlative term are set to zero, it becomes a predictive model. The ideal number of parameters in the correlation was then approximated using standard deviations (σ). For mix_1, V^E_{m123} was only negative and Δk_{s123} was only positive, while for mix_2 both negative and positive results were found for each property. Also, quantitative results point out that mix_1 is closer to ideal behavior than mix_2. The modeling for mix_2 employed more complex equations, with more parameters, and even so presented worse deviations than for mix_1. These results evidence the effect of one CH_2 in the acid chain on the thermodynamic properties of these mixtures.



1. INTRODUCTION

Ionic liquids (ILs) are typically classified as a family of salts with low asymmetry/symmetry bulky organic cations and organic or inorganic anions that are liquids below 100 °C.[1−3] Due to their remarkable physicochemical characteristics, such as excellent thermal and chemical stability, low volatility, good electrical conductivity, and low flammability, these salts have attracted a lot of attention in a variety of sectors of chemistry and electrochemistry.[4−9] The most desirable quality of these is their adaptability to specific requirements for a variety of applications. This is accomplished by adding the proper cosolvent to the IL or by changing the cationic or anionic component of the IL. To employ ILs as solvents, one must be aware of how they react with other substances, such as water and conventional solvents used in extraction and separation processes, including alcohols or carboxylic acids.[10,11]

ILs, which were initially investigated for their thermophysical and thermodynamic properties, are today believed to have applications in a wide range of areas, including materials science, cell engineering, lunar mirrors, and so on.[12] The thermodynamic properties of IL ternary mixtures are not well-understood despite a large amount of research on the thermodynamic properties of ILs and their binary mixtures with organic solvents. Understanding the IL mixture structural features and intermolecular interactions (such as cosolvent, solute−solute, and solute−solvent) that occur among the ions of ILs and solvent molecules, especially where hydrogen bonding occurs, is critical.[13,14]

In our previous work,[15] we carried out an investigation on the excess molar volume and deviation in isentropic compressibility of ternary mixtures consisting of 1-butyl-3-methylimidazolium tetrafluoroborate or 1-butyl-3-methylimidazolium hexafluorophosphate with acetophenone and acetic acid or propionic acid. The subject of the present research is to extend our investigation to ternary mixtures consisting of 1-ethyl-3-methylimidazolium tetrafluoroborate [EMIM][BF_4], acetophenone, and acetic acid or propionic acid, where we report their densities, ρ_{123}, speeds of sound, u_{123}, excess molar volumes, V^E_{m123}, and deviations in isentropic compressibility,

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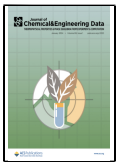

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J. Chem. Eng. Data 2024, 69, 25−37

Table 1. Specifications of the Pure Chemicals

chemical name	molecular weight/ g·mol^{-1}	CAS number	provenance	water content/ ppm[a]	mass-fraction purity[b]	purification method	mass-fraction purity[c]
[EMIM][BF_4]	197.97	143314-16-3	IoLiTec	≤400	>0.97	none	–
acetic acid	60.05	64-19-7	Sigma-Aldrich Pty Ltd.	≤300	≥0.99	none	≥0.99
propionic acid	74.08	79-09-4	Sigma-Aldrich Pty Ltd.	≤200	≥0.995	none	≥0.995
acetophenone	120.15	98-86-2	Sigma-Aldrich Pty Ltd.	≤400	>0.99	none	>0.98

[a]The water contents of the pure chemicals were measured using a Karl Fisher coulometer (756 KF coulometer, Metrohm, South Africa). [b]Stated by the supplier. [c]GC analysis.

Table 2. Comparison between Experimental and Literature Data for ρ and u of Pure [EMIM][BF_4], Acetic Acid, Propionic Acid, and Acetophenone Used in the Current Study at Different Temperatures and Pressure p = 0.1 MPa

		ρ/(g·cm^{-3})		u/m·s^{-1}	
component	T/K	expt	lit	expt	lit
[EMIM][BF_4]	293.15	1.283	1.283[34]	1642	1631[37]
			1.288[35]		1632[38]
			1.286[36]		1640[36]
	303.15	1.275	1.276[34]	1618	1608[37]
			1.279[35]		1609[38]
			1.278[36]		1616[36]
	313.15	1.267	1.268[34]	1595	1586[38]
			1.271[35]		1593[36]
			1.271[36]		
	323.15	1.260	1.261[34]	1572	1563[38]
			1.264[35]		1571[36]
			1.263[36]		
	333.15	1.253	1.253[34]	1550	1548[36]
			1.257[35]		
			1.256[36]		
acetic acid	293.15	1.056	1.049[39]	1158	1152[43]
			1.049[40]		1168[44]
			1.049[41]		1159[45]
			1.049[42]		
	303.15	1.048	1.038[39]	1124	1118[43]
			1.038[40]		1135[44]
			1.027[41]		1126[45]
			1.040[42]		
	313.15	1.035	1.027[40]	1092	1084[43]
			1.038[41]		1101[44]
			1.030[42]		1095[45]
	323.15	1.025	1.015[39]	1061	–
			1.015[40]		
			1.018[41]		
			1.021[42]		
	333.15	1.007	1.004[39]	1033	–
			1.004[40]		
propionic acid	293.15	0.998	0.994[40]	1171	1165[43]
			0.993[41]		1171[44]
			0.992[42]		1166[45]
			0.993[46]		
	303.15	0.988	0.984[40]	1134	1127[43]
			0.982[41]		1134[44]
			0.983[42]		1130[45]
			0.982[46]		
	313.15	0.977	0.972[40]	1097	1090[43]
			0.971[41]		1097[44]
			0.973[42]		1093[45]
			0.972[46]		
	323.15	0.966	0.961[40]	1060	–
			0.960[41]		
			0.964[42]		
			0.961[46]		
	333.15	0.955	0.950[40]	1025	–
acetophenone	293.15	1.028	1.028[47]	1497	–
			1.028[48]		
			1.028[49]		
	303.15	1.019	1.019[50]	1460	1452[50]
			1.011[51]		1422[51]
			1.020[52]		1462[53]
			1.020[53]		1460[54]
			1.020[54]		1452[63]
			1.019[63]		
			1.020[64]		
	313.15	1.010	1.011[47]	1423	1424[50]
			1.011[50]		1436[53]
			1.011[52]		1438[54]
			1.011[53]		1422[63]
			1.011[53]		
			1.011[63]		
			1.014[64]		
	323.15	1.002	0.999[51]	1387	1385[51]
			0.999[52]		
			0.999[53]		
			0.999[54]		
	333.15		0.995[47]	1352	–

Δk_{s123}, over the temperature range (293.15−333.15) K at 0.1 MPa.

A review of the literature revealed that thermodynamic properties of ternary mixtures containing the IL [EMIM]-[BF_4] with various organic solvents have been explored at varying temperatures by a number of researchers.[16−29] There have been no data published on the thermodynamic properties of the currently explored ternary mixtures. As a result, the originality of the current study is emphasized.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The details of purchase and purities of chemicals utilized are given in Table 1. Highly pure analytical grade samples of acetic acid, propionic acid, and acetophenone were collected from Sigma-Aldrich (Pty) Ltd. The IL

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J. Chem. Eng. Data 2024, 69, 25−37

Table 3. Predictive Terms Tested in This Work

model	$Y_{123}^{predictive}$
1. Redlich–Kister[55]	$Y_{12}(x_1, x_2) + Y_{13}(x_1, x_3) + Y_{23}(x_2, x_3)$
2. Tao-Smith[55]	$\frac{x_2}{1-x_1}Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1}Y_{13}(x_1, 1-x_1) + (1-x_1)Y_{23}(x_2', x_3')$
3. Kohler[55]	$(x_1 + x_2)^2 Y_{12}(x_1', x_2') + (x_1 + x_3)^2 Y_{13}(x_1', x_3') + (x_2 + x_3)^2 Y_{23}(x_2', x_3')$
4. Colinet[55]	$\frac{1}{2}\left[\frac{x_2}{1-x_1}Y_{12}(x_1, 1-x_1) + \frac{x_1}{1-x_2}Y_{12}(1-x_2, x_2) + \frac{x_3}{1-x_1}Y_{13}(x_1, 1-x_1) + \frac{x_1}{1-x_3}Y_{13}(1-x_3, x_3) + \frac{x_3}{1-x_2}Y_{23}(x_2, 1-x_2) + \frac{x_2}{1-x_3}Y_{23}(1-x_3, x_3)\right]$ $x_2 1-x_3 Y_{23}(1-x_3, x_3)]$
5. Scatchard et al.[55]	$\frac{x_2}{1-x_1}Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1}Y_{13}(x_1, 1-x_1) + Y_{23}(x_2, x_3)$
6. Toop[55]	$\frac{x_2}{1-x_1}Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1}Y_{13}(x_1, 1-x_1) + (1-x_1)^2 Y_{23}(x_2', x_3')$
7. Muggianu et al.	$\frac{x_1x_2}{\chi_1^{12}\chi_2^{12}}Y_{12}(\chi_1^{12}, \chi_2^{12}) + \frac{x_1x_3}{\chi_1^{13}\chi_3^{13}}Y_{13}(\chi_1^{13}, \chi_3^{13}) + \frac{x_2x_3}{\chi_2^{23}\chi_3^{23}}Y_{23}(\chi_2^{23}, \chi_3^{23})$, where $\chi_i^{ij} = (1 + x_i - x_j)/2$
8. Hiller[55]	$\frac{x_2}{1-x_1}Y_{12}(x_1, 1-x_1) + \frac{x_3}{1-x_1}Y_{13}(x_1, 1-x_1) + \frac{x_2x_3}{\chi_2^{23}\chi_3^{23}}Y_{23}(\chi_2^{23}, \chi_3^{23})Y_{23}(\chi_2^{23}, \chi_3^{23})$, where $\chi_i^{ij} = (1 + x_i - x_j)/2$
9. "average"[56]	$[(x_1 + x_2)Y_{12}' + (x_2 + x_3)Y_{23}' + (x_1 + x_3)Y_{13}']/2$

Table 4. Correlative Terms Tested in This Work

model	$Y_{123}^{correlative}$	ref[a]
1. Cibulka	$x_1x_2x_3[A_0 + A_1x_1 + A_2x_2]$	57, tw
2. 1p-Cibulka	$x_1x_2x_3A_0$	57
3. Rastogi et al.	$x_1x_2x_3[A_0 + A_1x_1(x_2 - x_3) + A_2x_1^2(x_2 - x_3)^2]$	56
4. 5p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2]$	58, tw
5. 7p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2 + A_5(x_2 - x_1)^3 + A_6(x_3 - x_2)^3]$	tw
6. 9p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2 + A_5(x_2 - x_1)^3 + A_6(x_3 - x_2)^3 + A_7(x_2 - x_1)^4 + A_8(x_3 - x_2)^4]$	tw
7. 11p-model	$x_1x_2x_3[A_0 + A_1(x_2 - x_1) + A_2(x_3 - x_2) + A_3(x_2 - x_1)^2 + A_4(x_3 - x_2)^2 + A_5(x_2 - x_1)^3 + A_6(x_3 - x_2)^3 + A_7(x_2 - x_1)^4 + A_8(x_3 - x_2)^4 + A_9(x_2 - x_1)^5 + A_{10}(x_3 - x_2)^5]$	tw

[a]tw stands for this work.

[EMIM][BF_4] was supplied by IoLiTec. The purities of the organic solvents were tested by gas chromatography (GC), and the mass-fraction purities of all the chemicals were >97.0. A Karl Fisher coulometer (756 KF coulometer, Metrohm, South Africa) was used to determine the water content of the pure chemicals prior to preparing the sample mixtures, and a water content of roughly 0.06% was obtained. All the chemicals were used as supplied, without any further purification.

We conducted comparative studies between experimental densities and speeds of sound of the currently investigated IL, carboxylic acids, and acetophenone in prior publications,[30−33] so they are not repeated here.

2.2. Apparatus and Procedure. In order to prepare the ternary mixtures, the necessary quantities of the pure chemicals were weighed using a weighing balance with a precision of 0.0004 g. The required amounts of pure components were weighed out using a disposable syringe into airtight 10 cm^3 glass vials for forming the ternary mixtures. The uncertainty in the mole fraction of the mixtures was around 0.0008.

A digital vibrating-tube densitometer and speed of sound analyzer (DSA 5000M, Anton-Paar) was used to determine the densities and speeds of sound automatically and simultaneously. The speeds of sound were determined by employing a propagation time technique with frequency around 3 MHz. The temperature regulator (integrated Pt-100 platinum thermometers together with Peltier elements) in the Anton-Paar digital vibrating-tube densitometer and speed of sound analyzer (DSA 5000M) kept the samples within a predetermined temperature with an uncertainty of 0.02 K. The equipment was automatically cleaned with ethanol, water, and dry air before each measurement. This process was repeated until all of the dissolved residue in the measuring cells had been removed.

Prior to performing the actual measurements, the instrument was calibrated using a certified standard liquid that was obtained from the manufacturer. After a series of measurements were made of the sample mixtures, density and sound

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J. Chem. Eng. Data 2024, 69, 25−37

Table 5. Mole Fractions (x_1, x_2, x_3), Densities, ρ_{123}, and Speeds of Sound, u_{123}, for the Ternary Mixtures {[EMIM][BF_4] (x_1) + Acetic Acid (x_1) + Acetophenone (x_1)} over the Temperature Range (293.15−333.15) K at Atmospheric Pressure (0.1 MPa)[a]

x_1	x_2	x_3	ρ/g·cm^{-3}	u/m·s^{-1}
		T = 293.15 K		
0.2688	0.5254	0.2058	1.155	1500
0.3724	0.3465	0.2812	1.169	1527
0.4331	0.2400	0.3269	1.184	1559
0.1291	0.8333	0.0376	1.127	1338
0.3097	0.5997	0.0906	1.179	1476
0.4363	0.4327	0.1310	1.188	1536
0.5060	0.3507	0.1433	1.212	1563
0.5856	0.2451	0.1693	1.195	1578
0.6819	0.1224	0.1956	1.230	1606
0.4120	0.5490	0.0390	1.205	1507
0.5680	0.3683	0.0637	1.230	–
0.6780	0.2570	0.0651	–	–
0.7909	0.1349	0.0741	1.256	–
0.8563	0.0599	0.0837	1.261	1625
0.0372	0.6556	0.3072	–	–
0.0493	0.5433	0.4074	1.065	1361
0.0616	0.4317	0.5067	1.068	–
0.0737	0.3223	0.6039	1.069	–
0.0841	0.2230	0.6928	1.069	1484
0.0967	0.1069	0.7964	1.070	1505
0.1083	0.7056	0.1861	1.105	1373
0.1935	0.4767	0.3297	1.126	1466
0.2283	0.3815	0.3902	1.103	1468
0.2947	0.2073	0.4980	1.142	1535
		T = 303.15 K		
0.2688	0.5254	0.2058	1.147	–
0.3724	0.3465	0.2812	1.161	1498
0.4331	0.2400	0.3269	1.176	1532
0.1291	0.8333	0.0376	1.117	1307
0.3097	0.5997	0.0906	1.171	1448
0.4363	0.4327	0.1310	1.180	1509
0.5060	0.3507	0.1433	1.204	1537
0.5856	0.2451	0.1693	1.186	1552
0.6819	0.1224	0.1956	1.222	1581
0.4120	0.5490	0.0390	1.196	1480
0.5680	0.3683	0.0637	1.222	–
0.6780	0.2570	0.0651	–	–
0.7909	0.1349	0.0741	1.248	–
0.8563	0.0599	0.0837	1.253	1601
0.0372	0.6556	0.3072	1.053	–
0.0493	0.5433	0.4074	1.056	–
0.0616	0.4317	0.5067	1.059	1404
0.0737	0.3223	0.6039	1.059	1428
0.0841	0.2230	0.6928	1.060	1449
0.0967	0.1069	0.7964	1.061	1471
0.1083	0.7056	0.1861	1.095	1340
0.1935	0.4767	0.3297	1.117	1435
0.2283	0.3815	0.3902	1.094	1435
0.2947	0.2073	0.4980	1.134	1504
		T = 313.15 K		
0.2688	0.5254	0.2058	1.138	–
0.3724	0.3465	0.2812	1.152	1470
0.4331	0.2400	0.3269	1.168	1504
0.1291	0.8333	0.0376	1.107	1276
0.3097	0.5997	0.0906	1.162	1421
0.4363	0.4327	0.1310	1.171	1481
0.5060	0.3507	0.1433	1.196	1511
0.5856	0.2451	0.1693	1.177	1527
0.6819	0.1224	0.1956	1.215	1556
0.4120	0.5490	0.0390	1.187	1454
0.5680	0.3683	0.0637	1.214	–
0.6780	0.2570	0.0651	–	–
0.7909	0.1349	0.0741	1.24	–
0.8563	0.0599	0.0837	1.245	1577
0.0372	0.6556	0.3072	1.044	–
0.0493	0.5433	0.4074	1.046	–
0.0616	0.4317	0.5067	1.050	1370
0.0737	0.3223	0.6039	1.051	1393
0.0841	0.2230	0.6928	1.052	1415
0.0967	0.1069	0.7964	1.053	1436
0.1083	0.7056	0.1861	1.085	1308
0.1935	0.4767	0.3297	1.109	1404
0.2283	0.3815	0.3902	1.086	1403
0.2947	0.2073	0.4980	1.125	1474
		T = 323.15 K		
0.2688	0.5254	0.2058	1.130	–
0.3724	0.3465	0.2812	1.143	1442
0.4331	0.2400	0.3269	1.160	1477
0.1291	0.8333	0.0376	1.098	1247
0.3097	0.5997	0.0906	1.153	1394
0.4363	0.4327	0.1310	1.163	1455
0.5060	0.3507	0.1433	1.188	1486
0.5856	0.2451	0.1693	1.167	1502
0.6819	0.1224	0.1956	1.207	1531
0.4120	0.5490	0.0390	1.179	1429
0.5680	0.3683	0.0637	1.206	–
0.6780	0.2570	0.0651	–	–
0.7909	0.1349	0.0741	–	–
0.8563	0.0599	0.0837	1.237	1553
0.0372	0.6556	0.3072	1.035	–
0.0493	0.5433	0.4074	1.036	–
0.0616	0.4317	0.5067	1.042	1336
0.0737	0.3223	0.6039	1.043	1360
0.0841	0.223	0.6928	1.044	1381
0.0967	0.1069	0.7964	1.045	1402
0.1083	0.7056	0.1861	1.076	1276
0.1935	0.4767	0.3297	1.100	1373
0.2283	0.3815	0.3902	1.077	1372
0.2947	0.2073	0.498	1.117	1444
		T = 333.15 K		
0.2688	0.5254	0.2058	1.121	1385
0.3724	0.3465	0.2812	1.135	1414
0.4331	0.2400	0.3269	1.152	1450
0.1291	0.8333	0.0376	1.089	1218
0.3097	0.5997	0.0906	1.145	1368
0.4363	0.4327	0.1310	1.155	1429
0.5060	0.3507	0.1433	1.180	1461
0.5856	0.2451	0.1693	1.159	1478
0.6819	0.1224	0.1956	1.199	1507
0.4120	0.5490	0.0390	–	–
0.5680	0.3683	0.0637	–	–
0.6780	0.2570	0.0651	–	–
0.7909	0.1349	0.0741	1.224	–
0.8563	0.0599	0.0837	1.229	1530
0.0372	0.6556	0.3072	1.025	–
0.0493	0.5433	0.4074	1.027	1224
0.0616	0.4317	0.5067	1.032	–
0.0737	0.3223	0.6039	1.033	–

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J. Chem. Eng. Data 2024, 69, 25−37

Table 5. continued

x_1	x_2	x_3	ρ/g·cm^{-3}	u/m·s^{-1}
		T = 333.15 K		
0.0841	0.2230	0.6928	1.034	1348
0.0967	0.1069	0.7964	1.036	1369
0.1083	0.7056	0.1861	1.067	1245
0.1935	0.4767	0.3297	1.091	1344
0.2283	0.3815	0.3902	1.068	1341
0.2947	0.2073	0.498	1.107	1415

[a]The standard uncertainties u are $u(T)$ = 0.02 K and $u(p)$ = 0.04 MPa, and the combined expanded uncertainties are $U_c(x)$ = 0.0008, $U_c(\rho)$ = 0. 011 g·cm^{-3}, and $U_c(u)$ = 3 m·s^{-1} (0.95 level of confidence).

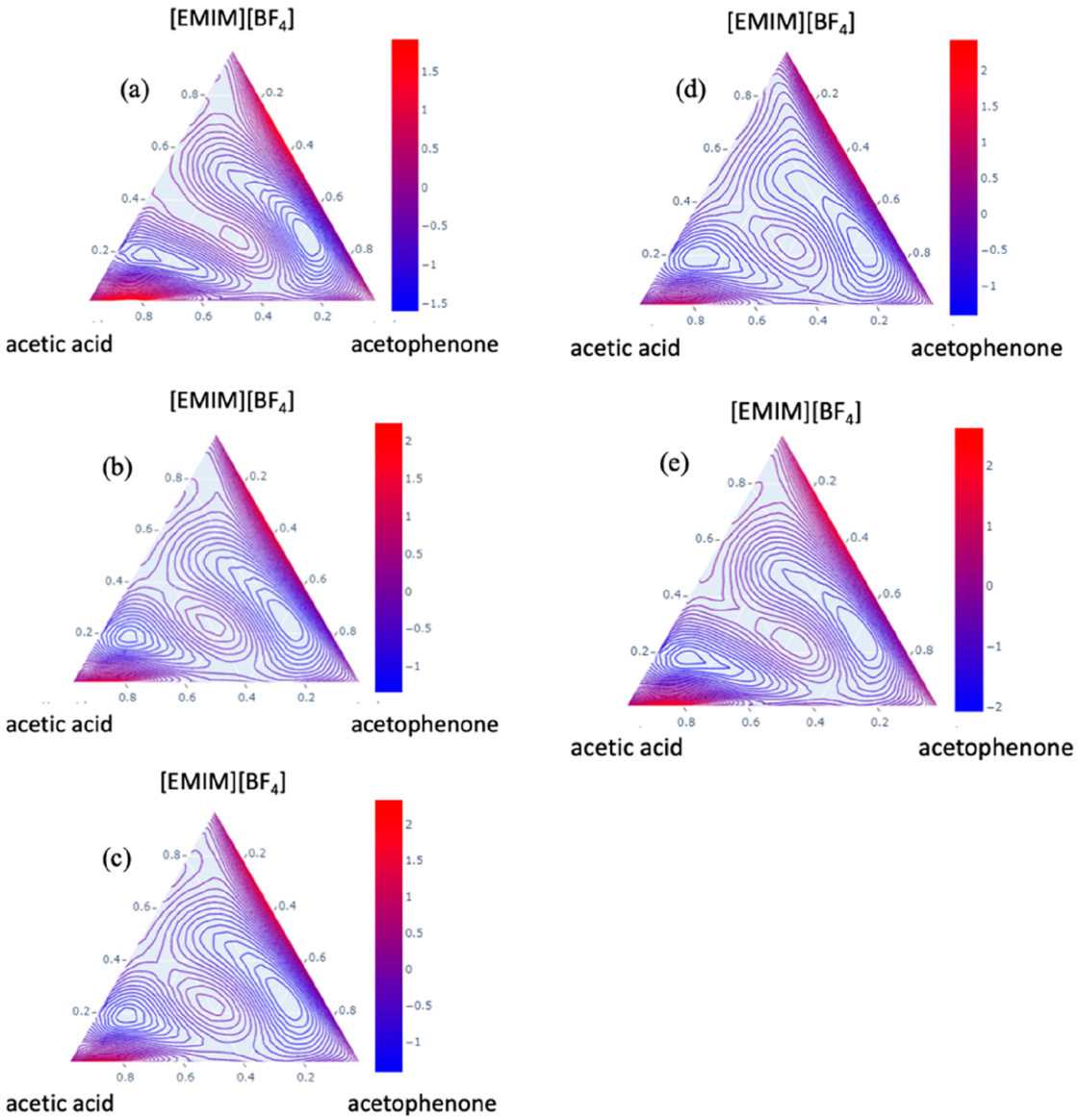

Figure 1. Plot of excess molar volume (V^E_{m123}) as a function IL mole fraction (x_1) for ternary mixtures {[EMIM][BF$_4$] (x_1) + acetic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K, and (e) 333.15 K.

speed measurements of pure water were performed to verify the precision of the ρ and u measurements.

The purities of all the pure compounds were assessed by comparing our previously measured densities and speeds of sound with those reported in the literature,[34−54] and the results are displayed in Table 2. Table 2 demonstrates that the ρ and u values have a slight variance that falls within the experimental error. Different experimental methods and/or tools as well as varying levels of sample purity could be responsible for the observed variance. The combined expanded uncertainties in the densities, ρ_{123}, speeds of sound, u_{123}, excess molar volumes, V^E_{m123}, and deviations in isentropic compressibility, Δk_{s123}, are 0.011 g·cm^{-3}, 3 m·s^{-1}, 0.185 cm^3·mol^{-1}, and 3.5 × 10^3 TPa^{-1}, respectively. The measurements were determined over the temperature range (293.15−333.15) K.

2.3. Modeling. Equation 1 illustrates how the V^E_{m123} and Δk_{s123} properties for the ternary mixtures were modeled

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J. Chem. Eng. Data 2024, 69, 25−37

Table 6. Mole Fractions (x_1, x_2, x_3), Densities, ρ_{123}, and Speeds of Sound, u_{123}, for the Ternary Mixtures {[EMIM][BF_4] (x_1) + Propionic Acid (x_2) + Acetophenone (x_3)} over the Temperature Range (293.15−333.15) K at Atmospheric Pressure (0.1 MPa)[a]

x_1	x_2	x_3	ρ/g·cm^{-3}	u/m·s^{-1}
		T = 293.15 K		
0.2990	0.4743	0.2266	1.139	1463
0.4019	0.2944	0.3037	1.160	1521
0.4526	0.2054	0.3420	1.173	1550
0.1544	0.8013	0.0444	1.034	1486
0.3490	0.5490	0.1020	1.158	1460
0.4789	0.3764	0.1447	1.189	1526
0.5425	0.3044	0.1531	1.203	1552
0.6131	0.2090	0.1779	1.211	1574
0.7004	0.1012	0.1984	1.231	1604
0.4614	0.4952	0.0434	1.189	1495
0.6254	0.3154	0.0593	1.228	1542
0.713	0.2195	0.0675	1.236	1587
0.8131	0.1110	0.0759	–	–
0.8711	0.0440	0.0850	1.312	1624
0.0507	0.5344	0.4149	1.044	1384
0.0554	0.4904	0.4542	–	–
0.0672	0.3810	0.5517	1.054	–
0.0782	0.2786	0.6432	1.058	1462
0.0880	0.1881	0.7239	1.064	–
0.0989	0.0889	0.8122	1.042	1484
0.1252	0.6615	0.2132	1.050	1416
0.2122	0.4258	0.3619	1.110	1457
0.2477	0.3314	0.4210	1.120	1489
0.3054	0.1743	0.5203	1.136	1536
		T = 303.15 K		
0.2990	0.4743	0.2266	1.131	1434
0.4019	0.2944	0.3037	1.152	1492
0.4526	0.2054	0.3420	1.165	1522
0.1544	0.8013	0.0444	1.028	1451
0.3490	0.5490	0.1020	1.148	1433
0.4789	0.3764	0.1447	1.180	1499
0.5425	0.3044	0.1531	1.195	1526
0.6131	0.2090	0.1779	1.203	1547
0.7004	0.1012	0.1984	1.223	1578
0.4614	0.4952	0.0434	1.181	1465
0.6254	0.3154	0.0593	1.211	1517
0.7130	0.2195	0.0675	1.228	1562
0.8131	0.1110	0.0759	–	–
0.8711	0.0440	0.0850	1.304	1600
0.0507	0.5344	0.4149	1.035	1349
0.0554	0.4904	0.4542	1.038	1365
0.0672	0.3810	0.5517	1.045	1399
0.0782	0.2786	0.6432	1.049	1427
0.0880	0.1881	0.7239	1.055	1450
0.0989	0.0889	0.8122	1.033	1449
0.1252	0.6615	0.2132	1.044	1386
0.2122	0.4258	0.3619	1.101	1426
0.2477	0.3314	0.4210	1.111	1459
0.3054	0.1743	0.5203	1.127	1505
		T = 313.15 K		
0.2990	0.4743	0.2266	1.122	1405
0.4019	0.2944	0.3037	1.143	1464
0.4526	0.2054	0.3420	1.157	1494
0.1544	0.8013	0.0444	1.021	1436
0.3490	0.5490	0.1020	1.136	1397
0.4789	0.3764	0.1447	1.172	1473
0.5425	0.3044	0.1531	1.187	1500
0.6131	0.2090	0.1779	1.196	–
0.7004	0.1012	0.1984	1.215	1553
0.4614	0.4952	0.0434	1.172	1433
0.6254	0.3154	0.0593	1.206	1490
0.7130	0.2195	0.0675	1.220	1538
0.8131	0.1110	0.0759	–	–
0.8711	0.0440	0.0850	1.296	1576
0.0507	0.5344	0.4149	1.026	1314
0.0554	0.4904	0.4542	1.029	1330
0.0672	0.3810	0.5517	1.036	–
0.0782	0.2786	0.6432	1.040	1392
0.0880	0.1881	0.7239	1.046	–
0.0989	0.0889	0.8122	1.025	1413
0.1252	0.6615	0.2132	1.037	1353
0.2122	0.4258	0.3619	1.093	1395
0.2477	0.3314	0.4210	1.103	1428
0.3054	0.1743	0.5203	1.119	1475
		T = 323.15 K		
0.2990	0.4743	0.2266	1.114	1378
0.4019	0.2944	0.3037	1.135	1436
0.4526	0.2054	0.3420	1.149	1467
0.1544	0.8013	0.0444	1.014	1417
0.3490	0.5490	0.1020	1.126	1368
0.4789	0.3764	0.1447	1.164	1447
0.5425	0.3044	0.1531	1.179	1474
0.6131	0.2090	0.1779	1.187	1496
0.7004	0.1012	0.1984	1.208	1528
0.4614	0.4952	0.0434	1.161	–
0.6254	0.3154	0.0593	1.196	1464
0.7130	0.2195	0.0675	1.212	1514
0.8131	0.1110	0.0759	–	–
0.8711	0.0440	0.0850	1.288	1553
0.0507	0.5344	0.4149	1.017	1279
0.0554	0.4904	0.4542	1.020	1296
0.0672	0.3810	0.5517	1.027	1330
0.0782	0.2786	0.6432	1.032	1358
0.0880	0.1881	0.7239	1.038	1382
0.0989	0.0889	0.8122	1.016	1378
0.1252	0.6615	0.2132	1.027	1320
0.2122	0.4258	0.3619	1.084	1365
0.2477	0.3314	0.4210	1.095	1398
0.3054	0.1743	0.5203	1.111	1445
		T = 333.15 K		
0.2990	0.4743	0.2266	1.106	1351
0.4019	0.2944	0.3037	1.127	1409
0.4526	0.2054	0.3420	1.141	1440
0.1544	0.8013	0.0444	1.006	1385
0.3490	0.5490	0.1020	1.115	1342
0.4789	0.3764	0.1447	1.156	1422
0.5425	0.3044	0.1531	1.171	1449
0.6131	0.2090	0.1779	1.179	1471
0.7004	0.1012	0.1984	1.200	1504
0.4614	0.4952	0.0434	1.149	1364
0.6254	0.3154	0.0593	1.185	1439
0.7130	0.2195	0.0675	1.204	–
0.8131	0.1110	0.0759	–	–
0.8711	0.0440	0.0850	1.280	1530
0.0507	0.5344	0.4149	1.008	1245
0.0554	0.4904	0.4542	1.011	1262

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J. Chem. Eng. Data 2024, 69, 25−37

Table 6. continued

x_1	x_2	x_3	ρ/g·cm^{-3}	u/m·s^{-1}
		T = 333.15 K		
0.0672	0.3810	0.5517	1.019	–
0.0782	0.2786	0.6432	1.023	1325
0.0880	0.1881	0.7239	1.029	1349
0.0989	0.0889	0.8122	1.007	1343
0.1252	0.6615	0.2132	1.017	1287
0.2122	0.4258	0.3619	1.076	1336
0.2477	0.3314	0.421	1.086	1369
0.3054	0.1743	0.5203	1.103	1416

[a]The standard uncertainties u are $u(T)$ = 0.02 K and $u(p)$ = 0.04 MPa, and the combined expanded uncertainties are $U_c(x)$ = 0.0008, $U_c(\rho)$ = 0.011 g·cm^{-3}, and $U_c(u)$ = 3 m·s^{-1} (0.95 level of confidence).

Table 7. Parameters for the Ternary Mixtures {[EMIM][BF$_4$] (x_1) + Acetic acid (x_2) + Acetophenone (x_3)}: For V^E_{m123}, the Model Is Predictive 5 (Scatchard) + Correlative 7 (11p-model); For Δk_{s123}, the Model Is Predictive 1 (Redlich−Kister) + Correlative 7 (11p-model)[a]

$Y_{123} = V^E_{m123}$, Parameters in cm^3·mol^{-1}												
T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	−13.1	167	69.6	−338	−151	−769	−443	757	−93	1971	1094	0.08
303.15	−20.1	182	56.6	−189	−169	−631	−84	346	−41	1701	504	0.13
313.15	−20.6	188	59.3	−197	−184	−606	−74	373	−31	1669	503	0.14
323.15	−24.0	166	78.9	−215	−172	−402	−210	339	−31	1526	716	0.32
333.15	−21.3	214	92.8	−421	−152	−964	−460	822	−134	2430	1287	0.20
$Y_{123} = \Delta k_{s123}$, Parameters in 10^5·TPa^{-1}												
T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	−10.7	7.83	−63.0	−50.9	159	−308	276	145	−208	885	−362	0.32
303.15	−11.3	−25.8	−52.4	120	95.4	238	355	−186	−79.6	−179	−521	0.12
313.15	−9.57	−31.9	−49.5	128	83.9	268	350	−214	−50.1	−301	−524	0.11
323.15	−8.11	−36.4	−47.2	135	82.2	293	342	−236	−36.7	−393	−514	0.11
333.15	−7.47	−20.1	−23.2	−6.11	99.5	0	0	0	0	0	0	0.28

[a]For Δk_{s123} with parameters A_7 to A_{10} equal to 0, the model is equivalent to 9 ("average") + 5 (7p-model); with parameters A_5 and A_{10} equal to 0, the model is equivalent to 1 (Redlich−Kister) + 4 (5p-model).

Table 8. Parameters for the Ternary Mixtures {[EMIM][BF$_4$] (x_1) + Propionic Acid (x_2) + Acetophenone (x_3)}: For V^E_{m123} and k_{s123}, the Model is Predictive 3 (Kohler) + Correlative 7 (11p-model)

$Y_{123} = V^E_{m123}$, Parameters in cm^3·mol^{-1}												
T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	26.6	391	224	−1790	−303	−5757	−2395	5443	394	17750	5386	0.26
303.15	1.53	347	101	−1133	−248	−5068	−1226	3320	701	15825	3358	0.25
313.15	11.0	386	171	−1184	−254	−4997	−2218	3113	874	15247	4722	0.39
323.15	−29.2	320	129	−297	88.9	−3816	−2441	−112	842	11194	4748	0.62
333.15	−36.3	153	179	488	−10.8	−765	−3195	−4412	2196	4072	4603	0.44
$Y_{123} = \Delta k_{s123}$, Parameters in 10^5·TPa^{-1}												
T/K	A_0	A_1	A_2	A_3	A_4	A_5	A_6	A_7	A_8	A_9	A_{10}	σ
293.15	−5.68	−19.8	−51.9	−468	−173	−473	871	2171	858	3350	−2317	0.22
303.15	−4.35	−34.1	−42.3	−345	−211	−250	723	1767	942	2580	−2151	0.21
313.15	−3.04	−40.0	−65.6	−360	−170	−337	1026	1885	773	2787	−2473	0.19
323.15	−4.85	−39.3	−64.5	56.9	−363.7	47.6	1227	−430	1570	−96.4	−3544	0.35
333.15	−6.73	−35.1	−36.9	85.5	−256.9	−57.8	840	−654	1238	−41.6	−2696	0.29

utilizing the sum of a predictive term (no estimated parameters) and a correlative term (estimated parameters):

$$Y_{123} = Y_{123}^{\text{predictive}} + Y_{123}^{\text{correlative}} \quad (1)$$

where Y is the property being modeled. The entire model is correlative; however, when the correlative parameters become zeroed, it turns into a predictive model.

Table 3 and Table 4 display the predictive terms and correlative terms that were investigated.[55−58] All of the correlative models and predictive models were tested together, which resulted in a total of 63 options of models (from a sum of each of nine predictive terms (no estimated parameters) with each of seven correlative terms (estimated parameters)). The procedure followed in selecting the best model for each property at each temperature for each mixture involved is provided in our previous publication.[15]

Moreover, the standard deviation was evaluated using eq 5:

$$\sigma = \sqrt{\sum_{i=1}^{N_{\text{exp}}} \frac{(Y_i^{\text{calc}} - Y_i^{\text{exp}})^2}{N_{\text{exp}} - N_{\text{par}}}} \quad (5)$$

where Y is the property being modeled, N_{exp} defines the quantity of experimental data, and N_{par} defines the quantity of estimated parameters. As this measure takes into account the

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J. Chem. Eng. Data 2024, 69, 25−37

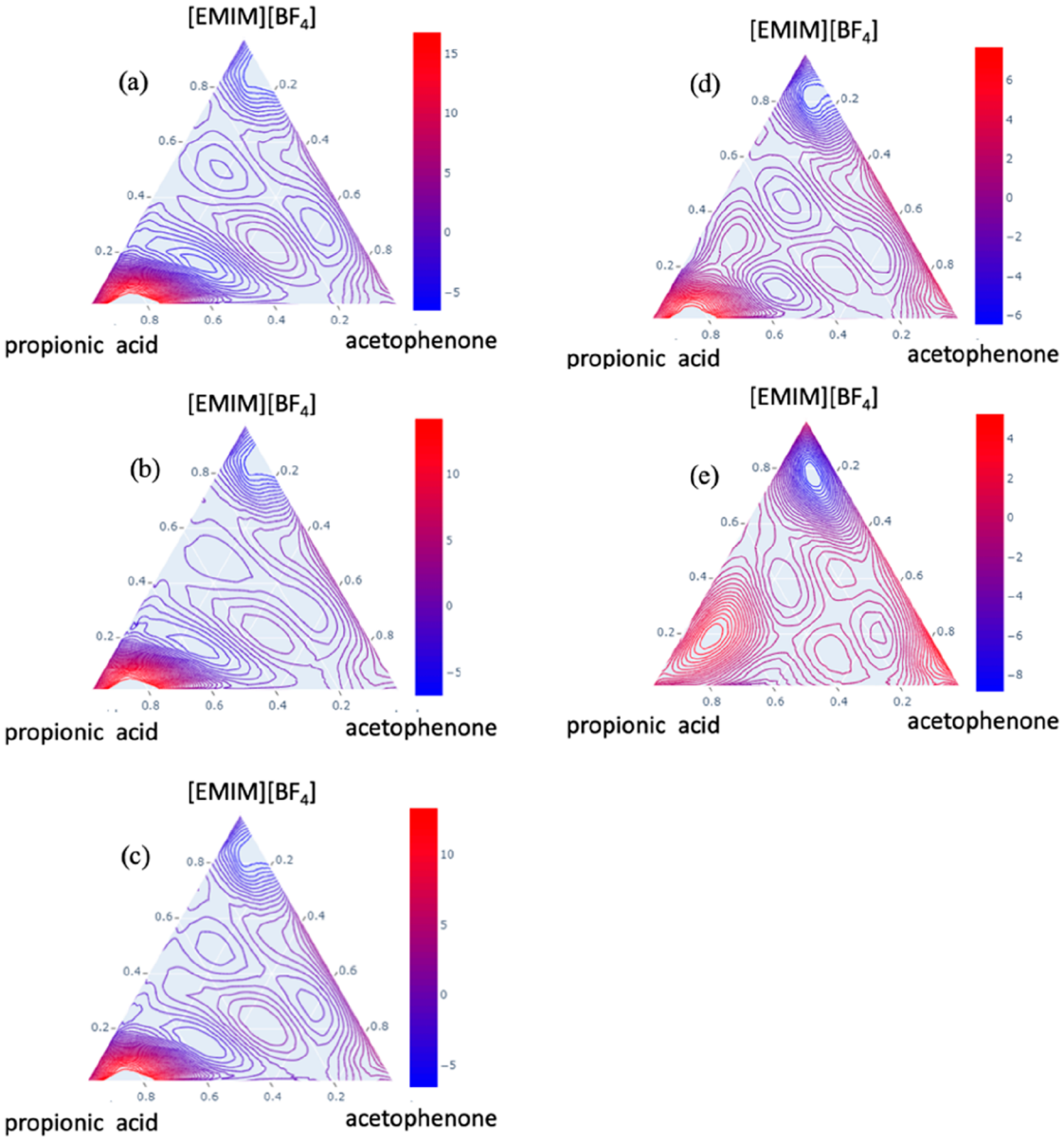

Figure 2. Plot of excess molar volume (V^{E}_{m123}) as a function IL mole fraction (x_1) for ternary mixtures {[EMIM][BF_4] (x_1) + propionic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K, and (e) 333.15 K.

quantity of degrees of freedom while determining the parameters, a model with more parameters than another could have a larger σ.

3. RESULTS AND DISCUSSION

The thermophysical and thermodynamic properties including densities, ρ_{123}, speeds of sound, u_{123}, excess molar volumes, V^{E}_{m123}, and deviations in isentropic compressibility, Δk_{s123}, of ternary mixtures {[EMIM][BF_4] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_1) and {[EMIM][BF_4] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_2) were investigated over the temperature range (293.15−333.15) K at atmospheric pressure (0.1 MPa). Tables 5 and 6 present the findings for the experimental densities and speeds of sound. The following equation was used to compute the excess molar volumes V^{E}_{m123} from the experimental ρ_{123} of ternary liquid mixtures:

$$V^{E}_{m123} = \frac{\sum_{i=1}^{n} x_i M_i}{\rho_m} - \sum_{i=1}^{n} \frac{x_i M_i}{\rho_i} \quad (6)$$

where n is the number of components present in the mixture, ρ_m is the density of the ternary mixture, and x_i, ρ_i, and M_i signify the mole fraction, density, and molar mass of pure component i, respectively.

The deviations in isentropic compressibility, Δk_{s123}, were computed utilizing eq 7:

$$\Delta k_{s123} = k_{s123} - \sum_{i=1}^{n} x_i k_{si} \quad (7)$$

where k_s denotes the isentropic compressibility computed using the Newton−Laplace equation as described in eq 8:

$$k_{s123} = \frac{1}{u_{123}^{2} \rho_m} \quad (8)$$

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J. Chem. Eng. Data 2024, 69, 25−37

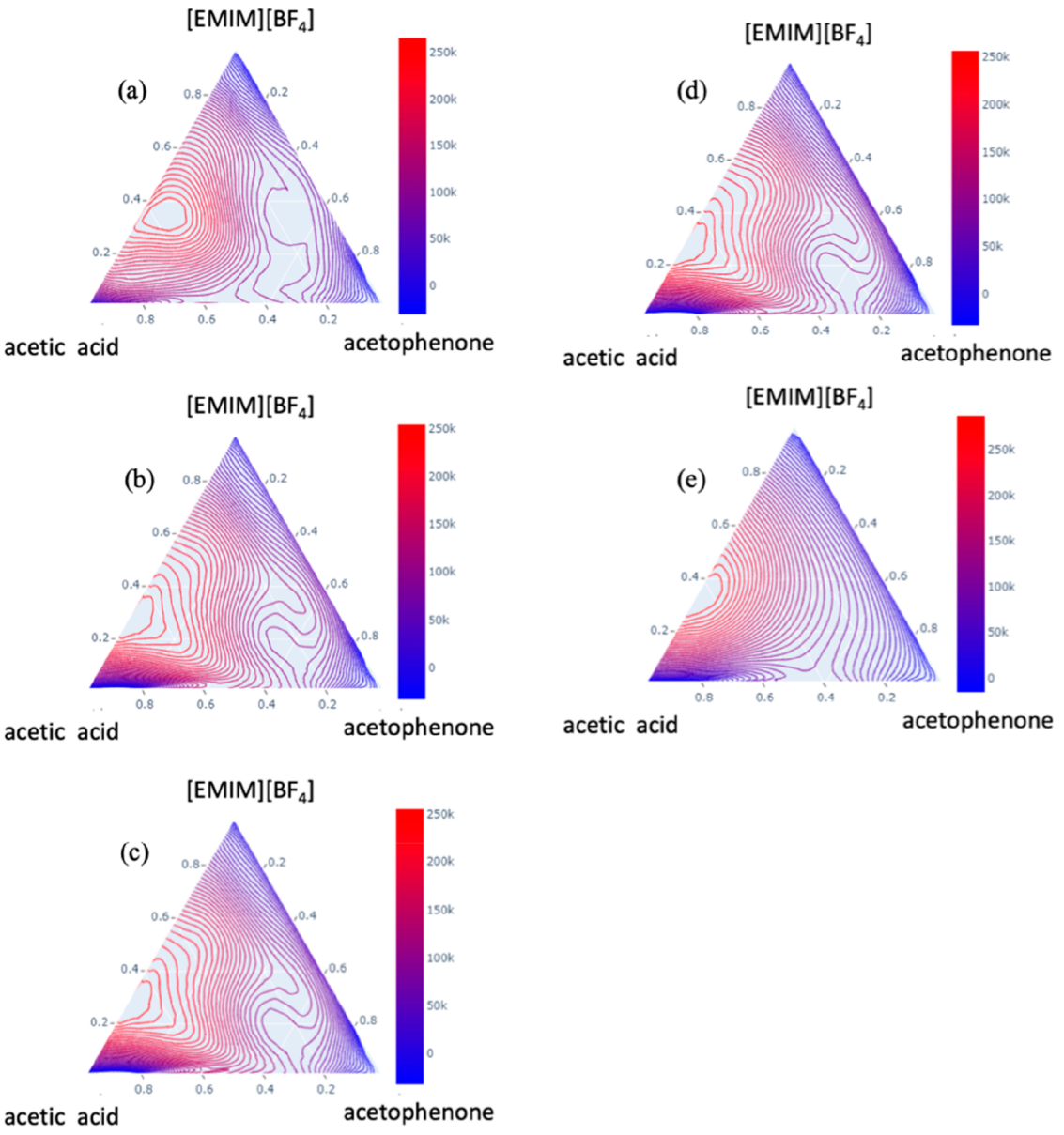

Figure 3. Plot of deviation in isentropic compressibility (Δk_{s123}) as a function IL mole fraction (x_1) for ternary mixtures {[EMIM][BF_4] (x_1) + acetic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K, and (e) 333.15 K.

The V^E_{m123} and Δk_{s123} values for mix_1 and mix_2 are displayed in Tables S1 and S2, and the fitted coefficients (A_i) and standard deviations (σ) of the Redlich−Kister equation for the corresponding binary mixtures are given in Tables S3−S5. As observed from the results, completely negative values of V^E_{m123} were obtained for mix_1, with the most negative value about −1.4 $cm^3 \cdot mol^{-1}$, and for mix_2 both positive and negative values of V^E_{m123} were obtained, from (−6.0 to 3.7) $cm^3 \cdot mol^{-1}$. Completely positive values of Δk_{s123} were obtained for mix_1, up to about 2.7×10^5 TPa^{-1}, and for mix_2 both positive and negative values of Δk_{s123} were obtained, from $(-0.6 \text{ to } 7.1) \times 10^5$ TPa^{-1}.

The positive values of V^E_{m123} and Δk_{s123} demonstrate that hydrogen bonds are formed among the molecules of acetophenone, acetic acid, and propionic acid and the anions of the IL. These hydrogen bonds are created when the IL ion pairs dissociate from one another.[15] The negative values of V^E_{m123} and Δk_{s123} are caused by the packing effect of acetophenone, acetic acid, and propionic acid in the gaps between the IL as well as the ion−dipole interactions between the solvent molecules in the mixture and the cations of the ILs.[15] Furthermore, the positive values of V^E_{m123} in mix_2 were found at a higher mole fraction of propionic acid or acetophenone, which may be attributed to less dominance of the ion−dipole interactions among the solvent molecules in the mixture and the cations of the IL. Based on these results, one can come to the conclusion that mix_1 is closer to an ideal solution in comparison to mix_2. As the temperature increases for both ternary mixtures, the negative values of V^E_{m123} get increasingly negative. A more efficient occupation of the free volumes among the IL ions was enabled by the component molecules' improved thermal mobility with temperature, which raised the negative V^E_{m123} values.[59,60]

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J. Chem. Eng. Data 2024, 69, 25−37

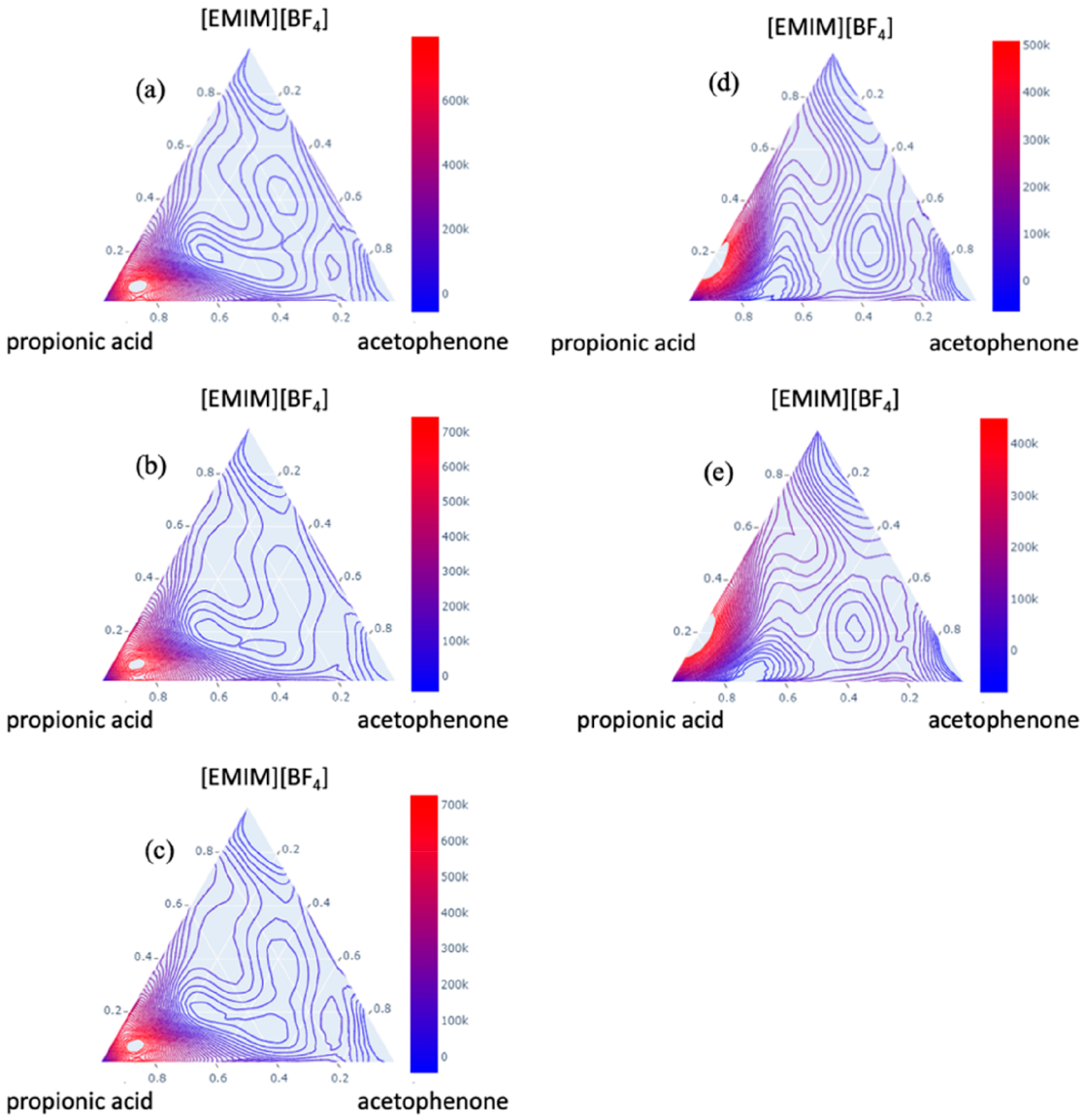

Figure 4. Plot of deviation in isentropic compressibility (Δk_{s123}) as a function IL mole fraction (x_1) for ternary mixtures {[EMIM][BF_4] (x_1) + propionic acid (x_2) + acetophenone (x_3)} at (a) 293.15 K, (b) 303.15 K, (c) 313.15 K, (d) 323.15 K, and (e) 333.15 K.

In our previous work,[30,31,61] we investigated V^E_{m123} and Δk_{s123} properties of the corresponding binary mixtures of the current studied ternary mixtures. When compared with the binary mixtures, it was found that acetophenone + carboxylic acid mixtures have extreme V^E_{m123} values from −0.6 $cm^3 \cdot mol^{-1}$ (293 K) to −1.1 $cm^3 \cdot mol^{-1}$ (333 K), while they range from −1.0 $cm^3 \cdot mol^{-1}$ (293 K) to −1.6 $cm^3 \cdot mol^{-1}$ (333 K) for [EMIM][BF_4] + acetic acid mixtures and from 2.6 $cm^3 \cdot mol^{-1}$ (293 K) to −3.4 $cm^3 \cdot mol^{-1}$ (333 K) for [EMIM][BF_4] + propionic acid mixtures and are mainly positive up to 5 $cm^3 \cdot mol^{-1}$ for [EMIM][BF_4] + acetophenone. Even for binaries, higher temperatures lead to more negative V^E_{m123} values, probably due to the free volume. For mix_1, the highly positive V^E_{m123} values found in the IL + acetophenone mixture are not present, which suggests that the interactions between IL and acetophenone are not so present in the ternary mixtures (mix_1).

It is also evident from Tables S3−S5 that the values of V^E_{m123} for mix_2 were more negative compared to the V^E_{m123} of mix_1. The extended alkyl chain of the propionic acid caused the effect of the interaction to rise because propionic acid has a larger electron donor capacity than acetic acid.[62]

The modeling results displayed in Tables 7 and 8 and Figures 1−4 show that the best predictive terms for mix_1 were 5 (Scatchard) for V^E_{m123} and 1 (Redlich−Kister) and 9 ("average") for Δk_{s123}. The results obtained for mix_2 show that the best predictive term was 3 (Kohler) for both V^E_{m123} and Δk_{s123}. The best correlative terms for mix_1 were 7 (11p-model) for V^E_{m123} and 7 (11p-model), 4 (5p-model), or 5 (7p-model) for Δk_{s123} depending on the temperature. The results obtained for mix_2 show that the best correlative term was 7 (11p-model) for both V^E_{m123} and Δk_{s123}. The most nonideal mixture required a more complex model according to these data, and as anticipated, the most effective modeling for mix_1 was achieved with a less complex model than for mix_2.

The mean standard deviation, σ, for V^E_{m123} of mix_2 was around 3 times higher than the values for mix_1 at

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J. Chem. Eng. Data 2024, 69, 25−37

temperatures of (293.15 and 315.15) K and twice as high as those at temperatures of (303.15, 323.15, and 333.15) K. For both ternary mixtures at temperatures of (293.15 and 333.15) K, the σ values for Δk_{s123} were within the same range. However, at temperatures of (303.15 and 313.15) K, σ for Δk_{s123} of mix_2 was double the values for Δk_{s123} of mix_1, and it was triple at 323.15 K.

4. CONCLUSION

In the present work, we have reported the densities, ρ_{123}, speeds of sound, u_{123}, excess molar volumes, V^E_{m123}, and deviations in isentropic compressibility, Δk_{s123}, of ternary mixtures {[EMIM][BF_4] (x_1) + acetic acid (x_2) + acetophenone (x_3)} (mix_1) and {[EMIM][BF_4] (x_1) + propionic acid (x_2) + acetophenone (x_3)} (mix_2) at T = (293.15−333.15) K and 0.1 MPa. The results obtained revealed that for mix_1, the values were wholly negative for V^E_{m123} and wholly positive for Δk_{s123}. On the contrary, both positive and negative values of V^E_{m123} and Δk_{s123} were obtained for mix_2. With regard to temperature effect, the values of V^E_{m123} for mix_1 and mix_2 decreased with an increase in temperature. Based on these quantitative results, the acetic acid-containing mixture was closer to an ideal solution in comparison to the propionic acid-containing mixture.

Furthermore, the V^E_{m123} and Δk_{s123} values of the ternary mixtures were modeled using the sum of a predictive term (no estimated parameters) and a correlative term (estimated parameters). The whole sum and/or model is a correlative model, and if all of the parameters of the correlative term are zeroed, it becomes a predictive model. The ideal number of parameters in the correlation was determined using the standard deviations (σ). The modeling results of mix_1 for V^E_{m123} was predictive model 5 (Scatchard) + correlative model 7 (11p-model), and for Δk_{s123} the model was predictive model 1 (Redlich−Kister) + correlative model 7 (11p-model). The modeling results of mix_2 for V^E_{m123} and Δk_{s123} was predictive model 3 (Kohler) + correlative model 7 (11p-model). A simpler model worked better for mix_1 than mix_2, necessitating a more complex model for the more nonideal mixture. More complex models were used for the modeling of mix_2, and mix_2 presented worse deviations than mix_1.

■ ASSOCIATED CONTENT

Data Availability Statement

The data are presented in both the article and the Supporting Information. The calculations were done in Python, and the ternary contour plots were developed with Plotly's Figure Factory Module. The code can be found at https://github.com/MLLP/TEP.[15]

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.3c00420.

Excess molar volumes, V^E_{m123}, and deviations in isentropic compressibility, Δk_{s123}, for the ternary mixtures {[EMIM][BF_4] (x_1) + acetic acid (x_2) + acetophenone (x_3)} and {[EMIM][BF_4] (x_1) + propionic acid (x_2) + acetophenone (x_3)} over the temperature range (293.15−333.15) K at atmospheric pressure (0.1 MPa) (Tables S1 and S2) and Redlich−Kister coefficients, A_i, and standard deviations, σ, obtained for the binary systems {[EMIM][BF_4] (x_1) + acetophenone (x_2)}, {[EMIM][BF_4] (x_1) + acetic acid (x_2)}, {[EMIM][BF_4] (x_1) + propionic acid (x_2)}, {acetic acid (x_1) + acetophenone (x_2)}, and {propionic acid (x_1) + acetophenone (x_2)} over the temperature range (293.15−333.15) K at atmospheric pressure (0.1 MPa) (Tables S3−S5) (PDF)

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Notes

The authors declare no competing financial interest.

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