Ternary Excess Molar Volumes of {Methyltrioctylammonium Bis[(trifluoromethyl)sulfonyl]imide + Methanol + Methyl Acetate or Ethyl Acetate} Systems at (298.15, 303.15, and 313.15) K

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The densities of the ternary systems {methyltrioctylammonium bis[(trifluoromethyl)sulfonyl]imide + methanol + methyl acetate or ethyl acetate} have been measured at the temperatures (298.15, 303.15, and 313.15) K. The ternary excess molar volumes, V^E_{123}, were calculated from the experimental densities at each temperature. The V^E_{123}values are negative for all mole fractions of the ionic liquid (IL). For the system {$[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate}, the minimum ternary excess molar volumes, $V^E_{123,min}$, decrease with decreasing *z* values (increasing the mole fraction of the IL) except at *z* equal to 0.30 at temperatures (298.15 and 313.15) K. The $V^E_{123,min}$decreases with an increase in the temperature. For the system {$[MOA]^+[Tf_2N]^-$ + methanol + ethyl acetate}, $V^E_{123,min}$ increases with decreasing *z* values at each temperature. The Cibulka equation was used to correlate the ternary excess molar volume data from the Redlich−Kister parameters obtained from fitting the Redlich−Kister equation to the five binary systems obtained from the literature. There is a good correlation between the Cibulka equation and experimental V^E_{123}data.

Introduction

Ionic liquids (ILs) have unique physical properties, such as low melting point, high thermal stability, nonflammability, and no measurable vapor pressure, and good dissolution properties for most inorganic and organic compounds,[1−6] which make them suitable substitutes for volatile organic compounds (VOCs). ILs are organic salts with melting points of less than <373.15 K. ILs belong to a class of neoteric solvents that are constituted of bulky, asymmetric organic cations and inorganic or organic anions to create a nonaqueous solvating medium.[7,8] There are numerous publications on IL properties or their applications in catalytic reactions, separation processes, membrane technology, chemical analysis, batteries, solar cells, or lubricants.[9,10]

Thermodynamic properties are used to understand the nature of molecular interactions, e.g., van der Waals interactions in binary or ternary liquid mixtures. Furthermore, thermodynamic properties of binary or ternary mixtures containing components capable of undergoing specific interactions exhibit significant deviations from ideality due to differences in the molecular size, shape, and structure.[11]

Thermodynamic data for the system (alkanol + alkanoate) are useful in the pharmaceutical, food, and flavor industries[12] and are of interest from a theoretical point of view because alcohols are hydrogen-bonded in the pure state and new hydrogen bonds are formed between the alcohol and ester when mixing occurs.[13,14] There is a lack of data on ternary excess molar volumes V^E_{123} for IL multicomponent systems.[15−19] Gómez et al.[15] studied the V^E_{123} for the IL system (ethanol + water + 1,3-dimethylimidazolium methylsulfate) at several temperatures. Deenadayalu et al.[16] used the graph theory to correlate V^E_{123} for the (1-ethyl-3-methylimidazolium diethylene glycol monomethyl ether sulfate + methanol + water) ternary IL system. González et al.[17] studied V^E_{123} for the ternary IL system (ethanol + water + 1-butyl-3-methylimidazolium methyl sulfate) at several temperatures. Andreatta et al.[18] studied V^E_{123} for the IL system {methyl acetate + methanol + 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide} at temperature 298.15 K and atmospheric pressure. Deenadayalu et al.[19] studied V^E_{123} for ILs $[EMIM]^+[BETI]^-$ or ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol or acetone) at temperatures (298.15, 303.15, and 313.15) K.

In this work, ternary V^E_{123} values for IL systems have been determined at three temperatures and at atmospheric pressure. The IL methyltrioctylammonium bis[(trifluoromethyl)sulfonyl]imide ($[MOA]^+[Tf_2N]^-$) was used. The experimental densities were determined for the ternary system ($[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate or ethyl acetate) over the entire composition range at temperatures (298.15, 303.15, and 313.15) K and at atmospheric pressure.

This work is a continuation of our research group's work on the thermodynamic properties of ILs.[16,19−24]

Experimental Section

The solvents were purchased from Aldrich and Fluka with mass purity >99.0 % for methanol, methyl acetate, and ethyl acetate and mass purity >98.0 % for the IL. The IL, methanol, methyl acetate, and ethyl acetate were used without any further purification. The water content in the IL was determined by using a Karl Fischer coulometer (model Metrohm 797), and the mass percent of water content was found to be <0.04 %. The purities of the solvents were assessed by a comparison of the experimental density values with the literature density values where available.[9,24,25]

The experimental technique was tested by determination of the excess molar volumes of the test system (octane + toluene)[26]

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Table 1. Literature and Experimental Densities of the Pure Compounds at T = (298.15, 303.15, and 303.15) K

		ρ/g·cm^{-3}			
		lit.		exptl	
compound	% mass purity	T/K = 298.15	T/K = 298.15	T/K = 303.15	T/K = 313.15
$[MOA]^+[Tf_2N]^-$	98.0	1.1093[a]	1.1069	1.1032	1.0957
methanol	99.8	0.7864[b]	0.7860	0.7834	0.7746
methyl acetate	99.0	0.9270[c]	0.9271	0.9205	0.9079
ethyl acetate	99.7	0.8944[c]	0.8947	0.8885	0.8751

[a] Reference 24. [b] Reference 9. [c] Reference 25.

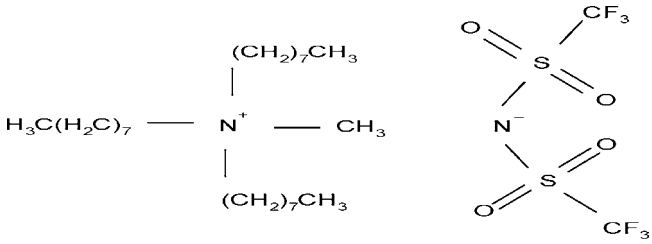

Figure 1. Structure of the IL {methyltrioctylammonium bis[(trifluoromethyl)sulfonyl]imide}.

Table 2. Densities and Excess Molar Volumes for IL (x_1) + Methyl Acetate (x_2) at T = (298.15, 303.15, and 313.15) K

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
		T = 298.15 K			
0.0577	0.9836	−0.088	0.5029	1.0905	−1.397
0.1318	1.0245	−0.368	0.6690	1.0994	−1.376
0.2042	1.0490	−0.747	0.7587	1.1028	−1.224
0.2502	1.0600	−0.975	0.8076	1.1042	−1.099
0.2939	1.0685	−1.213	0.8382	1.1048	−0.927
0.4075	1.0826	−1.345	0.8902	1.1059	−0.713
0.4564	1.0870	−1.385	0.9534	1.1079	−0.405
		T = 303.15 K			
0.0577	0.9809	−0.480	0.6106	1.0884	−2.223
0.1318	1.0218	−0.802	0.6690	1.0963	−1.879
0.2042	1.0462	−1.208	0.7587	1.0992	−1.624
0.2502	1.0571	−1.438	0.8076	1.1004	−1.417
0.2939	1.0657	−1.719	0.8382	1.1009	−1.200
0.4075	1.0800	−1.961	0.8902	1.1019	−0.936
0.4564	1.0841	−1.945	0.9534	1.1028	−0.520
		T = 313.15 K			
0.0577	0.9699	−0.571	0.6106	1.0894	−3.333
0.1318	1.0114	−0.842	0.6690	1.0917	−3.231
0.2042	1.0366	−1.270	0.7587	1.0927	−2.239
0.2502	1.0494	−1.819	0.8076	1.0931	−1.662
0.2939	1.0577	−2.015	0.8382	1.0938	−1.531
0.4075	1.0725	−2.317	0.8902	1.0942	−0.956
0.4564	1.0769	−2.365	0.9534	1.0951	−0.499
0.5029	1.0809	−2.538			

at temperature 298.15 K and comparison with literature values. The difference between the experimental and literature V_m^E values for the test system was within experimental error. The experimental uncertainty in V_{123}^E is ±0.01 cm^3·mol^{-1}. The ternary mixtures were prepared by the transfer by syringe of the pure liquids into stoppered bottles to prevent evaporation. The IL was first filled into the airtight glass-stoppered 5 cm^3 glass vial and weighed. An OHAUS mass balance was used to determine of the mass of each component of the mixture. The mass balance has a precision of 0.0001 g. The uncertainty in the mole fraction was estimated to be 0.0006.

The ternary mixtures were prepared to obtained a constant ratio of $z = x_3/x_1$, where x_1 is the mole fraction of the IL and x_3 is the mole fraction of methyl acetate or ethyl acetate, with varying mole fraction of methanol x_2. The densities were measured by an Anton Paar DMA 38 vibrating U-tube densimeter. Ultrapure water supplied by SH Calibration Service GmbH Graz and dried air were used for calibration of the

Table 3. Densities and Excess Molar Volumes for IL (x_1) + Ethyl Acetate (x_2) at T = (298.15, 303.15, and 313.15) K

x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}	x_1	ρ/g·cm^{-3}	V_m^E/cm^3·mol^{-1}
		T = 298.15 K			
0.0985	0.9792	−0.187	0.4848	1.0797	−1.458
0.1414	1.0018	−0.387	0.5450	1.0858	−1.579
0.1935	1.0229	−0.669	0.5859	1.0891	−1.552
0.2468	1.0394	−0.939	0.6761	1.0954	−1.537
0.2837	1.0483	−1.034	0.7589	1.0999	−1.422
0.3472	1.0612	−1.296	0.8319	1.1030	−1.197
0.3967	1.0688	−1.343	0.8859	1.1049	−0.975
0.4484	1.0756	−1.425			
		T = 303.15 K			
0.0985	0.9737	−0.201	0.4848	1.0750	−1.483
0.1414	0.9977	−0.613	0.5450	1.0810	−1.551
0.1935	1.0182	−0.780	0.5859	1.0843	−1.508
0.2468	1.0341	−0.901	0.6761	1.0906	−1.460
0.2837	1.0433	−1.052	0.7589	1.0950	−1.270
0.3472	1.0559	−1.212	0.8319	1.0983	−1.104
0.3967	1.0640	−1.368	0.8859	1.1002	−0.861
0.4484	1.0710	−1.491			
		T = 313.15 K			
0.0985	0.9836	−0.286	0.4848	1.0675	−1.792
0.1414	1.0245	−0.595	0.5450	1.0735	−1.834
0.1935	1.0490	−0.898	0.5859	1.0769	−1.808
0.2468	1.0600	−1.078	0.6761	1.0832	−1.722
0.2837	1.0685	−1.328	0.7589	1.0875	−1.452
0.3472	1.0482	−1.578	0.8319	1.0909	−1.297
0.3967	1.0562	−1.631	0.8859	1.0926	−0.931
0.4484	1.0634	−1.786			

densimeter at each temperature.[24] The temperature maintenance and control were regulated by a built-in thermostat controller with a temperature uncertainty of ±0.01 K and capable of measuring the density to ±0.0001 g·cm^{-3}. The uncertainty in the density for the ternary system was 0.002 g·cm^{-3}. The ternary excess molar volumes V_{123}^E were calculated from the experimental density. The literature and experimental densities (ρ) are given in Table 1. The deviation between the reference and experimental density for the IL in Table 1 is due to different suppliers. The structure of the IL is given in Figure 1.

Results and Discussion

In Tables 2 to 5, the densities, ρ, and the excess molar volumes for the binary, V_m^E, and ternary V_{123}^E, systems are given as a function of the composition at the three temperatures. The V_{123}^E values were calculated from the experimental density values using the following equation:

$$V_{123}^E = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} - \frac{x_3M_3}{\rho_3} \quad (1)$$

where x_1, x_2, and x_3 are mole fractions, M_1, M_2, and M_3 are the molecular masses, ρ_1, ρ_2, and ρ_3 are the densities of pure components 1 to 3, respectively, where 1 refers to the IL, 2 to methanol, and 3 to methyl acetate or ethyl acetate and ρ is the density of the mixture.

Table 4. Densities and Excess Molar Volumes for IL (x_1) + Methanol (x_2) + Methyl Acetate (x_3) at T = (298.15, 303.15, and 313.15) K

x_1	x_2	ρ/g·cm^{-3}	V^E_{123}/cm^3·mol^{-1}
		T = 298.15 K	
		z = 9.00	
0.0397	0.6030	0.9401	−0.30
0.0696	0.3023	0.9866	−0.57
0.0899	0.1012	1.0042	−0.49
0.1000	0.0000	1.0106	−0.37
		z = 4.00	
0.0596	0.7022	0.9620	−0.67
0.1006	0.4969	1.0045	−0.88
0.1434	0.2835	1.0298	−1.02
0.1637	0.1812	1.0380	−1.03
0.1999	0.0000	1.0485	−0.89
		z = 1.50	
0.1564	0.6090	1.0295	−0.85
0.2382	0.4046	1.0566	−1.08
0.2791	0.3018	1.0650	−1.13
0.3329	0.1681	1.0735	−1.21
0.3995	0.0000	1.0814	−1.33
		z = 1.00	
0.0641	0.8718	0.9545	−0.42
0.1195	0.7608	1.0070	−0.62
0.2418	0.5164	1.0565	−1.00
0.3478	0.3045	1.0754	−1.21
0.4567	0.0867	1.0865	−1.31
0.5000	0.0000	1.0898	−1.38
		z = 0.50	
0.2615	0.6078	1.0605	−1.02
0.3983	0.4026	1.0812	−1.20
0.5309	0.2037	1.0921	−1.32
0.5997	0.1004	1.0960	−1.36
0.6659	0.0000	1.0989	−1.34
		z = 0.30	
0.1867	0.7573	1.0385	−0.78
0.3606	0.5313	1.0768	−1.14
0.5182	0.3263	1.0914	−1.28
0.6259	0.1863	1.0975	−1.35
0.7709	0.0000	1.1029	−1.28
		T = 303.15 K	
		z = 9.00	
0.0397	0.6030	0.9374	−0.44
0.0696	0.3023	0.9855	−0.98
0.0899	0.1012	1.0016	−0.81
0.1000	0.0000	1.0069	−0.59
		z = 4.00	
0.0596	0.7022	0.9610	−0.93
0.1006	0.4969	1.0040	−1.32
0.1434	0.2835	1.0280	−1.41
0.1637	0.1812	1.0363	−1.49
0.1999	0.0000	1.0460	−1.30
		z = 1.50	
0.1564	0.6090	1.0285	−1.24
0.2382	0.4046	1.0556	−1.63
0.2791	0.3018	1.0635	−1.66
0.3329	0.1681	1.0720	−1.83
0.3995	0.0000	1.0792	−1.88
		z = 1.00	
0.0641	0.8718	0.9530	−0.58
0.1195	0.7608	1.0065	−0.97
0.2418	0.5164	1.0560	−1.60
0.3478	0.3045	1.0740	−1.81
0.4567	0.0867	1.0845	−1.91
0.5000	0.0000	1.0875	−1.93
		z = 0.50	
0.2615	0.6078	1.0590	−1.43
0.3983	0.4026	1.0797	−1.79
0.5309	0.2037	1.0902	−1.95
0.5997	0.1004	1.0938	−1.96
0.6659	0.0000	1.0965	−1.92
		z = 0.30	
0.1867	0.7573	1.0370	−1.07
0.3606	0.5313	1.0752	−1.63
0.5182	0.3263	1.0898	−1.95
0.6259	0.1863	1.0955	−2.00
0.7709	0.0000	1.1002	−1.78
		T = 313.15 K	
		z = 9.00	
0.0397	0.6030	0.9267	−0.49
0.0696	0.3023	0.9750	−1.05
0.0899	0.1012	0.9916	−0.92
0.1000	0.0000	0.9983	−0.87
		z = 4.00	
0.0596	0.7022	0.9526	−1.15
0.1006	0.4969	0.9960	−1.60
0.1434	0.2835	1.0206	−1.80
0.1637	0.1812	1.0278	−1.71
0.1999	0.0000	1.0370	−1.43
		z = 1.50	
0.1564	0.6090	1.0210	−1.54
0.2382	0.4046	1.0485	−2.01
0.2791	0.3018	1.0570	−2.17
0.3329	0.1681	1.0652	−2.30
0.3995	0.0000	1.0720	−2.27
		z = 1.00	
0.0641	0.8718	0.9433	−0.65
0.1195	0.7608	0.9970	−1.02
0.2418	0.5164	1.0485	−1.88
0.3478	0.3045	1.0672	−2.25
0.4567	0.0867	1.0778	−2.41
0.5000	0.0000	1.0805	−2.35
		z = 0.50	
0.2615	0.6078	1.0520	−1.78
0.3983	0.4026	1.0730	−2.22
0.5309	0.2037	1.0840	−2.57
0.5997	0.1004	1.0876	−2.61
0.6659	0.0000	1.0905	−2.69
		z = 0.30	
0.1867	0.7573	1.0295	−1.33
0.3606	0.5313	1.0686	−2.07
0.5182	0.3263	1.0834	−2.48
0.6259	0.1863	1.0891	−2.57
0.7709	0.0000	1.0932	−2.12

The binary V^E_m data for (IL + methanol),[24] (methanol + methyl acetate),[25] and (methanol + ethyl acetate)[25] were published in the literature, while V^E_m data for the binary systems (IL + methyl acetate) and (IL + ethyl acetate) are given in Tables 2 and 3. The Redlich−Kister equation[27] was fitted to the binary literature data to obtained the Redlich−Kister parameters at the temperatures (298.15, 303.15, and 313.15) K, except for (methanol + methyl acetate) and (methanol + ethyl acetate), which were only obtained for the temperatures (298.15 and 303.15) K because the literature data were not available at the temperature 313.15 K and the binary V^E_m data are relatively small and do not vary greatly with temperature. The binary parameters calculated from the Redlich−Kister equation are given in Table 6. The Redlich−Kister equation is given as

$$V^E_m = x_1 x_2 \sum_{i=1}^{N} A_i (1 - 2x_1)^{i-1} \quad (2)$$

The ternary excess molar volumes were correlated with the Cibulka equation,[28] which is given as

$$V^E_{123} = \sum_{i,j=1.2;1.3;2.3;} V^E_{ij}(x_i, x_j) - x_1 x_2 x_3 (b_0 - b_1 x_1 - b_2 x_2) \quad (3)$$

where x_1, x_2, and x_3 are the mole fractions of the IL, methanol, methyl acetate, or ethyl acetate, respectively. The Cibulka

Table 5. Densities and Excess Molar Volumes for IL (x_1) + Methanol (x_2) + Ethyl Acetate (x_3) at T = (298.15, 303.15, and 313.15) K

x_1	x_2	ρ/g·cm^{-3}	V^E_{123}/cm^3·mol^{-1}
		T = 298.15 K	
		z = 0.10	
0.9077	0.0000	1.1045	−0.57
0.7075	0.2218	1.0986	−0.72
0.6265	0.3103	1.0955	−0.87
0.5123	0.4369	1.0895	−1.03
0.4200	0.5381	1.0823	−1.09
0.3364	0.6294	1.0727	−1.09
0.2604	0.7133	1.0585	−0.86
0.1850	0.7964	1.0371	−0.76
0.0890	0.9021	0.9762	−0.19
		z = 0.43	
0.6987	0.0000	1.0965	−1.58
0.6273	0.1024	1.0938	−1.61
0.5613	0.1987	1.0908	−1.64
0.4837	0.3085	1.0857	−1.51
0.4165	0.4048	1.0808	−1.61
0.3460	0.5047	1.0734	−1.59
0.2786	0.6019	1.0623	−1.34
0.1999	0.7139	1.0429	−1.14
0.1330	0.8099	1.0135	−0.83
0.0864	0.8764	0.9764	−0.45
		z = 1.00	
0.5009	0.0000	1.0815	−1.59
0.4467	0.1065	1.0779	−1.60
0.3995	0.2022	1.0742	−1.62
0.3453	0.3073	1.0689	−1.67
0.2937	0.4119	1.0621	−1.64
0.2509	0.5004	1.0547	−1.60
0.1982	0.6035	1.0410	−1.38
0.1465	0.7071	1.0212	−1.17
0.0484	0.9033	0.9315	−0.54
		z = 1.80	
0.0852	0.7613	0.9825	−1.18
0.1371	0.6161	1.0185	−1.67
0.1918	0.4630	1.0391	−1.96
0.2564	0.2820	1.0528	−2.00
0.3312	0.0727	1.0613	−1.64
0.3571	0.0000	1.0627	−1.30
		z = 3.36	
0.1053	0.5406	1.0018	−1.96
0.1292	0.4363	1.0145	−2.13
0.1534	0.3307	1.0232	−2.13
0.1771	0.2272	1.0293	−2.02
0.2028	0.1153	1.0339	−1.77
		z = 7.50	
0.0421	0.6392	0.9450	−1.78
0.0775	0.3360	0.9840	−2.30
0.1032	0.1156	0.9950	−1.93
		T = 303.15 K	
		z = 0.10	
0.9077	0.0000	1.1006	−0.50
0.7075	0.2218	1.0943	−0.52
0.6265	0.3103	1.0915	−0.81
0.5123	0.4369	1.0859	−1.11
0.4200	0.5381	1.0781	−1.02
0.3364	0.6294	1.0679	−0.92
0.2604	0.7133	1.0535	−0.69
0.1850	0.7964	1.0291	−0.23
0.0890	0.9021	0.9724	−0.25
		z = 0.43	
0.6987	0.0000	1.0921	−1.40
0.6273	0.1024	1.0895	−1.49
0.5613	0.1987	1.0865	−1.54
0.4837	0.3085	1.0819	−1.58
0.4165	0.4048	1.0765	−1.55
0.3460	0.5047	1.0691	−1.55
0.2786	0.6019	1.0580	−1.32
0.1999	0.7139	1.0388	−1.16
0.1330	0.8099	1.0095	−0.87
0.0864	0.8764	0.9731	−0.56

Table 5. Continued

x_1	x_2	ρ/g·cm^{-3}	V^E_{123}/cm^3·mol^{-1}
		z = 1.00	
0.5009	0.0000	1.0769	−1.46
0.4467	0.1065	1.0734	−1.52
0.3995	0.2022	1.0698	−1.58
0.3453	0.3073	1.0644	−1.62
0.2937	0.4119	1.0576	−1.61
0.2509	0.5004	1.0498	−1.50
0.1982	0.6035	1.0366	−1.38
0.1465	0.7071	1.0169	−1.20
0.0484	0.9033	0.9269	−0.55
		z = 1.80	
0.0852	0.7613	0.9799	−1.39
0.1371	0.6161	1.0144	−1.75
0.1918	0.4630	1.0354	−2.10
0.2564	0.2820	1.0492	−2.18
0.3312	0.0727	1.0575	−1.80
0.3571	0.0000	1.0582	−1.29
		z = 3.36	
0.1053	0.5406	0.9978	−2.08
0.1292	0.4363	1.0115	−2.39
0.1534	0.3307	1.0198	−2.36
0.1771	0.2272	1.0255	−2.20
0.2028	0.1153	1.0304	−2.02
		z = 7.50	
0.0421	0.6392	0.9420	−1.99
0.0775	0.3360	0.9820	−2.71
0.1032	0.1156	0.9915	−2.21
		T = 313.15 K	
		z = 0.10	
0.9077	0.0000	1.0933	−0.67
0.7075	0.2218	1.0865	−0.49
0.6265	0.3103	1.0830	−0.55
0.5123	0.4369	1.0762	−0.55
0.4200	0.5381	1.0683	−0.54
0.3364	0.6294	1.0579	−0.49
0.2604	0.7133	1.0438	−0.41
0.1850	0.7964	1.0213	−0.30
0.0890	0.9021	0.9631	−0.19
		z = 0.43	
0.6987	0.0000	1.0848	−1.71
0.6273	0.1024	1.0815	−1.53
0.5613	0.1987	1.0778	−1.35
0.4837	0.3085	1.0723	−1.16
0.4165	0.4048	1.0665	−1.09
0.3460	0.5047	1.0580	−0.92
0.2786	0.6019	1.0472	−0.86
0.1999	0.7139	1.0272	−0.70
0.1330	0.8099	0.9977	−0.52
0.0864	0.8764	0.9620	−0.35
		z = 1.00	
0.5009	0.0000	1.0693	−1.80
0.4467	0.1065	1.0650	−1.60
0.3995	0.2022	1.0606	−1.45
0.3453	0.3073	1.0543	−1.31
0.2937	0.4119	1.0470	−1.24
0.2509	0.5004	1.0386	−1.07
0.1982	0.6035	1.0249	−0.95
0.1465	0.7071	1.0046	−0.78
0.0484	0.9033	0.9181	−0.59
		z = 1.80	
0.0852	0.7613	0.9710	−1.47
0.1371	0.6161	1.0055	−1.83
0.1918	0.4630	1.0271	−2.30
0.2564	0.2820	1.0410	−2.43
0.3312	0.0727	1.0490	−2.01
0.3571	0.0000	1.0504	−1.68
		z = 3.36	
0.1053	0.5406	0.9904	−2.43
0.1292	0.4363	1.0026	−2.59
0.1534	0.3307	1.0109	−2.58
0.1771	0.2272	1.0172	−2.54
0.2028	0.1153	1.0215	−2.28
		z = 7.50	
0.0421	0.6392	0.9330	−2.18
0.0775	0.3360	0.9730	−3.01
0.1032	0.1156	0.9820	−2.51

Table 6. Redlich−Kister Parameters for the Five Binary Systems at T = (298.15, 303.15, and 313.15) K

T/K	A_0	A_1	A_2	A_3	A_4	σ/cm^3·mol^{-1}
			$[MOA]^+[Tf_2N]^-$ + Methanol[a]			
298.15	3.01	−3.91	−0.68	−4.54		0.03
303.15	5.05	−5.47	−6.58	−2.76	3.00	0.03
313.15	4.74	−3.75	0.31	−11.29		0.03
			$[MOA]^+[Tf_2N]^-$ + Methyl Acetate			
298.15	−5.65	−0.17	−2.23	4.65	4.87	0.04
303.15	−8.37	−1.27				0.46
313.15	−11.30	−7.70	2.70	12.23		0.25
			$[MOA]^+[Tf_2N]^-$ + Ethyl Acetate			
298.15	−6.00	1.64	−2.33	4.64	3.90	0.03
303.15	−6.01	1.30	−0.29	2.83	0.18	0.06
313.15	−7.25	0.99	−0.21	4.18	1.81	0.04
			Methanol + Methyl Acetate[b]			
298.15	−0.29	0.04	0.05	0.05		0.00
303.15	−0.27	0.02	0.06	0.05		0.00
			Methanol + Ethyl Acetate[b]			
298.15	−0.30	−0.04	−0.08			0.00
303.15	−0.27	−0.05	−0.07			0.00

[a] Reference 24. [b] Reference 25.

Table 7. Smoothing Coefficients and Standard Deviations for the Cibulka Equation at T = (298.15, 303.15, and 313.15) K

T/K	b_0	b_1	b_2	σ_s
$[MOA]^+[Tf_2N]^-$ (x_1) + Methanol (x_2) + Methyl Acetate (x_3)				
298.15	17.48	−34.92	−110.91	0.22
303.15	15.59	−43.06	−144.46	0.28
313.15	18.49	−44.98	−172.17	0.37
$[MOA]^+[Tf_2N]^-$ (x_1) + Methanol (x_2) + Ethyl Acetate (x_3)				
298.15	−32.53	57.30	−111.75	0.45
303.15	−48.60	86.45	−113.99	0.50
313.15	−62.20	122.03	−88.56	0.63

Table 8. Minimum Excess Molar Volumes for Five Binary Systems at T = (298.15, 303.15, and 313.15) K Obtained from the Literature

T/K	x_1	x_2	$V^E_{m,min}$/cm^3·mol^{-1}
		$[MOA]^+[Tf_2N]^-$ + Methanol[a]	
298.15	0.8522	0.1478	−0.234
303.15	0.8522	0.1478	−0.292
313.15	0.9345	0.0655	−0.344
		$[MOA]^+[Tf_2N]^-$ + Methyl Acetate	
298.15	0.5029	0.4971	−1.397
303.15	0.6106	0.3894	−2.223
313.15	0.6106	0.3894	−3.333
		$[MOA]^+[Tf_2N]^-$ + Ethyl Acetate	
298.15	0.5450	0.4550	−1.579
303.15	0.5450	0.4550	−1.551
313.15	0.5450	0.4550	−1.834
		Methanol + Ethyl Acetate[b]	
298.15	0.5006	0.4994	−0.072
303.15	0.5006	0.4994	−0.065
		Methanol + Ethyl Acetate[b]	
298.15	0.5963	0.4037	−0.077
303.15	0.5963	0.4037	−0.071

[a] Reference 24. [b] Reference 25.

equation contains three parameters (b_0, b_1, and b_2) corrected over the five binary contributions and is included in the last term of eq 3. The values of b_0, b_1, and b_2 were adjusted to the experimental ternary excess molar volumes. The distinctive function was in the form of the sum of squares of residuals. The Cibulka equation parameters were adjusted to the differences between the ternary excess volumes and a sum of the binary contributions. The correlation coefficients and the standard deviation (rmsd), σ_s, values are given in Table 7. Table 8 lists all of the binary $V^E_{m,min}$ data.

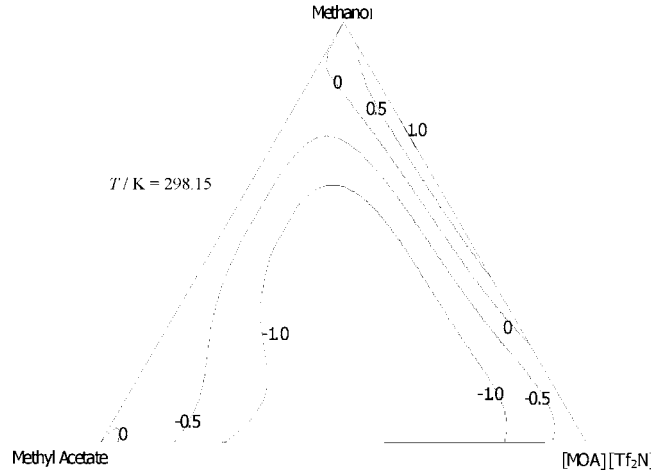

Figure 2. Graph of excess molar volumes, V^E_{123}, of the ternary mixture for $[MOA]^+[Tf_2\ N]^-$ (x_1) + methanol (x_2) + methyl acetate (x_3) at 298.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

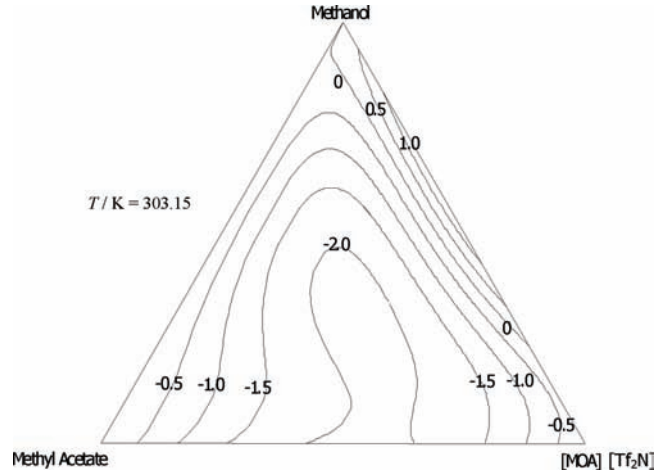

Figure 3. Graph of excess molar volumes, V^E_{123}, of the ternary mixture for $[MOA]^+[Tf_2N]^-$ (x_1) + methanol (x_2) + methyl acetate (x_3) at 303.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

From Table 4, for the ternary system {$[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate}, the minimum ternary excess molar

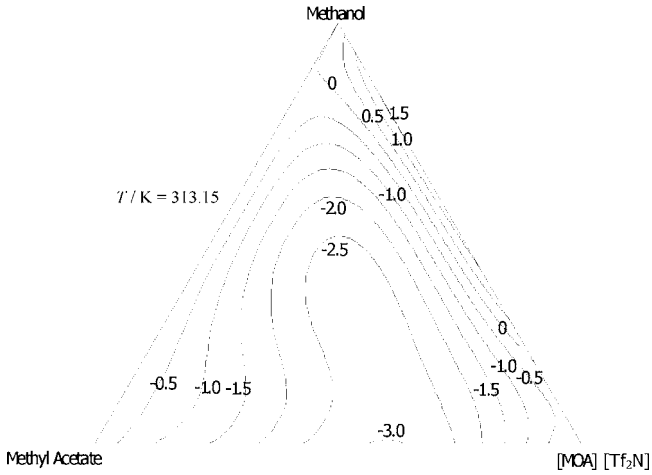

Figure 4. Graph of excess molar volumes, V^E_{123}, of the ternary mixture for $[MOA]^+[Tf_2N]^-$ (x_1) + methanol (x_2) + methyl acetate (x_3) at 313.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

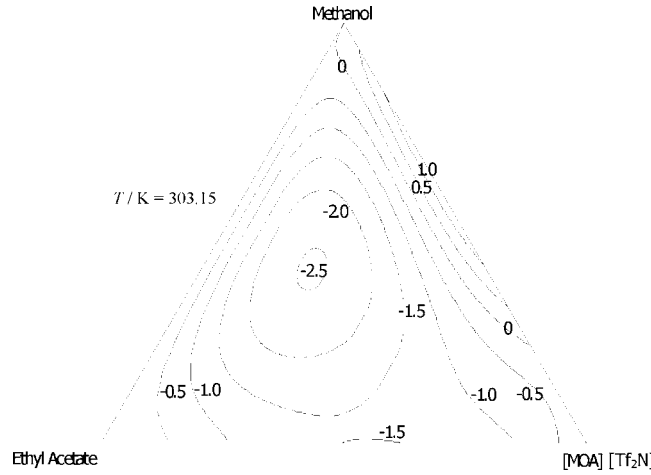

Figure 6. Graph of excess molar volumes, V^E_{123}, of the ternary mixture for $[MOA]^+[Tf_2N]^-$ (x_1) + methanol (x_2) + ethyl acetate (x_3) at 303.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

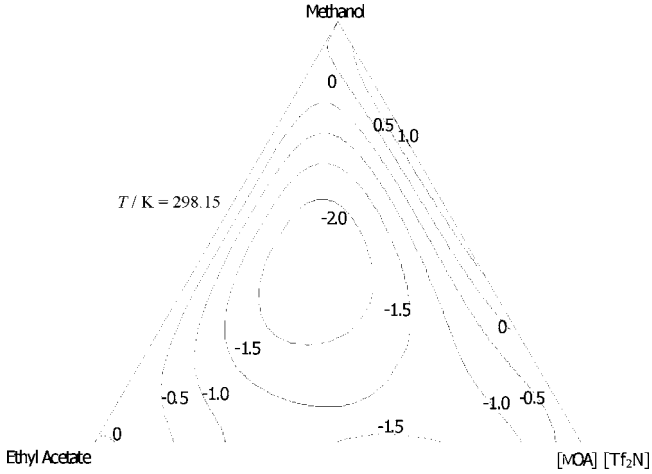

Figure 5. Graph of excess molar volumes, V^E_{123}, of the ternary mixture for $[MOA]^+[Tf_2N]^-$ (x_1) + methanol (x_2) + ethyl acetate (x_3) at 298.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

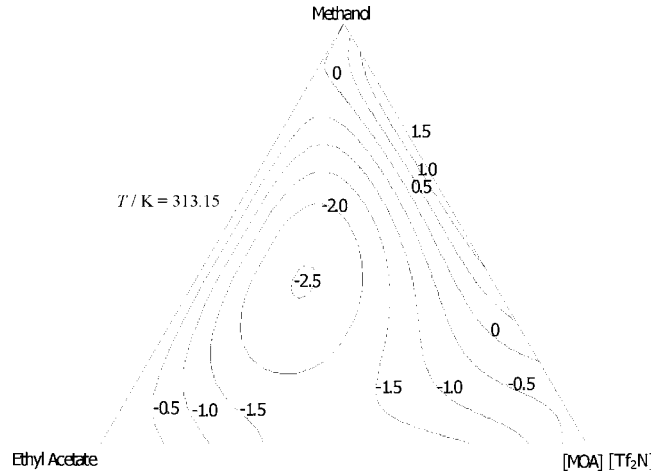

Figure 7. Graph of excess molar volumes, V^E_{123}, of the ternary mixture for $[MOA]^+[Tf_2N]^-$ (x_1) + methanol (x_2) + ethyl acetate (x_3) at 313.15 K. The solid lines were calculated by the Cibulka equation with the values of the parameters fitted to the binary and ternary data.

volumes, $V^E_{123,min}$, decrease with decreasing z values (increasing mole fractions of the IL) except at $z = 0.30$ at temperatures (298.15 and 313.15) K, where the z value is the ratio of the third and first components of the system ($z = x_3/x_1$). The negative values of V^E_{123} for (IL + methanol + methyl acetate) show that the (ion−dipole) interactions and packing effect between methanol, methyl acetate, and the IL are dominating over dissociation of the intermolecular hydrogen bonds in methanol and methyl acetate.[19] Figures 2 to 4 are the ternary excess molar volume graphs obtained from using the Cibulka equation parameters for the system {$[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate} at the three temperatures.

From Table 5, it can be seen that for the system {$[MOA]^+[Tf_2N]^-$ + methanol + ethyl acetate} $V^E_{123,min}$ increases with decreasing z values at each temperature. $V^E_{123,min}$ decreases with an increase in the temperature in the range of the z values from 7.50 to 1.80 and increases with the temperature from the range of the z values from 1.00 to 0.10 except at temperature 303.15 K and $z = 0.10$, where it decreases. The negative values of V^E_{123} for (IL + methanol + ethyl acetate) are due to the same effects that occur in the ternary (IL + methanol + methyl acetate) system.

Figures 5 to 7 are the ternary excess molar volume graphs obtained from using the Cibulka equation parameters for the system {$[MOA]^+[Tf_2N]^-$ + methanol + ethyl acetate} at the three temperatures. The V^E_{123} values are more negative for the {$[MOA]^+[Tf_2N]^-$ + methanol + ethyl acetate} system than for the {$[MOA]^+[Tf_2N]^-$ + methanol + methyl acetate} system at all temperatures and also decrease for both ternary systems with an increase in the temperature. The Cibulka equation indicated that the ternary contribution (three-body effect) is dominant.

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