Density, Speed of Sound, and Derived Thermodynamic Properties of Ionic Liquids $[EMIM]^+[BETI]^-$ or ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + Methanol or + Acetone) at T = (298.15 or 303.15 or 313.15) K

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The densities of binary and ternary mixtures were measured for the system 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide ($[EMIM]^+[BETI]^-$) + methanol or + acetone and $[EMIM]^+[BETI]^-$ + methanol + acetone, respectively, at T = (298.15, 303.15, and 313.15) K, and the speed of sound data for the binary system 1-ethyl-3-methylimidazolium diethyleneglycol monomethylethersulfate ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$) + methanol were measured at T = 298.15 K. The excess molar volumes were calculated from the experimental densities and were fitted to the Redlich-Kister equation for the binary system. The excess molar volumes, V_m^E, for the binary system ($[EMIM]^+[BETI]^-$ + methanol) were positive for low mole fractions of methanol, and for the binary system ($[EMIM]^+[BETI]^-$ + acetone), excess molar volumes were negative throughout the whole composition range. The ternary excess molar volumes were negative for all three temperatures. The isentropic compressibility for the binary system ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol) was negative over the entire composition range. The results have been interpreted in terms of the intermolecular interactions between the ionic liquid and the organic solvents.

Introduction

Ionic liquids (ILs) are liquid at room temperature (t < 100 °C).[1] They have been investigated as "green solvents" for electrochemistry, catalysts, solvent extraction, and extractive distillation.[2–9] Physico-chemical properties of ionic liquids have not been extensively investigated, and the molecular interactions between the ionic liquid and the organic molecules are not thoroughly understood. More recently, Meindersema[10] investigated the effect of the alkyl substituent on the properties of the ionic liquid for liquid-liquid extraction.

Zafarani-Moattar[11] has investigated the densities and speed of sound data for binary (1-butyl-3-methylimidazolium hexaflurophosphate + methanol or + acetonitrile). Esperança et al.[12] determined the density and speed of sound of pure 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide and 1-pentyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide at different temperatures and pressures. Esperança et al.[13] also determined the densities and excess molar volumes for a phosphonium-based IL. Ortega et al.[13] determined the density and excess molar volumes for a pyridinium IL with water, methanol, ethanol, 1-propanol, and 1-butanol over a range of temperatures. Densities and excess molar volumes were determined by Singh and Kumar[14] for binary dialkylimidazolium with a tetrafluoroborate anion. Iglesias et al.[16] reported the excess molar volumes and isentropic compressibilities for binary mixtures containing a new IL: 2-hydroxy ethyl ammonium formate + water or methanol or ethanol at different temperatures.

This work is a continuation of our research work on the physicochemical properties of ILs.[17–25] There is only one publication in the literature on the excess molar volumes of ternary mixtures containing ionic liquid with organic solvents.[25] The IL investigated in this work for the excess molar volumes represents an IL similar to the structure of the bis(trifluoromethylsulfonyl) imide anion except that an additional CF_2 group is in the anion structure for the $[BETI]^-$ ion. The thermal properties of the IL 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide ($[EMIM]^+[BETI]^-$) used in work was investigated by Ngo et al.[26] The structures of the ILs used in this work are given in Figure 1. The densities for the binary and ternary mixtures were determined for the systems 1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide ($[EMIM]^+[BETI]^-$) + methanol or + acetone and $[EMIM]^+[BETI]^-$ + methanol + acetone, respectively, at T = (298.15, 303.15, and 313.15) K, and the speed of sound data for the binary mixture 1-ethyl-3-methylimidazolium diethyleneglycol monomethylethersulfate ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$) + methanol were determined at T = 298.15 K. Methanol and acetone were used in this investigation because they are common solvents for background electrolytes in nonaqueous capillary electrophoresis.[27]

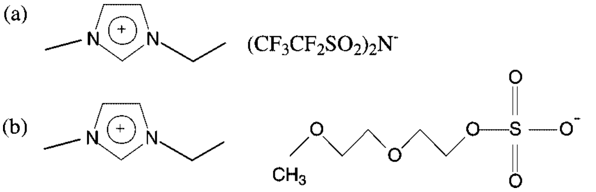

Figure 1. Structure of the ionic liquids. (a) 1-Ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide $[EMIM]^+[BETI]^-$. (b) 1-Ethyl-3-methylimidazolium diethyleneglycol monomethylethersulfate $[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$.

The excess molar volumes, V_m^E, and the isentropic compressibilities, k_S, have been derived from the experimental data. The calculated data are used to explain the intermolecular interactions between the IL and the organic molecules to relate structural modifications to the effectiveness of an IL for a particular purpose.[28,29]

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Table 1. Experimental Densities, ρ, and Excess Molar Volume, V_m^E, Data for the Binary System {1-Ethyl-3-methylimidazolium Bis(perfluoroethylsulfonyl)imide (($[EMIM]^+[BETI]^-$ + Methanol or Acetone)} at T = (298.15, 303.15, and 313.15) K

x_2	ρ / $(g \cdot cm^{-3})$	V_m^E / $(cm^3 \cdot mol^{-1})$	ρ / $(g \cdot cm^{-3})$	V_m^E / $(cm^3 \cdot mol^{-1})$	ρ / $(g \cdot cm^{-3})$	V_m^E / $(cm^3 \cdot mol^{-1})$
			$[EMIM]^+[BETI]^-$ (x_1) + Methanol (x_2)			
	T/K = 298.15		T/K = 303.15		T/K = 313.15	
0.0000	1.5932	0.00	1.5876	0.00	1.5767	0.00
0.0584	1.5862	0.06	1.5805	0.03	1.5695	0.06
0.1116	1.5794	0.08	1.5737	0.06	1.5626	0.10
0.1686	1.5713	0.11	1.5656	0.09	1.5545	0.13
0.2956	1.5497	0.14	1.544	0.12	1.5328	0.16
0.5104	1.4946	0.09	1.4889	0.07	1.4777	0.09
0.6083	1.4553	0.04	1.4496	0.02	1.4383	0.04
0.7060	1.3989	−0.01	1.3932	−0.02	1.3820	−0.03
0.8237	1.2859	−0.04	1.2802	−0.05	1.2693	−0.08
0.9033	1.1482	−0.04	1.1426	−0.05	1.1320	−0.08
1.0000	0.7866	0.00	0.7819	0.00	0.7726	0.00
			$[EMIM]^+[BETI]^-$ (x_1) + Acetone (x_2)			
	T/K = 298.15		T/K = 303.15		T/K = 313.15	
0.0000	1.5932	0.00	1.5873	0.00	1.5767	0.00
0.0807	1.5768	−0.08	1.5711	−0.10	1.5602	−0.11
0.1417	1.5631	−0.15	1.5574	−0.18	1.5464	−0.19
0.2521	1.5346	−0.33	1.5288	−0.35	1.5177	−0.39
0.2791	1.5266	−0.36	1.5208	−0.39	1.5096	−0.42
0.4150	1.4792	−0.53	1.4733	−0.56	1.4622	−0.66
0.5195	1.4318	−0.68	1.4258	−0.72	1.4148	−0.86
0.5676	1.4055	−0.76	1.3995	−0.79	1.3884	−0.94
0.7092	1.3031	−0.92	1.2972	−0.98	1.2857	−1.12
0.7550	1.2582	−0.92	1.2522	−0.98	1.2408	−1.13
0.8137	1.1884	−0.89	1.1825	−0.95	1.1708	−1.08
0.8927	1.0620	−0.72	1.0559	−0.75	1.0443	−0.87
0.9502	0.9350	−0.50	0.9291	−0.53	0.9176	−0.62
1.000	0.7841	0.00	0.7784	0.00	0.7669	0.00

Experimental

The ionic liquids were supplied by Solvent Innovation and Associated Solvents and had a quoted mass fraction > 98 %. The acetone was supplied by Merck and had a quoted mass fraction of 99.9 % and was used as is. Methanol was dried by refluxing with Grignard reagents ($Mg + I_2$) for 6 h and then distilled over 4 nm molecular sieves. The methanol was stored in a desiccator with molecular sieves. The ionic liquid once opened was stored in a desiccator and sealed with parafilm to prevent any absorption of moisture. The water content was determined by Karl Fischer titration (DL 35 Mettler Toledo) for the ionic liquids $[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ and $[EMIM]^+[BETI]^-$, and the mass fraction was 0.16 % and 0.06 %, respectively.

For each density determination, a known mass of ionic liquid was first injected into a sealed glass vial. The second component was then injected into the vial through a stopper by means of a syringe. In this way, the loss of solvent was minimized. The mass of each component was determined on an Ohaus mass balance which had an accuracy of 0.0001 g. The mixtures were injected into an Anton Paar digital vibrating glass tube densimeter (model DMA 38), and the density readings obtained at each temperature were obtained with a precision of 0.0002 $g \cdot cm^{-3}$. The temperature of the densimeter was controlled by means of a built-in thermostat (a semiconductor Peltier element and a resistance thermometer control system). Dry air and distilled water were used as reference fluids to calibrate the densimeter at each temperature. The uncertainty in ρ is less than 0.0004 $g \cdot cm^{-3}$ and in V_m^E less than 0.002 $cm^3 \cdot mol^{-1}$. The uncertainty in temperature was ± 0.1 K.

The speed of sound (u) for the binary system ($[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol) was measured at T = 298.15 K and at atmospheric pressure. The sound measurements were made with a crystal controlled Mittal ultrasonic interferometer (M-81G) at a frequency of 3 MHz. The precision of the speed of sound data was ± 0.5 $m \cdot s^{-1}$, and the uncertainty was 1 $m \cdot s^{-1}$. Isentropic compressibilities were determined for the test system (hexane + 1-butanol) to validate the technique. The uncertainty in the isentropic compressibilities, k_S, is estimated to be less than 2 TPa^{-1}.

Results and Discussion

The density and excess molar volumes for the binary system ($[EMIM]^+[BETI]^-$ + methanol or + acetone) for each temperature are given in Table 1. The excess molar volumes for the binary system were calculated from eq 1 using the experimental densities of the mixture and the pure components.

$$V_m^E = \frac{x_1 M_1 + x_2 M_2}{\rho} - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \qquad (1)$$

where x_1 and x_2 are mole fractions; M_1 and M_2 denote molar masses; ρ_1 and ρ_2 are the densities of the pure components, ionic liquid and methanol or acetone, respectively; and ρ is the density of the binary system.

The binary experimental data was fitted to the Redlich-Kister equation below

$$V_m^E/(cm^3 \cdot mol^{-1}) = x_1(1 - x_1)\sum_{i=0}^{N} A_i(2x_1 - 1)^i \qquad (2)$$

where A_i is the polynomial coefficient and N is the polynomial degree.

The standard deviations $\sigma(V_m^E)$ is defined as

Table 2. Experimental Densities, ρ, and Excess Molar Volume, V_m^E, Data for the Ternary System {1-Ethyl-3-methylimidazolium Bis(perfluoroethylsulfonyl)imide {($[EMIM]^+[BETI]^-$ (1) + Methanol (2) + Acetone (3))} at T = (298.15, 303.15, and 313.15) K

thermodynamic properties	mole fraction (x_1)	mole fraction (x_2)	T/K = 298.15	T/K = 303.15	T/K = 313.15
$\rho/(g\cdot cm^{-3})$	0.0211	0.7657	0.8894	0.8841	0.8735
$V_m^E/(cm^3\cdot mol^{-1})$			−0.33	−0.34	−0.35
$\rho/(g\cdot cm^{-3})$	0.0245	0.6613	0.8975	0.8922	0.8813
$V_m^E/(cm^3\cdot mol^{-1})$			−0.40	−0.42	−0.44
$\rho/(g\cdot cm^{-3})$	0.0272	0.2130	0.8825	0.8770	0.8657
$V_m^E/(cm^3\cdot mol^{-1})$			−0.45	−0.49	−0.55
$\rho;/(g\cdot cm^{-3})$	0.0549	0.4019	0.9781	0.9724	0.9610
$V_m^E/(cm^3\cdot mol^{-1})$			−0.54	−0.57	−0.62
$\rho/(g\cdot cm^{-3})$	0.0795	0.5957	1.0640	1.0584	1.0471
$V_m^E/(cm^3\cdot mol^{-1})$			−0.46	−0.49	−0.53
$\rho/(g\cdot cm^{-3})$	0.1454	0.5467	1.1941	1.1884	1.1767
$V_m^E/(cm^3\cdot mol^{-1})$			−0.45	−0.48	−0.51
$\rho/(g\cdot cm^{-3})$	0.1999	0.6292	1.2871	1.2812	1.2699
$V_m^E/(cm^3\cdot mol^{-1})$			−0.25	−0.26	−0.30
$\rho/(g\cdot cm^{-3})$	0.2294	0.1188	1.2533	1.2475	1.2356
$V_m^E/(cm^3\cdot mol^{-1})$			−0.69	−0.75	−0.83
$\rho/(g\cdot cm^{-3})$	0.2818	0.4481	1.3501	1.3441	1.3328
$V_m^E/(cm^3\cdot mol^{-1})$			−0.36	−0.37	−0.43
$\rho/(g\cdot cm^{-3})$	0.3221	0.2227	1.3548	1.3490	1.3373
$V_m^E/(cm^3\cdot mol^{-1})$			−0.53	−0.58	−0.64
$\rho/(g\cdot cm^{-3})$	0.4927	0.2348	1.4633	1.4576	1.4459
$V_m^E/(cm^3\cdot mol^{-1})$			−0.31	−0.34	−0.34
$\rho/(g\cdot cm^{-3})$	0.5038	0.0711	1.4502	1.4445	1.4328
$V_m^E/(cm^3\cdot mol^{-1})$			−0.47	−0.52	−0.55
$\rho/(g\cdot cm^{-3})$	0.5472	0.2722	1.4923	1.4867	1.4751
$V_m^E/(cm^3\cdot mol^{-1})$			−0.18	−0.21	−0.20
$\rho/(g\cdot cm^{-3})$	0.6055	0.3074	1.5192	1.5135	1.5022
$V_m^E/(cm^3\cdot mol^{-1})$			−0.07	−0.07	−0.07

Table 3. Redlich-Kister Parameters, A_i, and the Standard Deviation, ρ, for the Binary System {1-Ethyl-3-methylimidazolium Bis(perfluoroethylsulfonyl)imide {($[EMIM]^+[BETI]^-$ + Methanol or Acetone)} at T = (298.15, 303.15, and 313.15) K

T	A_o	A_1	A_2	A_3	A_4	$\sigma/cm^3\cdot mol^{-1}$
			$[EMIM]^+[BETI]^-$ + Methanol			
298.15 K	0.381	0.873	−0.275	−0.151	−0.044	0.002
303.15 K	0.292	0.896	−0.250	−0.313	−0.280	0.002
313.15 K	0.353	0.993	−0.132	0.347	−0.455	0.006
			$[EMIM]^+[BETI]^-$ + Acetone			
298.15 K	−2.66	2.56	−2.19	2.59	−1.32	0.023
303.15 K	−2.78	2.77	−2.65	2.54	−1.04	0.025
313.15 K	−3.33	3.29	−1.88	2.92	−2.78	0.029

$$\sigma(V_m^E) = \left[\sum_{i=1}^{N} \frac{(V_{m,exp}^E - V_{m,cal}^E)^2}{n-k}\right]^{1/2} \tag{3}$$

where n is the number of experimental points and k is the number of coefficients used in the Redlich-Kister correlation. The Redlich-Kister coefficients are given in Table 3 together with the standard deviations. The experimental data for the excess molar volumes for binary systems (1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide ($[EMIM]^+[BETI]^-$ + acetone) and (1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide ($[EMIM]^+[BETI]^-$ + methanol) have been plotted in Figures 2 and 3.

Molar excess volumes, V_m^E, for the ternary system were calculated from experimental densities using eq 4

$$V_m^E = \frac{x_1M_1 + x_2M_2 + x_3M_3}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_1M_2}{\rho_2} - \frac{x_3M_3}{\rho_3} \tag{4}$$

where x_1, x_2, and x_3 are mole fractions; M_1, M_2, and M_3 denote molar masses; ρ_1, ρ_2, and ρ_3 are the densities of the pure components 1, 2, and 3, respectively; and ρ is the density of the ternary system. Experimental densities and the calculated excess molar volumes are given in Table 2.

V_m^E of $[EMIM]^+[BETI]^-$ + Acetone. The V_m^E is negative for all temperatures, decreasing with an increase in temperature; i.e., V_m^E at T = 298.15 K > T = 303.15 K > T = 313.15 K with $V_{m,min}^E$ occurring at a high mole fraction of acetone similar to the findings for $[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + methanol (see Figure 2).[20] $V_{m,min}^E$ values for T = 298.15 K, T = 303.15 K, and T = 313.15 K are −0.920 $cm^3\cdot mol^{-1}$, −0.975 $cm^3\cdot mol^{-1}$, and −1.133 $cm^3\cdot mol^{-1}$, respectively. The values are similar ($V_{m,min}^E$ ranged from (−0.55 to −1.2) $cm^3\cdot mol^{-1}$) to that obtained by Singh and Kumar for a dialkylimidazolium cation with a $[BF_4]^-$anion.[15]

V_m^E of $[EMIM]^+[BETI]^-$ + Methanol. V_m^E values for $x_1 \leq 0.294$ are negative for all temperatures and also decrease with temperature for the same composition. V_m^E values for $x_1 > 0.294$ are positive, but the V_m^E values increase in the order T = 303.15 K < T = 298.15 K < T = 313.15 K (see Figure 3). In the IL-rich region, the positive V_m^E is probably due to breakdown effects of the intramolecular hydrogen bonding in the methanol molecules, and for the high mole fraction of methanol ($x_2 \geq 0.7$), the breakdown of intramolecular hydrogen bonds is less than the association effects between the IL and methanol

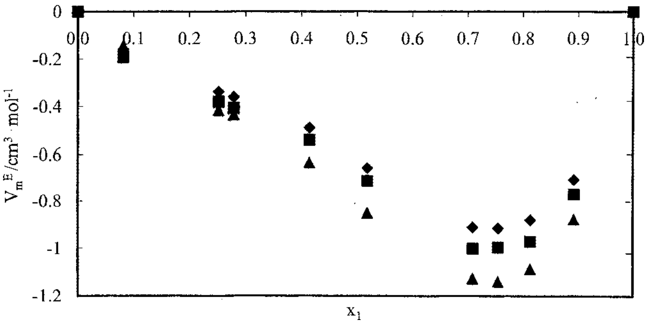

Figure 2. Excess molar volumes for binary system (1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide $[EMIM]^+[BETI]^-$ + acetone); ◆, T = 298.15 K; ■, T = 303.15 K; ▲, T = 313.15 K.

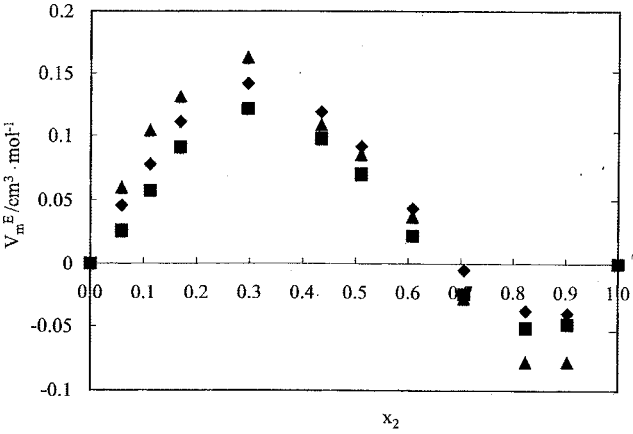

Figure 3. Excess molar volumes for binary system (1-ethyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide $[EMIM]^+[BETI]^-$ + acetone): ◆, T = 298.15 K; ■, T = 303.15 K; ▲, T = 313.15 K.

molecules. A more favorable packing of the IL in the vast hydrogen bonded methanol matrix can also contribute to the negative V_m^E. In the literature, V_m^E values for an (IL + methanol) were for $[BF_4]^-$, $[PF_6]^-$, or $[CH_3(OCH_2CH_2)_2OSO_3]^-$, $[OOCH]^-$ anions. There is no similar anion in the literature for which V_m^E data are published with which a suitable comparison can be made.

V_m^E of $[EMIM]^+[BETI]^-$ + Methanol + Acetone. The ternary V_m^E is negative for all compositions of the IL and decreases with an increase in temperature. The smaller acetone and methanol molecules are probably incorporated into the vast IL matrix (a packing effect) which is further enhanced by intermolecular hydrogen bonding between the methanol and acetone molecules and ion-dipole interactions between the IL ions and the acetone and methanol molecules (structural effect).

k_S $[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ + Methanol. The isentropic compressibilities, k_s, were calculated from the Newton-Laplace equation

$$k_s = \frac{1}{\rho u^2} \tag{5}$$

$$\Delta Q = Q - \sum_{i=1}^{2} x_i Q_i \tag{6}$$

The isentropic compressibilities deviation, Δk_s, and the speed of sound deviations, Δu, were evaluated for each composition point using eqs 5 and 6 where Q is k or u and ΔQ is the property Δk_s or Δu and the quantities with subscripts refer to the pure liquids. Tables 4 give the densities, ρ, speeds of sound, u, isentropic compressibilities, k_s, change in isentropic compressibilities, Δk_s, speed of sound deviations, Δu, Redlich-Kister parameters, A_i, and standard deviation, σ, for the binary mixture $\{[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ (x_1) + methanol $(x_2)\}$ at T = 298.15 K. The densities for the binary mixture $\{[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ (x_1) + methanol $(x_2)\}$were taken from an earlier paper.[20]

The densities and speed of sound do not vary much in the IL-rich region ($x_2 < 0.5$), but with increasing methanol mole fractions, there is a rapid decrease in the speed of sound. The decrease in densities and the speed of sound leads to an inverse increase in the isentropic compressibilities with increasing methanol mole fraction. The Δk_s values are large and negative, whereas the speed of sound deviations are large and positive over the entire composition range. The negative Δk_s values indicate the dominance of weak but structure making interactions between methanol and $[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$; i.e., when methanol is mixed with $[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$, ion–dipole interactions will tend to occur between the methanol molecules and the imidazolium ring of the IL. This reduces the ionic bonding between the cation and anion of the IL leading to a negative Δk_s. Asymmetric Δk_s and Δu are skewed toward the higher mole fraction region of the methanol. The minimum Δk_s and maximum Δu values lie in the methanol-rich region. We can postulate a 2-fold reason for this: (1) the stronger interactions exit between the methanol and the IL due to ion–dipole interactions and (2) a larger number of the smaller methanol molecules are accommodated into the ionic liquid structure.

Table 4. Densities, ρ, Speed of Sound, u, Isentropic Compressibilities, k_s, Isentropic Compressibility Deviations, Δk_s, Speed of Sound Deviations, Δu, Redlich-Kister Parameters, A_i, and Standard Deviation, σ, for the Binary System $\{[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-(x_1)$ + Methanol $(x_2)\}$ at T = 298.15 K

	ρ	u	k_s	Δk_s	Δu
x_2	(g·cm^{-3})	(m·s^{-1})	(TPa^{-1})	(TPa^{-1})	(m·s^{-1})
$\{[EMIM]^+[CH_3(OCH_2CH_2)_2OSO_3]^-$ (x_1) + Methanol $(x_2)\}$					
0.1791	1.2220[a]	1677.6	291	−124	79
0.3560	1.2025[a]	1647.0	307	−244	155
0.4548	1.1874[a]	1620.0	321	−305	188
0.5356	1.1716[a]	1597.2	335	−353	213
0.6298	1.1473[a]	1563.6	357	−403	237
0.7412	1.1050[a]	1499.4	403	−442	239
0.7987	1.0722[a]	1453.2	442	−447	228
0.8527	1.0314[a]	1387.5	504	−427	195
0.9011	0.9807[a]	1324.8	581	−386	161
0.9298	0.9408[a]	1270.8	658	−331	125
0.9620	0.8831[a]	1201.2	785	−229	74
0.9829	0.8356[a]	1158.0	892	−138	44

	A_o	A_1	A_2	A_3	$\sigma\Delta k_s$/TPa^{-1}
Δk_s/(TPa^{-1})	−86.8	75.2	50.9	43.0	0.7

[a] Data from Deenadayalu.[20]

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