

Binary mixtures containing imidazolium ionic liquids: properties measurement

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Abstract: Densities and transport properties (dynamic viscosity) of pure imidazolium ionic liquids 1-butyl-3-methylimidazolium acetate and 1-butyl-3-methylimidazolium dicyanamide and their binary mixtures with water and ethanol were measured within the temperature range of 293.15–333.15 K. Obtained experimental data were used to calculate excess molar volume and viscosity deviation. For the chosen binary mixtures, variations of excess molar volume, partial molar volumes of mixture components and of the viscosity deviation with the binary mixture composition were correlated using the Redlich-Kister equation. In addition, variation of viscosity with the binary mixture composition and temperature was fitted using the Jouyban-Acree model.

Keywords: Imidazolium ionic liquids, density, dynamic viscosity, excess molar volume, viscosity deviation, Redlich-Kister equation, Jouyban-Acree equation

Introduction

Ionic liquids (ILs) are characterized as salts in the liquid state (molten salts) that present several interesting properties (Welton, 1999). Especially, their negligible saturated vapor pressure over a large temperature range makes ILs different compared to commercially used ‘traditional’ solvents. Although, ILs are considered novel solvents in chemical technology, they already have found application or have been indicated as interesting medium for numerous processes, e.g. in carbon capture (Galán Sánchez et al., 2007), absorption of sour gases (Zeng et al., 2014), construction of fuel cells (Armand et al., 2009), separations of interesting metabolites from aqueous media (Perreiro et al., 2012; Gracsová & Steltenpohl, 2015), as extraction solvents in petroleum and hydrocarbon industries (Meindersma et al., 2010) or as a solvent and, at the same time, a catalyst for organic syntheses (Greaves & Drummond, 2008), etc.

The success of ILs application dwells in their unique thermophysical and phase-equilibria properties. It is further busted by the versatility of ILs synthesis that allows preparing tailor-made ionic liquids for each application (Nieto de Castro et al., 2010). Among others, volumetric and transport properties of ILs are important in the analysis of fluid flow as well as in chemical-engineering correlations and heat-transfer calculations (Bajić et al., 2014).

Although several computer-based contribution procedures for the prediction of the properties of ILs and their mixtures have recently been developed, experimental estimation of these properties is applied as an approval of computed properties

as well as a new input for the calculation procedure database (Jacquemin et al., 2008).

Here, density and viscosity of two ionic liquids, 1-butyl-3-methylimidazolium acetate ([bmim]Ac) and 1-butyl-3-methylimidazolium dicyanamide ([bmim]DCA) and their binary mixtures with water and with ethanol at temperatures of 20 °C, 40 °C and 60 °C are presented. Experimental data were correlated in terms of excess molar volume and the density difference was determined by the Redlich-Kister equation (Redlich & Kister, 1948). Viscosity data were also correlated using the Jouyban-Acree model (Acree, 1992).

Theoretical

Volumetric properties of the binary mixtures of chosen ionic liquids with water and ethanol were expressed as excess molar volumes and component partial molar volumes. Variation of the excess molar volumes of binary mixtures and that of component partial molar volumes with the mixture composition were correlated using the Redlich-Kister equation (Redlich & Kister, 1948).

Excess properties represent deviation of the binary liquid mixture behavior from that of the ideal mixture. Excess molar volume, V^E , is defined by the following equation:

$$V^E = V_m - \sum_i x_i V_i^* \quad (1)$$

where V_m represents the mixture molar volume, x_i is the mole fraction of i -th component of the binary mixture and V_i^* is the i -th component’s molar volume.

Molar volumes of binary mixtures and that of pure

component i ($x_i = 1$) were computed using experimental density values (Eq. (2)).

$$V_m = \frac{\sum_i x_i M_i}{\rho} \quad (2)$$

The excess molar volume values are frequently correlated using the Redlich-Kister equation that adopts the following form:

$$V^E = x_1 x_2 \sum_n C_n (x_1 - x_2)^{n-1} \quad (3)$$

C_n being the model parameters and n the polynomial order.

Partial molar volumes of mixture components, \bar{V}_i , were expressed in the following form (see e.g. Wood & Battino, 1990).

$$\bar{V}_i = V^E + V_i^* + (1 - x_i) \left(\frac{\partial V^E}{\partial x_i} \right)_{p,T} \quad i = 1, 2 \quad (4)$$

The term representing the variation of excess molar volume with mixture composition was derived by differentiating Eq. (3).

Viscosity of the studied binary mixtures was fitted either in terms of density differences variation with mixture composition using the Redlich-Kister equation or directly applying the Jouyban-Acree model equation.

Viscosity deviation, $\Delta\eta$, expresses the difference between the measured binary mixture viscosity and the value computed as linear combination of pure components' viscosities (Eq. (5)).

$$\Delta\eta = \eta_m - \sum_i x_i \eta_i \quad (5)$$

where η_m is the measured mixture viscosity and η_i is the i -th component viscosity.

The Redlich-Kister equation used to correlate the viscosity difference is given as:

$$\Delta\eta = x_1 x_2 \sum_n C_n (x_1 - x_2)^{n-1} \quad (6)$$

Viscosity variation with the mixture composition and temperature was also correlated using the Jouyban-Acree equation in the following form:

$$\ln \eta_{m,T} = \sum_i x_i \ln \eta_{i,T} + x_1 x_2 \sum_n J_n \frac{(x_1 - x_2)^{n-1}}{T} \quad (7)$$

where J_n represents the model parameters, n is the polynomial order and T stands for thermodynamic temperature.

The values of model parameters given in Eqs. (3), (6) and (7) were obtained by minimizing objective function, OF , as follows:

$$OF = \sum_N (Y_{\text{exp},j} - Y_{\text{calc},j})^2 = \min \quad (8)$$

$Y_{\text{exp},j}$ and $Y_{\text{calc},j}$ are experimental and computed values of the excess molar volume, viscosity difference and viscosity, respectively, and N is the number of experimental points.

Standard residual deviations of experimental data, σ_Y , were calculated as follows:

$$\sigma_Y = \left(\sum_N \frac{(Y_{\text{exp},j} - Y_{\text{calc},j})^2}{N - n} \right)^{1/2} \quad (9)$$

Experimental

Both ionic liquids used in this study were purchased from Iolitec, USA. De-ionized water was used for the aqueous solutions preparation. Absolute ethanol (purity above 99.9 %) was supplied by Slavus, Slovakia. Basic data of these chemicals are collected in Table 1.

Samples of supplied ionic liquids were purified using a laboratory film evaporator MO 15 (Agrokombinát Lehnice, Slovakia). After purification at the pressure of 1.4–1.8 kPa and temperature of 150–170 °C, the content of water in [bmim]Ac and [bmim]DCA ILs decreased to 0.1835 mass % and 0.0595 mass %, respectively (Graczová et al., 2020). Water content in purified IL samples was estimated using a Karl Fischer titrator (Mettler Toledo DL53).

Binary mixtures were prepared by precisely weighing individual mixture components using a Mettler AE 200 analytical balance. Accuracy of the mass reading was $\pm 1 \times 10^{-4}$ g.

Tab. 1. Basic data of studied chemicals.

Component	CAS	$M/(\text{kg}\cdot\text{mol}^{-1})$	Declared purity
[bmim]Ac	284049-75-8	0.19826	> 98 mass %
[bmim]DCA	448245-52-1	0.20526	> 99 mass %
water	7732-18-5	0.01802	de-ionized
ethanol	64-17-5	0.04607	> 99.9 mass %

Density of samples containing selected ionic liquids at ambient pressure was measured using an Anton Paar Densimeter DMA 5000. Declared standard uncertainty of density measurements using this equipment was $\pm 2 \times 10^{-2} \text{ kg}\cdot\text{m}^{-3}$. Densities of the prepared binary mixtures were determined at 20 °C, 40 °C and 60 °C. Accuracy of the temperature reading was $\pm 1 \times 10^{-3} \text{ }^\circ\text{C}$.

Estimation of transport properties of the samples was carried out using a Malvern Kinexus parallel plate rheometer. Viscosities of the prepared binary mixtures were determined at 20 °C, 40 °C and 60 °C. Accuracy of the temperature reading was $\pm 1 \times 10^{-2} \text{ }^\circ\text{C}$.

Results and Discussion

Measured densities and viscosities of pure components at chosen temperatures are summarized in Tables 2 and 3, respectively. For comparison literature data are also included.

Results of the excess molar volume and partial molar volume calculation for the four binary systems [bmim]Ac (1)–water (2), [bmim]DCA (1)–water (2), [bmim]Ac (1)–ethanol (2) and [bmim]DCA (1)–ethanol (2) are given in Tables 4–7, respectively.

Optimum values of the Redlich-Kister equation parameters used for the experimental excess molar

Tab. 2. Experimental and literature densities of components at chosen temperatures.

Component	Density, $\rho/(\text{kg}\cdot\text{m}^{-3})$						Source
	experimental			literature			
	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	
[bmim]Ac	1054.48	1042.26	1030.49	1054.3	1042.0	1029.9	Harris, 2020
[bmim]DCA	1063.30	1050.60	1038.16	1063.4	1050.6	1038.2	Almeida et al., 2016
water	998.22	-	-	998.22	991.29	973.05	NIST database
ethanol	789.59	772.22	754.14	789.45	772.44	754.30	NIST database

Tab. 3. Experimental and literature viscosities of components at chosen temperatures.

Component	Dynamic viscosity, $\eta/(\text{mPa}\cdot\text{s})$						Source
	experimental			literature			
	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	
[bmim]Ac	418.09	110.45	42.19	562.4	136.6	48.77	Harris, 2020
[bmim]DCA	35.04	16.83	9.65	36.83	17.86	10.38	Almeida et al., 2016
water	1.001	-	-	1.002	0.653	0.466	NIST database
ethanol	1.139	-	-	1.144	0.794	0.570	NIST database

Tab. 4. Excess molar volume of the binary system [bmim]Ac (1)–water (2) and component partial molar volumes at 20 °C, 40 °C and 60 °C.

Sample	Composition		$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_1/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_2/(\text{cm}^3\cdot\text{mol}^{-1})$		
	x_1	x_2	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
1	0.0808	0.9192	-0.9117	-0.7800	-0.6743	181.30	184.10	186.82	16.58	17.23	17.86
2	0.2044	0.7956	-1.3560	-1.2376	-1.1359	184.39	186.53	188.71	15.92	16.66	17.35
3	0.2864	0.7136	-1.5083	-1.4274	-1.3562	186.20	188.16	190.21	15.69	16.31	16.88
4	0.3662	0.6338	-1.5038	-1.4526	-1.4046	187.00	188.98	191.03	15.66	16.13	16.59
5	0.4230	0.5770	-1.4204	-1.3967	-1.3720	187.53	189.57	191.67	15.66	16.00	16.36
6	0.5255	0.4745	-1.2379	-1.2457	-1.2451	187.91	190.03	192.16	15.69	15.90	16.18
7	0.5970	0.4030	-0.9493	-0.9666	-1.0088	188.13	190.31	192.46	15.73	15.85	16.07
8	0.6733	0.3267	-0.7279	-0.7642	-0.8062	188.20	190.41	192.57	15.80	15.88	16.04
9	0.7439	0.2561	-0.5015	-0.5251	-0.5674	188.20	190.41	192.58	15.91	15.98	16.07

Tab. 5. Excess molar volume of the binary system [bmim]DCA (1)–water (2) and component partial molar volumes at 20 °C, 40 °C and 60 °C.

Sample	Composition		$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_1/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_2/(\text{cm}^3\cdot\text{mol}^{-1})$		
	x_1	x_2	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
1	0.0962	0.9038	0.0336	0.1536	0.2584	193.34	196.40	199.36	17.99	18.47	18.98
2	0.1968	0.8032	0.0723	0.2210	0.3521	193.34	195.87	198.37	17.98	18.50	19.10
3	0.2977	0.7023	0.1079	0.2517	0.3796	193.29	195.65	198.00	18.02	18.40	18.98
4	0.3774	0.6226	0.1296	0.2608	0.3777	193.25	195.58	197.91	18.06	18.30	18.87
5	0.4598	0.5402	0.1484	0.2633	0.3668	193.19	195.54	197.87	18.11	18.22	18.80
6	0.5387	0.4613	0.1546	0.2540	0.3445	193.15	195.49	197.82	18.18	18.17	18.80
7	0.6158	0.3842	0.1577	0.2414	0.3181	193.11	195.44	197.76	18.25	18.15	18.87
8	0.6976	0.3024	0.1499	0.2174	0.2811	193.07	195.38	197.69	18.35	18.15	18.99

Tab. 6. Excess molar volume of the binary system [bmim]Ac (1)–ethanol (2) and component partial molar volumes at 20 °C, 40 °C and 60 °C.

Sample	Composition		$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_1/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_2/(\text{cm}^3\cdot\text{mol}^{-1})$		
	x_1	x_2	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
1	0.0999	0.9001	-0.6905	-0.8106	-1.0047	184.23	185.69	186.77	56.07	57.05	57.94
2	0.2002	0.7998	-0.8131	-0.9677	-1.2045	186.98	188.90	190.74	55.88	56.80	57.59
3	0.2991	0.7009	-0.7933	-0.9523	-1.1917	187.72	189.83	191.94	56.46	57.41	58.30
4	0.3787	0.6213	-0.7620	-0.9173	-1.1462	187.81	189.95	192.11	56.93	57.94	58.95
5	0.4598	0.5402	-0.6860	-0.8311	-1.0415	187.83	189.98	192.14	57.20	58.27	59.37
6	0.5300	0.4700	-0.6089	-0.7438	-0.9357	187.93	190.07	192.22	57.25	58.34	59.48
7	0.6105	0.3895	-0.4905	-0.6126	-0.7799	188.12	190.26	192.42	57.16	58.25	59.38
8	0.6893	0.3107	-0.3780	-0.4901	-0.6338	188.31	190.46	192.65	57.10	58.15	59.24
9	0.7580	0.2420	-0.2202	-0.3271	-0.4568	188.41	190.58	192.79	57.25	58.23	59.26

Tab. 7. Excess molar volume of the binary system [bmim]DCA (1)–ethanol (2) and component partial molar volumes at 20 °C, 40 °C and 60 °C.

Sample	Composition		$V^E/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_1/(\text{cm}^3\cdot\text{mol}^{-1})$			$\bar{V}_2/(\text{cm}^3\cdot\text{mol}^{-1})$		
	x_1	x_2	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C	20 °C	40 °C	60 °C
1	0.0999	0.9001	-0.7147	-0.8060	-0.9690	188.44	190.12	191.43	56.59	57.70	58.73
2	0.1999	0.8001	-0.9297	-1.0623	-1.2737	191.17	193.17	195.09	56.18	57.22	58.16
3	0.2999	0.7001	-0.9919	-1.1379	-1.3609	192.30	194.47	196.64	56.38	57.43	58.42
4	0.3799	0.6201	-0.9351	-1.0778	-1.2919	192.63	194.87	197.11	56.67	57.73	58.79
5	0.4599	0.5401	-0.8643	-0.9983	-1.1967	192.75	195.03	197.30	56.91	57.98	59.09
6	0.5399	0.4601	-0.7660	-0.8863	-1.0628	192.81	195.11	197.40	57.03	58.11	59.24
7	0.6199	0.3801	-0.6531	-0.7564	-0.9068	192.88	195.19	197.50	57.02	58.09	59.21
8	0.6999	0.3001	-0.5618	-0.6465	-0.7695	192.96	195.28	197.62	56.91	57.97	59.07
9	0.7699	0.2301	-0.4342	-0.5002	-0.5953	193.02	195.35	197.71	56.79	57.84	58.92

volume data correlation are collected in Table 8. For all binaries, the polynomial order $n = 4$ was chosen when fitting the experimental excess molar volume data. In Table 8, also the values of standard residual deviations are included for each temperature considered.

In Figs. 1–4, variation of excess molar volume and excess partial molar volume of individual components vs. mixture composition is presented for the four chosen binary systems [bmim]Ac (1)–water (2), [bmim]DCA (1)–water (2), [bmim]Ac (1)–ethanol (2) and [bmim]DCA (1)–ethanol (2), respectively.

Tab. 8. Summary of excess molar volume correlation: optimum values of the 4th order Redlich-Kister model parameters and computed standard residual deviations.

Parameter	$t/^\circ\text{C}$	Binary system			
		[bmim]Ac–H ₂ O	[bmim]DCA–H ₂ O	[bmim]Ac–EtOH	[bmim]DCA–EtOH
C_1	20	-5.1965	0.5873	-2.5619	-3.2508
	40	-5.1764	1.0128	-3.1109	-3.7604
	60	-5.1341	1.3966	-3.8984	-4.5076
C_2	20	4.2619	0.1953	1.8712	2.2216
	40	3.7574	-0.1648	2.1168	2.5610
	60	3.2671	-0.4707	2.5707	3.0560
C_3	20	-1.2705	-0.0082	-1.1302	-2.5380
	40	-0.3172	0.4307	-1.7937	-2.7773
	60	0.1388	0.8361	-2.6434	-3.2685
C_4	20	1.1405	0.0925	5.2082	2.1527
	40	0.4904	-0.5811	5.4482	2.3043
	60	-0.3272	-1.1345	6.1911	2.9074
$\sigma_{V^E}/(\text{cm}^3 \cdot \text{mol}^{-1})$	20	0.0237	0.0010	0.0196	0.0163
	40	0.0213	0.0023	0.0226	0.0166
	60	0.0162	0.0039	0.0285	0.0195

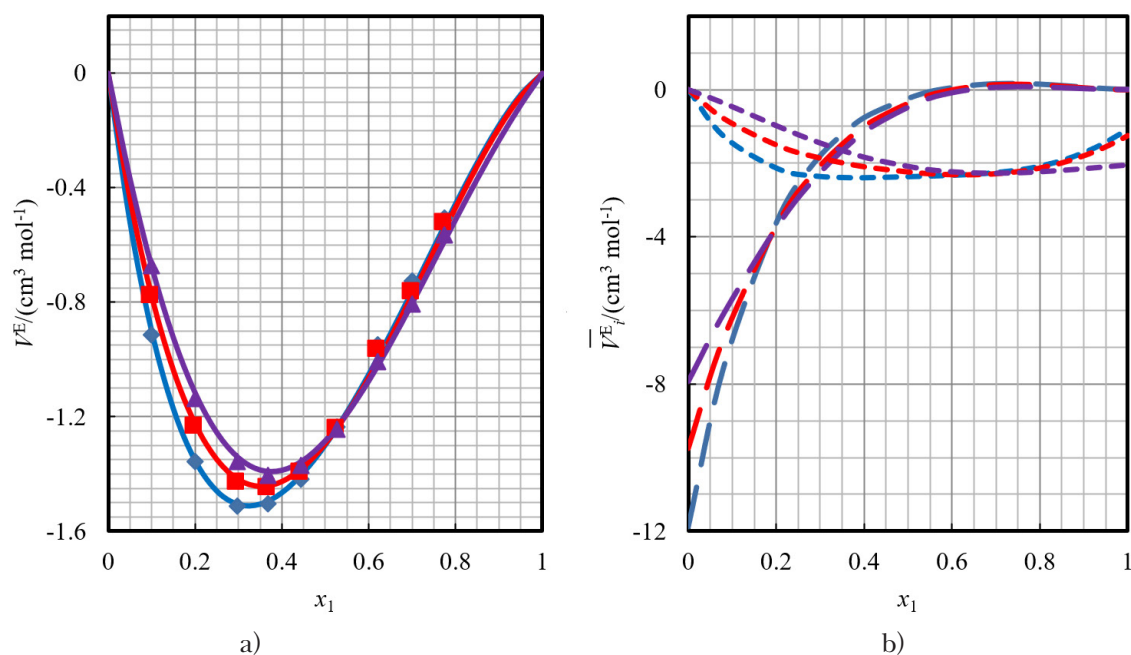


Fig. 1. Variation of a) excess molar volume of binary mixture [bmim]Ac (1)–water (2) and b) components excess partial molar volumes with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values; values for IL (dashed line) and water (dotted line).

Excess partial molar volumes of the respective components are defined as follows.

$$\bar{V}_i^E = \bar{V}_i - V_i^* \quad (10)$$

Results of the viscosity difference calculation according to Eq. (5) are presented in Tables 9–12 for binaries [bmim]Ac (1)–water (2), [bmim]DCA (1)–water (2), [bmim]Ac (1)–ethanol (2) and [bmim]DCA (1)–ethanol (2), respectively.

Optimum values of the Redlich-Kister equation parameters used for the experimental viscosity difference data correlation are collected in Table 13. For all binary systems considered, the polynomial order $n = 4$ was chosen when fitting the experimental viscosity difference data. In Table 13, also the values of standard residual deviations are included separately for each temperature.

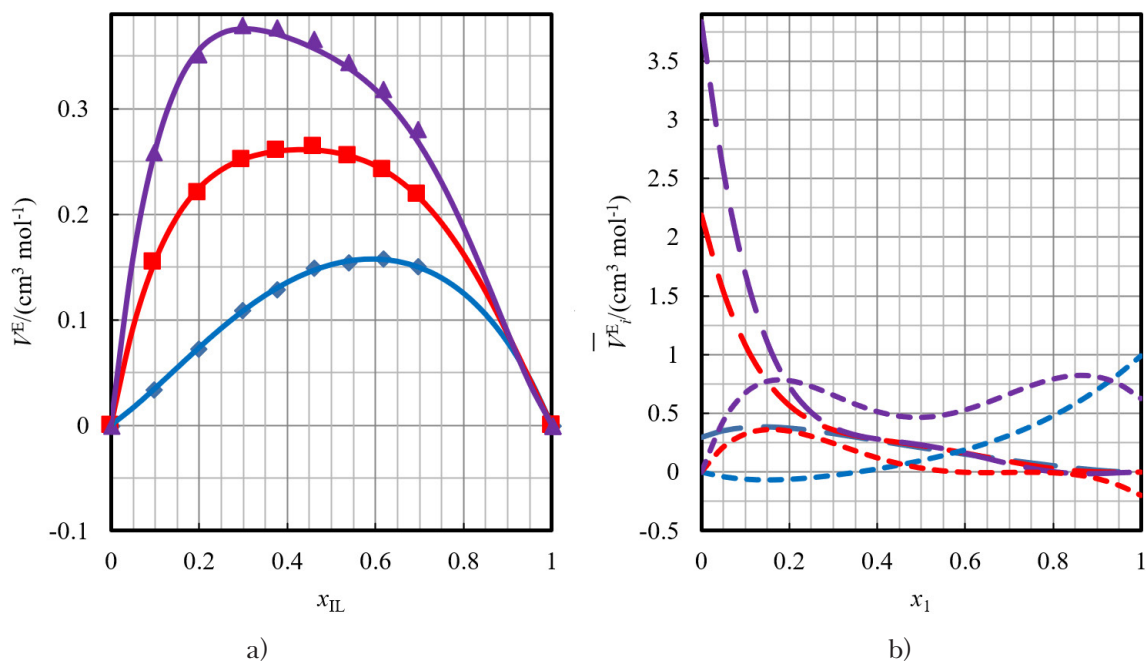


Fig. 2. Variation of a) excess molar volume of binary mixture [bmim]DCA (1)–water (2) and b) components excess partial molar volumes with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values; values for IL (dashed line) and water (dotted line).

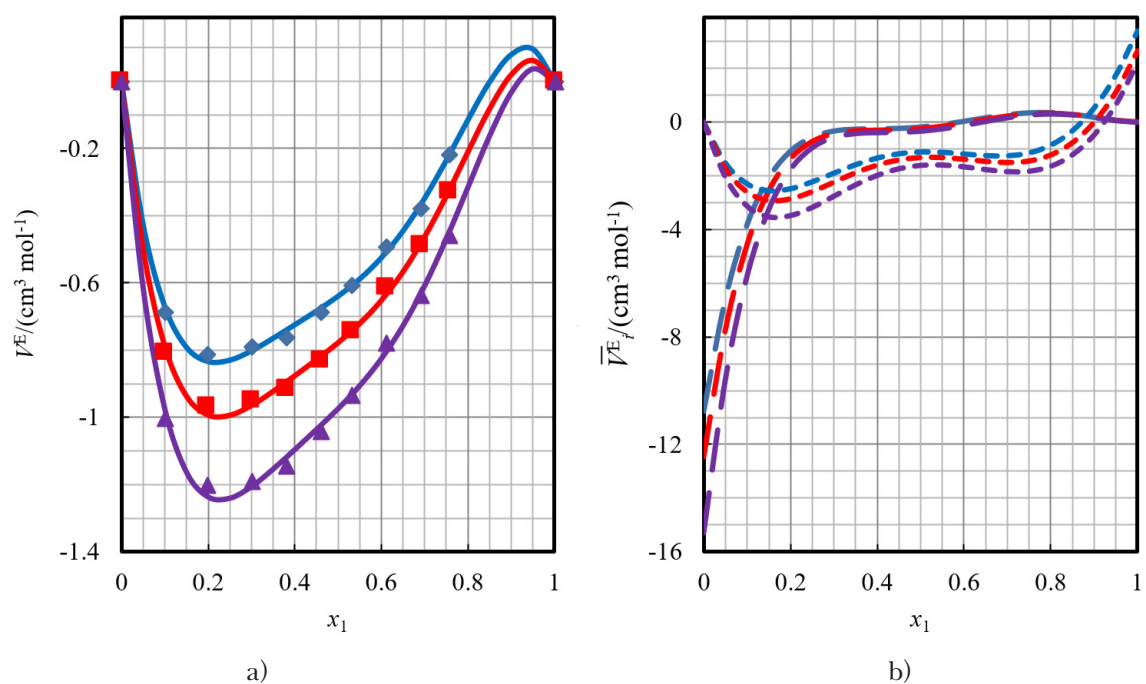


Fig. 3. Variation of a) excess molar volume of binary mixture [bmim]Ac (1)–ethanol (2) and b) components excess partial molar volumes with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values; values for IL (dashed line) and water (dotted line).

In Figs. 5–8, variation of viscosity difference with binary mixture composition is presented for the four chosen binary systems [bmim]Ac (1)–water (2), [bmim]DCA (1)–water (2), [bmim]Ac (1)–ethanol

(2) and [bmim]DCA (1)–ethanol (2), respectively. In these figures, also experimental viscosity values and their fit according to the Jouyban-Acree model (Eq. (7)) are included.

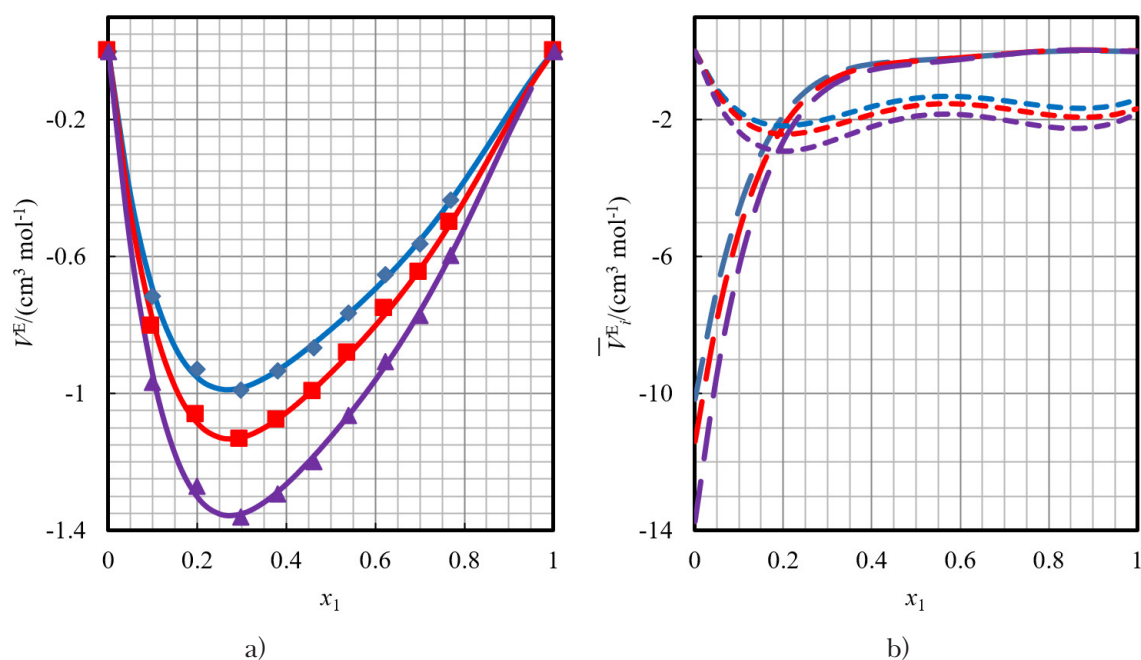


Fig. 4. Variation of a) excess molar volume of binary mixture [bmim]DCA (1)–ethanol (2) and b) components excess partial molar volumes with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values; values for IL (dashed line) and water (dotted line).

Tab. 9. Calculated viscosity difference of binary system [bmim]Ac (1)–water (2) at 20 °C, 40 °C and 60 °C.

Sample	Composition		$\Delta\eta$ /(Pa·s)		
	x_1	x_2	20 °C	40 °C	60 °C
1	0.0996	0.9004	-0.04642	-0.00922	-0.00242
2	0.1981	0.8019	-0.08070	-0.01508	-0.00370
3	0.2969	0.7031	-0.10687	-0.01861	-0.00418
4	0.3680	0.6320	-0.11233	-0.01779	-0.00341
5	0.4410	0.5590	-0.11855	-0.01787	-0.00330
6	0.5255	0.4745	-0.12014	-0.01732	-0.00307
7	0.6198	0.3802	-0.07136	-0.00551	0.00102
8	0.7007	0.2993	-0.08512	-0.00909	-0.00054
9	0.7755	0.2245	-0.01842	0.00255	0.00228

Tab. 10. Calculated viscosity difference of binary system [bmim]DCA (1)–water (2) at 20 °C, 40 °C and 60 °C.

Sample	Composition		$\Delta\eta$ /(Pa·s)		
	x_1	x_2	20 °C	40 °C	60 °C
1	0.0962	0.9038	-0.0007	-0.0001	0.0000
2	0.1968	0.8032	-0.0008	-0.0001	0.0001
3	0.2977	0.7023	0.0005	0.0008	0.0003
4	0.3774	0.6226	-0.0007	0.0004	0.0003
5	0.4598	0.5402	-0.0012	-0.0001	0.0004
6	0.5387	0.4613	-0.0022	-0.0005	0.0001
7	0.6158	0.3842	-0.0028	-0.0005	0.0001
8	0.6976	0.3024	-0.0040	-0.0011	-0.0003

Tab. 11. Calculated viscosity difference of binary system [bmim]Ac (1)–ethanol (2) at 20 °C, 40 °C and 60 °C.

Sample	Composition		$\Delta\eta$ /(Pa·s)		
	x_1	x_2	20 °C	40 °C	60 °C
1	0.0999	0.9001	-0.0541	-0.0122	-0.0038
2	0.2002	0.7998	-0.1071	-0.0238	-0.0073
3	0.2991	0.7009	-0.1567	-0.0342	-0.0102
4	0.3787	0.6213	-0.1927	-0.0409	-0.0118
5	0.4598	0.5402	-0.2237	-0.0463	-0.0131
6	0.5300	0.4700	-0.2430	-0.0487	-0.0133
7	0.6105	0.3895	-0.2545	-0.0490	-0.0130
8	0.6893	0.3107	-0.2490	-0.0458	-0.0117
9	0.7580	0.2420	-0.2273	-0.0401	-0.0098

Tab. 12. Calculated viscosity difference of binary system [bmim]DCA (1)–ethanol (2) at 20 °C, 40 °C and 60 °C.

Sample	Composition		$\Delta\eta$ /(Pa·s)		
	x_1	x_2	20 °C	40 °C	60 °C
1	0.0999	0.9001	-0.0025	-0.0009	-0.0004
2	0.1999	0.8001	-0.0047	-0.0017	-0.0007
3	0.2999	0.7001	-0.0062	-0.0021	-0.0007
4	0.3799	0.6201	-0.0072	-0.0024	-0.0007
5	0.4599	0.5401	-0.0080	-0.0027	-0.0009
6	0.5399	0.4601	-0.0083	-0.0027	-0.0009
7	0.6199	0.3801	-0.0082	-0.0026	-0.0009
8	0.6999	0.3001	-0.0077	-0.0024	-0.0008
9	0.7699	0.2301	-0.0066	-0.0021	-0.0007

Tab. 13. Summary of viscosity difference correlation: optimum values of the 4th order Redlich-Kister model parameters and computed standard residual deviations.

Parameter	t /°C	Binary system			
		[bmim]Ac–H ₂ O	[bmim]DCA–H ₂ O	[bmim]Ac–EtOH	[bmim]DCA–EtOH
C_1	20	-0.4657	-0.0069	-0.9444	-0.0331
	40	-0.0650	-0.0008	-0.1918	-0.0110
	60	-0.0101	0.0010	-0.0533	-0.0037
C_2	20	0.1948	-0.0279	-0.5430	-0.0088
	40	0.0722	-0.0121	-0.0687	0.0002
	60	0.0272	-0.0019	-0.0088	0.0002
C_3	20	0.4380	-0.0117	-0.0965	0.0028
	40	0.0697	-0.0015	0.0198	0.0015
	60	0.0143	-0.0046	0.0116	0.0002
C_4	20	0.3769	0.0355	0.0645	0.0045
	40	0.0524	0.0209	0.0237	0.0038
	60	0.0086	-0.0020	0.0071	0.0003
$\sigma_{\Delta\eta}$ /(Pa·s)	20	0.0151	0.0005	0.0005	0.0002
	40	0.0032	0.0003	0.0001	0.0002
	60	0.0011	0.0001	0.0001	0.0001

Optimum values of the Jouyban-Acree model parameters used for experimental viscosity data correlation are collected in Table 14. For all binary systems considered, the polynomial order $n = 4$ was chosen when fitting the experimental viscosity data. In Table 14, also the values of standard residual deviations are included.

Conclusions

Volumetric and transport properties of four binary mixtures containing [bmim]Ac and [bmim]DCA were measured at temperatures of 20 °C, 40 °C and 60 °C, and within the entire concentration range. Based on the experimental density values, excess

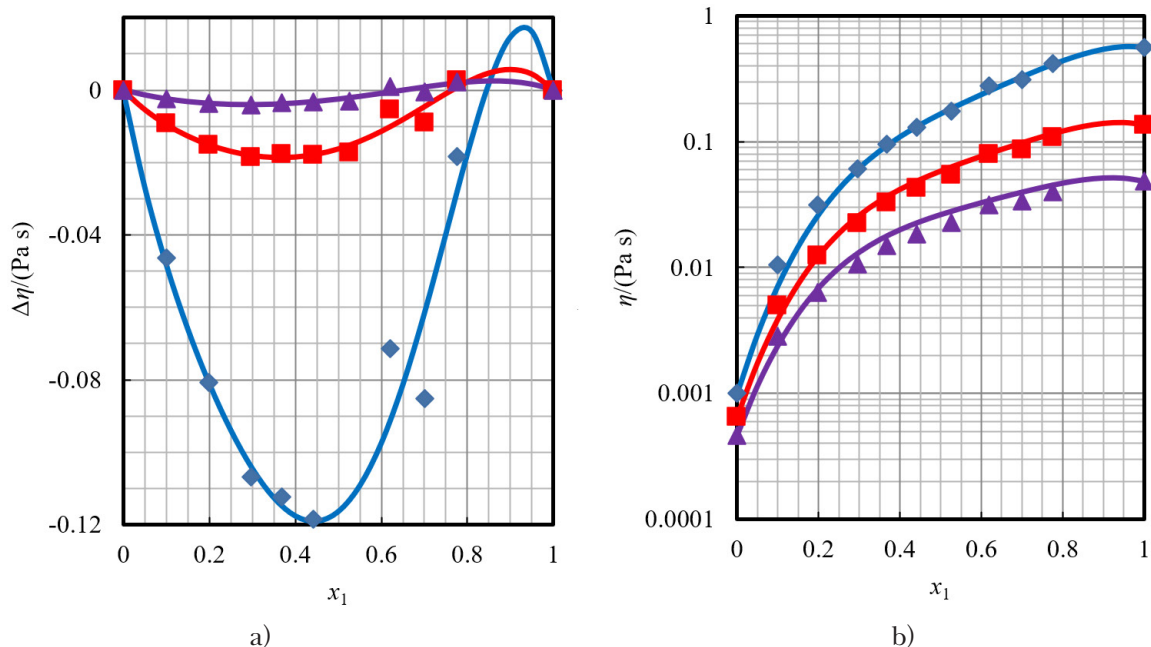


Fig. 5. Variation of a) viscosity difference of binary mixture [bmim]Ac (1)–water (2) and b) viscosity change with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values.

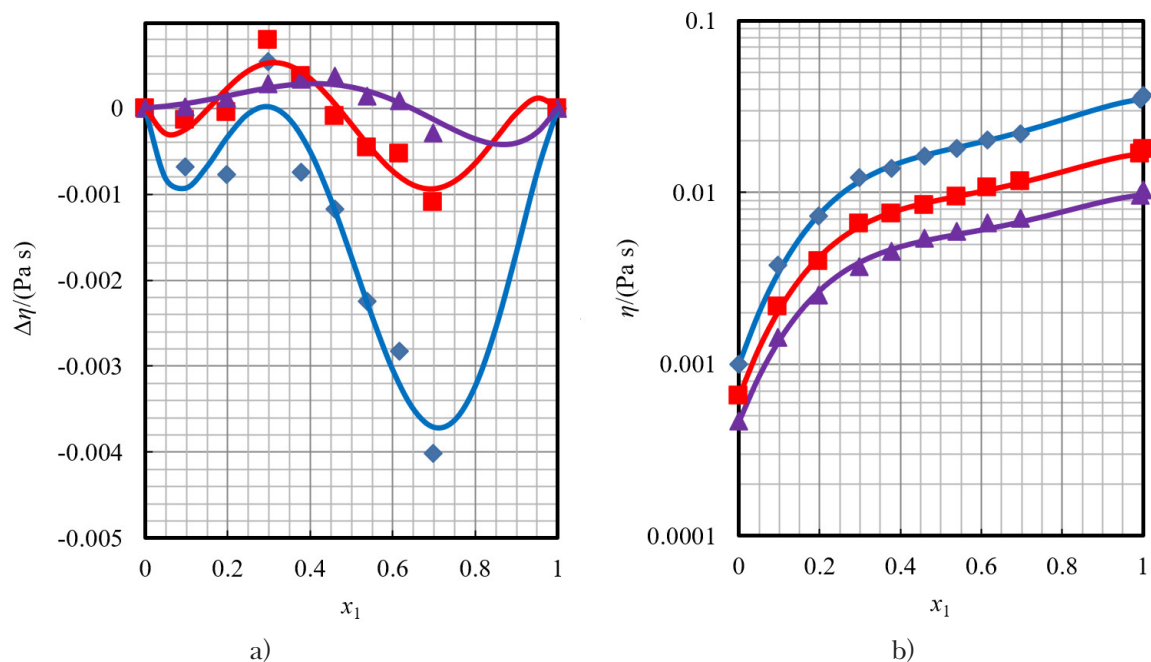


Fig. 6. Variation of a) viscosity difference of binary mixture [bmim]DCA (1)–water (2) and b) viscosity change with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values.

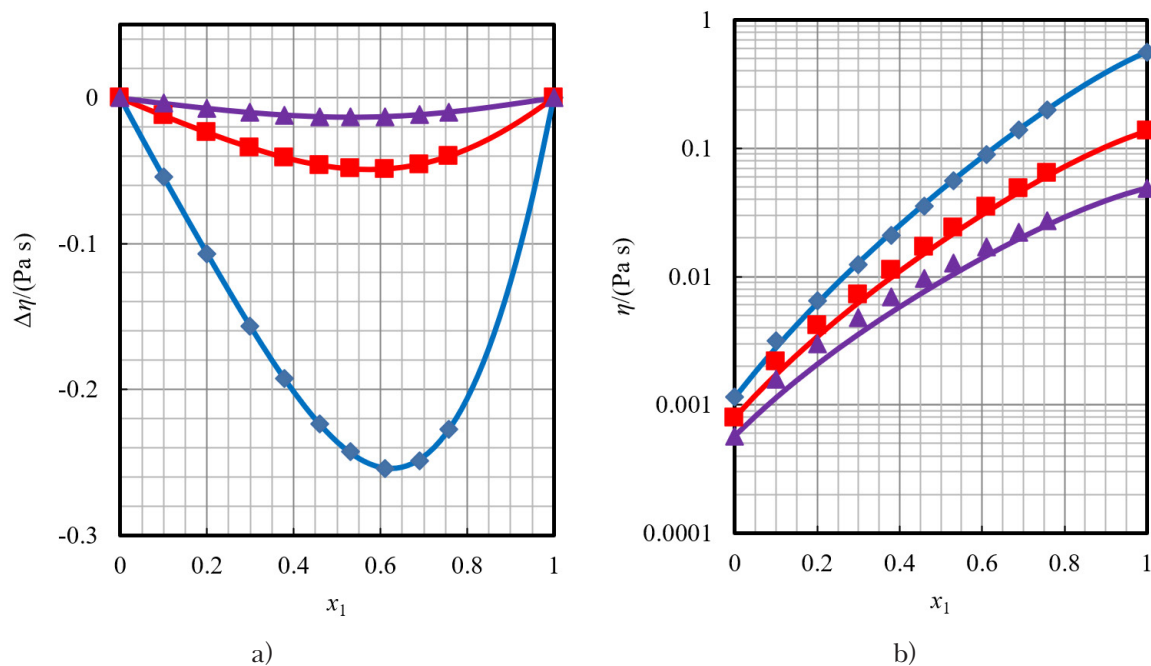


Fig. 7. Variation of a) viscosity difference of binary mixture [bmim]Ac (1)–ethanol (2) and b) viscosity change with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values.

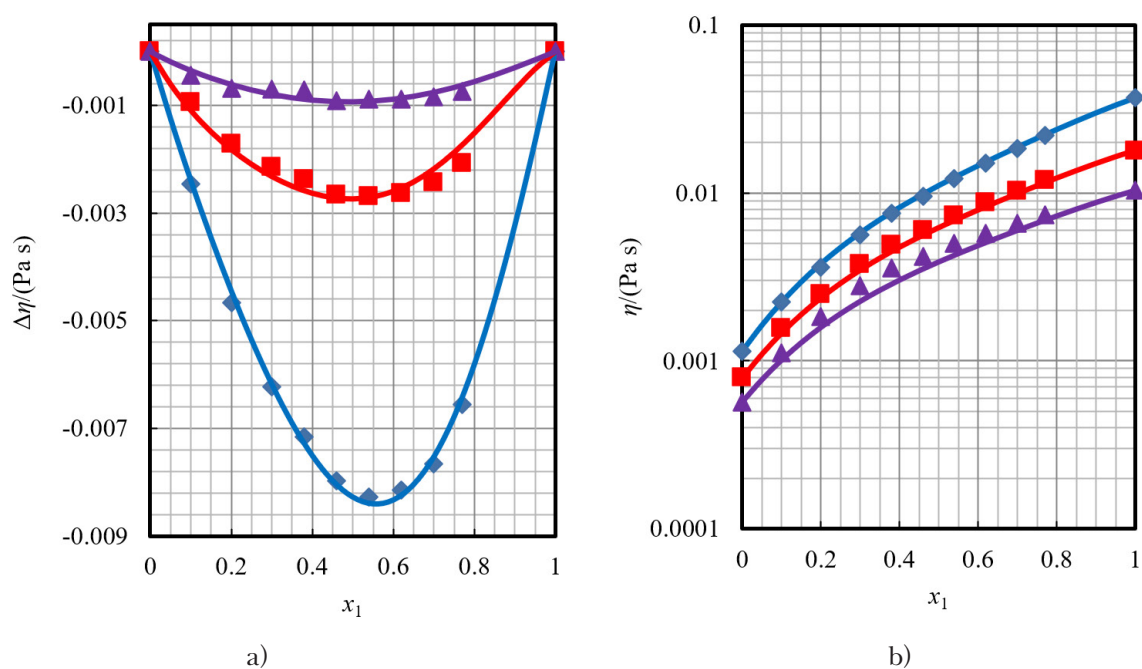


Fig. 8. Variation of a) viscosity difference of binary mixture [bmim]DCA (1)–ethanol (2) and b) viscosity change with mixture composition at 20 °C (blue color), 40 °C (red color) and 60 °C (violet color). Experimental (symbols) and calculated (curves) values.

molar volume and component partial molar volume data were computed. Their variation with mixture composition was correlated using the fourth-order Redlich-Kister equation. Compared to the behavior of other binary systems studied, positive values of excess molar volume were observed in case of

[bmim]DCA–water. Also, the variation of viscosity difference with mixture composition showed quite complex behavior.

Slightly worse goodness of fit of excess molar volume correlation was observed in case of binaries comprising [bmim]Ac ionic liquid. Average stand-

Tab. 14. Summary of viscosity difference correlation: optimum values of the three-parameters Jouyban-Acree model and computed standard residual deviations

Parameter	Binary system			
	[bmim]Ac–H ₂ O	[bmim]DCA–H ₂ O	[bmim]Ac–EtOH	[bmim]DCA–EtOH
J_1	2281.70	1260.10	723.70	626.53
J_2	-1509.04	-1332.52	-53.81	-370.80
J_3	1345.03	907.18	188.57	202.55
σ_r /(Pa·s)	0.0112	0.0003	0.0038	0.0010

ard deviation of the excess molar volume oscillated around the value of $0.02 \text{ cm}^3 \cdot \text{mol}^{-1}$. The same trend was observed when fitting the viscosity difference with an average standard deviation of around $0.3 \text{ mPa} \cdot \text{s}$. Only in case of the binary [bmim]Ac–water, the standard deviation value was by one order of magnitude higher. Better fit of experimental viscosity data using the Jouyban-Acree model were achieved for binaries containing [bmim]DCA ionic liquid.

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