



High-pressure densities and derived volumetric properties (excess and partial molar volumes, vapor-pressures) of binary methanol + ethanol mixtures

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ABSTRACT

The densities of five (0.08564, 0.19998, 0.41971, 0.68017, and 0.84236 mol fraction of methanol) binary methanol + ethanol mixtures have been measured with a vibrating-tube densimeter. Measurements were performed at temperatures from $T = (298.15 \text{ to } 423.15) \text{ K}$ and at pressures up to 40 MPa. The total uncertainty of density, temperature, pressure, and concentration measurements were estimated to be less than 0.15 kg m^{-3} , 15 mK, 5 kPa, and 10^{-4} , respectively. The uncertainties reported in this paper are expanded uncertainties at the 95% confidence level with a coverage factor of $k = 2$. The effect of temperature, pressure, and concentration on the density and derived volumetric properties such as excess and partial molar volumes was studied. Using the analytical extrapolating technique the vapor-pressure and saturation liquid densities of the mixture were derived. The measured densities were used to develop polynomial type equation of state for the mixture. The structural properties such as direct and total correlation function integrals and clusters size (excess coordination number) were calculated using the Krichevskii function concept and equation of state for the mixture at infinite dilution.

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1. Introduction

Both methanol and ethanol are small and highly polar molecules (gas-phase dipole moment at normal boiling point are 1.7 D and 1.6909 D, respectively), high acentric factor ($\omega = 0.5625$ and $\omega = 0.644$, respectively) and may be expected to interact strongly with other fluid in an H-bonded network. In mixtures in which methanol or ethanol one of the component, the thermodynamic properties exhibit some anomaly. Methanol and ethanol are structured, self-associated liquids. Methanol and ethanol are often present together in ternary mixtures with other components (for example, methanol + ethanol + water, methanol + ethanol + DMC, methanol + ethanol + ILs, methanol + ethanol + hydrocarbon). Ternary systems that contain two highly associated species are very important for technological applications. Methanol is also an inevitable companion of ethanol in many industrial processes [1]. Therefore, the design of engineering systems utilizing methanol and ethanol and their mixtures requires an accurate knowledge of thermodynamic properties. However, available thermodynamic

properties data for methanol + ethanol mixtures are not satisfactory. Methanol is one of the main additives used in natural gas processing and pipeline transport and used as a hydrate inhibitor and as secant following hydraulic tests of natural gas pipelines. Methanol and ethanol are very important fluids as a fuel and feedstock and interest in view of its connection with coal gasification; various applications such as: transport and storage of hydrogen, natural refrigerants, and working fluids in new power cycles. Ethanol also can be used as a renewable bio-fuel. Both methanol and ethanol also used as polar modifiers to increase solvating power of supercritical carbon dioxide in SCFE processes [2,3] (yield) and SCF chromatography [4] and improve selectivity. Alcohol molecules strongly affect, for example, water and other fluids structure. In pure fluids, strong attractive interactions between like molecules result in the formation of molecular clusters that have considerable effect on the thermodynamic and structural properties of the species. In mixtures, hydrogen-bonding interactions can occur between molecules of the same species (self-association) or between molecules of different species (solvation). So far statistical mechanics (calculation the structural and thermodynamic properties of fluids from knowledge of the intermolecular interactions) can give inaccurate or even physically impossible results when applied to hydrogen-bonded fluids. Because of the complexity of the mixtures (high polarity both components), there are neither experimental data on representative systems nor predictive

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thermodynamic models available that will offer sufficient insight for optimum process design. Precise experimental p - v - T - x data will also prove to be useful to develop a physico-chemical model of the thermodynamic properties of strong hydrogen-bonding mixtures.

Mixtures of methanol and ethanol with other fluids form highly nonideal systems, for example, excess molar properties exhibit unusually large deviations from ideal mixture behavior. However, very little known about ideality of the methanol + ethanol mixture. We do not have a sufficient understanding of microscopic properties of associated fluids including the nature of hydrogen bonds and their effect on thermodynamic and structural properties. A deeper understanding of the structure and nature of hydrogen bonding fluids and their effect on the thermodynamic and structural behavior will lead to marked improvements in important practical applications in the environmental, mechanical, chemical, biological, and geothermal industries. The volumetric properties (density, excess and partial molar volumes) provide very useful information on the structural and intermolecular interaction between the solvent and solute molecules with different sizes, shapes, and chemical nature.

A survey of the literature reveals that measurement of the density of methanol + ethanol mixtures were performed by several authors [5–14]. Albuquerque et al. [5] reported the densities of this mixture at 298 K and 0.1 MPa in the entire concentration range. Measurements were performed with DMA 512 (Anton Paar) with an uncertainty of $5 \times 10^{-5} \text{ g cm}^{-3}$. Rodriguez et al. [6] used also Anton Paar DMA-60/602 VTD with an uncertainty of $10^{-5} \text{ g cm}^{-3}$. The measurements were made at 298 and 0.1 MPa and cover the whole concentration range. Dizechi and Marschall [8] reported the densities of methanol + ethanol mixtures at temperatures from 293 to 323 K at pressure of 0.1 MPa in the whole concentration range. Measurements were made with a Paar Model DMA 46 with an accuracy of $10^{-4} \text{ g cm}^{-3}$ (or 0.013%). Kumagi and Yokoyama [9] used glass pycnometer to measure the density of methanol + ethanol mixtures at temperatures from 273 to 333 K at atmospheric pressure for four compositions. The uncertainty of the measured densities claimed by the authors is 0.04%. The measurements by Arce et al. [11] also were performed at 298 K and 0.1 MPa for the concentration from 0 to 1 mol fraction. They also used Anton Paar DSA-48 densimeter with uncertainty of $10^{-4} \text{ g cm}^{-3}$. Benson and Pflug [12] reported the excess molar volumes for methanol + ethanol mixtures from the density measurements at 298 K and 0.1 MPa. The volumes of the mixtures were measured directly with a dilatometer. The uncertainty in measured values of excess molar volumes is 0.5% for equimolar mixture and 5% in cases where the molar excess volume is small ($0.2 \text{ cm}^3 \text{ mol}^{-1}$). Wei and Rowley [13] used Anton Paar VTD (Model DMA-45) to measure the density of the mixture at 298 K and at ambient pressure. The uncertainty in density measurements is $10^{-4} \text{ g cm}^{-3}$. Zarei et al. [14] reported densities for methanol + ethanol mixtures at temperatures from 283 to 313 K at 0.1 MPa over the entire range of compositions and at ambient pressure (81.5 kPa). Measurements were made with Anton Paar DMA 4500 (oscillating U-tube densimeter) with an uncertainty of $10^{-5} \text{ g cm}^{-3}$. The measurements of the density of methanol + ethanol mixtures by Konobeev and Lyapin [7] were made at saturation curve for three temperatures (293, 313, and 333 K). Measurements were made with pycnometer (25 cc in volume). The uncertainty in measured densities is 0.2 kg m^{-3} (or about 0.03%). Thus, all of the previous measurements of density of methanol + ethanol mixtures were performed at atmospheric pressure and in the limited temperature range (from 273.15 to 333.15 K). To our knowledge no density data are available for this mixture under pressure. The main objective of this work is to provide new accurate experimental density data for methanol + ethanol mixtures at high temperatures (up to 423.15 K) and at high pressures

(up to 40 MPa) over entire concentration range using a vibrating tube densimeter technique. This technique previously was used to accurate measurements on pure methanol, 1-propanol, and alcohol containing binary mixtures (Abdulagatov et al. [15–20]). The present results considerably expand the temperature and pressure ranges in which density data for the solutions are available. Another objective of the work is to use the measured results to study of derive thermodynamic and structural properties of the methanol + ethanol mixtures. We also developed equation of state for this mixture which accurately reproduce the present density results.

2. Experimental

The details of the experimental method, the description of the apparatus and procedures used for the density measurements of the methanol + ethanol mixtures have been described in our previous several publications (Abdulagatov et al. [15–20]). Only brief and essential information will be given here. The (p , ρ , T , x) relationship of methanol + ethanol solutions were studied using high pressure–high temperature Anton-Paar vibrating-tube densimeter. Vibrating tube is fixed to the thermostated block of the cell located inside two thermostated jackets. The temperature was maintained constant to 10 mK. The period of oscillation measurement and the temperature control is implemented within the DMA-HDT control system, which consists from the measurement cell and a modified DMA 5000 control unit, connected to PC. For the present VTD the period of vibration is within 2550–2670 μs depending on density, temperature, and pressure. The period of oscillation is measured with an uncertainty of 1 ns. Pressure was created by hand pump (759.1100–HMEL, SITEC) and measured by pressure sensor from WIKA Manometer AG, Switzerland with the uncertainty of 5 kPa. Temperature was measured using the (ITS-90) Pt100 thermometer with the uncertainty of 15 mK.

In this method the relation between the period of vibration τ and density ρ is given as

$$\rho - \rho_0 = B(\tau^2 - \tau_0^2), \quad (1)$$

where $B(T, p)$ calibrating constant, subscript 0 relates to the reference fluid. Parameter B is the linear function of temperature. Usually the temperature and pressure dependences of B is determined using the calibration procedures with a several reference fluids (such as water, benzene, nitrogen, air, and toluene) whose (p , ρ , T) properties are well known. Calibration of a VTD with one fluid of well-known density cannot satisfactorily be used for another with different properties. Minimum two reference fluids are requiring to accurate calibration the VTD. Liquids with densities close to the densities of the fluids under study are more suitable to calibrate the instrument. The accuracy of the method is limited by the calibration procedure and should be performed very carefully. The reference (p , ρ , T) properties of pure water [21] and methanol [22] were used for the calibration. The uncertainty in density measurements is 0.05 kg m^{-3} at low pressures (near the atmospheric pressure) and 0.15 kg m^{-3} at high pressures (the combined expanded uncertainty, coverage factor is $k=2$). For the measured liquid densities between 650 and 860 kg m^{-3} this leads to relative uncertainty between 0.01% and 0.02%. All mixtures were prepared by mass. A balance with a precision of 10^{-4} g was used. The uncertainty in the concentration of the mole fraction of methanol was less than 10^{-4} . To verify the experimental apparatus and procedure the density of pure ethanol was measured at the selected T and p and compared with the reported data and calculated with fundamental EOS by Dillon and Penoncello [23]. Our instrument reproduces the available density data for pure ethanol

Table 1
Experimental values of density, pressure, apparent molar volume, temperature, and concentration of methanol + ethanol mixtures

$x = 0.0$ (pure ethanol) ^a		$x = 0.08564$		$x = 0.19998$	
p (MPa)	ρ (kg m ⁻³)	p (MPa)	ρ (kg m ⁻³)	p (MPa)	ρ (kg m ⁻³)
$T = 298.15$ K					
0.101	785.57	0.15	785.63	0.41	785.97
5	789.79	5.03	789.89	5.67	790.59
10	793.98	10.02	794.08	10.1	794.34
15	797.97	15.62	798.60	15.45	798.70
20	801.79	20.03	802.01	20.36	802.53
25	805.45	25.85	806.32	25.23	806.18
30	808.96	30.15	809.36	30.27	809.79
35	812.35	35.62	813.05	35.55	813.38
40	815.62	39.89	815.80	39.84	816.17
$T = 323.15$ K					
0.101	763.61	0.18	763.63	0.24	763.54
5	768.64	5.03	768.54	5.38	768.79
10	773.47	10.06	773.41	11.12	774.38
15	778.04	15.21	778.18	15.35	778.31
20	782.37	20.08	782.48	21.25	783.53
25	786.51	25.61	787.11	25.78	787.33
30	790.46	30.04	790.63	30.52	791.12
35	794.24	35.14	794.48	35.22	794.68
40	797.88	39.97	797.91	40.05	798.14
$T = 348.15$ K					
0.101	739.72	0.21	739.68	0.36	739.54
5	745.70	5.04	745.44	5.45	745.65
10	751.37	10.09	751.17	10.63	751.55
15	756.67	15.84	757.34	15.86	757.19
20	761.67	20.08	761.65	21.21	762.64
25	766.39	25.41	766.77	25.89	767.14
30	770.87	29.96	770.89	30.85	771.62
35	775.14	35.98	775.97	35.05	775.20
40	779.22	39.96	779.10	39.97	779.14
$T = 373.15$ K					
0.25	713.15	0.41	713.39	0.48	713.11
5	720.25	5.62	720.77	5.82	720.71
10	727.05	10.08	726.76	10.39	726.87
15	733.34	15.42	733.53	16.62	734.74
20	739.18	19.98	738.96	20.42	739.25
25	744.65	25.12	744.71	25.08	744.48
30	749.80	29.98	749.77	30.97	750.61
35	754.67	35.62	755.19	35.52	754.97
40	759.30	39.96	759.03	39.96	758.93
$T = 398.15$ K					
0.55	683.03	0.79	683.99	0.94	683.88
5	691.50	4.98	691.25	6.35	693.19
10	699.93	9.86	699.24	10.88	700.52
15	707.55	15.41	707.73	15.58	707.67
20	714.52	20.07	714.35	20.94	715.26
25	720.97	25.63	721.66	25.92	721.78
30	726.97	29.98	726.93	30.83	727.69
35	732.59	35.01	732.52	35.36	732.69
40	737.88	39.99	737.54	40.02	737.40
$T = 423.15$ K					
1.05	648.45	1.51	650.94	1.65	650.85
5	658.34	5.98	660.55	6.19	660.60
10	669.22	10.86	670.36	10.83	669.93
15	678.75	15.62	679.26	15.06	677.89
20	687.28	20.09	687.01	21.13	688.39
25	695.02	25.41	695.47	25.69	695.56
30	702.12	29.94	702.01	30.24	702.11
35	708.69	35.64	709.38	35.69	709.15
40	714.82	39.97	714.34	39.89	713.98
$x = 0.41971$		$x = 0.68017$		$x = 0.84236$	
p (MPa)	ρ (kg m ⁻³)	p (MPa)	ρ (kg m ⁻³)	p (MPa)	ρ (kg m ⁻³)
$T = 298.15$ K					
0.35	786.13	0.21	786.23	0.21	786.36
5.75	790.97	5.08	790.71	5.06	790.89
10.49	795.05	10.81	795.77	10.04	795.36
15.93	799.55	15.26	799.54	15.62	800.16

Table 1 (Continued)

x = 0.41971		x = 0.68017		x = 0.84236	
p (MPa)	ρ (kg m ⁻³)	p (MPa)	ρ (kg m ⁻³)	p (MPa)	ρ (kg m ⁻³)
20.66	803.30	20.46	803.77	20.06	803.82
25.35	806.87	25.28	807.52	25.94	808.45
30.51	810.63	29.83	810.91	30.51	811.88
35.59	814.15	34.82	814.47	35.62	815.53
39.61	816.81	39.35	817.55	39.96	818.50
T = 323.15 K					
0.23	763.28	0.23	763.05	0.41	763.13
5.37	768.63	5.77	768.91	5.23	768.28
10.44	773.67	10.53	773.72	10.32	773.49
15.53	778.50	15.34	778.36	15.64	778.67
20.33	782.83	20.41	783.03	20.08	782.80
25.14	786.97	24.45	786.57	25.64	787.70
30.47	791.31	30.31	791.45	30.08	791.42
35.52	795.19	34.25	794.55	35.74	795.88
39.94	798.39	39.52	798.47	39.94	799.00
T = 348.15 K					
0.35	739.02	0.35	738.58	0.26	738.25
4.84	744.50	5.58	745.01	4.98	744.11
10.56	751.13	9.92	750.10	10.62	750.76
15.72	756.79	15.21	756.01	15.32	756.02
20.24	761.49	20.07	761.14	20.06	761.04
25.33	766.49	24.25	765.32	25.94	766.91
30.35	771.12	29.81	770.57	30.08	770.79
35.73	775.76	35.26	775.36	35.61	775.65
39.72	778.98	40.02	779.25	39.98	779.23
T = 373.15 K					
0.97	713.23	0.64	712.22	0.53	711.80
5.29	719.45	5.41	719.15	5.06	718.43
10.63	726.72	10.85	726.62	10.52	725.98
15.61	733.11	15.78	732.98	15.68	732.69
20.74	739.28	20.42	738.61	20.09	738.07
25.42	744.55	25.22	744.07	25.61	744.38
31.03	750.42	30.61	749.78	30.07	749.12
35.61	754.85	35.12	754.19	35.61	754.56
39.83	758.63	39.57	758.23	39.91	758.44
T = 398.15 K					
1.02	683.44	0.98	682.85	0.94	682.53
5.4	691.06	6.13	691.82	4.98	689.63
10.55	699.51	10.22	698.54	10.32	698.49
15.91	707.70	15.11	706.11	15.06	705.84
21.31	715.35	20.63	714.05	20.45	713.62
26.52	722.15	25.68	720.75	25.83	720.78
30.74	727.24	30.64	726.81	29.94	725.83
36.34	733.41	35.73	732.48	35.16	731.72
39.77	736.87	39.75	736.57	39.92	736.59
T = 423.15 K					
1.87	650.75	1.75	649.98	1.96	650.20
5.45	658.46	5.82	658.74	5.64	658.12
10.72	669.14	10.42	668.06	10.47	667.91
15.96	678.96	15.44	677.53	15.84	678.02
21.25	688.05	20.86	686.94	20.64	686.34
25.05	694.08	25.18	693.82	25.94	694.75
30.66	702.20	30.51	701.57	29.12	699.41
35.62	708.62	34.77	707.17	35.62	708.03
40.08	713.77	39.74	713.03	39.98	713.12
x = 1.0 (pure methanol) ^{b,c}					
T = 298.15 K ^b					
0.24					785.98
5.00					790.69
10.00					795.40
15.01					799.88
19.99					804.10
25.01					808.17
30.00					812.04
34.99					815.76
39.98					819.34

Table 1 (Continued)

$x = 1.0$ (pure methanol) ^{b,c}	
$T = 323.15 \text{ K}^b$	
0.27	762.14
4.99	767.53
9.98	772.87
14.98	777.91
19.99	782.69
24.99	787.21
29.99	791.53
34.99	795.64
39.99	799.60
$T = 348.15 \text{ K}^b$	
0.37	737.29
4.99	743.46
9.99	749.65
14.99	755.42
20.00	760.84
25.02	765.94
30.01	770.76
34.99	775.32
40.00	779.70
$T = 373.15 \text{ K}^b$	
0.53	710.55
4.98	717.67
9.99	724.99
15.00	731.69
19.98	737.88
24.99	743.68
30.00	749.13
35.00	754.27
40.00	759.14
$T = 398.15 \text{ K}^b$	
0.93	680.93
4.98	689.00
10.00	697.91
14.99	705.88
19.99	713.16
24.99	719.87
29.99	726.11
35.01	731.99
40.00	737.47

^a Dillon and Penoncello [23].

^b Abdulagatov et al. [17].

^c de Reuck and Craven [22].

0.01–0.05%. This is good confirmation of the accuracy of the method and correct calibration of the instrument.

Pure methanol and ethanol was supplied from Merck, Germany and was degassed by vacuum distillation using a Vigreux column with a height of 90 cm. The final purity of the methanol and ethanol were checked by gas chromatography (>99.9 mass%) and Karl-Fischer titration (water content <50 ppm).

3. Results and discussion

3.1. Density

Measurements of the density of methanol + ethanol mixtures as a function of temperature, pressure, and concentration were performed at five concentrations (0.08564, 0.19998, 0.41971, 0.68017, and 0.84236 mol fraction of methanol) for the temperatures between 298.15 and 423.15 K. The pressure ranged from 0.1 to 40 MPa. The experimental results are presented in Table 1. Some selected experimental results for the mixture are shown in Figs. 1–3 as projections in the ρ - p , ρ - x , and ρ - T planes. As Figs. 1 and 2 demonstrate, the pressure (ρ - p), temperature (ρ - T), and concentration (ρ - x) dependences of density are nearly linear (very small curvature) in the measured temperature and pressure ranges. The concentration dependence of the densities (see Fig. 2, ρ - x

curves) shows almost ideality. Very small positive deviations up to 0.07 kg m^{-3} from the ideality, $\rho_{\text{ide}} = x\rho_1 + (1-x)\rho_2$, was found at temperature of 298.15 K and 0.1 MPa, although at high pressures the differences between measured densities for the mixture and ρ_{ide} almost zero. This is not surprise because both components of the mixture thermodynamically very similar. Therefore, for the mixtures like this it is very difficult to accurately determine the excess properties (excess molar volumes, for example, see Abdulagatov and Azizov [24]). Detailed comparison between the present measured densities for methanol + ethanol mixtures and reported data is shown in Fig. 4. As Fig. 4 shows, all of the available experimental density data for methanol + ethanol mixtures at 298.15 K and at 0.1 MPa lied within 0.08% (maximum deviation). Especially large deviations are found at low concentration (near the pure ethanol data). Most published data for pure methanol agree well (within 0.04%) with each other, while our result deviate from the published values within 0.06%, although the present values for the density of pure methanol excellent (0.008%) agree with the values calculated with IUPAC [22] accepted reference EOS. The present result for the pure ethanol is good (within 0.02%) agrees with all of the reported data and with the values calculated from EOS by Dillon and Penoncello [23]. In general the present data for the mixture at atmospheric pressure shows good agreement within 0.05% at concentration below 0.3 mol fraction of methanol and excellent agree

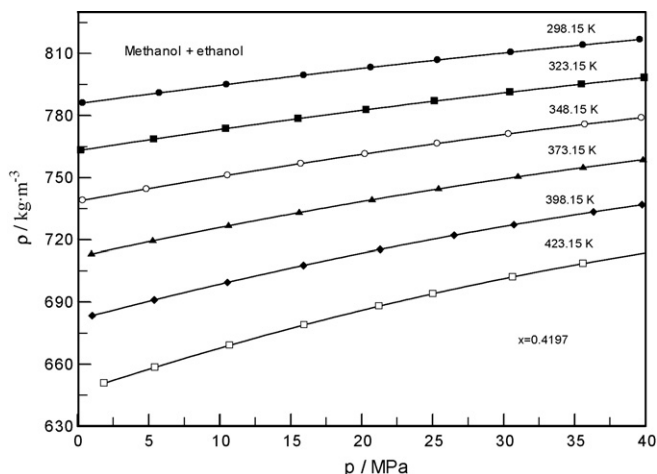


Fig. 1. Experimental densities ρ of methanol + ethanol mixture as a function of pressure p along the selected concentration of 0.4197 mol fraction of methanol and at various isotherms together with values calculated with Eq. (4).

within 0.02–0.03% at high concentrations (above 0.3 mol fraction). Therefore, the agreement between all reported data at atmospheric pressure is almost within their experimental uncertainties.

We in detailed compared the present density data for the mixtures with the values calculated from $\rho_{\text{ide}} = x\rho_1 + (1-x)\rho_2$ for the ideal mixture, where $\rho_1(p, T)$ and $\rho_2(p, T)$ are the density of pure methanol calculated with IUPAC EOS [22] and pure ethanol calculated with Dillon and Penoncello [23], respectively. The differences are within 0.010% and 0.025%.

3.2. Excess molar volumes

The present density results for the methanol + ethanol mixtures together with the values for pure components calculated from

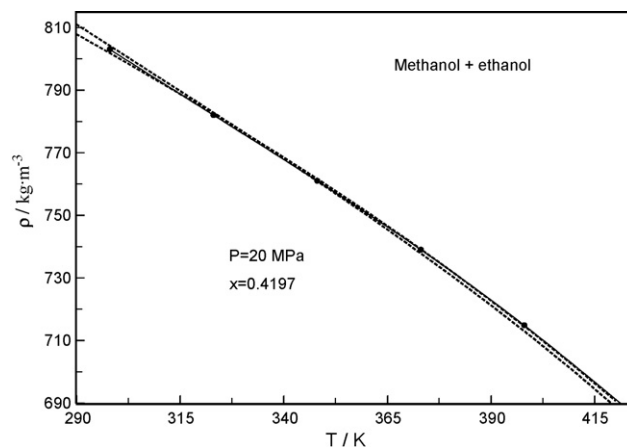


Fig. 3. Experimental densities ρ of methanol + ethanol mixtures as a function of temperature T along the selected isobar of 20 MPa and concentration of 0.4197 mol fraction of methanol together with values for pure components calculated with IUPAC [22] and Dillon and Penoncello [23] EOS. (●) Experimental values; (—), calculated values Eq. (4); (---), pure component values calculated from EOS [22,23].

IUPAC [22] and Dillon and Penoncello [23] EOS (see also Table 1) were used to calculate the excess molar volumes with the following relation

$$V_m^E(p, T, x) = V_m(p, T, x) - xV_m(p, T, 1) - (1-x)V_m(p, T, 0), \quad (2)$$

where x is the mole fraction of methanol, $V_m(p, T, x)$ is the experimentally determined molar volume of the mixture of concentration x at temperature T and pressure p , and $V_1 = V_m(p, T, 1)$ and $V_2 = V_m(p, T, 0)$ are the molar volumes of the pure components (methanol and ethanol, respectively) at the same pressure p and temperature T . Excess molar volumes account for the non-ideality of the mixture and reflect the nature of the solute and solvent molecules interactions. The derived values of V_m^E for the selected temperatures and

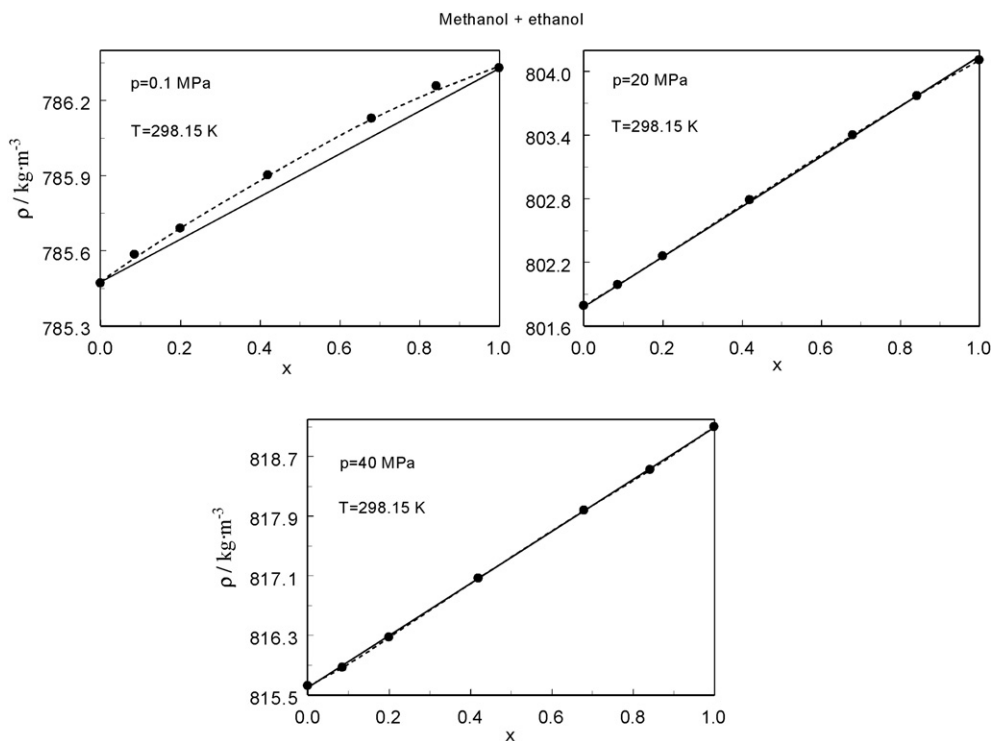


Fig. 2. Experimental densities ρ of methanol + ethanol mixture as a function of composition x along three selected isobars of (0.1, 20, and 40 MPa) and at temperature 298.15 K. (---), Eq. (4); (—), ideal mixture values, $\rho_{\text{ide}} = x\rho_2 + (1-x)\rho_1$.

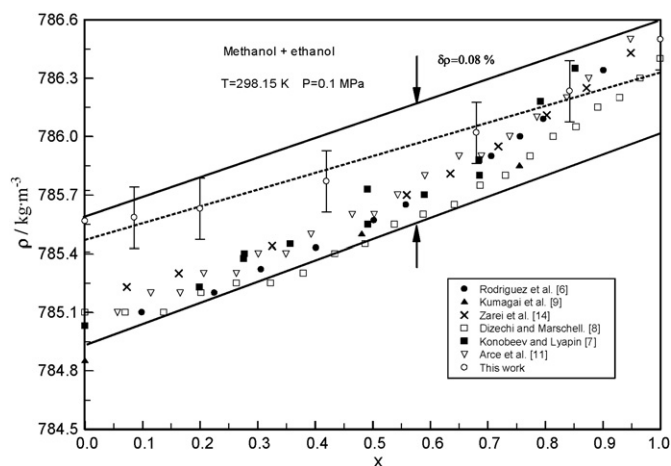


Fig. 4. Experimental densities ρ of methanol + ethanol mixture as a function of composition x at constant temperature of 298.15 K and at atmospheric pressure together with reported data. (---) Ideal mixture values, $\rho_{\text{ide}} = x\rho_2 + (1-x)\rho_1$, where ρ_1 and ρ_2 calculated with IUPAC [22] and Dillon and Penoncello [23] EOS.

pressures are given in Table 2 and depicted in Fig. 5 as a function of mole fraction of methanol, x , at selected temperature of 298.15 K and at various selected pressures. As one can see from Fig. 5 the derived values of V_m^E for the methanol + ethanol mixtures are very small (maximal value is about $-0.02 \text{ cm}^3 \text{ mol}^{-1}$) and negative for all measured temperatures and pressures over the whole composition range (except single data point). $V_m^E - x$ curves are almost symmetric with the maximum at 0.5 mol fraction. The small values of the V_m^E is the result of the ideality of the methanol + ethanol mixture, i.e. the difference between the mixture molar volume V_{mix} and the ideal mixture molar volume $V_{\text{ide}} = xV_1 + (1-x)V_2$ is very small (maximum value of about $-0.02 \text{ cm}^3 \text{ mol}^{-1}$ at 298.15 K and 30 MPa). The maximum relative uncertainty, δV_m^E , in the derived values of V_m^E is very large and can be approximately estimated from the relation reported in our previous paper (Abdulagatov and Azizov [25,24]). The uncertainty in V_m^E determination is inversely proportional to the difference between V_{mix} and V_{ide} , $\delta V_m^E \cong (V_{\text{mix}} - V_{\text{ide}})^{-1}$, therefore, due to small amount of V_m^E (or $(V_{\text{mix}} - V_{\text{ide}}) \rightarrow 0$), the values of δV_m^E can be reach up to 50–100% and more. Fig. 6 shows the comparison between present derived values of the excess molar volumes and those reported by other authors. As this figure shows, majority reported values of V_m^E are positive and agree well with each other, except the data reported by Albuquerque et al. [5]. The agreement

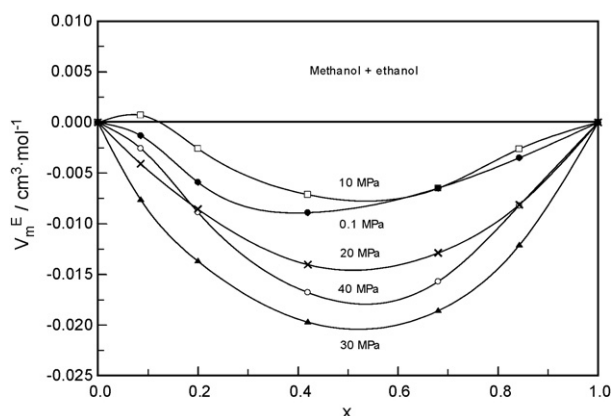


Fig. 5. Excess molar volumes V_m^E of methanol + ethanol mixtures as a function of concentration x at temperature of 298.15 K and for various isobars derived from present density measurements.

Table 2

Excess molar volumes for methanol + ethanol mixtures derived from the present density measurements

x	V_m^E ($\text{cm}^3 \text{ mol}^{-1}$)	\bar{V}_1 ($\text{cm}^3 \text{ mol}^{-1}$)	\bar{V}_2 ($\text{cm}^3 \text{ mol}^{-1}$)
$p = 0.1 \text{ MPa}$ ($T = 298.15 \text{ K}$)			
0.0	0.0	58.650	76.584
0.08564	-0.00130	58.648	73.506
0.19998	-0.00592	58.648	69.401
0.41971	-0.00891	58.644	61.519
0.68017	-0.00648	58.635	52.188
0.84236	-0.00349	58.628	46.383
1.0	0.0	58.619	40.746
$p = 10 \text{ MPa}$ ($T = 298.15 \text{ K}$)			
0.0	0.0	58.022	75.802
0.08564	0.00072	58.025	72.755
0.19998	-0.00257	58.023	68.684
0.41971	-0.00712	58.017	60.868
0.68017	-0.00649	58.009	51.617
0.84236	-0.00261	58.003	45.863
1.0	0.0	57.993	40.273
$p = 20 \text{ MPa}$ ($T = 298.15 \text{ K}$)			
0.0	0.0	57.456	75.124
0.08564	-0.00408	57.457	72.090
0.19998	-0.00855	57.455	68.042
0.41971	-0.01403	57.447	60.276
0.68017	-0.01287	57.430	51.092
0.84236	-0.00811	57.415	45.385
1.0	0.0	57.399	39.848
$p = 30 \text{ MPa}$ ($T = 298.15 \text{ K}$)			
0.0	0.0	56.947	74.512
0.08564	-0.00763	56.945	71.490
0.19998	-0.01369	56.943	67.463
0.41971	-0.01970	56.933	59.742
0.68017	-0.01858	56.908	50.620
0.84236	-0.01212	56.887	44.956
1.0	0.0	56.864	39.466
$p = 40 \text{ MPa}$ ($T = 298.15 \text{ K}$)			
0.0	0.0	56.482	73.918
0.08564	-0.00256	56.485	70.924
0.19998	-0.00886	56.482	66.927
0.41971	-0.01677	56.471	59.261
0.68017	-0.01569	56.450	50.202
0.84236	-0.00820	56.435	44.577
1.0	0.0	56.413	39.119

between the present and the data by Albuquerque et al. [5] is good. It is obviously that the values of V_m^E very sensitive to the values of pure component density. Because of our values of the density of pure ethanol at 298.15 K and at 0.1 MPa slightly (by 0.02%, this is within experimental uncertainty) higher than other reported data, therefore our result for V_m^E lower than other published data (i.e. $V_{\text{ide}} > V_m$). If the value of the density of pure ethanol slightly change (even within their experimental uncertainty), the derived values of V_m^E significantly increases up to positive values as this shown in Fig. 6 dashed line. Thus, the agreement between our results for V_m^E and reported data are excellent if slightly (by 0.02%, within their experimental uncertainty) decrease the value of the pure ethanol density. This is the result of the ideality of the mixture. The pressure dependence of the derived values of excess molar volumes for selected compositions is shown in Fig. 7.

3.3. Partial molar volumes

The partial molar volumes, \bar{V}_i , $i = 1, 2$, were obtained from the measured molar volumes V_m using the well-known relation

$$\bar{V}_1 = V_m - x \left(\frac{\partial V_m}{\partial x} \right)_{p,T}, \quad \bar{V}_2 = V_m + (1-x) \left(\frac{\partial V_m}{\partial x} \right)_{p,T}. \quad (3)$$

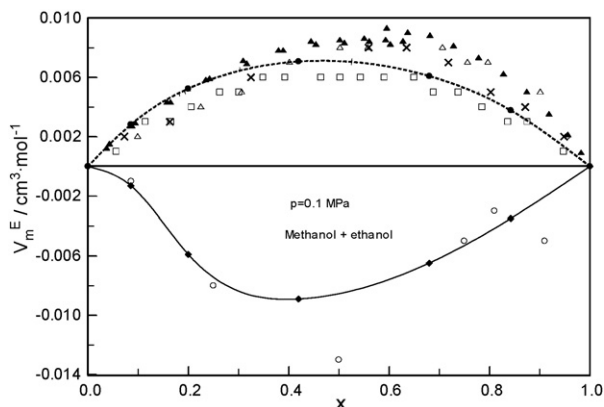


Fig. 6. Comparison reported values of excess molar volumes V_m^E of methanol + ethanol mixtures at 0.1 MPa and 298.15 K with the present results. \square , Arce et al. [11]; \circ , Albuquerque et al. [5]; \bullet , this work (calculated with the value of for pure ethanol density calculated from [23]); \blacktriangle , Benson and Pflug [12]; \times , Zarei et al. [14]; \blacktriangle , Rodriguez et al. [6]; \blacklozenge , this work (calculated with the corrected within experimental uncertainty value of density for pure ethanol).

Derived values of the partial molar volumes are presented in Table 2. The values of the derivative $(\partial V_m / \partial x)_{p,T}$ were calculated using the EOS for the methanol + ethanol mixture (see below Section 3.5). As Table 2 shows, partial molar volume, \bar{V}_1 , almost linearly decrease with pressure increasing and very slightly changes with concentration. The opposite behavior is found for the partial molar volume, \bar{V}_2 . This is typical behavior for the ideal mixtures. For non-ideal mixtures (alcohol + water, alcohol + ionic liquids, for example), $\bar{V}_1 - x$ and $\bar{V}_2 - x$ isotherm-isobar shows minimum and maximum, respectively, near the $x=0$ and $x=1.0$ (dilute mixtures), see, for example, Kubota et al. [37] and Abdulagatov et al. [17].

3.4. Vapor-pressures and saturated densities of methanol + ethanol mixtures

There are several publications on the vapor-pressure of methanol + ethanol mixture (see for example, refs. [26–36]). We use analytical extrapolation technique to calculate the vapor-pressure for methanol + ethanol mixtures. The experimental p – ρ curves (see Fig. 8) at constant temperature of 298.15 K for each measured concentrations were extrapolated to the saturation density reported by Konobeev and Lyapin [7]. The derived values of vapor-pressures for selected isotherms are presented in Table 3. The uncertainty in derived values of p_s is good enough (within 0.1–0.2%) because

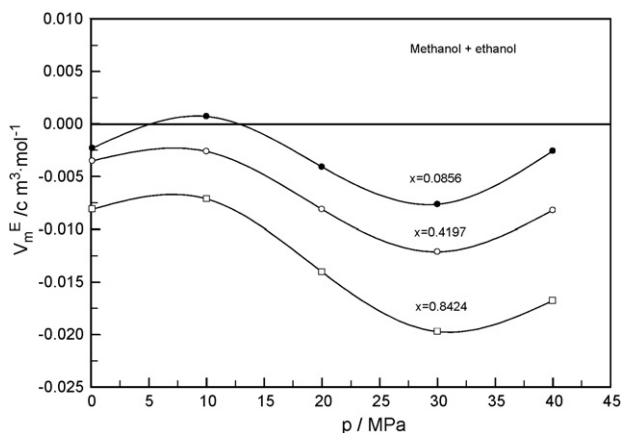


Fig. 7. Excess molar volumes V_m^E of methanol + ethanol mixtures as a function of pressure p at temperature of 298.15 K and at three selected concentrations.

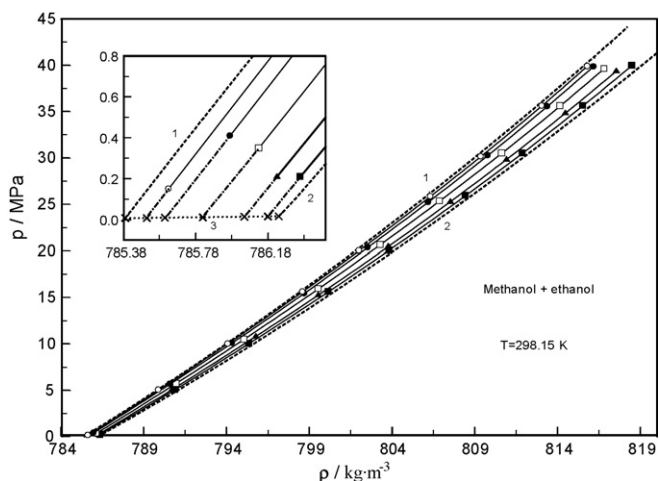


Fig. 8. Density dependence of the pressure along fixed temperature of 298.15 K at various concentrations. \circ , $x=0.0856$; \square , $x=0.1999$; \blacktriangle , $x=0.4197$; \blacklozenge , $x=0.6802$; \blacksquare , $x=0.8424$; 1–pure ethanol [23]; 2–vapor-pressure curve; (– – –), linear extrapolation of the experimental p – ρ curve to the saturation densities by Konobeev and Lyapin [5]; \times , vapor-pressures.

the experimental p – ρ isotherms are almost linear and the range of extrapolation is very small (maximum is within 0.1–0.4 MPa). Therefore, the extrapolation is very reliable. The basic source of the uncertainty of derived values of the vapor-pressure is the accuracy of the saturated densities [7]. The total uncertainty in derived values of the vapor-pressure including the uncertainty in the reported saturated densities is about 1–2%, because small changes in saturated densities are caused large changes in the pressure. The same technique was used to calculate the values of saturated density, ρ_s , by extrapolating experimental p – ρ curves to the vapor-pressures reported by other authors [26–36] for each experimental isotherm. The results are presented also in Table 3. The comparison between the derived values of the vapor-pressure and the reported data by other authors are shown in Fig. 9. The agreement between the published data and the present values is good (within 1.0–1.5%) except the old data reported by Schmidt [30] which are considerable lower than all of the available datasets. Fig. 9 also includes the values of vapor-pressure for ideal methanol + ethanol mixtures (solid lines). As one can see, departs from the ideality is negligible small (within their experimental uncertainty). The discrepancies for saturated densities are within 0.02–0.04% (see Fig. 10). The comparison between the present derived vapor-pressures and the reported data for selected concentration of 0.4197 mol fraction is shown in Fig. 11 together with vapor-pressure curves for pure components.

3.5. Equation of state

The measured densities for methanol + ethanol mixtures were used to develop polynomial type equations of state

$$p = [(a_{10} + a_{11}x)T + a_{20}T^2 + a_{30}T^3]\rho^m + (b_{00} + b_{01}x + b_{10}T)\rho^n + (c_{01} + c_{10}T + c_{20}T^2)\rho^k, \quad (4)$$

where the optimal values of the parameters m , n , and k are 2, 8, and 12, respectively. The derived values of parameters (a_{ij}) , (b_{ij}) , and (c_{ij}) of the equation of state (4) for methanol + ethanol mixture are given in Table 4. To accurately represent measured densities of pure components at atmospheric pressure we used quadratic functions

$$\rho_{01}(T, x = 1, p_0 = 0.1) = 893.6835 + 0.1582T - 0.1746 \times 10^{-2}T^2, \quad (5)$$

for pure methanol

Table 3

Pressures and densities at saturation for methanol+ ethanol mixtures derived from the present density measurements as a function of concentration at 298.15 K

x (mole fraction of methanol)	p_s (MPa)	ρ_s (kg m ⁻³)
T = 298.15 K		
0.0	0.0079	785.39
0.08564	0.0087	785.51
0.19998	0.0097	785.61
0.41971	0.0117	785.82
0.68017	0.0140	786.05
0.84236	0.0155	786.18
1.0	0.0170	786.24
T = 323.15 K		
0.0	0.0297	763.54
0.08564	0.0314	763.47
0.19998	0.0346	763.30
0.41971	0.0411	763.11
0.68017	0.0468	762.85
0.84236	0.0521	762.73
1.0	0.0557	762.53
T = 373.15 K		
0.0	0.2253	713.14
0.08564	0.2357	713.14
0.19998	0.2533	712.76
0.41971	0.2773	712.20
0.68017	0.3155	711.72
0.84236	0.3370	711.52
1.0	0.3537	710.95

$$\rho_{02}(T, x = 0, p_0 = 0.1) = 885.5504 + 0.159604T - 0.16624 \times 10^{-2} T^2,$$

for pure ethanol

(6)

The values of thermal expansion coefficient, $\alpha_{0i} = (1/\rho_{0i})(\partial\rho_{0i}/\partial T)_{p_0}$, calculated with Eqs. (5) and (6) for the pure methanol and ethanol at temperature 298.15 K and at 0.1 MPa

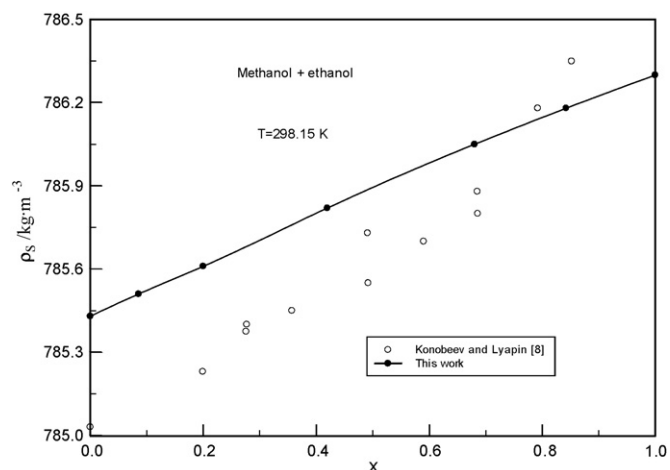


Fig. 10. Derived values of saturated density for methanol+ ethanol mixtures as a function of concentration at selected temperatures of 298.15 K together with reported data.

are ($1.124 \times 10^{-3} \text{ K}^{-1}$ and 1.059×10^{-3} , respectively) in a good (within 5% and 2%) agreement with the values reported by Benson and Pflug [12], Mori et al. [10], and Zarei et al. [14]. Equation of state (4) was used to calculate the some derived thermodynamic and structural properties of the methanol+ ethanol mixture such as partial molar volumes (see above Section 3.3), direct and

Table 4

Values of the coefficients a_{ij} , b_{ij} , and c_{ij} in Eq. (4)

$a_{10} = -2.12982 \times 10^0$	$b_{00} = -1.00241 \times 10^4$	$c_{01} = -3.65560 \times 10^3$
$a_{11} = -1.03039 \times 10^{-2}$	$b_{01} = 1.47273 \times 10^3$	$c_{10} = 6.97594 \times 10^0$
$a_{20} = 6.06462 \times 10^{-2}$	$b_{10} = 5.73137 \times 10^0$	$c_{20} = -1.85118 \times 10^{-2}$
$a_{30} = -3.38814 \times 10^{-5}$	–	–

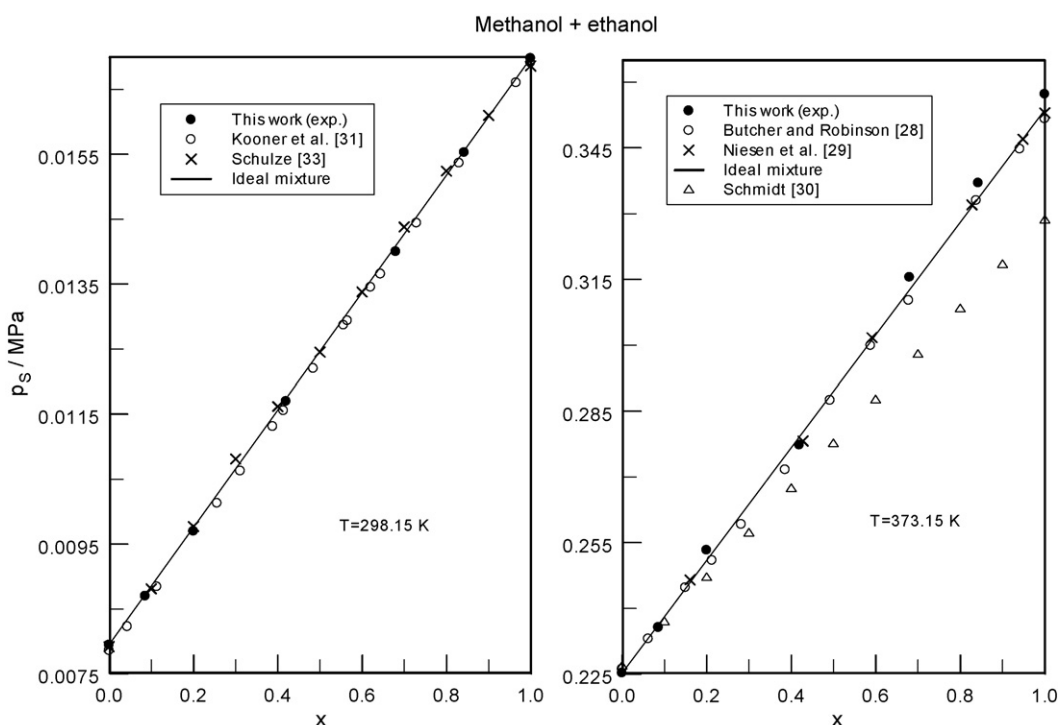


Fig. 9. Derived values of vapor-pressure for methanol+ ethanol mixtures as a function of concentration at two selected temperatures of 298.15 and 373.15 K together with reported data.

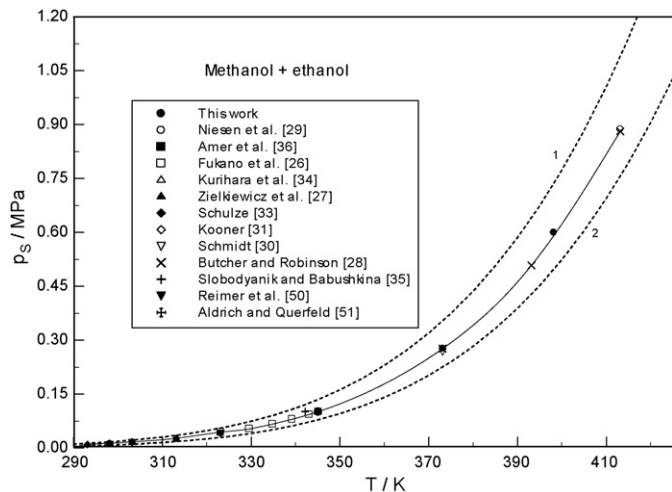


Fig. 11. Derived values of vapor-pressure for methanol + ethanol mixtures as a function of temperature at selected concentration of 0.4197 mol fraction of methanol together with reported data. 1-vapor-pressure of methanol IUPAC [22]; 2-vapor-pressure of ethanol [23].

total correlation function integrals, and the Krichevskii function (see below Section 3.6). Eq. (4) represent the present measured densities for the methanol + ethanol mixtures within 0.018% in the temperature range from 298 to 423 K at pressures up to 40 MPa and for the whole concentration range from 0 to 1 mol fraction of methanol.

3.6. Partial molar volume and structural properties of dilute mixtures of methanol + ethanol

As was shown above, measured and derived volumetric properties for the methanol + ethanol mixtures showed the ideality of the mixture. In this section, we studied the ideality of the mixtures

from the structural properties view point. As well know, the structural and thermodynamic properties of the dilute mixtures can be study using the Krichevskii function concept, which is defined as derivative $J = (\partial P / \partial x)_{VT}^{\infty}$ at $x \rightarrow 0$ [38–43]. The Krichevskii function directly related with the total (TCFI) and direct (DCFI) correlation function integrals [38–46]

$$J = \frac{\rho_1(H_{11} - H_{12})}{K_T}, \quad (7)$$

$$J = RT\rho_1^2(C_{11} - C_{12}) \quad (8)$$

where H_{11} and H_{12} are the TCFI defined as $H_{ij} = \int h_{ij}(r) dr$; $h_{ij}(r) = g_{ij}(r) - 1$ is the total correlation function for i - j pair interactions; $g_{ij}(r)$ is the radial distribution function; $H_{11} = (K_T RT) - \rho_1^{-1}$ is the TCFI for i - i pair (pure solvent molecules) interactions; C_{11} and C_{12} are DCFI defined as $C_{ij} = \int c_{ij}(r) dr$; $c_{ij}(r)$ is the direct correlation function for i - j pair interactions; and $(1 - \rho_1 C_{11}) = (\rho_1 K_T RT)^{-1}$ is the DCFI for i - i (pure solvent molecules) pair interactions; ρ_1 is the density of pure solvent. As Eqs. (7) and (8) shows, the Krichevskii function J expresses the difference between (1–2) and (1–1) interactions, i.e. account the ideality of the mixture. If the differences between $(C_{11} - C_{12})$ and $(H_{11} - H_{12})$ are also very small or zero ($C_{11} = C_{12}$) and $(H_{11} = H_{12})$, i.e. the interactions between solvent and solute molecules (1–2 interactions) and solvent–solvent (1–1 interactions) molecules are identical. This is can be considered as the microscopic definition of the ideality of the dilute mixtures. Krichevskii function concept is useful technique to study of the microstructural properties of dilute mixtures. Kirkwood and Buff [47] (see also Refs. [48,49]) showed that thermodynamic properties of fluid mixtures can be expressed in terms of DCFI and TCFI. The DCFI's are related to the TCFI by the integrated Ornstein–Zernike equation [45]

$$H_{12} = C_{12} + \rho C_{12} H_{11} \quad (9)$$

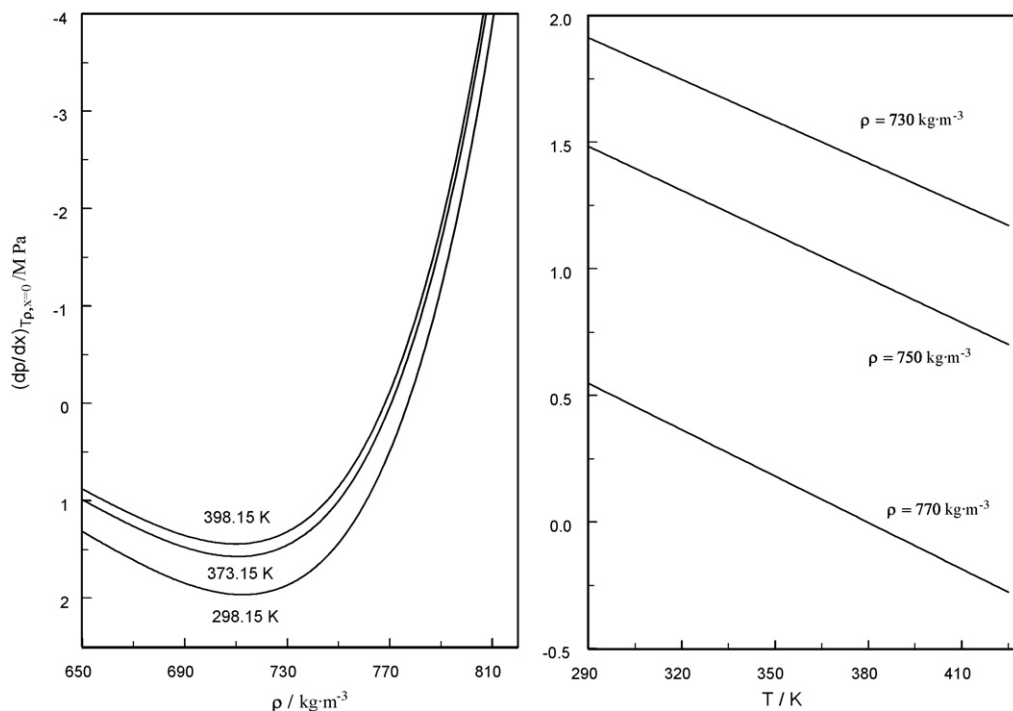


Fig. 12. Krichevskii function for methanol + ethanol mixture as a function of pure solvent (ethanol) density and temperature along the various selected isotherms (left) and isochores (right) calculated with EOS (4).

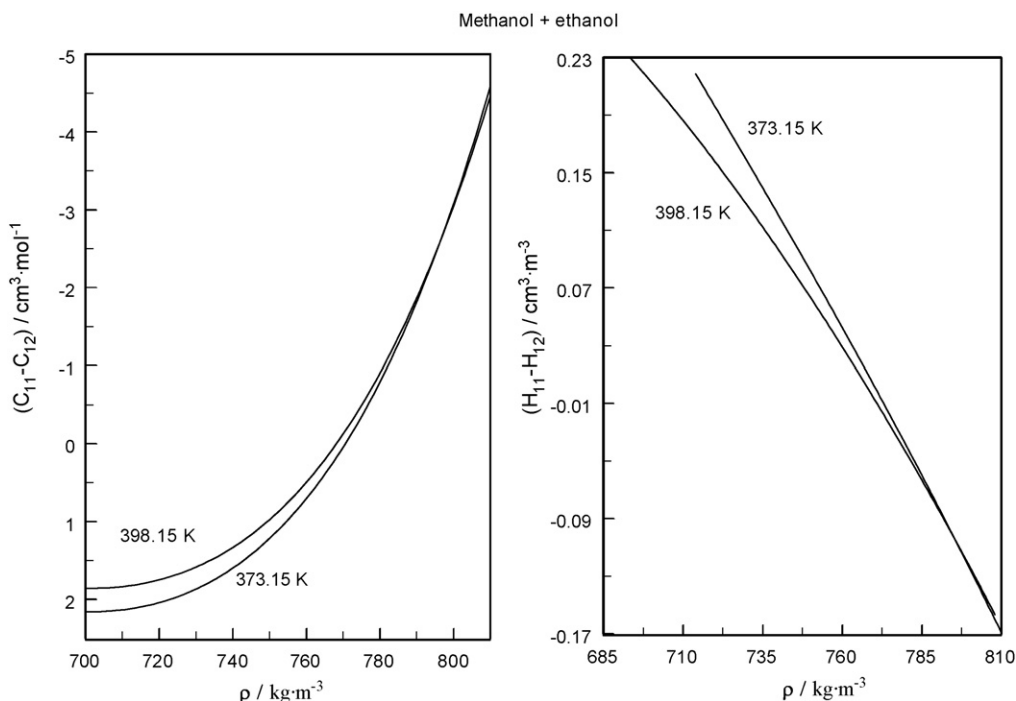


Fig. 13. Direct and total correlation function integrals differences for 1–1 and 1–2 pair interactions between ethanol–ethanol and methanol–ethanol as a function of density at two selected isotherms.

Thus, Krichevskii function takes into account the effects of the intermolecular interactions between solvent and solute molecules that determine the structural and thermodynamic properties of dilute solutions.

We used the equation of state (4) to calculate the Krichevskii function for methanol+ethanol mixtures. The calculated values of the Krichevskii function for this mixture as a function of density for the selected isotherms are shown in Fig. 12. As Fig. 12 shows, the Krichevskii function for this mixture is very small (for most alcohol containing binary mixtures Krichevskii function is about 200–500) and changing the sign in depending on the density. The negative values of the Krichevskii function means that the interaction between the methanol and ethanol molecules is attractive, while positive values mean that the interaction is repulsive.

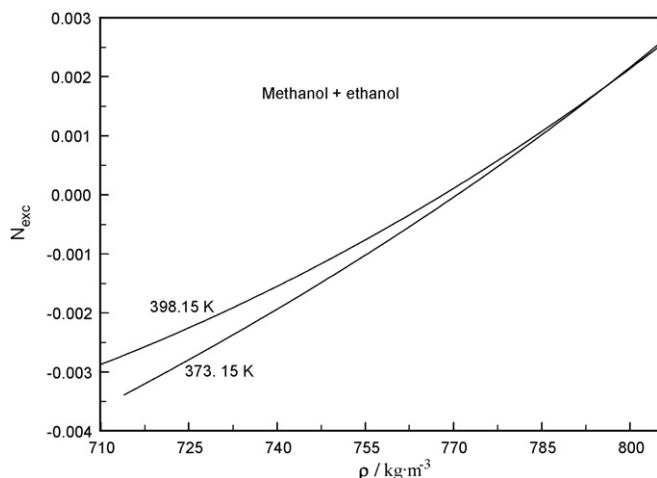


Fig. 14. The number of ethanol molecules (cluster size N_{exc} or coordination number) around a methanol molecule in excess of that found around an ethanol molecule, as a function of ethanol density along two isotherms.

The Krichevskii function is reflects the variation of the pressure of the system when exchanging a solvent (ethanol) molecule by one solute (methanol) molecule at constant volume and temperature. Derived values of the Krichevskii parameter were used to calculate the difference between the DCFI and TCFI for methanol–ethanol and ethanol–ethanol molecules in the methanol+ethanol dilute mixtures. The results are depicted in Fig. 13. As we expected, the values of $(C_{11} - C_{12})$ and $(H_{11} - H_{12})$ for the mixture are small (variation around the zero). Therefore, in microscopic view point the dilute methanol+ethanol mixture is ideal system. Another verification of the ideality of the methanol+ethanol mixture is the microstructural parameter, N_{exc}^{∞} , which defined the excess number (or excess coordination number, $N_{exc}^{\infty} = N_{12} - N_{11}$, where N_{12} indicate that the each methanol molecule surrounding by a cage of N_{12} molecules of ethanol, while N_{11} indicating that each ethanol molecule in the bulk surrounding by a cage of N_{11} other ethanol molecules) of solvent (ethanol) molecules around the infinitely dilute solute (methanol) relative to that number around any other solvent (ethanol) molecule. Microscopic definition of the excess coordination number is

$$N_{exc}^{\infty} = 4\pi\rho \int_0^{R_{shell}} [g_{12}(r) - g_{11}(r)]r^2 dr, \quad (10)$$

where $g_{11}(r)$ and $g_{12}(r)$ are the radial distribution functions for the solvent–solvent (1–1) and solvent–solute (1–2) interactions. The values of N_{exc}^{∞} are also related with the Krichevskii function as

$$N_{exc}^{\infty} = -K_T \left(\frac{\partial P}{\partial x} \right)_{TV}^{\infty}, \quad (11)$$

Thus, Krichevskii function is also define the microscopic phenomena involving local density perturbations induced by the presence of the solute molecules. Therefore, Krichevskii function is measure the finite microscopic rearrangement of the solvent structure around the infinitely dilute solute relative to the solvent structure ideal mixture. We calculated the values of N_{exc}^{∞} for the dilute methanol+ethanol mixture using the relation (11). As

one can see from Fig. 14, the excess number of solvent (ethanol) molecules N_{exc}^{∞} around the solute (methanol) molecules in the infinite dilution limit is nearly zero. This means that $N_{12} = N_{11}$, i.e. when exchanging a solvent (ethanol) molecule by one solute (methanol) molecule at constant volume and temperature, the local density (coordination number) of ethanol molecules around methanol molecule is not changing like ideal mixture or bulk density of pure ethanol (local environment around an infinitely dilute methanol not differ from the bulk average). Thus, methanol + ethanol are ideal mixtures. Unfortunately, there is no in the literature MD or MK simulations for this mixture to compare with the present results.

4. Conclusions

Density measurements (p , ρ , T data) and some derived properties such as excess and partial molar volumes of methanol + ethanol mixtures at temperatures from 298.15 to 423.15 K and at pressures up to $p = 40$ MPa for five concentrations (0.08564, 0.19998, 0.41971, 0.68017, and 0.84236 mol fraction of methanol) are reported. Analytical extrapolation technique was used to calculate the vapor-pressure and saturated densities for the mixture. Measured densities were used to develop accurate polynomial type equation of state of the mixture. This EOS represents the present density data within 0.018%. These data also were used to calculate the excess and partial molar volumes for the mixture. The derived values of excess molar volumes are very small which are confirming that the mixture is almost ideal. Method of correlation functions integral is applied to study of the structural and thermodynamic properties of dilute methanol + ethanol mixtures. Calculated values of the DCFI and TCFI and the excess coordination number of solvent (ethanol) molecules, N_{exc}^{∞} , around the infinitely dilute solute (methanol) at any measured temperatures and pressures is almost zero. This is microscopically confirmation of the ideality of mixture. All volumetric and structural properties for methanol + ethanol mixtures are found ideal.

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