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Vapour–liquid equilibrium for the 2-methylpropane + methanol, +ethanol, +2-propanol, +2-butanol and +2-methyl-2-propanol systems at 313.15 K

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Abstract

An automated total pressure measurement apparatus was used to measure PT_z data that was regressed into PT_{xy} data using the method of Barker (1953). The isothermal vapour–liquid equilibrium measurements were carried out for the five binary systems 2-methylpropane + methanol, +ethanol, +2-propanol, +2-butanol and +2-methyl-2-propanol at 313.15 K. Error analysis of the measured results is presented. Measurements were compared with predictions given by UNIFAC and COSMO-RS. All systems exhibited positive deviation from Raoult's law and azeotropic behaviour was found for the systems 2-methylpropane + methanol and 2-methylpropane + ethanol. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

Vapour–liquid equilibrium (VLE) data is needed for modelling separation processes in various stages of development, design, optimisation and revamping of chemical plants.

Theoretical prediction of VLE can be based on extrapolation methods like UNIFAC [1] or performed with Cosmo-RS [2], in which quantum mechanical calculation of single molecules in a solvent is combined with statistical thermodynamical calculations of a solution.

These methods have been found to be particularly useful in the preliminary stages of process development when sufficient amount and quality of experimental information of the system is not available. However, when the performance of the studied process is sensitive to accuracy of the vapour–liquid equilibrium data, the accuracy of the predictive models is seldom adequate. This is encountered for example within azeotropic distillations.

Vapour–liquid equilibrium data for 1-butene, 2-methylpropane, cis-2-butene and trans-2-butene with methanol,

ethanol, 2-propanol, 2-butanol and 2-methyl-2-propanol has been presented in our earlier papers [3–6]. Vapour–liquid equilibrium data for the systems presented in this work was found for the systems 2-methylpropane + methanol [7] at temperatures 273.15, 323.15, 373.15, 398.15, 404.15, 406.15 and 423.15 K, 2-methylpropane + ethanol [8] at 308.6, 318.4 and 363.5 K and 2-methylpropane + 2-propanol [9] at 331.5 K and 363.6 K. Excess enthalpies have been determined for the 2-methylpropane + 2-propanol system at 298.15 and 325.15 K at a pressure of 5, 10 and 15 MPa [10]. Miyano et al. measured Henry's constants for 2-methylpropane in methanol [11], 2-propanol [12], 2-butanol [13] and 2-methylpropanol [14] at temperatures from 250 to 330 K. Most of the earlier VLE measurements for these systems utilize sampling of the liquid and vapour phases. Sampling of the vapour phases poses problems especially at lower pressures, which leads to inconsistencies in the measured results.

In this work, total pressure–temperature–total composition (pT_z) measurements were carried out for 2-methylpropane with methanol, ethanol, 2-propanol, 2-butanol and 2-methyl-2-propanol at 313.15 K. The experimental data were used for a comparative analysis of the predictive ability of UNIFAC and COSMO-RS.

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2. Experimental section

2.1. Materials

Methanol (99.8 wt.%), was provided by Merck, ethanol (99.5 wt.%) by Primalco Oy, 2-propanol (99.8 wt.%) by Riedel-de Haën, and 2-butanol (>99.5 wt.%) and 2-methyl-2-propanol (>99.7 wt.%) by Fluka. 2-Methylpropane (99.4 mol%) was provided by Messer Finland Oy.

2-Methylpropane was used as supplied. The alcohols were dried over molecular sieves (Merck3A) at least for 24 h before the degassing procedure. Degassing was performed in a round-bottomed flask, which was placed in an ultrasonic bath. Small pieces of steel packing were added to the flask to enhance the boiling. A column packed with steel mesh was used as a reflux condenser in the system. The cooling water flowed inside the cooling jacket around the condenser. The condenser returned the vaporised material back to the flask with very high reflux ratio. Evacuation of the system through the reflux condenser caused the boiling. Usually from 10 to 30 vol.% of the material was vaporised to the liquid nitrogen trap during the degassing. Degassing was continued for at least 5 h. Success of the degassing procedure was checked through comparing the measured vapour pressures, listed in Table 1, with the values calculated from literature correlations. A schematic figure of the apparatus used for degassing is presented in our earlier paper [15].

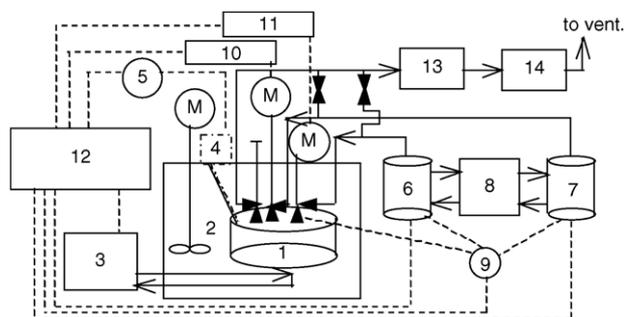


Fig. 1. Schematic of the automated apparatus: (1) equilibrium cell with a magnetic stirrer; (2) 70 dm³ water bath; (3) circulator thermostat; (4) electrically traced pressure transducer connected to the equilibrium cell with electrically traced 1/16 in. tubing; (5) pressure display; (6, 7) syringe pumps; (8) circulator thermostat; (9) temperature display; (10, 11) stepper motor interface card; (12) PC with a SmartIO C168H card at PCI bus; (13) liquid nitrogen trap; (14) vacuum pump.

2.2. Apparatus

Details of the VLE apparatus were presented in our earlier paper [4]. The experimental set-up is presented in Fig. 1. Temperature was measured with a thermometer (Thermolyzer S2541 (Frontek)), which was equipped with Pt-100 probes. The temperature meter and the probes were calibrated at the Finnish National Standards Laboratory. The resolution of the temperature measurement system was 0.005 K and the calibration uncertainty was ± 0.015 K. The overall uncertainty

Table 1
Measured vapor pressures and values calculated from literature correlations

	T (K)	Vapor pressure (kPa)			
		a	b	c	d
2-Methylpropane	529.65	526.77			
	313.06			533.33	
		530.05	527.05		531.06
	313.08	529.95		533.60	531.34
	313.12	530.75	527.60	534.16	531.89
	313.07	529.95	526.91		
Methanol	313.07	35.27		35.20	35.28
			35.35		
				17.81	17.93
Ethanol	313.07	17.77			
			17.85		
2-Propanol	313.11	13.77		14.29	14.26
			13.95		
2-Butanol	313.10	5.97		6.24	6.29
			6.00		
2-Methyl-2-propanol	313.08	13.77			
			13.77	13.70	13.83

^a This work.

^b Reid et al. [30].

^c Yaws [31].

^d Perry et al. [20].

of the temperature measurement system is estimated to be ± 0.03 K. The equilibrium cell temperature was measured with a temperature probe that was located in contact with the equilibrium cell wall.

The pressure was measured with a Digiquartz 2100A-101-CE pressure transducer (0–689 kPa, compensated temperature range 219–380 K) equipped with a Digiquartz 740 intelligent display-unit. The uncertainty of the pressure measurement was ± 0.069 kPa, according to data provided by the manufacturers of the pressure measurement device. The overall accuracy of the pressure measurement system, which includes pressure transducer, heated pressure measurement line and equilibrium cell is ± 0.2 kPa. To eliminate systematic errors, the pressure measurement system including the pressure measurement line (1/16") tube between the pressure meter and the cell was checked against a DHPPC-2 pressure calibrator. A calibrator was connected to the fitting in the cell lid. Also the temperature compensation of the pressure transducer was checked, for which a portable calibrator with an accuracy of 0.3 kPa was used. Checking indicated that the pressure measurement line tube or the cell did not have detectable effect to the pressure measurement.

Injections of the components were made with syringe pumps (Isco 260 D and Isco 100 DM). The temperatures and the pressures of the barrels of the syringe pumps were controlled. The temperatures of the syringe pumps were measured with temperature probes located in contact with the syringe pump barrels. The pressures of the syringe pump barrels were controlled with built-in strain gauge pressure meters in the pumps. The injection volumes of the pumps were calibrated gravimetrically prior to measurements with distilled water.

The total volume of the equilibrium cell was 113.5 cm^3 . The cell volume was determined by injecting degassed distilled water in to the cell at 298.15 K. The estimated uncertainty of the total volume of equilibrium cell is $\pm 0.05 \text{ cm}^3$. The valves for filling and evacuation and the fitting for emptying the cell were welded to the cell lid. The pressure measurement line (1/16") tube was soldered to the cell lid. The content of the cell was agitated with a magnetic stirrer. Small baffles were put into the equilibrium cell in order to reduce the equilibration time.

The water bath was built of an insulated cylindrical vessel with a volume of approximately 70 dm^3 . The heating coil located on the inside wall of the bath held the bath temperature constant. Heating water circulated inside the heating coil. The temperature stability of the bath, ± 0.02 K, was discussed in our earlier paper [15].

2.3. Procedure

For investigated system an identical measuring procedure was followed. The composition range was measured in two steps; from the both ends of the composition scale to an approximately equimolar mixture. Injection volumes were optimized so that the equilibrium cell became nearly filled with

mixture in both steps of the measurement. This was done to improve the measurement accuracy of the overall compositions in the equilibrium cell. The syringe pumps were operated in constant pressure mode (900 kPa) to ensure the accuracy of the volume measurement, to prevent the contamination of degassed components and to keep isobutene in liquid phase. The Hankinson–Brobst–Thomson method [16] was used to take the pressure effects on the liquid densities in the syringe pumps into account. The temperatures of the syringe pumps were measured. The cell content and the bath were mixed continuously during the measurements.

Pure component vapour pressures and 23–26 equilibrium points were measured in each run. At first, component 1 was introduced into the cell and its vapour pressure was measured. The unchanged pressure after a second addition of the first component into the cell indicated the success of the degassing. The vapour pressure would rise due to incomplete degassing of the component as a result of dissolved gases in the equilibrium cell. After the vapour pressure measurement of component 1 a predetermined volume of component 2 was added to the equilibrium cell. The cell content was mixed with a magnetic mixer and the cell was let to equilibrate for approximately 30 min. The additions of component 2 were continued until the target composition was reached and cell became nearly filled with the mixture. The emptying and the evacuation of the equilibrium cell ended the first part of the measurement. Measuring the other side of the isotherm was initiated by injecting the pure component 2 and checking its vapour pressure. The additions of component 1 were continued to the target composition. The success of the run could be verified by comparing the coincidence of the cell pressures as a function of total composition when the different sides of the isotherm meet at the mole fraction of approximately 0.5.

The data transfer between water bath, temperature and pressure meters, stepping motors and syringe pumps and the PC were operated via a SmartIO C168H/8 ports card at a PCI bus. The actual run was programmed in a spreadsheet program. Once the program was started the proceeding of measurements could be followed with trend plots. Data written into file as a function of time allowed detailed analysis of the measurements and further calculation of final results.

2.4. Data reduction

The method proposed by Barker [17] was used to convert the total amount of moles fed in to the cell into mole fractions in both vapour and liquid phase. The method of Barker data reduction assumes that there is an activity coefficient model that can predict the bubble point pressure with higher accuracy than the experimental error of the measured total pressure. Barker's method is an iterative method, which needs vapour phase fugacities and liquid phase activities to be calculated. The method chosen for calculating fugacity coefficients was the Soave Redlich–Kwong equation of state with quadratic mixing rule [18]. Liquid phase activity coefficients were obtained using Legendre polynomials [19], which due

Table 2

Critical temperature T_c , critical pressure p_c , acentric factor ω , liquid molar volume V_i , UNIQUAC volume parameter R_{UNIQUAC} , UNIQUAC area parameter Q_{UNIQUAC}

Component	2-Methylpropane	Methanol	Ethanol
T_c (K ^a)	408.14 ± 4.08	512.58 ± 5.13	516.25 ± 5.16
p_c (MPa ^a)	3.648 ± 0.04	8.0959 ± 0.24	6.3835 ± 0.19
ω^a	0.1770	0.5656	0.6371
V_i (cm ³ /mol)	104.36 ^b	40.702 ± 0.41 ^a	58.515 ± 0.59 ^a
R_{UNIQUAC}^b	3.1502	1.4311	2.2668
Q_{UNIQUAC}^b	2.7720	1.4320	2.3283

Component	2-Propanol	2-Butanol	2-Methyl-2-propanol
T_c (K ^a)	508.31 ± 5.08	536.01 ± 5.36	506.2 ± 5.06
p_c (MPa ^a)	4.7643 ± 0.14	4.1938 ± 0.13	3.9719 ± 0.12
ω^a	0.6689	0.5711	0.6158
V_i (cm ³ /mol ^a)	76.784 ± 0.15	92.118 ± 0.92	94.861 ± 2.85
R_{UNIQUAC}^b	3.2491	3.9235	3.9228
Q_{UNIQUAC}^b	3.1240	3.6640	3.7440

^a Daubert and Danner [28].^b Poling et al. [29].

to their flexible nature are suitable for accurately describing non-ideal behaviour of the liquid phase. To avoid overfitting, as few parameters were used in Legendre polynomials as was necessary in terms of successful data reduction.

The scheme used here for data reduction is reported earlier by Uusi-Kyyny et al. [15]. The critical properties needed for data reduction by Barker's method are presented in Table 2.

2.5. Error analysis

Error estimates were obtained for all measured variables. For cell volume, temperature and pressure, absolute errors are reported above. For total mole fractions z_i , following analysis was done to determine error margins.

The uncertainty in vapour and liquid mole fractions depends on many quantities, such as uncertainties in the measurement of cell temperature, pressure, overall composition of the mixture in the cell, and the total volume of the cell. The uncertainty of the overall composition of the mixture in the cell depends on the uncertainty of injections. The uncertainty of injection volumes $\Delta V_1 = \pm 0.02 \text{ cm}^3$ was obtained from the calibration experiments with distilled water. The estimated inaccuracies of temperature and pressure measurement in the pumps are $\Delta T = \pm 0.1 \text{ K}$ and $\Delta p = \pm 20 \text{ kPa}$. Densities of components were calculated from the correlations in reference [20]. Uncertainties of density correlations were for 2-methylpropane, methanol, ethanol, 2-propanol and 2-methyl-2-propanol <1.0% ($\Delta \rho_1 = \pm 0.01 \rho_1$) and for 2-butanol <3.0% ($\Delta \rho_1 = \pm 0.03 \rho_1$) [21]. Mathematical treatment of the error analysis is discussed earlier in [4].

2.6. COSMO-RS calculations

All Cosmo-RS calculations were performed using a continuum model with density functional theory (RI-DFT) using BP functional with TZVP basis set as it was implemented

in Turbomole program [22] (version 5.7). Geometry optimisation for the molecules under investigation was performed with Turbomole software. Subsequent COSMO calculations were done with the CosmoTherm program (COSMOtherm-C12-0103 [23]).

Even though COSMO-RS is capable of predicting vapour pressures, to avoid any additional errors only experimentally determined pure component vapour pressures were used in calculations. For ethanol, 2-butanol and 2-propanol several conformers were taken into account in COSMO-RS calculations.

3. Results and discussion

3.1. Vapour–liquid equilibrium measurements

All five binary pairs measured show positive deviation from Raoult's law. The results of 2-methylpropane + methanol are presented in Table 3, of 2-methylpropane + ethanol in Table 4, of 2-methylpropane + 2-propanol in Table 5, of 2-methylpropane + 2-butanol in Table 6 and of 2-methylpropane + 2-methyl-2-propanol in Table 7. Estimated theoretical maximum errors are given in Tables 3–7 for the measured mole amounts and total composition. It is very unlikely that all measured quantities; temperature, pressure, composition of the mixture in the cell and total volume of the cell are simultaneously in their lower or upper boundaries of uncertainty. Therefore, the actual errors of calculated liquid and vapour compositions and activity coefficients are typically smaller. Injected amounts of moles are presented in Tables 3–7 using more significant digits than their errors would indicate. This is required, if someone wants to recalculate the measured data.

Fig. 2 presents the experimental pressure as a function of liquid and vapour composition. Parameters of the Legendre polynomial are summarised in Table 8.

Table 3

VLE data for the 2-methylpropane(1) + methanol(2) system at 326 K: n_1 and n_2 , moles of components in the equilibrium cell; total composition z_1 , calculated liquid phase x_1 , and vapour phase y_1 , mole fractions; experimental pressure p_{exp} , and pressure calculated from the Legendre-polynomial fit p_{leg} ; experimental temperature T ; and activity coefficient, γ_i

n_1 (mol)	n_2 (mol)	z_1	x_1	y_1	T (K)	p_{exp} (kPa)	p_{leg} (kPa)	γ_1	γ_2
0.0000 ± 0.0	0.9290 ± 0.0099	0.0000 ± 0.0	0.0000	0.0000	313.07	35.27	35.27	13.86	1.00
0.0321 ± 0.0005	0.9290 ± 0.0099	0.0334 ± 0.0009	0.0289	0.8133	313.07	190.96	190.96	11.10	1.00
0.0519 ± 0.0007	0.9290 ± 0.0099	0.0530 ± 0.0013	0.0467	0.8631	313.06	261.26	261.34	9.79	1.01
0.1051 ± 0.0013	0.9290 ± 0.0099	0.1016 ± 0.0021	0.0934	0.9065	313.06	383.35	383.35	7.31	1.03
0.1652 ± 0.0019	0.9290 ± 0.0099	0.1510 ± 0.0029	0.1429	0.9211	313.07	452.65	452.79	5.63	1.07
0.2321 ± 0.0026	0.9290 ± 0.0099	0.1999 ± 0.0035	0.1930	0.9275	313.07	490.25	490.25	4.49	1.12
0.3089 ± 0.0034	0.9290 ± 0.0099	0.2495 ± 0.0041	0.2443	0.9308	313.07	510.95	510.95	3.70	1.18
0.3961 ± 0.0043	0.9290 ± 0.0099	0.2989 ± 0.0045	0.2953	0.9327	313.07	522.55	522.54	3.12	1.25
0.4995 ± 0.0053	0.9290 ± 0.0099	0.3497 ± 0.0049	0.3477	0.9338	313.08	529.35	529.40	2.69	1.35
0.6171 ± 0.0065	0.9290 ± 0.0099	0.3991 ± 0.0051	0.3985	0.9345	313.07	533.35	533.33	2.36	1.46
0.6220 ± 0.0066	0.9290 ± 0.0099	0.4010 ± 0.0051	0.4004	0.9345	313.08	533.45	533.44	2.35	1.46
0.6015 ± 0.0064	0.9192 ± 0.0098	0.4516 ± 0.0051	0.4501	0.9350	313.06	535.55	535.67	2.10	1.59
0.6015 ± 0.0064	0.7483 ± 0.0081	0.5017 ± 0.0053	0.4997	0.9353	313.06	537.15	537.14	1.89	1.74
0.6015 ± 0.0064	0.6120 ± 0.0067	0.5508 ± 0.0054	0.5484	0.9355	313.06	538.35	538.30	1.73	1.92
0.6015 ± 0.0064	0.5026 ± 0.0056	0.6023 ± 0.0054	0.5997	0.9358	313.06	539.45	539.44	1.59	2.16
0.6015 ± 0.0064	0.4069 ± 0.0046	0.6525 ± 0.0053	0.6499	0.9362	313.06	540.45	540.52	1.47	2.47
0.6015 ± 0.0064	0.3282 ± 0.0038	0.7029 ± 0.0051	0.7004	0.9365	313.06	541.55	541.54	1.36	2.87
0.6015 ± 0.0064	0.2604 ± 0.0032	0.7531 ± 0.0048	0.7508	0.9370	313.06	542.55	542.54	1.27	3.43
0.6015 ± 0.0064	0.2021 ± 0.0026	0.8029 ± 0.0044	0.8010	0.9377	313.07	543.84	543.81	1.20	4.25
0.6015 ± 0.0064	0.1513 ± 0.0020	0.8534 ± 0.0039	0.8521	0.9391	313.07	545.34	545.43	1.13	5.61
0.6015 ± 0.0064	0.1059 ± 0.0016	0.9036 ± 0.0032	0.9030	0.9414	313.06	547.04	547.04	1.07	8.25
0.6015 ± 0.0064	0.0657 ± 0.0012	0.9540 ± 0.0025	0.9541	0.9479	313.06	548.44	547.89	1.02	15.54
0.6015 ± 0.0064	0.0297 ± 0.0008	0.9939 ± 0.0017	0.9941	0.9836	313.05	538.45	536.87	1.00	37.18
0.6015 ± 0.0064	0.0000 ± 0.0	1.0000 ± 0.0	1.0000	1.0000	313.06	529.65	529.65	1.00	44.39

Table 4

VLE data for the 2-methylpropane(1) + ethanol(2) system at 326 K: n_1 and n_2 , moles of components in the equilibrium cell; total composition z_1 , calculated liquid phase x_1 , and vapour phase y_1 , mole fractions; experimental pressure p_{exp} , and pressure calculated from the Legendre-polynomial fit p_{leg} ; experimental temperature T ; and activity coefficient, γ_i

n_1 (mol)	n_2 (mol)	z_1	x_1	y_1	T (K)	p_{exp} (kPa)	p_{leg} (kPa)	γ_1	γ_2
0.0000 ± 0.0	0.8055 ± 0.0085	0.0000 ± 0.0	0.0000	0.0000	313.07	17.77	17.77	7.30	1.00
0.0269 ± 0.0005	0.8055 ± 0.0085	0.0323 ± 0.0009	0.0305	0.8391	313.08	110.57	110.57	6.41	1.00
0.0436 ± 0.0006	0.8055 ± 0.0085	0.0514 ± 0.0012	0.0489	0.8874	313.08	157.77	157.77	5.95	1.01
0.0896 ± 0.0011	0.8055 ± 0.0085	0.1000 ± 0.0021	0.0972	0.9310	313.08	256.06	256.06	4.98	1.02
0.1398 ± 0.0016	0.8055 ± 0.0085	0.1479 ± 0.0028	0.1457	0.9465	313.08	326.76	326.80	4.23	1.04
0.1970 ± 0.0022	0.8055 ± 0.0085	0.1965 ± 0.0035	0.1959	0.9543	313.07	378.55	378.55	3.62	1.08
0.2610 ± 0.0029	0.8055 ± 0.0085	0.2447 ± 0.0040	0.2459	0.9589	313.07	415.25	415.20	3.15	1.12
0.3376 ± 0.0037	0.8055 ± 0.0085	0.2953 ± 0.0045	0.2985	0.9619	313.07	442.55	442.55	2.75	1.18
0.4233 ± 0.0046	0.8055 ± 0.0085	0.3445 ± 0.0048	0.3496	0.9639	313.07	461.45	461.45	2.45	1.25
0.5233 ± 0.0056	0.8055 ± 0.0085	0.3938 ± 0.0051	0.4006	0.9653	313.07	475.15	475.04	2.19	1.33
0.5026 ± 0.0054	0.6109 ± 0.0065	0.4513 ± 0.0053	0.4491	0.9663	313.07	484.45	484.49	1.99	1.43
0.5026 ± 0.0054	0.5004 ± 0.0054	0.5011 ± 0.0054	0.4981	0.9671	313.07	491.75	491.75	1.82	1.55
0.5026 ± 0.0054	0.4087 ± 0.0045	0.5515 ± 0.0054	0.5480	0.9678	313.07	497.65	497.58	1.67	1.70
0.5026 ± 0.0054	0.3327 ± 0.0037	0.6017 ± 0.0052	0.5978	0.9685	313.07	502.35	502.35	1.55	1.89
0.5026 ± 0.0054	0.2687 ± 0.0031	0.6516 ± 0.0050	0.6475	0.9691	313.08	506.35	506.46	1.44	2.13
0.5026 ± 0.0054	0.2136 ± 0.0025	0.7018 ± 0.0047	0.6978	0.9696	313.08	509.95	509.95	1.34	2.45
0.5026 ± 0.0054	0.1660 ± 0.0020	0.7517 ± 0.0043	0.7480	0.9703	313.09	513.45	513.36	1.26	2.89
0.5026 ± 0.0054	0.1241 ± 0.0016	0.8020 ± 0.0037	0.7987	0.9711	313.09	516.95	516.94	1.19	3.53
0.5026 ± 0.0054	0.0872 ± 0.0012	0.8521 ± 0.0031	0.8495	0.9724	313.09	520.85	520.98	1.13	4.55
0.5026 ± 0.0054	0.0543 ± 0.0009	0.9025 ± 0.0024	0.9008	0.9741	313.09	524.95	524.97	1.07	6.50
0.5026 ± 0.0054	0.0250 ± 0.0006	0.9526 ± 0.0015	0.9520	0.9773	313.09	529.35	528.78	1.02	11.83
0.5026 ± 0.0054	0.0047 ± 0.0004	0.9908 ± 0.0009	0.9908	0.9902	313.09	531.85	531.40	1.00	26.85
0.5026 ± 0.0054	0.0000 ± 0.0	1.0000 ± 0.0	1.0000	1.0000	313.08	530.05	530.04	1.00	35.23

Table 5

VLE data for the 2-methylpropane(1) + 2-propanol(2) system at 326 K: n_1 and n_2 , moles of components in the equilibrium cell; total composition z_1 , calculated liquid phase x_1 , and vapour phase y_1 , mole fractions; experimental pressure p_{exp} , and pressure calculated from the Legendre-polynomial fit p_{leg} ; experimental temperature T ; and activity coefficient, γ_i

n_1 (mol)	n_2 (mol)	z_1	x_1	y_1	T (K)	p_{exp} (kPa)	p_{leg} (kPa)	γ_1	γ_2
0.0000 ± 0.0	0.6257 ± 0.0067	0.0000 ± ± 0.0	0.0000	0.0000	313.11	13.77	13.77	5.04	1.00
0.0222 ± 0.0004	0.6257 ± 0.0067	0.0342 ± 0.0010	0.0318	0.8319	313.10	81.57	81.57	4.53	1.00
0.0357 ± 0.0006	0.6257 ± 0.0067	0.0540 ± 0.0014	0.0505	0.8828	313.11	116.67	116.67	4.29	1.00
0.0718 ± 0.0009	0.6257 ± 0.0067	0.1030 ± 0.0022	0.0977	0.9299	313.11	193.06	193.04	3.79	1.01
0.1127 ± 0.0014	0.6257 ± 0.0067	0.1526 ± 0.0030	0.1466	0.9479	313.11	255.96	256.13	3.36	1.03
0.1568 ± 0.0018	0.6257 ± 0.0067	0.2004 ± 0.0036	0.1945	0.9568	313.11	304.66	304.66	3.00	1.06
0.2085 ± 0.0023	0.6257 ± 0.0067	0.2500 ± 0.0041	0.2447	0.9624	313.11	344.86	344.76	2.69	1.09
0.2682 ± 0.0030	0.6257 ± 0.0067	0.3000 ± 0.0046	0.2958	0.9662	313.11	376.75	376.76	2.42	1.13
0.3355 ± 0.0036	0.6257 ± 0.0067	0.3491 ± 0.0049	0.3459	0.9688	313.11	401.55	401.55	2.19	1.18
0.4156 ± 0.0045	0.6257 ± 0.0067	0.3991 ± 0.0051	0.3972	0.9708	313.12	421.55	421.60	2.00	1.25
0.5093 ± 0.0054	0.6257 ± 0.0067	0.4488 ± 0.0053	0.4480	0.9724	313.12	437.55	437.29	1.83	1.33
0.5050 ± 0.0054	0.5073 ± 0.0055	0.4989 ± 0.0054	0.4971	0.9736	313.09	449.25	449.25	1.70	1.43
0.5050 ± 0.0054	0.4152 ± 0.0045	0.5488 ± 0.0053	0.5464	0.9747	313.09	459.75	459.74	1.58	1.55
0.5050 ± 0.0054	0.3385 ± 0.0037	0.5987 ± 0.0052	0.5957	0.9757	313.09	468.95	468.95	1.47	1.70
0.5050 ± 0.0054	0.2740 ± 0.0031	0.6483 ± 0.0050	0.6450	0.9767	313.10	477.15	477.31	1.38	1.88
0.5050 ± 0.0054	0.2180 ± 0.0025	0.6985 ± 0.0046	0.6950	0.9776	313.10	485.05	485.05	1.30	2.12
0.5050 ± 0.0054	0.1699 ± 0.0020	0.7483 ± 0.0042	0.7449	0.9787	313.10	492.55	492.43	1.23	2.45
0.5050 ± 0.0054	0.1280 ± 0.0016	0.7978 ± 0.0037	0.7946	0.9799	313.10	499.75	499.75	1.17	2.90
0.5050 ± 0.0054	0.0909 ± 0.0012	0.8474 ± 0.0031	0.8448	0.9814	313.10	506.95	507.09	1.12	3.60
0.5050 ± 0.0054	0.0577 ± 0.0009	0.8975 ± 0.0023	0.8956	0.9832	313.11	514.15	514.15	1.07	4.88
0.5050 ± 0.0 ± 0.054	0.0284 ± 0.0006	0.9468 ± 0.0015	0.9458	0.9859	313.11	521.45	520.72	1.03	7.98
0.5050 ± 0.0054	0.0067 ± 0.0003	0.9868 ± 0.0008	0.9867	0.9931	313.12	527.75	527.99	1.00	16.01
0.5050 ± 0.0054	0.0000 ± 0.0	1.0000 ± 0.0	1.0000	1.0000	313.12	530.75	530.74	1.00	22.14

Table 6

VLE data for the 2-methylpropane(1) + 2-butanol(2) system at 326 K: n_1 and n_2 , moles of components in the equilibrium cell; total composition z_1 , calculated liquid phase x_1 , and vapour phase y_1 , mole fractions; experimental pressure p_{exp} , and pressure calculated from the Legendre-polynomial fit p_{leg} ; experimental temperature T ; and activity coefficient, γ_i

n_1 (mol)	n_2 (mol)	z_1	x_1	y_1	T (K)	p_{exp} (kPa)	p_{leg} (kPa)	γ_1	γ_2
0.0000 ± 0.0	0.5078 ± 0.0054	0.0000 ± 0.0	0.0000	0.0000	313.10	5.97	5.97	3.73	1.00
0.0222 ± 0.0004	0.5078 ± 0.0054	0.0418 ± 0.0012	0.0389	0.9173	313.07	71.47	71.47	3.59	1.00
0.0312 ± 0.0005	0.5078 ± 0.0054	0.0579 ± 0.0015	0.0540	0.9382	313.07	95.27	95.33	3.50	1.00
0.0716 ± 0.0009	0.5078 ± 0.0054	0.1235 ± 0.0026	0.1173	0.9680	313.07	181.46	181.42	3.10	1.01
0.0939 ± 0.0012	0.5078 ± 0.0054	0.1561 ± 0.0031	0.1493	0.9736	313.07	217.46	217.52	2.91	1.02
0.1219 ± 0.0015	0.5078 ± 0.0054	0.1935 ± 0.0036	0.1866	0.9777	313.07	254.26	254.26	2.70	1.04
0.1663 ± 0.0019	0.5078 ± 0.0054	0.2467 ± 0.0042	0.2401	0.9814	313.07	298.76	298.76	2.45	1.07
0.2158 ± 0.0024	0.5078 ± 0.0054	0.2983 ± 0.0046	0.2925	0.9837	313.07	334.06	334.14	2.23	1.10
0.2779 ± 0.0031	0.5078 ± 0.0054	0.3537 ± 0.0050	0.3492	0.9854	313.08	365.05	365.04	2.03	1.15
0.327 ± 0.0036	0.5078 ± 0.0054	0.3917 ± 0.0052	0.3882	0.9863	313.06	382.45	382.45	1.91	1.20
0.4145 ± 0.0045	0.5078 ± 0.0054	0.4494 ± 0.0053	0.4473	0.9874	313.07	405.15	405.16	1.75	1.28
0.4538 ± 0.0049	0.4575 ± 0.0049	0.4980 ± 0.0054	0.4959	0.9881	313.07	421.35	421.02	1.63	1.36
0.5065 ± 0.0055	0.5078 ± 0.0054	0.4994 ± 0.0054	0.4984	0.9882	313.07	421.75	421.74	1.62	1.36
0.5812 ± 0.0062	0.5078 ± 0.0054	0.5337 ± 0.0053	0.5335	0.9886	313.07	431.85	431.85	1.55	1.43
0.4538 ± 0.0049	0.3745 ± 0.0041	0.5479 ± 0.0054	0.5449	0.9888	313.07	434.85	434.94	1.53	1.46
0.4538 ± 0.0049	0.3051 ± 0.0033	0.5979 ± 0.0052	0.5943	0.9894	313.07	447.05	447.26	1.44	1.58
0.4538 ± 0.0049	0.2463 ± 0.0027	0.6482 ± 0.0050	0.6441	0.9899	313.06	458.15	458.15	1.36	1.74
0.4538 ± 0.0049	0.1955 ± 0.0022	0.6989 ± 0.0047	0.6946	0.9905	313.09	468.65	468.65	1.28	1.94
0.4538 ± 0.0049	0.1524 ± 0.0018	0.7485 ± 0.0042	0.7442	0.9911	313.09	478.45	478.23	1.22	2.22
0.4538 ± 0.0049	0.1150 ± 0.0014	0.7978 ± 0.0037	0.7938	0.9917	313.09	487.65	487.65	1.16	2.59
0.4538 ± 0.0049	0.0813 ± 0.0011	0.8480 ± 0.0030	0.8446	0.9924	313.09	496.65	496.99	1.11	3.18
0.4538 ± 0.0049	0.0508 ± 0.0007	0.8992 ± 0.0023	0.8967	0.9933	313.09	505.75	505.75	1.06	4.29
0.4538 ± 0.0049	0.0219 ± 0.0004	0.954 ± 0.0014	0.9527	0.9947	313.09	516.25	515.39	1.02	7.43
0.4538 ± 0.0049	0.0031 ± 0.0003	0.9933 ± 0.0006	0.9931	0.9985	313.08	527.05	527.05	1.00	14.80
0.4538 ± 0.0049	0.0000 ± 0.0	1.0000 ± 0.0	1.0000	1.0000	313.10	529.95	529.95	1.00	17.30

Table 7

VLE data for the 2-methylpropane(1)+2-methyl-2-propanol(2) system at 326 K: n_1 and n_2 , moles of components in the equilibrium cell; total composition z_1 , calculated liquid phase x_1 , and vapour phase y_1 , mole fractions; experimental pressure p_{exp} , and pressure calculated from the Legendre-polynomial fit p_{leg} ; experimental temperature T ; and activity coefficient, γ_i

n_1 (mol)	n_2 (mol)	z_1	x_1	y_1	T (K)	p_{exp} (kPa)	p_{leg} (kPa)	γ_1	γ_2
0.0000 ± 0.0	0.4812 ± 0.0051	0.0000 ± 0.0	0.0000	0.0000	313.08	13.77	13.77	3.38	1.00
0.0198 ± 0.0004	0.4812 ± 0.0051	0.0396 ± 0.0012	0.0370	0.7986	313.08	67.47	67.54	3.11	1.00
0.0283 ± 0.0005	0.4812 ± 0.0051	0.0555 ± 0.0015	0.0521	0.8454	313.08	87.87	87.55	3.01	1.00
0.0555 ± 0.0 ± 008	0.4812 ± 0.0051	0.1033 ± 0.0023	0.0981	0.9068	313.08	142.67	142.67	2.76	1.01
0.0876 ± 0.0011	0.4812 ± 0.0051	0.1539 ± 0.0030	0.1477	0.9326	313.08	193.16	193.23	2.52	1.02
0.1225 ± 0.0015	0.4812 ± 0.0051	0.2029 ± 0.0037	0.1965	0.9459	313.08	235.36	235.36	2.31	1.04
0.1607 ± 0.0018	0.4812 ± 0.0051	0.2503 ± 0.0042	0.2441	0.9540	313.09	270.96	270.96	2.14	1.06
0.2072 ± 0.0023	0.4812 ± 0.0051	0.3010 ± 0.0046	0.2955	0.9601	313.08	304.26	304.20	1.98	1.10
0.2592 ± 0.0029	0.4812 ± 0.0051	0.3501 ± 0.0049	0.3455	0.9645	313.08	332.46	332.56	1.85	1.13
0.3210 ± 0.0035	0.4812 ± 0.0051	0.4001 ± 0.0052	0.3966	0.9680	313.08	357.96	357.95	1.73	1.18
0.3937 ± 0.0043	0.4812 ± 0.0051	0.4500 ± 0.0053	0.4476	0.9708	313.08	380.45	380.28	1.62	1.23
0.4473 ± 0.0048	0.5431 ± 0.0057	0.4517 ± 0.0053	0.4506	0.9709	313.09	381.45	381.57	1.61	1.24
0.4473 ± 0.0048	0.4442 ± 0.0047	0.5017 ± 0.0053	0.4997	0.9732	313.09	400.65	400.65	1.52	1.30
0.4473 ± 0.0048	0.3633 ± 0.0039	0.5519 ± 0.0053	0.5490	0.9752	313.09	418.05	418.01	1.44	1.38
0.4473 ± 0.0048	0.2971 ± 0.0032	0.6009 ± 0.0052	0.5975	0.9770	313.10	433.65	433.69	1.37	1.48
0.4473 ± 0.0048	0.2387 ± 0.0026	0.6521 ± 0.0049	0.6482	0.9787	313.09	448.45	448.45	1.31	1.61
0.4473 ± 0.0048	0.1902 ± 0.0021	0.7017 ± 0.0046	0.6975	0.9803	313.09	461.55	461.60	1.25	1.77
0.4473 ± 0.0048	0.1480 ± 0.0017	0.7514 ± 0.0042	0.7472	0.9819	313.09	473.75	473.75	1.19	1.99
0.4473 ± 0.0048	0.1105 ± 0.0013	0.8020 ± 0.0036	0.7981	0.9836	313.08	485.25	485.20	1.14	2.30
0.4473 ± 0.0048	0.0784 ± 0.0010	0.8508 ± 0.0030	0.8475	0.9853	313.09	495.75	495.90	1.10	2.77
0.4473 ± 0.0048	0.0494 ± 0.0007	0.9005 ± 0.0022	0.8980	0.9873	313.09	505.95	505.95	1.06	3.62
0.4473 ± 0.0048	0.0237 ± 0.0005	0.9496 ± 0.0014	0.9484	0.9902	313.08	516.25	515.70	1.02	5.59
0.4473 ± 0.0048	0.0127 ± 0.0003	0.9725 ± 0.0010	0.9718	0.9928	313.08	521.35	521.17	1.01	7.62
0.4473 ± 0.0048	0.0040 ± 0.0003	0.9911 ± 0.0006	0.9909	0.9968	313.08	526.85	526.83	1.00	10.61
0.4473 ± 0.0048	0.0019 ± 0.0002	0.9958 ± 0.0005	0.9957	0.9983	313.08	527.45	528.29	1.00	11.69
0.4473 ± 0.0048	0.0000 ± 0.0	1.0000 ± 0.0	1.0000	1.0000	313.08	529.95	529.94	1.00	12.83

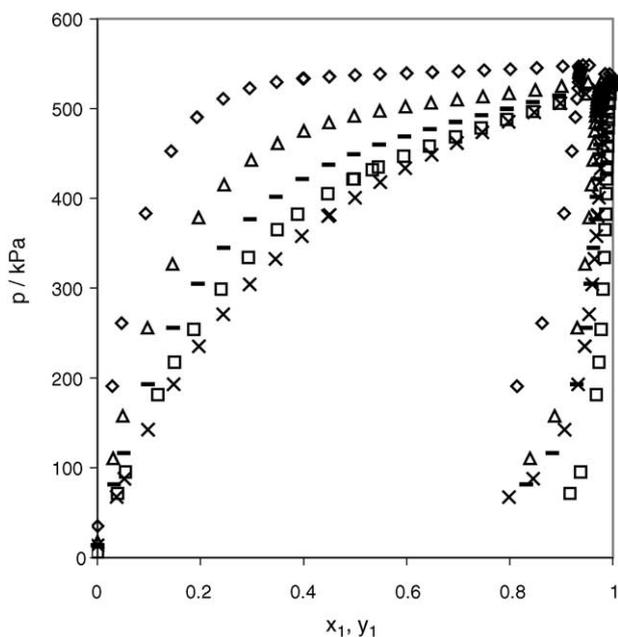


Fig. 2. Pressure composition diagram of 2-methylpropane (1)+alcohol (2) at 313.15 K: (\diamond) 2-methylpropane + methanol; (\triangle) 2-methylpropane + ethanol; (\square) 2-methylpropane + 2-propanol; (\times) 2-methylpropane + 2-methyl-2-propanol.

Azeotropic behaviour was observed for the system 2-methylpropane + methanol at $x(2\text{-methylpropane}) = 0.947$, $p = 548.25$ kPa and $T = 313.06$ K and for the system 2-methylpropane + ethanol at $x(2\text{-methylpropane}) = 0.990$, $p = 531.34$ kPa and $T = 313.08$ K.

Parameters of the Wilson [24], NRTL [25] and UNIQUAC [26] activity coefficient models are presented in Table 8. Volume and area parameters used in the UNIQUAC model are listed in Table 2.

3.2. Comparison with predictive methods and literature data

Activity coefficients at infinite dilution, average pressure residuals and average absolute pressure residuals obtained from Legendre fits, UNIFAC and COSMO-RS are listed in Table 9 and compared to ones found from literature.

In both UNIFAC and COSMO-RS, all interactions between molecules are considered as nearest neighbour interactions of pairwise contacting molecular surfaces. However, UNIFAC and COSMO-RS use a different approach in treating a single molecule. In UNIFAC the surfaces are represented by specific groups surfaces, and the binary interaction parameters are optimised based on experimental information for substances consisting of the interacting groups. COSMO-RS starts from quantum mechanical calculation of a molecule in

Table 8
Activity coefficient model parameters, Legendre [19], Wilson [22], NRTL [23], UNIQUAC [24]

	System 1	System 2	System 3	System 4	System 5
Legendre, $a_{1,0}$	2.5899	1.9446	1.9046	1.7052	1.4945
Legendre, $a_{2,0}$	0.34409	0.435	0.51203	0.53657	0.47491
Legendre, $a_{3,0}$	0.47737	0.2212	0.3248	0.28564	0.29079
Legendre, $a_{4,0}$	0.16949	0.079135	0.17313	0.17481	0.14694
Legendre, $a_{5,0}$	0.11144	0.02945	0.098876	0.078351	0.077412
Legendre, $a_{6,0}$	0.054445	1.9446	0.047	0.047236	0.038301
Legendre, $a_{7,0}$	0.027639	0.435	0.024753	0.015036	0.01905
Legendre, $a_{8,0}$	0.012643	0.2212	0.0081365	0.0081676	0.006954
Legendre, $a_{9,0}$	0	0.079135	0.0038975	0	0.0032083
Legendre, $a_{10,0}$	0	0.02945	0	0	0
$ \Delta p $ (kPa)	0.12	0.07	0.09	0.09	0.11
Wilson, $\lambda_{12}-\lambda_{11}$ (J/mol)	2257.77	1349.758	1063.131	988.534	493.084
Wilson, $\lambda_{21}-\lambda_{22}$ (J/mol)	10770.45	8760.878	6649.363	5761.937	5143.31
Δp (kPa)	0.56	0.13	1.27	-1.26	-1.91
$ \Delta p $ (kPa)	3.30	1.42	2.07	2.28	3.8
NRTL, $g_{12}-g_{11}$ (K)	769.17	725.11	639.66	610.47	563.31
NRTL, $g_{21}-g_{22}$ (K)	563.6	384.79	290.8	247.6	222.86
NRTL, $\alpha_{12} = \alpha_{21}$	0.43246	0.45855	0.51084	0.56373	0.66941
Δp (kPa)	-1.94	-0.62	1.13	-1.00	0.85
$ \Delta p $ (kPa)	3.40	3.27	2.94	2.56	1.6
UNIQUAC, $u_{12}-u_{11}$ (K)	634.14	452.8	320.12	156.26	229.35
UNIQUAC, $u_{21}-u_{22}$ (K)	34.462	-26.642	-33.776	22.318	-40.541
Δp (kPa)	-5.87	5.24	5.83	-4.46	-4.14
$ \Delta p $ (kPa)	15.56	10.8	8.10	6.32	6.26

Data regressed with the Legendre-polynomials, average pressure residual Δp , absolute average pressure residual $|\Delta p|$, 2-methylpropane + methanol (system 1), 2-methylpropane + ethanol (system 2), 2-methylpropane + 2-propanol (system 3), 2-methylpropane + 2-butanol (system 4), 2-methylpropane + 2-methyl-2-propanol (system 5).

a conductor surrounding with a screening charge density on the molecule surface. The binary surface interaction energies (electrostatic, hydrogen bonding) are calculated using those charge densities.

Considering a single molecule as an entity enables COSMO-RS to predict intramolecular interactions. Table 9 shows that a detailed description of a single molecule made by COSMO-RS results in a better representation of VLE for systems with low molecular mass alcohols, whereas UNIFAC interpolation is not accurate enough for the beginners of homological series. Methanol, however, is treated in UNIFAC as its own functional group, which increases the quality of the predictions. Compared to more than a hundred parameters of UNIFAC [1], COSMO-RS needs only few element-specific and universal parameters for quantum mechanical calculations [2] and no experimental data is needed. COSMO-RS is a relatively novel approach to VLE prediction and examination of its ability to describe different system is important for further model utilization.

From Table 9, it can be seen that the experimental data presented in this work are well in line with those reported previously in literature. For alcohols in 2-methylpropane, UNIFAC gives lower activity coefficients in the dilute region than found experimentally, whereas COSMO-RS tends to give higher activity coefficients for alcohols. For 2-methylpropane in alcohols, the activity coefficients given both by UNIFAC and COSMO-RS are lower than those

obtained from the Legendre fit. Overestimation of alcohol activity coefficients and underestimation of alkanes activity coefficients is a known fact for the COSMO-RS model [27]. For UNIFAC, the tendency of underestimating activity coefficients for both alcohols and 2-methylpropane may partly originate from the mathematical similarity of UNIFAC with UNIQUAC. The latter cannot accurately predict the activity coefficients for highly non-ideal mixtures, e.g. for binaries of 2-methylpropane and short-chain alcohols (Table 8).

In Fig. 3, the pressures predicted by COSMO-RS and UNIFAC are plotted for the 2-methylpropane + ethanol binary at 313.08 K and compared to the experimentally determined pressures. The tendency of predictive methods to underestimate the pressure of 2-methylpropane + ethanol system at the ethanol-rich end of the composition range can be seen from Fig. 3. This tendency originates from the underestimation of the activity coefficients of 2-methylpropane at the alcohol-rich end of the composition range in the 2-methylpropane + alcohol systems.

In Table 10, azeotropic compositions, pressures and temperatures for 2-methylpropane + methanol and 2-methylpropane + ethanol binaries found from literature are listed. Those are well in line with our results. In this work, azeotropes were found for 2-methylpropane + methanol and 2-methylpropane + ethanol binaries. As a result of the low activity coefficients, UNIFAC does not predict an azeotrope for 2-methylpropane + ethanol binary in 313.15 K.

Table 9

Comparison of VLE data produced with predictive methods UNIFAC and COSMO-RS with measured data and with data regressed with the Legendre-polynomials

	System 1	System 2	System 3	System 4	System 5
Legendre					
Δp (kPa)	0.07	0.04	0.02	0.02	0.00
$ \Delta p $ (kPa)	0.12	0.07	0.09	0.09	0.11
$\gamma_{\text{inf, IB}}$	13.86	7.30	5.04	3.73	3.38
$\gamma_{\text{inf, alcohol}}$	44.39	35.23	22.14	17.30	12.83
UNIFAC					
Δp (kPa)	-1.06	18.17	13.75	18.16	0.18
$ \Delta p $ (kPa)	16.06	18.36	16.19	19.27	10.64
$\gamma_{\text{inf, IB}}$	10.24	4.50	3.19	2.48	2.47
$\gamma_{\text{inf, alcohol}}$	21.67	24.52	18.69	14.60	14.63
COSMO-RS					
Δp (kPa)	-2.88	11.6	12.0	18.1	5.18
$ \Delta p $ (kPa)	8.67	12.5	13.3	19.4	5.34
$\gamma_{\text{inf, IB}}$	10.78	4.97	3.28	2.41	2.46
$\gamma_{\text{inf, alcohol}}$	109.94	47.52	24.74	12.69	13.65
Literature					
$\gamma_{\text{inf, IB}}$	14.10 ^a	2.83 ^b	5.00 ^c	4.30 ^d	4.08 ^e
$\gamma_{\text{inf, alcohol}}$		37.26 ^b			

Average pressure residual Δp , absolute average pressure residual $|\Delta p|$, activity coefficient at infinite dilution γ_{inf} , 2-methylpropane + methanol (system 1), 2-methylpropane + ethanol (system 2), 2-methylpropane + 2-propanol (system 3), 2-methylpropane + 2-butanol (system 4), 2-methylpropane + 2-methyl-2-propanol (system 5).

^a Miyano et al. [11].

^b Zabaloy et al. [9].

^c Miyano [12].

^d Miyano [13].

^e Miyano [14].

For the 2-methylpropane + methanol binary, UNIFAC predicts an azeotrope at $x_{2\text{-mp}} = 0.955$. COSMO-RS predicts an azeotrope for the 2-methylpropane + ethanol binary, but as a result of the high activity coefficients, for the 2-

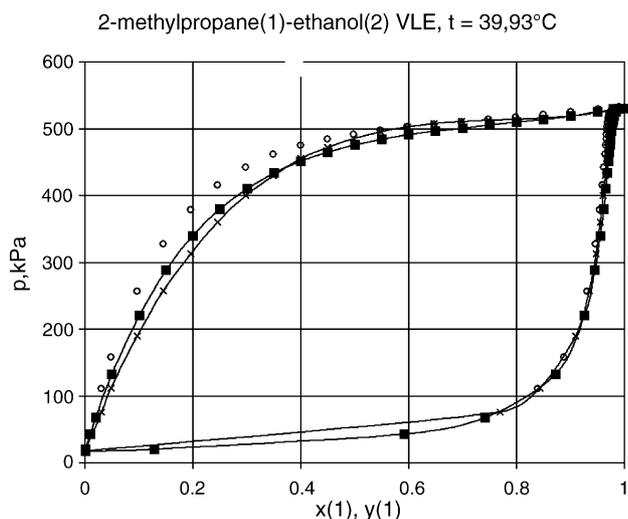


Fig. 3. Comparison, in terms of vapour pressures, between experimental data (○) and data predicted by COSMO-RS (■) and UNIFAC (×) for 2-methylpropane-ethanol binary at 39.93 °C (313.08 K).

Table 10

Comparison of azeotropic compositions for 2-methylpropane-alcohol binaries measured in this work, predicted by UNIFAC and COSMO-RS and found from literature

	x_1	T (K)	p (kPa)
2-Methylpropane (1) – methanol (2)			
This work	0.947	313.06	548.25
COSMO	0.949	313.06	537.73
UNIFAC	0.955	313.06	529.91
Literature ^a	0.9562	323.15	733.2
2-Methylpropane (1) – ethanol (2)			
This work	0.990	313.08	531.34
COSMO	0.9945	313.08	530.28
UNIFAC	–	–	–
Literature ^b	0.9944	308.6	–
	0.9911	318.4	–
	0.976	363.5	–

^a Leu and Robinson [7].

^b Zabaloy et al. [9].

methylpropane + methanol binary a heterogeneous azeotrope (a liquid–liquid phase split) is found. Our experimental results do not confirm the existence of a heterogeneous azeotrope for the methanol + 2-methylpropane binary at this temperature and pressure. Also Leu and Robinson [7] found no liquid–liquid miscibility gap for this binary at temperatures between 273 and 423.15 K.

4. Conclusion

Isothermal VLE for five binary systems of 2-methylpropane and alcohols were measured at 313.15 K using the total pressure method. Barker method [17] was used to convert PTz data into PTxy data. At 313.15 K, 2-methylpropane showed azeotropic behaviour with methanol at $p = 548.25$ kPa and $x_{\text{IB}} = 0.947$ and with ethanol at $p = 531.34$ kPa and $x_{\text{IB}} = 0.990$. All systems measured exhibited positive deviation from Raoult's law. Global error analysis was performed to the measured equilibria and the major source of error was found to be the uncertainty on the liquid density. The parameters of Wilson, NRTL and UNIQUAC activity coefficient model were optimised. Measured VLE was compared with VLE predicted by UNIFAC and COSMO-RS in terms of infinite dilution activity coefficients and predicted azeotropic compositions. UNIFAC was found to predict lower activity coefficients for 2-methylpropane and C1–C4-alcohols than the measurements show, whereas COSMO-RS predicts higher activity coefficients for the alcohols in 2-methylpropane than those calculated from measured data. In terms of average absolute pressure residuals between measured and predicted VLE, the predictions with UNIFAC and COSMO-RS can be considered relatively good; e.g. for 2-methyl-2-propanol–2-methylpropane binary, the residuals from COSMO-RS are smaller than the residuals from UNIQUAC with parameters fitted on top of the measured data.

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List of symbols

$a_{n,0}$	n th parameter of the Legendre polynomial
m	mass of injected liquid (g)
M	molecular weight (g mol^{-1})
n_i	number of moles
p_{exp}	experimental pressure
p_{leg}	pressure from Legendre polynomial fit
R_{UNIQ}	volume parameter in UNIQAC model
Q_{UNIQ}	area parameter in UNIQAC model
Δp	average pressure residuals between measured and calculated pressure (kPa)
$ \Delta p $	absolute average pressure residuals between measured and calculated pressure (kPa)
T	temperature (K)
V_i	injected liquid volume of component i (m^3)
x_i	composition of component i in liquid phase
y_i	composition of component i in vapor phase
z_i	overall composition of component i in equilibrium cell

Greek letters

α_{12}, α_{21}	nonrandomness constant for binary ij interactions in NRTL model
γ_i	activity coefficient of component i
Δ	difference
κ	isothermal compressibility of liquid (Pa^{-1})
λ_{ij}	binary interaction parameter of the Wilson equation (K)
ρ	density of liquid (mol m^{-3})
ω	acentric factor

Subscripts

c	critical
calc	calculated
exp	experimental
i, j	components of a mixture
2-mp	isobutane, 2-methylpropane

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