

Publication II

Helena Laavi, Anna Zaitseva, Juha-Pekka Pokki, Petri Uusi-Kyyny, Younghun Kim, and Ville Alopaeus. Vapor–Liquid Equilibrium, Excess Molar Enthalpies, and Excess Molar Volumes of Binary Mixtures Containing Methyl Isobutyl Ketone (MIBK) and 2-Butanol, *tert*-Pentanol, or 2-Ethyl-1-hexanol. *J. Chem. Eng. Data*, 57 (11) 3092–3101, October 15, 2012.

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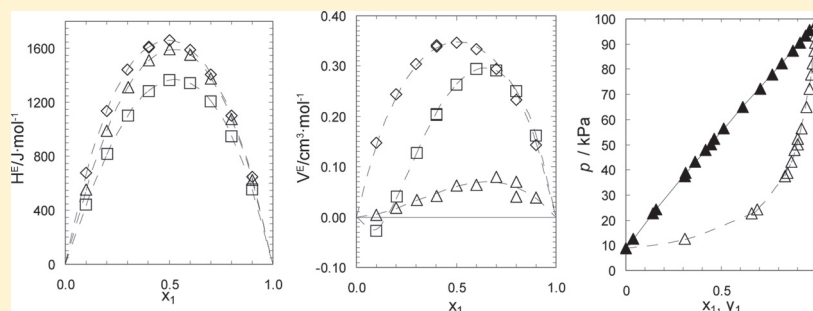
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Vapor–Liquid Equilibrium, Excess Molar Enthalpies, and Excess Molar Volumes of Binary Mixtures Containing Methyl Isobutyl Ketone (MIBK) and 2-Butanol, *tert*-Pentanol, or 2-Ethyl-1-hexanol

Paper presented at the 18th Symposium on Thermophysical Properties, Boulder, CO, June 24 to 29, 2012.

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ABSTRACT: Phase equilibrium and calorimetric measurements provide complementary data that are vital for process models. The combined use of vapor–liquid equilibrium (VLE) data and excess enthalpies (H^E) makes the thermodynamic model more reliable in extrapolation outside the conditions of the measurement. This is important during the tight time schedule of process development. In this work, phase equilibrium and excess enthalpies of binary mixtures were measured by using three apparatuses. Two types of VLE runs were conducted by using a circulation still of the Yerazunis-type and by using Agilent headspace sampler with a gas chromatograph (HS-GC). A SETARAM C80 calorimeter equipped with a flow mixing cells was taken into use for excess enthalpy measurements. New data of phase equilibrium, excess molar enthalpy, and excess molar volume were obtained for industrially relevant binary mixtures of methyl isobutyl ketone (MIBK) with alcohols (2-butanol, *tert*-pentanol, 2-ethyl-1-hexanol). Excess enthalpy data at 298.15 K are well in line with equilibrium data obtained in the range of (294 to 368) K. Azeotropic behavior was observed in the MIBK + *tert*-pentanol system. The experimental data were used for the optimization of Wilson and Redlich–Kister equation parameters.

INTRODUCTION

Methyl isobutyl ketone (MIBK) is widely used as a solvent of which the extraction properties can be tuned by using alcohols. Therefore, the thermodynamic properties of (MIBK + an alcohol) mixtures provide essential information for process design.

For the binary system of MIBK + 2-butanol (2-BuOH), vapor–liquid equilibria (VLE),¹ excess enthalpies (H^E),² excess volumes (V^E),^{3,4} and densities⁵ are reported in literature. For the binary system of MIBK + *tert*-pentanol (*t*-PnOH), no VLE data are found in literature, but H^E data⁶ by using an adiabatic Loiseleur calorimeter are reported. V^E data⁶ and densities⁷ are also available. For the binary system of MIBK + 2-ethyl-1-hexanol (2-EH) no VLE, H^E , or V^E data are reported in literature.

MATERIALS

The purities, water contents, densities, and manufacturers of the used chemicals are listed in Table 1.

The purity of the chemicals was checked by gas chromatography. In excess enthalpy and excess volume measurements, the chemicals were used as purchased. In the VLE experiments on circulation still, MIBK, *t*-PnOH, and 2-EH were distilled in vacuum prior to measurements of these binary systems. In the VLE experiments on headspace with a gas chromatograph (HS-GC), all chemicals were distilled in vacuum, and a molecular sieve (pore size 3 Å) was used on MIBK, *t*-PnOH, and 2-EH. The water content of the chemicals was determined using the Karl Fischer titrator (Mettler-Toledo DL38) applying one-component reagents (Hydrapoint Solvent G and Titrant 2 mgH₂O·cm⁻³) technique. Refraction indexes were measured by using a digital automatic refractometer Abbatemat (Dr. Kernchen, Germany) at 298.15 K. The accuracies of the measured refractive indexes and measurement temperatures

Received: June 22, 2012

Accepted: October 3, 2012

Published: October 15, 2012

Table 1. Purity, Water Content, Density ρ at Temperature T , Refractive Index n , and Supplier of Pure Liquid Components^a

	purity	water content	ρ_{exp}	ρ_{lit}	T	n_{exp}	n_{lit}	supplier
	%	wt %	kg·dm ⁻³	kg·dm ⁻³	K			
2-BuOH	≥ 99.5	0.016	0.8027	0.8026	297.83	1.3951	1.3949	Sigma-Aldrich
<i>t</i> -PnOH	≥ 99	0.036	0.8053	0.8052	297.85	1.4025	1.40238	Merck
2-EH	≥ 99.6	0.034	0.8288	0.8299	297.86	1.4295	1.429	Aldrich
MIBK	≥ 99.5	0.028	0.7964	0.7965	297.84	1.3935	1.3933	Sigma-Aldrich

^a ρ_{exp} is the measured density, kg·dm⁻³; ρ_{lit} is the density from DIPPR,⁸ kg·dm⁻³; n_{exp} is the measured refractive index at 298 K, n_{lit} is the refractive index at 298 K from DIPPR,⁸ T is the temperature at which the density was measured, K.

were ± 0.00002 and ± 0.03 K, respectively. The literature⁸ values of densities and refractive indexes for the pure chemicals are shown for comparison.

■ EQUIPMENT

Excess Molar Enthalpy. Excess molar enthalpies were measured at 298.15 K with a SETARAM C80 calorimeter equipped with a flow mixing cell.⁹ The temperature accuracy of the calorimeter was 0.1 K. The flows of the chemicals into the calorimeter were controlled by syringe pumps ISCO 260D and ISCO 500D of which the accuracies of the flows were 0.5 % of the set point. The calorimeter was calibrated by using two well-known recommended chemical reference systems: cyclohexane–hexane and methanol–water.¹⁰ The calibration procedure indicated for this type of equipment^{10,11} was utilized. The cyclohexane–hexane binary system was used to determine the sensitivity of the calorimeter, and the methanol–water binary system was used to check the accuracy of the calibration. The average accuracy of the calorimeter was found to be 1.3 % of the best straight line.

Excess Molar Volume. Densities of the binary mixtures were measured with a vibrating-tube Anton Paar DMA 512 P densimeter that was located after the calorimeter unit. The uncertainty of the densimeter was ± 0.00016 kg·dm⁻³. The densimeter temperature was controlled with a Lauda E200 water immersion thermostat. The temperature of the vibrating tube block was measured with a Thermolyzer S2541 temperature meter equipped with a Pt-100 probe calibrated at the Finnish National Standards Laboratory. The calibration uncertainty was ± 0.015 K, and the uncertainty of temperature was estimated to ± 0.02 K. The densimeter was calibrated based on deionized and degassed water¹² and dry air¹³ reference systems. The measured pure component densities corresponded well to the literature data,^{12,13} as can be seen from Table 1.

VLE Circulation Still. VLE were measured using a circulation still of Yerazunis-type¹⁴ with minor modifications to the original design.^{15,16} The liquid volume needed for running the apparatus was approximately 80 cm³. Pressure was measured with a pressure transducer PMP 4070 (Druck) connected to Red Lion panel meter at accuracy of 0.04 kPa. The pressure meter was compared against the Beamex MC2-PE field calibrator calibrated at the Finnish National Standards Laboratory. The temperature meter was a F200 Precision Thermometer (Automatic Systems Laboratories ASL) calibrated at Finnish National Standards Laboratory at calibration uncertainty of 0.015 K. As a check of the circulation still, the pure water vapor pressure was measured and compared to literature¹² showing a maximum ± 0.05 kPa deviation.

VLE Headspace. Agilent Technologies 7697A headspace sampler was used for sampling the gas phase for the VLE measurement. The thermal control of all temperature zones had set point increments in 1 K with 0.1 K resolution for actual

temperatures. The samples were prepared by using Precisa 410AM-FR balance (Oy Teo-Pal Ab) of which the uncertainty of weighing was ± 0.0002 g.

VLE Gas Chromatograph. Agilent 6890N Series Gas Chromatograph with Agilent 7683 Series injector (GC) was used for VLE composition analysis with circulation still apparatus as well as with the analysis of the headspace samples.

■ EXPERIMENTAL PROCEDURE

Excess Molar Enthalpy. The feed pumps were let to equilibrate to the feed temperature for 60 min prior starting the experiments. The total flow rate to the calorimeter was kept at 0.5 cm³·min⁻¹ by varying the flow rates of the feed pumps as recommended.^{9,11} The calorimeter signal stabilized in approximately 20 min, and an additional (10 to 15) min was waited prior recording the values of the experimental point.

Excess Molar Volume. Since the densimeter was located after the calorimeter unit, it was also utilized to check the perfect mixing of the calorimeter flow mixing cell. The thermostat of the densimeter was activated one hour prior to the measurements to guarantee the temperature in demand. The densimeter signal was let to stabilize the same time (30 to 45) min in which the calorimeter signal stabilized even though it took only approximately 10 min to get a stabilized signal from the densimeter.

VLE Circulation Still. The procedure is described in detail in our previous work.¹⁶ Pure component 1 was introduced in the circulation still, and its vapor pressure was measured. Then, component 2 was introduced into the cell, and it took approximately 30 min to achieve a constant temperature. The temperature was held constant for (30 to 45) min before sampling. After the pressure was measured, the vapor and liquid samples were simultaneously withdrawn with a 1 cm³ Hamilton Sample Lock syringe. The total volume of the syringe was 1.2 cm³. 0.7 cm³ of the content was injected into a GC vial, and the rest 0.5 cm³ was analyzed with the refractometer.

VLE Headspace. The binary mixtures for the HS analysis were gravimetrically prepared in 20 cm³ Agilent Technologies Class A borosilicate glass vials. A portion of 5 cm³ of the vial volume was occupied by the investigated mixture to ensure sufficient amount of the vapor phase. The HS vials were equilibrated at constant temperature in the HS apparatus oven for at least 30 min. Vapor phase sampling was made by using Agilent Technology valve and loop headspace sampling system (loop size 1 cm³). The sampler pressurized the vial with helium at 160 kPa absolute pressure and opened the vial to the loop at 110 kPa absolute pressure. Then, the vapor sample was automatically transferred with a 10 cm³·min⁻¹ helium flow into GC through the transfer line heated to 15 K above the equilibration temperature.

Gas Chromatograph. Compositions of liquid and condensed vapor phases of the circulation still measurements were determined by gas chromatography. Liquid samples of 1 mm³

were injected into GC with an Agilent 7683 Series injector. Prior to GC analysis, the condensed vapor and liquid phase samples of the circulation still equipment were diluted with toluene, in ratio approximately (700 to 600) mm³. Agilent GC 2 cm³ glass vials with aluminum grimp caps with PTFE/red rubber septa were used.

The following settings were used for the GC analysis for all measurements related to the circulation still apparatus. The front inlet temperature was set to 523 K and the pressure to 39 kPa over pressure; the split ratio was 50:1. The separation capillary column was a DB-WaxETR (length 30 m, inner diameter 320 μm, film thickness 1 μm). Helium was the carrier gas, and its flow rate in the GC column was 18 cm³·min⁻¹. The GC oven temperature was programmed to increase after 7 min of isothermal operation at 381 K at a rate of 50 K·min⁻¹ to the final temperature of 463 K, which was kept for 5 min. The flame ionization detector (FID) temperature was set at 523 K, hydrogen flow was set to 40 cm³·min⁻¹, and air flow was set to 450 cm³·min⁻¹.

The GC operational conditions were modified for the analysis of vapor samples made with the HS sampler. Due to the smaller size of the HS injected samples, the GC inlet split ratio was reduced to 20:1. The GC capillary column flow and the inlet pressure were also reduced to 14 cm³·s⁻¹ and 30 kPa to improve the capillary column separation and the accuracy of the GC peak area detection. These changes limited the broadening of the GC peaks. Due to similar polarity and vapor pressures, a complete separation of the 2-BuOH, *t*-PnOH, and MIBK GC peaks was a challenging task.

MODELING

The Hayden–O'Connell (HOC) model was applied to the vapor phase fugacity coefficients.^{17,18} The association parameters η_{ii} and solvation parameters η_{ij} were available⁸ for the systems except for the (MIBK + 2-EH). For this system, the values were approximated based on the chemical similarity.^{17,18} The modeling parameters are presented in Table 2.

Table 2. Physical Properties⁸ and Parameters^{17,18} Used in the Hayden–O'Connell Correlation with Chemical Theory^a

	MIBK	2-butanol	<i>tert</i> -pentanol	2-ethyl-1-hexanol
RGYR/10 ⁻¹⁰ m	3.83	3.18	3.42	4.809
DMOM/D	2.8	1.7	1.9	1.8
Association η_{ii} and Solvation Parameters η_{ij}				
MIBK	0.9	1	1	1
2-BuOH	1	1.75	1	1
<i>tert</i> -pentanol	1	1	1	1
2-ethyl-1-hexanol	1	1	1	1

^aRGYR is the radius of gyration, 10⁻¹⁰ m; DMOM is the dipole moment, D; η_{ii} are the association parameters (located in the diagonal of the table); η_{ij} are the solvation parameters.

The liquid activity coefficients were regressed by using the Wilson model¹⁹ where the temperature dependence was given by the polynomials (1) and (2)

$$\lambda_{12} - \lambda_{11} = a_{0,12} + a_{1,12}T + a_{2,12}T^2 \quad (1)$$

$$\lambda_{21} - \lambda_{22} = a_{0,21} + a_{1,21}T + a_{2,21}T^2 \quad (2)$$

where λ_{ij} are the Wilson model parameters (K), $a_{0,ij}$ (K), $a_{1,ij}$ (K), and $a_{2,ij}$ (K⁻¹) are the binary interaction parameters of the Wilson model, and T is the temperature (K).

The objective functions (OF) of the data regression were

$$OF_{\text{circ}} = \sum_{i=1}^{NP} \left(\frac{(p_{\text{calc},i} - p_{\text{meas},i})}{p_{\text{meas},i}} \right)^2 \quad (3)$$

at bubble point pressure at x_{meas} and T_{meas}

$$OF_{\text{HS}} = \sum_{i=1}^{NP} \sum_{j=1}^{NC} \left(\frac{(y_{j,\text{calc},i} - y_{j,\text{meas},i})}{y_{j,\text{meas},i}} \right)^2 \quad (4)$$

at bubble point pressure at x_{meas} and T_{meas}

$$OF_{\text{HE}} = \sum_{i=1}^{NP} \left(\frac{(H_{\text{calc},i}^E - H_{\text{meas},i}^E)}{H_{\text{meas},i}^E} \right)^2 \quad (5)$$

at x_{meas} and T_{meas} , where p is the pressure (kPa), x is the liquid mole fraction, T is the temperature (K), and H^E is the excess molar enthalpy (J·mol⁻¹).

RESULTS AND DISCUSSION

Excess Molar Enthalpy, Density, and Excess Molar Volume. Results of excess molar enthalpies, densities, and excess molar volumes for the mixtures of MIBK + an alcohol (2-BuOH, *t*-PnOH, or 2-EH) are given in Table 3.

The experimental excess molar enthalpies H^E (J·mol⁻¹) were fitted together with the measured VLE data by using the Wilson model¹⁹ for liquid phase activities and Hayden–O'Connell with chemical theory correlation^{17,18} for vapor phase fugacities. The values of H^E are positive in the entire mole fraction range for all of the studied binary mixtures as can be seen in Figure 1. The mixtures show very similar behavior, with the largest values found for (MIBK + 2-BuOH) and the smallest for (MIBK + *t*-PnOH). The values of the H^E for (MIBK + *t*-PnOH) are lower in literature⁶ than in our experiments, but according to the developer of the Loiseleur type of calorimeter this type of calorimeter is not convenient for measurements with high accuracy.²⁰

The excess molar volumes V^E (cm³·mol⁻¹) were fitted using the Redlich–Kister equation²¹ 6

$$V^E = x_1(1 - x_1) \sum_{i=0}^m A_i(2x_1 - 1)^i \quad (6)$$

where x_i is the mole fraction of MIBK and V^E is the excess molar volume (cm³·mol⁻¹). The values of the parameters A_i determined by least-squares analysis are listed in Table 4 together with the standard deviations. The correspondence of the Redlich–Kister equation with the experimental excess molar volumes is shown in Figure 2. The definition of the excess molar volume is given in eq 7

$$V^E = \frac{x_1M_1 + x_2M_2}{\rho} - \frac{x_1M_1}{\rho_1} - \frac{x_2M_2}{\rho_2} \quad (7)$$

where x_i is the molar fraction, M_i is the molar mass (g·mol⁻¹), and ρ_i the density (g·cm⁻³) of the component i .

The excess molar volumes are positive except for (MIBK + *t*-PnOH) at $x_1 = 0.1$ when the V^E is negative. For (MIBK + 2-BuOH) the V^E values are the highest and for (MIBK + 2-EH) the values are smallest indicating more ideal behavior.

Refractive Indexes and Response Factors. The refractive index measurement was used for an alternative analysis of vapor and liquid compositions of the binary mixtures of the circulation

Table 3. Excess Molar Enthalpy H^E , Excess Molar Volume V^E , and Density ρ at 298 K of Binary Systems of Methyl Isobutyl Ketone (MIBK) + an Alcohol (2-Butanol, *tert*-Pentanol, 2-Ethyl-1-hexanol)^a

x_1	H^E	ρ	V^E	T
	J·mol ⁻¹	kg·dm ⁻³	cm ³ ·mol ⁻¹	
		MIBK (x_1) + 2-BuOH (x_2)		
0.1009 ± 0.0004	674.6 ± 8.7	0.80064 ± 0.00016	0.14812 ± 0.01881	297.83 ± 0.02
0.2009 ± 0.0006	1138.0 ± 14.7	0.79914 ± 0.00016	0.24359 ± 0.01874	297.83 ± 0.02
0.3007 ± 0.0007	1438.9 ± 18.6	0.79802 ± 0.00016	0.30410 ± 0.01879	297.83 ± 0.02
0.4015 ± 0.0007	1605.1 ± 20.8	0.79716 ± 0.00016	0.34235 ± 0.01911	297.84 ± 0.02
0.4015 ± 0.0006	1612.1 ± 21.4	0.79713 ± 0.00016	0.33816 ± 0.01969	297.84 ± 0.02
0.5008 ± 0.0007	1658.7 ± 20.7	0.79655 ± 0.00016	0.34689 ± 0.01909	297.84 ± 0.02
0.6021 ± 0.0005	1588.6 ± 20.5	0.79612 ± 0.00016	0.33322 ± 0.02054	297.84 ± 0.02
0.7004 ± 0.0004	1407.9 ± 18.2	0.79590 ± 0.00016	0.29433 ± 0.02156	297.84 ± 0.02
0.7998 ± 0.0003	1097.7 ± 14.2	0.79584 ± 0.00016	0.23288 ± 0.02271	297.84 ± 0.02
0.8998 ± 0.0001	648.0 ± 8.4	0.79597 ± 0.00016	0.14316 ± 0.02394	297.84 ± 0.02
		MIBK (x_1) + <i>t</i> -PnOH (x_2)		
0.1012 ± 0.0004	441.7 ± 5.7	0.80447 ± 0.00016	-0.02694 ± 0.02231	297.85 ± 0.02
0.2017 ± 0.0007	818.1 ± 10.6	0.80300 ± 0.00016	0.04085 ± 0.02228	297.84 ± 0.02
0.3013 ± 0.0009	1099.3 ± 14.2	0.80145 ± 0.00016	0.12718 ± 0.02203	297.84 ± 0.02
0.4017 ± 0.0010	1283.1 ± 16.6	0.80001 ± 0.00016	0.20297 ± 0.02173	297.84 ± 0.02
0.4017 ± 0.0010	1283.0 ± 16.6	0.80000 ± 0.00016	0.20395 ± 0.02173	297.85 ± 0.02
0.5008 ± 0.0010	1367.4 ± 17.6	0.79873 ± 0.00016	0.26304 ± 0.02161	297.84 ± 0.02
0.6006 ± 0.0009	1343.3 ± 17.3	0.79767 ± 0.00016	0.29494 ± 0.02175	297.84 ± 0.02
0.7009 ± 0.0007	1206.8 ± 15.6	0.79687 ± 0.00016	0.29159 ± 0.02221	297.84 ± 0.02
0.8017 ± 0.0005	948.0 ± 12.2	0.79633 ± 0.00016	0.24989 ± 0.02300	297.84 ± 0.02
0.9007 ± 0.0003	550.8 ± 7.1	0.79612 ± 0.00016	0.16253 ± 0.02399	297.84 ± 0.02
		MIBK (x_1) + 2-EH (x_2)		
0.1009 ± 0.0005	550.2 ± 7.1	0.82611 ± 0.00017	0.00408 ± 0.03067	297.85 ± 0.02
0.2001 ± 0.0010	986.5 ± 12.7	0.82329 ± 0.00016	0.01780 ± 0.02931	297.85 ± 0.02
0.3019 ± 0.0014	1308.9 ± 16.9	0.82027 ± 0.00016	0.03392 ± 0.02731	297.84 ± 0.02
0.4014 ± 0.0017	1509.6 ± 19.5	0.81723 ± 0.00016	0.04259 ± 0.02488	297.84 ± 0.02
0.5009 ± 0.0020	1591.2 ± 20.5	0.81399 ± 0.00016	0.06290 ± 0.02221	297.84 ± 0.02
0.6018 ± 0.0021	1551.4 ± 20.0	0.81067 ± 0.00016	0.06428 ± 0.01955	297.84 ± 0.02
0.7019 ± 0.0020	1377.1 ± 17.8	0.80713 ± 0.00016	0.08014 ± 0.01752	297.84 ± 0.02
0.8009 ± 0.0017	1079.3 ± 13.9	0.80380 ± 0.00016	0.04077 ± 0.01686	297.84 ± 0.02
0.8009 ± 0.0017	1074.6 ± 13.9	0.80362 ± 0.00016	0.07101 ± 0.01697	297.84 ± 0.02
0.9004 ± 0.0010	622.2 ± 8.0	0.80006 ± 0.00016	0.03865 ± 0.01885	297.84 ± 0.02

^a x_1 is the mole fraction of the ketone; H^E is the excess molar enthalpy at 298 K, J·mol⁻¹; ρ is the density, kg·dm⁻³; V^E is the excess molar volume, cm³·mol⁻¹; T is the temperature at which the excess volumes have been measured, K.

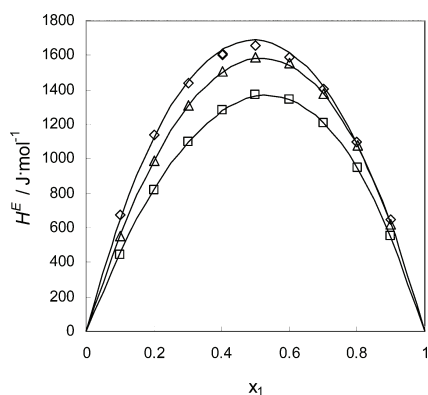


Figure 1. Excess molar enthalpies H^E at 298 K of binary systems of methyl isobutyl ketone (MIBK) + an alcohol { \diamond , 2-butanol; \square , *tert*-pentanol; \triangle , 2-ethyl-1-hexanol}, —, comparison with the model presented in this work.

Table 4. Parameters A_i of the Redlich–Kister Equation for the Excess Molar Volume V^E ^a

	A_0	A_1	A_2	A_3	S
	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹	cm ³ ·mol ⁻¹
MIBK (x_1) + 2-BuOH (x_2)	1.3907	0.0447	0.3441		0.01
MIBK (x_1) + <i>t</i> -PnOH (x_2)	1.0557	0.8893	-0.4327	0.6470	0.01
MIBK (x_1) + 2-EH (x_2)	0.2416	0.2244	-0.0039		0.03

^a A_0 to A_4 are the Redlich–Kister equation parameters for excess molar volume V^E , cm³·mol⁻¹; S is the standard deviation, cm³·mol⁻¹.

still. Gravimetrically prepared samples of the binary mixture were used for the determination of both the response factors of the GC FID detector and for refractive index calibration curve. The refractive indexes of binary mixture as a function of MIBK mole fraction at 298 K are tabulated in Table 5. The response factors are calculated as suggested in literature.²²

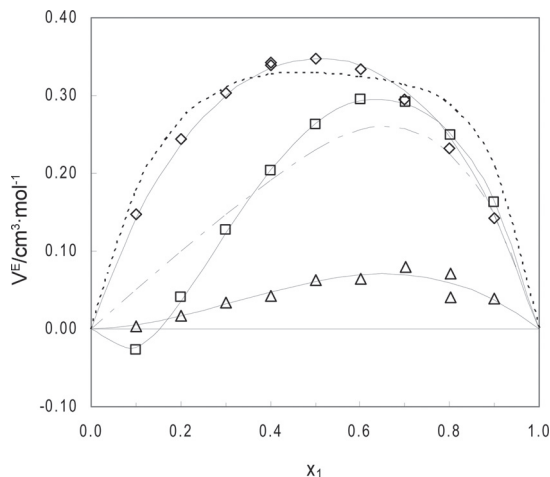


Figure 2. Excess molar volumes V^E at 298 K of binary systems of MIBK + an alcohol (\diamond , 2-butanol; \square , *tert*-pentanol; \triangle , 2-ethyl-1-hexanol), —, comparison with Redlich–Kister models presented in this work; - - -, comparison with MIBK + 2-butanol at 298 K,⁴ - · - ·, comparison with MIBK + *tert*-pentanol at 298 K.⁶

Table 5. Refractive Index n and Response Factor $F2 \cdot F1^{-1}$ as a Function of MIBK Mole Fraction x_1 of the Binary System at 298 K^a

MIBK (x_1) + 2-BuOH (x_2)		MIBK (x_1) + <i>t</i> -PnOH (x_2)		MIBK (x_1) + 2-EH (x_2)	
x_1	n	x_1	n	x_1	n
1.0000	1.393464	1.0000	1.393517	1.0000	1.393464
0.9508	1.393350	0.9563	1.393640	0.9491	1.395874
0.8985	1.393252	0.9177	1.393827	0.9051	1.398480
0.7988	1.393127	0.8202	1.394388	0.7986	1.402493
0.6020	1.393093	0.5982	1.396151	0.6050	1.409997
0.3998	1.393347	0.4095	1.398111	0.3970	1.417226
0.2005	1.393922	0.2171	1.400431	0.2045	1.423512
0.1005	1.394430	0.1216	1.401561	0.1017	1.426595
0.0502	1.394728	0.0598	1.402167	0.0516	1.428058
0.0000	1.395124	0.0000	1.402529	0.0000	1.429492
Response Factor $F2 \cdot F1^{-1}$					
		1.611716		1.077206	
				0.641469	

^a x_1 is the mole fraction of MIBK, n is the refractive index of the mixture at 298 K; $F2 \cdot F1^{-1}$ is the response factor.¹²

The system (MIBK + 2-BuOH) showed a minimum of the refractive index and thus requires a supplementary analysis method such as gas chromatography. In this work, gas chromatography was the primary method to determine the composition, but refractive index was used for (MIBK + *t*-PnOH) and for (MIBK + 2-EH) for comparison. The average absolute deviation of the MIBK mole fraction (x_1) between refractometer and GC analysis for (MIBK + 2-EH) was 0.008. For (MIBK + *t*-PnOH) the x_1 deviation was 0.009. Some of the samples were analyzed twice with GC, and the average repeatability of the x_1 was 0.0009.

Pure Component Vapor Pressure. Pure component vapor pressures were measured with the Yerazunis type apparatus before the VLE measurements of the binary systems. The

Table 6. Vapor Pressures p at Temperature T of MIBK, 2-Butanol, *tert*-Pentanol, and 2-Ethyl-1-hexanol^a

MIBK		2-BuOH	
T/K	p/kPa	T/K	p/kPa
340.18 ± 0.1	19.35 ± 0.04	358.16 ± 0.05	57.27 ± 0.04
340.66 ± 0.1	19.78 ± 0.04	367.97 ± 0.05	84.94 ± 0.04
343.42 ± 0.1	21.92 ± 0.04	372.43 ± 0.05	100.62 ± 0.04
351.55 ± 0.1	30.01 ± 0.04	372.71 ± 0.05	101.88 ± 0.04
352.71 ± 0.1	31.12 ± 0.04	<i>tert</i> -Pentanol	
353.11 ± 0.1	31.71 ± 0.04	336.04 ± 0.1	19.84 ± 0.04
359.22 ± 0.05	39.35 ± 0.04	344.75 ± 0.1	29.94 ± 0.04
359.39 ± 0.05	39.63 ± 0.04	351.29 ± 0.1	39.96 ± 0.04
359.58 ± 0.05	40.05 ± 0.04	356.60 ± 0.1	49.95 ± 0.04
362.88 ± 0.05	44.70 ± 0.04	361.18 ± 0.1	60.05 ± 0.04
365.90 ± 0.05	49.68 ± 0.04	365.40 ± 0.1	70.74 ± 0.04
366.61 ± 0.05	50.66 ± 0.04	368.16 ± 0.05	78.09 ± 0.04
368.06 ± 0.05	53.01 ± 0.04	368.75 ± 0.05	80.20 ± 0.04
368.07 ± 0.05	53.42 ± 0.04	371.97 ± 0.05	90.23 ± 0.04
368.14 ± 0.05	53.26 ± 0.04	375.14 ± 0.05	100.74 ± 0.04
368.15 ± 0.05	53.24 ± 0.04	375.38 ± 0.05	101.88 ± 0.04
368.70 ± 0.05	54.29 ± 0.04	375.53 ± 0.05	102.61 ± 0.04
371.34 ± 0.05	59.43 ± 0.04	2-Ethyl-1-hexanol	
371.64 ± 0.05	59.75 ± 0.04	389.76 ± 0.2	9.88 ± 0.04
371.91 ± 0.05	60.19 ± 0.04	407.11 ± 0.2	19.88 ± 0.04
374.37 ± 0.05	65.18 ± 0.04	418.24 ± 0.2	30.03 ± 0.04
376.26 ± 0.05	69.16 ± 0.04	426.95 ± 0.1	39.67 ± 0.04
376.49 ± 0.05	69.98 ± 0.04	430.79 ± 0.1	45.05 ± 0.04
378.80 ± 0.05	74.83 ± 0.04	433.51 ± 0.1	49.22 ± 0.04
380.65 ± 0.05	79.56 ± 0.04	437.24 ± 0.05	55.52 ± 0.04
381.06 ± 0.05	80.16 ± 0.04	439.49 ± 0.05	59.61 ± 0.04
382.66 ± 0.05	84.16 ± 0.04	442.12 ± 0.05	64.64 ± 0.04
384.99 ± 0.05	90.58 ± 0.04	445.00 ± 0.05	70.55 ± 0.04
388.31 ± 0.05	99.40 ± 0.04	447.04 ± 0.05	75.01 ± 0.04
388.63 ± 0.05	100.35 ± 0.04	449.02 ± 0.05	79.55 ± 0.04
388.65 ± 0.05	100.41 ± 0.04	451.06 ± 0.05	84.49 ± 0.04
389.06 ± 0.05	101.85 ± 0.04	456.77 ± 0.05	99.44 ± 0.04
389.49 ± 0.05	102.78 ± 0.04	457.83 ± 0.05	102.20 ± 0.04
		458.23 ± 0.05	102.91 ± 0.04
		458.24 ± 0.05	103.26 ± 0.04

^a T is the temperature, K; p is the pressure, kPa.

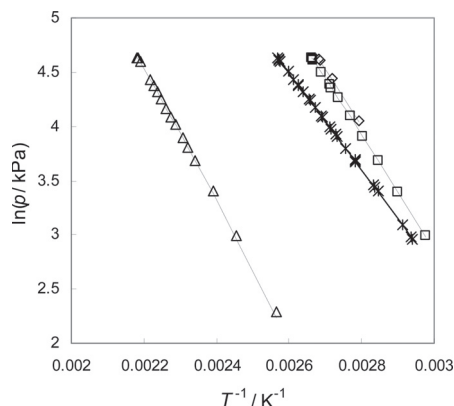


Figure 3. Vapor pressure of pure components: \times , MIBK; \diamond , 2-BuOH; \square , *t*-PnOH and \triangle , 2-EH, —, DIPPR⁸ correlation.

Table 7. Coefficients A to C for the Vapor-Pressure Correlation and the Absolute Average Pressure Deviation $|\Delta p|$ from the Literature^s from Temperature T_{\min} to T_{\max} ^a

this work	MIBK	2-BuOH	<i>tert</i> -pentanol	2-ethyl-1-hexanol
A	7.1654	8.2682	6.8905	7.6629
B	3097.02201	2980	2385.00609	3499.26149
C	-61.413631	-90.353	-115.39796	-105.79056
T_{\min}/K	340.2	358.2	336.0	389.8
T_{\max}/K	389.5	372.7	375.5	458.2
$ \Delta p /\text{kPa}$	0.37	0.75	0.06	0.30

^aA, B, and C are the parameters for the eq 8 in this work, T_{\min} (K) is the minimum temperature for the vapor pressure correlation; T_{\max} is the maximum pressure for the vapor pressure correlation; $|\Delta p|$ (kPa) is the absolute average pressure deviation from the DIPPR^s reference.

Table 8. Measured $xyTp$ Data for the Binary System of MIBK + 2-Butanol by Using the Circulation Still^a

x_1	y_1	T/K	p/kPa
0.000	0.000	367.97 ± 0.05	85.16 ± 0.04
0.107 ± 0.001	0.091 ± 0.001	368.10 ± 0.05	84.14 ± 0.04
0.160 ± 0.001	0.132 ± 0.001	368.10 ± 0.05	83.33 ± 0.04
0.206 ± 0.001	0.167 ± 0.001	368.10 ± 0.05	82.47 ± 0.04
0.302 ± 0.001	0.238 ± 0.001	368.09 ± 0.05	80.49 ± 0.04
0.363 ± 0.001	0.277 ± 0.001	367.99 ± 0.05	78.98 ± 0.04
0.390 ± 0.001	0.301 ± 0.001	368.09 ± 0.05	78.39 ± 0.04
0.424 ± 0.001	0.327 ± 0.001	368.11 ± 0.05	77.46 ± 0.04
0.456 ± 0.001	0.353 ± 0.001	368.01 ± 0.05	76.30 ± 0.04
0.494 ± 0.001	0.382 ± 0.001	368.05 ± 0.05	75.24 ± 0.04
0.537 ± 0.001	0.416 ± 0.001	368.05 ± 0.05	73.81 ± 0.04
0.581 ± 0.001	0.453 ± 0.001	368.08 ± 0.05	72.52 ± 0.04
0.629 ± 0.001	0.495 ± 0.001	367.98 ± 0.05	70.57 ± 0.04
0.685 ± 0.001	0.547 ± 0.001	368.17 ± 0.05	68.96 ± 0.04
0.738 ± 0.001	0.604 ± 0.001	368.04 ± 0.05	66.47 ± 0.04
0.800 ± 0.001	0.676 ± 0.001	368.00 ± 0.05	63.69 ± 0.04
0.859 ± 0.001	0.755 ± 0.001	367.99 ± 0.05	60.88 ± 0.04
0.929 ± 0.001	0.861 ± 0.001	367.96 ± 0.05	57.04 ± 0.04
1.000	1.000	368.04 ± 0.05	53.21 ± 0.04

^a x_1 is the MIBK liquid phase mole fraction; y_1 is the MIBK vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa.

measured vapor pressures of MIBK, 2-BuOH, *t*-PnOH, and 2-EH are presented in Table 6 and graphically in Figure 3.

The vapor pressure correlation is presented in eq 8

$$\ln\left(\frac{p}{\text{MPa}}\right) = A - \frac{B}{(T/\text{K}) + C} \quad (8)$$

where p is the vapor pressure (MPa), T is the temperature (K), and A , B , and C are the parameters of the equation. The coefficients (A to C) are given in Table 7. The objective function used for the eq 8 was the minimum of the sum of the absolute relative deviations between measured and correlated values. The correlation of DIPPR^s was used for the comparison of measured vapor pressures.

The measured vapor pressures were compared to the values calculated with DIPPR database correlation. The average pressure deviations were 0.37 kPa for MIBK, 0.75 kPa for 2-BuOH, 0.06 kPa for *t*-PnOH, and 0.3 kPa for 2-EH within the used temperature ranges.

VLE Circulation Still. Two techniques were used for the VLE measurements: circulation still and HS-GC. The measured results of the circulation still are presented in Tables 8, 9, and 10.

Table 9. Measured $xyTp$ Data for the Binary System of MIBK + *tert*-Pentanol by Using the Circulation Still^a

x_1	y_1	T/K	p/kPa
0.000	0.000	368.07 ± 0.05	78.27 ± 0.04
0.018 ± 0.001	0.015 ± 0.001	368.08 ± 0.05	78.07 ± 0.04
0.046 ± 0.001	0.037 ± 0.001	368.08 ± 0.05	77.63 ± 0.04
0.057 ± 0.001	0.047 ± 0.001	368.08 ± 0.05	77.44 ± 0.04
0.070 ± 0.001	0.056 ± 0.001	368.08 ± 0.05	77.24 ± 0.04
0.082 ± 0.001	0.066 ± 0.001	368.07 ± 0.05	77.00 ± 0.04
0.110 ± 0.001	0.088 ± 0.001	368.07 ± 0.05	76.53 ± 0.04
0.145 ± 0.001	0.116 ± 0.001	368.07 ± 0.05	75.93 ± 0.04
0.194 ± 0.001	0.155 ± 0.001	368.08 ± 0.05	75.05 ± 0.04
0.265 ± 0.001	0.212 ± 0.001	368.08 ± 0.05	73.71 ± 0.04
0.328 ± 0.001	0.261 ± 0.001	368.07 ± 0.05	72.40 ± 0.04
0.438 ± 0.001	0.354 ± 0.001	368.08 ± 0.05	70.24 ± 0.04
0.484 ± 0.001	0.393 ± 0.001	368.07 ± 0.05	69.44 ± 0.04
0.559 ± 0.001	0.464 ± 0.001	368.08 ± 0.05	67.49 ± 0.04
0.564 ± 0.001	0.468 ± 0.001	368.07 ± 0.05	66.93 ± 0.04
0.588 ± 0.001	0.490 ± 0.001	368.07 ± 0.05	66.74 ± 0.04
0.612 ± 0.001	0.513 ± 0.001	368.08 ± 0.05	65.78 ± 0.04
0.664 ± 0.001	0.565 ± 0.001	368.08 ± 0.05	64.45 ± 0.04
0.722 ± 0.001	0.627 ± 0.001	368.08 ± 0.05	62.96 ± 0.04
0.786 ± 0.001	0.704 ± 0.001	368.08 ± 0.05	60.88 ± 0.04
0.857 ± 0.001	0.792 ± 0.001	368.07 ± 0.05	58.26 ± 0.04
0.860 ± 0.001	0.795 ± 0.001	368.07 ± 0.05	58.24 ± 0.04
0.909 ± 0.001	0.862 ± 0.001	368.07 ± 0.05	56.87 ± 0.04
0.960 ± 0.001	0.936 ± 0.001	368.08 ± 0.05	54.77 ± 0.04
1.000	1.000	368.07 ± 0.05	53.42 ± 0.04

^a x_1 is the MIBK liquid phase mole fraction; y_1 is the MIBK vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa.

Table 10. Measured $xyTp$ Data for the Binary System of MIBK + 2-Ethyl-1-hexanol by Using the Circulation Still^a

x_1	y_1	T/K	p/kPa
0.000	0.000	388.1	8.80 ± 0.1 ^b
0.036 ± 0.005	0.306 ± 0.005	388.1 ± 0.2	12.52 ± 0.05
0.143 ± 0.003	0.658 ± 0.003	388.2 ± 0.1	22.78 ± 0.05
0.160 ± 0.002	0.688 ± 0.002	388.1 ± 0.1	24.17 ± 0.05
0.310 ± 0.001	0.834 ± 0.001	388.12 ± 0.05	37.46 ± 0.04
0.313 ± 0.001	0.844 ± 0.001	387.99 ± 0.05	38.77 ± 0.04
0.363 ± 0.001	0.865 ± 0.001	388.02 ± 0.05	43.29 ± 0.04
0.416 ± 0.001	0.885 ± 0.001	388.04 ± 0.05	48.05 ± 0.04
0.444 ± 0.001	0.899 ± 0.001	388.08 ± 0.05	50.04 ± 0.04
0.461 ± 0.001	0.902 ± 0.001	388.19 ± 0.05	52.30 ± 0.04
0.512 ± 0.001	0.919 ± 0.001	388.07 ± 0.05	56.40 ± 0.04
0.614 ± 0.001	0.945 ± 0.001	388.08 ± 0.05	64.89 ± 0.04
0.704 ± 0.001	0.962 ± 0.001	388.07 ± 0.05	72.28 ± 0.04
0.765 ± 0.001	0.971 ± 0.001	388.09 ± 0.05	77.94 ± 0.04
0.816 ± 0.001	0.978 ± 0.001	388.07 ± 0.05	82.43 ± 0.04
0.875 ± 0.001	0.985 ± 0.001	388.07 ± 0.05	87.44 ± 0.04
0.910 ± 0.001	0.990 ± 0.001	388.08 ± 0.05	90.61 ± 0.04
0.940 ± 0.001	0.993 ± 0.001	388.07 ± 0.05	93.25 ± 0.04
0.964 ± 0.001	0.996 ± 0.001	388.08 ± 0.05	95.48 ± 0.04
1.000	1.000	388.07 ± 0.05	98.70 ± 0.04

^a x_1 is the MIBK liquid phase mole fraction; y_1 is the MIBK vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa. ^bBoiling too unstable, estimated value by using the Antoine equation.

The sampling at the circulation still technique is dependent on the stability of the boiling. The apparatus was equipped with a large buffer tank to keep the pressure stable within 0.01 kPa, but in the case of the (MIBK + 2-EH) the large boiling point

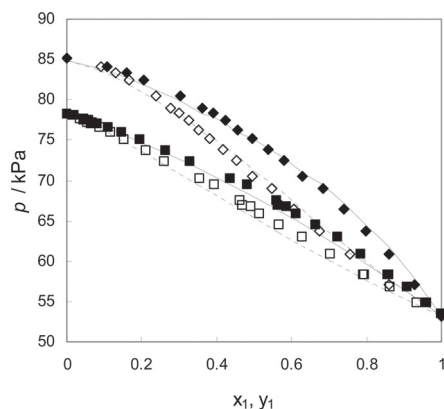


Figure 4. Circulation still measurements: \blacklozenge , liquid mole fraction; \diamond , vapor mole fraction for MIBK (1) + 2-BuOH (2) at 368 K; and \blacksquare , liquid mole fraction; \square , vapor mole fraction for MIBK (1) + *t*-PnOH (2) at 368 K, —, liquid phase comparison with the model presented in this work, - - -, vapor phase comparison with the model presented in this work.

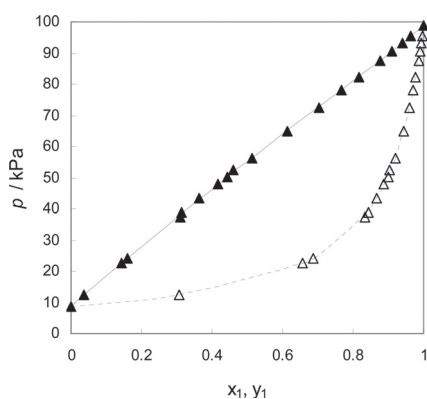


Figure 5. Circulation still measurements: \blacktriangle , liquid mole fraction; \triangle , vapor mole fraction for MIBK (1) + 2-EH (2) at 388 K; —, liquid phase comparison with the model presented in this work; - - -, vapor phase comparison with the model presented in this work.

difference between the pure components in addition to high viscosity of 2-EH made the boiling unstable at very low pressure. The equilibration at low pressure for 2-EH rich mixtures took over one hour compared to typical half of an hour for other investigated binary mixtures. Mixing of the liquid and condensed vapor inside the mixing chamber was inefficient due to approximately 15 times larger viscosity at 293 K of 2-EH compared to MIBK. Additionally the relative volatility had values from 9.5 to 10.5. The apparatus was successfully operated for relative volatilities up to 40 in earlier work²³ for less viscous systems. This lead to the conclusion that the combination of these two factors caused the fluctuation of temperature below 30 kPa. The graphical presentation of the measurements is shown in Figures 4 and 5.

The consistency of the measured data was first evaluated by using the area test.^{24–26} Second, the infinite dilution test^{24–26} was applied to the measured data. Third, the point test was

Table 11. Results of the Consistency Tests (Area, Infinite Dilution, Point) for Circulation Still Measurements of the Binary Systems of MIBK + an Alcohol (2-Butanol, *tert*-Pentanol, 2-Ethyl-1-hexanol) by Using the Hayden–O’Connell Method^a

	MIBK (x_1) + 2-BuOH (x_2)	MIBK (x_1) + <i>t</i> -PnOH (x_2)	MIBK (x_1) + 2-EH (x_2)
Area Test			
area	0.001	0.010	0.012
deviation/%	0.60	14.90	21.30
Infinite Dilution Test			
$x_1 = 0\%$	6.40	17.20	98.20
$x_1 = 1\%$	20.30	75.10	12.69
Point Test			
abs(y)	0.0019	0.0024	0.0018
abs(dp)/kPa	0.065	0.116	0.233

^a x_1 is the MIBK mole fraction; y is the vapor mole fraction; dp is the pressure deviation between the measured and calculated pressure, kPa.

Table 12. Measured xyT Data for the Binary System of MIBK (1) + 2-Butanol (2) by Using HS-GC^a

x_1	y_1	T/K
0.947 ± 0.003	0.894 ± 0.003	368.2 ± 0.1
0.897 ± 0.003	0.808 ± 0.003	368.2 ± 0.1
0.797 ± 0.003	0.668 ± 0.003	368.2 ± 0.1
0.698 ± 0.003	0.556 ± 0.003	368.2 ± 0.1
0.601 ± 0.003	0.464 ± 0.003	368.2 ± 0.1
0.503 ± 0.003	0.382 ± 0.003	368.2 ± 0.1
0.405 ± 0.003	0.306 ± 0.003	368.2 ± 0.1
0.304 ± 0.003	0.232 ± 0.003	368.2 ± 0.1
0.201 ± 0.003	0.156 ± 0.003	368.2 ± 0.1
0.100 ± 0.003	0.077 ± 0.003	368.2 ± 0.1
0.053 ± 0.003	0.038 ± 0.003	368.2 ± 0.1

^a x_1 is the MIBK mole fraction in the liquid phase; y_1 is the MIBK mole fraction in the vapor phase; T is temperature, K.

applied.²⁷ The results of the consistency tests for the circulation still measurements are given in Table 11.

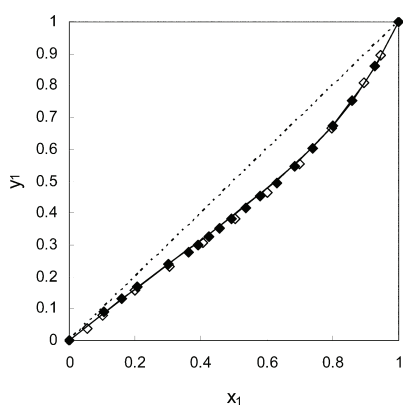
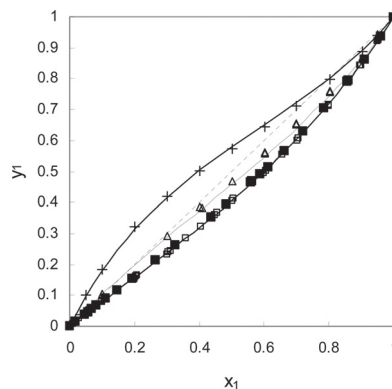
VLE HS-GC. Utilization of the HS-GC supported the data obtained with the circulation still and extended the measurements to lower temperatures where the stability of the circulation still is difficult to achieve. Liquid sample GC calibrations were used to determine the response factors needed for vapor phase analysis. Liquid phase concentrations were obtained from the gravimetric data of the preparation of the vials, and the liquid sample concentrations were corrected for the difference in component compositions due to vapor sampling.²⁸ The ideal gas law was utilized in the gas phase calculations together with approximate activity coefficients of the components in liquid phase calculated with the UNIFAC Dortmund activity coefficient model.²⁹ The correction of the liquid phase composition was at maximum 0.6 % of the more dilute component’s concentration. For (MIBK + 2-BuOH), one isotherm was measured, and for (MIBK + *t*-PnOH) three isotherms. The results are given in Tables 12 and 13. A comparison between the two techniques, circulation still and HS-GC, is shown in Figures 6 and 7.

The thermodynamic area consistency test³⁰ was used to evaluate the quality of the headspace data. Since pure component vapor peak areas were very unstable, correlations for the binary mixture areas were used to obtain pure component area.³¹ The results of the consistency test for the HS-GC measurements are presented in Table 14.

Table 13. Measured xyT Data for the Binary System of MIBK (1) + *tert*-Pentanol (2) by Using HS-GC^a

x_1	y_1	x_1	y_1
$T = 368.2 \pm 0.1$ K		$T = 333.2 \pm 0.1$ K	
0.010 ± 0.003	0.008 ± 0.003	0.048 ± 0.003	0.052 ± 0.003
0.010 ± 0.003	0.008 ± 0.003	0.099 ± 0.003	0.104 ± 0.003
0.010 ± 0.003	0.009 ± 0.003	0.300 ± 0.003	0.291 ± 0.003
0.030 ± 0.003	0.025 ± 0.003	0.403 ± 0.003	0.387 ± 0.003
0.030 ± 0.003	0.025 ± 0.003	0.407 ± 0.003	0.381 ± 0.003
0.049 ± 0.003	0.040 ± 0.003	0.503 ± 0.003	0.468 ± 0.003
0.050 ± 0.003	0.038 ± 0.003	0.601 ± 0.003	0.557 ± 0.003
0.050 ± 0.003	0.041 ± 0.003	0.603 ± 0.003	0.563 ± 0.003
0.051 ± 0.003	0.041 ± 0.003	0.697 ± 0.003	0.650 ± 0.003
0.100 ± 0.003	0.081 ± 0.003	0.700 ± 0.003	0.656 ± 0.003
0.101 ± 0.003	0.077 ± 0.003	0.802 ± 0.003	0.759 ± 0.003
0.101 ± 0.003	0.080 ± 0.003	0.803 ± 0.003	0.758 ± 0.003
0.202 ± 0.003	0.154 ± 0.003	0.902 ± 0.003	0.868 ± 0.003
0.206 ± 0.003	0.161 ± 0.003	0.950 ± 0.003	0.932 ± 0.003
0.209 ± 0.003	0.164 ± 0.003		
0.300 ± 0.003	0.232 ± 0.003	$T = 294.7 \pm 0.2$ K	
0.304 ± 0.003	0.241 ± 0.003	0.950 ± 0.003	0.942 ± 0.003
0.310 ± 0.003	0.244 ± 0.003	0.902 ± 0.003	0.889 ± 0.003
0.359 ± 0.003	0.286 ± 0.003	0.802 ± 0.003	0.798 ± 0.003
0.405 ± 0.003	0.324 ± 0.003	0.700 ± 0.003	0.713 ± 0.003
0.449 ± 0.003	0.359 ± 0.003	0.603 ± 0.003	0.645 ± 0.003
0.455 ± 0.003	0.366 ± 0.003	0.501 ± 0.003	0.573 ± 0.003
0.502 ± 0.003	0.406 ± 0.003	0.403 ± 0.003	0.502 ± 0.003
0.505 ± 0.003	0.411 ± 0.003	0.300 ± 0.003	0.418 ± 0.003
0.597 ± 0.003	0.495 ± 0.003	0.202 ± 0.003	0.320 ± 0.003
0.604 ± 0.003	0.503 ± 0.003	0.099 ± 0.003	0.183 ± 0.003
0.656 ± 0.003	0.555 ± 0.003	0.048 ± 0.003	0.100 ± 0.003
0.703 ± 0.003	0.598 ± 0.003		
0.705 ± 0.003	0.605 ± 0.003		
0.799 ± 0.003	0.713 ± 0.003		
0.800 ± 0.003	0.715 ± 0.003		
0.897 ± 0.003	0.844 ± 0.003		
0.899 ± 0.003	0.844 ± 0.003		
0.950 ± 0.003	0.920 ± 0.003		
0.954 ± 0.003	0.926 ± 0.003		

^a x_1 is the MIBK mole fraction in the liquid phase; y_1 is the MIBK mole fraction in the vapor phase; T is temperature, K.

**Figure 6.** Binary system of MIBK (1) + 2-BuOH (2) at 368 K: \blacklozenge , circulation still; \diamond , HS-GC; —, comparison with the model presented in this work.**Figure 7.** Binary system of MIBK (1) + *t*-PnOH (2): \blacksquare , circulation still at 368 K; \square , HS-GC at 368 K; \triangle , HS-GC at 333 K; +, HS-GC at 294 K; —, comparison with the model presented in this work.**Table 14.** Results of the Area Consistency Test for the Binary Systems of MIBK (1) + an Alcohol (2) (2-Butanol or *tert*-Pentanol) with the Hayden–O'Connell (HOC) Correlation^a

	T/K	no. points	area	deviation%
MIBK (x_1) + 2-BuOH (x_2)	368	11	0.04	30.7
MIBK (x_1) + <i>t</i> -PnOH (x_2)	368	35	0.005	6.2
MIBK (x_1) + <i>t</i> -PnOH (x_2)	333	14	0.035	30.7
MIBK (x_1) + <i>t</i> -PnOH (x_2)	294.6	11	0.009	3.5

^a T is the temperature, K.

Table 15. Wilson Model Parameters a_{ij} and Model Deviations of Vapor Mole Fraction y , Pressure p , and Excess Molar Enthalpy H^E from the Measured Values for the Binaries MIBK (1) + an Alcohol (2) (2-Butanol, *tert*-Pentanol, or 2-Ethyl-1-hexanol)^a

	MIBK (x_1) + 2-BuOH (x_2)	MIBK (x_1) + <i>t</i> -PnOH (x_2)	MIBK (x_1) + 2-EH (x_2)
$a_{0,12}$	728.5	3228.5	571.7
$a_{0,21}$	316.1	-1198.2	383.7
$a_{1,12}$	-2.449	-21.085	-1.560
$a_{1,21}$	0.037	10.587	-0.660
$a_{2,12}$	0	0.0344	0
$a_{2,21}$	0	-0.0203	0
$ \bar{y} , xyTp$	0.005	0.002	0.001
$ \bar{p} , xyTp$	0.47	0.48	0.23
$\bar{y}, xyT, 368$ K	0.009	0.002	
$\bar{y}, xyT, 333$ K		0.009	
$\bar{y}, xyT, 294$ K		0.004	
$ H^E $	22.5	4.9	4.5

^a $a_{0,ij}$, $a_{1,ij}$, and $a_{2,ij}$ are the Wilson model binary interaction parameters for eqs 2 and 3; x is the liquid phase mole fraction; y is the vapor phase mole fraction; T is the temperature, K; p is the pressure, kPa; H^E is the excess molar enthalpy, $J \cdot mol^{-1}$.

The regressed Wilson model parameters and the deviations of the objective functions are listed in Table 15. Modeled activity coefficients based on the excess VLE measurements (circulation still, HS-GC) and the excess molar enthalpy measurements are presented in Figure 8.

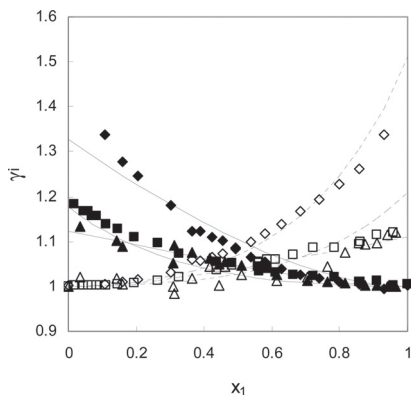


Figure 8. Activity coefficients of circulation still measurements: \blacklozenge , MIBK; \diamond , 2-BuOH for MIBK (1) + 2-BuOH (2) at 368 K; \blacksquare , MIBK; \square , *t*-PnOH for MIBK (1) + *t*-PnOH (2) at 368 K; and \blacktriangle , MIBK; \triangle , (2-EH) for MIBK (1) + 2-EH (2) at 388 K; —, comparison of the MIBK activity coefficients with the model presented in this work; - - -, comparison of 2-BuOH and *t*-PnOH activity coefficients with the model presented in this work.

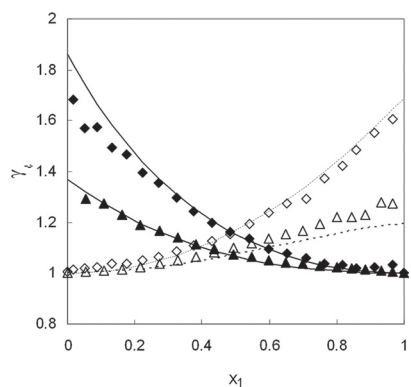


Figure 9. A comparison of activity coefficients obtained from literature² against modeled activity coefficients at (20 and 101) kPa for MIBK (1) + 2-BuOH (2), \blacklozenge , MIBK; \diamond , 2-BuOH measurements¹ at 20 kPa; and \blacktriangle , MIBK; \triangle , 2-BuOH measurements² at 101 kPa; —, comparison of the MIBK activity coefficients with the model presented in this work; - - -, comparison of the alcohol activity coefficients with the model presented in this work.

The regressed parameters of this work of the MIBK + 2-BuOH system were tested against literature measurements¹ at two isobars at (20 and 101) kPa. As shown in Figure 9, the model corresponds to this experimental data. This is due to the fact that complementary VLE and H^E data provide sufficient data sets for extrapolation.

CONCLUSIONS

Excess molar enthalpies (H^E) and excess molar volumes (V^E) have been measured at 298.15 K for the systems consisting of MIBK and an alcohol (2-butanol, *tert*-pentanol, or 2-ethyl-1-hexanol). Redlich–Kister equation parameters are provided for both H^E and for V^E .

VLE has been determined for the systems MIBK + 2-butanol at 368 K, MIBK + *tert*-pentanol at 368 K, at 333 K, and at 295 K,

and MIBK + 2-ethyl-1-hexanol at 388 K by using circulation still and HS-GC apparatuses. The binary system MIBK + *tert*-pentanol showed azeotropic behavior.

The chemical theory was applied to vapor phase fugacity coefficients and the Wilson model to liquid phase activity coefficients. The VLE model was capable of correlating the VLE and H^E data for all of the binary systems. Furthermore, the model reliably represented literature¹ data of the binary system (MIBK + 2-butanol) at lower temperatures.

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Funding

The authors acknowledge the Academy of Finland and H. Laavi acknowledges the Research Foundation of Helsinki University of Technology, and Jenny and Antti Wihuri Foundation for financial support.

Notes

The authors declare no competing financial interest.

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