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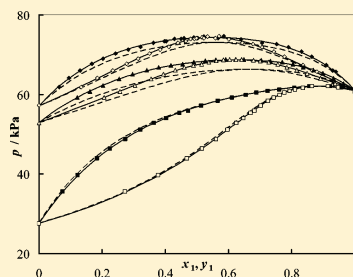
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Vapor–Liquid Equilibria, Excess Enthalpy, and Excess Volume of Binary Mixtures Containing an Alcohol (1-Butanol, 2-Butanol, or 2-Methyl-2-butanol) and 2-Ethoxy-2-methylbutane

Aarne T. Sundberg,* Helena Laavi, Younghun Kim, Petri Uusi-Kyyny, Juha-Pekka Pokki, and Ville Alopaeus

Department of Biotechnology and Chemical Technology, Aalto University, Finland

ABSTRACT: Pure component vapor pressure between (324 and 374) K, isothermal vapor–liquid equilibria at 358 K, excess enthalpy, excess volume, and density at 298 K were determined for three binary systems consisting of 2-ethoxy-2-methylbutane + 1-butanol, + 2-butanol, or + 2-methyl-2-butanol. Excess enthalpy was measured with a microflow calorimeter and excess volume with a vibrating-tube densimeter. A recirculation still was used to measure both the pure component vapor pressures and the phase equilibria of binary systems. The measured data were well-represented with local composition models. A maximum pressure azeotrope was observed for all measured systems.



■ INTRODUCTION

The incomplete combustion of fuel causes harmful emissions of carbon monoxide and hydrocarbons. Improved combustion can be achieved by the addition of oxygen compounds, such as alcohols or ethers.¹

2-Ethoxy-2-methylbutane, also known as *tert*-amyl ethyl ether or TAE, is produced from isoamylenes and ethanol. Ethanol and butanol are both derived by a fermentation process from biomass; thus their use as a petroleum component or the use of bioethanol in the production of TAE is promoted by legislation.²

The Reid vapor pressure of gasoline blends containing ethanol is relatively high due to formation of azeotropes, which can limit the maximum ethanol content. To reach higher ethanol content, the use of components with lower vapor pressure is required. The Reid vapor pressure of both TAE and butanol is significantly lower than the level permitted for gasoline.³

To find the optimal composition for a gasoline mixture, a phase equilibria model for the systems involved is required. For this reason, a comprehensive review detailing the phase equilibria measurements for mixtures containing 2-methoxy-2-methylpropane, 2-methoxy-2-methylbutane, 2-ethoxy-2-methylpropane, 1-propoxypropane, and 2-isopropoxypropane was compiled by Marsh et al.⁴ However, for mixtures containing TAE and an alcohol, only a few works have been published. Arce et al.⁵ measured the vapor–liquid equilibria (VLE) of TAE and water and Everson and Jansen⁶ the VLE of TAE, ethanol, and 2-methyl-1-butene. The purpose of this work was to complement those works with measurements of binary systems containing TAE and 1-butanol, 2-butanol, or 2-methyl-2-butanol.

■ EXPERIMENTAL SECTION

Materials. TAE was synthesized as presented in our earlier work.⁷ After the synthesis, TAE was purified by extraction

with distilled water to remove ethanol, followed by drying over molecular sieves (Merck 3 Å), and a batch distillation at atmospheric pressure.

The purity of all components was analyzed by using an Agilent 6850A gas chromatograph (GC) equipped with an autosampler and a flame ionization detector (FID). All components were dried over molecular sieves (Merck 3 Å), and the water content was analyzed with Karl Fischer titration.

The refractive index was measured with an automatic refractometer (ABBEMAT-HP, Dr. Kernchen, Germany), with an accuracy of ± 0.00002 . The temperature accuracy of the refractometer was ± 0.03 K.

The density was measured with a vibrating-tube densimeter (Anton Paar DMA 512P), with a relative accuracy of ± 0.02 %. The temperature of the densimeter was measured with a Pt-100 resistance temperature probe connected to a temperature meter (Thermolyzer S2541, Frontec), with a calibration uncertainty of ± 0.015 K. The excess volumes were evaluated based on the density measurements with an uncertainty of ± 0.03 cm³·mol⁻¹.

The measured densities and refractive indices corresponded well with the literature values,^{8–10} as presented in Table 1.

Recirculation Still. The recirculation still used in the measurements was Yerazunis-type¹¹ with minor modifications to the original design.¹² The experimental setup has been described in detail in the previous works.^{12,13} Approximately 80 cm³ of components were needed to run the apparatus. Temperatures were measured with a Pt-100 resistance temperature probe located at the bottom of the packed section of the equilibrium chamber. Temperatures were read with a precision thermometer

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Table 1. Supplier and Purity of the Components

component	supplier	GC purity	water content	T^a	ρ_{measured}^a	ρ_{lit}^5	n_D^b	
		mass %	mass %	K	kg·m ⁻³	kg·m ⁻³	measured	lit.
2-ethoxy-2-methylbutane	synthesized ^d	≥ 99.8	0.027	297.82	760.52	761.61	1.38858	1.38857 ⁵ 1.39112 ^c 1.3912 ^{c,6}
1-butanol	Sigma-Aldrich	≥ 99.9	0.003	297.82	805.97	804.31	1.3972	1.3971 ⁸
2-butanol	Sigma-Aldrich	≥ 99.5	0.016	297.83	802.71	802.61	1.3951	1.3949 ⁸
2-methyl-2-butanol	Merck	≥ 99	0.036	297.85	805.29	805.15	1.40248	1.40238 ⁸

^aDensity, ρ , $u(\rho) = 0.16 \text{ kg}\cdot\text{m}^{-3}$, at temperature, T , $u(T) = 0.015 \text{ K}$. ^bRefractive index, n_D , $u(n_D) = 0.00002$, at temperature of 298.15 K, $u(T) = 0.03 \text{ K}$.

^cRefractive index, n_D , at 293.15 K.

Table 2. Pure Component Physical Properties

component	2-ethoxy-2-methylbutane	1-butanol	2-butanol	2-methyl-2-butanol
CAS no.	919-94-8	71-36-3	78-92-2	75-85-4
T_C^a/K	546	563.1	535.9	543.7
P_C^b/MPa	2.74	4.414	4.1885	3.71
ω^c	0.338194	0.58828	0.580832	0.481975
$\nu_i^d/\text{cm}^3\cdot\text{mol}^{-1}$	152.635	92.19	92.39	109.5
Q^e	4.712	3.048	3.032	3.446
R^f	5.417	3.454	3.598	4.254
A^g	58.933 ^h	106.29483 ⁱ	122.552 ⁱ	115.78 ⁱ
B^g	-5897 ^h	-9866.35511 ⁱ	-10236.2 ⁱ	-9860.05 ⁱ
C^g	-5.4 ^h	-11.6553 ⁱ	-14.125 ⁱ	-13.1617 ⁱ
D^g	0.0000024 ^h	1.08318·10 ⁻¹⁷ⁱ	2.35591·10 ⁻¹⁷ⁱ	1.46808·10 ⁻¹⁷ⁱ
E^g	2 ^h	6 ⁱ	6 ⁱ	6 ⁱ
$T_{\text{min}}^g/\text{K}$	274.2 ^h	183.85 ⁱ	158.45 ⁱ	264.15 ⁱ
$T_{\text{max}}^g/\text{K}$	411.65 ^h	563.1 ⁱ	535.9 ⁱ	543.7 ⁱ
$ \Delta p_{\text{AVG}}^s ^{j,5}/\text{kPa}$	0.22	0.06	0.67	0.19
$ \Delta p_{\text{AVG}}^s ^{j,8}/\text{kPa}$	not available	0.78	0.45	0.55

^aCritical temperature, T_C . ^bCritical pressure, P_C . ^cAcentric factor, ω . ^dLiquid molar volume at 298 K, ν_i . ^eRelative van der Waals volume, R^8 . ^fRelative van der Waals surface area, Q^8 . ^gNormalization factors for volume and surface parameters are given in Abrams et al.^{2,5} ^hVapor pressure correlation (1) parameters A through E , for the temperature range from T_{min} to T_{max} . ⁱParameters fitted in this work. ^jParameters from ref. 8. ^kAverage absolute deviation of vapor pressure, $|\Delta p_{\text{AVG}}^s| = ((\sum_{i=1}^N |p_{i,\text{calc}} - p_{i,\text{exp}}|)/N)$.

Table 3. Experimental Vapor Pressure for Temperature T and Pressure p of Pure Components^a

T/K	p/kPa	T/K	p/kPa	T/K	p/kPa	T/K	p/kPa
2-Ethoxy-2-methylbutane				1-Butanol			
324.31	17.7	358.09	61.3	345.91	15.6	376.72	60.1
331.83	24.0	359.96	65.1	358.05	27.4	378.46	64.2
343.83	37.6	362.13	69.7	359.46	29.4	380.74	70.2
345.82	40.3	364.42	74.9	366.26	39.3	382.55	75.1
349.21	45.4	366.44	79.6	369.57	45.1	384.30	80.1
351.71	49.5	367.36	81.8	372.02	49.8	385.78	84.6
355.12	55.5	368.16	83.8	374.43	54.9	390.41	100.0
357.39	59.9	373.70	98.9				
358.01	61.0	374.41	101.0				
2-Butanol				2-Methyl-2-butanol			
330.11	15.7	362.88	69.9	334.98	18.8	361.21	59.7
337.99	23.3	365.08	76.3	344.45	29.4	363.43	65.2
345.15	32.7	366.13	79.5	351.18	39.5	365.23	69.8
354.49	49.4	367.13	82.9	354.10	44.7	367.10	75.0
357.15	55.3	371.51	98.3	356.81	50.1	368.88	80.1
358.16	57.3	372.43	100.6	358.12	52.8	371.04	86.7
358.98	59.6			359.14	55.0	375.78	102.7

^a $u(T) = 0.05 \text{ K}$, $u(p) = 0.17 \text{ kPa}$.

(F200, Tempcontrol), with an accuracy of $\pm 0.02 \text{ K}$, as reported by the manufacturer. The temperature calibration uncertainty was $\pm 0.015 \text{ K}$. The uncertainty of the whole temperature measurement system was estimated to be $\pm 0.05 \text{ K}$.

The pressure was measured with a pressure transducer [Druck PMP 4070, (0 to 100) kPa] connected to a panel meter (Red Lion). The combined pressure inaccuracy of the instruments was reported to be $\pm 0.07 \text{ kPa}$ by the manufacturer.

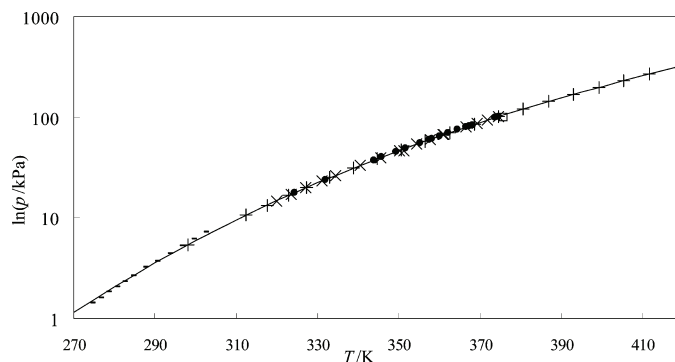


Figure 1. Saturated vapor pressure p , for temperature T , of 2-ethoxy-2-methylbutane. \square , Reboul and Truchot;¹⁷ $+$, Steele et al.;¹⁸ \times , Krähenbühl and Gmehling;¹⁹ $-$, Verevkin et al.;²⁰ \bullet , this work. The solid line represents the extended form of Antoine's equation.

The pressure measurement system was calibrated against a pressure calibrator (BEAMEX PC 105-1166). The uncertainty of the whole pressure measurement system including the calibration uncertainty was expected to be less than ± 0.17 kPa.

Calorimeter. A calorimeter (SETARAM C80) equipped with mixing vessels was used to measure excess molar enthalpies. Syringe pumps (ISCO 260D and 500D) were used to feed the components to the calorimeter. The relative accuracy of the pump flow rate was ± 0.5 % of the set point value. The pump syringe was kept at 293.15 ± 0.5 K by using a temperature controlled water bath. The combined total flow rate of the components was $0.5 \text{ cm}^3 \cdot \text{min}^{-1}$. The calorimeter was calibrated as recommended by Wadsö and Goldberg¹⁴ with two reference systems: cyclohexane + hexane and methanol + water. The calibration procedure indicated for this type of equipment^{15,16} was utilized. The cyclohexane + hexane binary system was used to determine the sensitivity of the calorimeter, and the methanol + water binary was used to evaluate the accuracy of the calibration. The average relative accuracy of the calorimeter was found to be ± 1.3 %. The accuracy of the calorimeter temperature was ± 0.1 K and precision ± 0.05 K, as given by the manufacturer for the whole operating temperature range of the calorimeter (from ambient temperature to 573 K). The density measurement was directly after the calorimeter to verify complete mixing in the calorimeter. The outlet was at atmospheric pressure.

VLE Measurement. Pure component 1 was introduced in the recirculation still, and its vapor pressure was measured at several temperatures. Then component 2 was injected into the recirculation still. It took (45 to 60) min to achieve constant temperature. The temperature was held constant for (30 to 45) min before sampling. A steady temperature was assumed as an indication of reaching phase equilibrium.

After equilibration, the temperature in the equilibrium cell was measured, and vapor and liquid samples were withdrawn with a 1 cm^3 Hamilton Sample Lock syringe and injected into a cooled 2 cm^3 autosampler vial containing approximately 1 cm^3 of solvent (toluene), which was used as a diluent. The compositions of both samples were immediately measured by the GC.

The GC-column used was a HP-1 dimethylpolysiloxane ($60.0 \text{ m} \times 250 \mu\text{m} \times 1.0 \mu\text{m}$). The injector and FID were kept at 250 °C. Helium was used as the carrier gas at a constant flow rate of $1 \text{ cm}^3 \cdot \text{min}^{-1}$. The inlet split ratio was 100:1. The oven temperature was initially kept at 70 °C for 2 min, then

Table 4. Experimental (Vapor + Liquid) Equilibrium Data for Temperature T , Pressure p , Liquid-Phase Mole Fraction x , Vapor-Phase Mole Fraction y , and Liquid Activity Coefficient γ , for the System 2-Ethoxy-2-methylbutane (1) + 1-Butanol (2)^a

T/K	p/kPa	x_1	y_1	γ_1^b	γ_2^b
358.05	27.4	0.000	0.000		1.00
358.11	35.5	0.074	0.273	2.30	0.99
358.11	39.7	0.123	0.378	2.10	1.00
358.10	43.8	0.183	0.469	1.89	1.02
358.02	46.3	0.225	0.518	1.78	1.04
358.02	48.8	0.273	0.562	1.68	1.05
358.14	51.1	0.321	0.598	1.58	1.08
358.11	52.8	0.364	0.626	1.50	1.12
358.10	54.0	0.402	0.648	1.44	1.15
358.07	55.3	0.445	0.671	1.38	1.18
358.01	55.9	0.472	0.684	1.34	1.21
358.14	57.2	0.514	0.703	1.28	1.26
358.14	58.3	0.567	0.726	1.23	1.33
358.14	59.2	0.611	0.745	1.18	1.40
358.13	59.9	0.655	0.763	1.14	1.48
358.16	60.5	0.688	0.778	1.12	1.56
358.11	60.9	0.723	0.793	1.09	1.64
358.05	61.2	0.761	0.812	1.07	1.75
358.09	61.7	0.809	0.837	1.05	1.91
358.15	62.0	0.856	0.865	1.03	2.10
358.16	62.0	0.922	0.914	1.01	2.45
358.12	61.7	0.956	0.947	1.00	2.74
358.01	61.0	1.000	1.000	1.00	

^a $u(T) = 0.05$ K, $u(p) = 0.17$ kPa, $u(x_1) = u(y_1) = 0.003$, $u(\gamma_1) = u(\gamma_2) = 0.08$. ^bDerived from the experimental data by using eq 2.

increased subsequently to 150 °C at a rate of 8 °C \cdot min⁻¹, and kept at 150 °C for 3 min. The total run time was 15 min.

Pure components were used to determine the retention times; then the GC was calibrated with eight mixtures of known composition that were prepared gravimetrically. Solvent was added in advance in the autosampler vials to reduce the volume of the sample. The maximum error of liquid and vapor composition measurements was estimated to be 0.003 mole fraction.

The saturated vapor pressure used in the modeling of the data was calculated from the extended form of Antoine's equation.

$$P_i^s = \exp\left(A + \frac{B}{T} + C \ln T + DT^E\right) \quad (1)$$

Table 5. Experimental (Vapor + Liquid) Equilibrium Data for Temperature T , Pressure p , Liquid-Phase Mole Fraction x , Vapor-Phase Mole Fraction y , and Liquid Activity Coefficient γ , for the System 2-Ethoxy-2-methylbutane (1) + 2-Butanol (2)^a

T/K	p/kPa	x_1	y_1	γ_1^b	γ_2^b
358.16	57.3	0.000	0.000		1.00
358.00	61.8	0.064	0.135	2.35	0.99
358.12	64.1	0.095	0.187	2.18	1.00
358.15	66.1	0.130	0.235	2.01	1.01
358.11	67.7	0.167	0.279	1.88	1.02
358.11	69.0	0.203	0.316	1.76	1.04
358.07	70.3	0.242	0.351	1.67	1.05
358.06	71.3	0.283	0.384	1.59	1.07
358.01	72.0	0.321	0.412	1.52	1.09
358.06	73.0	0.363	0.440	1.45	1.12
358.02	73.4	0.398	0.462	1.40	1.15
358.10	73.4	0.402	0.465	1.38	1.15
358.12	74.0	0.429	0.481	1.36	1.17
358.13	73.9	0.450	0.493	1.32	1.19
358.07	74.1	0.459	0.498	1.31	1.20
358.04	74.3	0.491	0.516	1.28	1.23
358.11	74.2	0.502	0.523	1.26	1.24
358.08	74.5	0.523	0.534	1.25	1.27
358.08	74.2	0.567	0.559	1.20	1.32
358.10	74.6	0.585	0.569	1.19	1.35
358.06	73.9	0.640	0.601	1.14	1.43
358.06	72.9	0.706	0.643	1.10	1.52
358.07	72.7	0.753	0.676	1.07	1.66
358.03	71.8	0.790	0.705	1.05	1.77
358.06	70.7	0.831	0.743	1.04	1.89
358.03	69.5	0.864	0.777	1.02	2.00
358.06	67.4	0.910	0.835	1.01	2.18
358.03	66.1	0.930	0.864	1.01	2.26
358.09	65.7	0.940	0.879	1.01	2.25
358.09	61.3	1.000	1.000		1.01

^a $u(T) = 0.05$ K, $u(p) = 0.17$ kPa, $u(x_1) = u(y_1) = 0.003$, $u(\gamma_1) = u(\gamma_2) = 0.06$. ^bDerived from the experimental data by using eq 2.

where P_i^s is the saturated vapor pressure expressed in Pa at the system temperature, T is the system temperature expressed in K, and A through E are the fitted parameters. The model parameters for TAEE were adjusted based on the literature data^{17–20} and the vapor pressures measured in this work.

The activity coefficients were calculated for the VLE data by using eq 2

$$\gamma_i = \frac{y_i P \phi_i}{x_i P_i^s \phi_i^s} \exp \int_P^{P_i^s} \frac{V_i^L}{RT} dP \quad (2)$$

where y_i is the mole fraction of component i in the vapor phase, P is the total pressure of the system, ϕ_i is the fugacity coefficient of component i in the vapor phase, x_i is the mole fraction of the component i in the liquid phase, ϕ_i^s is the pure component-saturated liquid fugacity coefficient, V_i^L is the molar volume of pure component i in liquid phase at the system temperature, and R is the universal gas constant ($8.31441 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The Rackett equation²¹ was used to calculate the liquid molar volume in the Poynting factor.

The experimental excess enthalpy (H^E) data were used to improve the accuracy of the activity coefficient model

Table 6. Experimental (Vapor + Liquid) Equilibrium Data for Temperature T , Pressure p , Liquid-Phase Mole Fraction x , Vapor-Phase Mole Fraction y , and Liquid Activity Coefficient γ , for the System 2-Ethoxy-2-methylbutane (1) + 2-Methyl-2-butanol (2)^a

T/K	p/kPa	x_1	y_1	γ_1^b	γ_2^b
358.12	52.8	0.000	0.000		1.00
358.10	59.3	0.121	0.207	1.74	1.00
358.03	60.7	0.161	0.258	1.63	1.01
358.02	62.2	0.202	0.305	1.56	1.02
358.06	63.9	0.253	0.357	1.48	1.04
358.11	65.1	0.296	0.395	1.42	1.05
358.11	66.1	0.341	0.432	1.37	1.07
358.12	66.8	0.379	0.461	1.33	1.09
358.06	67.3	0.417	0.489	1.29	1.11
358.02	67.6	0.455	0.515	1.26	1.13
358.10	68.1	0.490	0.538	1.22	1.16
358.10	68.5	0.526	0.562	1.20	1.19
358.09	68.6	0.560	0.584	1.17	1.22
358.10	68.8	0.592	0.604	1.15	1.25
358.11	68.8	0.622	0.624	1.13	1.28
358.10	68.8	0.649	0.641	1.11	1.32
358.10	68.5	0.704	0.679	1.08	1.40
358.10	68.4	0.733	0.699	1.07	1.44
358.13	68.1	0.769	0.727	1.05	1.51
358.12	67.6	0.804	0.755	1.04	1.59
358.04	66.8	0.837	0.784	1.03	1.65
358.03	66.1	0.868	0.815	1.02	1.73
358.09	65.4	0.898	0.848	1.01	1.81
358.06	64.0	0.933	0.891	1.01	1.90
358.09	62.8	0.964	0.936	1.00	1.97
358.01	61.0	1.000	1.000		1.00

^a $u(T) = 0.05$ K, $u(p) = 0.17$ kPa, $u(x_1) = u(y_1) = 0.003$, $u(\gamma_1) = u(\gamma_2) = 0.06$. ^bDerived from the experimental data by using eq 2.

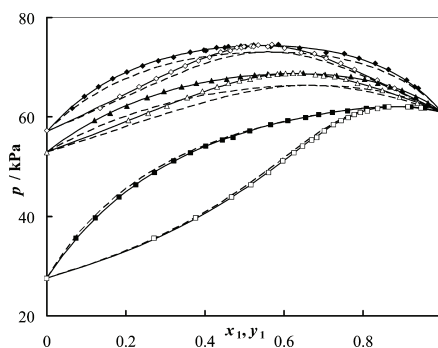


Figure 2. Experimental (vapor + liquid) equilibrium for pressure p , liquid-phase mole fraction x , and gas-phase mole fraction y , at a temperature of 358 K. 2-Ethoxy-2-methylbutane (1) + 1-butanol (2): \blacksquare , x ; \square , y ; 2-ethoxy-2-methylbutane (1) + 2-butanol (2): \blacklozenge , x ; \diamond , y ; 2-ethoxy-2-methylbutane (1) + 2-methyl-2-butanol (2): \blacktriangle , x ; \triangle , y . The solid lines represent the Wilson model, and the dashed lines represent UNIFAC (Dortmund).

outside the experimental temperature range by using the Gibbs–Duhem eq 3.²²

$$H^E = -RT^2 \sum x_i \left(\frac{\partial \ln \gamma_i}{\partial T} \right)_{P,x} \quad (3)$$

Table 7. Azeotropic Composition (x, y) at Temperature T and Pressure p for the Binary Systems of 2-Ethoxy-2-methylbutane (1) + 1-Butanol (2), 2-Butanol (2), and 2-Methyl-2-butanol (2) as Estimated by the Wilson Model^a

2-ethoxy-2-methylbutane (1)	1-butanol (2)	2-butanol (2)	2-methyl-2-butanol (2)
T/K	358.17	358.15	358.16
P/kPa	62.2	74.6	68.9
$x_1 = y_1$	0.883	0.546	0.626

^a $u(T) = 0.05$ K, $u(p) = 0.4$ kPa, $u(x_1) = u(y_1) = 0.006$.

Table 8. Experimental Excess Enthalpy (H^E) Data for Temperature $T_1 = 298.15$ K, Experimental Density ρ and Excess Volume V^E for Temperature T_2 , and Liquid-Phase Mole Fraction x_1 , for the Binary Systems of 2-Ethoxy-2-methylbutane (1) + 1-Butanol (2), 2-Butanol (2), and 2-Methyl-2-butanol (2)^a

x_1	H^E		ρ	V^E
	J·mol ⁻¹	T_2 K		
2-Ethoxy-2-methylbutane (1) + 1-Butanol (2)				
0.9020	381.9	297.70	764.8	-0.295
0.7999	556.3	297.71	769.2	-0.497
0.7009	615.7	297.71	773.3	-0.612
0.6005	613.1	297.71	777.5	-0.667
0.5023	566.9	297.70	782.0	-0.699
0.4010	485.0	297.70	786.6	-0.669
0.3022	378.8	297.71	791.1	-0.580
0.2005	251.0	297.70	796.1	-0.458
0.1010	119.2	297.70	801.0	-0.261
2-Ethoxy-2-methylbutane (1) + 2-Butanol (2)				
0.8990	556.9	297.68	763.8	-0.118
0.8001	819.2	297.67	766.9	-0.162
0.7012	944.8	297.67	770.2	-0.194
0.6008	986.0	297.68	774.0	-0.255
0.5005	957.7	297.68	777.9	-0.258
0.4013	868.4	297.69	782.0	-0.240
0.3008	719.2	297.69	786.6	-0.224
0.2007	515.8	297.69	791.6	-0.192
0.1011	271.3	297.69	796.8	-0.119
2-Ethoxy-2-methylbutane (1) + 2-Methyl-2-butanol				
0.9003	663.6	297.72	763.7	0.012
0.8011	900.2	297.71	767.1	0.003
0.7003	972.7	297.71	770.9	-0.005
0.6010	961.1	297.71	774.7	0.002
0.5013	893.7	297.71	778.9	-0.012
0.4018	781.3	297.71	783.4	-0.022
0.3013	632.3	297.71	788.2	-0.033
0.2006	448.0	297.71	793.2	-0.017
0.1005	236.2	297.70	798.8	-0.023

^a $u_1(H^E) = u(H^E)/H^E = 0.013$, $u(T_1) = 0.1$ K, $u(x_1) = 0.002$, $u(T_2) = 0.015$ K, $u(\rho) = 0.16$ kg·m⁻³, $u(V^E) = 0.03$ cm³·mol⁻¹.

The liquid activity coefficients were calculated with Wilson,²³ NRTL,²⁴ UNIQUAC,²⁵ and UNIFAC (Dortmund)²⁶ models. For the local composition models, temperature-dependent parameters were used. For a binary system, the Wilson model for the excess Gibbs energy can be expressed as eq 4

$$\frac{g^E}{RT} = -x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(\Lambda_{21}x_1 + x_2) \quad (4)$$

Table 9. Liquid Activity Model Parameters a , Liquid Activity Coefficients at Infinite Dilution γ , Average Absolute Pressure Deviation $|\Delta p_{AVG}^S|$, Average Absolute Vapor-Phase Composition Deviation ($|\Delta y_{AVG}|$) at Temperature $T_1 = 358.17$ K, and Average Absolute Excess Enthalpy Deviation ($|\Delta H_{AVG}^E|$) at Temperature $T_2 = 298.15$ K, for the Binary System of 2-Ethoxy-2-methylbutane (1) + 1-Butanol (2)^a

	Wilson	NRTL	UNIQUAC	UNIFAC
$a_{0,12}^b/K$	-48.8647	597.915	289.013	N/A
$a_{0,21}^b/K$	695.857	-70.5333	-79.9395	N/A
$a_{1,12}^b$	-0.0435984	-0.868524	0.0108235	N/A
$a_{1,21}^b$	-0.595909	0.498735	-0.134133	N/A
γ_1^∞	2.43	2.42	2.30	2.62
γ_2^∞	3.07	2.91	3.00	2.96
$ \Delta p_{AVG}^S /kPa$	0.1	0.1	0.1	0.2
$ \Delta y_{AVG} ^d$	0.003	0.003	0.004	0.003
$ \Delta H_{AVG}^E /J\cdot mol^{-1}$	8	7	7	73

^a $u(T_1) = 0.05$ K, $u(T_2) = 0.015$ K. ^bTemperature dependence of energy interaction parameters: $\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (Wilson), $\Delta g_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (NRTL), $\Delta U_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (UNIQUAC). ^cAverage absolute deviation of pressure, $|\Delta p_{AVG}^S| = ((\sum_{i=1}^N |p_{i,calc} - p_{i,exp}|)/N)$. ^dAverage absolute deviation of vapor phase concentration, $|\Delta y_{AVG}| = ((\sum_{i=1}^N |y_{i,calc} - y_{i,exp}|)/N)$. ^eAverage absolute deviation of excess enthalpy, $|\Delta H_{AVG}^E| = ((\sum_{i=1}^N |H_{i,calc}^E - H_{i,exp}^E|)/N)$.

Table 10. Liquid Activity Model Parameters a , Liquid Activity Coefficients at Infinite Dilution γ , Average Absolute Pressure Deviation $|\Delta p_{AVG}^S|$, Average Absolute Vapor-Phase Composition Deviation ($|\Delta y_{AVG}|$) at Temperature $T_1 = 358.15$ K, and Average Absolute Excess Enthalpy Deviation ($|\Delta H_{AVG}^E|$) at Temperature $T_2 = 298.15$ K, for the Binary System of 2-Ethoxy-2-methylbutane (1) + 2-Butanol (2)^a

	Wilson	NRTL	UNIQUAC	UNIFAC
$a_{0,12}^b/K$	68.6944	615.194	296.83	N/A
$a_{0,21}^b/K$	803.376	112.367	-59.0624	N/A
$a_{1,12}^b$	-0.257839	-1.03014	-0.171845	N/A
$a_{1,21}^b$	-1.13048	-0.00386699	-0.114754	N/A
γ_1^∞	2.43	2.30	2.38	2.19
γ_2^∞	2.63	2.62	2.58	2.52
$ \Delta p_{AVG}^S /kPa$	0.2	0.1	0.2	1.2
$ \Delta y_{AVG} ^d$	0.002	0.003	0.003	0.006
$ \Delta H_{AVG}^E /J\cdot mol^{-1}$	14	17	23	230

^a $u(T_1) = 0.05$ K, $u(T_2) = 0.015$ K. ^bTemperature dependence of energy interaction parameters: $\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (Wilson), $\Delta g_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (NRTL), $\Delta U_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (UNIQUAC). ^cAverage absolute deviation of pressure, $|\Delta p_{AVG}^S| = ((\sum_{i=1}^N |p_{i,calc} - p_{i,exp}|)/N)$. ^dAverage absolute deviation of vapor phase concentration, $|\Delta y_{AVG}| = ((\sum_{i=1}^N |y_{i,calc} - y_{i,exp}|)/N)$. ^eAverage absolute deviation of excess enthalpy, $|\Delta H_{AVG}^E| = ((\sum_{i=1}^N |H_{i,calc}^E - H_{i,exp}^E|)/N)$.

where g^E is the Gibbs excess energy, Λ_{ij} are the interaction parameters, expressed as eqs 5 and 6

$$\Lambda_{12} = \frac{V_2^L}{V_1^L} \exp\left(\frac{-\Delta\lambda_{12}}{RT}\right) \quad (5)$$

$$\Lambda_{21} = \frac{V_1^L}{V_2^L} \exp\left(\frac{-\Delta\lambda_{21}}{RT}\right) \quad (6)$$

where $\Delta\lambda_{ij}$ are the binary parameters.

The temperature dependency of the binary parameters for the Wilson model is expressed as eq 7. The temperature

Table 11. Liquid Activity Model Parameters a , Liquid Activity Coefficients at Infinite Dilution γ , Average Absolute Pressure Deviation $|\Delta p_{AVG}^s|$, Average Absolute Vapor-Phase Composition Deviation ($|\Delta y_{AVG}^l|$) at Temperature $T_1 = 358.16$ K, and Average Absolute Excess Enthalpy Deviation ($|\Delta H_{AVG}^E|$) at Temperature $T_2 = 298.15$ K, for the Binary System of 2-Ethoxy-2-methylbutane (1) + 2-Methyl-2-butanol (2)^a

	Wilson	NRTL	UNIQUAC	UNIFAC
$a_{0,12}^b/K$	-24.6158	899.983	398.135	N/A
$a_{0,21}^b/K$	1096.87	7.54605	-116.996	N/A
$a_{1,12}^b$	-0.118992	-1.72332	-0.498429	N/A
$a_{1,21}^b$	-2.05965	-0.00060647	-0.00473707	N/A
γ_1^∞	1.88	1.82	1.87	1.59
γ_2^∞	2.24	2.25	2.18	1.93
$ \Delta p_{AVG}^s /kPa$	0.1	0.2	0.1	2.1
$ \Delta y_{AVG}^l $	0.001	0.003	0.002	0.011
$ \Delta H_{AVG}^E /J\cdot mol^{-1}$	37	40	40	233

^a $u(T_1) = 0.05$ K, $u(T_2) = 0.015$ K. ^bTemperature dependence of energy interaction parameters: $\Delta\lambda_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (Wilson), $\Delta g_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (NRTL), $\Delta U_{ij} = a_{0,ij} + a_{1,ij}(T/K)$ (UNIQUAC). ^cAverage absolute deviation of pressure, $|\Delta p_{AVG}^s| = ((\sum_{i=1}^N |p_{i,calc} - p_{i,exp}|)/N)$. ^dAverage absolute deviation of vapor phase concentration, $|\Delta y_{AVG}^l| = ((\sum_{i=1}^N |y_{i,calc} - y_{i,exp}|)/N)$. ^eAverage absolute deviation of excess enthalpy, $|\Delta H_{AVG}^E| = ((\sum_{i=1}^N |H_{i,calc}^E - H_{i,exp}^E|)/N)$.

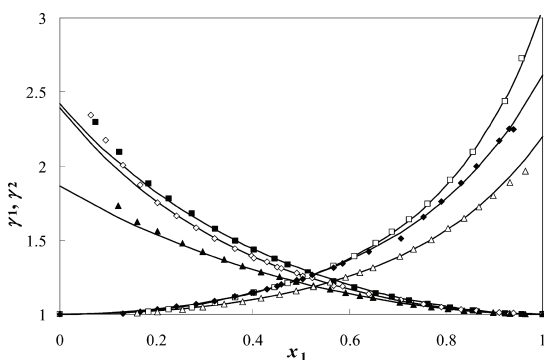


Figure 3. Liquid-phase activity coefficients γ , for liquid-phase mole fraction x , at temperature of 358 K. \square , 2-Ethoxy-2-methylbutane (1) + 1-butanol (2); \blacklozenge , 2-ethoxy-2-methylbutane (1) + \diamond , 2-butanol (2); \triangle , 2-ethoxy-2-methylbutane (1) + \blacktriangle , 2-methyl-2-butanol (2). The lines represent the Wilson model.

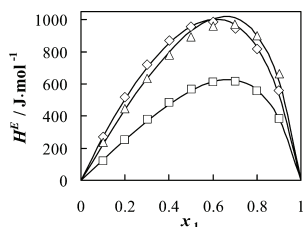


Figure 4. Excess molar enthalpy, H^E , for liquid-phase mole fraction x , at temperature of 298.15 K. \square , 2-Ethoxy-2-methylbutane (1) + 1-butanol (2); \diamond , 2-ethoxy-2-methylbutane (1) + 2-butanol (2); \triangle , 2-ethoxy-2-methylbutane (1) + 2-methyl-2-butanol (2). The lines represent the Wilson model.

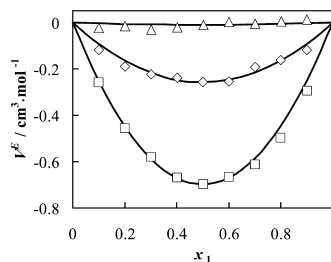


Figure 5. Excess molar volume V^E , for liquid-phase mole fraction x , at temperature of 298.15 K. \square , 2-Ethoxy-2-methylbutane (1) + 1-butanol (2); \diamond , 2-ethoxy-2-methylbutane (1) + 2-butanol (2); \triangle , 2-ethoxy-2-methylbutane (1) + 2-methyl-2-butanol (2). The lines represent the Redlich–Kister model.

Table 12. Redlich–Kister Equation Parameters C_i for Excess Volume V^E at Temperature $T = 298.15$ K^a

2-ethoxy-2-methylbutane (1)	1-butanol (2)	2-butanol (2)	2-methyl-2-butanol (2)
C_0	-2.7950	-1.0339	-0.0476
$ \Delta V_{AVG}^E /cm^3\cdot mol^{-1}$	0.02	0.01	0.01

^a $u(T) = 0.15$ K. ^bAverage absolute deviation of excess volume, $|\Delta V_{AVG}^E| = ((\sum_{i=1}^N |V_{i,calc}^E - V_{i,exp}^E|)/N)$.

dependency for the NRTL and UNIFAC model parameters was calculated in a similar manner.

$$\Delta\lambda_{ij} = \lambda_{ij} - \lambda_{ii} = a_{0,ij} + a_{1,ij}(T/K) \quad (7)$$

The liquid activity coefficients for the Wilson model are calculated from eqs 8 and 9

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \quad (8)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2} \right) \quad (9)$$

The vapor phase fugacity was calculated with the Hayden–O'Connell equation.^{27,28} The physical property values and correlation parameters used are presented in Table 2. All measurements were processed with VLEFIT software.²⁹ The objective function (OF) used is presented in eq 10, where N_i is the number of points used in the fit.

$$OF = \sum_{k=1}^{N_{VLE}} \sum_{i=1}^2 \left| \frac{\gamma_{i,calc}^k - \gamma_{i,exp}^k}{\gamma_{i,exp}^k} \right| + \sum_{i=1}^{N_{HE}} \left| \frac{H_{i,calc}^E - H_{i,exp}^E}{H_{i,exp}^E} \right| \quad (10)$$

The excess volume was modeled with the Redlich–Kister equation³⁰ 11.

$$V^E = x_1x_2 \sum_{n=0}^m C_n(x_1 - x_2)^n \quad (11)$$

RESULTS AND DISCUSSION

As the literature correlation⁸ for the vapor pressure of 2-ethoxy-2-methylbutane was based on a relatively small amount of data, the correlation parameters were refitted using both the experimental

vapor pressures presented in Table 3 and the literature values.^{17–20} The agreement between the data and the correlation was excellent, as shown in Figure 1. For the alcohols, parameters taken from literature⁸ were used. The experimental values for alcohols agreed well with the calculated values; the average absolute pressure deviation was less than 0.8 kPa, as presented in Table 2.

The experimental isothermal VLE data ($xyTp$) and the calculated activity coefficients are presented in Tables 4, 5, and 6. The measured data passed the integral test,³¹ the infinite dilution test,³² and the point test;³¹ thus the data were considered to be of good quality. As presented in Figure 2, all measured systems had a maximum pressure azeotrope. The azeotropic conditions are presented in Table 7. All three systems showed a positive deviation from the Raoult's law.

Measured molar excess enthalpies, densities, and excess volumes are presented in Table 8. The molar excess enthalpies determined in this work were positive over the whole composition range. The binary systems of 2-ethoxy-2-methylbutane + 2-butanol and + 2-methyl-2-butanol had the highest excess enthalpies, up to 986 J·mol⁻¹. The 1-butanol system showed excess enthalpies no higher than 616 J·mol⁻¹.

The average absolute pressure deviation was no higher than 0.3 kPa for the local composition models and no higher than 1.8 kPa for the UNIFAC model, as presented in Tables 9, 10, and 11. Similarly, the average absolute deviation of vapor phase composition for the local composition models was no higher than 0.003 and the average absolute deviation of excess enthalpy no higher than 44 J·mol⁻¹.

The correlation between the experimental values and the models was in general good, although they failed to fully describe the deviation from ideality for the measured systems at two temperatures, as presented for the Wilson model in Figures 3 and 4.

Excess volumes were negative for the binary systems of 2-ethoxy-2-methylbutane + 2-butanol and + 1-butanol throughout the composition range. The excess volume data were modeled by using the Redlich–Kister equation; one parameter was sufficient to obtain an average absolute deviation no higher than 0.02 cm³·mol⁻¹, as shown in Figure 5. The equation parameters are presented in Table 12.

AUTHOR INFORMATION

Corresponding Author

*E-mail: aarne.sundberg@iki.fi.

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REFERENCES

- (1) Oxygenates fact book, published by Clean fuels development coalition. <http://www.cleanfuelsdc.org/pubs/documents/oxyfactbook.pdf> (accessed June 2, 2012).
- (2) European Fuel Oxygenates Association. <http://www.efoa.eu/> (accessed May 26, 2012).
- (3) Di Girolamo, M.; Brianti, M.; Conte, M.; Marchionna, M. Octane Enhancers. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley: New York, 2009.
- (4) Marsh, K. N.; Niamskul, P.; Gmehling, J.; Bölts, R. Review of thermophysical property measurements on mixtures containing MTBE, TAME, and other ethers with non-polar solvents. *Fluid Phase Equilib.* **1999**, *156*, 207–227.

(5) Arce, A.; Arce, A., Jr.; Rodil, E.; Soto, A. Isobaric vapor–liquid equilibria for systems composed by 2-ethoxy-2-methylbutane, methanol or ethanol and water at 101.32 kPa. *Fluid Phase Equilib.* **2005**, *233*, 9–18.

(6) Everson, R. C.; Jansen, W. Isobaric Vapor-Liquid Equilibria of Binary and Ternary Mixtures of Heavy Ethers, Isoamylenes, and Alcohols. 2. Tertiary Amyl Ethyl Ether, 2-Methyl-1-butene, and Ethanol. *J. Chem. Eng. Data* **2001**, *46*, 247–250.

(7) Sundberg, A.; Uusi-Kyyny, P.; Jakobson, K.; Alopaeus, V. A small scale pilot plant demonstration – case study of the synthesis of 2-Ethoxy-2-methylbutane. *AIChE Spring meeting*, Houston, Texas, April 1–5, 2012; p 7.

(8) Design Institute for Physical Properties. *DIPPR Project 801 - Full Version*; Design Institute for Physical Property Research/AIChE: New York, 2005, 2008, 2009, 2010; accessed at Knovel.com.

(9) Evans, T. W.; Edlund, K. R. Tertiary Alkyl Ethers Preparation and Properties. *Ind. Eng. Chem.* **1936**, *28* (10), 1186–1188.

(10) Yaws, C., L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds*; Knovel: New York, 2003; accessed at Knovel.com.

(11) Yerazunis, S.; Plowright, J. D.; Smola, F. M. Vapor-Liquid Equilibrium Determination by a New Apparatus. *AIChE J.* **1964**, *10*, 660–665.

(12) Uusi-Kyyny, P.; Pokki, J.-P.; Aittamaa, J.; Liukkonen, S. Vapor–Liquid Equilibrium for the Binary Systems of 3-Methylpentane + 2-Methyl-2-propanol at 331 K and + 2-Butanol at 331 K. *J. Chem. Eng. Data* **2001**, *46*, 754–758.

(13) Sapei, E.; Zaytseva, A.; Uusi-Kyyny, P.; Keskinen, K. I.; Aittamaa, J. Vapor–liquid equilibrium for binary system of thiophene + 2,2,4-trimethylpentane at 343.15 and 353.15 K and thiophene + 2-ethoxy-2-methylpropane at 333.15 and 343.15 K. *Fluid Phase Equilib.* **2007**, *261*, 115–121.

(14) Wadsö, I.; Goldberg, R. N. Standards in isothermal microcalorimetry (IUPAC Technical Report). *Pure Appl. Chem.* **2001**, *73* (10), 1625–1639.

(15) Polednicek, M. *Development of instruments for obtaining thermodynamic data in systems of environmental and energetic interest*. Doctoral dissertation, Blaise Pascal University, Clermont-Ferrand, France, 2000.

(16) *Technical note 12 - C80 Flow mixing cell*; SETARAM: Caluire, France, March 3, 2010.

(17) Reboul, E.; Truchot, P. Ueber einen mit dem Aethylamyläther isomeren Aether: das Amylenäthylat, und Beobachtungen bezüglich der Bildung der gemischten Aether. *Justus Liebigs Ann. Chem.* **1867**, *144* (2), 241–245.

(18) Steele, W. V.; Nguyen, A.; Knipmeyer, S. E.; Chirico, R. D. Final Report. DIPPR Project 821. Vapor Pressure of Organic Chemicals of Industrial Interest. *The 1991 Project Results National Institute for Petroleum and Energy Research*, Bartlesville, OK, 1992.

(19) Krähenbühl, M. A.; Gmehling, J. Vapor Pressures of Methyl tert-Butyl Ether, Ethyl tert-Butyl Ether, Isopropyl tert-Butyl Ether, tert-Amyl Methyl Ether, and tert-Amyl Ethyl Ether. *J. Chem. Eng. Data* **1994**, *39* (4), 759–762.

(20) Verevkin, S. P.; Krashnykh, E. L.; Vasilitsova, T. V.; Heintz, A. Determination of Ambient Temperature Vapor Pressures and Vaporization Enthalpies of Branched Ethers. *J. Chem. Eng. Data* **2003**, *48*, 591–599.

(21) Rackett, H. G. Equation of state for saturated liquids. *J. Chem. Eng. Data* **1970**, *15*, 514–517.

(22) Walas, S. M. *Phase equilibria in Chemical Engineering*; Butterworth-Heinemann: Oxford, U.K., 1985.

(23) Wilson, G. M. Vapor–Liquid Equilibrium. XI. A new expression for the excess free energy of mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.

(24) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1978**, *14*, 135–144.

(25) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(26) Weidlich, U.; Gmehling, J. A modified UNIFAC model. 1. Prediction of VLE, h^E , and γ^∞ . *Ind. Eng. Chem. Res.* **1987**, *26*, 1372–1381.

(27) Hayden, J. G.; O'Connell, J. P. Generalized method for predicting second virial coefficients. *Ind. Eng. Chem. Process. Des. Dev.* **1975**, *14*, 209–216.

(28) Prausnitz, J. M.; Anderson, T. F.; Grens, E. A.; Eckert, C. A.; Hsieh, R.; O'Connell, J. P. *Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria*; Prentice-Hall Inc.: Englewood Cliffs, NJ, 1980.

(29) Aittamaa, J.; Pokki, J.-P. *User Manual of Program VLEFIT*; Helsinki University of Technology: Espoo, Finland, 2003.

(30) Redlich, O.; Kister, A. T. Algebraic representation of thermodynamic properties and the classification of solutions. *Ind. Eng. Chem.* **1948**, *40* (2), 345–358.

(31) Gmehling, J.; Onken, U. *Vapour-Liquid Data Collection; DECHEMA Chemistry Data Series, Part 1*; DECHEMA: Frankfurt/Main, 1977, Vol. 1.

(32) Kojima, K.; Moon, H.; Ochi, K. Thermodynamic consistency test of vapor-liquid equilibrium data: Methanol + water, benzene + cyclohexane and ethyl methyl ketone + water. *Fluid Phase Equilib.* **1990**, *56*, 269–284.