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Isobaric Vapor Liquid Equilibrium for 2,3-Dimethyl-2-butene + Methanol, + Ethanol, + 2-Propanol, or + 2-Butanol at Atmospheric Pressure

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Isobaric vapor liquid equilibrium (VLE) was measured for the systems 2,3-dimethyl-2-butene + methanol, + ethanol, + 2-propanol, and + 2-butanol at atmospheric pressure. The measurements were made with a recirculation still. Gas chromatography was used for analyzing the samples from the equilibrium measurements. The VLE measurements were correlated with the Wilson, NRTL, and UNIQUAC activity coefficient models and the Soave−Redlich−Kwong equation of state.

Introduction

Vapor liquid equilibrium data for the systems 2,3-dimethyl-2-butene + methanol, + ethanol, + 2-propanol, and + 2-butanol were measured at atmospheric pressure using a recirculation still. No VLE data have been reported previously for the systems measured.

Experimental Section

Materials. Methanol (99.8 mass %) was provided by Merck, ethanol (99.5 mass %) by Primalco Oy, 2-propanol (99.8 mass %) by Riedel-de Haen, and 2-butanol (>99.5 mass %) by Fluka. 2,3-Dimethyl-2-butene (99.4% GC) was provided by Aldrich. The purities of the components are according to the manufacturers' specifications. The materials were used without further purification except for drying over molecular sieves (Merck 3A).

Apparatus. A recirculation still of the Yerazunis type[1,2] was used. The liquid volume needed for running the apparatus was approximately 80 mL. The temperature was measured with a Thermolyzer S2541 (Frontek) temperature meter (resolution 0.005 K) equipped with a Pt-100 probe. The thermometers were calibrated at an accredited calibration laboratory (Inspecta Oy, Finland), with a calibration uncertainty of 0.015 K. The uncertainty in the temperature measurement of the system is estimated to be ±0.07 K, due to the uncertainty of the calibration, the location of the probes, and the small pressure fluctuations. The Pt-100 probe was located at the bottom of the packed section of the equilibrium chamber.

The pressure was measured with a Druck pressure transducer (0 to 100 kPa) equipped with a Red Lion panel meter. The uncertainty of the pressure measurement was ±0.07 kPa, according to the data provided by the manufacturer of the pressure measurement devices. The pressure measurement system was calibrated with a DHPPC-2 pressure calibrator. Including the calibration uncertainty, the uncertainty in the pressure measurement system is ±0.15 kPa.

Table 1. Vapor Pressure of 2,3-Dimethyl-2-butene

T/K	p/kPa	T/K	p/kPa
346.28	101.43	333.00	65.23
344.13	94.64	330.28	59.32
342.81	90.74	327.70	54.12
340.98	85.40	324.24	47.72
339.12	80.30	318.44	38.40
337.15	75.19	312.39	30.29
335.11	70.15		

Table 2. VLE Data, Measured Liquid Phase Mole Fractions x_1, Measured Vapor Phase Mole Fractions y_1, Pressure P, Temperature T, and Activity Coefficients γ_i, for the 2,3-Dimethyl-2-butene (1) + Methanol (2) System at Atmospheric Pressure

x_1	y_1	T/K	P^a/kPa	γ_1	γ_2
1.0000	1.0000	346.25	101.1	1.00	
0.9866	0.7717	338.02	101.2	1.01	16.83
0.9657	0.6181	331.68	101.2	1.02	14.10
0.9331	0.5491	328.61	101.2	1.04	9.67
0.8258	0.4976	326.34	101.2	1.16	4.55
0.7203	0.4825	325.81	101.2	1.31	2.98
0.6233	0.4758	325.62	101.2	1.50	2.26
0.5402	0.4718	325.51	101.2	1.73	1.87
0.4261	0.4663	325.44	101.2	2.17	1.52
0.3804	0.4642	325.44	101.2	2.42	1.42
0.3426	0.4607	325.45	101.2	2.66	1.34
0.2891	0.4559	325.51	101.2	3.12	1.25
0.2324	0.4468	325.67	101.2	3.78	1.17
0.1842	0.4344	325.97	101.2	4.59	1.11
0.1290	0.4081	326.72	101.2	5.99	1.05
0.0197	0.1652	333.77	101.9	12.59	1.00
0.0164	0.1440	334.25	101.9	12.98	1.00
0.0110	0.1007	335.19	101.8	13.11	1.01
0.0028	0.0278	336.97	101.8	13.43	1.01
0.0000	0.0000	337.64	101.8		1.00

[a] Atmospheric pressure changed during the experiment.

Gas Chromatographic Analysis. The condensed vapor phase and the liquid phase of the 2,3-dimethyl-2-butene + methanol, 2,3-dimethyl-2-butene + ethanol, and 2,3-dimethyl-2-butene + 2-propanol were analyzed with a HP 6850A gas chromatograph with an autosampler and a flame ionization detector. The GC column used was an HP-1 (cross-linked methyl siloxane, length 30 m, column inner diameter 0.25 mm, film thickness 1.0 μm). The GC program was isothermal, with an oven temperature of 373 K. For the 2,3-dimethyl-2-butene + 2-butanol system the isothermal GC program was modified to separate the components by using a temperature program (initial temperature 323 K, temperature ramp 10 K·min^{-1} to 373 K; temperature was maintained at 373 K for 4 min, giving a total run time of 9 min). The calibration and sampling procedures were similar to those of earlier measure-

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Table 3. VLE Data, Measured Liquid Phase Mole Fractions x_1, Measured Vapor Phase Mole Fractions y_1, Pressure P, Temperature T, and Activity Coefficients γ_i, for the 2,3-Dimethyl-2-butene (1) + Ethanol (2) System at Atmospheric Pressure

x_1	y_1	T/K	P^a/kPa	γ_1	γ_2
1.0000	1.0000	346.01	100.7	1.00	
0.9685	0.8200	340.32	100.7	1.01	8.88
0.9350	0.7411	337.68	100.7	1.03	6.92
0.8623	0.6730	335.84	100.7	1.08	4.47
0.7823	0.6433	335.18	100.7	1.16	3.17
0.7071	0.6278	334.94	100.7	1.26	2.49
0.6213	0.6149	334.84	100.6	1.41	2.00
0.5355	0.6030	334.86	100.6	1.61	1.68
0.4461	0.5889	335.03	100.6	1.87	1.45
0.3581	0.5702	335.41	100.6	2.23	1.28
0.2737	0.5429	336.12	100.6	2.71	1.17
0.2114	0.5113	337.06	100.6	3.21	1.11
0.1585	0.4695	338.65	100.6	3.74	1.05
0.0995	0.3907	340.92	100.6	4.61	1.02
0.0706	0.3283	342.81	100.7	5.15	1.01
0.0342	0.2053	346.29	100.6	5.98	1.00
0.0236	0.1545	347.61	100.7	6.27	1.00
0.0162	0.1132	348.56	100.6	6.50	1.00
0.0103	0.0761	349.39	100.6	6.69	1.00
0.0000	0.0000	351.30	101.5		1.00

[a] Atmospheric pressure changed during the experiment.

Table 4. VLE Data, Measured Liquid Phase Mole Fractions x_1, Measured Vapor Phase Mole Fractions y_1, Pressure P, Temperature T, and Activity Coefficients γ_i, for the 2,3-Dimethyl-2-butene (1) + 2-Propanol (2) System at Atmospheric Pressure

x_1	y_1	T/K	P^a/kPa	γ_1	γ_2
1.0000	1.0000	345.78	99.9	1.00	
0.9787	0.9148	343.56	100.0	1.00	6.40
0.9387	0.8243	340.97	100.0	1.02	5.13
0.8845	0.7745	339.71	100.0	1.06	3.69
0.8112	0.7354	338.99	100.0	1.12	2.74
0.7320	0.7066	338.70	100.0	1.21	2.17
0.6444	0.6804	338.68	100.0	1.32	1.78
0.5589	0.6577	338.77	99.8	1.47	1.53
0.4794	0.6331	339.10	99.8	1.63	1.37
0.3903	0.6027	339.74	99.8	1.87	1.23
0.3055	0.5623	340.76	99.8	2.15	1.14
0.2191	0.5025	342.42	99.8	2.55	1.07
0.1531	0.4338	344.48	99.8	2.96	1.03
0.1066	0.3591	346.57	99.8	3.30	1.01
0.0682	0.2713	348.85	99.8	3.64	1.00
0.0451	0.1992	350.59	99.8	3.84	1.00
0.0294	0.1438	351.86	99.8	4.10	1.00
0.0192	0.1017	352.82	99.8	4.31	1.00
0.0129	0.0675	353.48	99.8	4.19	1.01
0.0087	0.0476	353.93	99.8	4.31	1.01
0.0000	0.0000	355.22	101.5		1.00

[a] Atmospheric pressure changed during the experiment.

ments.[2,3] The gravimetric calibration mixtures were prepared in 2 mL vials with approximately 1 mL of toluene as a solvent for the GC calibration for all systems measured. The accuracy of the analysis of the compositions of the phases is estimated to be 0.003 in mole fraction.

Procedure of the VLE Measurement. Pure component 1 was introduced to the recirculation still, and its vapor pressure was measured. Component 2 was added to the equilibrium still. Atmospheric pressure was used for all runs. It took from (15 to 30) min to achieve constant temperature. The run continued for approximately another 35 min to further enhance the steady-state condition before sampling.

Table 5. VLE Data, Measured Liquid Phase Mole Fractions x_1, Measured Vapor Phase Mole Fractions y_1, Pressure P, Temperature T, and Activity Coefficients γ_i, for the 2,3-Dimethyl-2-butene (1) + 2-Butanol (2) System at Atmospheric Pressure

x_1	y_1	T/K	P^a/kPa	γ_1	γ_2
1.0000	1.0000	346.49	102.1	1.00	
0.9860	0.9757	346.09	102.1	1.00	5.06
0.9706	0.9536	345.76	102.1	1.01	4.65
0.9189	0.9065	345.24	102.1	1.03	3.48
0.8764	0.8859	345.11	101.8	1.05	2.80
0.8375	0.8695	345.24	101.8	1.08	2.42
0.7885	0.8548	345.54	101.7	1.11	2.04
0.7448	0.8402	345.92	101.7	1.15	1.83
0.6887	0.8009	346.54	101.7	1.16	1.81
0.5390	0.7769	347.44	101.7	1.40	1.32
0.4652	0.7521	348.49	101.7	1.52	1.21
0.3917	0.7184	349.90	101.7	1.66	1.13
0.3263	0.6784	351.51	101.7	1.79	1.09
0.2908	0.6561	352.41	101.3	1.89	1.06
0.2407	0.6125	354.24	101.3	2.02	1.03
0.2123	0.5858	355.52	101.3	2.12	1.01
0.1590	0.5114	358.28	101.3	2.28	1.00
0.1348	0.4740	359.74	101.3	2.40	0.98
0.1146	0.4277	361.23	101.3	2.45	0.99
0.0900	0.3750	362.95	101.4	2.61	0.98
0.0680	0.3014	365.06	101.3	2.63	0.98
0.0544	0.2598	366.25	101.2	2.74	0.98
0.0375	0.1991	367.95	101.2	2.92	0.98
0.0224	0.1223	369.56	101.2	2.89	0.99
0.0150	0.0868	370.44	101.2	2.98	0.99
0.0103	0.0611	371.05	101.2	3.02	0.99
0.0000	0.0000	372.61	102.1		1.00

[a] Atmospheric pressure changed during the experiment.

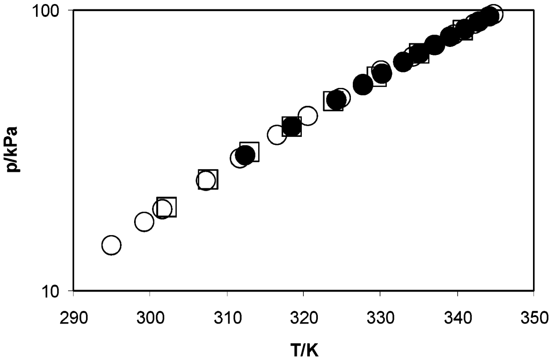

Figure 1. Vapor pressure of 2,3-dimethyl-2-butene: ●, this work; ○, Baghdoyan et al.;[16] □, Scott et al.[17]

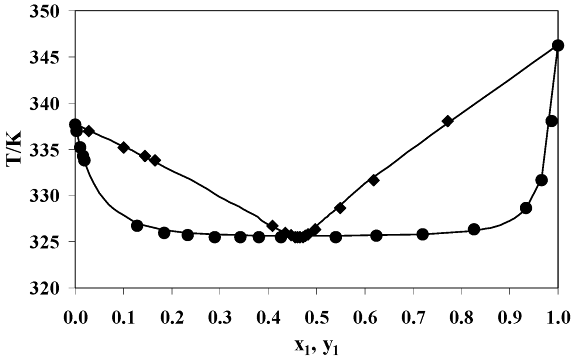

Figure 2. Temperature−composition diagram for the 2,3-dimethyl-2-butene (1) + methanol (2) system at atmospheric pressure: ●, x_1 measured; ◆, y_1 measured; —, x_1 calculated; —, y_1 calculated.

Results and Discussion

The measured pure component vapor pressure for 2,3-dimethyl-2-butene and the VLE data measured with the calculated activity coefficients are reported in Tables 1−5 and Figures 1−7. The activity coefficients for the species i, γ_i, were calculated from eq 2

$$y_i P \phi_i = \gamma_i x_i P_{\mathrm{vp}i} \phi_i^{\mathrm{s}} \exp \int_{P_{\mathrm{vp}i}}^{P} \frac{v_i^{\mathrm{L}}\, \mathrm{d}P}{RT} \tag{1}$$

where y_i is the mole fraction of component i in the vapor

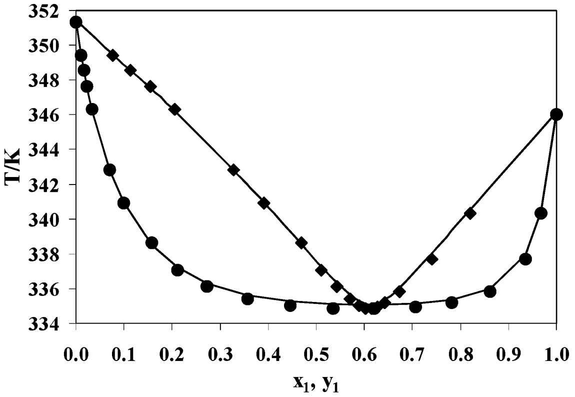

Figure 3. Temperature−composition diagram for the 2,3-dimethyl-2-butene (1) + ethanol (2) system at atmospheric pressure: ●, x_1 measured; ◆, y_1 measured; —, x_1 calculated; —, y_1 calculated.

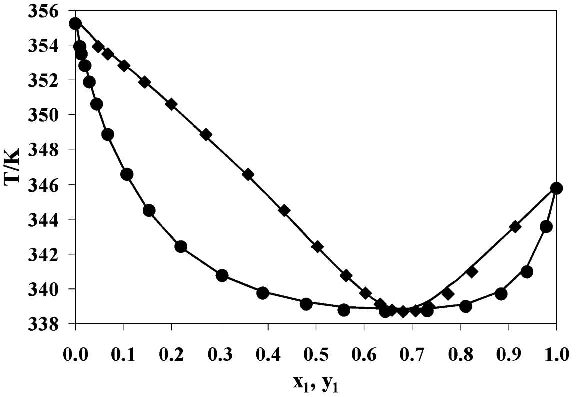

Figure 4. Temperature−composition diagram for the 2,3-dimethyl-2-butene (1) + 2-propanol (2) system at atmospheric pressure: ●, x_1 measured; ◆, y_1 measured; —, x_1 calculated; —, y_1 calculated.

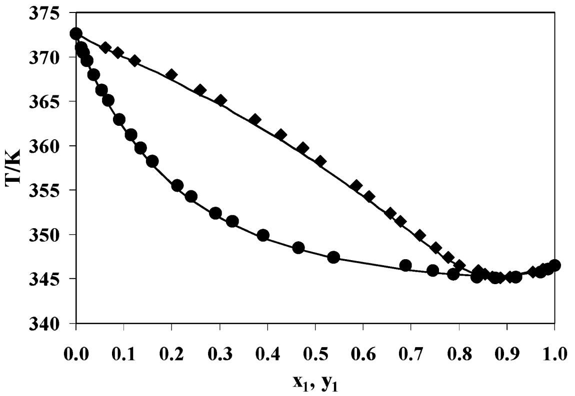

Figure 5. Temperature−composition diagram for the 2,3-dimethyl-2-butene (1) + 2-butanol (2) system at atmospheric pressure: ●, x_1 measured; ◆, y_1 measured; —, x_1 calculated; —, y_1 calculated.

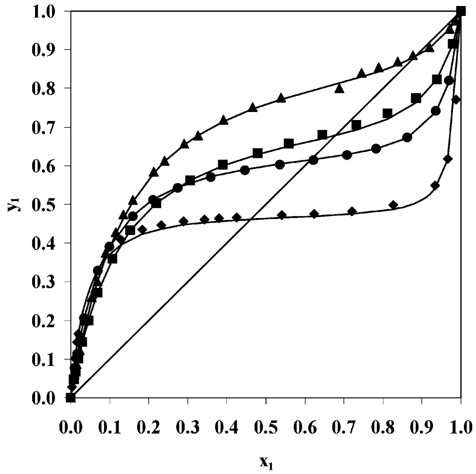

Figure 6. *xy*-diagram for the 2,3-dimethyl-2-butene (1) + methanol (2), + ethanol (2), + 2-propanol (2), and + 2-butanol (2) systems at atmospheric pressure: ◆, measured for the methanol system; ●, measured for the ethanol system; ■, measured for the 2-propanol system; ▲, measured for the 2-butanol system; —, calculated with the Wilson model.

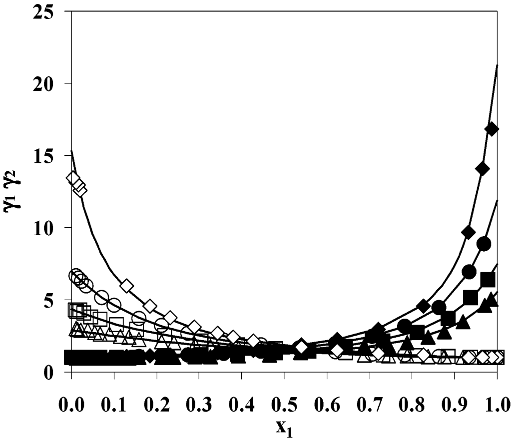

Figure 7. Activity coefficient−composition diagram for the 2,3-dimethyl-2-butene (1) + methanol (2) system: ◆, γ calculated from measurements for methanol; ◇, γ calculated from measurements for 2,3-dimethyl-2-butene. 2,3-Dimethyl-2-butene (1) + ethanol (2) system: ●, γ calculated from measurements for ethanol; ○, γ calculated from measurements for 2,3-dimethyl-2-butene. 2,3-Dimethyl-2-butene (1) + 2-propanol (2) system: ■, γ calculated from measurements for 2-propanol; □, γ calculated from measurements for 2,3-dimethyl-2-butene. 2,3-Dimethyl-2-butene (1) + 2-butanol (2) system: ▲, γ_1 calculated from measurements for 2-butanol; △, γ calculated from measurements for 2,3-dimethyl-2-butene. —, γ_1 and γ_2 predicted by the Wilson model.

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 component i in the liquid phase, P_{vpi} is the vapor pressure of pure component i at the system temperature, ϕ_i^s is the pure component saturated vapor fugacity coefficient at the system temperature, v_i^L is the liquid phase molar volume of component i at the system temperature, T is temperature in Kelvin, and R is the universal gas constant. The Soave−Redlich−Kwong equation of state with a quadratic mixing rule for the attractive parameter and a linear mixing rule for the covolume parameter for the evaluation of vapor phase fugacity coefficients was used.[4] The binary interaction parameter in the quadratic mixing rule was set to the value zero. The liquid phase was modeled with the Wilson equation.[5] NRTL[6] and UNIQUAC[7] equation parameters were also acquired. The critical temperatures, critical pressures, acentric factors, liquid molar volumes, and UNIQUAC volume and area parameters used in the calculations are presented in Table 6. For the NRTL equation, the α parameter was fixed to the value 0.4. The vapor pressure of the pure substances was calculated from the Antoine equation, eq 2. The vapor pressure equation parameters

$$p/\mathrm{MPa} = \exp\left(A - \frac{B}{(T/\mathrm{K} + C)}\right) \qquad (2)$$

in Table 6 were fitted from data measured with the same

Table 6. Critical Temperature T_c, Critical Pressure P_c, Acentric Factor ω, Liquid Molar Volume (Used for Fitting the Wilson Equation Parameters) v_i, UNIQUAC Volume Parameter R_{UNIQ}, UNIQUAC Area Parameter Q_{UNIQ}, Pure Component Vapor Pressure Equation Parameters *A*, *B*, and *C* for the Antoine Equation (Vapor Pressure Data Measured with the Apparatus Used in the VLE Measurements Was Fitted), and Recommended Temperature Range of the Vapor Pressure Correlation T_{min}, T_{max}

	methanol	ethanol	2-propanol	2-butanol	2,3-dimethyl-2-butene
$T_c{}^a$/K	512.6 ± 5	516.25 ± 5	508.31 ± 5	536.01 ± 5.36	524.0 ± 26.2
$P_c{}^a$/MPa	8.096 ± 0.24	6.384 ± 0.19	4.764 ± 0.14	4.1938 ± 0.13	3.16 ± 0.32
ω^a	0.5656	0.6371	0.669	0.5711	0.2333
$v_i{}^a$/cm^3·mol^{-1}	40.7 ± 0.4	58.515 ± 0.6	76.784 ± 0.8	92.118 ± 0.92	119.643 ± 3.6
$R_{UNIQ}{}^b$	1.4311	2.2668	3.2491	3.9235	4.2649
$Q_{UNIQ}{}^b$	1.4320	2.3283	3.1240	3.6640	3.8770
A	9.5334^c	9.9417^d	9.8016^e	8.364	6.574^f
B	3550.3^c	3799.7^d	3635.8^e	3026.1	2500.8^f
C	−37.353^c	−40.781^d	−54.710^e	−88.316	−64.19^f
T_{min}/K	296	316	321	325	312
T_{max}/K	377	383	383	373	373

[a] Reference 12. [b] Reference 13. [c] The vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in ref 14 at vapor pressures from 110 kPa to 398 kPa (from 340 K to 377 K). [d] The vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in ref 15 at vapor pressures from 136 kPa to 240 kPa (from 359 K to 375 K). [e] The vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in ref 14 at vapor pressures from 131 kPa to 218 kPa (from 362 K to 376 K). [f] The vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in ref 12 at vapor pressures from 110 kPa to 219 kPa (from 347 K to 373 K).

Table 7. Fitted Wilson, NRTL, and UNIQUAC Equation Parameters for the Mixtures, Averages of Absolute Vapor Fraction Residuals Δy and Temperature Residuals ΔT for the Wilson, NRTL ($\alpha_{12} = \alpha_{21} = 0.4$), and UNIQUAC Fits, Averages of the Absolute Vapor Fraction and Temperature Residuals for the UNIFAC−Dortmund Modification ($\Delta y_{Do-UNIF}$) and the Original UNIFAC Estimation Method (Δy_{UNIF}), Results of the Area Test *D* and *D* − *J*, and Azeotropic Composition x_{1az}

Wilson$_{12}$ J·mol^{-1}	Wilson$_{21}$ J·mol^{-1}	Δy ΔT/K	NRTL$_{12}$ K	NRTL$_{21}$ K	Δy ΔT/K	UNIQUAC$_{12}$ K	UNIQUAC$_{21}$ K	Δy ΔT/K	$\Delta y_{Do-UNIF}$ ΔT/K	Δy_{UNIF} ΔT/K	*D* *D* − *J*^{a}	x_{1az}, T_{az}/K p_{az}/kPa
					2,3-Dimethyl-2-butene (1) + Methanol (2)							
2110.7	9488.5	0.0059 0.14	691.87	513.14	0.0124 0.41	803.69	−39.410	0.0194 0.56	0.0067 0.28	0.0209 1.07	1.3 −8.3	0.468 325.4 101.2
					2,3-Dimethyl-2-butene (1) + Ethanol(2)							
1173.4	7235.4	0.0008 0.14	543.83	378.28	0.0072 0.24	459.47	−58.460	0.0108 0.32	0.0103 0.41	0.0069 0.18	1.0 −6.4	0.614 334.8 100.7
					2,3-Dimethyl-2-butene (1) + 2-Propanol (2)							
771.15	5594.8	0.0037 0.11	497.72	229.40	0.0064 0.19	370.92	−88.701	0.0081 0.24	0.0140 0.66	0.0104 0.50	0.2 −7.2	0.696 338.7 100.0
					2,3-Dimethyl-2-butene (1) + 2-Butanol (2)							
261.63	4821.6	0.0052 0.23	451.10	117.42	0.0055 0.28	221.95	−65.977	0.0056 0.31	0.0115 0.36	0.0148 1.21	0.6 −11.3	0.895 345.1 101.8

[a] The criterion for passing the area test is *D* − *J* ≤ 10.

apparatus that was used for the VLE-measurements.[2] The parameters of the pure component vapor pressure equation with the recommended temperature range of the vapor pressure equations are also presented in Table 6.

The systems measured show positive deviations from Raoult's law and exhibit azeotropic behavior. The azeotropic data for the systems measured are presented in Table 7. Azeotropic data were determined graphically from the measured values. The objective function[8] OF used for fitting of the activity coefficient equation parameters is given by eq 3

$$\mathrm{OF} = \frac{1}{N(\mathrm{NC})}\sum_{i=1}^{N}\sum_{j=1}^{\mathrm{NC}}\left|\frac{\gamma_{i,j}^{\mathrm{model}} - \gamma_{i,j}^{\mathrm{measured}}}{\gamma_{i,j}^{\mathrm{measured}}}\right| \tag{3}$$

where *N* is the number of points used in the fit and NC is the number of components used in the fit. The activity coefficient equation parameters (Wilson, UNIQUAC, NRTL) for the mixtures with the averages of the absolute values of the residuals for the vapor phase and temperature are presented in Table 7. In the point test,[9] a set of data is considered consistent if the averages of the absolute values of the residuals for the vapor phase in mole fraction are smaller than 0.01. The measured data were found to satisfy the point test criterion if the Wilson equation is used as presented in Figures 8 and 9. The NRTL equation also gives a good fit of the data except for the 2,3-dimethyl-2-butene + methanol system. The UNIQUAC equation can

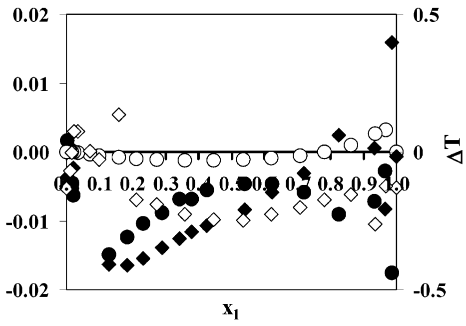

Figure 8. Point test for the 2,3-dimethyl-2-butene (1) + methanol (2) and 2,3-dimethyl-2-butene (1) + ethanol (2) systems at atmospheric pressure (Wilson model): ●, Δy for the methanol system; ◆, ΔT for the methanol system; ○, Δy for the ethanol system; ◇, ΔT for the ethanol system.

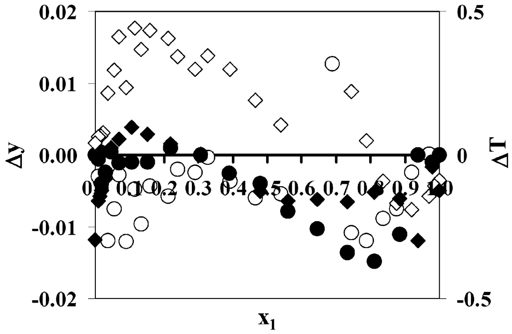

Figure 9. Point test for the 2,3-dimethyl-2-butene (1) + 2-propanol (2) and 2,3-dimethyl-2-butene (1) + 2-butanol (2) systems at atmospheric pressure (Wilson model): ●, Δ*y* for the 2-propanol system; ◆, Δ*T* for the 2-propanol system; ○, Δ*y* for the 2-butanol system; ◇, Δ*T* for the 2-butanol system.

describe the systems with 2-propanol and 2-butanol, but for the methanol and ethanol systems, the fit is worse. The estimations made with the different UNIFAC models[10,11] gave a worse description of the data if compared to that given by fitting the data with the Wilson equation. For the other activity coefficient models, the situation differs from case to case. All the data sets measured passed the integral test.[9]

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