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Articles

Vapor−Liquid Equilibrium for the *trans*-2-Butene + Methanol, + Ethanol, + 2-Propanol, + 2-Butanol, and + 2-Methyl-2-propanol Systems at 332 K

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An automated static total pressure measurement apparatus was used to measure isothermal vapor−liquid equilibria for five binary systems: *trans*-2-butene + methanol, + ethanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol at 332.3 K. Error analysis of the measured results has been presented. All systems exhibited positive deviation from Raoult's law. The *trans*-2-butene + methanol and *trans*-2-butene + ethanol systems showed azeotropic behavior.

Introduction

Vapor−liquid equilibrium data for the C4 alkanes and C4 alkenes with alcohols are used in designing processes for producing different gasoline components: 2-methoxy-2-methylpropane, 2-ethoxy-2-methylpropane, and isooctane. These measurements are part of a measurement project for which earlier measurements were made with a manually operated version of the apparatus.[1,2] As high a temperature as possible with this experimental setup with a small safety margin in order not to damage the pressure transducer was chosen. For the systems measured in this work, only VLE data for the *trans*-2-butene + ethanol system were found in the literature.[3] Miyano[4] measured the activity coefficient at infinite dilution for *trans*-2-butene in 2-propanol from 250 K to 330 K. An automated VLE-measurement apparatus enables rapid measurement with a reasonably small amount of labor,[5] thus it lowers the cost of acquiring data.

Experimental Section

Materials. The following reagents were used: *trans*-2-butene, Messer Griesheim, 99.4 vol %; methanol, Merck, 99.8 wt %; ethanol, Primalco Oy, 99.5 wt %; 2-propanol, Riedel-de Haën, 99.8 wt %; 2-butanol, Fluka >99.8 wt %; and 2-methyl-2-propanol, Fluka, >99.7 wt %. The alcohols were used without further purification except for drying over molecular sieves and degassing. The *trans*-2-butene was degassed in the syringe pump by opening the vacuum line valve 10 times for a period of 10 s. The syringe pump temperature was approximately 288 K.

Apparatus. A schematic depiction of the apparatus is presented in Figure 1. The equilibrium cell (113.10 cm^3, AISI 316L) is immersed in a 70-dm^3 water bath. Communication between the PC and the devices was through RS232 ports. The large water bath was heated with a Lauda Ecoline RE206 water bath whose set point can be changed from the PC. The pressure of the equilibrium cell was measured with a Digiquartz 2100A-101-CE pressure transducer (0 to 689 kPa) equipped with a model 740 intelligent display (uncertainty ±0.069 kPa). The total uncertainty in the pressure measurements was ±0.2 kPa due to limitations in the automation software. The transducer temperature was recorded through the same channel that was used for the recording of the pressure. The transducer and the $^1/_{16}$-in. tube connecting it to the equilibrium cell were electrically heated to a temperature higher than the equilibrium cell temperature to avoid condensation effects on the pressure measurement. The temperature of the water bath and two syringe pumps were measured with Pt-100 probes connected to the Systemteknik S2541 temperature meter (uncertainty ±0.03 K) equipped with a CNV 232 MA converter, which transferred the measurements to the PC.

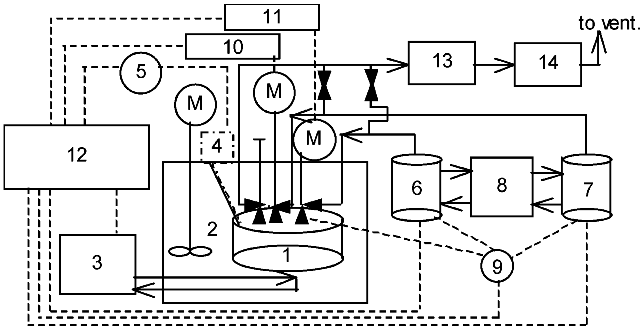

Figure 1. Schematic of the automated apparatus: 1, equilibrium cell with a magnetic stirrer; 2, 70-dm^3 water bath; 3, circulator thermostat; 4, electrically heated pressure transducer connected to the equilibrium cell with electrically heated $^1/_{16}$-in. tubing; 5, pressure display; 6 and 7, syringe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

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Table 1. Critical Temperature T_c, Critical Pressure p_c, Acentric Factor ω, Liquid Molar Volume v_i, UNIQUAC Volume Parameter R_{UNIQ}, and UNIQUAC Area Parameter Q_{UNIQ}

component	*trans*-2-butene	methanol	ethanol	2-propanol	2-butanol	2-methyl-2-propanol
T_c/K[a]	428.63 ± 4.29	512.58 ± 5.13	516.25 ± 5.16	508.31 ± 5.08	536.01 ± 5.36	506.2 ± 5.06
p_c/MPa[a]	4.1024 ± 0.04	8.0959 ± 0.24	6.3835 ± 0.19	4.7643 ± 0.14	4.1938 ± 0.13	3.9719 ± 0.12
ω[a]	0.2182	0.5656	0.6371	0.6689	0.5711	0.6158
v_i/cm^3/mol[a]	89.415 ± 0.89	40.702 ± 0.41	58.515 ± 0.59	76.784 ± 0.15	92.118 ± 0.92	94.861 ± 2.85
R_{UNIQ}[b]	2.9189	1.4311	2.2668	3.2491	3.9235	3.9228
Q_{UNIQ}[b]	2.8720	1.4320	2.3283	3.1240	3.6640	3.7440

[a] Daubert and Danner.[8] [b] Poling et al.[9]

Table 2. Measured Vapor Pressures and Values Calculated from Literature Correlations

		vapor pressure/kPa				
	T/K	this work	ref 7	ref 8	ref 9	ref 18
trans-2-butene	332.04	605.54	606.98	607.03	603.05	607.08
	332.06	605.74	607.28	607.33	603.35	607.39
	332.07	606.94	607.44	607.49	603.50	607.54
	332.08	606.14	607.59	607.64	603.65	607.69
		606.44				
methanol	332.08	80.97	81.08	80.85	80.93	80.88
ethanol	332.06	44.67	44.79	44.48	44.65	44.48
2-propanol	332.03	36.47	36.89	36.90	36.80	36.90
2-butanol	332.08	17.27	17.74	17.59	17.10	17.59
2-methyl-2-propanol	332.06	36.97	36.91	36.55	36.69	36.55

The valves welded to the lid of the equilibrium cell were operated with Vexta stepping motors equipped with gear boxes. The interface cards connected the stepping motors to the PC. Isco 260 D and Isco 100 DM syringe pumps injected the components into the equilibrium cell, and the pump volumes were read from Isco control units.

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

Procedure. The degassing procedure for the alcohols was described by Fischer and Gmehling.[6] The degassed alcohol was transferred from the degassing round-bottom flask to the evacuated Isco 100 syringe pump. The Isco 260 syringe pump was charged with degassed *trans*-2-butene. The syringe pumps were operated in constant-pressure mode. After the stepping motor opened the valve, the syringe pump injected the degassed component into the evacuated cell until the target volume was reached, and then the valve was closed. The pump operates until the constant-pressure set point is reached (in this case 1 MPa). The vapor pressure of the pure component was measured. The amount of injected component was computed from the displacement of the piston of the pump, the correlated density of the component, and the pump temperature. After the vapor pressure measurement, a small amount of the other component was injected. The equilibration time for one experimental point of these systems with this apparatus was found to be less than 20 min. The measurements were continued until a mole fraction of approximately 0.5 was reached. The cell was emptied and evacuated, and the measurement was continued with the other half of the isotherm after the target temperature had been reached and stabilized.

Error Analysis. The uncertainty in vapor and liquid mole fractions depends on many quantities such as uncertainties in the measurement of cell temperature, pressure, and injected molar amount of mixture components in the cell and the total volume of the cell. The uncertainty in injection volumes $\Delta V_1 = \pm 0.02$ cm^3 was obtained from the calibration experiments with distilled water. The estimated uncertainties in temperature and pressure measurements in the pumps are $\Delta T = \pm 0.1$ K and $\Delta p = \pm 20$ kPa. The densities of the components were calculated from correlations.[7] Uncertainties in density correlations for *trans*-2-butene, methanol, ethanol, 2-propanol, and 2-methyl-2-propanol were less than 1.0% ($\Delta\rho_1 = \pm 0.01\rho_1$), and for 2-butanol, they were less than 3.0% ($\Delta\rho_1 = \pm 0.03\rho_1$).[8]

To estimate the uncertainty of experimental molar amounts of mixture components in the cell, we derive the theoretical standard error for an injectionbelow. By differentiating the injected number of moles n_1, we obtain

$$dn_1 = d\left(\frac{\rho_1(T, p)V_1}{M_1}\right) \tag{1}$$

which results as an equation for the theoretical standard error

$$\Delta n_1 = \frac{V_1}{M_1}\Delta\rho_1 + \frac{V_1}{M_1}\left(\left|\frac{d\rho_1}{dT}\right|\Delta T + \frac{d\rho_1}{dp}\Delta p\right) + \frac{\rho_1}{M_1}\Delta V_1 \tag{2}$$

The modification of the pressure derivative of density gives

$$\Delta n_1 = \frac{V_1}{M_1}\Delta\rho_1 + \frac{V_1}{M_1}\left(\left|\frac{d\rho_1}{dT}\right|\Delta T + \left(-\frac{m_1}{V_1^{\,2}}\frac{dV_1}{dp}\Delta p\right)\right) + \frac{\rho_1}{M_1}\Delta V_1 \tag{3}$$

By taking the term $\rho_1 V_1/M_1 = n_1$ as a multiplier

$$\Delta n_1 = n_1\left(\frac{\Delta\rho_1}{\rho_1} + \frac{1}{\rho_1}\left|\frac{d\rho_1}{dT}\right|\Delta T + \left(-\frac{1}{V_1}\left(\frac{dV_1}{dp}\right)_T\right)\Delta p + \frac{\Delta V_1}{V_1}\right) \tag{4}$$

and setting

$$\kappa_1 = -\frac{1}{V_1}\left(\frac{dV_1}{dp}\right)_T \tag{5}$$

Table 3. VLE Data for the *trans*-2-Butene(1) + Methanol(2) System at 332 K[a]

								Legendre		
T/K	n_1/mol	Δn_1	n_2/mol	Δn_2	p_{exptl}/kPa	x_1	y_1	p_{leg}/kPa	γ_1	γ_2
332.06	0.6237	0.007	0	0	605.74	1	1	605.74	1.00	18.57
332.07	0.6237	0.007	0.0087	0.0006	622.84	0.987	0.969	619.99	1.00	15.73
332.06	0.6237	0.007	0.0336	0.0008	639.44	0.949	0.9240	636.43	1.01	10.50
332.06	0.6237	0.007	0.0697	0.0012	640.44	0.899	0.9023	639.47	1.05	6.83
332.06	0.6237	0.007	0.1113	0.002	638.84	0.848	0.8948	638.16	1.10	4.85
332.06	0.6237	0.007	0.1567	0.002	636.44	0.798	0.8918	636.45	1.17	3.74
332.06	0.6237	0.007	0.2092	0.003	633.84	0.747	0.8899	634.57	1.24	3.04
332.05	0.6237	0.007	0.2672	0.003	631.34	0.698	0.8882	632.22	1.32	2.58
332.06	0.6237	0.007	0.3362	0.004	628.54	0.647	0.8864	629.48	1.42	2.23
332.05	0.6237	0.007	0.4162	0.005	625.54	0.597	0.8845	625.86	1.52	1.98
332.05	0.6237	0.007	0.5108	0.006	621.74	0.547	0.8826	621.74	1.65	1.78
332.05	0.6237	0.007	0.6236	0.007	617.34	0.498	0.8807	617.03	1.80	1.62
332.05	0.6237	0.007	0.7619	0.008	611.74	0.449	0.8786	611.38	1.97	1.49
332.05	0.6237	0.007	0.9332	0.010	604.34	0.400	0.8763	604.23	2.19	1.38
332.08	0.5758	0.006	0.8694	0.009	604.34	0.397	0.8760	604.24	2.20	1.37
332.08	0.5427	0.006	0.8694	0.009	601.64	0.382	0.8752	601.64	2.27	1.35
332.08	0.4553	0.005	0.8694	0.009	592.14	0.341	0.8724	592.46	2.51	1.27
332.08	0.3576	0.004	0.8694	0.009	574.84	0.287	0.8672	575.35	2.89	1.19
332.08	0.2821	0.003	0.8694	0.009	551.94	0.239	0.8603	552.39	3.32	1.14
332.08	0.2171	0.002	0.8694	0.009	519.45	0.193	0.8498	519.44	3.86	1.09
332.08	0.0977	0.0012	0.8694	0.009	385.55	0.094	0.7924	384.96	5.66	1.02
332.07	0.0457	0.0007	0.8694	0.009	259.86	0.045	0.6898	259.86	7.14	1.01
332.08	0	0	0.8694	0.009	80.97	0	0	80.97	9.19	1.00

[a] Experimental temperature T, moles of components in the equilibrium cell n_1 and n_2, experimental pressure p_{exptl}, liquid-phase x_1 mole fractions, vapor-phase mole fractions y_1, and pressure p_{calcd} calculated from the Legendre polynomial fit; Δn_1 and Δn_2 are absolute errors in calculation of corresponding variables.

Table 4. VLE Data for the *trans*-2-Butene(1) + Ethanol(2) System at 332 K[a]

								Legendre		
T/K	n_1/mol	Δn_1	n_2/mol	Δn_2	p_{exptl}/kPa	x_1	y_1	p_{leg}/kPa	γ_1	γ_2
332.07	0.5370	0	0	0	606.94	1	1	606.94	1.0	13.71
332.07	0.5370	0.006	0.0053	0.0004	608.64	0.990	0.990	607.86	1.00	12.24
332.08	0.5370	0.006	0.0284	0.0006	607.24	0.949	0.964	605.50	1.01	8.11
332.07	0.5370	0.006	0.0591	0.0009	601.54	0.900	0.952	599.09	1.05	5.46
332.07	0.5370	0.006	0.0941	0.0013	595.54	0.849	0.947	593.48	1.09	3.99
332.07	0.5370	0.006	0.1338	0.002	589.64	0.798	0.944	588.62	1.15	3.13
332.07	0.5370	0.006	0.1782	0.002	583.74	0.748	0.942	583.78	1.22	2.59
332.08	0.5370	0.006	0.2291	0.003	577.64	0.698	0.940	578.44	1.29	2.22
332.07	0.5370	0.006	0.2875	0.003	571.14	0.648	0.938	571.92	1.38	1.95
332.07	0.5370	0.006	0.3566	0.004	563.94	0.598	0.936	564.38	1.47	1.75
332.07	0.5370	0.006	0.4409	0.005	555.34	0.546	0.933	555.34	1.58	1.58
332.07	0.5370	0.006	0.5390	0.006	545.34	0.497	0.931	545.09	1.71	1.46
332.07	0.5370	0.006	0.6584	0.007	533.05	0.448	0.928	532.86	1.85	1.35
332.07	0.5370	0.006	0.8072	0.008	517.95	0.399	0.925	517.87	2.02	1.27
332.08	0.5168	0.006	0.7789	0.008	518.05	0.398	0.925	517.70	2.03	1.27
332.07	0.4175	0.004	0.7789	0.008	497.45	0.347	0.920	497.45	2.23	1.20
332.07	0.3335	0.004	0.7789	0.008	471.05	0.296	0.914	471.47	2.47	1.14
332.06	0.2594	0.003	0.7789	0.008	436.25	0.245	0.906	436.60	2.76	1.09
332.06	0.1954	0.002	0.7789	0.008	391.75	0.195	0.893	391.75	3.10	1.06
332.06	0.1412	0.002	0.7789	0.008	337.36	0.148	0.873	336.79	3.49	1.03
332.06	0.0908	0.0011	0.7789	0.008	264.86	0.100	0.836	264.30	3.96	1.02
332.06	0.0453	0.0007	0.7789	0.008	172.97	0.052	0.745	172.96	4.55	1.00
332.06	0.0295	0.0005	0.7789	0.008	133.07	0.034	0.668	133.31	4.80	1.00
332.06	0	0	0.7789	0.008	44.67	0	0	44.67	5.37	1.00

[a] Experimental temperature T, moles of components in the equilibrium cell n_1 and n_2, experimental pressure p_{exptl}, liquid-phase x_1 mole fractions, vapor-phase mole fractions y_1, and pressure p_{calcd} calculated from the Legendre polynomial fit; Δn_1 and Δn_2 are absolute errors in calculation of corresponding variables.

which is the isothermal compressibility, we finally obtain

$$\Delta n_1 = n_1\left(\frac{\Delta\rho_1}{\rho_1} + \frac{1}{\rho_1}\left|\frac{d\rho_1}{dT}\right|\Delta T + \kappa_1\Delta p + \frac{\Delta V_1}{V_1}\right) \qquad (6)$$

The corresponding equation is also valid for component 2 with subscript 2. In eq 6, the temperature derivative of density was calculated from the density correlation,[7] and the isothermal compressibility of a liquid was obtained from the Hankinson−Brobst−Thompson model.[9]

Data Reduction. The method proposed by Barker[10] was used to convert the moles of each component injected into the cell to the mole fractions of the vapor and liquid phases with the VLEFIT software.[11] The method of Barker data reduction assumes that there is an activity coefficient model that can predict the bubble-point pressure, p_{calcd}, at higher accuracy than the experimental error of the measured total pressure. Our scheme for the data reduction is reported in ref 12. The data were reduced with the Legendre[13] polynomial as the activity coefficient model and

Table 5. VLE Data for the *trans*-2-Butene(1) + 2-Propanol(2) System at 332 K[a]

								Legendre		
T/K	n_1/mol	Δn_1	n_2/mol	Δn_2	p_{exptl}/kPa	x_1	y_1	p_{leg}/kPa	γ_1	γ_2
332.08	0.5342	0	0	0	606.44	1	1	606.44	1.00	9.18
332.08	0.5342	0.006	0.0045	0.0003	604.54	0.992	0.9948	604.45	1.00	8.44
332.08	0.5342	0.006	0.0271	0.0005	595.24	0.951	0.9784	594.26	1.01	5.89
332.08	0.5342	0.006	0.0579	0.0009	584.94	0.901	0.9686	582.93	1.04	4.15
332.08	0.5342	0.006	0.0926	0.0012	574.94	0.850	0.9633	573.24	1.08	3.17
332.09	0.5342	0.006	0.1320	0.002	564.84	0.799	0.9596	564.21	1.13	2.58
332.08	0.5342	0.006	0.1759	0.002	554.54	0.749	0.9565	554.73	1.18	2.19
332.08	0.5342	0.006	0.2274	0.003	543.54	0.698	0.9535	544.21	1.24	1.92
332.08	0.5342	0.006	0.2858	0.003	532.05	0.649	0.9505	532.72	1.31	1.72
332.08	0.5342	0.006	0.3536	0.004	519.65	0.599	0.9475	520.03	1.38	1.57
332.08	0.5342	0.006	0.4350	0.005	505.75	0.549	0.9442	505.75	1.47	1.45
332.08	0.5342	0.006	0.5310	0.006	490.55	0.500	0.9407	490.17	1.56	1.36
332.08	0.5342	0.006	0.6491	0.007	473.15	0.451	0.9368	472.47	1.67	1.28
332.00	0.4275	0.005	0.3959	0.004	494.05	0.515	0.9420	494.07	1.53	1.38
332.01	0.3841	0.004	0.3959	0.004	484.95	0.488	0.9399	484.90	1.59	1.33
332.01	0.3188	0.003	0.3959	0.004	467.15	0.440	0.9360	467.09	1.70	1.26
332.01	0.2699	0.003	0.3959	0.004	449.25	0.397	0.9320	449.25	1.81	1.20
332.01	0.2139	0.002	0.3959	0.004	420.75	0.341	0.9254	420.96	1.97	1.14
332.02	0.1702	0.002	0.3959	0.004	389.35	0.290	0.9173	389.69	2.14	1.10
332.02	0.1378	0.002	0.3959	0.004	357.96	0.246	0.9081	358.05	2.31	1.07
332.02	0.1053	0.001	0.3959	0.004	315.76	0.198	0.8934	315.76	2.52	1.05
332.03	0.0787	0.0010	0.3959	0.004	270.46	0.154	0.8730	270.28	2.73	1.03
332.03	0.0505	0.0007	0.3959	0.004	207.06	0.103	0.8306	207.18	3.02	1.01
332.03	0.0408	0.0006	0.3959	0.004	181.16	0.085	0.8047	181.04	3.13	1.01
332.03	0.0196	0.0004	0.3959	0.004	114.07	0.042	0.6849	114.07	3.44	1.00
332.03	0	0	0.3959	0.004	36.47	0	0	36.47	3.80	1.00

[a] Experimental temperature T, moles of components in the equilibrium cell n_1 and n_2, experimental pressure p_{exptl}, liquid-phase x_1 mole fractions, vapor-phase mole fractions y_1, and pressure p_{calcd} calculated from the Legendre-polynomial fit; Δn_1 and Δn_2 are absolute errors in calculation of corresponding variables.

Table 6. VLE Data for the *trans*-2-Butene(1) + 2-Butanol(2) System at 332 K[a]

								Legendre		
T/K	n_1/mol	Δn_1	n_2/mol	Δn_2	p_{exptl}/kPa	x_1	y_1	p_{leg}/kPa	γ_1	γ_2
332.04	0.5135	0.005	0	0	605.54	1	1	605.54	1.00	7.21
332.04	0.5135	0.005	0.0058	0.0003	599.64	0.989	0.9973	599.75	1.00	6.49
332.04	0.5135	0.005	0.0278	0.0005	582.64	0.947	0.9907	582.42	1.01	4.68
332.04	0.5135	0.005	0.0578	0.0008	567.44	0.897	0.9864	566.31	1.04	3.42
332.04	0.5135	0.005	0.0910	0.0011	554.14	0.847	0.9838	553.26	1.07	2.70
332.04	0.5135	0.005	0.1282	0.002	541.15	0.797	0.9818	541.05	1.12	2.25
332.05	0.5135	0.005	0.1713	0.002	527.65	0.747	0.9800	528.33	1.17	1.94
332.06	0.5135	0.005	0.2200	0.002	513.85	0.697	0.9782	514.77	1.22	1.73
332.06	0.5135	0.005	0.2767	0.003	498.85	0.647	0.9764	499.64	1.28	1.58
332.06	0.5135	0.005	0.3423	0.004	482.95	0.598	0.9745	483.29	1.34	1.46
332.07	0.5135	0.005	0.4200	0.004	465.55	0.548	0.9724	465.55	1.41	1.36
332.07	0.5135	0.005	0.5130	0.005	446.45	0.499	0.9702	446.12	1.49	1.28
332.06	0.5188	0.006	0.5164	0.005	446.95	0.500	0.9702	446.44	1.48	1.29
332.06	0.4254	0.005	0.5164	0.005	425.05	0.450	0.9676	424.43	1.57	1.22
332.07	0.3474	0.004	0.5164	0.005	400.25	0.399	0.9645	399.84	1.67	1.17
332.09	0.2837	0.003	0.5164	0.005	373.15	0.351	0.9608	373.15	1.78	1.12
332.10	0.2264	0.003	0.5164	0.005	340.86	0.300	0.9559	341.11	1.91	1.09
332.09	0.1777	0.002	0.5164	0.005	304.56	0.251	0.9494	304.72	2.04	1.06
332.09	0.1346	0.002	0.5164	0.005	262.66	0.201	0.9397	262.66	2.19	1.04
332.09	0.0974	0.0012	0.5164	0.005	216.06	0.153	0.9249	215.86	2.35	1.02
332.09	0.0639	0.0009	0.5164	0.005	162.77	0.105	0.8981	162.54	2.53	1.01
332.09	0.0309	0.0005	0.5164	0.005	95.97	0.053	0.8238	96.11	2.75	1.00
332.09	0.0207	0.0004	0.5164	0.005	72.27	0.036	0.7641	72.27	2.83	1.00
332.08	0	0	0.5164	0.005	17.27	0	0	17.27	3.02	1.00

[a] Experimental temperature T, moles of components in the equilibrium cell n_1 and n_2, experimental pressure p_{exptl}, liquid-phase x_1 mole fractions, vapor-phase mole fractions y_1, and pressure p_{calcd} calculated from the Legendre polynomial fit; Δn_1 and Δn_2 are absolute errors in calculation of corresponding variables.

the Soave−Redlich−Kwong[14] cubic equation of state with quadratic mixing rules in the attractive parameter and linear in covolume. Binary interaction parameters k_{ij} in the attraction term of the equation-of-state model were set equal to zero. The critical properties used in data reduction are presented in Table 1. The validity of the models used in the Barker data reduction procedure used in this work has been experimentally proven to produce activity coefficients that are correct for hydrocarbon + alcohol systems.[12]

Results and Discussion

Vapor pressures measured for the pure components are presented in Table 2, with values calculated from different correlations from the literature. All five binary pairs measured show positive deviation from Raoult's law. The

Table 7. VLE Data for the *trans*-2-Butene(1) + 2-Methyl-2-propanol(2) System at 332 K[a]

								Legendre		
T/K	n_1/mol	Δn_1	n_2/mol	Δn_2	p_{exptl}/kPa	x_1	y_1	p_{leg}/kPa	γ_1	γ_2
332.08	0.5203	0.006	0	0	606.14	1	1	606.14	1.00	5.80
332.08	0.5203	0.006	0.0056	0.0003	601.64	0.989	0.9956	601.91	1.00	5.31
332.08	0.5203	0.006	0.0275	0.0005	587.64	0.949	0.9841	587.48	1.01	3.97
332.08	0.5203	0.006	0.0570	0.0008	573.34	0.900	0.9758	572.49	1.03	3.00
332.09	0.5203	0.006	0.0905	0.0011	559.64	0.849	0.9703	559.01	1.06	2.42
332.10	0.5203	0.006	0.1277	0.002	545.94	0.800	0.9659	545.94	1.10	2.05
332.11	0.5203	0.006	0.1704	0.002	531.65	0.750	0.9618	532.08	1.14	1.80
332.12	0.5203	0.006	0.2187	0.002	516.55	0.701	0.9578	517.20	1.19	1.63
332.11	0.5203	0.006	0.2746	0.003	500.45	0.652	0.9537	500.69	1.24	1.50
332.12	0.5203	0.006	0.3405	0.004	482.75	0.602	0.9492	482.75	1.29	1.39
332.13	0.5203	0.006	0.4173	0.004	463.95	0.553	0.9444	463.55	1.35	1.31
332.13	0.5203	0.006	0.5101	0.005	443.25	0.504	0.9391	442.51	1.41	1.25
332.09	0.3139	0.003	0.4804	0.005	386.75	0.392	0.9240	386.47	1.58	1.14
332.09	0.2578	0.003	0.4804	0.005	359.45	0.345	0.9156	359.45	1.67	1.10
332.08	0.2096	0.002	0.4804	0.005	329.76	0.299	0.9052	329.90	1.76	1.08
332.08	0.1701	0.002	0.4804	0.005	299.46	0.256	0.8927	299.61	1.85	1.05
332.07	0.1352	0.002	0.4804	0.005	266.66	0.214	0.8763	266.65	1.95	1.04
332.08	0.1058	0.0013	0.4804	0.005	233.16	0.175	0.8551	233.16	2.05	1.03
332.08	0.0803	0.0010	0.4804	0.005	198.46	0.138	0.8261	198.42	2.16	1.02
332.08	0.0569	0.0008	0.4804	0.005	161.27	0.101	0.7815	161.07	2.27	1.01
332.07	0.0368	0.0006	0.4804	0.005	123.27	0.068	0.7098	123.38	2.39	1.00
332.07	0.0189	0.0004	0.4804	0.005	84.37	0.036	0.570	84.64	2.52	1.00
332.07	0.0117	0.0003	0.4804	0.005	67.37	0.022	0.456	67.37	2.58	1.00
332.06	0	0	0.4804	0.005	36.97	0	0	36.97	2.68	1.00

[a] Experimental temperature T, moles of components in the equilibrium cell n_1 and n_2, experimental pressure p_{exptl}, liquid-phase x_1 mole fractions, vapor-phase mole fractions y_1, and pressure p_{calcd} calculated from the Legendre polynomial fit; Δn_1 and Δn_2 are absolute errors in calculation of corresponding variables.

Table 8. Parameters[a] for *trans*-2-Butene + Methanol (System 1), *trans*-2-Butene + Ethanol (System 2), *trans*-2-Butene + 2-Propanol (System 3), *trans*-2-Butene + 2-Butanol (System 4), and *trans*-2-Butene + 2-Methyl-2-propanol (System 5)

	system				
	1	2	3	4	5
Legendre, $a_{1,0}$	2.2671	1.9197	1.5817	1.3650	1.2035
Legendre, $a_{2,0}$	0.28815	0.39996	0.37849	0.37577	0.33586
Legendre, $a_{3,0}$	0.27802	0.20925	0.17523	0.15829	0.15331
Legendre, $a_{4,0}$	0.063931	0.068467	0.062327	0.058969	0.049387
Legendre, $a_{5,0}$	0.024545	0.020941	0.019225	0.016749	0.015922
Legendre, γ_1^∞	9.19	5.37	3.80	3.02	2.68
Legendre, γ_2^∞	18.57	13.71	9.18	7.21	5.80
Δp/kPa	0.21	0.27	0.16	0.05	0.04
$|\Delta p|$/kPa	0.57	0.50	0.37	0.31	0.22
Wilson, λ_{12}/K	184.6	124.4	116.1	109.2	62.3
Wilson λ_{21}/K	1061.5	878.2	629.6	521.4	515.9
Wilson, γ_1^∞	9.51	5.42	3.77	2.99	2.53
Wilson, γ_2^∞	23.26	15.94	8.48	6.41	5.65
Δp/kPa	−0.25	−0.23	0.93	1.10	−0.78
$|\Delta p|$/kPa	1.29	0.78	1.32	1.38	1.91
NRTL, λ_{12}/K	607.76	585.31	511.36	484.81	451.38
NRTL, λ_{21}/K	428.18	260.79	156.34	88.83	49.15
NRTL, $\alpha_{12} = \alpha_{21}$	0.4	0.4	0.4	0.4	0.4
NRTL, γ_1^∞	8.75	5.24	3.68	2.95	2.55
NRTL, γ_2^∞	13.47	10.34	6.89	5.48	4.48
Δp/kPa	1.90	2.73	2.43	2.41	2.10
$|\Delta p|$/kPa	6.30	4.20	3.86	3.44	3.62
UNIQUAC, λ_{12}/K	653.223	337.896	203.056	144.688	143.277
UNIQUAC, λ_{21}/K	−11.276	−22.808	−3.834	8.870	−5.166
UNIQUAC, γ_1^∞	7.75	5.03	3.59	2.92	2.53
UNIQUAC, γ_2^∞	13.01	8.89	6.50	5.31	4.56
Δp/kPa	4.10	5.27	2.78	2.67	1.32
$|\Delta p|$/kPa	8.13	7.33	5.06	4.04	3.64

[a] Activity coefficient model parameters, Legendre,[13] Wilson,[15] NRTL,[16] UNIQUAC,[17] average pressure residual Δp, and absolute average pressure residual $|\Delta p|$.

results of the *trans*-2-butene + methanol system are presented in Table 3. The azeotropic point was found by the Legendre polynomial fit for the *trans*-2-butene + methanol system at x(*trans*-2-butene) = 0.902, p = 639.5 kPa at 332.06 K (experimental pressure maximum of 640.4 kPa at 332.06 K). The results of the *trans*-2-butene + ethanol system are presented in Table 4. For the *trans*-2-butene + ethanol system, an azeotropic point was also found by the Legendre polynomial fit at x(*trans*-2-butene) = 0.988, p = 607.9 kPa at T = 332.07 K (experimental pressure maximum of 608.6 kPa at 332.07 K). The *trans*-2-butene + 2-propanol measurements are presented in Table 5. The infinite dilution activity coefficient value for *trans*-2-butene in 2-propanol reported by Miyano[4] (3.9 at

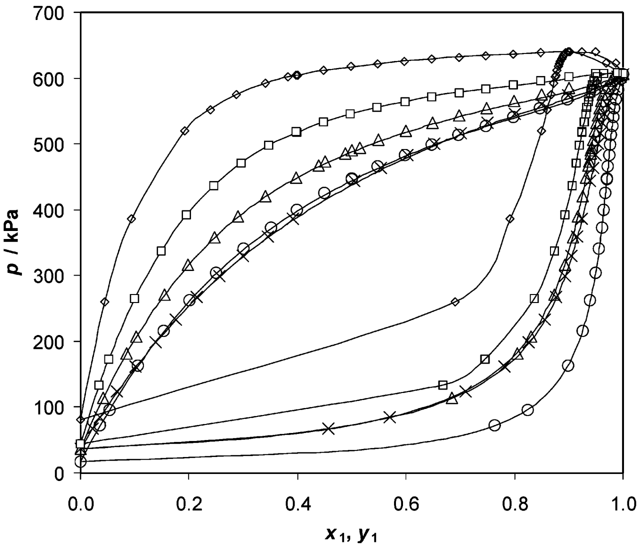

Figure 2. Pressure−composition diagram of *trans*-2-butene(1) + alcohol(2) at 332 K: ◇, *trans*-2-butene + methanol; □, *trans*-2-butene + ethanol; △, *trans*-2-butene + 2-propanol; ○, *trans*-2-butene + 2-butanol; ×, *trans*-2-butene + 2-methyl-2-propanol; −, calculated with the Legendre polynomial.

330.00 K) is well in-line with this work (3.8 at 320.03 K). The *trans*-2-butene + 2-butanol measurements are presented in Table 6, and the *trans*-2-butene + 2-methyl-2-propanol measurements are presented in Table 7. The Tables consist of temperature, amount of material injected, and experimental pressure, which enable with the reported cell volume the use of different data reduction techniques for the interested reader. The resulting liquid-phase and vapor-phase compositions from the regression procedure used[12] with the calculated pressure and activity coefficients are also presented in the Tables.

The *trans*-2-butene + 2-methyl-2-propanol data set was chosen for a comparison of the results regressed with the Barker method using the Wilson, NRTL, and UNIQUAC activity coefficient models. (See Δp and $|\Delta p|$ in Table 8.) The prediction of pressure is satisfactory with the Wilson model and much worse with the NRTL and UNIQUAC models. These results are typical for measurements with these systems. The accuracy of the activity coefficients calculation is about 2% in the dilute region and 0.5% at higher component concentrations. Injected numbers of moles are presented in Tables 3−7 using more significant digits than their errors would indicate. This is required if someone wants to recalculate the measured data.

In Figures 2 and 3, the symbols present the experimental pressure as a function of liquid and vapor composition calculated with the Legendre polynomial parameters. The solid line presents the calculated pressure as a function of liquid and vapor composition. In Figure 3, the systems exhibiting azeotropic behavior are presented. The polynomial function with the regressed parameters can reproduce the location of the pressure maximum well with respect to composition for the *trans*-2-butene + methanol system. The reproduction of pressure with the Legendre polynomial falls short in the dilute methanol range, and the activity coefficient receives a value that is too small. The Wilson[15] equation represents the dilute methanol range well, but the representation of pressure residuals in ranges other than the dilute methanol range is far worse than with the Legendre polynomial. Similar behavior for the *trans*-2-butene + ethanol system compared to that of the *trans*-2-butene + methanol system can be detected.

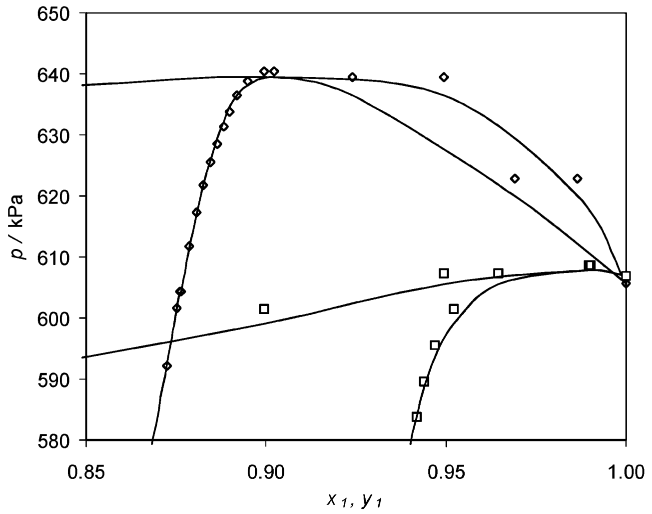

Figure 3. Pressure−composition diagram of *trans*-2-butene(1) + alcohol(2) systems which exhibit azeotropic behavior at 332 K: ◇, *trans*-2-butene + methanol; □, *trans*-2-butene + ethanol; −, calculated with the Legendre polynomial.

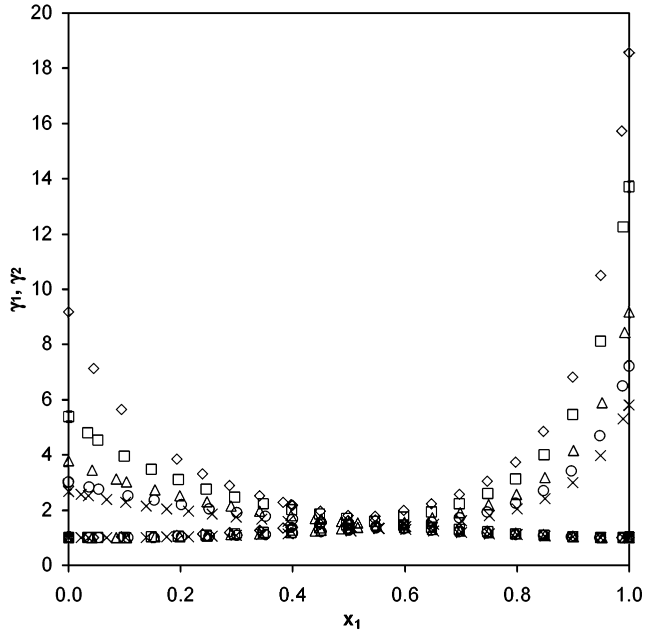

Figure 4. Activity coefficient−composition diagram of *trans*-2-butene(1) + alcohol(2) at 326 K: ◇, *trans*-2-butene + methanol; □, *trans*-2-butene + ethanol; △, *trans*-2-butene + 2-propanol; ○, *trans*-2-butene + 2-butanol; ×, *trans*-2-butene + 2-methyl-2-propanol.

Figure 4 presents activity coefficients as a function of the liquid composition. Parameters of the Legendre polynomial are summarized in Table 8.

According to the error analysis, the most significant source of error is the uncertainty in the density correlation, causing subsequent errors first at injected molar amounts and then at calculated pressure and compositions. It is possible that the large deviation in the calculated system total pressure (Tables 3−7) compared to the experimental system total pressure is caused by the errors in density. Therefore, it would be beneficial to measure the densities prior to VLE experiments for all pure components at pump pressure and temperature. One additional cause of the large pressure deviations can be difficulties in optimizing the activity coefficient model parameters properly. The pressure deviations are systematically larger for the systems that are less ideal.

Parameters of the Wilson,[15] NRTL,[16] and UNIQUAC[17] activity coefficient models are presented in Table 8. Volume and area parameters used in the UNIQUAC model are listed in Table 1.

Conclusions

Five isotherms at 332 K of *trans*-2-butene and alcohols were measured with a total pressure measurement approach leading to *PTz* data and treated using the method of Barker[10] to provide *PTxy* data. The *trans*-2-butene + methanol and *trans*-2-butene + ethanol systems showed azeotropic behavior. All systems measured exhibited positive deviation from Raoult's law. Error analysis was performed on the measured data, and the major source of error was found to be the uncertainty in the liquid density. Parameters of the Wilson, NRTL, and UNIQUAC activity coefficient models were optimized.

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