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Vapor−Liquid Equilibrium for the Binary Systems of Methanol + 2,4,4-Trimethyl-1-pentene at 331 K and 101 kPa and Methanol + 2-Methoxy-2,4,4-trimethylpentane at 333 K

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Isothermal and isobaric vapor−liquid equilibrium data were measured for the system methanol + 2,4,4-trimethyl-1-pentene at 331 K and at 101 kPa. Isothermal vapor−liquid equilibrium data were also measured for methanol + 2-methoxy-2,4,4-trimethylpentane at 333 K. Vapor pressures were measured for 2-methoxy-2,4,4-trimethylpentane. The measurements were made with a recirculation still. The results were correlated with the Soave−Redlich−Kwong equation of state and the Wilson activity coefficient models.

Introduction

MTBE (2-methoxy-2-methyl-propane) will be banned in California no later than December 31, 2002, because of groundwater pollution problems.[1] Thus, MTBE will have to be replaced with other fuel components. The consumption[2] of MTBE in California was about 4 million gallons per day during the first quarter of 2000. It is economically feasible to convert existing MTBE plants to produce chemicals such as diisobutylene (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) or, by hydrogenating the diisobutylene, the high-quality fuel component isooctane (2,2,4-trimethylpentane).[3] Karinen has proposed that it is also possible to produce 2-methoxy-2,4,4-trimethylpentane[4] by etherification of diisobutylene with methanol. The water solubility of ethers with higher molecular weight is expected to be less than the water solubility of ethers with lower molecular weights,[4] which could make 2-methoxy-2,4,4-trimethylpentane an attractive oxygenated fuel component. The systems measured have relevance in the design of 2-methoxy-2,4,4-trimethylpentane processes. Data for the systems measured were not available in the literature.

Experimental Section

Materials. Methanol (99.7%, by gas chromatography (GC)) was provided by Merck, and 2,4,4-trimethyl-1-pentene (99.5%, by GC) was provided by Fluka. 2-Methoxy-2,4,4-trimethylpentane, with analysis results, was provided by Fortum Oy. Results of the GC analysis of 2-methoxy-2,4,4-trimethylpentane are presented in Table 1. The materials were used without further purification except for drying over molecular sieves (Merck 3A).

Apparatus. A recirculation still of the Yerazunis type[5] was used. The liquid volume needed for running the apparatus was approximately 80 mL. The experimental setup is presented schematically in Figure 1. Small magnetic stirrers were used to enhance mixing in the sampling chambers and in the mixing chamber. For temperature measurements, a Thermolyzer S2541 (Frontec) temperature meter with a Pt 100 probe calibrated at the Finnish National Standards Laboratory was used. The resolution of the temperature measurement system was 0.005 K, and the calibration uncertainty was ±0.015 K; the uncertainty in the temperature measurement of the system is believed to be ±0.05 K. The Pt 100 probe was located at the bottom of the packed section of the equilibrium chamber.

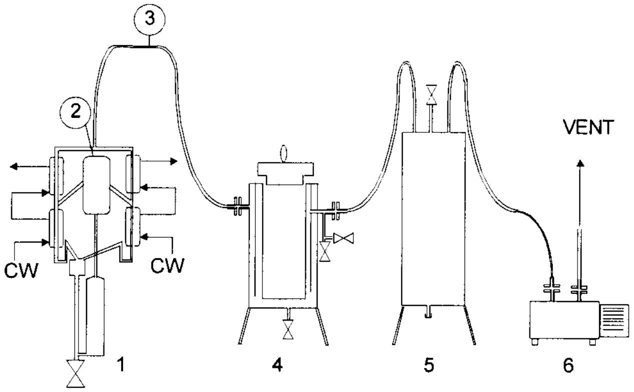

Figure 1. Experimental setup: (1) recirculation still, (2) temperature probe (Pt 100), (3) pressure transducer, (4) liquid nitrogen trap, (5) buffer tank 30 dm^3, (6) vacuum pump.

Table 1. Results of the GC Analysis of 2-Methoxy-2,4,4-trimethylpentane

component	mass %
2-methoxy-2,4,4-trimethylpentane	98.982
2,4,4-trimethyl-2-pentanol	0.764
2,4,4-trimethyl-2-pentene	0.162
2,4,4-trimethyl-1-pentene	0.074
other components	0.108

The pressure measurements were made with a Druck pressure transducer (0−100 kPa) and a Red Lion panel meter. The uncertainty in 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 against a DHP-PC-2 pressure calibrator. Including the calibration uncertainty, the uncertainty in the pressure measurement system is ±0.15 kPa

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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 Methanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 331 K

x_1	y_1	T (K)	P (kPa)	γ_1	γ_2
1.000	1.000	331.12	78.0		
0.9870	0.9366	331.12	82.5	1.00	15.98
0.9797	0.9081	331.12	84.4	1.00	15.15
0.9717	0.8849	331.13	86.1	1.00	13.96
0.96.5	0.8641	331.12	88.0	1.01	11.97
0.9476	0.8418	331.12	89.6	1.02	10.68
0.9339	0.8265	331.12	90.8	1.03	9.40
0.9172	0.8122	331.12	91.9	1.04	8.21
0.8998	0.7995	331.13	92.5	1.05	7.29
0.8829	0.7910	331.12	93.0	1.07	6.53
0.8630	0.7737	331.12	93.3	1.07	6.06
0.8393	0.7776	331.13	93.6	1.11	5.09
0.8120	0.7733	331.12	93.6	1.14	4.44
0.6270	0.7625	331.13	93.6	1.46	2.34
0.5756	0.7611	331.12	93.4	1.58	2.07
0.4844	0.7570	331.13	93.0	1.86	1.72
0.3910	0.7563	331.12	92.4	2.29	1.45
0.3233	0.7515	331.13	91.8	2.73	1.33
0.2872	0.7440	331.12	91.3	3.03	1.29
0.2489	0.7451	331.12	90.7	3.48	1.21
0.2195	0.7417	331.13	90.0	3.89	1.17
0.1467	0.7303	331.13	87.0	5.55	1.08
0.0642	0.6886	331.15	76.6	10.54	1.01
0.0366	0.6344	331.15	66.0	14.70	1.00
0.0000	0.0000	331.12	24.4		

Analysis and GC Calibration. The condensed vapor phase and the liquid phase were analyzed with an HP 6850A gas chromatograph with an autosampler, a capillary column (HP-1, cross-linked methyl siloxane, length 30 m, column inner diameter 0.25 mm, film thickness 1.0 μm), and a flame ionization detector. Gravimetric calibration mixtures were prepared in 2-mL vials with approximately 1 mL of toluene as the solvent. The errors in the analysis for the systems measured is believed to be less than 0.003 in mole fraction.

Procedure. Pure component 1 was introduced to the recirculation still, and its vapor pressure was measured. After the vapor pressure measurements, component 2 was added to the equilibrium still. In the isothermal runs, the temperature was adjusted to the desired value by adjusting the pressure of the system. In the isobaric runs, the ambient pressure was the same as the system pressure. It took from 15 to 30 min to achieve constant temperature because of the large boiling point difference of the pure components. The temperature was held constant for approximately 35 min to further enhance the steady-state condition before sampling. Approximately 1 mL of toluene was added to the 2-mL autosampler vials before sampling was facilitated. Toluene was used as the solvent in order to reduce the volume of the sample needed to fill the 2-mL vial. Samples of the liquid and the vapor condensate were taken with a 1-mL Hamilton Sample Lock syringe after the steady-state condition was achieved. At first, the syringe was flushed with 0.1−0.2 mL of sample, and then a 0.4−0.5-mL sample was taken and injected into the cooled 2-mL autosampler vial.

Results and Discussion

The measured and calculated activity coefficients are reported in Tables 2−4 and Figures 2−7. Azeotropic behavior was observed for the methanol + 2,4,4-trimethyl-1-pentene systems (x_{az}(methanol) = 0.771, T = 331.12 K, P = 93.6 kPa, and x_{az}(methanol) = 0.773, T = 332.98 K, P = 101.0 kPa). Azeotropic data were determined graphically from measured values.

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 Methanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 101 kPa

x_1	y_1	T (K)	P (kPa)	γ_1	γ_2
1.0000	1.0000	337.35	100.2	1.00	
0.9869	0.9385	336.16	100.9	1.00	15.51
0.9764	0.9042	335.37	100.9	1.01	13.79
0.9632	0.8718	334.67	100.9	1.01	12.12
0.9351	0.8297	333.76	100.9	1.03	9.43
0.8503	0.7833	333.06	101.0	1.10	5.33
0.7997	0.7752	332.99	101.0	1.16	4.14
0.6793	0.7659	333.01	101.0	1.35	2.69
0.6103	0.7629	333.07	101.0	1.49	2.24
0.5489	0.7614	333.12	101.0	1.65	1.94
0.4751	0.7577	333.22	101.0	1.89	1.69
0.4198	0.7568	333.32	101.0	2.13	1.53
0.3619	0.7517	333.43	101.0	2.44	1.41
0.3002	0.7503	333.61	100.9	2.91	1.29
0.2450	0.7481	333.92	100.9	3.52	1.19
0.1995	0.7410	334.29	100.9	4.22	1.14
0.1438	0.7301	335.14	100.9	5.57	1.08
0.0950	0.7075	336.99	100.9	7.61	1.03
0.0642	0.6817	339.05	100.9	10.02	1.01
0.0514	0.6599	341.06	100.9	11.22	0.99
0.0399	0.6192	343.76	100.9	12.27	1.00
0.0311	0.5689	347.66	100.9	12.54	0.99
0.0218	0.5024	351.47	100.8	13.79	1.00
0.0000	0.0000	374.15	100.7		1.00

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 Methanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 333 K

x_1	y_1	T (K)	P (kPa)	γ_1	γ_2
1.0000	1.0000	333.24	85.0		
0.9284	0.9722	333.13	82.4	1.02	5.61
0.8749	0.9636	333.12	80.7	1.05	4.13
0.8324	0.9594	333.13	79.6	1.09	3.39
0.8065	0.9574	333.13	79.1	1.11	3.06
0.7729	0.9556	333.12	78.4	1.15	2.70
0.7410	0.9534	333.13	77.6	1.18	2.46
0.7000	0.95.3	333.12	76.5	1.23	2.23
0.6301	0.9482	333.11	74.9	1.34	1.85
0.5503	0.9442	333.13	72.9	1.48	1.60
0.4286	0.9384	333.13	69.1	1.79	1.32
0.3971	0.9359	333.12	67.4	1.89	1.27
0.3702	0.9342	333.12	66.4	1.99	1.23
0.2970	0.9267	333.15	61.8	2.29	1.14
0.2379	0.9205	333.15	57.9	2.66	1.08
0.1917	0.9117	333.15	53.4	3.02	1.04
0.1615	0.9012	333.15	49.8	3.31	1.05
0.1321	0.8942	333.15	46.3	3.73	1.01
0.0000	0.0000	333.35	5.47		

It was not possible to reach a steady state for the methanol + 2-methoxy-2,4,4-trimethylpentane system in the composition range from x(methanol) = 0 to 0.13 with this apparatus. The measured points, x(methanol) = 0.1329, 0.1625, and 0.1928, had temperature fluctuations of ±0.5, ±0.3, and ±0.3 K, respectively, even after long equilibration periods. The relative volatility of methanol at these points has values of 55.6, 47.3, and 43.5, respectively. These results show that the still design used is best suited for measurements of systems for which the maximum relative volatility is below 40. The methanol + 2-methoxy-2,4,4-trimethylpentane system at 333 K measured did not show azeotropic behavior.

The activity coefficients for species i, γ_i, were calculated from eq 1

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

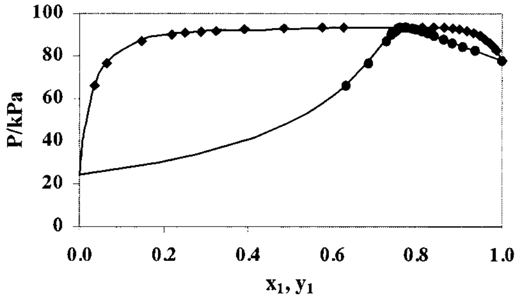

Figure 2. Pressure−composition diagram for the methanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 331 K: ♦, x_1 measured; ●, y_1 measured; —, x_1 calculated; —, y_1 calculated.

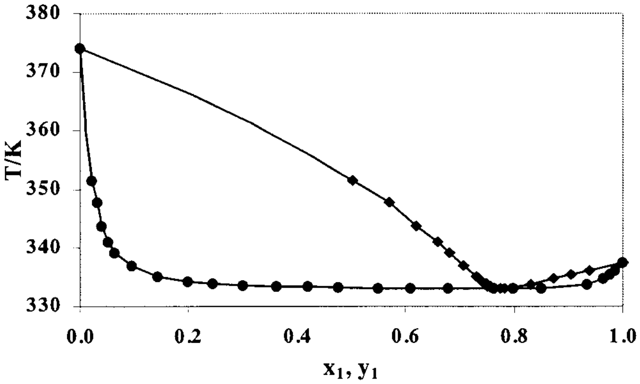

Figure 3. Temperature−composition diagram for the methanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa: ●, x_1 measured; ♦, y_1 measured; —, x_1 calculated; —, y_1 calculated.

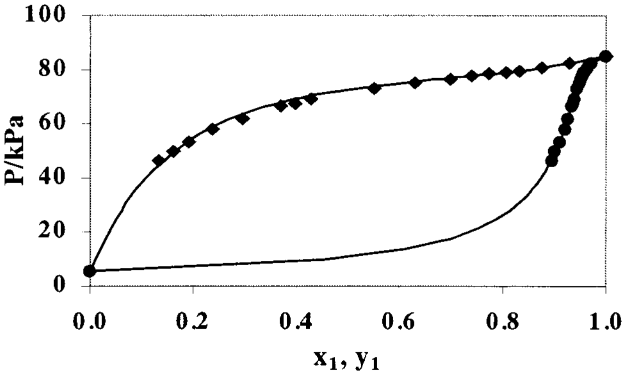

Figure 4. Pressure−composition diagram for the methanol (1) + 2-methoxy-2,4,4-trimethylpentane (2) system at 333 K: ♦, x_1 measured; ●, y_1 measured; —, x_1 calculated; —, y_1 calculated.

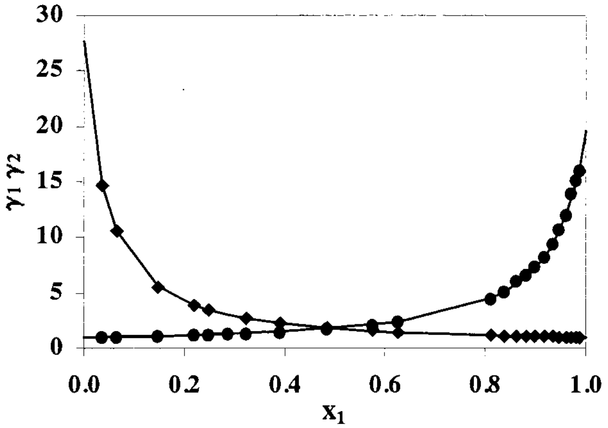

Figure 5. Activity coefficient−composition diagram for the methanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 331 K: ♦, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

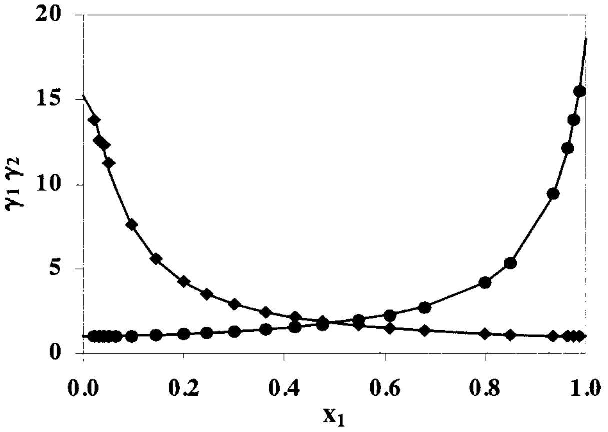

Figure 6. Activity coefficient−composition diagram for the methanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa: ♦, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

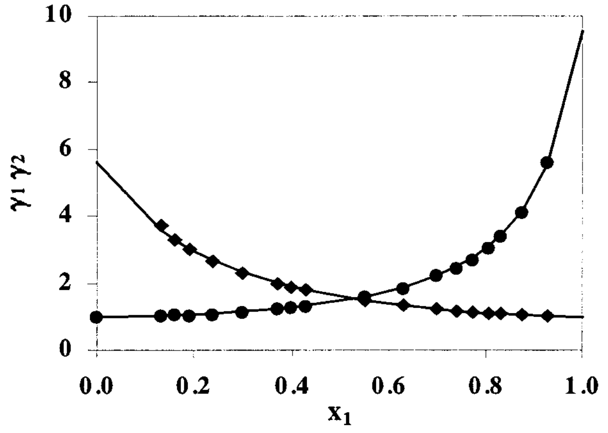

Figure 7. Activity coefficient−composition diagram for the methanol (1) + 2-methoxy-2,4,4-trimethylpentane (2) system at 333 K: ♦, γ_1 calculated from measurements; ●, γ_2 calculated from measurements; —, γ_1 predicted by the model; —, γ_2 predicted by the model.

where y_i is the mole fraction of component i in the vapor phase, P is the system total pressure, 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, $P_{\mathrm{vp}i}$ is the vapor pressure of pure component i at the system temperature, ϕ_i^{s} is the pure-component saturated liquid fugacity coefficient at the system temperature, v_i^{L} is the component-i liquid-phase molar volume at the system temperature, T is the temperature in Kelvin, and R is the universal gas constant (8.314 J K^{-1} mol^{-1}). The Soave−Redlich−Kwong equation of state with quadratic mixing rules in the attractive parameter and linear mixing rules in the covolume was used for vapor phase calculation.[6] The binary interaction parameter in the quadratic mixing rule was set to zero. The liquid phase was modeled with the Wilson equation.[7] The critical temperatures, critical pressures, critical volumes, acentric factors, and the liquid molar volumes used in the calculations are presented in Table 5. The vapor pressures of the pure substances were calculated from the Antoine equation, eq 2. The vapor pressure equation parameters were fitted from data measured with the same apparatus that was used for the VLE measure-

Table 5. Critical Temperatures T_c; Critical Pressures P_c; Critical Molar Volumes V_c; Acentric Factors ω; Liquid Molar Volumes v_i;[a] Pure-Component Vapor Pressure Equation Parameters *A*, *B*, and *C* for the Antoine Equation;[b] and Recommended Temperature Range of the Vapor Pressure Correlation T_{min} and T_{max}

component	T_c (K)	P_c (MPa)	V_c ($cm^3\ mol^{-1}$)	ω	v_i ($cm^3\ mol^{-1}$)	*A*	*B*	*C*	T_{min} (K)	T_{max} (K)
methanol	512.6 ± 5	8.096 ± 0.24	118 ± 6	0.5656	40.7 ± 0.4	9.5334[f]	3550.3[f]	−37.353[f]	295.8	377
2,4,4-trimethyl-1-pentene	553.0 ± 28[c]	2.630 ± 0.26[c]	465 ± 116[c]	0.2695[c]	157.9 ± 4.7[c]	6.9460	2999.3	−49.678	333.1	374.3
2-methoxy-2,4,4-trimethylpentane	601.5[d]	2.350[d]	535.5[d]	0.3408	181.9 ± 3.8[e]	6.5126	3000.8	−77.355	326.5	418.0

[a] Used for fitting the Wilson equation parameters. [b] Vapor pressure data measured with the apparatus used in the VLE measurements was fitted. [c] Daubert and Danner.[12] [d] Estimated Joback−Lydersen method.[13] [e] From measured density with an Anton-Paar-40 vibrating tube densimeter ($\rho = 0.793$ g cm^{-3} at 298.15 K and $M = 144.25$ g mol^{-1}). [f] Vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in Smith and Srivastava[14] at vapor pressures from 110 to 398 kPa (from 340 to 377 K).

Table 6. Pure-Component Vapor Pressures, Methanol

T (K)	*P* (kPa)	*T* (K)	*P* (kPa)
337.32	100.16	320.73	50.03
336.01	95.06	318.33	44.95
334.62	89.97	315.77	40.03
333.24	85.06	312.85	34.97
331.73	79.97	309.62	30.01
331.12	77.99	305.82	24.95
330.14	74.88	301.40	19.99
328.49	69.92	295.82	14.95
326.77	65.02	331.12	77.99
324.89	60.00	337.35	100.24
322.81	54.84		

Table 7. Pure-Component Vapor Pressures, 2-Methoxy-2,4,4-trimethylpentane

T (K)	*P* (kPa)	*T* (K)	*P* (kPa)
417.95	100.56	376.76	29.78
416.10	95.75	371.61	24.95
413.91	90.52	365.16	19.88
411.51	85.16	360.89	17.00
409.20	80.09	355.67	13.93
407.00	75.11	351.12	11.66
404.43	69.90	345.16	9.16
401.70	64.86	339.93	7.33
399.15	60.08	336.52	6.29
396.18	55.03	335.13	5.94
392.97	49.98	333.35	5.47
389.59	45.10	331.13	4.94
385.68	39.89	329.11	4.49
381.61	34.98	326.45	3.96

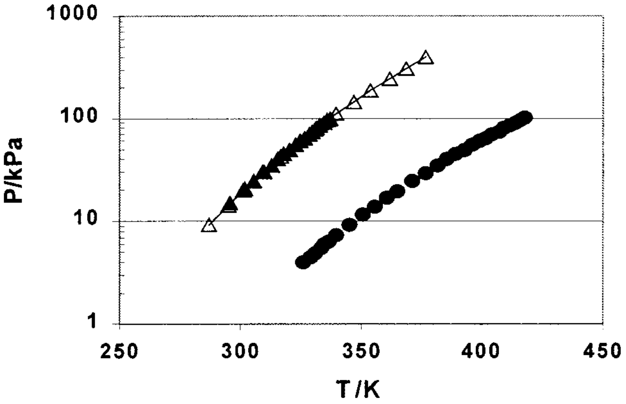

Figure 8. Vapor pressure of: ▲, methanol, this work; −△−, methanol, literature[14]; ●, 2-methoxy-2,4,4-trimethylpentane, this work.

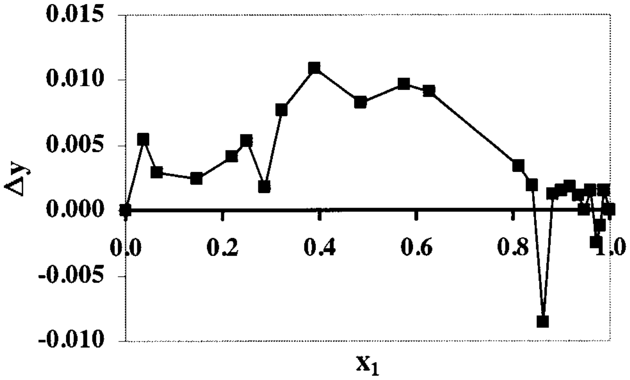

Figure 9. Point test for the methanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 331 K.

ments. The pure-component vapor pressure equation parameters with the recommended temperature range of the vapor pressure equations are also presented in Table 5. Methanol and 2-methoxy-2,4,4-trimethylpentane vapor pressure data are presented in Tables 6 and 7 and Figure 8. Pure-component vapor pressures for 2,4,4-trimethyl-1-pentene were measured previously.[8] The recommended minimum temperature of the pure-component vapor pressure equation parameters for the 2,4,4-trimethyl-1-pentene system is only to 333.1 K. If calculated vapor pressure values are compared with the measured value at 331.12 K, the difference between measured and calculated is 0.05 kPa, which makes it possible to use the vapor pressure equation parameters in Table 5 for 2,4,4-trimethyl-1-pentene in modeling the measured isothermal and isobaric data.

$$P/\text{MPa} = \exp\left[A - \frac{B}{(T/\text{K} + C)}\right] \qquad (2)$$

Both systems measured indicate positive deviations from Raoult's law. The objective function, OF, used to fit the Wilson equation parameters is presented in eq 3.[9] The Wilson equation parameters for the mixtures with the averages of the absolute values of the residuals for the vapor phase and pressure are presented in Table 8.

$$\text{OF} = \frac{1}{NN_C}\sum_{i=1}^{N}\sum_{j=1}^{N_C}(\gamma_{i,j}^{\text{model}} - \gamma_{i,j}^{\text{measured}})^2 \qquad (3)$$

where N is the number of points used in the fit and N_C is the number of components used in the fit.

The data sets measured passed the integral[10] test and the infinite dilution test.[11] The results of the integral test and the infinite dilution test are presented in Table 8. In the point test, a set of data is considered consistent[10] if the averages of the absolute values of the residuals for the vapor phase in terms of mole fraction are smaller than 0.01 by the point test. The data sets were found to satisfy the point test criterion (Table 8, Figures 9−11).

Table 8. Wilson Equation Parameters $\lambda_{ij} - \lambda_{ii}$ for the Mixtures, Averages of the Absolute Vapor Fraction Residuals Δy, Averages of Absolute Pressure Residuals ΔP for the Wilson Fit, Results of the Integral Test D, and Results of the Infinite Dilution Test I

system	$\lambda_{12} - \lambda_{11}$ (J mol^{-1})	$\lambda_{21} - \lambda_{22}$ (J mol^{-1})	ΔP or ΔT (kPa or K)	Δy	D^a (%)	I
methanol (1) + 2,4,4-trimethyl-1-pentene (2), 331 K	10454	1957.3	0.30 kPa	0.0038	0.8	pass
methanol (1) + 2,4,4-trimethyl-1-pentene (2), 101 kPa	9979.7	1916.9	0.22 K	0.0046	0.3	pass
methanol (1) + 2-methoxy-2,4,4-trimethylpentane (2), 333 K	6689.7	443.01	0.62 kPa	0.0008	2.5	pass

[a] The criterion for passing the test is $D < 10\%$.[10]

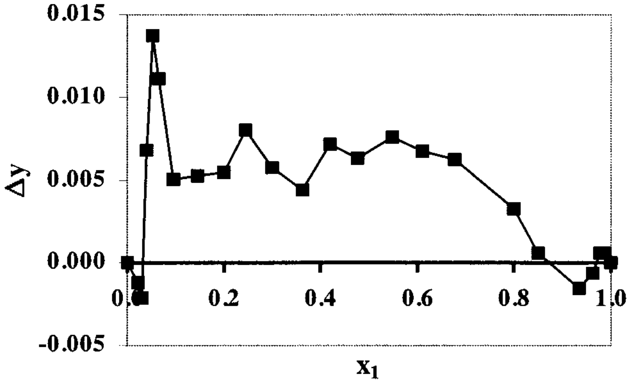

Figure 10. Point test for the methanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa.

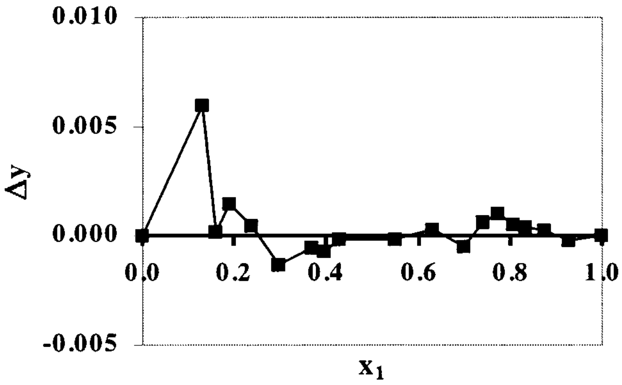

Figure 11. Point test for the methanol (1) + 2-methoxy-2,4,4-trimethylpentane (2) system at 333 K.

Acknowledgment

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