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Vapor−Liquid Equilibrium Data at 343 K and Excess Molar Enthalpy Data at 298 K for the Binary Systems of Ethanol + 2,4,4-Trimethyl-1-pentene and 2-Propanol + 2,4,4-Trimethyl-1-pentene

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Isothermal vapor−liquid equilibrium data were measured for two binary systems, ethanol + 2,4,4-trimethyl-1-pentene and 2-propanol + 2,4,4-trimethyl-1-pentene, at 343 K. The measurements were made with a circulation still. The composition of liquid and condensed vapor phase was determined with a gas chromatograph. Excess molar enthalpy data were measured for the same binary systems at 298 K. Both systems indicate positive deviations from Raoult's law and exhibit azeotropic behavior.

Introduction

Production of MTBE (2-methoxy-2-methyl-propane) has been one of the fastest growing in the past decade. It is made from isobutylene and methanol. It has caused some groundwater pollution problems,[1] particularly in California, and it is planned to be banned in California by the end of 2002. One alternative to the existing MTBE plants is to convert the production to make isooctane.[2] It is made by dimerization of isobutylene in the presence of alcohol.[2,3] That is why the behavior of alcohol and 2,4,4-trimethyl-1-pentene is of great interest today. To provide reliable data for process design purposes, both vapor−liquid equilibrium and excess enthalpy were measured.

Experimental Section

Materials for Vapor−Liquid Equilibrium (VLE) Measurements. The 2,4,4-trimethyl-1-pentene (>98% by gas chromatography (GC)) was provided by Fluka; ethanol (99.7%, GC) was provided by Oy Alko Ab; and 2-propanol (99.7%, GC) was provided by Riedel de Haën. The materials were used without further purification except for drying over molecular sieves (Merck 3A).

Materials for Excess Enthalpy (H^E) Measurements. The 2,4,4-trimethyl-1-pentene, (>98%, GC, water content 0.010 wt %, exp. density 0.7113 $g\cdot cm^{-3}$ (at 298.15 K), literature[4] 0.71089 $g\cdot cm^{-3}$), was provided by Fluka; ethanol (99.9%, GC, water content 0.012 wt %, exp. density 0.7853 $g\cdot cm^{-3}$ (at 298.15 K), literature[5] 0.78509 $g\cdot cm^{-3}$) was provided by Merck; and 2-propanol (>99.7%, GC, water content 0.008 wt %, exp. density 0.7810 $g\cdot cm^{-3}$ (at 298.15 K), literature[5] 0.78126 $g\cdot cm^{-3}$) was provided by Lachema. The water content in the chemicals was determined by the Karl Fischer titration, and their densities were measured by means of an Anton Paar vibrating-tube density meter, model DMA 5000.

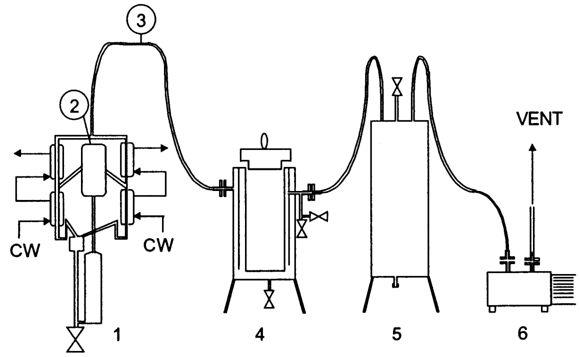

Figure 1. Experimental setup: (1) circulation still; (2) temperature probe (Pt-100); (3) pressure transducer; (4) liquid nitrogen trap; (5) buffer tank 30 dm^3; (6) vacuum pump.

Apparatus for VLE Measurements. A circulation still of the Yerazunis type[6] was built at the glass workshop of Helsinki University of Technology with minor modifications to the original design.[7] The total volume of mixture needed for the measurements was approximately 80 mL. Temperature was measured using an Ametek DTI100 temperature meter with a Pt-100 probe calibrated at the Inspecta Oy (Accredited Calibration Laboratory). The Pt-100 probe was located at the bottom of the packed section of the circulation still. The resolution of the temperature measurement system was 0.01 K, and the calibration uncertainty was ±0.05 K. The uncertainty in the temperature measurement, estimated to be ±0.07 K, was mostly due to fine-tuning of pressure at a measured isotherm.

Pressure was measured using a Druck pressure transducer (0 to 100 kPa) connected to a Red Lion panel meter. According to the data provided by the manufacturers of the pressure measurement devices, the uncertainty of the pressure measurement was ±0.07 kPa. The pressure measurement system was calibrated against a DHPPC-2 pressure calibrator. Including the calibration uncertainty, the uncertainty in the pressure measurement system is estimated to be ±0.15 kPa. An overview of our setup is presented in Figure 1.

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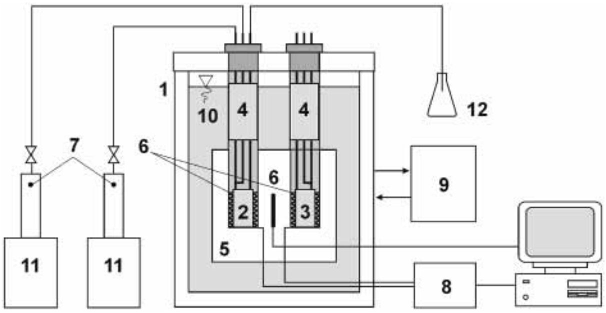

Figure 2. Schematic diagram of the flow mixing microcalorimeter setup: 1, microcalorimeter; 2, sample cell; 3, reference cell; 4, heat exchangers; 5, heat sink; 6, thermoelectric sensors; 7, thermometers; 8, differential amplifier; 9, cooling thermostat; 10, water bath; 11, HPLC syringe pumps; 12, waste bottle.

Apparatus for HE Measurements. Excess molar enthalpies were measured with an isothermal microcalorimeter model 4400 manufactured by Calorimetry Science Corp. (CSC), Provo, USA. This instrument of differential heat conduction design incorporates two test wells (sample and reference) in a large aluminum heat sink that is immersed in an ultrastable termostating bath. The microcalorimeter is equipped with flow mixing cells, model 4442, that have been reconstructed by CSC to improve their performance. Contrary to the original construction using a inefficient mixing tee, in the new design, mixing is achieved in a concentric tube arrangement in which the inner tube and the outer tube provide the inlets for the two liquids to be mixed.

A schematic diagram of the flow mixing microcalorimeter assembly is given in Figure 2. Two high-pressure liquid chromatography syringe pumps, model HPP 5001 by Laboratorní Přístroje (Praha, Czech Republic), were employed to inject the components into the calorimeter. The components are continuously delivered into the sample cell at a constant total flow rate chosen from the range 0.20 to 0.31 mL·min^{-1}, whereas the ratio of individual flow rates is varied to carry out measurements for different compositions. The flow rates can be set with the resolution of 0.01 mL·min^{-1}, and the temperature of the fluid in the pump cylinder is measured with a digital thermometer. Calibration of the pump flow rates was done by flowing water through the system while timing and then weighing the delivered amount. Replicates showed flow rate reproducibility within 0.3%. The reference cell, which is used to compensate for electronic noise and any heat flux due to temperature fluctuations in the heat sink, is left empty. The differential signal from the calorimeter test wells thus corresponds to the rate of heat production from the sample cell itself. The signal is calibrated using a Joule effect produced by a built-in calibration heater on the pure liquid (before and after each set of experiments). Data acquisition and calibration is controlled by a PC. Details concerning the calorimeter are given elsewhere.[8]

Table 1. Isothermal VLE Data, Liquid Phase (x_1), and Vapor Phase (y_1), Mole Fractions, Pressure (P), Temperature (T), and Activity Coefficient (γ_i) for the Ethanol (1) + 2,4,4-Trimethyl-1-pentene (2) System

x_1	y_1	T/K	P/kPa	γ_1	γ_2
0.000	0.000	343.43	38.4		1.00
0.028	0.353	343.53	57.7	10.05	0.99
0.050	0.444	343.53	67.9	8.14	1.02
0.097	0.523	343.45	77.5	5.70	1.05
0.153	0.564	343.46	82.9	4.16	1.09
0.230	0.593	343.42	86.7	3.05	1.17
0.297	0.610	343.48	88.9	2.48	1.25
0.363	0.623	343.42	90.0	2.10	1.35
0.413	0.630	343.43	90.7	1.88	1.45
0.507	0.644	343.44	91.7	1.59	1.68
0.546	0.649	343.43	91.9	1.49	1.81
0.578	0.655	343.43	92.1	1.42	1.92
0.628	0.662	343.43	92.3	1.32	2.12
0.668	0.670	343.43	92.1	1.26	2.32
0.714	0.680	343.43	92.0	1.19	2.62
0.754	0.691	343.43	91.6	1.14	2.93
0.793	0.707	343.43	91.1	1.11	3.28
0.831	0.723	343.43	90.3	1.07	3.76
0.868	0.748	343.44	88.9	1.04	4.33
0.895	0.767	343.43	87.4	1.02	4.93
0.917	0.791	343.43	85.8	1.01	5.53
0.960	0.864	343.43	81.1	0.99	7.04
0.978	0.918	343.43	78.0	1.00	7.39
0.989	0.957	343.44	75.6	1.00	7.83
0.997	0.988	343.43	73.8	1.00	7.47
1.000	1.000	343.43	73.0	1.00	

Table 2. Isothermal VLE Data, Liquid Phase (x_1), and Vapor Phase (y_1), Mole Fractions, Pressure (P), Temperature (T) and Activity Coefficient (γ_i) for the 2-Propanol (1) + 2,4,4-Trimethyl-1-pentene (2) System

x_1	y_1	T/K	P/kPa	γ_1	γ_2
0.000	0.000	343.43	38.2		1.00
0.023	0.205	343.43	47.3	6.95	1.00
0.057	0.336	343.43	55.9	5.43	1.02
0.099	0.407	343.43	61.9	4.16	1.05
0.153	0.461	343.43	65.9	3.23	1.08
0.199	0.489	343.43	68.4	2.74	1.12
0.255	0.511	343.43	70.5	2.30	1.19
0.309	0.533	343.43	71.9	2.02	1.25
0.368	0.557	343.43	73.0	1.80	1.31
0.423	0.570	343.43	74.2	1.63	1.42
0.482	0.590	343.43	74.9	1.49	1.52
0.537	0.607	343.43	75.3	1.38	1.64
0.597	0.625	343.43	75.5	1.29	1.80
0.654	0.645	343.43	75.5	1.21	1.98
0.686	0.656	343.43	75.5	1.17	2.12
0.729	0.674	343.44	75.3	1.13	2.31
0.774	0.697	343.43	74.7	1.09	2.57
0.816	0.718	343.43	73.9	1.06	2.91
0.850	0.741	343.44	73.0	1.03	3.24
0.881	0.773	343.43	71.6	1.02	3.52
0.912	0.799	343.43	70.0	1.00	4.10
0.941	0.842	343.43	67.9	0.99	4.70
0.988	0.961	343.43	63.1	1.00	5.13
1.000	1.000	343.44	61.3	1.00	

Analysis of VLE and GC Calibration. The condensed vapor phase and the liquid phase were analyzed with a HP 6850A gas chromatograph with an autosampler and a flame ionization detector (FID). The GC column used was a HP-1 (methyl siloxane, length 30 m, nominal diameter 320 μm, nominal film thickness 0.25 μm). The oven temperature was 100 °C; run time, 9 min; inlet split ratio, 50:1; carrier gas, He (1.4 mL·min^{-1}); FID temperature, 250 °C. Toluene was used as a solvent for the samples to reduce the volume of the sample. Gravimetric calibration mixtures were prepared in 2 mL vials with approximately 1 mL of toluene as a solvent. The response factors [9] were calculated from

$$\frac{A_1}{A_2}\frac{F_1}{F_2} = \frac{x_1}{x_2} \tag{1}$$

where A_1 and A_2 are the GC peak areas, F_1 and F_2 are response factors, and x_1 and x_2 are mole fractions of components 1 and 2, respectively. The nine gravimetrically prepared samples per binary system were analyzed, and then the ratio of A_1/A_2 was plotted as a function of x_1/x_2. The slope of the regressed linear trend is F_2/F_1 and the

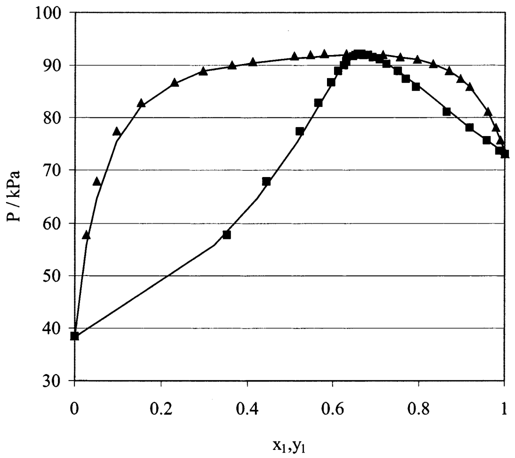

Figure 3. Pressure−composition diagram for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343 K: ▲, x_1; ■, y_1; —, x_1, y_1 by the Wilson model.

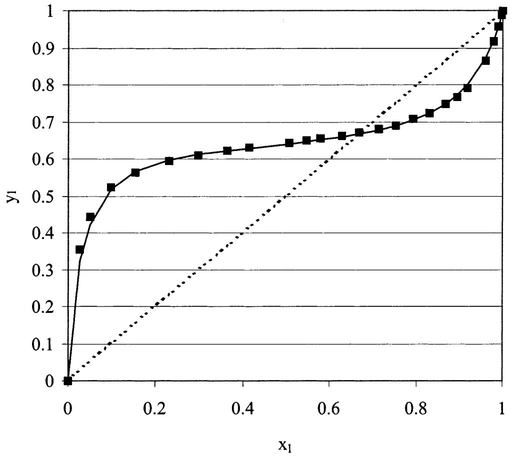

Figure 4. Vapor−liquid composition diagram for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343 K: ■, y_1; —, y_1 by the Wilson model.

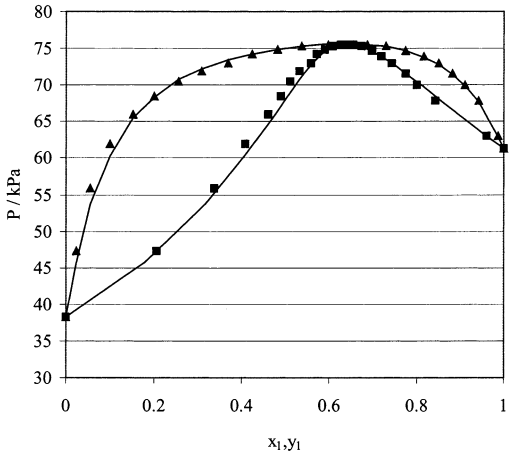

Figure 5. Pressure-composition diagram for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343 K: ▲, x_1; ■, y_1; —, x_1, y_1 by the Wilson model.

deviation from origin is called bias. The bias was very small and ignored. Composition of component 1 was solved from

$$x_1 = \frac{A_1F_1}{A_2F_2}\bigg/\left(1 + \frac{A_1F_1}{A_2F_2}\right) \qquad (2)$$

Procedure. Pure component 1 was introduced to the circulation still, and its vapor pressure was measured. After vapor pressure measurements, component 2 was added to the still. The temperature was adjusted to the desired value by adjusting the pressure of the system. Two manual valves, a small globe valve at the top of the buffer tank and a small needle valve between liquid nitrogen trap and buffer tank are adjusted manually, see Figure 1. The small needle valve was used for a fine-tuning of pressure to meet the isotherm. At steady state, it was possible to fine-tune

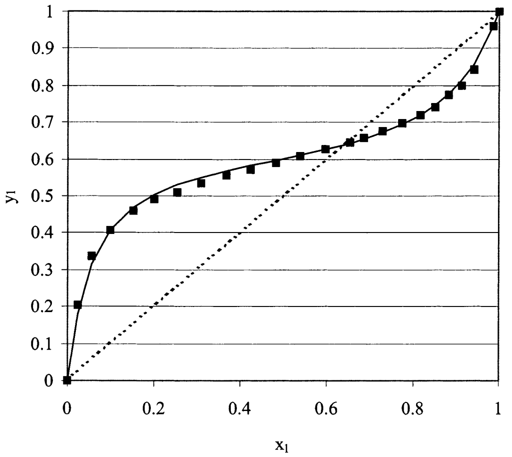

Figure 6. Vapor−liquid composition diagram for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343 K: ■, y_1; —, y_1 by the Wilson model.

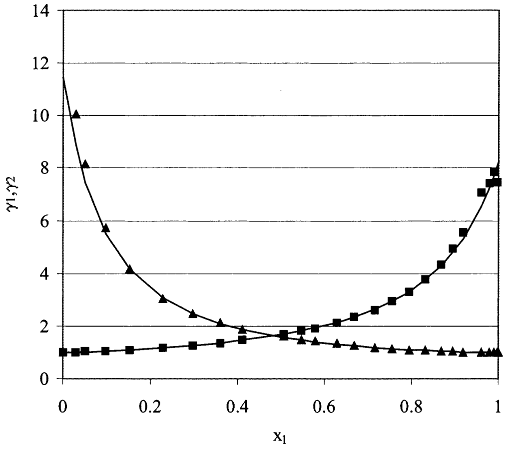

Figure 7. Activity coefficient-composition diagram for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343 K: ▲, γ_1 from data; ■, γ_2 from data; —, γ_1, γ_2 by the Wilson model.

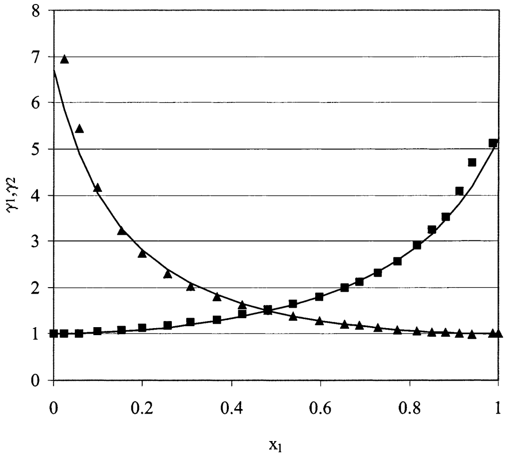

Figure 8. Activity coefficient-composition diagram for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343 K: ▲, γ_1 from data; ■, γ_2 from data; —, γ_1, γ_2 by the Wilson model.

Table 3. Wilson Interaction Parameters ($\lambda_{12}-\lambda_{11}$) and ($\lambda_{21}-\lambda_{22}$) for Ethanol + 2,4,4-Trimethyl-1-pentene (System 1) and 2-Propanol + 2,4,4-Trimethyl-1-pentene (System 2) $\lambda_{12}-\lambda_{11} = a_{0,12} + a_{1,12}T + a_{2,12}T^2$, $\lambda_{21}-\lambda_{22} = a_{0,21} + a_{1,21}T + a_{2,21}T^2$

	$a_{0,12}$[a]	$a_{1,12}$[b]	$a_{2,12}$[c]	$a_{0,21}$[a]	$a_{1,21}$[b]	$a_{2,21}$[c]
system 1	5773.6	22.4412	−0.0488	1071.1	2.42855	−0.009
system 2	5718.7	17.8814	−0.0517	842.67	0.66721	−0.0042

[a] In units of $\mathrm{J{\cdot}mol^{-1}}$. [b] In units of $\mathrm{J{\cdot}mol^{-1}K^{-1}}$. [c] In units of $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-2}}$.

Table 4. Physical Property Data for Pure Components[a]

component	ethanol	2-propanol	2,4,4-trimethyl-1-pentene
T_c/K	516.25 ± 5.16[b]	508.31 ± 5.1[b]	553.00 ± 28[b]
P_c/MPa	6.3835 ± 0.19[b]	4.764 ± 0.14[b]	2.630 ± 0.26[b]
V_c/cm^3·mol^{-1}	166.92 ± 8.3[b]	220.13 ± 11[b]	465 ± 116[b]
ω	0.6371[b]	0.6689[b]	0.2695[b]
v_i/cm^3·mol^{-1}	58.515 ± 0.58[b]	76.784 ± 0.15[b]	157.9 ± 4.7[b]
A	9.98531[c]	9.78226[c]	6.9460[d]
B	3799.739[c]	3635.779[c]	2999.3[d]
C	−41.8417[c]	−54.2868[c]	−49.678[d]
T_{min}/K	316[c]	333[c]	333.11[d]
T_{max}/K	351[c]	355[c]	374.33[d]
T_b/K	351.4[c]	355.47[c]	374.44[d]
T_b/K	351.44[b]	355.41[b]	374.33[d]

[a] Critical temperature (T_c), critical pressure (P_c), critical molar volumes (V_c), acentric factor (ω), liquid molar volume (v_i), pure component vapor pressure equation parameters (A, B, and C) for the Antoine equation (vapor pressure data measured), recommended temperature range of the vapor pressure correlation (T_{min} and T_{max}), and normal boiling point, (T_b). [b] Daubert and Danner.[17] [c] This work. [d] Uusi-Kyyny et al.[7]

Table 5. Experimental Vapor Pressures of Pure Components

ethanol				2-propanol			
T/K	P/kPa	T/K	P/kPa	T/K	P/kPa	T/K	P/kPa
316.30	21.07	345.48	79.75	333.72	39.54	349.48	79.34
326.49	34.61	346.68	83.77	340.98	55.03	351.19	85.15
335.03	51.22	348.31	89.52	343.19	60.66	352.63	90.34
338.70	59.97	348.87	91.55	344.86	65.23	353.46	93.41
342.65	70.90	349.49	93.88	346.33	69.47	355.42	101.07
344.11	75.37	351.36	101.18	348.21	75.27		
344.57	76.84						

the pressure in ±0.01 kPa, but taking into account the uncertainty ±0.15 kPa in pressure measurements system, we estimate the oscillations in temperature to be ±0.07 K. For the most part, uncertainty in pressure and the boiling of the mixture inside the still caused the oscillations in temperature. Before sampling, a steady state condition was maintained for approximately 35 min by adjusting the pressure of the system. Approximately 1 mL of toluene was added to the 2 mL autosampler vials before sampling was carried out. Sample 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 to 0.2 mL of sample, and then a 0.4 to 0.5 mL sample was taken and injected to the cooled 2 mL autosampler vial.

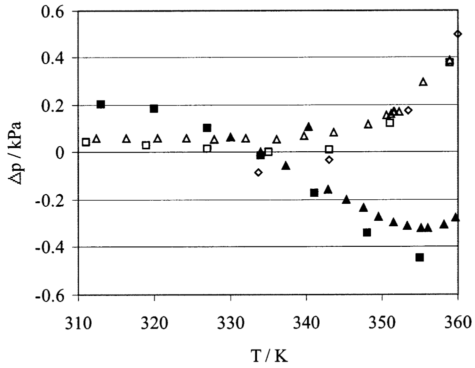

Figure 9. Deviation plot (p, literature − p, this work) of vapor pressure of ethanol and 2-propanol compared to earlier measurements: □, Smith,[12] ethanol; △, Ambrose,[13] ethanol; ◇, Sauermann,[14] ethanol; ■, Smith,[12] 2-propanol; ▲, Ambrose,[13] 2-propanol.

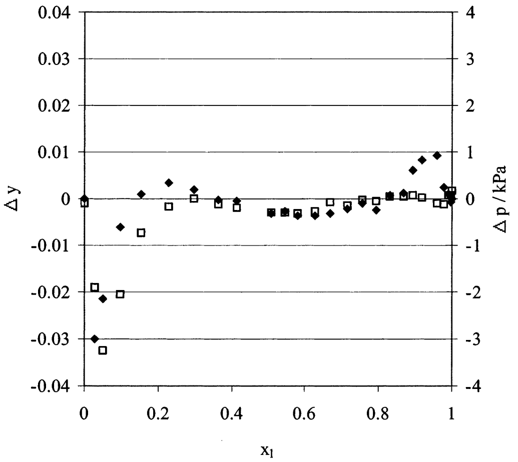

Figure 10. Point test for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343.43 K: ◆, Δy; □, Δp.

Table 6. Results of the Consistency Tests for Ethanol + 2,4,4-Trimethyl-1-pentene (System 1) and 2-Propanol + 2,4,4-Trimethyl-1-pentene (System 2) at 343.43 K

binary pair	integral test	infinite dilution test	point test
system 1	0.02%	22.3% ($x(1) = 0$)	$\lvert\Delta y_{\mathrm{aver}}\rvert = 0.004$
		29.6% ($x(1) = 1$)	$\lvert\Delta p_{\mathrm{aver}}\rvert = 0.41$ kPa
system 2	3.09%	17.6% ($x(1) = 0$)	$\lvert\Delta y_{\mathrm{aver}}\rvert = 0.008$
		25.6% ($x(1) = 1$)	$\lvert\Delta p_{\mathrm{aver}}\rvert = 0.35$ kPa

Results and Discussion

The measured data and calculated activity coefficients are reported in the Tables 1 and 2 and shown in Figures 3−8. Both systems indicate positive deviations from Raoult's law. Azeotropic behavior was observed for both the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) (T = 343.43 K, p = 92.1 kPa, x_1 = 0.66) and the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) (T = 343.43 K, p = 75.5 kPa, x_1 = 0.65) system. The azeotropic data were interpolated graphically from measured values. The activity coefficients for the species i, were calculated from

$$y_i P \phi_i = \gamma_i x_i P_{vpi} \phi_i^{s} \exp \int_{P_{\mathrm{vp}i}}^{P} \frac{v_{L,i}}{RT}\, \mathrm{d}P \qquad (3)$$

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 mole fraction of the 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, $v_{L,i}$ is the component i liquid-phase molar volume at the system temperature, T is temperature in Kelvin, and R is the universal gas constant (8.31441 J K^{-1} mol^{-1}). The Soave−Redlich−Kwong (SRK) equation of state with quadratic mixing rules in the attractive parameter and linear in covolume was used to calculate fugacity coefficients.[10] The binary interaction parameters of the SRK equation were set to zero for these two systems. It was found that SRK binary interac-

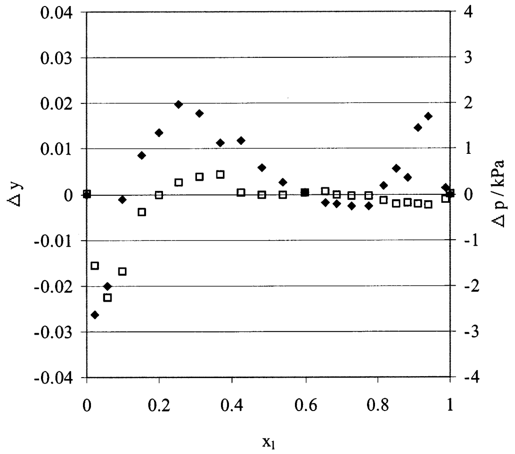

Figure 11. Point test for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 343.43 K: ◆, Δy; □, Δp.

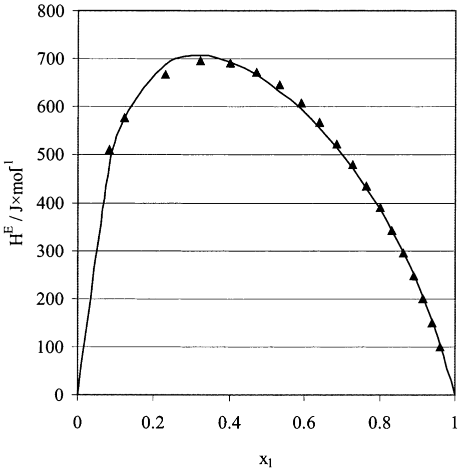

Figure 12. Excess molar enthalpy for ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 298.15 K: ▲, measured; —, by the Wilson model.

Table 7. Excess Molar Enthalpy for Ethanol (1) + 2,4,4-Trimethyl-1-pentene (2) (System 1) and 2-propanol (1) + 2,4,4-Trimethyl-1-pentene (2) (System 2) at 298.15 K

system 1				system 2			
x_1	H^E J·mol^{-1}	x_1	H^E J·mol^{-1}	x_1	H^E J·mol^{-1}	x_1	H^E J·mol^{-1}
0.0817	510.9	0.7274	479.8	0.0646	522.1	0.6711	671.3
0.1231	577.5	0.7654	434.6	0.0983	618.6	0.7137	606.2
0.2287	667.5	0.8001	388.8	0.1858	778.0	0.7537	541.6
0.3201	694.4	0.8321	342.1	0.2655	858.2	0.7911	470.6
0.4001	691.6	0.8616	294.6	0.3384	896.4	0.8264	400.2
0.4707	671.8	0.8889	246.2	0.4052	899.7	0.8595	333.1
0.5334	645.1	0.9144	198.5	0.4668	881.4	0.8908	258.7
0.5896	608.4	0.9380	148.6	0.5236	848.5	0.9203	197.2
0.6401	566.7	0.9600	99.0	0.5765	799.0	0.9483	125.8
0.6858	522.7			0.6254	740.0	0.9748	62.3

tion parameters had minor effect on the objective function. The activity coefficients of liquid phase were modeled using a Wilson equation[11] and drawn in Figures 7 and 8. The parameters of the Wilson model are given in Table 3. The critical temperature, critical pressure, critical volume, acentric factor, and liquid molar volume for each component needed in the calculation are presented in Table 4. The vapor pressure of the pure substances was calculated from Antoine type equation

$$P/\mathrm{MPa} = \exp\left(A - \frac{B}{(T/\mathrm{K} + C)}\right) \tag{4}$$

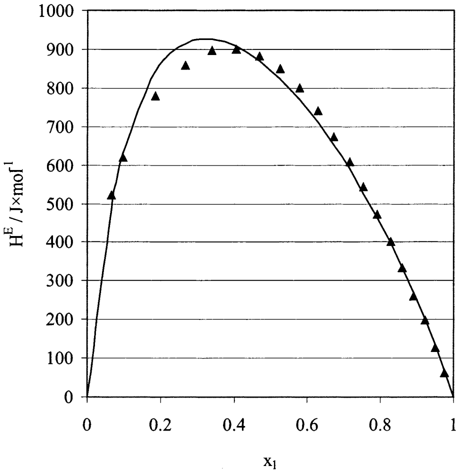

Figure 13. Excess molar enthalpy for 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 298.15 K: ▲, measured; —, by the Wilson model.

The parameters of this equation were optimized with the data measured in our apparatus. These parameters with the recommended temperature range of the vapor pressure equations are also presented in Table 4. Pure component vapor pressure for 2,4,4-trimethyl-1-pentene was measured earlier,[7] and ethanol and 2-propanol vapor pressure data measured in this work are presented in Table 5. Comparisons to earlier measurements for ethanol[12,13,14] and 2-propanol[12,13] are shown in Figure 9.

For the fitting the Wilson equation parameters, both the VLE and HE data were used simultaneously. The following objective function was used:

$$\mathrm{O.F.} = \frac{1}{N_{\mathrm{VLE}}}\sum_{1}^{N_{\mathrm{VLE}}}\frac{(P_{i,\mathrm{model}} - P_{i,\mathrm{meas}})}{P_{i,\mathrm{meas}}} + \frac{1}{N_{\mathrm{HE}}}\sum_{1}^{N_{\mathrm{HE}}}\frac{(H^E_{i,\mathrm{model}} - H^E_{i,\mathrm{meas}})}{H^E_{i,\mathrm{meas}}} \tag{5}$$

where, the excess enthalpy was computed from the relation

$$H^E = -RT^2\left(\sum_{i=1}^{NC} x_i \frac{\partial(\ln\gamma_i)}{\partial T}\right)_{p,x} \tag{6}$$

The consistency was tested with integral test,[15] infinite dilution test,[16] and point test.[15] Results of these tests are collected in Table 6. The Wilson equation with optimized parameters was used in the point test, and polynomials in the integral and infinite dilution tests. Both systems passed the integral test. At the high mole fractions of alcohol, the infinite dilution test is worse than at low mole fractions of alcohol. However, the infinite dilution test was passed. The point test was not properly passed because there are some points where the pressure deviation is greater than the uncertainty (±0.15 kPa) in pressure measurement. This is shown in Figures 10 and 11.

Measured molar excess enthalpy data are presented in Table 7 and Figures 12 and 13. The modeling shows a good agreement both in the excess enthalpy and in the VLE data.

Literature Cited

(1) California Energy Commission. *Commission Findings: Timetable for the Phaseout of MTBE from California's Gasoline Supply, Docket NO. 99-GEO-1*, 1999.

(2) Sloan, D.; Birkhoff, R.; Gilbert, M.; Nurminen, M.; Pyhälahti, A. *Isooctane Production from C4's as an Alternative to MTBE*; National Petrochemical & Refiners Association Paper AM-00−34; NPRA: Washington, DC, 2000.

(3) Jakobsson, K.; Pyhälahti, A.; Pakkanen, S.; Keskinen, K.; Aittamaa, J. Modelling of a side reaction configuration combining reaction and distillation. *Chem. Eng. Sci.* **2002**, *57*, 1521−1524.

(4) Camin, D. L.; Rossini, F. D. *J. Chem. Eng. Data* **1960**, *5*, 368−372

(5) Frenkel, M., ed.; *TRC Thermodynamic Tables Non-Hydrocarbons*; Thermodynamic Research Center: College Station, TX, 1999.

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

(7) Uusi-Kyyny, P.; Pokki, J.-P.; Aittamaa, J.; Liukkonen, S. Vapor Liquid Equilibrium for the Binary Systems of 2-Methyl-2-propanol + 2,4,4-Trimethyl-1-pentene at 333 K and 348 K and 2-Butanol + 2,4,4-Trimethyl-1-pentene at 360. *J. Chem. Eng. Data* **2001**, *46*, 686−691.

(8) Fenclová, D.; Vrbka, P.; Dohnal, V.; Řehák, K.; Miaja, G. G. (Vapour + liquid) equilibria and excess molar enthalpies for mixtures with strong complex formation. Trichloromethane or 1-bromo-1-chloro-2,2,2-trifluoroethane (halothane) with tetrahydropyran or piperidine, *J. Chem. Thermodyn.* **2002**, *34*, 361−376.

(9) Raal, J. D.; Mühlbauer, A. L. *Phase Equilibria, Measurement and Computation*; Taylor & Francis, Washington DC, 1998.

(10) Soave, G. Equilibrium Constants from a Modified Redlich − Kwong Equation of State. *Chem. Eng. Sci.* **1972**, *27*, 1197−1203.

(11) 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.

(12) Smith, B. D.; Srivastava, R. *Thermodynamic Data for Pure Compounds, Part A Hydrocarbons and Ketones, Physical Sciences Data 25*; Elsevier: Amsterdam, 1986.

(13) Ambrose, D.; Sprake, H. S. Thermodynamic properties of organic oxygen compounds, XXV. Vapour pressures and normal boiling temperatures of aliphatic alcohols. *J. Chem. Thermodyn.* **1970**, *2*, 631−645.

(14) Sauermann, P.; Holzapfel, K.; Oprzynski, J.; Kohler, F.; Poot, W.; de Loos, T. W. The pρT properties of ethanol + hexane. *Fluid Phase Equilib.* **1995**, *112*, 249−272.

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

(16) Kojima, K.; Moon, H.; Ochi, K. Thermodynamic Consistency Test of Vapor-Liquid Equilibrium Data. *Fluid Phase Equilib.* **1990**, *56*, 269−284.

(17) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere: New York, 1989.

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