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Vapor Liquid Equilibria for Ethanol + 2,4,4-Trimethyl-1-pentene and 2-Propanol + 2,4,4-Trimethyl-1-pentene at 101 kPa

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Isobaric vapor liquid equilibrium (VLE) data were measured for the systems ethanol + 2,4,4-trimethyl-1-pentene and 2-propanol + 2,4,4-trimethyl-1-pentene at 101 kPa. The measurements were made with a recirculation still. The determination of the equilibrium compositions was made with two analyzers, a mass spectrometer, and a gas chromatograph. Two novel sampling systems were tested for introducing the samples of liquid and condensed vapor phases to the analyzers. The VLE data were correlated with the Wilson activity coefficient model and the Soave−Redlich−Kwong equation of state.

Introduction

Demand for MTBE (2-methoxy-2-methyl-propane) has been one of the most growing in the last century. Its use has created serious concerns, particularly in California, where the groundwater sources of the Santa Barbara area were polluted. Consequently, MTBE was banned in California originally by the end of 2002,[1] but the ban has been recently postponed by one year.[2] The consumption[3] of MTBE in California was about 3.7 million gallons per day during the last quarter of 2001. One alternative replacement for MTBE is isooctane.[4,5] The design and optimization of this new production scheme require a knowledge of the physical properties reported in this article. Data for the systems measured were not available in the literature.

VLE measurements made with a recirculation still require analysis of the circulating phases. For the analysis of organic mixtures, gas chromatography is the method employed most widely.[6] In this work, VLE measurements were made and two different analysis methods, gas chromatography (GC) and mass spectrometry (MS), were used for analyzing the composition of the samples from the equilibrium still. Mass spectrometry has been used as an analysis method in high-pressure fluid phase equilibria.[7] To our knowledge it has not been used for analyzing organic samples from VLE experiments at atmospheric pressure. Continuous analysis of samples from a recirculation apparatus with a refractometer has also been reported.[8] When measuring the first two data sets, GC analysis was used for the systems measured (2-propanol + 2,4,4-trimethyl-1-pentene and ethanol + 2,4,4-trimethyl-1-pentene systems). The VLE measurements were repeated with runs in which the samples were analyzed with mass spectrometry (2-propanol + 2,4,4-trimethyl-1-pentene and ethanol + 2,4,4-trimethyl-1-pentene systems). The goal of these experiments was to test if it was possible to use mass spectrometry to analyze samples from VLE measurements and also to produce data of industrial interest.

Experimental Section

Materials. The ethanol (99.7%, by volume) was provided by Oy Primalco Ab, and 2,4,4-trimethyl-1-pentene was provided by Fluka (99.5%, GC). The 2-propanol was provided by Riedel de Haën (99.7%, GC). The materials were used without further purification except for drying over molecular sieves (Merck 3A).

Apparatus. A recirculation still of the Yerazunis type[9,10] was used. The liquid volume needed for running the apparatus was approximately 80 mL. Small magnetic stirrers were used in order to enhance mixing in the sampling chambers and in the mixing chamber. For the 2-propanol + 2,4,4,-trimethyl-1-pentene system (GC analysis), the temperature measurements were made with a Thermolyzer S2541 (Frontek) temperature meter (resolution 0.005 K) equipped with a Pt-100 probe. For the other system, an AMETEK DT-100 temperature meter equipped with a Pt-100 probe was used. The temperature meters were calibrated at an accredited calibration laboratory (Inspecta Oy), 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 measurement was done with a Druck pressure transducer (0 to 100) kPa and 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.

Analysis and Calibration

Gas Chromatographic Analysis. The condensed vapor phase and the liquid phase of the 2-propanol + 2,4,4-trimethyl-1-pentene and ethanol + 2,4,4-trimethyl-1-pentene systems were analyzed with a HP 6850A gas chromatograph with an autosampler, a liquid sample valve, and a flame ionization detector. The GC column used was a

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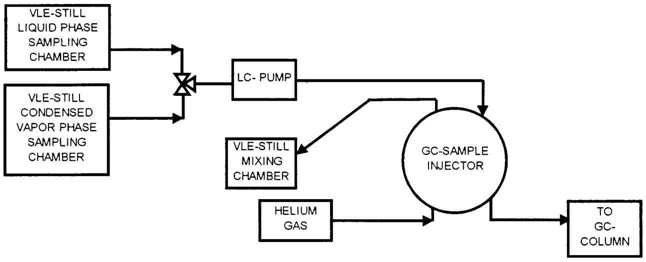

Figure 1. GC sampling system.

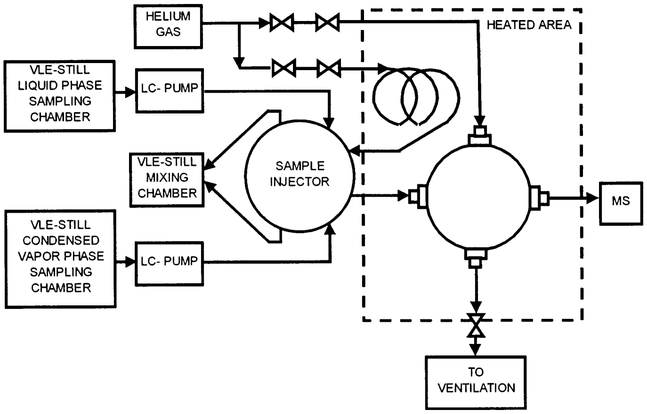

Figure 2. Sampling system for mass spectrometric analysis.

HP-1 (cross-linked methylsiloxane, 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. The calibration and sampling procedures were similar to those for earlier measurements.[10,11] The gravimetric calibration mixtures were prepared in 2 mL vials with approximately 1 mL of toluene as a solvent for the GC calibration.

On-Line Gas Chromatographic Analysis. For the ethanol + 2,4,4-trimethyl-1-pentene system gravimetric calibration mixtures were prepared in 10 mL vials. The calibration mixtures were pumped to the GC sampling valve, and the analysis was repeated three times. The uncertainty of the analysis for the systems measured with GC is estimated to be less than 0.004 in mole fraction. The uncertainty results from uncertainties of calibration and sampling. The sampling system is presented in Figure 1. The sampling lines were connected to a GC liquid sampling valve, and only one LC pump was used. The on-line GC system was not acceptable due to the large hold-up in the circulating lines. The total composition of the circulating mixture changed, when the position of the three-way valve was switched, equilibrium points of the vapor and the liquid phases did not correspond, and a slight shift in temperature was also noted. Both phases should be continuously circulated in order to minimize the change in the circulating mixture.

Mass Spectrometric Analysis. The VLE measurements of the 2-propanol + 2,4,4-trimethyl-1-pentene system and the ethanol + 2,4,4-trimethyl-1-pentene system were repeated, and the samples were analyzed with a mass spectrometer. The sampling system enables an extraction of samples from both phases on-line. The problems resulting from the change of total composition in the equilibrium still are avoided by continuous recirculation of both phases. The sampling system used is presented schematically in Figure 2. The sampling system consisted of a Valco dual microvolume sample injector (0.2 μL) with a microelectric actuator and a sample dilutor. The volume of the dilutor was approximately 25 cm^3 in the 2-propanol + 2,4,4-trimethyl-1-pentene runs. The dilutor was locally manufactured in the workshop of the Department of Chemical Technology. The dilutor was placed in a temperature-controlled, electrically heated box, and the temperature of the dilutor was held at 473 K. The mass spectrometer was calibrated for the 2-propanol + 2,4,4-trimethyl-1-pentene system with gravimetrically prepared calibration mixtures in 10 mL vials. The calibration mixtures were pumped through the sample injector and injected into the dilutor with the carrier gas (He 5.7, AGA). The flow rate of the carrier gas was approximately 7.5 mL·min^{-1}. The sampling procedure was as follows: the flushing line of the dilutor was first closed, and a waiting period of 10 s was used to release a possible small overpressure condition; the sample was flushed into the dilutor chamber by pushing the injector actuator switch, and simultaneously the outlet line valve was closed; the intensities of the selected ions were tracked, and after they reached a maximum and the intensities were decreasing, the outlet and the flushing valves were reopened (usually after 2 min); the flushing took approximately 1 min; from the beginning to the end the whole sampling sequence took approximately 3 min. The problem associated with this sampling system was that the repeatability of the samples was not better than that for the GC analysis. This is believed to be caused by the small volume of the sample cavity (0.2 μL).

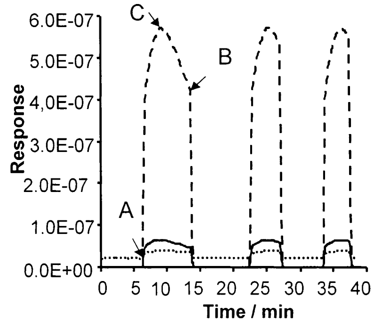

Figure 3. SIM chromatogram of a VLE experiment in which a calibration standard (60 mol % TMP and 40 mol % ethanol) was measured by mass spectrometry. Ions recorded were as follows: - - -, *m*/*z* 57 for 2,2,4-trimethyl-1-pentene; —, *m*/*z* 45 for ethanol; · · ·, *m*/*z* 18 for background. (A) The sample injector is operated, and the calibration mixture is released into the dilution chamber; simultaneously the valve of the ventilation line is closed. (B) The valve of the flushing gas is opened, and the valve of the ventilation line is opened, and the whole dilution chamber is flushed rapidly with helium. (C) The time when the concentration of a compound reaches its maximum as the compound is first vaporized into the dilution chamber while a small flow of helium is purged into the chamber; the measurement contains three successive repetitions of the same calibration mixture.

For the ethanol + 2,4,4-trimethyl-1-pentene runs two minor modifications to the sampling system were made; namely, the volume of the sample cavity was increased to 2 μL and the dilutor volume was increased to approximately 50 cm^3. The calibration mixtures were made in 10 mL vials, and the mixtures were injected into the sample cavity with a syringe manually, instead of by pumping. The samples from the actual experimental run were also taken with a syringe, and they were injected manually into the sample cavity. Only one sampling cavity was used in these experiments. The flushing time for this system was approximately 2 min, and the maximum intensity was reached after 5 min. Seven minutes was required to complete a single analysis from the beginning to the end. The repeatability of the new sampling system was better than that for the earlier MS sampling system. The sam-

Table 1. 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 Ethanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 101 kPa Analyzed by GC

x_1	y_1	*T*/K	P^a/kPa	γ_1	γ_2
0.0000	0.0000	374.50	101.2		1.00
0.0218	0.2413	364.14	100.4	6.90	1.03
0.0430	0.3824	357.73	100.4	6.98	1.03
0.0727	0.4723	353.08	100.4	6.06	1.05
0.1475	0.5537	348.92	100.4	4.11	1.11
0.2186	0.5843	347.49	100.4	3.09	1.18
0.2806	0.6037	346.92	100.4	2.55	1.24
0.3321	0.6135	346.47	100.4	2.23	1.33
0.3866	0.6270	346.18	100.4	1.98	1.41
0.4345	0.6328	346.00	100.5	1.79	1.51
0.4860	0.6402	345.84	100.5	1.63	1.64
0.5233	0.6476	345.92	101.3	1.54	1.74
0.5330	0.6490	345.73	100.5	1.51	1.77
0.5763	0.6549	345.66	100.5	1.42	1.92
0.6065	0.6613	345.80	101.3	1.36	2.03
0.6475	0.6693	345.78	101.3	1.29	2.22
0.6828	0.6777	345.78	101.3	1.24	2.40
0.7462	0.6937	345.87	101.3	1.16	2.85
0.7893	0.7069	346.00	101.3	1.11	3.27
0.8275	0.7234	346.22	101.3	1.07	3.74
0.8580	0.7395	346.51	101.3	1.05	4.24
0.8852	0.7560	346.87	101.3	1.02	4.86
0.9102	0.7859	347.37	101.3	1.01	5.36
0.9327	0.8108	347.94	101.3	1.00	6.21
0.9747	0.8971	349.70	101.5	0.99	8.51
1.0000	1.0000	351.43	100.9	1.00	

[a] Atmospheric pressure changed during the experiment.

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 Ethanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 101 kPa Analyzed by MS

x_1	y_1	*T*/K	P^a/kPa	γ_1	γ_2
0.0000	0.0000	373.11	97.6		1.00
0.0901	0.5370	350.23	98.2	6.07	1.01
0.2560	0.6123	346.56	98.3	2.81	1.17
0.3852	0.6380	345.68	98.4	2.02	1.36
0.5085	0.6572	345.30	98.6	1.60	1.63
0.5521	0.6495	345.32	99.3	1.47	1.84
0.6241	0.6636	345.25	99.3	1.33	2.11
0.7004	0.6848	345.25	99.3	1.22	2.49
0.7704	0.7073	345.34	99.2	1.14	3.00
0.8164	0.7276	345.55	99.2	1.10	3.47
0.8559	0.7512	345.87	99.2	1.07	4.00
1.0000	1.0000	351.36	101.2	1.00	

[a] Atmospheric pressure changed during the experiment.

pling cavity was flushed with helium gas coming out from the dilutor before analysis of a new sample.

Samples of the condensed vapor phase and the liquid phase of the 2-propanol + 2,4,4-trimethyl-1-pentene and ethanol + 2,4,4-trimethyl-1-pentene systems were analyzed using a Balzers Omnistar quadrupole mass spectrometer with a mass range of 1 to 300 atomic mass units (Balzers, Liechtenstein). It was equipped with a closed electron impact (70 eV) ion source and an electron multiplier detector. A direct inlet was used for the sample introduction. The inlet was electrically heated to 150 °C. The steel capillary of the direct inlet was connected to the custom-made dilution chamber with 1/16 in. fittings.

Measurement data were collected using a selected ion monitoring mode (SIM). The following characteristic ions were recorded for the analyzed compounds: *m*/*z* 45 for 2-propanol; *m*/*z* 57 for 2,2,4-trimethyl-1-pentene; and, *m*/*z* 45 for ethanol. A typical ion chromatogram measured for the VLE experiment is presented in Figure 3.

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-Propanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 101 kPa Analyzed by GC

x_1	y_1	*T*/K	P^a/kPa	γ_1	γ_2
0.0000	0.0000	374.05	100.1		1.00
0.0213	0.1618	368.33	100.0	4.65	1.00
0.0473	0.2953	362.87	99.5	4.63	1.01
0.0964	0.4023	357.98	99.5	3.72	1.04
0.1496	0.4707	354.22	101.9	3.32	1.13
0.2200	0.5206	353.17	101.9	2.60	1.15
0.3664	0.5665	351.65	99.3	1.76	1.31
0.4092	0.5879	352.07	101.8	1.65	1.35
0.4640	0.6059	351.74	101.8	1.52	1.44
0.4696	0.6016	351.03	99.4	1.50	1.47
0.5037	0.6167	351.47	101.6	1.44	1.52
0.5592	0.6331	351.34	101.6	1.33	1.65
0.6226	0.6541	351.34	101.6	1.24	1.81
0.6809	0.6747	351.12	101.6	1.18	2.03
0.7373	0.6995	351.19	101.6	1.13	2.27
0.7883	0.7265	351.38	101.7	1.09	2.55
0.8321	0.7558	351.67	101.7	1.06	2.85
0.8824	0.7969	352.24	101.7	1.03	3.33
0.9189	0.8401	352.88	101.7	1.01	3.72
0.9556	0.8985	353.81	101.7	1.00	4.19
0.9756	0.9394	354.46	101.7	1.00	4.47
0.9889	0.9709	354.98	101.8	1.00	4.64
0.9948	0.9860	355.24	101.7	1.00	4.73
1.0000	1.0000	355.37	101.3	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-Propanol (1) + 2,4,4-Trimethyl-1-pentene (2) System at 101 kPa Analyzed by MS

x_1	y_1	*T*/K	P^a/kPa	γ_1	γ_2
0.0000	0.0000	374.33	100.6		1.00
0.0049	0.0635	371.64	100.7	7.12	1.01
0.0058	0.0663	371.60	100.7	6.29	1.01
0.0154	0.1365	368.71	100.7	5.39	1.02
0.0153	0.1389	368.66	100.7	5.53	1.02
0.0369	0.2831	364.16	100.7	5.49	0.99
0.0351	0.2784	364.24	100.7	5.66	0.99
0.5556	0.6357	351.06	100.7	1.35	1.62
0.5569	0.6330	351.06	100.7	1.34	1.64
0.7498	0.6993	350.64	100.0	1.11	2.39
0.7549	0.7027	350.63	100.0	1.11	2.42
0.9334	0.8695	352.77	99.9	1.02	3.65
0.9341	0.8697	352.77	99.9	1.02	3.68
0.9620	0.9185	353.54	99.8	1.01	3.90
0.9621	0.9181	353.54	99.9	1.01	3.93
0.9831	0.9568	354.28	99.8	1.00	4.54
0.9832	0.9559	354.28	99.8	1.00	4.66
1.0000	1.0000	355.37	101.3	1.00	

[a] Atmospheric pressure changed during the experiment.

Gravimetric calibration mixtures were used for the calibration of the MS measurements. In ethanol + 2,4,4-trimethyl-1-pentene analysis calibration curves were straight lines. The correlation coefficient was 0.9991 for 2,4,4-trimethyl-1-pentene and 0.9981 for ethanol. Due to the construction of the sampling system, for a 2-propanol + 2,4,4-trimethyl-1-pentene analysis the calibration was done separately for the two valves of the sampling system. For better precision of the results, the calibration was also done separately for the ranges below 10 wt % and also between (10 and 100) wt %. The intensity values were 2 orders of magnitude. In the lower concentration range the calibration points exhibited a behavior that was modeled best with a separate linear correlation; thus, the relative error could be reduced compared to just one linear correlation over the whole concentration range.

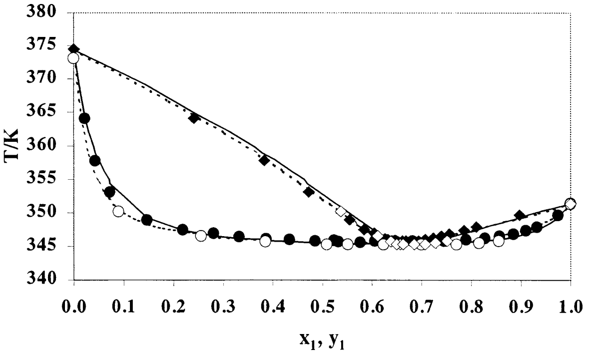

Figure 4. Temperature−composition diagram for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa. Lower: ●, x_1 measured (GC); —, x_1 calculated (GC fit of data); ○, x_1 measured (MS); - - -, x_1 calculated (MS fit of data). Upper: ◆, y_1 measured (GC); —, y_1 calculated (GC fit of data); ◇, y_1 measured (MS); - - -, y_1 calculated (MS fit of data).

For a 2-propanol + 2,4,4-trimethyl-1-pentene analysis, the correlation coefficients for 2,4,4-trimethyl-1-pentene ranged from 0.9999 to 0.9932, and for 2-propanol, they ranged from 0.9989 to 0.9932.

The results in weight percent units were calculated from the heights of the SIM ion chromatogram peaks. The results were normalized before the calculation of the activity coefficients. For the 2-propanol + 2,4,4-trimethyl-1-pentene measurements, the average uncertainty was 6.7% for sample injector position A and 3.4% in composition for sample injector position B. For the ethanol + 2,4,4-trimethyl-1-pentene measurements, the average uncertainty in composition was 2.4%.

The repeatability of the MS analysis was good. The relative standard deviation was less than 5% for a 2-propanol + 2,4,4-trimethyl-1-pentene analysis and less than 2% for an ethanol + 2,4,4-trimethyl-1-pentene analysis.

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 in all runs. It took from (15 to 30) min to achieve constant temperature due to the large boiling point difference of the components. The temperature was held constant for approximately 35 min to further enhance the steady-state condition before sampling.

Results and Discussion

The data measured and the calculated activity coefficients are reported in Tables 1−4 and Figures 4−9.

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

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

where y_i is the mole fraction of component i in the vapor phase, P is the total pressure of the system, ϕ_i is the fugacity coefficient of component i in the vapor phase, x_i is 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 vapor fugacity coefficient at the system temperature, $v_{\mathrm{i}}^{\mathrm{L}}$ 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.[12] The binary interaction parameter in the quadratic mixing rule was set to the value zero. The liquid phase was modeled with the Wilson equation.[13] Critical temperatures, critical pressures, acentric factors, and liquid molar volumes used in the calculations are presented in Table 5. The vapor pressures of the pure substances were calculated

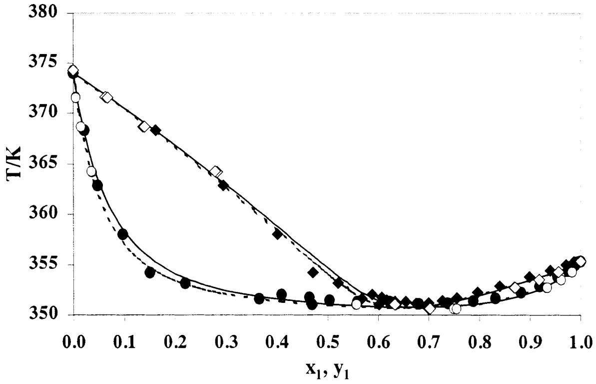

Figure 5. Temperature−composition diagram for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa. Lower: ●, x_1 measured (GC); —, x_1 calculated (GC fit of data); ○, x_1 measured (MS); - - -, x_1 calculated (MS fit of data). Upper: ◆, y_1 measured (GC); —, y_1 calculated (GC fit of data); ◇, y_1 measured (MS); - - -, y_1 calculated (MS fit of data).

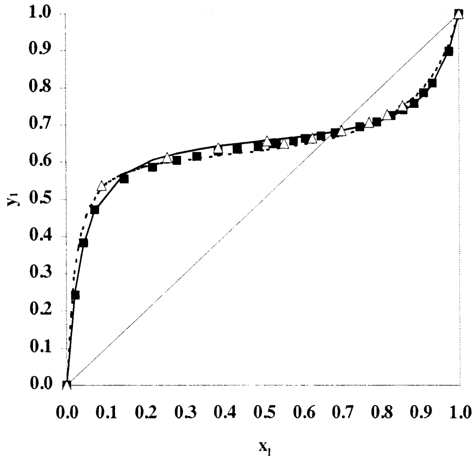

Figure 6. *xy* diagram for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa: ■, x_1 measured (GC); —, x_1 calculated (GC fit of data); △, x_1 measured (MS); - - -, x_1 calculated (MS fit of data).

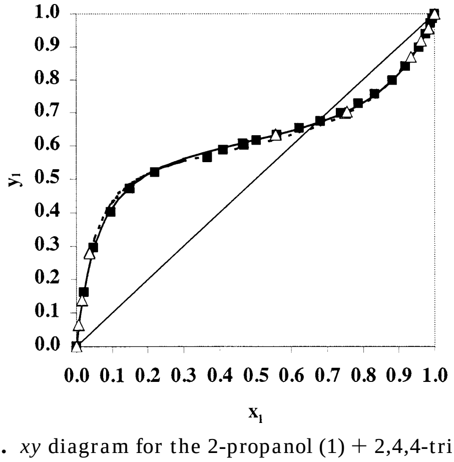

Figure 7. *xy* diagram for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa: ■, x_1 measured (GC); —, x_1 calculated (GC fit of data); △, x_1 measured (MS); - - -, x_1 calculated (MS fit of data).

Table 5. Critical Temperature, T_c, Critical Pressure, P_c, Acentric Factor, ω, Liquid Molar Volume (Used for Fitting the Wilson Equation Parameters), v_i, 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 Were Fitted.), Absolute Average Deviation of the Vapor Pressure Fit, AAD, and Recommended Temperature Range of the Vapor Pressure Correlation, T_{min}, T_{max}

	ethanol	2-propanol	2,4,4-trimethyl-1-pentene
T_c/K	516.25 ± 5	508.31 ± 5	553.0 ± 28[a]
P_c/MPa	6.384 ± 0.19	4.764 ± 0.14	2.630 ± 0.26[a]
ω	0.6371[a]	0.669[a]	0.2695[a]
v_i/cm^3·mol^{-1}	58.515 ± 0.6	76.784 ± 0.8	157.9 ± 4.7[a]
A	9.9417[b]	9.8016[c]	6.9460
B	3799.7[b]	3635.8[c]	2999.3
C	−40.781[b]	−54.710[c]	−49.678
AAD/kPa	0.09	0.26	0.04
T_{min}/K	316.33	320.51	333.1
T_{max}/K	383	383	374.3

[a] Daubert and Danner.[18] [b] The vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in ref 19 at vapor pressures from 136 kPa to 240 kPa (from 359 K to 375 K). [c] The vapor pressure function parameter range was increased by fitting measured values from this work combined with the values in ref 20 at vapor pressures from 131 kPa to 218 kPa (from 362 K to 376 K).

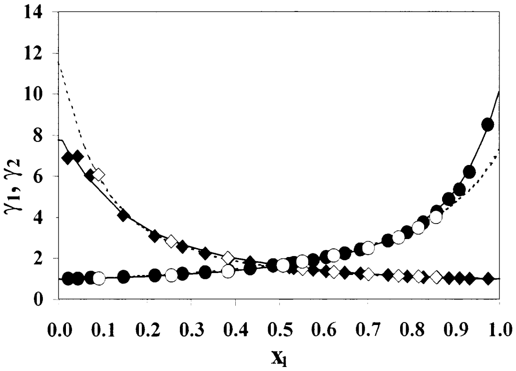

Figure 8. Activity coefficient−composition diagram for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa. ◆, γ_1 calculated from measurements (GC); ◇, γ_1 calculated from measurements (MS); —, γ_1 predicted by the model (fit of GC data); - - -, γ_1 predicted by the model (fit of MS data). ●, γ_2 calculated from measurements (GC); ○, γ_2 calculated from measurements (MS); —, γ_2 predicted by the model (fit of GC data); - - -, γ_2 predicted by the model (fit of MS data).

from the Antoine equation, eq 2.

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

The vapor pressure equation parameters were fitted from data measured with the same apparatus that was used for the VLE-measurements.[10,14] The parameters of the pure component vapor pressure equation with the recommended temperature range of the vapor pressure equations are also presented in Table 5.

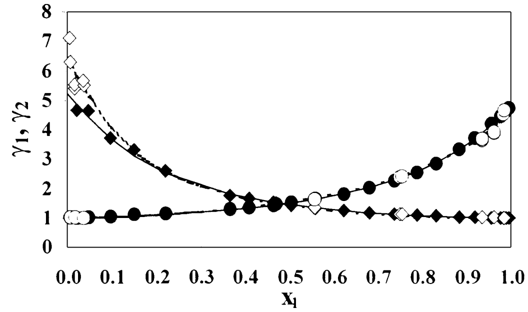

Figure 9. Activity coefficient−composition diagram for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa. ◆, γ_1 calculated from measurements (GC); ◇, γ_1 calculated from measurements (MS); —, γ_1 predicted by the model (fit of GC data); - - -, γ_1 predicted by the model (fit of MS data). ●, γ_2 calculated from measurements (GC); ○, γ_2 calculated from measurements (MS); —, γ_2 predicted by the model (fit of GC data); - - -, γ_2 predicted by the model (fit of MS data).

Both systems measured show positive deviations from Raoult's law and exhibit azeotropic behavior. The azeotropic data for the systems measured are presented in Table 6. Azeotropic data were determined graphically from the measured values. The objective function,[15] OF, used for fitting of the Wilson equation parameters is given by eq 3

$$\text{OF} = \frac{1}{N\cdot\text{NC}}\sum_{i=1}^{N}\sum_{j=1}^{\text{NC}}(\gamma_{i,j}^{\text{model}} - \gamma_{i,j}^{\text{measured}})^2 \tag{3}$$

where N is the number of points used in the fit and NC is the number of components used in the fit. 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 6. While the measurements of the ethanol + 2,4,4-trimethyl-1-pentene system (GC analysis) and the 2-propanol + 2,4,4-trimethyl-1-pentene system (MS analysis) did not pass the infinite dilution test,[16] the other systems measured did pass this test. The results of the infinite dilution test are presented in Table 6. In the point test[17] 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 except for the ethanol + 2,4,4-trimethyl-1-pentene data set (MS analysis, Table 6, Figures 10 and 11).

Conclusions

VLE measurements with a recirculation still of the Yerazunis type were made for the systems ethanol + 2,4,4-trimethyl-1-pentene and 2-propanol + 2,4,4-trimethyl-1-pentene at atmospheric pressure. Analysis of the phase

Table 6. Wilson Equation Parameters, $\lambda_{ij} - \lambda_{ii}$, for the Mixtures, Averages of Absolute Temperature Residuals, ΔT, for the Wilson Fit, Averages of the Absolute Vapor Fraction Residuals, Δy, Azeotropic Composition, x_{1az}, and Results of the Infinite Dilution Test, I

system/analysis method	$\lambda_{12} - \lambda_{11}$ J·mol^{-1}	$\lambda_{21} - \lambda_{22}$ J·mol^{-1}	ΔT K	Δy	x_{1az}	I[a] $x_1 \to 0/x_2 \to 0$
ethanol (1) + 2,4,4-trimethyl-1-pentene (2), 101 kPa/GC	7043.8	1631.8	0.39	0.0080	0.676	44.7/−14.8
ethanol (1) + 2,4,4-trimethyl-1-pentene (2), 101 kPa/MS	8596.0	371.64	0.24	0.0105	0.661	−0.7/14.6
2-propanol (1) + 2,4,4-trimethyl-1-pentene (2), 101 kPa/GC	5544.2	521.03	0.22	0.0036	0.670	5.5/13.7
2-propanol (1) + 2,4,4-trimethyl-1-pentene (2), 101 kPa/MS	6373.1	123.75	0.16	0.0061	0.672	65.6/2.2

[a] The criterion for passing the infinite dilution test is $I < 30$ both at $x_1 \to 0$ and at $x_2 \to 0$.

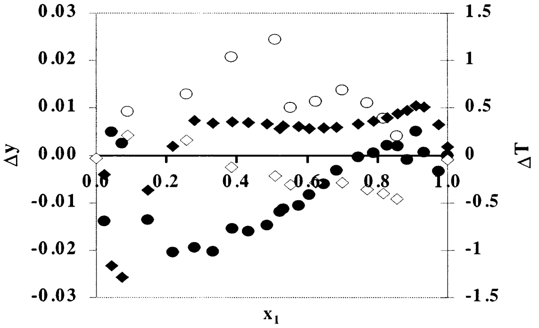

Figure 10. Point test for the ethanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa: ●, Δy (GC analysis); ◆, ΔT (GC analysis); ○, Δy (MS analysis); ◇, ΔT (MS analysis).

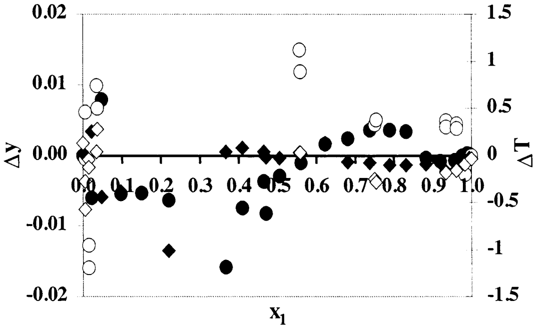

Figure 11. Point test for the 2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 101 kPa: ●, Δy (GC analysis); ◆, ΔT (GC analysis); ○, Δy (MS analysis); ◇, ΔT (MS analysis).

compositions was made with gas chromatography or mass spectrometry. Various sampling systems were tested, and mass spectrometry was found to be suitable for analyzing the samples both on-line and off-line. On-line sampling systems enable the determination of the steady-state point with regard to composition when using a recirculation still for VLE measurements, because the total composition does not change significantly in the still due to the small amount of sample withdrawn. Further developments will be made in order to reduce the analysis time, enhance the reliability, and simplify the calibration procedure.

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