

Vapor–Liquid Equilibrium for the Binary Systems of 3-Methylpentane + 2-Methyl-2-propanol at 331 K and + 2-Butanol at 331 K

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Isothermal vapor–liquid equilibrium data were measured for two binary systems, 3-methylpentane + 2-methyl-2-propanol at 331 K and 3-methylpentane + 2-butanol at 331 K. 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 model.

Introduction

MTBE (2-methoxy-2-methylpropane) will be banned in California not later than December 31, 2002, due to groundwater pollution problems.¹ The consumption² of MTBE in California was about 4 million gallons per day during the first quarter of 2000. MTBE will have to be replaced with other fuel components. It is economically sound to convert existing MTBE plants in order to produce new chemicals such as di-isobutylene (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene) or, by hydrogenating the di-isobutylene, produce a high-quality fuel component, isooctane (2,2,4-trimethylpentane).³ The systems measured have relevance in the design of the di-isobutylene processes. Isobaric data for the system 3-methylpentane + 2-methyl-2-propanol at 1 atm were found in the literature.⁴ Isothermal data for the systems measured were not found in the literature.

Experimental Section

Materials. The 2-methyl-2-propanol (99.7%, by gas chromatography (GC)), 2-butanol (99.5%, GC), and 3-methylpentane ($\geq 99\%$, GC) were provided by Fluka. The materials were used without further purification except for drying over molecular sieves (Merck 3A).

Apparatus. A recirculation still of the Yerazunis type⁵ was used. The liquid volume needed for running the apparatus was approximately 80 mL. The experimental setup is presented schematically in Figure 1. A minor modification was made to the apparatus after earlier measurements⁶—small magnets were used in order 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.

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

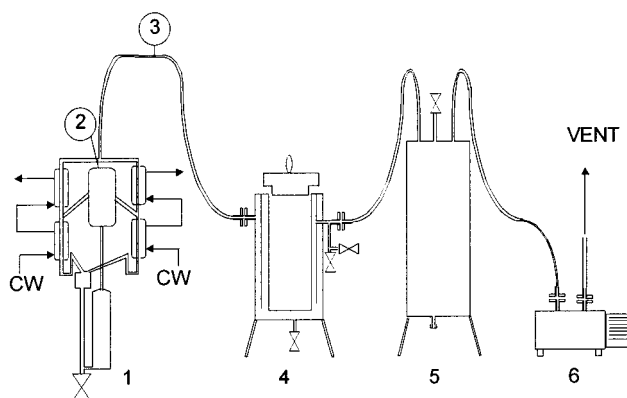


Figure 1. Experimental setup: (1) recirculation still; (2) temperature probe (Pt-100); (3) pressure transducer; (4) liquid nitrogen trap; (5) 30 dm³ buffer tank; (6) vacuum pump.

± 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.

Analysis 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. The GC-column used was a HP-1 (cross-linked methyl siloxane, length 30 m, column inner diameter 0.25 mm, film thickness 1.0 μ m). Isooctane was used as a solvent for the samples to avoid the precipitation of 2-methyl-2-propanol (its melting point is 298.8 K) and to reduce the volume of the sample. Isooctane was also used as a solvent for the system 3-methylpentane + 2-butanol. Gravimetric calibration mixtures were prepared in 2 mL vials with approximately 1 mL of isooctane as a solvent. The 3-methylpentane response factors were set to the value of 1; thus, it is possible to calculate the 2-methyl-2-propanol and 2-butanol response factors for the binary systems with eq 1

$$Q = \frac{m_1 A_2}{m_2 A_1} \quad (1)$$

Table 1. 2-Methyl-2-propanol and 2-Butanol Response Factor, Q , Number of Calibration Mixtures, n , and Average Deviation of the Response Factor, $\text{av dev } Q$, for the Systems 3-Methylpentane + 2-Methyl-2-propanol at 331 K (System 1) and 3-Methylpentane + 2-Butanol at 331 K (System 2)

system	Q	n	av dev Q
1	1.369	6	0.008
2	1.568	6	0.007

Table 2. VLE Data, Liquid-Phase, x_1 , and Vapor-Phase, y_1 , Mole Fractions, Pressure, P , Temperature, T , and Activity Coefficient, γ_b , for the 3-Methylpentane (1) + 2-Methyl-2-propanol (2) System at 331 K

x_1	y_1	T/K	P/kPa	γ_1	γ_2
1.0000	1.0000	331.15	86.7		
0.9571	0.9076	331.15	91.5	1.01	5.43
0.9067	0.8677	331.15	93.3	1.04	3.64
0.7992	0.8210	331.14	93.8	1.12	2.30
0.7623	0.8105	331.15	93.5	1.15	2.05
0.6946	0.7895	331.15	92.7	1.22	1.76
0.6253	0.7693	331.15	91.4	1.31	1.55
0.5340	0.7417	331.15	88.9	1.44	1.36
0.4545	0.7131	331.14	86.1	1.57	1.25
0.3767	0.6822	331.15	82.4	1.74	1.16
0.3122	0.6484	331.15	78.6	1.91	1.11
0.2533	0.6125	331.14	74.0	2.10	1.07
0.2017	0.5656	331.15	69.4	2.28	1.05
0.1655	0.5247	331.14	65.4	2.44	1.04
0.1252	0.4648	331.15	59.7	2.61	1.02
0.0941	0.3944	331.15	54.4	2.69	1.02
0.0668	0.3285	331.14	50.0	2.91	1.01
0.0417	0.2357	331.15	44.8	3.01	1.00
0.0000	0.0000	331.15	35.0		

where m_1 is the mass of 2-methyl-2-propanol or 2-butanol in the gravimetrically prepared sample, m_2 is the mass of the 3-methylpentane in the gravimetrically prepared sample, A_1 is the GC peak area of the 2-methyl-2-propanol or 2-butanol, and A_2 is the GC peak area of the 3-methylpentane. The GC runs were repeated three times for each calibration mixture. GC response factors with average deviations of response factors for the systems measured are presented in Table 1. The results obtained with these response factors were converted to mole fractions when analyzing samples.

Procedure. Pure component 1 was introduced to the recirculation still, and its vapor pressure was measured. After vapor pressure measurements, component 2 was added to the equilibrium still. The temperature was adjusted to the desired value by adjusting the pressure of the system. The temperature was held constant for approximately 35 min to further enhance the steady-state condition before sampling. Approximately 1 mL of isoctane was added to the 2 mL autosampler vials before sampling was carried out. The 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 to 0.2 mL of sample, and then a 0.4 to 0.5 mL sample was taken and injected into the cooled 2 mL autosampler vial.

Results and Discussion

The measured data and calculated activity coefficients are reported in Tables 2 and 3 and Figures 2–5. Azeotropic behavior was observed for the 3-methylpentane + 2-methyl-2-propanol system and also for the 3-methylpentane + 2-butanol system. The azeotropic data for the systems measured are presented in Table 4. The azeotropic data were determined graphically from measured values.

Table 3. VLE Data, Liquid-Phase, x_1 , and Vapor-Phase, y_1 , Mole Fractions, Pressure, P , Temperature, T , and Activity Coefficient, γ_b , for the 3-Methylpentane (1) + 2-Butanol (2) System at 331 K

x_1	y_1	T/K	P/kPa	γ_1	γ_2
1.0000	1.0000	331.15	85.8		
0.9492	0.9413	331.15	87.8	1.01	5.97
0.9387	0.9358	331.15	87.8	1.02	5.41
0.9275	0.9309	331.15	87.8	1.03	4.92
0.9053	0.9230	331.15	87.7	1.04	4.20
0.8602	0.9110	331.15	87.3	1.08	3.27
0.7972	0.8982	331.15	86.3	1.13	2.55
0.7265	0.8869	331.15	85.0	1.21	2.07
0.6685	0.8780	331.15	83.7	1.28	1.82
0.6106	0.8690	331.15	82.1	1.36	1.63
0.5399	0.8579	331.15	79.8	1.48	1.46
0.4746	0.8465	331.15	77.3	1.61	1.34
0.4191	0.8356	331.14	74.8	1.75	1.25
0.3640	0.8220	331.15	71.6	1.90	1.19
0.3084	0.8052	331.15	67.8	2.08	1.13
0.2631	0.7864	331.16	63.7	2.24	1.10
0.1929	0.7414	331.15	55.4	2.52	1.06
0.1401	0.6908	331.10	48.9	2.86	1.06
0.0484	0.4637	331.15	30.3	3.47	1.03
0.0000	0.0000	331.15	16.3		

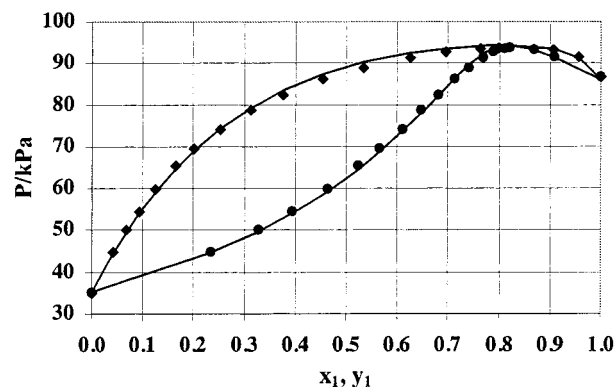


Figure 2. Pressure–composition diagram for the 3-methylpentane (1) + 2-methyl-2-propanol (2) system at 331 K: \blacklozenge , x_1 ; \bullet , y_1 ; \circ , x_1 calculated; \circ , y_1 calculated.

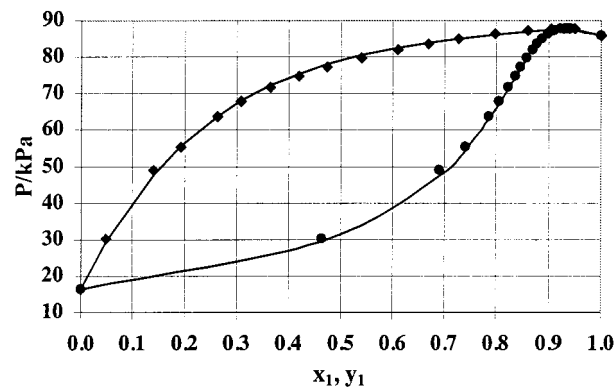


Figure 3. Pressure–composition diagram for the 3-methylpentane (1) + 2-butanol (2) system at 331 K: \blacklozenge , x_1 ; \bullet , y_1 ; \circ , x_1 calculated; \circ , y_1 calculated.

The activity coefficients for species i , γ_i , were calculated from eq 2

$$y_i P \phi_i = \gamma_i x_i P_{\text{vpi}} \phi_i^s \exp \int_{P_{\text{vpi}}}^P \frac{v_i^L dP}{RT} \quad (2)$$

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

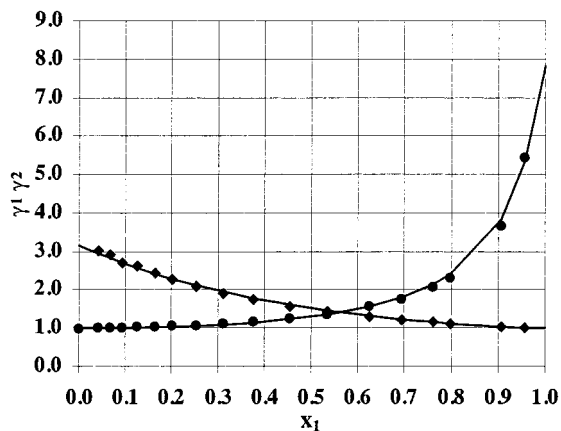


Figure 4. Activity coefficient–composition diagram for the 3-methylpentane (1) + 2-methyl-2-propanol (2) system at 331 K: \blacklozenge , γ_1 from data; \bullet , γ_2 from data; $-$, γ_1 from model; $-$, γ_2 from model.

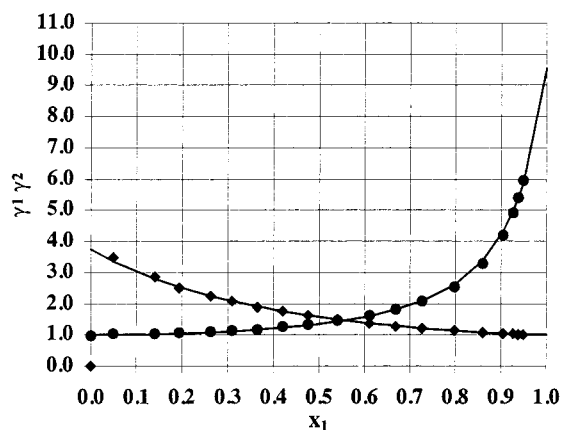


Figure 5. Activity coefficient–composition diagram for the 3-methylpentane (1) + 2-butanol (2) system at 331 K: \blacklozenge , γ_1 from data; \bullet , γ_2 from data; $-$, γ_1 from model; $-$, γ_2 from model.

Table 4. Azeotropic Pressure, P , Temperature, T , and Composition, x_1

binary pair	P/kPa	T/K	x_1
3-methylpentane (1) + 2-methyl-2-propanol (2)	94.0	331.15	0.838
3-methylpentane (1) + 2-butanol (2)	88.0	331.15	0.934

fraction of component i in the liquid phase, P_{vpi} is the vapor pressure of pure component i at the system temperature, ϕ_i^s is the pure component saturated liquid fugacity coefficient at the system temperature, v_i^l is the component i liquid-phase molar volume at the system temperature, T is temperature in Kelvin, and R is the universal gas constant ($8.314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). The Soave–Redlich–Kwong equation of state with quadratic mixing rules in the attractive parameter and which is linear in covolume was used for vapor-phase calculation.⁸ The liquid phase was modeled with the Wilson equation.⁹ Critical temperatures, critical pressures, critical volumes, acentric factors, and 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 3. The vapor pressure equation parameters were fitted with data measured in the same apparatus used for the VLE-measurements. The pure component vapor pressure equation parameters with the recommended temperature range of the vapor pressure equations are also presented in Table 5. Pure component vapor pressures for 2-methyl-2-propanol and 2-butanol were measured earlier,⁶ and 3-methylpen-

Table 5. Critical Temperature, T_c , Critical Pressure, P_c , Critical Molar Volumes, V_c , Acentric Factor, ω , Liquid Molar Volume (Used for Fitting the Wilson Equation Parameters), v_i^l , Pure Component Vapor Pressure Equation Parameters, A , B , and C , for the Antoine Equation,^a and Recommended Temperature Range of the Vapor Pressure Correlation, T_{min} , T_{max}

component	2-methyl-2-propanol	2-butanol	3-methylpentane
T_c/K	506.2 ± 5^b	536.01 ± 5^b	504.43 ± 5^b
P_c/MPa	3.9719 ± 0.12^b	4.1938 ± 0.12^b	3.124 ± 0.03^b
$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	275 ± 11^b	268 ± 13^b	366.4 ± 18^b
ω	0.6158^b	0.5711^b	0.2737^b
$v_i^l/\text{cm}^3\cdot\text{mol}^{-1}$	94.861 ± 2.8^b	92.12 ± 0.9^b	130.575 ± 1.3^b
A	10.401	8.3640	6.5835
B	3982.9	3026.1	2500.2
C	-41.420	-88.316	-54.549
T_{min}/K	329.76	325.05	302.35
T_{max}/K	355.24	372.20	336.09

^aVapor pressure data measured with the apparatus used in the VLE measurements was fitted. ^bDaubert and Danner.⁷

Table 6. Pure Component Vapor Pressures for 3-Methylpentane

T/K	P/kPa	T/K	P/kPa
336.09	100.5	331.15	85.8
336.06	100.5	330.15	83.1
335.44	98.5	329.15	80.3
335.04	97.2	328.16	77.7
334.42	95.3	325.04	69.9
333.28	92.0	320.59	59.9
333.15	91.6	315.58	50.0
332.62	90.0	309.60	40.0
332.16	88.7	302.35	30.0
331.16	85.8		

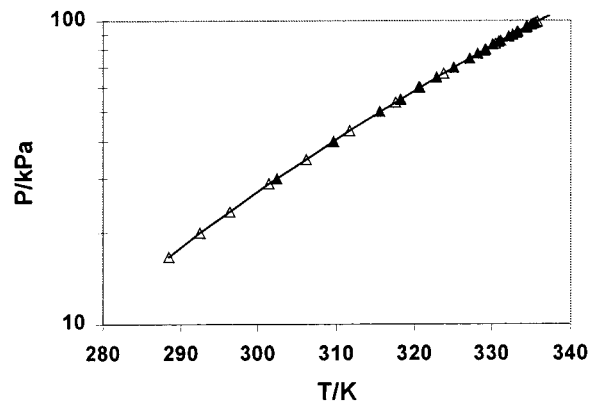


Figure 6. Vapor pressures: \blacktriangle , 3-methylpentane, this work; \triangle , 3-methylpentane, Boublik et al.¹³

tane vapor pressure data are presented in Table 6 and Figure 6.

$$P/\text{MPa} = \exp\left(A - \frac{B}{(TK + C)}\right) \quad (3)$$

Both systems measured indicate positive deviations from Raoult's law. The objective function¹⁰ O.F. used for fitting of the Wilson equation parameters is presented in eq 4

$$\text{O.F.} = \frac{1}{N \cdot NC} \sum_{i=1}^N \sum_{j=1}^{NC} (\gamma_{ij}^{\text{model}} - \gamma_{ij}^{\text{measured}})^2 \quad (4)$$

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 and the averages of the absolute values of the residuals for the vapor phase and pressure are presented in Table 7.

Table 7. Wilson Equation Parameters, $\lambda_{ij} - \lambda_{ji}$ for the Mixtures, Averages of the Absolute Vapor Fraction Residuals, Δy , Averages of the Absolute Pressure Residuals, Δp , for the Wilson Fit, and Results of the Integral Test, D

system	$\lambda_{12} - \lambda_{11}$ J·mol ⁻¹	$\lambda_{21} - \lambda_{22}$ J·mol ⁻¹	ΔP kPa	Δy	$D^a/\%$
3-methylpentane (1) + 2-methyl-2-propanol (2)	-4.0417	5788.7	0.7	0.0041	0.1 (pass)
3-methylpentane (1) + 2-butanol (2)	335.63	6135.8	0.4	0.0026	1.4 (pass)

^a The criterion for passing the test is $D < 10\%$.¹¹

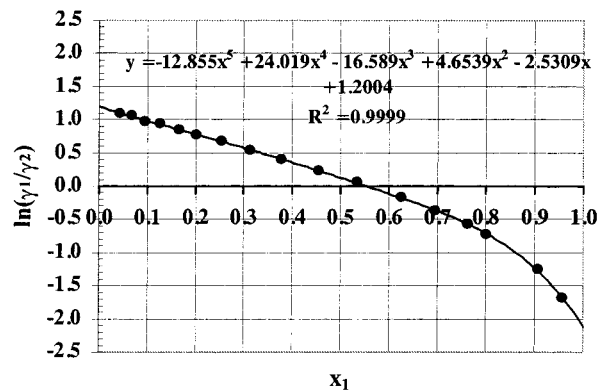


Figure 7. Integral test for the 3-methylpentane (1) + 2-methyl-2-propanol (2) system at 331 K.

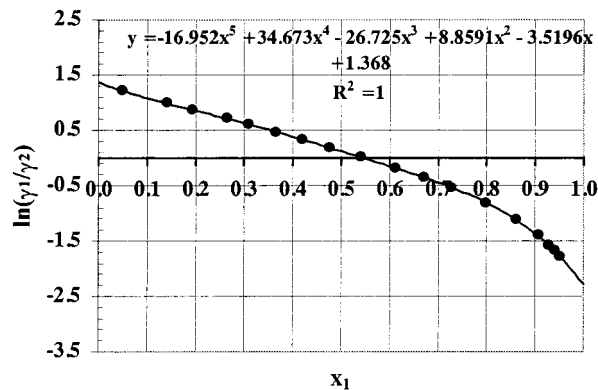


Figure 10. Integral test for the 3-methylpentane (1) + 2-butanol (2) system at 331 K.

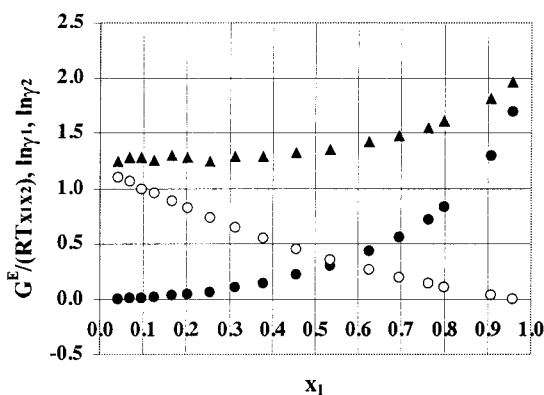


Figure 8. Infinite dilution test for the 3-methylpentane (1) + 2-methyl-2-propanol (2) system at 331 K: \blacktriangle , $G^E/(RTx_1x_2)$; \circ , $\ln \gamma_1$; \bullet , $\ln \gamma_2$.

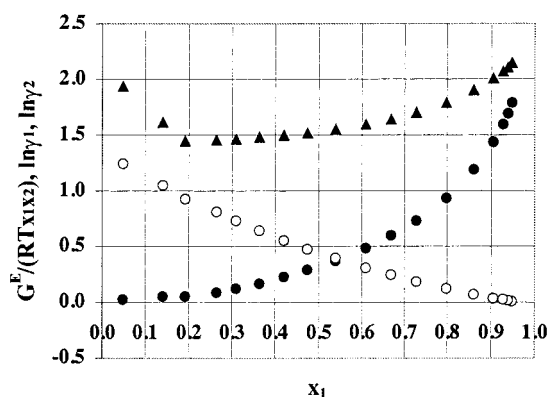


Figure 11. Infinite dilution test for the 3-methylpentane (1) + 2-butanol (2) system at 331 K: \blacktriangle , $G^E/(RTx_1x_2)$; \circ , $\ln \gamma_1$; \bullet , $\ln \gamma_2$.

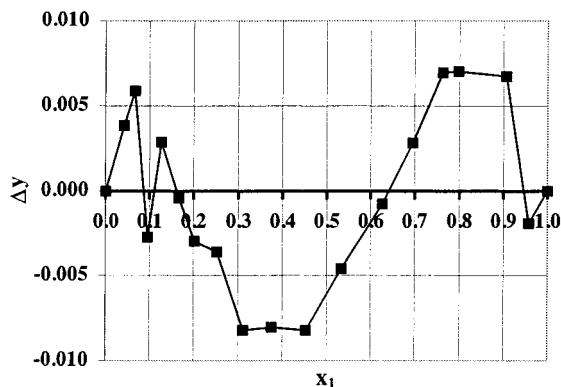


Figure 9. Point test for the 3-methylpentane (1) + 2-methyl-2-propanol (2) system at 331 K.

The data sets measured passed the integral¹¹ test (Figures 7 and 10). The results of the integral test are presented in Table 7. The infinite dilution test plots¹² (Figures 8 and 11) show that the 3-methylpentane + 2-butanol data set in the dilute 3-methylpentane region shows some inconsistency. The 3-methylpentane + 2-methyl-2-propanol data set can be considered consistent according to the infinite dilution test. In the point test a set of

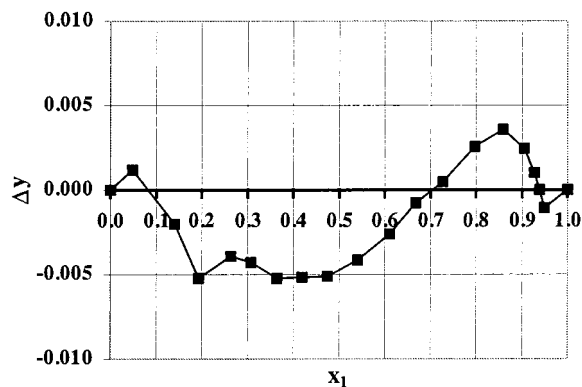


Figure 12. Point test for the 3-methylpentane (1) + 2-butanol (2) system at 331 K.

data is considered consistent¹¹ if the averages of the absolute values of the residuals for the vapor phase in mole fraction are < 0.01 by the point test. The data sets were found to satisfy the point test criterion (Table 7, Figures 9 and 12).

Acknowledgment

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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) California Energy Commission. *Quarterly Report Concerning MTBE Use in California Gasoline*, January 1 through March 31, 2000, 2000.
- (3) Sloan, D.; Birkhoff, R.; Gilbert, M.; Nurminen, M.; Pyhälähti, A. Isooctane Production from C₄'s as an Alternative to MTBE; National Petrochemical & Refiners Association Paper AM-00-34; NPRA: Washington, DC, 2000.
- (4) Gabaldón, C.; Marzal, P.; Montón, J.; Peña-roja, J. Isobaric Vapor-Liquid Equilibria for the Binary System 3-Methylpentane + 2-Methyl-2-propanol and for the Ternary System Methyl 1,1-Dimethylethyl Ether + 3-Methylpentane + 2-Methyl-2-propanol at 101.3 kPa. *J. Chem. Eng. Data* **1999**, *44*, 1386-1390.
- (5) Yerazunis, S.; Plowright, J. D.; Smola, F. M. Vapor-Liquid Equilibrium Determination by a New Apparatus. *AIChE J.* **1964**, *10*, 660-665.
- (6) 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 K. Submitted to *J. Chem. Eng. Data*.
- (7) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere: New York, 1989.
- (8) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197-1203.
- (9) 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.
- (10) Aittamaa, J.; Keskinen, K.; Keurulainen, T. *VLEFIT manual, VLEFIT manuaali*; 1995, in Finnish.
- (11) Gmehling, J.; Onken, U. *Vapor-Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series, Vol 1, Part 1; DECHEMA: Frankfurt/Main, 1977.
- (12) Kojima, K.; Moon, H.; Ochi, K. Thermodynamic consistency test of vapor-liquid equilibrium data. *Fluid Phase Equilib.* **1990**, *56*, 269-284.
- (13) Boublik, T.; Fried, V.; Hala, E. *Vapor Pressures of Pure Substances, Selected Values of the Temperature Dependence of the Vapor Pressures of Some Pure Substances in the Normal and Low-Pressure Region, 2nd Revised Edition*. *Physical Science Data 17*; Elsevier: Amsterdam, 1984.

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