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Vapor−Liquid Equilibrium for the 2-Methylpentane + 2-Methyl-2-propanol and + 2-Butanol Systems at 329 K

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Isothermal vapor−liquid equilibrium data were measured for two binary systems, 2-methylpentane + 2-methyl-2-propanol and 2-methylpentane + 2-butanol at 329 K. The measurements were made with a recirculation still and the composition of liquid and condensed vapor phase was analyzed with a gas chromatograph. Both systems measured indicate positive deviations from Raoult's law and exhibit azeotropic behavior. The pure component vapor pressure of 2-methylpentane was also measured.

Introduction

MTBE (2-methoxy-2-methylpropane) will be banned in California by the end of 2002 due to groundwater pollution problems.[1] The consumption[2] of MTBE in California was about 4 million gal/day during the first quarter of 2000. MTBE will have to be replaced with other fuel components. One of the alternatives is to convert existing MTBE units, which use isobutylene and methanol as feeds, to isooctane units. Isobutylene is dimerized to diisobutylene (2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene), which is hydrogenated to a high-quality fuel component, isooctane (2,2,4-trimethylpentane).[3] The systems measured are important in the design of the diisobutylene processes. Isobaric data for the system 2-methylpentane + 2-methyl-2-propanol at 101.3 kPa was found in the literature.[4] Isothermal data for the systems measured was 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 2-methylpentane (≥99%, GC) were provided by Fluka. Normal boiling point calculated from the Antoine equation is shown in Table 5. The parameters of Antoine were optimized with the data measured in this and earlier work.[6] The materials were used without further purification except for drying over molecular sieves (Merck3A).

Apparatus. A recirculation still of the Yerazunis type[5] was used. Since the first presentation[6] of our apparatus, small magnets were added to the apparatus to enhance mixing in the sampling and the mixing chambers. The total volume of mixture needed for the measurements was ≈80 mL. Temperature was measured using a Thermolyzer S2541 (Frontec) temperature meter with a Pt-100 probe calibrated at the Finnish National Standards Laboratory. The Pt-100 probe was located at the bottom of the packed section of the recirculation still. 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, estimated to be ±0.05 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. The overview of our setup is presented in Figure 1.

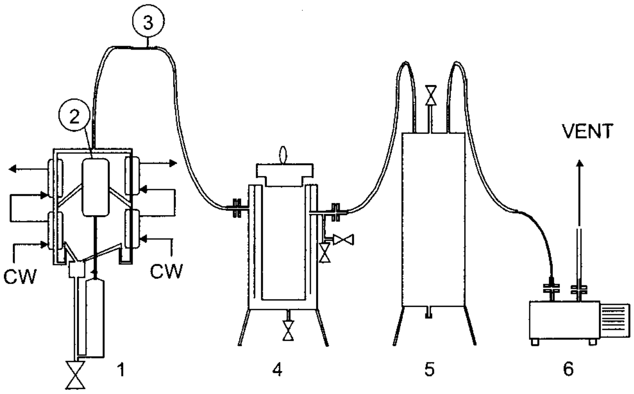

Figure 1. The experimental setup: (1) recirculation still; (2) temperature probe (Pt-100); (3) pressure transducer; (4) liquid nitrogen trap; (5) buffer tank 30 dm^3; (6) vacuum pump.

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 (FID). 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 μm). At 2-methylpentane + 2-methyl-2-propanol runs the oven temperature was 100 °C, run time 4 min, inlet split ratio 100:1, carrier gas He (1.1 mL/min), and FID temperature 250 °C. At 2-methylpentane + 2-butanol runs the oven temperature was initially 31 °C for 4 min, and then the temperature was raised 10 °C/min to the final temperature 70 °C, inlet split ratio 100:1, carrier gas He (2.7 mL/min), and FID temperature 250 °C. Isooctane was used as a solvent for the samples to avoid the precipitation of 2-methyl-2-propanol (its melting point is 298.97 K[7]) and to reduce the volume of the sample. Isooctane was also used as a solvent for the system 2-methylpentane + 2-butanol. Gravimetric calibration mixtures were prepared in 2-mL vials with ≈1 mL of isooctane as a solvent. The 2-methylpentane re-

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Table 1. 2-Methyl-2-propanol and 2-Butanol Response Factor *Q*, Number of Calibration Mixtures *N*, Average Deviation of the Response Factor Av. Dev. *Q*, for the Systems 2-Methylpentane + 2-Methyl-2-propanol (System 1) and 2-Methylpentane + 2-Butanol at 329 K (System 2)

system	*Q*	*N*	av. dev. *Q*	system	*Q*	*N*	av. dev. *Q*
1	1.373	6	0.009	2	1.576	6	0.011

sponse 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 given by

$$Q = \frac{m_2 A_1}{m_1 A_2} \tag{1}$$

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 2-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 2-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.

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 still. The temperature was adjusted to the desired value by adjusting the pressure of the system. Two manual valves, a small ball valve at the top of the buffer tank and a small needle valve between the 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 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 ±0.05 K. Mostly 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 ≈35 min by adjusting the pressure of the system. Approximately 1 mL of isooctane was added to the 2-mL autosampler vials before sampling was carried out. 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 the Tables 2 and 3 and are shown in Figures 2−7. Both systems indicate positive deviations from Raoult's law. Azeotropic behavior was observed for both the 2-methylpentane + 2-methyl-2-propanol system and the 2-methylpentane + 2-butanol system. The azeotropic data for the systems measured are presented in Table 4. The azeotropic data were interpolated graphically from measured values.

Table 2. VLE Data, Liquid Phase x_1 and Vapor Phase y_1, Mole Fractions, Pressure *P*, MPa, Temperature *T*, K, and Activity Coefficient, γ_i, for the 2-Methylpentane (1) + 2-Methyl-2-propanol(2) System at 329 K

x_1	y_1	T/K	P/kPa	γ_1	γ_2
0.0000	0.0000	329.15	32.0		1.00
0.0165	0.1429	329.14	36.5	3.68	0.99
0.0554	0.3380	329.12	45.5	3.20	0.99
0.0854	0.4244	329.14	51.3	2.93	1.00
0.1559	0.5438	329.15	62.0	2.47	1.03
0.1719	0.5401	329.14	63.7	2.29	1.09
0.1930	0.5799	329.16	66.9	2.29	1.07
0.1937	0.5834	329.14	67.4	2.32	1.07
0.2327	0.6283	329.14	71.6	2.20	1.07
0.2836	0.6605	329.14	76.1	2.02	1.11
0.3384	0.6920	329.14	80.1	1.86	1.14
0.4068	0.7201	329.15	84.0	1.68	1.21
0.4597	0.7403	329.14	86.5	1.58	1.27
0.5127	0.7555	329.15	88.6	1.48	1.36
0.5438	0.7634	329.15	89.6	1.42	1.42
0.5896	0.7774	329.14	91.1	1.36	1.51
0.6608	0.7991	329.15	92.9	1.27	1.68
0.7279	0.8164	329.15	94.1	1.19	1.93
0.7894	0.8350	329.15	95.0	1.13	2.27
0.8507	0.8556	329.15	95.4	1.08	2.81
0.9141	0.8838	329.14	94.9	1.03	3.91
0.9505	0.9111	329.14	93.9	1.01	5.13
0.9716	0.9361	329.14	92.5	1.01	6.35
1.0000	1.0000	329.14	88.4	1.00	

Table 3. 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-Methylpentane(1) + 2-Butanol (2) System at 329 K

x_1	y_1	T/K	P/kPa	γ_1	γ_2
0.0000	0.0000	329.15	15.0		1.01
0.0504	0.5644	329.18	31.0	4.03	0.95
0.0831	0.6357	329.24	37.8	3.33	1.00
0.1215	0.7089	329.06	46.2	3.12	1.02
0.1873	0.7679	329.13	56.3	2.65	1.06
0.2480	0.7949	329.17	61.2	2.24	1.10
0.3071	0.8239	329.17	68.6	2.10	1.15
0.3911	0.8490	329.16	74.5	1.84	1.21
0.4613	0.8614	329.14	78.0	1.66	1.32
0.5580	0.8754	329.16	82.0	1.46	1.51
0.6372	0.8857	329.14	84.4	1.33	1.74
0.7094	0.8950	329.14	86.4	1.23	2.04
0.7864	0.9064	329.15	88.1	1.15	2.52
0.8606	0.9197	329.16	89.4	1.08	3.35
0.9219	0.9358	329.15	90.1	1.03	4.83
0.9600	0.9531	329.15	90.2	1.01	6.88
0.9829	0.9737	329.15	89.6	1.00	8.96
1.0000	1.0000	329.14	88.4	1.00	

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

$$y_i P \phi_i = \gamma_i x_i P_{\mathrm{vpi}} \phi_i^{\mathrm{s}} \exp \int_{P_{\mathrm{vpi}}}^{P} \frac{v_i^{\mathrm{L}}\, \mathrm{d}P}{RT} \tag{2}$$

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 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 the temperature in Kelvin, and R is the universal gas constant (8.314 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$). The Soave−Redlich−Kwong equation of state with quadratic mixing rules in the attractive parameter and linear in covolume was used for vapor-phase calculation.[8] The binary interaction parameters of SRK were set to zero for these two systems. The activity coefficients of the liquid phase were modeled using a five-parameter Legendre polynomial[9] and Wilson model.[15] Figures 2−7 are drawn with the Legendre model and the

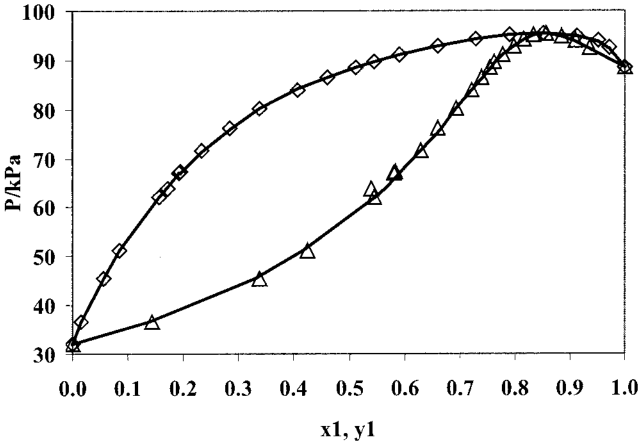

Figure 2. Pressure-composition diagram for the 2-methylpentane(1) + 2-methyl-2-propanol(2) system at 329 K: ◇, x_1; △, y_1; —, x_1 model; —, y_1 model.

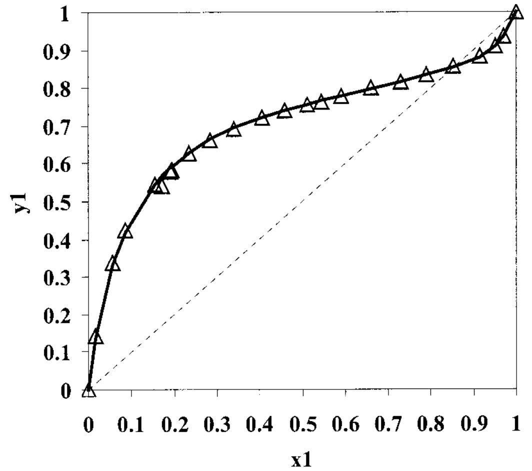

Figure 3. Vapor−liquid composition diagram for the 2-methylpentane(1) + 2-methyl-2-propanol(2) system at 329 K: △, y_1; —, y_1 model.

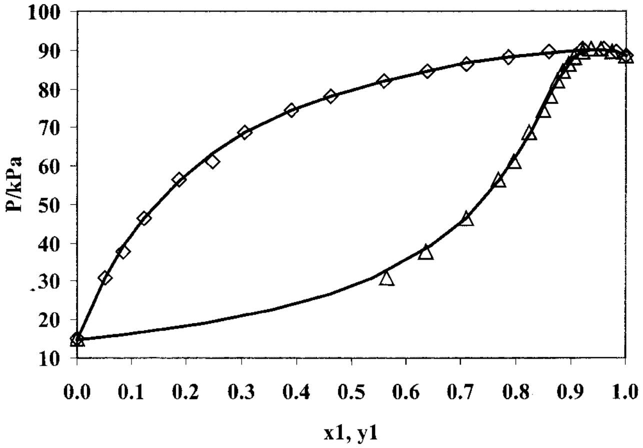

Figure 4. Pressure−composition diagram for the 2-methylpentane(1) + 2-butanol(2) system at 329 K: ◇, x_1; △, y_1; —, x_1 model; —, y_1 model.

Table 4. Azeotropic Pressure P, Temperature T, and Composition x_1, Interpolated from Measurements, Wilson Interaction Parameters $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$

binary pair	P kPa	T K	x_1	$\lambda_{12} - \lambda_{11}$ J·mol^{-1}	$\lambda_{21} - \lambda_{22}$ J·mol^{-1}
2-methylpentane(1) + 2-methyl-2-propanol(2)	95.4	329.14	0.85	182.87	5312.2
2-methylpentane(1) + 2-butanol(2)	90.2	329.15	0.95	551.78	5860.7

Table 5. 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 $T_{\min}$, T_{Max}, and Normal Boiling Point T_b

component	2-methyl-2-propanol	2-butanol	2-methylpentane
T_c/K	506.2 ± 5[a]	536.01 ± 5[a]	497.5[b]
P_c/MPa	3.9719 ± 0.12[a]	4.1938 ± 0.12[a]	3.01[b]
V_c/cm^3·mol^{-1}	275 ± 11[a]	268 ± 13[a]	367[b]
ω	0.6158[a]	0.5711[a]	0.278[b]
v_i/cm^3·mol^{-1}	94.861 ± 2.8[a]	92.12 ± 0.9[a]	132.0[b]
A	10.401[c]	8.3640[c]	6.6319
B	3982.9[c]	3026.1[c]	2500.2
C	−41.420[c]	−88.316[c]	−53.098
$T_{\min}$/K	329.76[c]	325.05[c]	300.00
$T_{\max}$/K	355.24[c]	372.20[c]	334.00
T_b/K	355.29[c]	372.37[c]	333.35
T_b/K	355.57[a]	372.7[a]	333.4[b]

[a] Daubert and Danner.[7] [b] Reid et al.[13] [c] Uusi-Kyyny et al.[6]

Table 6. Pure Component Vapor Pressures, 2-Methylpentane

T K	P kPa	T K	P kPa	T K	P kPa	T K	P kPa
333.33	101.33	329.63	89.87	324.72	76.30	310.13	45.24
332.58	98.91	329.15	88.44	322.42	70.55	306.89	39.97
331.26	94.83	329.15	88.51	319.75	64.28	304.83	36.90
331.00	93.95	327.94	85.00	313.80	51.92	300.78	31.35
330.15	91.38	327.28	83.16	311.97	48.52		

parameters of the Wilson model are given in Table 4. The critical temperature, critical pressure, critical volume, acentric factor, and the liquid molar volume for each component needed in the calculation are presented in Table 5. The vapor pressure of the pure substances was calculated from Antoine-type equation, (3).

$$P/\mathrm{MPa} = \exp\left(A - \frac{B}{(T/\mathrm{K} + C)}\right) \tag{3}$$

The parameters of the vapor pressure 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 5. Pure component vapor pressures for 2-methyl-2-propanol and 2-butanol were measured earlier[6] and 2-methylpentane vapor pressure data measured in this work are presented in Table 6 and a comparison to earlier measurements[12,14] is shown in Figure 8.

The consistency was tested with an integral[9] test, infinite dilution test,[11] and point test.[9] During these tests the objective function was the deviation between the measured and modeled pressure[10] as shown in eq 4. The activity coefficients were calculated from the Legendre polynomial.

$$\mathrm{O.F.} = \frac{1}{N}\sum_{i=1}^{N}\frac{(P_{i,\mathrm{model}} - P_{i,\mathrm{meas}})}{P_{i,\mathrm{meas}}} \tag{4}$$

The results of these tests are collected Table 7. Both systems passed the integral test. The infinite dilution test reveals better quality of measurements at high concentrations of 2-methylpentane than alcohol. However, the

Table 7. Results of Consistency Tests Using Legendre Polynomial

system	integral test	infinite dilution test	point test
2-methylpentane(1) + 2-methyl-2-propanol(2)	0.6% (passed)	−25.5% ($x(1) = 0$) 19.8% ($x(1) = 1$)	$\lvert\Delta p_{\text{aver}}\rvert = 0.12$ kPa $\lvert\Delta y_{\text{aver}}\rvert = 0.004$
2-methylpentane(1) + 2-butanol(2)	0.2% (passed)	−22.9% ($x(1) = 0$) 10.3% ($x(1) = 1$)	$\lvert\Delta p_{\text{aver}}\rvert = 0.29$ kPa $\lvert\Delta y_{\text{aver}}\rvert = 0.003$

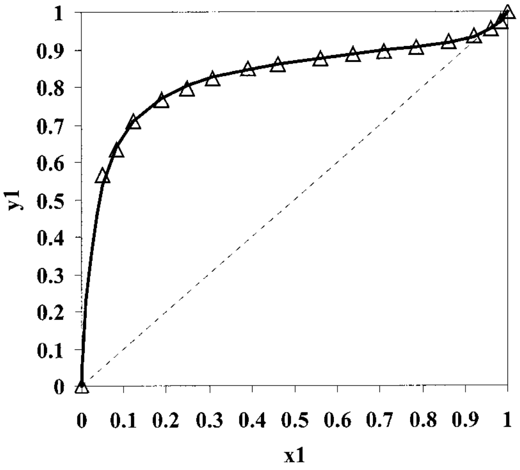

Figure 5. Vapor−liquid composition diagram for the 2-methylpentane(1) + 2-butanol(2) system at 329 K: △, y_1; —, y_1 model.

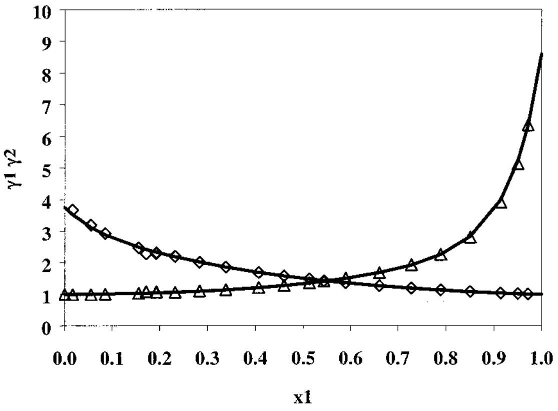

Figure 6. Activity coefficient−composition diagram for the 2-methylpentane(1) + 2-methyl-2-propanol(2) system at 329 K: ◇, γ_1 from data; △, γ_2 from data; —, γ_1 model; —, γ_2 model.

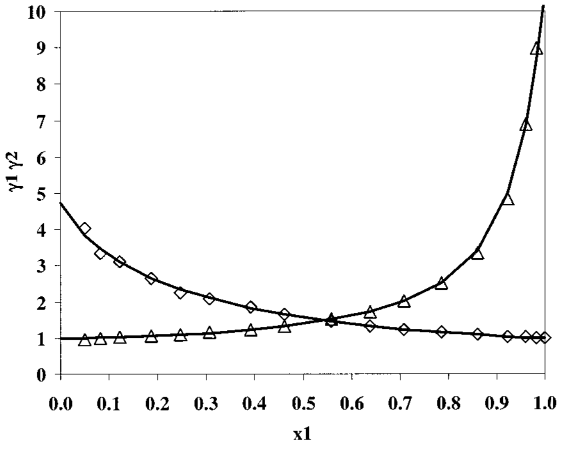

Figure 7. Activity coefficient−composition diagram for the 2-methylpentane(1) + 2-butanol(2) system at 329 K: ◇, γ_1 from data; △, γ_2 from data; —, γ_1 model; —, γ_2 model.

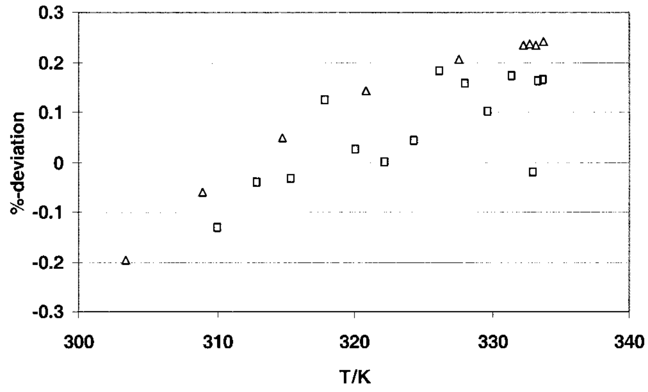

Figure 8. Percent pressure deviation (100% × (p, this work − p, literature)/p, literature) of 2-methylpentane vapor pressure: △, Boublik et al.;[12] □, Aucejo et al.[14]

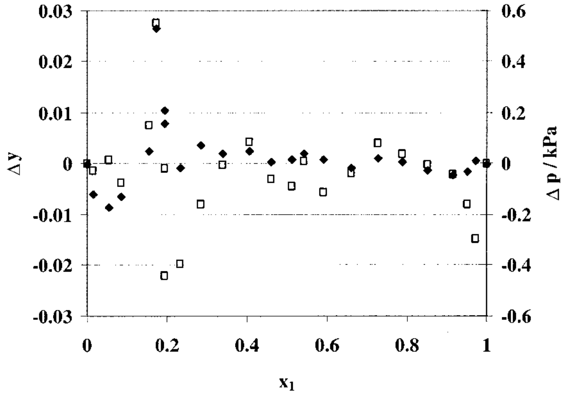

Figure 9. Point test for the 2-methylpentane(1) + 2-methyl-2-propanol(2) system at 329 K: ◆; Δy, □; Δp, model.

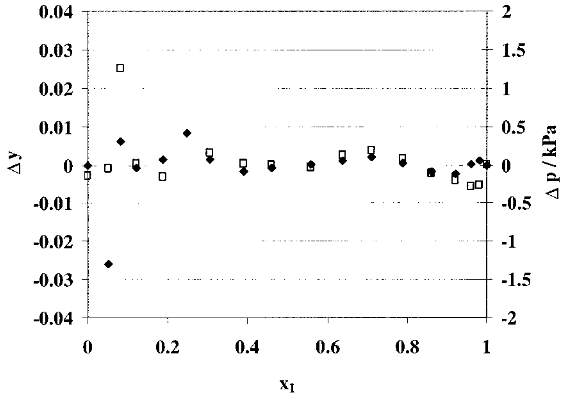

Figure 10. Point test for the 2-methylpentane(1) + 2-butanol(2) system at 329 K: ◆; Δy, □; Δp, model.

infinite dilution test is passed. The point test is 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 9 and 10.

Acknowledgment

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