Excess Enthalpy and Vapor−Liquid Equilibrium at Atmospheric Pressure for the Binary Systems 2-Methyl-2-propanol + 2,4,4-Trimethyl-1-pentene and 2-Butanol + 2,4,4-Trimethyl-1-pentene

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Excess molar enthalpies were measured for the binary systems 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene at 300 K and for 2-butanol + 2,4,4-trimethyl-1-pentene at 298 K. Vapor−liquid equilibria were also measured for the same systems at atmospheric pressure with a circulation still, and the liquid and condensed vapor phase samples were analyzed with a gas chromatograph. The experimental data were correlated with a Wilson activity coefficient model. Experimental results and the fitted model were also compared with the predictive activity coefficient model UNIFAC (Dortmund).

Introduction

MTBE (2-methoxy-2-methylpropane) production has increased continuously during the past decade. It is used as an octane-enhancing component, and it enabled the ban of lead in gasoline. It also enhances gasoline burning, and this improves air quality in populated areas. Leaks in gasoline storage tanks have produced smell and contamination of groundwater in some areas, particularly in California,[1] where MTBE will be banned by the end of 2003. The originally planned ban at the end of 2002 had been postponed for one year. New initiatives are required for replacement of MTBE. One option is to transform old MTBE plants to produce isooctene from isobutylene and then hydrogenate isooctene to isooctane.[2] In the design of new processes, information on the physical properties of isooctenes is required, particularly to develop reliable phase equilibrium models for the design of the separation units. Excess molar enthalpy and VLE data for the systems 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene and 2-butanol + 2,4,4-trimethyl-1-pentene at atmospheric pressure were measured, and the results were correlated. This work extends the previous isothermal data[3] on VLE by excess enthalpy (H^E), and thus, the new correlation has a better representation of the temperature dependence of the activity coefficient.

Experimental Section

Materials. The 2,4,4-trimethyl-1-pentene (>98% purity, by gas chromatography (GC) peak area, water content 0.010 mass %, experimental density 0.7113 g·cm^{-3} (at 298.15 K), literature[4] density 0.71089 g·cm^{-3}), 2-butanol (>99.5%, by GC peak area, water content 0.006 mass %, experimental density 0.8024 g·cm^{-3} (at 298.15 K), literature[5] density 0.8026 g·cm^{-3}), and 2-methyl-2-propanol (>99.7%, by GC peak area, water content 0.009 mass %, experimental density 0.7755 g·cm^{-3} (at 303.15 K), literature[6] density 0.77521 g·cm^{-3}) were supplied by Fluka. The water content in the chemicals was determined by Karl Fischer titration, and their densities were measured by means of an Anton Paar vibrating-tube density meter, model DMA 5000. The materials were used without further purification except for drying over molecular sieves (Merck 3A).

Apparatus for H^E Measurements. Excess molar enthalpies were measured with an isothermal microcalorimeter model 4400 manufactured by Calorimetry Science Corp. (CSC), Provo, UT. This differential heat conduction instrument incorporates two test wells (sample and reference) in a large aluminum heat sink that is immersed in an ultrastable thermostating bath. The microcalorimeter is equipped with flow mixing cells (model 4442) that have been recently reconstructed by CSC to improve their performance. Contrary to the original construction using an inefficient mixing tee, mixing in the new design is achieved in a concentric tube arrangement in which the inner tube and the outer tube provide the inlets for two liquids to be mixed. A schematic diagram of the flow mixing microcalorimeter assembly was described previously.[12] 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 combined flow rate chosen from the range (0.20 to 0.31) mL·min^{-1} while the ratio of individual flow rates is varied to carry out measurements for different compositions. The flow rates can be set within the resolution of 0.01 mL·min^{-1}. 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 that 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). A PC controls data acquisition and calibration. Details concerning the calorimeter are given elsewhere.[9]

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

x_1	y_1	T/K	P/kPa	$\gamma_{1,\text{meas}}$	$\gamma_{2,\text{meas}}$	$\Delta\gamma_1{}^a$	$\Delta\gamma_2{}^b$
0.0000	0.0000	374.34	101.4		1.00		0.00
0.0182	0.0931	371.26	101.5	2.85	1.01	0.30	−0.01
0.0367	0.1725	368.50	101.5	2.89	1.01	0.16	−0.01
0.0693	0.2719	364.78	101.5	2.75	1.03	0.10	−0.02
0.1221	0.3689	361.03	101.5	2.43	1.05	0.08	−0.03
0.1776	0.4304	358.79	101.5	2.12	1.09	0.08	−0.03
0.3266	0.5251	355.38	100.5	1.59	1.22	0.06	−0.05
0.3637	0.5450	354.97	100.6	1.51	1.25	0.05	−0.04
0.4194	0.5745	354.39	100.5	1.41	1.30	0.03	−0.03
0.4910	0.6064	353.82	100.5	1.30	1.40	0.01	−0.02
0.5432	0.6330	353.51	100.5	1.24	1.47	0.00	−0.01
0.5826	0.6522	353.34	100.5	1.20	1.53	0.00	0.00
0.6274	0.6755	353.18	100.5	1.16	1.61	−0.01	0.02
0.6673	0.6955	353.07	100.4	1.13	1.69	−0.01	0.02
0.7037	0.7158	353.05	100.5	1.10	1.78	−0.01	0.03
0.7410	0.7446	353.04	100.5	1.09	1.83	−0.02	0.08
0.7781	0.7615	353.09	100.5	1.06	1.99	−0.01	0.03
0.8144	0.7872	353.20	100.5	1.04	2.12	−0.01	0.02
0.8514	0.8190	353.35	100.5	1.03	2.24	−0.01	0.03
0.9113	0.8742	353.80	100.5	1.01	2.57	0.00	−0.05
0.9458	0.9155	354.20	100.5	1.00	2.79	0.00	−0.11
0.9692	0.9489	354.55	100.6	1.00	2.94	0.00	−0.15
0.9834	0.9721	354.81	100.6	1.00	2.96	0.00	−0.09
1.0000	1.0000	355.13	100.6	1.00		0.00	

[a] $\Delta\gamma_1 = \gamma_{1,\text{model}} - \gamma_{1,\text{meas}}$. [b] $\Delta\gamma_2 = \gamma_{2,\text{model}} - \gamma_{2,\text{meas}}$.

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

x_1	y_1	T/K	P/kPa	$\gamma_{1,\text{meas}}$	$\gamma_{2,\text{meas}}$	$\Delta\gamma_1{}^a$	$\Delta\gamma_2{}^b$
0.0000	0.0000	374.34	101.3		1.00		0.00
0.0108	0.0383	373.26	101.3	3.43	1.00	0.08	0.00
0.0373	0.1196	370.90	101.3	3.39	1.01	−0.08	0.00
0.0780	0.2025	368.40	101.3	3.01	1.02	−0.01	−0.01
0.1285	0.2704	366.57	101.3	2.61	1.04	0.02	−0.01
0.1823	0.3182	365.40	101.3	2.26	1.07	0.05	−0.02
0.2309	0.3513	364.75	101.3	2.02	1.11	0.05	−0.02
0.2732	0.3754	364.37	101.3	1.85	1.14	0.05	−0.02
0.3303	0.4050	364.01	101.2	1.68	1.19	0.04	−0.02
0.3814	0.4285	363.83	101.2	1.55	1.24	0.03	−0.02
0.4368	0.4524	363.74	101.2	1.43	1.31	0.02	−0.01
0.4884	0.4745	363.73	101.2	1.34	1.39	0.02	−0.01
0.5419	0.4980	363.83	101.2	1.27	1.47	0.01	0.00
0.5895	0.5211	363.99	101.2	1.21	1.56	0.01	0.00
0.6509	0.5552	364.20	100.9	1.15	1.69	0.00	0.02
0.6659	0.5626	364.31	100.9	1.14	1.73	0.00	0.01
0.6992	0.5814	364.57	100.9	1.11	1.83	0.00	0.01
0.7231	0.5964	364.77	100.8	1.09	1.90	0.00	0.01
0.7439	0.6139	365.01	100.8	1.08	1.95	0.00	0.02
0.7716	0.6316	365.35	100.8	1.06	2.07	0.01	0.00
0.8034	0.6573	365.85	100.7	1.04	2.20	0.01	−0.01
0.8398	0.6915	366.51	100.6	1.02	2.39	0.01	−0.05
0.8696	0.7288	367.17	100.6	1.01	2.53	0.01	−0.05
0.8973	0.7653	367.93	100.5	1.00	2.72	0.02	−0.11
0.9165	0.8013	368.52	100.4	1.00	2.78	0.01	−0.07
0.9314	0.8224	369.01	100.3	0.99	2.99	0.02	−0.19
0.9775	0.9325	370.95	100.5	1.00	3.28	0.00	−0.21
0.9900	0.9713	371.59	100.5	1.00	3.07	0.00	0.08
1.0000	1.0000	372.14	100.5	1.00		0.00	

[a] $\Delta\gamma_1 = \gamma_{1,\text{model}} - \gamma_{1,\text{meas}}$. [b] $\Delta\gamma_2 = \gamma_{2,\text{model}} - \gamma_{2,\text{meas}}$.

Apparatus for VLE Measurements. The VLE runs were conducted with a circulation still of the Yerazunis-type[7] built at the glass workshop of Helsinki University of Technology with minor modifications to the original design.[8] Approximately 80 mL of reagents was needed to run the apparatus.

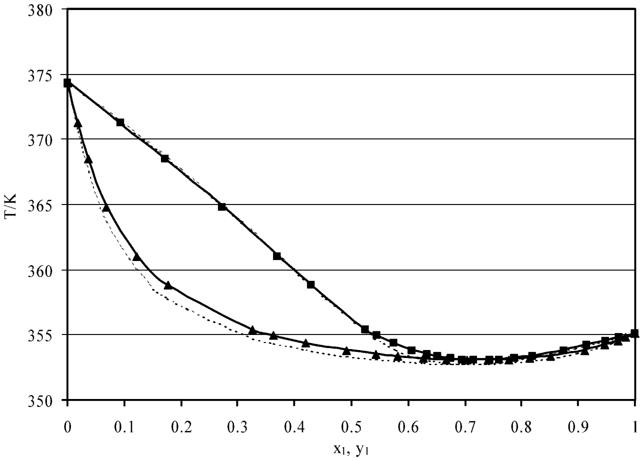

Figure 1. Temperature−composition diagram for the 2-methyl-2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at atmosphere pressure: ▲, x_1 from data; ■, x_2 from data; —, x_1 and x_2 by the Wilson model-extended data; - - -, x_1 and y_1 by the UNIFAC−Dortmund model.

Temperature was measured with a Thermolyzer S2541 (Frontec) temperature meter with a Pt-100 probe calibrated at the Inspecta Oy (Helsinki, Finland). The Pt-100 probe was located at the bottom of the packed section of the equilibrium chamber. The resolution of the temperature measurement system was 0.005 K, and the calibration uncertainty was ±0.015 K. The uncertainty of the whole temperature measurement system is estimated to be ±0.05 K. Pressure was measured with a Druck pressure transducer (0 to 100 kPa) and a Red Lion panel meter. The inaccuracy of the instruments was reported to be ±0.07 kPa by the manufacturer. The pressure measurement system was calibrated against a DHPPC-2 pressure calibrator. The inaccuracy of the whole pressure measurement system, including the calibration uncertainty, is expected to be less than ±0.15 kPa. The experimental setup was described previously.[12]

Analysis of VLE and GC Calibration. The equilibrated liquid phase was cooled and withdrawn from the sample chamber. The equilibrated vapor phase was first condensed and then sampled in liquid phase from the sample chamber. The liquid and vapor samples were analyzed with an 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, the run time was 9 min, the inlet split ratio was 50:1, the carrier gas was He (1.4 mL·min^{-1}), and the FID temperature was 250 °C. Toluene was used as a solvent for the samples to reduce the volume of the sample.

Procedure. Pure component 1 was introduced to the circulation still, and its vapor pressure was measured; then component 2 was introduced into the equilibrium still. It took approximately (15 to 30) min to achieve constant boiling temperature when the differences in boiling point of the pure components were large. The temperature was held constant for approximately 35 min to guarantee the steady state condition before sampling. Approximately 1 mL of toluene was added to the 2 mL autosampler vials before sampling was carried out. The samples from the liquid phase and from the vapor condensate were taken with a 1 mL Hamilton Sample Lock syringe. The syringe was flushed with (0.1 to 0.2) mL of sample before a (0.4 to 0.5) mL sample was taken and injected into the cooled 2 mL autosampler vial.

Results and Discussion

The measured equilibrium data and calculated activity coefficients are reported in Tables 1 and 2 and shown in Figures 1−4. Both systems exhibit positive deviations from

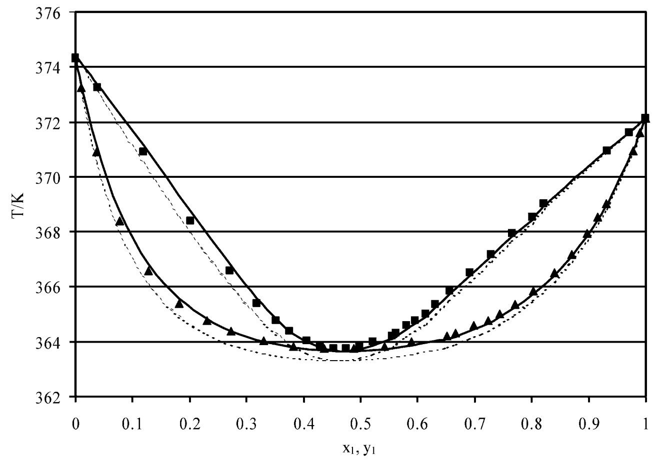

Figure 2. Temperature−composition diagram for the 2-butanol (1) + 2,4,4-trimethyl-1-pentene (2) system at atmosphere pressure: ▲, x_1 from data; ■, y_1 from data; —, x_1 and y_1 by the Wilson model-extended data; - - -, x_1 and y_1 by the UNIFAC−Dortmund model.

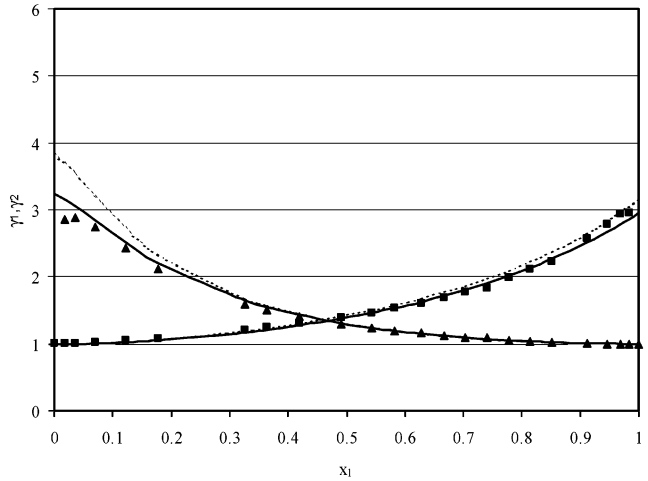

Figure 3. Activity coefficient−composition diagram for the 2-methyl-2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at atmosphere pressure: ▲, γ_1 from data; ■, γ_2 from data; —, γ_1 and γ_2 by the Wilson model-extended data; - - -, γ_1 and γ_2 by the UNIFAC−Dortmund model.

Raoult's law. Azeotropic behavior with a minimum boiling temperature was observed for both the 2-methyl-2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) (T = 352.83 K, P = 100.5 kPa, x_1 = 0.73) and 2-butanol (1) + 2,4,4-trimethyl-1-pentene (2) (T = 363.72 K, P = 101.2 kPa, x_1 = 0.46) systems, respectively. The activity coefficients γ_i were calculated from the following equation

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

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 the mole fraction of component i in the liquid phase, $P_{\mathrm{vp}i}$ is the vapor pressure of pure component i at the system temperature, ϕ_i^{s} is the pure component saturated liquid fugacity coefficient at the system temperature, $V_{\mathrm{L},i}$ is the molar volume of component i in the liquid phase at the system temperature, T is the temperature in Kelvin, and R is the universal gas constant (8.314 41 J·K^{-1}·mol^{-1}).

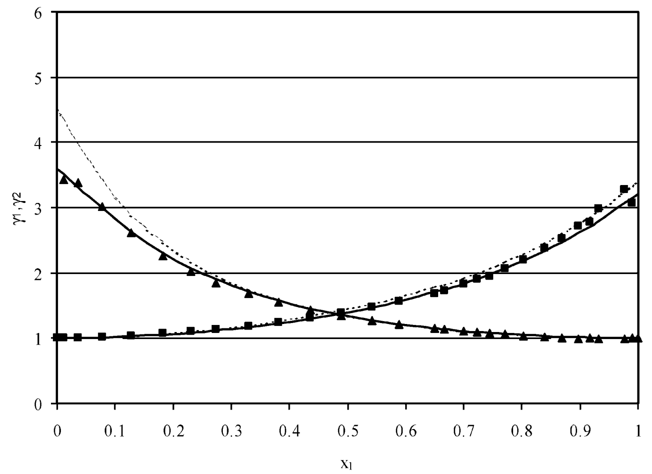

Figure 4. Activity coefficient−composition diagram for the 2-butanol (1) + 2,4,4-trimethyl-1-pentene (2) system at atmosphere pressure: ▲, γ_1 from data; ■, γ_2 from data; —, γ_1 and γ_2 by the Wilson model-extended data; - - -, γ_1 and γ_2 by the UNIFAC−Dortmund model.

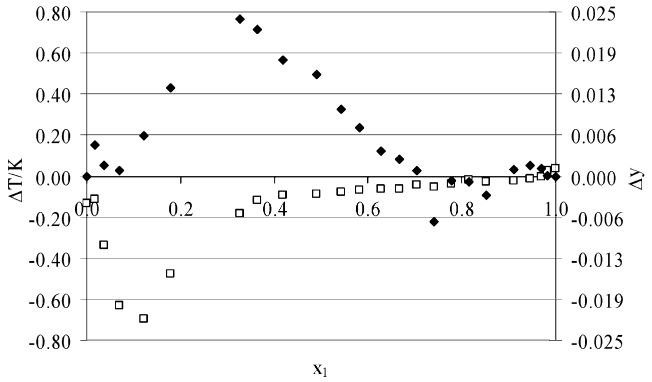

Figure 5. Point test for the 2-methyl-2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at atmospheric pressure: ◆, Δy; □, ΔT.

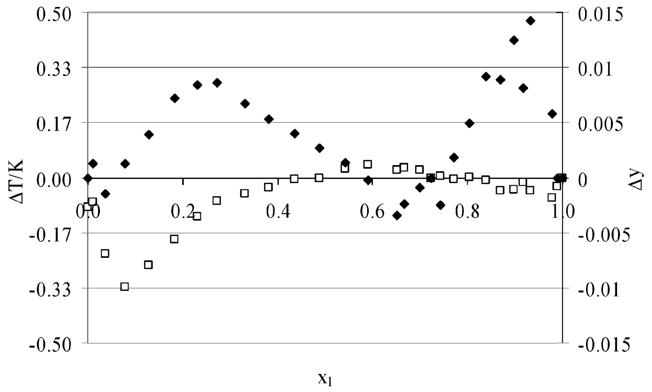

Figure 6. Point test for the 2-butanol (1) + 2,4,4-trimethyl-1-pentene (2) system at atmospheric pressure: ◆, Δy; □, ΔT.

The Soave−Redlich−Kwong (SRK) equation of state that has quadratic mixing rules in the attractive parameter and is linear in covolume was used for calculation of fugacity coefficients.[10] The binary interaction parameters of the SRK equation were set to zero for these two systems. This is justified by the low pressure, which makes the vapor phase nearly ideal.

The critical temperature, critical pressure, critical volume, acentric factor, and liquid molar volume for each component needed in the calculation are presented in Table

Table 3. Physical Properties of the Pure Components: 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,[a] and the Recommended Temperature Range of the Vapor Pressure Correlation (T_{min}, T_{max})

	2-methyl-2-propanol	2-butanol	2,4,4-trimethyl-1-pentene
T_c/K	506.2 ± 5[b]	536.01 ± 5[b]	553.00 ± 28[b]
P_c/MPa	3.9719 ± 0.12[b]	4.1938 ± 0.12[b]	2.630 ± 0.26[b]
V_c/cm^3·mol^{-1}	275 ± 11[b]	268 ± 13[b]	465 ± 116[b]
ω	0.6158[b]	0.5711[b]	0.2695[b]
v_i/cm^3·mol^{-1}	94.861 ± 2.8[b]	92.118 ± 0.9[b]	157.915 ± 4.7[b]
A	10.401[c]	8.3640[c]	6.9460[c]
B	3982.9[c]	3026.1[c]	2999.3[c]
C	−41.420[c]	−88.316[c]	−49.678[c]
T_{min}/K	329.76[c]	325.05[c]	333.11[c]
T_{max}/K	355.24[c]	372.20[c]	374.33[c]

[a] See eq 2 for dimensions and details (vapor pressure data measured). [b] Daubert and Danner.[15] [c] Uusi-Kyyny et al.[3]

3. The vapor pressures of the pure substances were calculated with an Antoine type equation,

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

The parameters of this equation were optimized from the data measured in our apparatus. These parameters with the recommended temperature range of the vapor pressure equations are also presented in Table 3. Pure component vapor pressures for 2-methyl-2-propanol, 2-butanol, and 2,4,4-trimethyl-1-pentene were measured previously in our laboratory.[8,12]

During the parameter fitting of the Wilson equation, both VLE and HE measurements were correlated simultaneously. The following objective function was used.

$$\mathrm{OF} = \frac{1}{N_{\mathrm{VLE}}}\sum_{i=1}^{N_{\mathrm{VLE}}}\sum_{j=1}^{2}\left|\frac{\gamma_{i,j,\mathrm{model}} - \gamma_{i,j,\mathrm{meas}}}{\gamma_{i,j,\mathrm{meas}}}\right| + \frac{1}{N_{\mathrm{HE}}}\sum_{1}^{N_{\mathrm{HE}}}\left|\frac{H^{\mathrm{E}}_{i,\mathrm{model}} - H^{\mathrm{E}}_{i,\mathrm{meas}}}{H^{\mathrm{E}}_{i,\mathrm{meas}}}\right| \tag{3}$$

The Gibbs−Helmholtz equation interrelates the excess Gibbs energy and the excess enthalpy. The excess enthalpy was computed from the relation

$$H^{\mathrm{E}}_{\mathrm{model}} = -RT^2\left(\sum_{i=1}^{NC} x_i \frac{\partial(\ln \gamma_{i,\mathrm{model}})}{\partial T}\right)_{p,x} \tag{4}$$

The parameters of the Wilson model[11] are given in Table 4. Comparisons of the experimental points and the fitted Wilson model are given in Figures 1−4 and 7−8.

The activity coefficients were also predicted using a variation of the group contribution method, the modified UNIFAC (Dortmund) method.[16] The predictions are also presented in Figures 1−4 and 7−8. It is seen that predictive method can predict the azeotropic concentrations reasonably well. Also temperature and pressure predictions

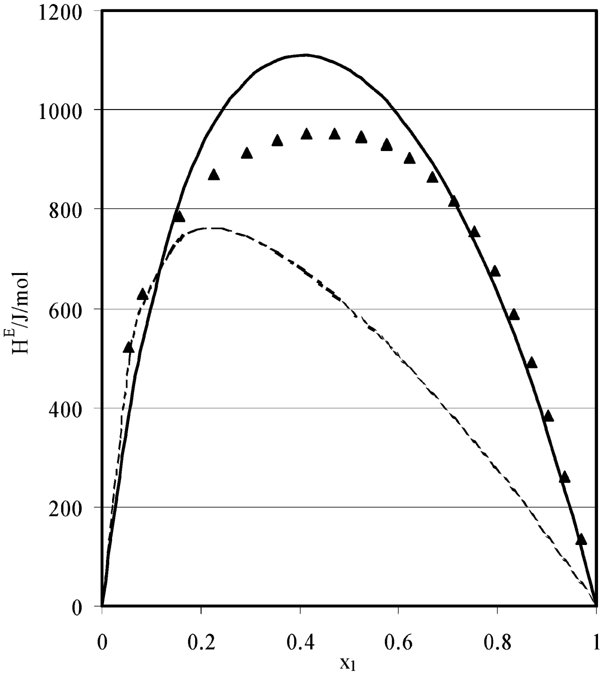

Figure 7. Excess molar enthalpy for the 2-methyl-2-propanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 300 K: ▲, measured; —, Wilson model-extended data; - - -, UNIFAC−Dortmund model.

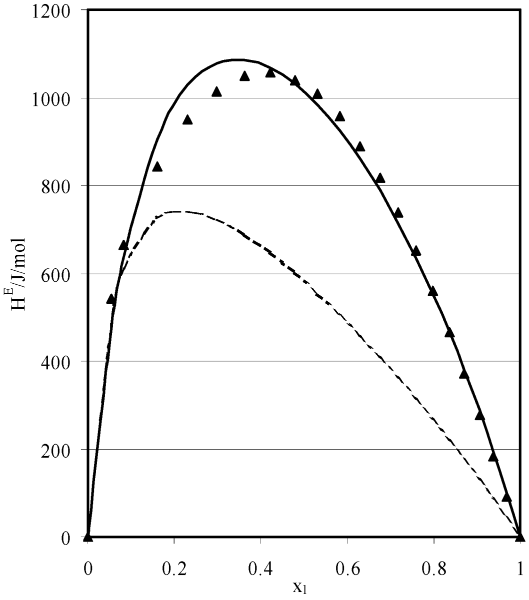

Figure 8. Excess molar enthalpy for the 2-butanol (1) + 2,4,4-trimethyl-1-pentene (2) system at 298 K: ▲, measured; —, Wilson model-extended data; - - -, UNIFAC−Dortmund model.

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

	$a_{0,12}$[a]	$a_{1,12}$[b]	$a_{2,12}$[c]	$a_{0,21}$[a]	$a_{1,21}$[b]	$a_{2,21}$[c]
extended system 1[d]	3849.176	16.665 56	−0.0414	−1254.9096	17.244 17	−0.040 25
extended system 2[e]	5665.996	17.862 56	−0.05763	962.9221	0.6798 11	−0.007 65

[a] In units of J·mol^{-1}. [b] In units of J·mol^{-1}·K^{-1}. [c] In units of J·mol^{-1}·K^{-2}. [d] Data of this work + data for the binary system 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene at 333 K and 348 K.[3] [e] Data of this work + data for the binary system 2-butanol + 2,4,4-trimethyl-1-pentene at 360 K.[3]

Table 5. Results of the Consistency Tests for 2-Methyl-2-propanol + 2,4,4-Trimethyl-1-pentene (System 1) and 2-Butanol + 2,4,4-Trimethyl-1-pentene (System 2) at Atmospheric Pressure

binary pair	integral test	infinite dilution test	point test
system 1	$D = 8.5\%$ $J = 8.9\%$ $D - J = -0.5\%$	36.1% ($x_1 = 0$) −3.0% ($x_1 = 1$)	$\lvert\Delta y_{\text{aver}}\rvert = 0.006$ $\lvert\Delta T_{\text{aver}}\rvert = 0.137$ K
system 2	$D = 4.0\%$ $J = 4.4\%$ $D - J = -0.4\%$	16.9% ($x_1 = 0$) −16.2% ($x_1 = 1$)	$\lvert\Delta y_{\text{aver}}\rvert = 0.004$ $\lvert\Delta T_{\text{aver}}\rvert = 0.065$ K

Table 6. Excess Molar Enthalpy for 2-Methyl-2-propanol (1) + 2,4,4-Trimethyl-1-pentene (2) (System 1) at 300.15 K and 2-Butanol (1) + 2,4,4-Trimethyl-1-pentene (2) (System 2) at 298.15 K

	system 1			system 2	
	H^E	$\Delta H^{E\,a}$		H^E	$\Delta H^{E\,a}$
x_1	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$	x_1	$J\cdot mol^{-1}$	$J\cdot mol^{-1}$
0.0529	521.8	−139.1	0.0544	542.0	−68.2
0.0811	630.4	−97.5	0.0832	665.0	−28.6
0.1559	786.6	26.8	0.1597	843.8	60.9
0.2264	869.6	102.4	0.2314	949.2	79.0
0.2928	914.2	144.9	0.2987	1015.1	63.3
0.3555	939.4	160.7	0.3621	1048.5	37.9
0.4148	950.9	158.4	0.4217	1056.3	11.6
0.4710	952.0	143.2	0.4781	1040.5	−8.8
0.5241	946.3	117.2	0.5313	1010.1	−27.0
0.5242	942.9	120.5	0.5818	957.9	−32.8
0.5747	930.0	87.4	0.6296	890.1	−30.0
0.5747	930.1	87.5	0.6750	818.7	−29.1
0.6229	902.9	57.0	0.7182	738.5	−24.2
0.6687	865.9	26.9	0.7593	651.2	−16.0
0.7124	817.2	0.0	0.7986	559.5	−7.0
0.7541	754.2	−19.8	0.8360	466.9	0.0
0.7939	675.6	−30.5	0.8717	372.7	5.9
0.8320	589.6	−39.7	0.9059	278.3	9.3
0.8685	492.5	−43.3	0.9386	182.7	11.4
0.9034	382.7	−38.9	0.9699	91.5	6.9
0.9369	262.1	−28.5			
0.9691	136.3	−17.5			

[a] $\Delta H^E = H^E_{\text{model}} - H^E_{\text{meas}}$.

are adequate for preliminary design, since the deviations in temperature are less than 2 °C. There are clear deviations in the predicted activity coefficients (Figures 3 and 4) in low concentration areas. Since the azeotropic points are in the middle concentration area, these deviations in the low concentration area do not cause serious problems for distillation design by using the predictive UNIFAC model. The results of the integral test,[13] the infinite dilution test,[14] and the point test[13] are presented in Table 5. The two data sets passed both the integral test and the point test. In the point test, the data set is considered consistent[13] if the average deviations between the measured and the calculated values for the vapor phase are smaller than 0.01 mol fraction unit (see Table 5 and Figures 5 and 6). For the evaluation of the deviations Δy_1 and ΔT in the point test, the Wilson model with the parameters given in Table 4 was used. The parameters were obtained by the simultaneous correlation of several series of VLE data (this work and the previous one[3]) and the excess enthalpy data (this work). Slight inconsistency of the correlated data series caused the deviations Δy_1 and ΔT to be not randomly scattered about their zero values. Considering the infinite dilution test, the data set of 2-methyl-2-propanol is not consistent in the dilute region. This is probably due to the lack of mixing in the sampling chambers and in the mixing chamber of the condensed vapor phase and the liquid phase.

The comparison between the measured molar excess enthalpy and the one calculated by the Wilson model is presented in Table 6 and in Figures 7 and 8. It is seen that the Wilson equation can model the excess enthalpies very well. In these two figures, excess enthalpies are also estimated by the Dortmund modification of the UNIFAC model. It underpredicts the maximum of the excess enthalpy.

Conclusions

VLE at atmospheric pressure and excess enthalpy data were measured for two alcohol + hydrocarbon systems, namely 2-methyl-2-propanol + 2,4,4-trimethyl-1-pentene and 2-butanol + 2,4,4-trimethyl-1-pentene. The data in this study extended with previous isothermal data[3] on VLE were correlated by the Wilson activity coefficient model, and an excellent fit was obtained for VLE data and a good fit for excess enthalpy data. The group contribution method modified UNIFAC (Dortmund) was also used to predict the behavior of the measured systems and gives reasonable predictions for VLE data of the systems.

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