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Isothermal Vapor−Liquid Equilibrium Data of Propan-1-ol + 2,2,4-Trimethylpentane and Butan-1-ol + 2,2,4-Trimethylpentane at 318.15 K

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ABSTRACT: In this research, vapor−liquid equilibrium (VLE) data were determined at 318.15 K for the mixtures propan-1-ol + 2,2,4-trimethylpentane and butan-1-ol + 2,2,4-trimethylpentane in an isothermic Othmer still with recirculation, where the temperature was kept constant by means of a proportional-integral (PI) cascade control for the vapor phase. The equilibrium concentration for each phase was determined by gas chromatography, and the vapor phase was considered as nonideal. The consistency of the data was verified by means of the Van Ness direct test of thermodynamic consistency, supported by several thermodynamic methods based on the Gibbs−Duhem equation. The correlation of the VLE data was carried out using the Wilson local composition model. The alkanol + 2,2,4-trimethylpentane mixtures studied exhibit positive contributions from ideality and azeotropic behavior.

INTRODUCTION

Quantitative information concerning the phase equilibria, specifically the vapor−liquid equilibrium (VLE) relations, is required for the design of equipment for separation processes such as distillation, absorption, and extraction. Therefore, an essential step for separation process simulation, design, and optimization is obtaining consistent VLE data. The VLEs of alkanol + 2,2,4-trimethylpentane mixtures have been widely studied because of their extended applicability as gasoline antiknock agents. Nevertheless, some studies also point to propan-1-ol and butan-1-ol as potential oxygenating agents in gasoline.[1−3] Among the published investigations of solutions of alcohols in nonpolar solvents, only a few have studied the mixtures presented in this work. The current literature includes some references about the VLE of propan-1-ol + 2,2,4-trimethylpentane under isothermal conditions,[4−6] but none of them was conducted at 318.15 K. No studies of butan-1-ol + 2,2,4-trimethylpentane mixtures using a condensate circulation technique have been reported to date.

EXPERIMENTAL SECTION

Materials. In this work, propan-1-ol and butan-1-ol were provided by Scharlau and were of the highest purity available [stated mass-fraction purities of 0.999 and 0.997, respectively, as determined by gas chromatography (GC)]. 2,2,4-Trimethylpentane (mass-fraction purity ≥ 0.99 by GC) was provided by Aldrich. The materials were used without additional purification.

Apparatus for VLE Measurements. The experimental measurments of isothermal VLE data were conducted with an Othmer-type circulating glass still[7] with a volume of 40 cm^3. Minor modifications were made to the original design. A schematic of the experimental setup is shown in Figure 1. The heating system for the liquid and vapor phases consisted of two electrical heating tapes (Brisk Heat) and power semiconductor devices. The temperatures were measured with two platinum resistance thermometers (Pt-100) calibrated against a mercury thermometer (0.1 K per division scale) with a thermostatted bath (Haake DC50-B3). The uncertainties in the temperature measurements were estimated as ± 0.07 K for the system containing 1-propan-1-ol and ± 0.05 K for the system containing 1-butan-1-ol. Temperature acquisition and control were performed using a data acquisition device (National Instruments NI-PCI-6014) with an interface (NI-SCC-68) and LabVIEW software.

The pressure measurement was made with a U-tube mercury manometer (1 cm^3 per division scale), and atmospheric pressure was measured by means of an absolute pressure gauge (Penwalt Wallace & Tiernan) with a range of (53.33 to 106.70) kPa. The pressure was carried to subatmospheric levels using a high-vacuum pump (Welch Scientific model 1402). The uncertainty of the pressure measurements was estimated as 0.02 kPa. The condensation system associated with the cell consisted of two glass condensers in series. The cooling liquid was an ethylene glycol solution (0.1053 mass fraction) in distilled water. The cooling liquid was refrigerated by means of an immersion cooler (Prolab).

Procedure. The experimental procedure was based on that proposed by Zudkevitch,[7] in which each liquid mixture having a

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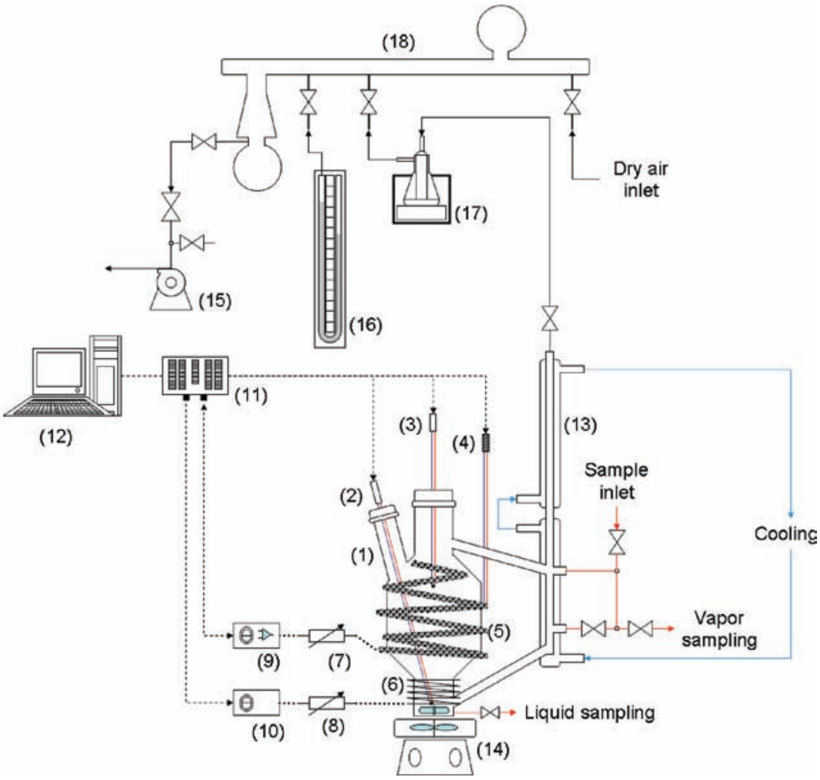

Figure 1. Experimental setup: VLE Othmer still (1); Pt-100 temperature probes (2, 3); K-type thermocouple (4); electric heating tapes (5, 6); rheostats (7, 8); power semiconductor devices (9, 10); NI-SCC-68 interface module (11); computer (12); double shell and tube condenser (13); magnetic stirrer (14); vacuum pump (15); U-tube mercury manometer (16); cold trap (17); manifold (18).

specific composition was prepared and charged in the cell to reach a volume of 40 cm^3. The liquid-phase temperature controller was set, and the liquid was heated by the electric heating tape. The liquid temperature was adjusted to the desired value by manual control of the the system's pressure. A proportional-integral controller was set up to control the temperature of the vapor phase, and it governed the heating tape for that phase by means of a power control circuit with a thyristor. The system was considered to be in equilibrium when temperature (T) and pressure (P) remained constant for about 1200 s, at which point extracted vapor condensate and liquid samples were immediately analyzed by gas chromatography.

Analysis of the Samples. Three liquid-phase and vapor-condensate-phase samples were analyzed with a gas chromatograph (PerkinElmer model 1020) equipped with a flame ionization detector and an HP-20 Carbowax 20 M column (30 m × 0.53 mm × 1.33 μm). Nitrogen was used as the carrier gas (0.05 cm$^3\cdot$s^{-1}) with an inlet split flow of 45 cm$^3\cdot$min^{-1} and an injection volume of 0.001 cm^3. The following temperature program was used: initial column temperature, 333.15 K (hold 1 min at 333.15 K); rate of temperature program, 315.15 K$\cdot$min^{-1} for (333.15 to 413.15) K; injector and detector temperatures, (523.15 and 573.15) K, respectively. The analysis time for each injection was about 180 s. The quantitative analysis of the samples was based on the internal standardization method of calibration.[8] Calibration was made by analysis of standard solutions having known mass compositions. Ethanol was selected as an internal standard, whereas samples were diluted with hexane. The uncertainty of the measured liquid (x_i) and vapor (y_i) mole fractions was ± 0.004.

Table 1. Experimental VLE Data for Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (y_1), Pressure (P),[a] and Activity Coefficients (γ_1, γ_2) for the Propan-1-ol (1) + 2,2,4-Trimethylpentane (2) System at 318.15 K

P/kPa	x_1	y_1	γ_1	γ_2
19.00	0.0475	0.1888	8.1388	1.0093
19.13	0.0539	0.1948	7.4497	1.0154
19.93	0.0759	0.2467	6.9703	1.0128
20.53	0.1262	0.2719	4.7559	1.0660
20.53	0.1265	0.2742	4.7845	1.0630
20.66	0.1507	0.2903	4.2772	1.0758
20.66	0.1514	0.2906	4.2618	1.0763
20.93	0.1966	0.3083	3.5257	1.1229
21.06	0.2416	0.3186	2.9824	1.1790
21.06	0.2751	0.3206	2.6356	1.2299
20.93	0.2784	0.3294	2.6590	1.2123
21.13	0.3925	0.3317	1.9171	1.4485
21.06	0.3997	0.3371	1.9067	1.4494
21.00	0.4225	0.3534	1.8829	1.4666
21.00	0.4294	0.3596	1.8891	1.4684
20.93	0.5060	0.3491	1.5498	1.7191
20.66	0.5673	0.3679	1.4376	1.8822
20.66	0.6061	0.3707	1.3558	2.0586
20.33	0.6248	0.3634	1.2473	2.1188
20.27	0.6810	0.3897	1.2443	2.4200
19.47	0.7875	0.4062	1.0774	3.3983
15.47	0.9182	0.5673	1.0254	5.1391

[a] Standard uncertainties (u) are $u(P) = 0.02$ kPa, $u(x) = u(y) = 0.004$, $u(T) = 0.07$ K.

■ RESULTS AND DISCUSSION

The measured VLE data (P, x_1, y_1) and the calculated activity coefficients for the propan-1-ol (1) + 2,2,4-trimethylpentane (2) and butan-1-ol (1) + 2,2,4-trimethylpentane (2) systems at 318.15 K are reported in Tables 1 and 2 and are presented in Figures 2 and 3 along with modeled data.

Table 2. Experimental VLE Data for Liquid-Phase Mole Fraction (x_1), Vapor-Phase Mole Fraction (y_1), Pressure (P),[a] and Activity Coefficients (γ_1, γ_2) for the Butan-1-ol (1) + 2,2,4-Trimethylpentane (2) System at 318.15 K

P/kPa	x_1	y_1	γ_1	γ_2
16.40	0.0797	0.0991	6.0309	1.0038
16.40	0.1015	0.0960	4.5881	1.0317
16.40	0.1020	0.1012	4.8118	1.0263
16.33	0.1066	0.1013	4.5891	1.0272
16.13	0.3039	0.1572	2.4616	1.2219
16.00	0.3633	0.1671	2.1704	1.3098
15.93	0.3638	0.1691	2.1837	1.3021
15.87	0.3837	0.1700	2.0736	1.3377
15.53	0.4933	0.1768	1.6414	1.5797
15.27	0.5897	0.1888	1.4413	1.8910
15.07	0.6242	0.1905	1.3560	2.0337
14.93	0.6624	0.2011	1.3360	2.2139
14.93	0.6657	0.2033	1.3438	2.2297
14.40	0.7458	0.2220	1.2629	2.7637
13.60	0.8359	0.2470	1.1838	3.9173
13.00	0.8623	0.2524	1.1213	4.4330
12.53	0.8831	0.2574	1.0765	5.0018
11.40	0.9191	0.2834	1.0364	6.3537
11.27	0.9230	0.2936	1.0568	6.5069
9.33	0.9483	0.3532	1.0251	7.3629
7.20	0.9751	0.4642	1.0119	9.8003

[a] Standard uncertainties (u) are $u(P) = 0.02$ kPa, $u(x) = u(y) = 0.004$, $u(T) = 0.05$ K.

The experimental activity coefficients of component i (γ_i) were computed using eq 1:

$$\phi_i P y_i = (\gamma_i P_i^{\circ} x_i \phi_i^{\circ}) \exp\left[v_i^{\mathrm{L}}(P - P_i^{\circ})/RT\right] \qquad (1)$$

wherein the fugacity coefficients of component i in the mixture and under saturated conditions (ϕ_i and ϕ_i°, respectively) were calculated using eq 2, which takes into account vapor-phase deviations from the perfect gas law by using the virial equation of state truncated after the second virial coefficient (B):[9,10]

$$\ln \phi_i = \frac{P}{RT}\left[2\sum_{j=1}^{n} y_i B_{ij} - B\right] \qquad (2)$$

In a mixture of n components, B is expressed in terms of the second virial coefficients B_{ij} characterizing pair interactions between molecules i and j. The second virial coefficients were estimated according the Hayden−O'Connell method,[10] which accounts for the association and chemical bonding in the vapor phase. The vapor pressures of the pure components (P_i°) were calculated using the equations compiled by Reid et al.,[11] and the liquid-phase molar volumes (v_i^{L}) were obtained using the Rackett equation.[12] Calculations of the experimental activity coefficients were obtained with the ASPEN PLUS Process Simulator, version 10. Values of second virial coefficients and v_i^{L} are given in Table 3.

The correlation of the data was performed using the Wilson equation[13] according to the type of mixtures and extensive and successful use by previous researchers.[5,6,14,15] Regression was done using Barker's method,[16] and optimum Wilson binary interaction parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) were obtained by minimization of the following objective function (OF):

$$\mathrm{OF} = \sum_{i=1}^{n} (P_{\mathrm{exptl},\,i} - P_{\mathrm{calcd},\,i})^2 \qquad (3)$$

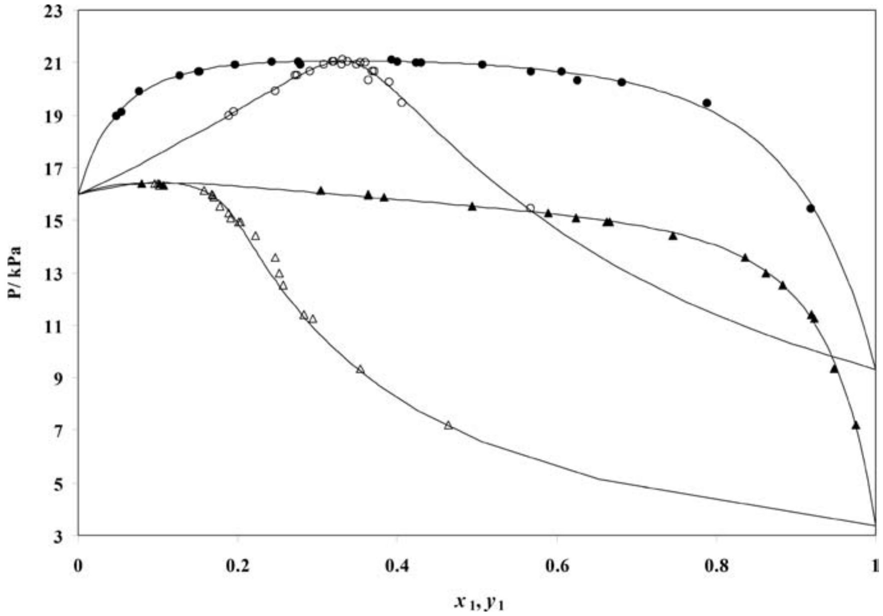

Figure 2. Pressure−composition diagram for the two binary systems at 318.15 K. Propan-1-ol (1) + 2,2,4-trimethylpentane (2): ●, measured x_1; ○, measured y_1. Butan-1-ol (1) + 2,2,4-trimethylpentane (2): ▲, measured x_1; △, measured y_1. Solid curves were obtained using the Wilson model.

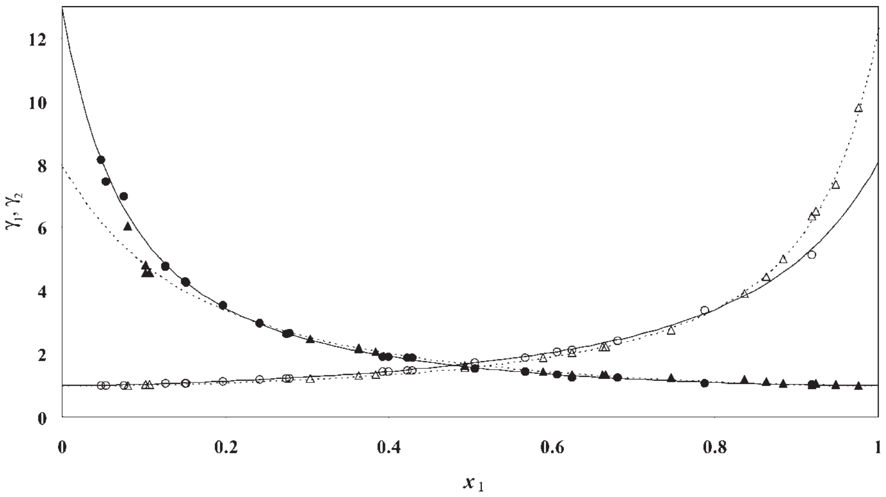

Figure 3. Activity coefficient—composition diagram for the two binary systems at 318.15 K. Propan-1-ol (1) + 2,2,4-trimethylpentane (2): ●, γ_1 obtained from the data; ○, γ_2 obtained from the data. Butan-1-ol (1) + 2,2,4-trimethylpentane (2): ▲, γ_1 obtained from the data; △, γ_2 obtained from the data. The curves were obtained using the Wilson model.

Table 3. Molar Volumes of Pure Liquids (v_i^L) and Second Virial Coefficients (B_{ii}, B_{ij}) at T = 318.15 K

	propan-1-ol		butan-1-ol		2,2,4-trimethylpentane	
	this work	literature	this work	literature	this work	literature
v_i^L/cm^3·mol^{-1}	75.6	76.70 [a]	94.8	–	167.05	–
B_{ii}/cm^3·mol^{-1}	−1731.10	−1862, [a] −1769.42[b]	−1940.96	−2136.47[b]	−950.26	–
B_{ij}/cm^3·mol^{-1}	−512.17	–	−638.84	–	–	–

[a] Reference 20. [b] Reference 21.

Table 4. Regressed Wilson Interaction Parameters ($\lambda_{12} - \lambda_{11}$) and ($\lambda_{21} - \lambda_{22}$) for the Measured Binary Systems at 318.15 K and the Root-Mean-Square Deviation between the Experimental and Modeled Values of the Pressure (δP)

	($\lambda_{12} - \lambda_{11}$)	($\lambda_{21} - \lambda_{22}$)	δP[a]
binary system	J·mol^{-1}	J·mol^{-1}	kPa
propan-1-ol (1) + 2,2,4-trimethylpentane (2)	6945.424	1244.389	0.09
butan-1-ol (1) + 2,2,4-trimethylpentane (2)	4824.458	3113.257	0.09

[a] $\delta P = [\sum_{i=1}^{n} (P_{\mathrm{exptl},i} - P_{\mathrm{calcd},i})^2/n]^{1/2}$.

Table 5. Results of the Direct Test of Consistency, the Integral Test, and the Infinite Dilution Test for the Measured Systems

				infinite dilution test[c]	
	direct test[a]		integral test[b]	extrapolation error/%	
binary system	$\delta \ln(\gamma_1/\gamma_2)$	consistency index	error function	$x_1 = 0$	$x_1 = 1$
propan-1-ol (1) + 2,2,4-trimethylpentane (2)	0.034	2	4.0×10^{-7}	1	7
butan-1-ol (1) + 2,2,4-trimethylpentane (2)	0.049	2	3.0×10^{-9}	1	12

[a] Criterion for passing the direct test of consistency: $0.025 < \delta \ln(\gamma_1/\gamma_2) \leq 0.050$ and consistency index = 2, where $\delta \ln(\gamma_1/\gamma_2)$ is the rmsd of $\ln(\gamma_1/\gamma_2)$, calculated as $\delta \ln(\gamma_1/\gamma_2) = \{\sum_{i=1}^{n} [\ln(\gamma_1/\gamma_2)_{\mathrm{exptl},i} - \ln(\gamma_1/\gamma_2)_{\mathrm{calcd},i}]^2/n\}^{1/2}$. [b] Criterion for passing the integral test: error function <5.0×10^{-5}. [c] Criterion for passing the infinite dilution test: extrapolation error closer to 10%.

The values of the regressed parameters and δP, the root-mean-square deviation (rmsd) between the experimental and calculated pressures, are presented in Table 4. Thermodynamic consistency was verified using the "direct test of consistency" suggested by Van Ness,[17] the integral test,[18] and the infinite dilution test.[18] The results of these tests are collected in Table 5.

Both binary systems exhibit positive deviations from Raoult's law and form a maximum-pressure azeotrope, in agreement with previously measured results for alkanol + hydrocarbon systems.[4−6,14,15] The azeotropic points were estimated to be (x_1 = 0.333, P = 21.06 kPa) for the propan-1-ol (1) + 2,2,4-trimethylpentane (2) system and (x_1 = 0.101, P = 16.42 kPa) for the butan-1-ol (1) + 2,2,4-trimethylpentane (2) system. The large values of the activity coefficients at low alkanol mole fractions is produced by the interactions of the alkanol molecules (hydrogen-bond rupture), as suggested in the literature,[10,19] and the association of the alkanols decreases with increasing alkanol chain length.

The Wilson model used to fit the experimental data gave good correlations for both systems. The rmsd of the pressure was δP = 0.09 kPa.

All sets of experimental data presented a "consistency index"[17] equal to 2 on a scale that starts at 1 for highly consistent data and goes to 10 for data of very poor quality. Also, both systems passed the integral and infinite dilution tests, proving that the data are consistent.

SUMMARY AND CONCLUSIONS

Consistent VLE data for propan-1-ol (1) + 2,2,4-trimethylpentane (2) and butan-1-ol (1) + 2,2,4-trimethylpentane (2) were measured at 318.15 K. No published VLE data for the butan-1-ol system obtained using a condensate circulation technique were found in the literature; three sets of VLE data are available for propan-1-ol (1) + 2,2,4-trimethylpentane (2), but these were obtained under different isotherm conditions. Both mixtures are highly nonideal, exhibiting positive deviations from Raoult's law and azeotropic behavior. The activity coefficients of the alkanols and 2,2,4-trimethylpentane were fit to the Wilson equation. Thermodynamic consistency tests showed that the data are consistent.

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