

Vapor–Liquid Equilibria for Pentane + Dodecane and Heptane + Dodecane at Low Pressures

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A Fischer recirculating still has been used to measure isobaric vapor–liquid equilibrium data for pentane + dodecane and heptane + dodecane at 70 and 100 kPa and 40, 70, and 100 kPa, respectively. The concentrations of the vapor and liquid mixtures have been determined with the aid of an oscillating tube densimeter. The excess volume behavior has also been found on the basis of density–composition calibration curves. Vapor pressure data of the pure components as function of the temperature have also been measured and indicated the reliability of the experimental procedure. Thermodynamic consistency tests of the vapor–liquid data have been checked using a maximum likelihood data reduction and the UNIQUAC model.

Introduction

Vapor–liquid equilibrium (VLE) data for hydrocarbon systems are of great importance to the design and operation of separation units and also to develop mixture models. A literature search indicated a complete lack of VLE data for the subject hydrocarbon systems, probably due to the weak deviations from ideal behavior. This work presents complete isobaric VLE data for the systems pentane + dodecane and heptane + dodecane, that had not been reported in the literature.¹ The measured VLE data and density–composition curves express the magnitude of nonidealities that originate mainly from size difference and may be used to test mixture theories. These data are also helpful for the description of the behavior of petroleum reservoir and petrochemical processes.

Experimental Section

Apparatus and Procedures. The VLE measurements were carried out in an all-glass Fisher ebulliometer model 602, manufactured by Fischer Labor und Verfahrenstechnik (Germany) and developed by Stage and Müller in 1961.² The still provides for the recirculation of the liquid and condensed vapor phases. The first steady state was usually reached after 1.5 h of operation. The temperature was measured with a platinum resistance thermometer, which was calibrated with pure component vapor pressures and was determined to be accurate within ± 0.05 K over the range of 278 to 503 K. A heating mantle was placed around the equilibrium cell with a controlled temperature of 1 K lower than the inside equilibrium temperature to minimize heat transfer, especially for high boiling point systems. Pressure was measured by a digital transducer, which was calibrated against a mercury barometer.³ A buffer tank was used to minimize the fluctuations of pressure, which was controlled by an automatic vacuum-pressure system to within ± 0.02 kPa. The compositions of the liquid and condensed vapor phases were determined by measuring the

Table 1. Sources, Purities, Density, ρ , and Refractive Index, n_D , of the Pure Components

component	supplier	purity mol %	$\rho(298.15 \text{ K})/\text{g}\cdot\text{cm}^{-3}$		$n_D(298.15 \text{ K})$	
			exp	lit. ¹	exp	lit. ⁶
pentane	Merck	≥ 99	0.622 75	0.621 40	1.3565	1.3547
heptane	Merck	≥ 99	0.682 99	0.679 50	1.3855	1.3851
dodecane	Merck	≥ 99	0.748 02	0.745 13	1.4198	1.4151

Table 2. Density for Pentane (1) + Dodecane (2) and Heptane (1) + Dodecane (2) at 298.15 K and Excess Volume Redlich–Kister Correlation^a

Pentane (1) + Dodecane (2) ^b				Heptane (1) + Dodecane (2) ^c			
x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$	x_1	$\rho/\text{g}\cdot\text{cm}^{-3}$
0.1851	0.736 70	0.7471	0.677 86	0.1475	0.742 04	0.6996	0.710 55
0.3293	0.726 24	0.8211	0.664 82	0.2796	0.735 94	0.7840	0.703 81
0.4571	0.714 29	0.8872	0.651 56	0.3998	0.729 75	0.8615	0.697 14
0.5671	0.702 49	0.9465	0.637 63	0.5094	0.723 43	0.9334	0.690 19
0.6629	0.690 36			0.6086	0.717 08		

^a $\text{AAD}(v^E) = (1/N)\sum_1^N |v_{\text{exp}}^E - v_{\text{calc}}^E|$; ^b $v^E = x_1(1 - x_1)(-4.0487 - 2.3041(2x_1 - 1) - 2.1840(2x_1 - 1)^2)$; $\text{AAD}(v^E) = 0.020 \text{ cm}^3\cdot\text{mol}^{-1}$.
^c $v^E = x_1(1 - x_1)(-1.4929 - 0.5957(2x_1 - 1) - 0.3639(2x_1 - 1)^2)$; $\text{AAD}(v^E) = 0.005 \text{ cm}^3\cdot\text{mol}^{-1}$.

density at 298.15 K and comparing the results with densities of mixtures of known composition, via inverse interpolation. The densities were measured with an Anton Paar Model DMA-60 digital densimeter with a precision of $\pm 5 \times 10^{-5} \text{ g}\cdot\text{cm}^{-3}$. The temperature of the density-cell was fixed by circulating thermostated water from a Heto thermostatic bath, and it is considered to be accurate within ± 0.05 K. The experimental procedure for determining VLE data may be summarized in the following steps: (1) charge a mixture of adequate composition in the ebulliometer; (2) fix the desired pressure and start the heating at the recommended rate and set-point of the control system; (3) wait for the recirculation and steady-state condition, observing the nature of the liquid and condensed flows, with the goal of a smooth type and the stabilization of the temperatures; (4) after 1 h of steady state at the fixed pressure, record the temperature of the cell and withdraw samples of the liquid and vapor phases

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Table 3. Vapor Pressures, P^S , of Pentane, Heptane, and Dodecane as a Function of Temperature, T

Pentane				Heptane				Dodecane			
T/K	P^S/kPa	T/K	P^S/kPa	T/K	P^S/kPa	T/K	P^S/kPa	T/K	P^S/kPa	T/K	P^S/kPa
278.15	30.00	302.49	80.00	325.32	20.00	359.57	70.00	432.17	20.00	474.03	70.00
284.76	40.00	305.79	90.00	335.33	30.00	363.57	80.00	444.68	30.00	479.13	80.00
290.27	50.00	308.80	100.00	343.14	40.00	367.38	90.00	454.20	40.00	483.64	90.00
294.88	60.00	309.20	101.41	349.35	50.00	370.98	100.00	461.54	50.00	487.94	100.00
298.88	70.00			354.66	60.00	371.48	101.69	468.22	60.00	488.64	101.87

Table 4. Estimated Antoine Parameters (Eq 1), Using Observed (obs) and Literature (lit.) Data

component	A_i	B_i	C_i	T range/K	N	source	AAD(P^S)/kPa
pentane	6.369 00	1312.963	-8.314	274-454	43	obs and lit. ^{7,8}	1.32
heptane	6.139 06	1338.993	-47.620	324-463	41	obs and lit. ^{1,7}	0.21
dodecane	6.860 29	2178.646	-39.637	298-489	32	obs and lit. ¹	0.10

$$^a \text{AAD}(P^S) = (1/N) \sum_i^N |P_{\text{exp}}^S - P_{\text{calc}}^S|_i$$

for analysis in the density meter. The still permits simultaneous sampling of the liquid and condensed vapor phases, without interruption of the recirculation. After sampling, either the mixture may be submitted to another pressure or the composition may be changed. In the last case, the experiment has to be interrupted. The rate of data collection is about two equilibrium points per day. This procedure was shown to produce accurate data⁴ for this system and also for hydrocarbon systems operating isothermally.⁵

Materials. Table 1 shows the pure components used, their suppliers, and their minimum guaranteed purities. Further purification of these chemicals was considered unnecessary, since significant secondary peaks were not found from gas chromatographic analysis and the chemicals presented a high grade of purity. Double-distilled water has also been used for the procedures of calibration of the thermometer and densimeter. To characterize the quality of the linear hydrocarbons used, density (ρ) and refractive index (n_D) were determined and compared with data reported in the literature.

Density-Composition Calibration Curves. About nine mixtures of known composition were prepared gravimetrically for each binary system, with a precision of 0.1 mg. The compositions covered the whole concentration range. The measured densities of the calibration curves were fitted with a third-order polynomial. The fitted composition-density function was used to determine the unknown compositions of liquid samples from the ebulliometer. The accuracy in the compositions with this procedure is estimated to be better than 0.0005 mole fraction. Table 2 presents the density-composition calibration curves for the studied systems and also the corresponding excess volume fitted functions.

Results and Discussion

Vapor Pressures for the Pure Components. The experiments were carried out at fixed pressures with the aid of the Fischer control system, measuring the boiling temperatures. Negligible differences were observed between the set and actual values of pressure. Table 3 presents the observed vapor pressures for the pure components. It should be noted that these measurements are in agreement with the reported values in the literature.^{1,6,7,8} This has also been checked by the relatively low deviations of pressure for the Antoine correlation of the observed and literature data together in a wide range of temperature, shown in Table 4. The values of vapor pressure and temperature used for the estimation of each set of Antoine constants were composed of the observed values and literature values retrieved from databases^{7,8} or

Table 5. Vapor-Liquid Equilibrium Data for Pentane (1) + Dodecane (2) at 70.00 and 100.00 kPa: Liquid Mole Fraction, x_i , Temperature, T , Vapor Mole Fraction, y_i , and Pressure, P

x_1	T/K	y_1	P/kPa	x_1	T/K	y_1	P/kPa
0.0114	463.81 ^a	0.3184	70.00	0.0011	480.93 ^a	0.2693	100.00
0.0428	453.60	0.5307	70.00	0.0095	478.53 ^a	0.3643	100.00
0.0847	425.76	0.8228	70.00	0.0642	456.10	0.6539	100.00
0.1885	389.51	0.9832	70.00	0.0989	431.57	0.8225	100.00
0.2334	367.58	0.9900	70.00	0.1559	396.62	0.9455	100.00
0.3854	345.35	0.9983	70.00	0.3698	355.06	0.9790	100.00
0.4210	338.34	0.9990	70.00	0.4831	338.94	0.9869	100.00
0.4882	328.52	0.9990	70.00	0.7661	315.80	0.9930	100.00
0.7872	304.69	0.9990	70.00	0.9832	309.40	0.9980	100.00
0.9592	299.59	0.9990	70.00				

^a Temperature is higher than the critical temperature of pentane; point was not included in the UNIQUAC data reduction.

generated by DDB and DIPPR correlations,^{1,6} in order to cover the desired temperature range of the binary VLE data.

The form of the Antoine correlation used is given by eq 1, and the objective function was defined in terms of the absolute value of pressure. The correlation for pentane resulted in higher deviations regarding the wide ranges of temperature and pressure. Correlation with the DIPPR equation with five adjusted constants for pentane was also tested but did not improve the order of magnitude of the deviations. Therefore, the Antoine equation was also used for pentane, regarding that it may affect the VLE correlation.

$$\log_{10}(P_i^S/kPa) = A_i - \frac{B_i}{(T/K) + C_i} \quad (1)$$

Vapor-Liquid Equilibrium Measurements. Isobaric VLE measurements for the systems pentane + dodecane and heptane + dodecane are presented in Tables 5 and 6, respectively. It was originally planned to measure an isobaric for the binary system with pentane at 40 kPa, but due to the low pressure and to the high volatility difference, an appropriate steady state could not be obtained, because it presented problems with reflux of the liquid phase. Figures 1 and 2 illustrate the observed VLE data for the systems pentane + dodecane at 100 kPa and heptane + dodecane at 40 kPa, respectively. The thermodynamic description was realized with the aid of the UNIQUAC model,⁹ representing the nonidealities of the liquid phase and virial equation of state, truncated after the second term, to express the deviations of the vapor phase, as presented by Hayden and O'Connell.¹⁰ The correction of the vapor phase in terms of the fugacity coefficients in the

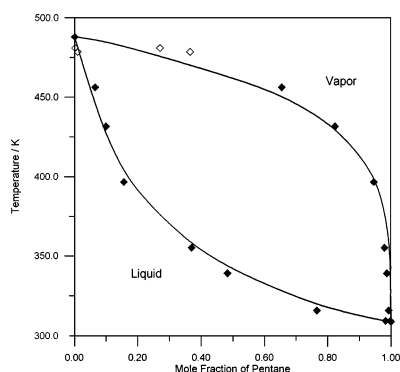
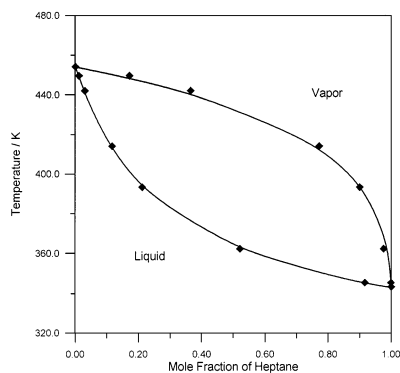
Table 6. Vapor–Liquid Equilibrium Data for Heptane (1) + Dodecane (2) at 40.00, 70.00, and 100.00 kPa: Liquid Mole Fraction, x_1 , Temperature, T , Vapor Mole Fraction, y_1 , and Pressure, P

x_1	T/K	y_1	P/kPa	x_1	T/K	y_1	P/kPa	x_1	T/K	y_1	P/kPa
0.0111	449.69	0.1709	40.00	0.0045	470.32	0.0909	70.00	0.0179	482.14	0.1866	100.00
0.0298	442.08	0.3641	40.00	0.0288	463.91	0.2182	70.00	0.0253	475.03	0.3111	100.00
0.1157	414.14	0.7714	40.00	0.2924	407.13	0.8894	70.00	0.0452	468.92	0.3984	100.00
0.2112	393.31	0.8997	40.00	0.5109	379.99	0.9655	70.00	0.2895	416.95	0.8945	100.00
0.5201	362.27	0.9759	40.00	0.6678	371.78	0.9905	70.00	0.7374	380.59	0.9835	100.00
0.9163	345.25	0.9990	40.00	0.9054	361.97	0.9989	70.00	0.9112	373.89	0.9966	100.00

Table 7. UNIQUAC Estimated^a Parameters and Mean Deviations

T range/K	P range/kPa	a_{12}^b/K	a_{21}/K	AAD(x_1) ^c	ΔT^d (%)	AAD(y_1)	ΔP (%)
298.9–487.9	Pentane (1) ($r = 3.8253$, $q = 3.3160$) + Dodecane (2) ($r = 8.5458$, $q = 7.0906$)	–115.7	91.48	0.0082	0.66	0.0092	0.51
343.1–487.9	Heptane (1) ($r = 5.1740$, $q = 4.3960$) + Dodecane (2) ($r = 8.5458$, $q = 7.0906$)	329.2	–226.2	0.0046	0.23	0.0066	0.35

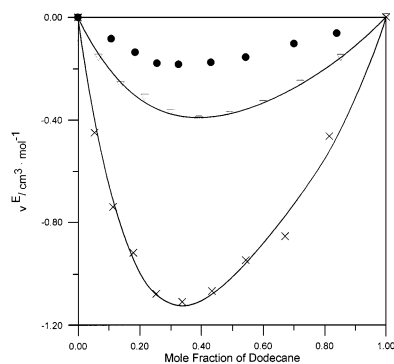
^a Uncertainties assigned: $\sigma_x = \sigma_y = 0.0005$; $\sigma_T = 0.10$ K; and $\sigma_P = 3.0$ kPa. ^b Binary UNIQUAC parameter: $a_{ij} \equiv (u_{ij} - u_{jj})/R$. ^c AAD = $(1/N)\sum_i^N |\text{exp} - \text{calc}|_i$. ^d $\Delta = (100/N)\sum_i^N |(\text{exp} - \text{calc})/\text{exp}|_i$.

**Figure 1.** Diagram T – x , y for the system pentane + dodecane at 100 kPa: ◆, experimental; ◇, experimental values at temperatures higher than the critical temperature of pentane; –, UNIQUAC.**Figure 2.** Diagram T – x , y for the system heptane + dodecane at 40 kPa: ◆, experimental; –, UNIQUAC.

mixture for the components was found to be relevant, and the order of magnitude ranged from 0.81 to 1.48 and 0.93 to 1.20, for the systems with pentane and heptane, respectively. The maximum likelihood principle¹¹ was applied to correlate the VLE data and provided a deviation test of the consistency of each isobaric data set. The binary estimated UNIQUAC parameters, together with the deviations between experimental and calculated values of the temperature, pressure, and liquid and vapor mole fractions, are listed in Table 7. On the basis of these calculations, the data measured are considered to be consistent.

Conclusions

It has been shown that the Fischer VLE cell is applicable for hydrocarbon systems with marked differences of volatil-

**Figure 3.** Excess volume at 298.15 K: ×, pentane + dodecane; ∇, heptane + dodecane; –, Redlich–Kister correlation (Table 2); ●, heptane + dodecane.¹²

ity and over ranges of temperature. Operating problems have occurred with the binary system with pentane at low pressures such as 40 kPa, even with extra refrigeration for the liquid phase.

Using the calibration density–composition curves, the excess volume behavior of the binary systems could be studied and described by a Redlich–Kister correlation, shown in Table 2 and Figure 3. The excess volume of the binary system with heptane has also been reported in the literature,¹² and the observed data present agreement in terms of shape and signal. However, the significant differences in terms of order of magnitude are due to the high sensitivity of the excess volume function with respect to the differences of the densities between the two sources. The negative signal of the excess volume curves indicates the accommodation and attraction of the molecules, which are more pronounced for the system with pentane.

Excess enthalpies for the binary system with heptane have also been reported in the literature,¹³ which are positive and indicate the coherence of the measured excess volumes and Gibbs energy in terms of signal.¹⁴

The consistency of the VLE data sets has been checked and found to be satisfactory with the maximum likelihood method. Negative and significant deviations in relation to the Raoult's law were found for the pentane + dodecane system. The experimental information obtained may be especially useful for the petroleum industry.

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