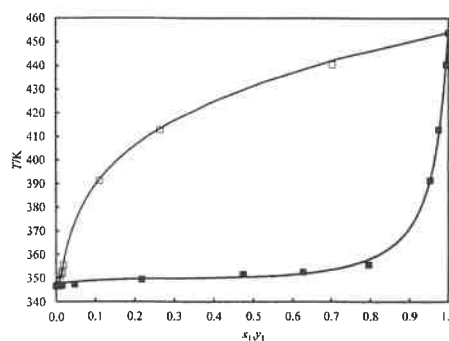


Vapor–Liquid Equilibrium Data for Binary Systems of *n*-Dodecane + {Propan-1-ol, Butan-1-ol, 2-Methylpropan-1-ol} at 40 kPaZoubir Tebbal,[†] Peterson Thokozani Ngema,[‡] Caleb Narasigadu,[‡] Latifa Negadi,^{*,†} and Deresh Ramjugernath[‡][†]LATA2M, Laboratoire de Thermodynamique Appliquée et Modélisation Moléculaire, University of Tlemcen, Post Office Box 119, Tlemcen 13000, Algeria[‡]Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, 4041, South Africa

ABSTRACT: Isobaric (T - x - y) binary vapor–liquid equilibrium (VLE) data were measured and modeled for the *n*-dodecane + {propan-1-ol, butan-1-ol, or 2-methylpropan-1-ol} systems at 40 kPa. A low pressure dynamic still, capable of measuring systems of high relative volatility, was used for the measurements. The vapor and liquid equilibrium compositions were determined using a gas chromatograph with a thermal conductivity detector. The experimental data were regressed using the combined method (γ - ϕ approach). The nonrandom two-liquid (NRTL) activity coefficient model was used to describe the liquid phase nonideality, and the vapor phase was assumed to be ideal. The NRTL model parameters were determined using nonlinear least-squares regression. The experimental data were found to be well correlated with the thermodynamic modeling. No azeotropic behavior has been observed. The three investigated systems show a large positive deviation from Raoult's law.



INTRODUCTION

To separate alcohols from water in chemical and petrochemical industries, *n*-dodecane can be used as a solvent for extraction. Once the extraction has been performed, it is easy to separate the alcohols from the solvent (*n*-dodecane) by distillation because of the large differences in boiling points between the two chemicals.

As part of a large research program in our research unit, a systematic study concerning the phase equilibria of mixtures (VLE and LLE) containing light alcohols, water, and *n*-dodecane have been undertaken.^{1–3} The open literature also contains VLE data for *n*-dodecane + butan-1-ol but at very low pressures (0.06–2.5) kPa.⁴ All these data however have been measured at isothermal conditions. Usually the design of distillation columns is based on constant pressure operation, and vacuum operation is used to lower the column temperatures where otherwise very high temperatures would be needed for distillation.⁵

Therefore, this paper reports the isobaric measurements, undertaken for *n*-dodecane + {propan-1-ol, butan-1-ol, or 2-methylpropan-1-ol}, systems at 40 kPa using a dynamic low pressure VLE apparatus. The experimental data were correlated using the combined method (γ - ϕ approach) with the NRTL⁶ activity coefficient model used to describe the liquid phase nonideality and the vapor phase assumed ideal. There are to our knowledge no VLE data (P - T - x - y) reported in the open literature for *n*-dodecane + {propan-1-ol, butan-1-ol, or 2-methylpropan-1-ol} at 40 kPa.

EXPERIMENTAL SECTION

Materials. The chemical purities listed in Table 1 were verified by analyzing both the refractive index and density. The refractive indices were measured using an ATAGO RX-7000 α refractometer with an overall uncertainty of 0.00013 ($k = 2$). The densities of the chemicals were measured using an Anton Paar DMA 5000 density meter with an overall uncertainty of 0.00078 kg·m⁻³ ($k = 2$). All chemicals were purchased from Merck. Gas chromatography (GC) analysis revealed no significant impurities, and the measured refractive indices and densities agree well with the literature.

Equipment. The VLE measurements were undertaken using the dynamic analytical method on a low pressure apparatus in our laboratories used primarily for systems of high relative volatility.¹ Details on the apparatus description and operating procedure are well documented in a previous work.^{1,7} The main feature of the apparatus is the spiral mixer which enhances the mixing of the recirculated vapor and liquid phases to eliminate the occurrence of flashing. Figure 1 shows the schematic layout of the experimental apparatus.

An A class Pt-100 temperature probe was used to measure the equilibrium temperature. The overall uncertainty in the temperature measurement is 0.03 K ($k = 2$). The Pt-100 temperature probe was calibrated using a silicon oil bath

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Table 1. Property Data for the Chemicals Studied

	propan-1-ol	butan-1-ol	2-methylpropan-1-ol	<i>n</i> -dodecane
CAS no.	71-23-8	71-36-3	78-83-1	112-40-3
measured	1.3851	1.3992	1.3954	1.4218
literature ⁹	1.3850	1.3993	1.3955	1.4216
	$\rho^b/\text{kg}\cdot\text{m}^{-3}$			
measured	804.9	810.4	802.7	750.0
literature ⁹	803.5	809.8	801.8	748.7
GC peak area (area fraction)	0.999	0.997	1.000	1.000
Claimed purity (mass fraction)	≥ 0.999	≥ 0.995	≥ 0.999	≥ 0.990
	Critical Properties ¹⁰			
T_c/K	536.78	563.05	547.78	658.00
P_c/kPa	5175.00	4423.00	4300.00	1820.00
$V_c/\text{cm}^3\cdot\text{mol}^{-1}$	219.00	275.00	273.00	754.00
acentric factor (ω)	0.629	0.590	0.590	0.573
	Antoine Constants ¹¹			
A	7.748 87	7.924 84	8.535 16	7.131 37
B	1440.74	1617.52	1950.94	1723.37
C	198.8	203.296	237.147	189.845

^aRefractive index at 293.15 K. $u(n_D) = 0.00013$ ($k = 2$). ^bDensity at 293.15 K. $u(\rho) = 0.00078 \text{ g}\cdot\text{cm}^{-3}$ ($k = 2$); ref 11, Antoine equation $\log_{10} P/\text{Pa} = A - B/(C + T/\text{K})$.

(WIKA CTB 9100) and WIKA primary temperature probe which was connected to a WIKA CTH 6500 multimeter.

The system pressure was measured with the P-10 WIKA pressure transducer ranging from 0 kPa to 100 kPa absolute. The pressure transducer was calibrated with a WIKA CPH 6000 unit. The overall uncertainty in the pressure reading is 0.03 kPa ($k = 2$).

The equilibrium phase samples were analyzed by gas chromatography using a Shimadzu GC 2010 Plus which was fitted with a thermal conductivity detector. A Zebtron ZB-Waxplus capillary GC column which was 30 m in length with a 0.25 μm film thickness was used for good separation with helium as the carrier gas. The overall uncertainty in the phase equilibrium compositions is 0.004 mole fraction for all systems measured in this work. The area ratio method as discussed by Raal and Muhlbauer⁸ was used for calibration of the GC detector.

Correlation. In this study, the combined (γ - ϕ) method was used to regress the experimental VLE data for the isobaric measurements. The γ - ϕ equation is represented in the form

$$y_i \Phi_i P = x_i \gamma_i P_i^{\text{sat}} \quad (1)$$

where y_i is the vapor phase mole fraction of species i , x_i is the liquid phase mole fraction of species i , γ_i is the activity coefficient of species i , Φ_i is the vapor correction factor which is

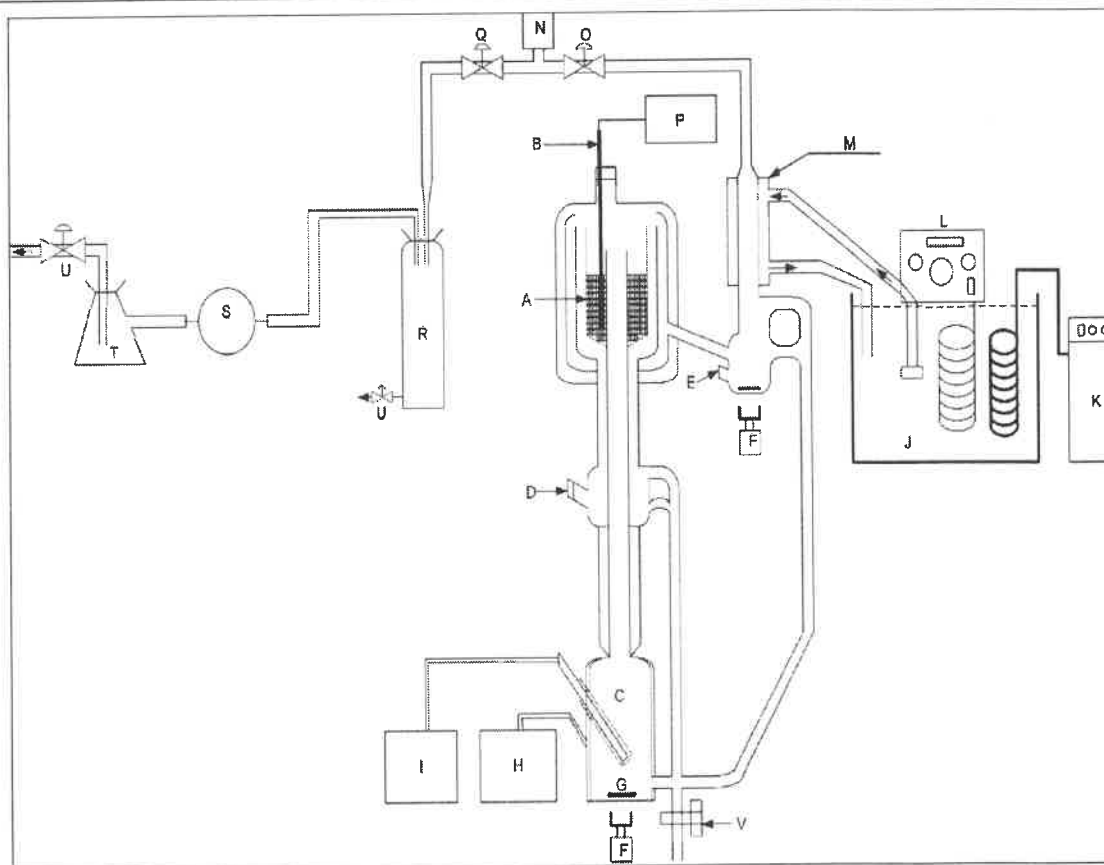


Figure 1. Schematic diagram for low pressure VLE still: A, packing chamber; B, reboiler; C, Pt-100; D, liquid sampling point; E, vapor sampling point; G, magnetic stirrer; H, external heater; I, internal heat; J, water bath with chilling fluid; K, coldfinger; L, temperature programmable circulator; M, condenser; N, pressure transducer; O, digital multimeter; P, control valve; Q, fine-tune valve; R, ballast; S, vacuum pump; T, vacuum flask; U, vent valve to atmosphere; and V, drain valve.

Table 2. T - x - y Data for the n -Dodecane + {Propan-1-ol, Butan-1-ol, or 2-Methylpropan-1-ol} Systems at 40 kPa^a

x_1	T/K	y_1	γ_1	x_1	T/K	y_1	γ_1	x_1	T/K	y_1	γ_1
n -Dodecane (1) + Propan-1-ol (2)				n -Dodecane (1) + Butan-1-ol (2)				n -Dodecane (1) + 2-Methylpropan-1-ol			
0.000	346.5	0.000		0.000	367.1	0.000		0.000	357.6	0.000	
0.010	346.6	0.002	15.56	0.007	366.1	0.002	7.85	0.036	358.2	0.004	4.57
0.015	346.8	0.002	10.25	0.015	366.5	0.004	7.21	0.059	358.7	0.005	3.41
0.047	347.4	0.005	7.93	0.076	367.1	0.016	5.51	0.105	359.8	0.010	3.61
0.218	349.3	0.009	2.75	0.133	368.2	0.020	3.73	0.178	361.0	0.011	2.21
0.474	351.7	0.014	1.73	0.250	369.6	0.027	2.50	0.295	362.7	0.015	1.67
0.627	352.6	0.015	1.33	0.387	371.3	0.034	1.88	0.442	364.2	0.017	1.16
0.796	355.6	0.018	1.07	0.510	372.7	0.038	1.49	0.536	365.5	0.019	1.01
0.954	391.3	0.111	1.02	0.608	374.4	0.043	1.31	0.922	402.6	0.161	0.97
0.975	412.9	0.265	1.02	0.712	376.6	0.052	1.22	0.955	420.8	0.329	0.98
0.995	440.5	0.703	1.05	0.786	379.2	0.058	1.09	1.000	453.7	1.000	1.00
1.000	453.7	1.000	1.00	0.863	385.9	0.085	1.09				
				0.891	392.6	0.116	1.08				
				0.934	408.2	0.220	1.05				
				0.953	423.5	0.381	1.03				
				0.957	426.6	0.428	1.04				
				1.000	453.7	1.000	1.00				

^a $u(T) = 0.03$ K ($k = 2$), $u(P) = 0.03$ kPa ($k = 2$), $u(x_1) = 0.004$, $u(y_1) = 0.004$; $u(\gamma_1) = 0.06$; $u(\gamma_2) = 0.06$.

the ratio of the fugacity coefficient to the saturated fugacity coefficient multiplied by the Poynting correction factor, P is the total pressure, and P_i^{sat} is the saturation pressure of species i .

Equation 1 reduces to the modified Raoult's law when $\Phi_i = 1$ (vapor assumed to be an ideal gas mixture). The modified Raoult's law was used for all VLE data correlation in this work. Bubble-temperature calculations were performed to regress the model parameters for the excess Gibbs energy model, namely, the NRTL⁶ model. The data reduction procedure requires the minimization of an objective function (OF). The objective function given in eq 2 was used where δT , the temperature residual, is the difference between the measured and the calculated temperatures:

$$\text{OF} = \sum |\delta T| \quad (2)$$

The bias, the average absolute deviations (AAD), and absolute deviations, where U represents T or y , are given in eqs 3, 4, and 5, respectively.

$$\text{BIAS}(U) = \frac{100}{N} \sum \left(\frac{U_{\text{exp}} - U_{\text{cal}}}{U_{\text{exp}}} \right) \quad (3)$$

$$\text{AAD}(U) = \frac{100}{N} \sum \left| \frac{U_{\text{exp}} - U_{\text{cal}}}{U_{\text{exp}}} \right| \quad (4)$$

$$\Delta(U) = \frac{1}{N} \sum |U_{\text{cal}} - U_{\text{exp}}| \quad (5)$$

RESULTS AND DISCUSSION

Table 1 lists the critical properties and the acentric factors for the chemicals used in this study. The measured refractive indices and densities agree well with literature.⁹ Table 1 also lists the pure component Antoine parameters reported in the literature for all chemicals used in this study.

The measured isobaric vapor-liquid equilibrium data for the binary systems of n -dodecane + {propan-1-ol, butan-1-ol, or 2-methylpropan-1-ol} at 40 kPa are shown in Table 2 and plotted in Figures 2 to 4. The model parameters for the NRTL model are

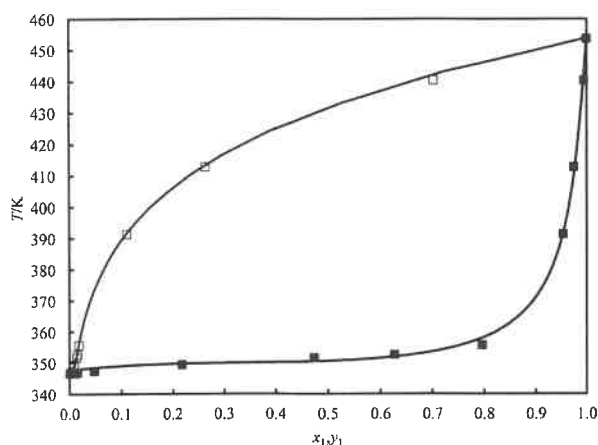


Figure 2. T - x - y data for the n -dodecane (1) + propan-1-ol (2) system at 40 kPa: ■, T - x (exp); □, T - y (exp); —, NRTL model.

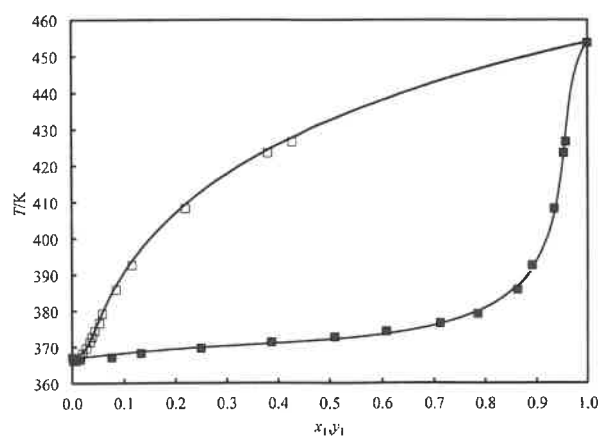


Figure 3. T - x - y data for the n -dodecane (1) + butan-1-ol (2) system at 40 kPa: ■, T - x (exp); □, T - y (exp); —, NRTL model.

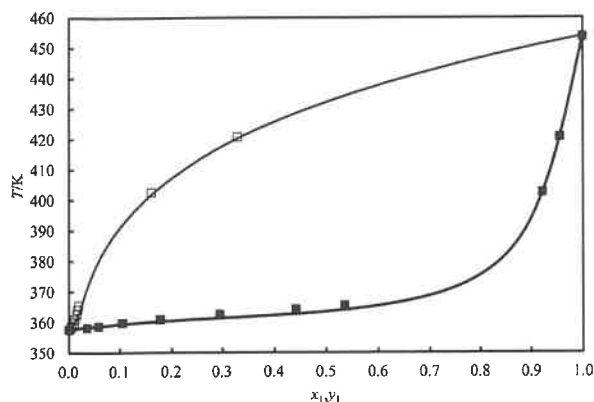


Figure 4. T - x - y data for the n -dodecane (1) + 2-methylpropan-1-ol (2) system at 40 kPa: ■, T - x (exp); □, T - y (exp); —, NRTL model.

provided in Table 3. The nonrandom parameter (α_{ij}) in the NRTL model was set to 0.5. The BIAS and the average absolute

Table 3. NRTL Parameters for the n -Dodecane (1) + {Propan-1-ol, Butan-1-ol, or 2-Methylpropan-1-ol} (2) Systems at 40 kPa

	n -dodecane (1) + propan-1-ol (2)	n -dodecane (1) + butan-1-ol (2)	n -dodecane (1) + 2- methylpropan-1-ol (2)
a_{12}^a	-3.994	-1.329	-3.209
a_{21}	1.898	-9.967	15.194
b_{12}/K^a	1825.231	944.493	1301.660
b_{21}/K	0.701	4160.782	-4989.770
α_{ij}	0.5	0.5	0.5

$${}^a\tau_{ij} = (a_{ij} + (b_{ij}/T)).$$

deviations (AAD) for the calculated temperature and vapor composition of the NRTL model are shown in Table 4.

Table 4. Error Analysis for the n -Dodecane (1) + {Propan-1-ol, Butan-1-ol, or 2-Methylpropan-1-ol} (2) Systems

	n -dodecane (1) + propan-1-ol (2)	n -dodecane (1) + butan-1-ol (2)	n -dodecane (1) + 2- methylpropan-1-ol (2)
rmsd ^a	1.225	0.433	0.614
$\Delta T/K$	0.956	0.379	0.489
Δy	0.005	0.003	0.002
AAD (T/K)	0.254	0.099	0.131
BIAS (T/K)	-0.154	-0.039	0.092
AAD (y)	10.400	3.276	8.407
BIAS (y)	-1.046	1.787	-3.268

^aRoot mean square deviation (rmsd):

$$\text{rmsd} = \sqrt{\frac{\sum_{j=1}^N (\delta T)^2}{N}}$$

All the systems studied in this work were well correlated using the modified Raoult's law with the NRTL model. No azeotropic behavior has been observed for the three investigated systems. They all show a large positive deviation from Raoult's law indicating easy separation of these binary pairs by conventional distillation.

CONCLUSIONS

New isobaric VLE (T - x - y) data for binary systems comprising n -dodecane + {propan-1-ol, butan-1-ol, or 2-methylpropan-1-ol} at 40 kPa are reported. The three isobaric systems do not exhibit azeotropic behavior. They all show a large positive deviation from Raoult's law. The experimental VLE data were successfully correlated with the NRTL activity coefficient model.

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Notes

The authors declare no competing financial interest.

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