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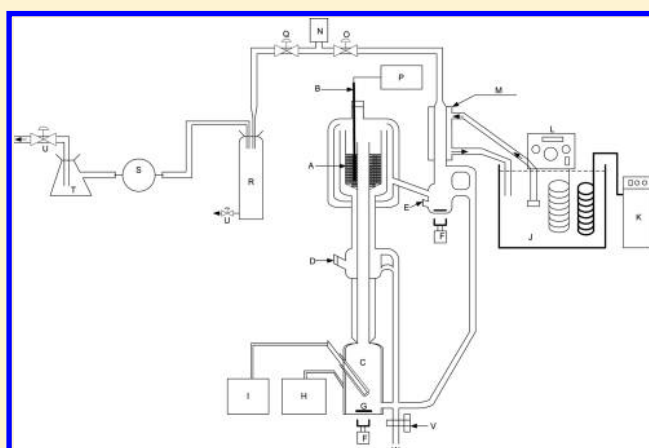
**Vapor–Liquid Equilibrium Data for Binary Systems of
1-Methyl-4-(1-methylethenyl)-cyclohexene + {Ethanol, Propan-1-ol,
Propan-2-ol, Butan-1-ol, Pentan-1-ol, or Hexan-1-ol} at 40 kPa**

Peterson Thokozani Ngema,[†] Dobrochna Matkowska,[‡] Paramespri Naidoo,[†] Tadeusz Hofman,[‡]
and Deresh Ramjugernath^{*,†}

[†]Thermodynamics Research Unit, School of Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, 4041, South Africa

[‡]Physical Chemistry Division, Faculty of Chemistry, Warsaw University of Technology, 00-664 Warsaw, Poland

ABSTRACT: Isobaric binary vapor–liquid equilibrium (VLE) data were measured for the 1-methyl-4-(1-methylethenyl)-cyclohexene (D-limonene) + {ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, or hexan-1-ol} systems at 40 kPa. A low pressure dynamic still was used for the measurements. The experimental data were regressed using the nonrandom two-liquid (NRTL) and Wilson activity coefficient models. Both models correlated the data well. The 1-methyl-4-(1-methylethenyl)-cyclohexene + {butan-1-ol or pentan-1-ol or hexan-1-ol} systems exhibit a minimum temperature azeotrope. The 1-methyl-4-(1-methylethenyl)-cyclohexene + {ethanol or propan-1-ol or propan-2-ol} systems show the largest positive deviation from Raoult's law, and these systems exhibit no azeotropic behavior.



■ INTRODUCTION

D-Limonene ((+)-limonene) is the R enantiomer of 1-methyl-4-(1-methylethenyl)-cyclohexene and is a naturally occurring cyclic monoterpene having the molecular formula $C_{10}H_{16}$. It is the major component of the oil extracted from citrus rinds, particularly oranges, as it constitutes 98% of the essential oil obtained from orange peel. This compound has been used for many years as a flavor and fragrance additive in many consumer products. As a nonpolar liquid under typical conditions, it has found a wide range of applications as a solvent and a cleaning product. It has also been widely used as a cleaner for petroleum-based greases. It may be an alternative for some popular solvents in industry because it is not toxic, biodegradable, and produced from renewable resources. Recently it has been used in the recycling of polystyrene.¹

Alcoholic solutions of citrus essential oils are particularly important from an industrial point of view because of at least three reasons: (i) as it is highly soluble in aqueous solutions it can be used to make drinks and perfumes; (ii) they enhance the aromatic strength of the mixture; (iii) oxidation reactions are reduced in the presence of an alcohol.² Although phase equilibrium studies provide essential information for design and optimization of industrial processes, only one literature¹ article concerning vapor-liquid equilibria of alcoholic solutions of D-limonene has been reported in the literature.

D-Limonene is soluble in hydrocarbons and alcohols except with methanol and water in which it is partially miscible.³ As

D-limonene is soluble in alcohols, previously reported¹ data are isobaric vapor–liquid equilibrium (VLE) data for ethanol + D-limonene and propan-1-ol + D-limonene at atmospheric pressure. The aim of this study is to begin and undertake systematic studies of the thermodynamic properties of mixtures containing D-limonene and an alcohol. Thus, isobaric VLE data were measured for the binary systems comprising D-limonene + {ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, or hexan-1-ol} at 40 kPa. The experimental VLE data are presented and correlated using the nonrandom two-liquid (NRTL)⁴ and Wilson⁵ activity coefficient models.

■ EXPERIMENTAL SECTION

Materials. The chemical purities listed in Table 1 were verified by analyzing both the refractive index and the density. All chemicals (except butan-1-ol) were purchased from Capital Laboratories; butan-1-ol was obtained from Merck. GC analysis revealed no significant impurities, and the measured refractive indices and densities agree well with the literature. The refractive indices were measured using an ATAGO RX-7000 α refractometer with an uncertainty in refractive index of ± 0.004 . The densities of the chemicals were measured using an Anton

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Table 1. Property Data for the Chemicals Studied

	ethanol	propan-1-ol	propan-2-ol	butan-1-ol	pentan-1-ol	hexan-1-ol	1-methyl-4-(1-methylethenyl)-cyclohexene
	n_D^{20} ^a						
measured	1.3612	1.3851	1.3771	1.3993	1.4097	1.4207	1.4730
literature ⁸	1.3605	1.3850	1.3750	1.3988	1.4101	1.4161	1.4701
	ρ^* ^b /kg·m ⁻³						
measured	789.91	801.33	785.42	810.28	814.16	816.31	814.83
literature ⁸	789.20	799.70	785.50	809.50	814.40	815.90	814.10
GC peak area (area fraction)	0.999	0.999	0.996	1.000	0.999	0.994	0.996
supplier stated purity (mass fraction)	≥0.998	≥0.998	≥0.998	≥0.999	≥0.994	≥0.990	≥0.970
	Critical Properties ¹⁰						
T_c /K	513.92	536.70	508.30	563.05	588.15	611.40	649.10 ^c
P_c /kPa	6148.00	5167.57	4762.27	4423.00	3909.00	3500.00	2720.00 ^c
V_c /cm ³ ·mol ⁻¹	167.0	218.5	220.0	275.0	326.0	381.0	470.0 ^c
acentric factor (ω)	0.649	0.629	0.665	0.590	0.579	0.573	0.374 ^c
	Antoine Constants ¹¹						
A	8.20417	7.74887	8.87829	7.92484	7.44287	7.90559	6.90868
B	1642.89	1440.74	2010.32	1617.52	1439.27	1819.57	1493.07
C	230.30	198.80	252.63	203.29	177.76	205.08	194.24

^aRefractive index at 293.2 K, uncertainty = ± 0.004 . ^bDensity at 293.2 K, uncertainty = ± 0.0016 g·cm⁻³. ^cReference 9. Antoine equation:

$$\log_{10}(P/\text{mmHg}) = A - B/(T/^\circ\text{C} + C)$$

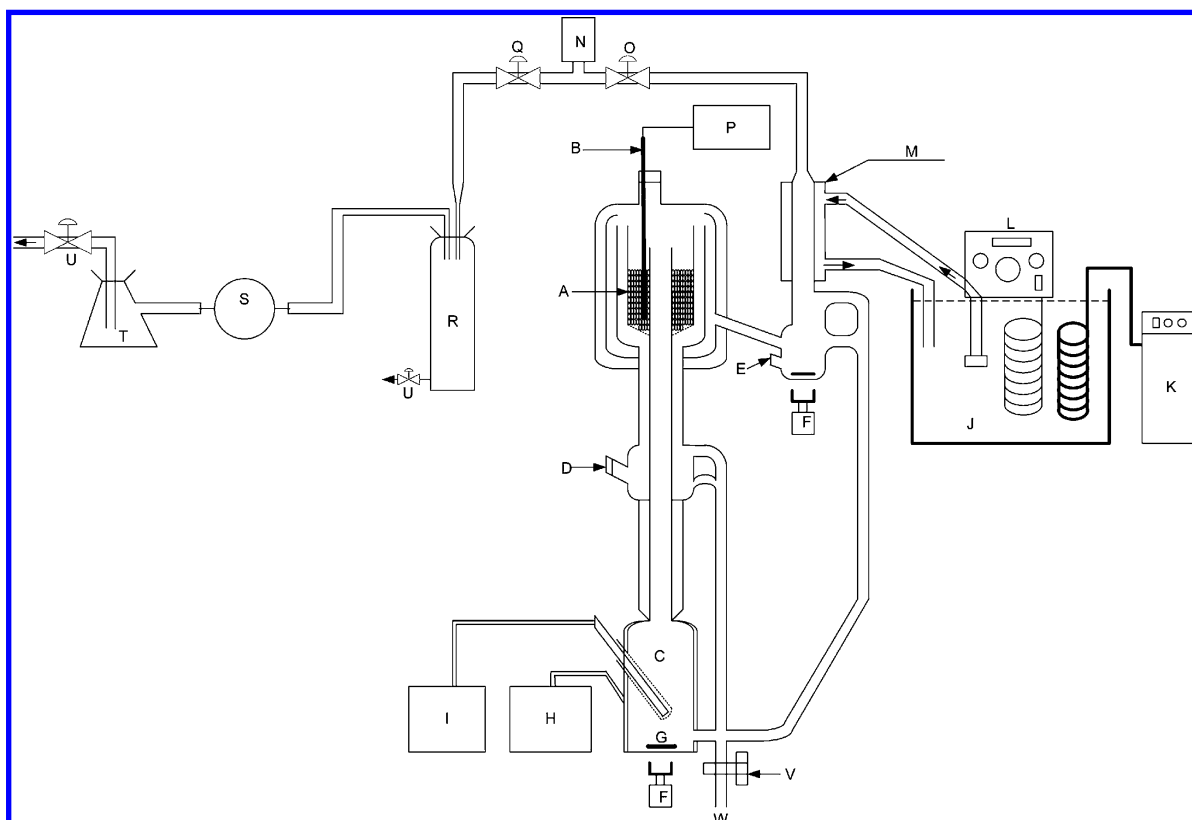


Figure 1. Schematic diagram for low pressure VLE still: A, packing chamber; B, reboiler; C, Pt-100; D, liquid sampling point; E, vapor sampling point; G, magnetic stirrer; H, external heater; I, internal heat; J, water bath with chilling fluid; K, cold finger; L, temperature programmable circulator; 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; V, drain valve and W, drain.

Paar DMA 5000 density meter with a maximum uncertainty of ± 0.0016 g·cm⁻³.

Equipment. A dynamic low pressure VLE still was used to measure the experimental data and has been described in detail previously by Joseph et al.⁶ The capacity of the VLE still is

approximately 180 cm³. A schematic of the experimental apparatus is shown in Figure 1.

A class A Pt-100 temperature probe was used to measure the equilibrium temperature. The uncertainty in the temperature measurement is ± 0.1 K. The Pt-100 temperature probe was

Table 2. Measured Vapor Pressures for the Chemicals Studied^{a,b}

P/kPa	exptl T/K	ΔT^c	exptl T/K	ΔT^c	exptl T/K	ΔT^c
1-Methyl-4-(1-methylethenyl)-cyclohexene						
10	375.5	0.07	Ethanol		Propan-1-ol	
20	394.5	0.08	302.4	0.08	319.6	0.08
30	406.6	0.09	315.5	0.08	332.8	0.04
40	415.8	0.07	323.7	0.07	341.3	0.03
50	423.4	0.10	329.7	0.01	347.7	0.02
60	429.8	0.09	334.6	0.03	352.7	0.07
70	435.4	0.10	338.8	0.05	357.1	0.06
80	440.4	0.09	342.5	0.04	360.8	0.09
90	444.9	0.07	345.7	0.04	364.1	0.08
99.7	448.9	0.05	348.5	0.04	367.1	0.07
			351.0	0.09	369.8	0.06
Propan-2-ol						
10	307.1	0.10	Butan-1-ol		Pentan-1-ol	
20	319.9	0.01	337.2	0.01	353.8	0.07
30	328.0	0.03	351.1	0.10	368.7	0.04
40	334.0	0.03	360.0	0.08	378.0	0.09
50	338.9	0.02	366.7	0.09	385.3	0.08
60	342.9	0.10	372.1	0.10	391.0	0.04
70	346.5	0.08	376.6	0.10	395.9	0.03
80	349.7	0.03	380.5	0.10	400.2	0.04
90	352.5	0.07	384.1	0.09	404.0	0.07
99.9	355.0	0.07	387.2	0.09	407.4	0.06
			390.1	0.01	410.3 ^d	0.06 ^d
Hexan-1-ol						
10	369.8	0.04				
20	385.7	0.10				
30	395.7	0.04				
40	403.4	0.09				
50	409.3	0.08				
60	414.5	0.01				
70	419.0	0.02				
80	423.0	0.08				
90	426.5	0.01				
99.7	429.6	0.04				

^a $u(T) = 0.1$ K. ^b $u(P) = 0.3$ kPa. ^cLiterature vapor pressure data obtained from DDB.¹¹ ^dMeasured at 99.7 kPa.

$$\Delta T = |T_{\text{lit}} - T_{\text{exp}}|$$

calibrated using a silicon oil bath (WIKA CTB 9100) and WIKA primary temperature probe which was connected to a WIKA CTH 6500 multimeter.

The pressure in the VLE still was controlled below atmospheric pressure using a KNF vacuum pump controller (type NC800). The system pressure was measured with the aid of a Sensotec Super TJE pressure transducer. The pressure transducer was calibrated with a WIKA CPH 6000 unit. The uncertainty in the reported pressure is ± 0.3 kPa.

Thermodynamic equilibrium was assumed to be reached when the measured equilibrium temperature remained constant for at least 45 min. Thereafter, vapor samples followed by liquid samples were withdrawn for composition analysis. A Shimadzu GC-2010 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) was used for the analysis of the equilibrium phases. The separation in the GC was effected with a Cwax 20 M bonded column. The area ratio method as discussed by Raal and Mühlbauer⁷ was used for the calibration of the GC detector. The estimated uncertainty in the phase equilibrium compositions is ± 0.006 mole fraction.

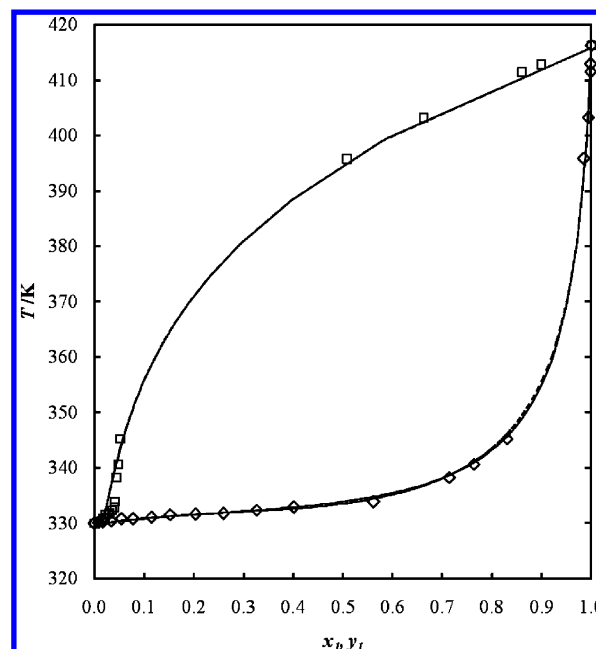


Figure 2. T - x - y data for the 1-methyl-4-(1-methylethenyl)-cyclohexene (1) + ethanol (2) system at 40 kPa: \square , T - y (exp); \diamond , T - x (exp); —, Wilson model; ---, NRTL model.

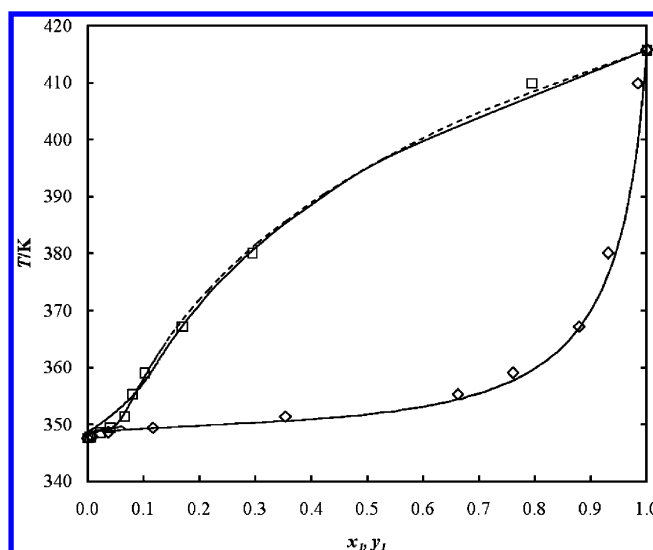


Figure 3. T - x - y data for the 1-methyl-4-(1-methylethenyl)-cyclohexene (1) + propan-1-ol (2) system at 40 kPa: \square , T - y (exp); \diamond , T - x (exp); —, Wilson model; ---, NRTL model.

Correlations. In this study, the γ - ϕ method was used to regress the experimental VLE data for both of the isobaric measurements. The γ - ϕ equation is represented in the form

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

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 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 $\Phi_i = 1$

Table 3. T - x - y Data for the 1-Methyl-4-(1-methylethenyl)-cyclohexene + {Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Pentan-1-ol, or Hexan-1-ol} Systems at 40 kPa^{a,b,c,d}

x_1	T/K	y_1	γ_1	x_1	T/K	y_1	γ_1	x_1	T/K	y_1	γ_1	x_1	T/K	y_1	γ_1
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Ethanol (2)				1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Propan-1-ol (2)				1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Propan-2-ol (2)				1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Butan-1-ol (2)			
0.000	330.0	0.000		0.000	347.7	0.000		0.340	337.3	0.030	1.96	0.385	370.3	0.139	1.78
0.007	330.2	0.010	46.24	0.008	347.9	0.004	6.58	0.589	340.6	0.045	1.44	0.646	373.8	0.189	1.25
0.016	330.3	0.010	20.12	0.037	348.6	0.022	7.57	0.789	345.0	0.060	1.15	0.792	379.1	0.239	1.05
0.034	330.5	0.014	13.11	0.117	349.5	0.040	4.17	0.874	350.6	0.086	1.14	0.879	386.3	0.321	0.97
0.055	330.6	0.017	9.79	0.354	351.5	0.066	2.07	0.959	385.3	0.369	1.06	0.957	403.4	0.669	1.03
0.077	330.8	0.019	7.73	0.662	355.4	0.080	1.12	0.977	399.9	0.633	1.08	0.989	413.4	0.913	0.99
0.114	331.1	0.021	5.68	0.760	359.1	0.102	1.06	1.000	415.8	1.000	1.00	1.000	415.7	1.000	1.00
0.152	331.6	0.022	4.34	0.879	367.3	0.169	1.07								
0.203	331.7	0.028	4.12	0.931	380.3	0.295	1.06								
0.259	331.8	0.030	3.44	0.984	409.9	0.794	0.97								
0.326	332.4	0.035	3.09	1.000	415.7	1.000	1.00								
0.402	332.9	0.039	2.72												
0.562	333.9	0.040	1.89												
0.714	338.3	0.043	1.27												
0.763	340.7	0.048	1.18												
0.830	345.3	0.051	0.92												
0.985	395.8	0.507	0.98												
0.993	403.2	0.662	0.99												
0.998	411.5	0.860	0.98												
0.999	412.9	0.899	0.98												
1.000	415.8	1.000	1.00												
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Propan-2-ol (2)				1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Butan-1-ol (2)											
0.000	334.1	0.000		0.000	366.7	0.000									
0.027	335.3	0.023	21.00	0.032	367.4	0.025	4.33								
0.077	335.6	0.019	5.99	0.060	367.6	0.035	3.21								
0.161	336.5	0.027	3.88	0.080	367.8	0.045	3.07								

^a $u(T) = 0.1$ K. ^b $u(P) = 0.3$ kPa. ^c $u(x_1) = 0.006$. ^d $u(y_1) = 0.006$.

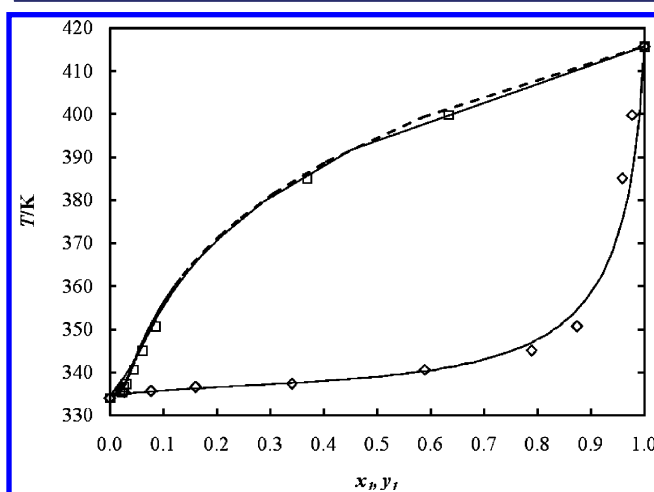


Figure 4. T - x - y data for the 1-methyl-4-(1-methylethenyl)-cyclohexene (1) + propan-2-ol (2) system at 40 kPa: \square , T - y (exp); \diamond , T - x (exp); —, Wilson model; ---, NRTL model.

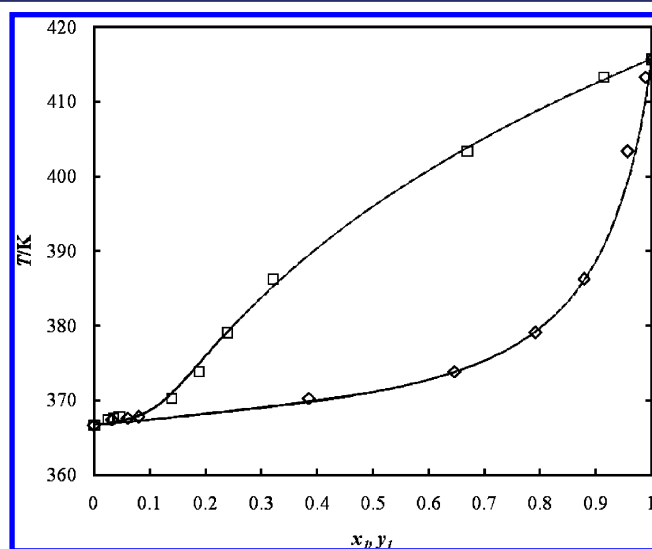


Figure 5. T - x - y data for the 1-methyl-4-(1-methylethenyl)-cyclohexene (1) + butan-1-ol (2) system at 40 kPa: \square , T - y (exp); \diamond , T - x (exp); —, Wilson model; ---, NRTL model.

(vapor assumed to be an ideal gas mixture). The modified Raoult's law was used for all VLE data correlation.

Bubble-temperature calculations were performed to regress the model parameters for each of the two excess Gibbs energy models, namely, the NRTL⁴ and the Wilson³

models. 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

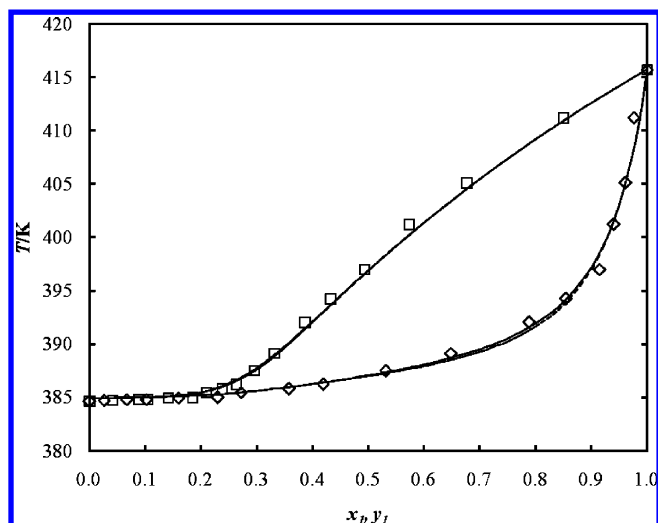


Figure 6. T - x - y data for the 1-methyl-4-(1-methylethenyl)-cyclohexene (1) + pentan-1-ol (2) system at 40 kPa: \square , T - y (exp); \diamond , T - x (exp); —, Wilson model; ---, NRTL model.

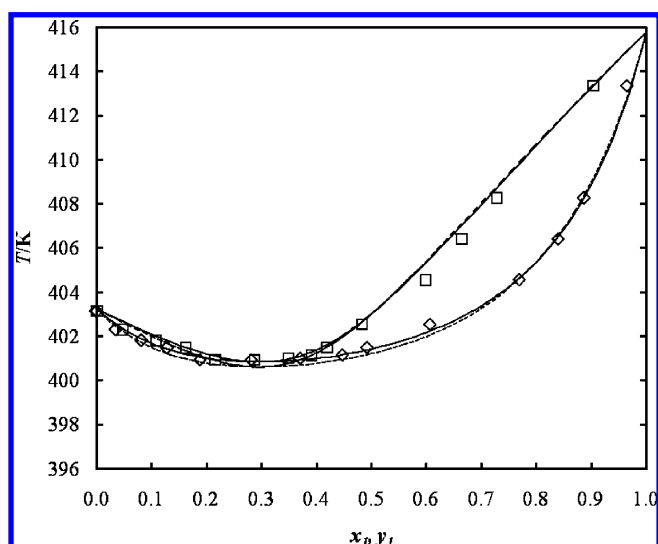


Figure 7. T - x - y data for the 1-methyl-4-(1-methylethenyl)-cyclohexene (1) + hexan-1-ol (2) system at 40 kPa: \square , T - y (exp); \diamond , T - x (exp); —, Wilson model; ---, NRTL model.

residual, is the difference between the measured and the calculated temperatures:

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

Table 4. NRTL Model Parameters for the 1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + {Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Pentan-1-ol, or Hexan-1-ol} (2) Systems at 40 kPa

system	$(g_{12} - g_{11})$ J·mol ⁻¹	$(g_{21} - g_{22})$ J·mol ⁻¹	ΔT^a /K	Δy_2^a	α_{12}
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + ethanol (2)	1219.8	5095.6	0.23	0.007	0.4
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + propan-1-ol (2)	917.0	5705.6	0.31	0.019	0.4
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + propan-2-ol (2)	704.9	5210.1	0.38	0.034	0.4
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + butan-1-ol (2)	3223.0	1642.9	0.21	0.020	0.4
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + pentan-1-ol (2)	3794.9	1546.8	0.37	0.013	0.4
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + hexan-1-ol (2)	1821.3	1801.0	0.15	0.013	0.4

^aCalculated using eq 5.

Table 5. Wilson Model Parameters for the 1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + {Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Pentan-1-ol, or Hexan-1-ol} (2) Systems at 40 kPa

system	$(\lambda_{12} - \lambda_{11})$ J·mol ⁻¹	$(\lambda_{21} - \lambda_{22})$ J·mol ⁻¹	ΔT^a /K	Δy_2^a
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + ethanol (2)	2437.8	4419.7	0.22	0.007
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + propan-1-ol (2)	4122.4	3377.1	0.40	0.019
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + propan-2-ol (2)	3818.2	2680.6	0.48	0.031
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + butan-1-ol (2)	3312.3	1895.1	0.34	0.020
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + pentan-1-ol (2)	675.1	4872.1	0.24	0.014
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + hexan-1-ol (2)	3434.9	1322.8	0.15	0.013

^aCalculated using eq 5.

Equations 3, 4, and 5 represent the bias, the average absolute deviations (AAD), and absolute deviations, respectively, where U represents T or y .

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

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

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

RESULTS AND DISCUSSION

Table 1 lists the critical properties and the acentric factors for the chemicals used in this study. The measured refractive indices agree well with literature.⁸ Table 2 lists the pure component vapor pressure data which were measured and the difference between the measured data and the literature for all chemicals used in this study.

The measured isobaric vapor–liquid equilibrium data for the binary systems of D-limonene + {ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, or hexan-1-ol} at 40 kPa are shown in Table 3 and plotted in Figures 2 to 7. The model parameters for the NRTL and Wilson models are provided in Tables 4 and 5. The NRTL nonrandom (α_{ij}) parameter (for systems containing alcohols) in the NRTL model was set to

Table 6. Error Analysis for the 1-Methyl-4-(1-methylethenyl)-cyclohexene + {Ethanol, Propan-1-ol, Propan-2-ol, Butan-1-ol, Pentan-1-ol, or Hexan-1-ol} Systems at 40 kPa

	NRTL		Wilson	
	y_2	T/K	y_2	T/K
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Ethanol (2)				
BIAS % ^a	0.488	0.00	−0.613	0.01
AAD % ^b	1.090	0.06	0.723	0.09
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Propan-1-ol (2)				
BIAS % ^a	−0.646	−0.12	1.479	−0.07
AAD % ^b	1.565	0.18	1.748	0.17
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Propan-2-ol (2)				
BIAS % ^a	−1.054	0.07	−1.172	−0.06
AAD % ^b	0.878	0.71	0.900	0.72
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Butan-1-ol (2)				
BIAS % ^a	0.622	0.17	0.689	0.18
AAD % ^b	0.761	0.19	0.842	0.20
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Pentan-1-ol (2)				
BIAS % ^a	−1.002	0.03	−1.036	0.03
AAD % ^b	0.175	0.11	0.473	0.11
1-Methyl-4-(1-methylethenyl)-cyclohexene (1) + Hexan-1-ol (2)				
BIAS % ^a	1.601	0.00	0.797	0.00
AAD % ^b	1.180	0.04	0.961	0.03

^aCalculated using eq 3. ^bCalculated using eq 4.

Table 7. Computed Azeotropic Conditions for the Systems Measured.

system	composition (x_1)	P/kPa	T/K
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + butan-1-ol (2)	0.003	40.0	367.4
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + pentan-1-ol (2)	0.106	40.0	384.8
1-methyl-4-(1-methylethenyl)-cyclohexene (1) + hexan-1-ol (2)	0.303	40.0	400.9

0.4 as was suggested by Zhingang et al.⁹ The BIAS and the average absolute deviations (AAD) for the calculated temperature and vapor composition of the NRTL and Wilson models are shown in Table 6. The D-limonene + {butan-1-ol, pentan-1-ol, or hexan-1-ol} systems exhibit a minimum temperature azeotrope. The D-limonene + {ethanol, propan-1-ol, or propan-2-ol} systems show the largest positive deviation from Raoult's law. Ethanol was found to be highly soluble in D-limonene with a high relative volatility; as a result measurements were quite difficult to perform in the dilute region.

Table 7 lists the azeotropic points for the systems measured which exhibited azeotropic behavior. These points were computed using a polynomial fit of the measured x - y data, and the remaining variable (temperature) was determined from the intersection of the T - x and T - y curves. Both NRTL and Wilson models provided a good correlation of the measured data.

CONCLUSIONS

New isobaric VLE data for binary systems comprising D-limonene + {ethanol, propan-1-ol, propan-2-ol, butan-1-ol, pentan-1-ol, or hexan-1-ol} at 40 kPa are reported. The isobaric

systems for the D-limonene + {butan-1-ol, pentan-1-ol, or hexan-1-ol} exhibit a minimum temperature azeotrope and the D-limonene + {ethanol, propan-1-ol, or propan-2-ol} systems show large deviations from Raoult's law. The experimental VLE data were successfully correlated with both the Wilson and the NRTL activity coefficient models.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ramjuger@ukzn.ac.za. Tel.: +27 31 260 3128. Fax: +27 31 260 1118.

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Notes

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