Vapor-liquid equilibria of the binary systems (cyclohexanone + 2-heptanone) and (cyclohexanone + hexanal) at different temperatures.

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ABSTRACT

Isothermal VLE data for (Cyclohexanone + 2-Heptanone) and (Cyclohexanone + Hexanal) mixtures are reported at T = (313.15, 333.15, 353.15, 393.15) K, which were measured using a static technique. Equilibrium properties are measured directly, and their standard uncertainties are: injected volume 0.03 mL, temperature 10 mK, and total pressure 0.05%. The non-ideality of the vapor phase was taken into account using the virial equation of state. VLE data were correlated using Margules, Wilson, NRTL and UNIQUAC equations obtaining good results. The binary mixture (Cyclohexanone + 2-Heptanone) presents a maximum pressure azeotrope which is broken at 393.15 K.

Keywords: VLE; Cyclohexanone; 2-Heptanone; Hexanal; azeotrope.

1. Introduction

Cyclohexanone is considered an intermediate key product in the industrial manufacture processes related to the production of caprolactam and adipic acid. Caprolactam is a widely used chemical (consumed as a monomer) for the production of Nylon-6. Also, adipic acid (obtained from cyclohexanone) is an important precursor for the manufacture of Nylon-6/6 [1, 2].

Nylon is the raw material for fibers production, with applications in textiles and industry. It is well known, Nylon is highly resilient, abrasion resistant and self-lubricating. Most of the nylon applications are in fibers for clothes, carpets, furniture and ropes. In addition, some industrial uses of nylon are, as a substitute of metal materials, in bearings, gears and parts where resistance and low friction are needed.

2-Heptanone and hexanal are by-products of the production of cyclohexanone, affecting the product quality. For 2-heptanone, due to its similar boiling point to cyclohexanone, the extraction of its traces becomes a separation problem in industry for conventional distillation processes [3]. The main purpose of this work is to explore the thermodynamic behaviour of the mixtures (Cyclohexanone + 2-Heptanone and Cyclohexanone + Hexanal) in order to solve the problem of removing these impurities.

Knowledge of the phase behaviour (vapor pressure, temperature and phase compositions) for these mixtures is carried out using an isothermal VLE technique. Measuring four isotherms (from 313.15 K to 393.15 K), we are able to find out which is the best temperature in order to increase the performance of cyclohexanone purification process. In addition, if the mixture presents an azeotropic behaviour, the effect of temperature in the azeotrope can be studied. We have no found VLE data for these mixtures in the literature so that the data presented in this paper are new.

2. Experimental section

2.1. Materials

The compounds were purchased from Sigma-Aldrich and were of the highest purity available, chromatography quality reagents with a purity >0.995 (GC) for cyclohexanone, 2-heptanone and hexanal. The details of the compounds are summarized in Table 1. In addition, the pure compounds were degasified, before charging them to the cell, by means of a modified distillation method [4].

Table 1. Material description.

Chemical name	**CAS**	**Source**	**Mass fraction purity**[a]	**Purification method**
Cyclohexanone	108-94-1	Sigma-Aldrich	≥0.995	None
2-Heptanone	110-43-0	Sigma-Aldrich	≥0.995	None
Hexanal	66-25-1	Sigma-Aldrich	≥0.995	None

[a] Stated by the supplier and checked by gas chromatography

Density of pure compounds at atmospheric pressure were measured by a Stabinger SVM 3000 with a standard uncertainty of $5 \cdot 10^{-4}$ kg·m^3. In table 2, density of pure hydrocarbons as function of temperature is shown.

Table 2. Atmospheric densities of pure hydrocarbons in the range of 288.15 K to 378.15 K. Laboratory pressure, 94.13 kPa.

		ρ^a / kg·m^3	
***T* / K**	**Cyclohexanone**	**2-Heptanone**	**Hexanal**
288.15		819.7	
293.15	947.2	815.5	822.6
298.15		811.1	

303.15	938.3	807.2	813.4
308.15		803.0	
313.15	929.3	798.7	804.3
323.15	920.3	789.8	795.3
333.15	911.3	780.9	786.0
343.15	902.2	772.0	776.8
353.15	893.1	763.0	767.5
363.15	883.8	754.0	
368.15			753.0
373.15	874.6	745.0	
378.15	870.0	740.4	743.7

[a] Standard uncertainties: u(ρ) = $5\cdot10^{-4}$ kg·m^3, u(T) = 0.02 K, u(p) = 0.22 kPa.

The experimental densities have been checked with the available literature, showing a maximum deviation of 0.6% with an average better of 0.3% which agrees with the uncertainty of the apparatus. Cyclohexanone was compared with [5, 6, 7, 8]. In addition, the sources used for 2-heptanone were [5, 9, 10] and finally, the literature data for hexanal is [11].

2.2. Experimental technique

A modified isothermal total pressure cell, described in previous papers [12, 13], was used for the measurements. The cell is a cylindrical stainless-steel piece with a volume of 180 mL which has an externally-operated magnetic stirrer. Known volumes of pure degassed components are injected into the cell by means of positive displacement pumps. First, around 50 mL of one component are injected into the evacuated cell, and the vapor pressure is recorded. Then, successive volume injections of the second compound modify the composition of the mixture and the corresponding vapor pressures are recorded up to a mole fraction of 0.4 of the first component. A second run is performed, starting with the pure second component and following the described procedure. There are repeated central compositions which are used for checking the repeatability of the measurements. The total amount of mass injected is accurately determined from the volume differences read between two stop-points of the piston, the temperature of the injector and the value of the density for that pure component giving a standard uncertainty in the mole fraction of 0.0005.

The cell is immersed in a high precision water bath assuring a temperature stability of ±0.5 mK. The temperature is measured by a calibrated standard PRT-100 connected to an a/c resistance bridge (calibrated and traceable to I.S. units) with a temperature resolution of 1 mK and the estimated standard uncertainty of the temperature measurement is 10 mK.

A new pressure measurement procedure is used. A Druck pressure transducer (model PDCR-910-1422), whose pressure range is from (3.5 to 200) kPa, is placed in the cell and pressure is directly measured using a pressure indicator (Druck DPI 145). The pressure system was calibrated with our own standards traceable to I.S. units and the estimated relative standard uncertainty of pressure is 0.05%.

3. Results

The VLE technique is based on the Duhem´s theorem [14] “for any closed system formed initially from given masses of prescribed chemical species, the equilibrium state is completely determined when any two independent variables are fixed”. It can be mathematically expressed in the equation 1 as the equality of chemical potentials of each component in each phase. The equivalent of equation 1 can be written in terms of fugacity, the fugacity of each component in a mixture (equation 2)

$$\mu_i^{\alpha} = \mu_i^{\beta} = \cdots = \mu_i^{\omega} \quad (1)$$

$$f_i^{\alpha} = f_i^{\beta} = \cdots = f_i^{\omega} \quad (2)$$

In the particular case of VLE for a binary system, the previous expression can be reduced at the next equality:

$$f_i^{l}(x_i, P, T) = f_i^{v}(y_i, P, T) \quad (3)$$

Where the fugacity of each component in each phase is function of pressure, temperature and the composition of every phases. The logic of the calculations is based on the Bubble pressure calculations with the gamma-phi approach (Poynting factor). It is an iterative process starting with the equation 3, using the definition of the fugacity in the liquid and vapor phase. The equation becomes:

$$x_i \cdot \gamma_i \cdot f_i = y_i \cdot \hat{\Phi}_i \cdot P \quad (4)$$

Where f_i represents the fugacity of the pure component *i* at the mixture temperature and pressure, $\hat{\phi}_i$ is the fugacity coefficient of the same component at the vapor phase and γ_i is the activity coefficient.

Substituting for f_i by its definition and the Poynting factor, the equation 4 becomes as:

$$x_i \cdot \gamma_i \cdot P = y_i \cdot \Phi_i \cdot P_i^{sat} \quad (5)$$

Where: $\Phi_i = \exp \dfrac{B_{ii}(P - P_i^{sat}) + P\dfrac{1}{2}\sum_k \sum_l y_k y_l (2\delta_{ki} - \delta_{kl})}{RT}$ (6)

Data reduction was performed using Barker's method and, due to this procedure and the use of a static technique, thermodynamic consistency has not necessary to be checked [15, 16, 17]. The vapor phase was modeled using the virial equation of state truncated after the second term. It means that the calculation of the fugacity coefficients is given by equation 6, where $\delta_{ki} \equiv 2B_{ki} - B_{kk} - B_{ii}$; $\delta_{kl} \equiv 2B_{kl} - B_{kk} - B_{ll}$ and B_{ii}, B_{ki}, B_{kk} ... are the values of the virial coefficients.

The pure-component and interaction second virial coefficients (B_{ii}, B_{ij}) were estimated using Hayden-O'Connell [18] method and the parameters published by Dymond and Smith [19], summarized in Table 3. Besides, this table contains the experimental vapor pressure of pure compounds and the literature values [20-25] for comparison.

Once the activity coefficients and the fugacity are well known, the total pressure of the mixture and the vapor phase composition are evaluated through and iterative process, following the next equations:

$$P = \sum_i \frac{x_i \gamma_i P_i^{sat}}{\Phi_i} \quad (7) \quad \text{and} \quad y_i = \frac{x_i \gamma_i P_i^{sat}}{\Phi_i P} \quad (8)$$

The iterative process starts with the experimental temperature, pressure, the initial liquid molar composition and $\Phi_i = 1$. Then, objective function $O.F. = \sum(\delta P)^2 = \sum\left(P_{cal} - P_{exp}\right)^2$ is minimized by Marquardt algorithm fitting procedure. As a result, a first approach of a calculated pressure and vapor molar fraction is obtained. When the solution converges, and all the thermodynamic equations are balanced; liquid and vapor composition and calculated pressure are restimated as can be seen in the following flow chart (figure 1).

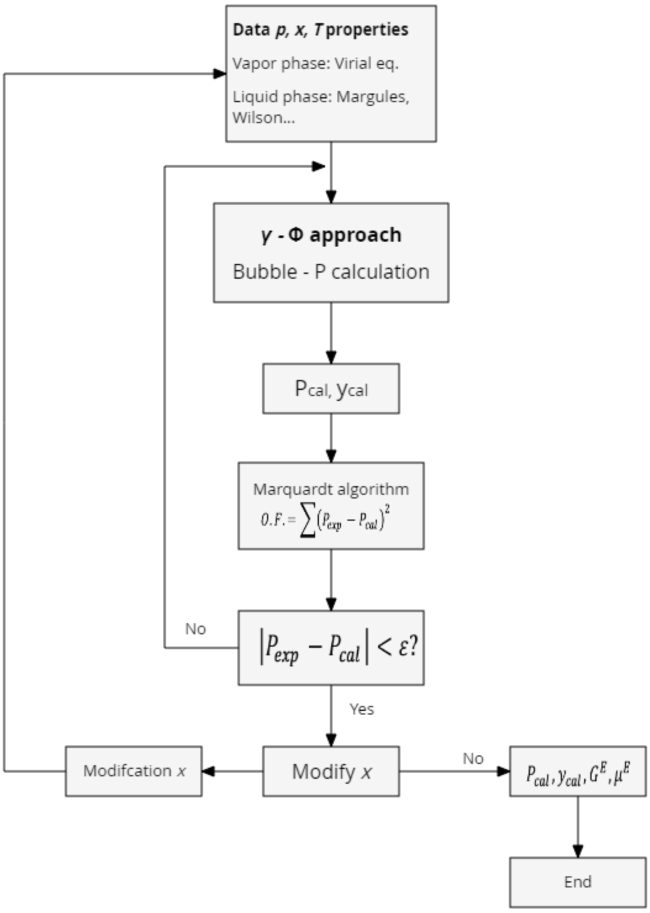

Figure 1. Data reduction flow chart

Table 3. Experimental vapor pressures p_i^s, literature values of vapor pressures p_i^s(lit) and calculated virial coefficients (B_{ii}, B_{ij}) at different temperatures.

	***T* /K**	**Cyclohexanone**[*] **(i = 1)**	**2-Heptanone** **(i = 2)**	**Hexanal** **(i = 3)**
p_i^s/kPa	313.15	1.307	1.281	3.604
p_i^s/kPa (lit)	313.15	1.290[a]	1.268[a]	3.502[e]
				3.281[f]
p_i^s/kPa	333.15	3.583	3.697	9.119
p_i^s/kPa (lit)	333.15	3.591[a]	3.672[a]	9.082[e]
			3.676[d]	8.558[f]

p_i^s/kPa	353.15	8.692	9.272	20.643
p_i^s/kPa (lit)	353.15	8.677[a]	9.144[a]	20.643[e]
		8.60[b]	9.153[d]	19.613[f]
p_i^s/kPa	393.15	36.563	40.990	79.036
p_i^s/kPa (lit)		36.753[a]	40.357[a]	79.035[e]
		36.753[c]	40.385[d]	76.614[f]
$B_{ii}/(\mathrm{cm}^3\ \mathrm{mol}^{-1})$[g]	313.15	-2796	-3571	-3100
	333.15	-2340	-2954	-2567
	353.15	-1987	-2480	-2158
	393.15	-1486	-1814	-1582
$B_{1i}/(\mathrm{cm}^3\ \mathrm{mol}^{-1})$[g]	313.15		-2980	-2841
	333.15		-2484	-2370
	353.15		-2101	-2006
	393.15		-1557	-1489

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[*] The values are the average of two experimental measurements.

[a] Calculated from Antoine equation using constants reported by Riddick et al. [20].

[b] Reported by Teodorescu et al. [21]

[c] Calculated from Antoine equation using constants reported by Meyer and Hotz [22].

[d] Calculated from Antoine equation using constants reported by Ambrose et al. [23].

[e] Calculated from Antoine equation using constants reported by Meneses et al. [24].

[f] Calculated from Antoine equation using constants reported by Palczewska-Tulińska and Oracz. [25].

[g] Calculated values using [18,19].

In figure 2, the residuals from the experimental saturation pressure at the working temperature are plotted in order to check the agreement with the literature data and our experimental data. Most of the deviations are better than 1.5%, only Palczewska-Tulińska et al [25] shows a maximum deviation of 9% for the pure hexanal at 313.15 K.

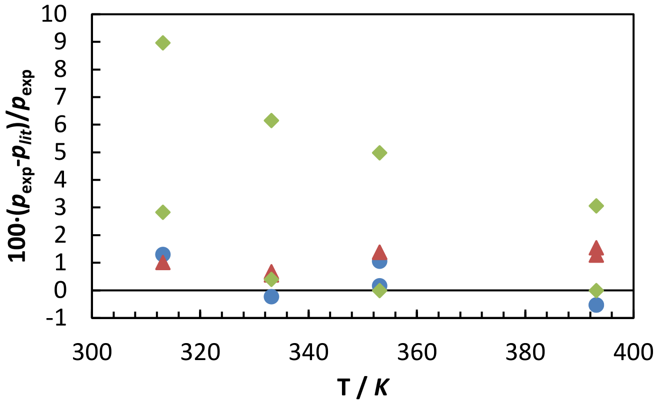

Figure 2. Relative saturation pressure residuals at different temperatures of the pure compounds: (●) Cyclohexanone, (▲) 2-Heptanone and (♦) Hexanal.

VLE data were correlated by four-parameter Margules equation [26], because with the addition of more parameters do not improve significantly the adjustment results:

$$G_m^E/(RT) = \left[A_{ji}x_i + A_{ij}x_j - \left(\lambda_{ji}x_i + \lambda_{ij}x_j\right)x_ix_j\right]x_ix_j \tag{9}$$

Additionally, data reduction was undertaken using Wilson [27], NRTL [28] and UNIQUAC [29] models, whose equations are shown below:

$$G_m^E/(RT) = -\sum_i x_i \ln\left(\sum_j x_j A_{ij}\right) \tag{10}$$

$$G_m^E/(RT) = \sum_i x_i \left(\sum_j A_{ji}G_{ji}x_j\right)/\left(\sum_k G_{ki}x_k\right) \tag{11}$$

$$G_m^E/(RT) = \sum_i x_i \ln(\phi_i/x_i) + (z/2)\sum_i q_ix_i \ln(\vartheta_i/q_i) - \sum_i q_ix_i \ln\left(\sum_j \vartheta_j A_{ji}\right) \tag{12}$$

Where A_{ij}, A_{ji} and α (only for NRTL model) are the adjustable parameters, and $G_{ji}=\exp(-\alpha_{ji}A_{ji})$; $\vartheta_i = q_i x_i/\sum_j q_j x_j$; $\phi_i = r_i x_i/\sum_j r_j x_j$ and $z = 10$.

VLE data were obtained at different temperatures (313.15 K, 333.15 K, 353.15 K and 393.15 K) and they are reported in Tables 4 and 5 for the binary systems (cyclohexanone + 2-heptanone) and (cyclohexanone + hexanal), respectively. The vapor phase mole fractions were calculated using four-parameter Margules equation.

Table 4. VLE data: total pressure, liquid mole fraction and calculated vapor mole fraction using four-parameter Margules equation for Cyclohexanone (1) + 2-Heptanone (2) at different temperatures.

x_1	$y_{1,\mathrm{calc}}$	p/kPa	x_1	$y_{1,\mathrm{calc}}$	p/kPa
		T = 313.15 K			
0.0000	0.0000	1.281	0.5007	0.5042	1.324
0.0428	0.0484	1.289	0.5501	0.5523	1.328
0.0965	0.1058	1.304	0.6002	0.6008	1.324
0.1415	0.1521	1.303	0.6501	0.6490	1.320
0.1966	0.2072	1.306	0.6967	0.6939	1.318
0.2477	0.2576	1.310	0.7504	0.7457	1.320
0.2981	0.3069	1.313	0.8009	0.7945	1.320
0.3479	0.3555	1.316	0.8530	0.8455	1.316
0.3977	0.4039	1.318	0.9045	0.8972	1.314
0.4486	0.4536	1.325	0.9582	0.9535	1.306
0.4502	0.4551	1.321	1.0000	1.0000	1.298
		T = 333.15 K			

0.0000	0.0000	3.697	0.5503	0.5334	3.715
0.0472	0.0508	3.712	0.6003	0.5825	3.707
0.0989	0.1054	3.726	0.6499	0.6321	3.694
0.1467	0.1544	3.735	0.7001	0.6830	3.683
0.1988	0.2057	3.743	0.7503	0.7344	3.670
0.2495	0.2539	3.751	0.8008	0.7864	3.655
0.2998	0.3006	3.756	0.8503	0.8376	3.631
0.3495	0.3460	3.759	0.9006	0.8902	3.613
0.3995	0.3916	3.763	0.9502	0.9435	3.583
0.4606	0.4482	3.738	1.0000	1.0000	3.563
0.5000	0.4852	3.728			

T = 353.15 K

0.0000	0.0000	9.272	0.5004	0.4770	9.243
0.0487	0.0498	9.290	0.5505	0.5242	9.200
0.0990	0.1034	9.303	0.6009	0.5735	9.160
0.1492	0.1558	9.317	0.6508	0.6241	9.109
0.1994	0.2058	9.330	0.7008	0.6760	9.065
0.2492	0.2531	9.336	0.7512	0.7292	9.017
0.2995	0.2987	9.340	0.8010	0.7820	8.964
0.3496	0.3429	9.346	0.8511	0.8351	8.907
0.3998	0.3867	9.350	0.9006	0.8877	8.847
0.4497	0.4309	9.325	0.9509	0.9425	8.779
0.4503	0.4314	9.293	1.0000	1.0000	8.689
0.4998	0.4764	9.327			

T = 393.15 K

0.0000	0.0000	40.990	0.5510	0.5191	39.234
0.0473	0.0464	40.960	0.6010	0.5688	38.935
0.0987	0.0953	40.866	0.6513	0.6199	38.718
0.1488	0.1419	40.763	0.7003	0.6704	38.467
0.1988	0.1879	40.648	0.7516	0.7242	38.170
0.2491	0.2339	40.525	0.8021	0.7781	37.832
0.2992	0.2799	40.399	0.8522	0.8326	37.650
0.3496	0.3265	40.249	0.9012	0.8869	37.331
0.3997	0.3734	40.082	0.9517	0.9441	37.069
0.4508	0.4219	39.762	1.0000	1.0000	36.687
0.5008	0.4699	39.435			

[a] Standard uncertainties: $u(x_1) = 0.0005$, $u_r(p) = 5\cdot10^{-4}\cdot\mathrm{Pa/Pa}$, $u(T) = 10$ mK.

Table 5. VLE data: total pressure, liquid mole fraction and calculated vapour mole fraction using Margules equation for Cyclohexanone (1) + Hexanal (2) at different temperatures.

x_1	$y_{1,\mathrm{calc}}$	p/kPa	x_1	$y_{1,\mathrm{calc}}$	p/kPa
		$T = 313.15$ K			
0.0000	0.0000	3.604	0.5513	0.3113	2.335
0.0489	0.0169	3.498	0.5514	0.3114	2.338
0.0992	0.0383	3.351	0.5990	0.3554	2.224
0.1502	0.0626	3.221	0.6511	0.4096	2.113
0.2005	0.0881	3.095	0.7011	0.4677	2.004
0.2504	0.1143	2.982	0.7514	0.5321	1.891
0.3007	0.1416	2.885	0.8017	0.6027	1.782

0.3506	0.1699	2.791	0.8526	0.6810	1.667
0.4010	0.2004	2.691	0.9016	0.7655	1.551
0.4510	0.2334	2.577	0.9494	0.8629	1.446
0.4511	0.2335	2.583	1.0000	1.0000	1.315
0.5012	0.2701	2.466			
		T = 333.15 K			
0.0000	0.0000	9.119	0.5010	0.2792	6.424
0.0481	0.0200	8.837	0.5523	0.3238	6.073
0.0993	0.0438	8.550	0.6011	0.3715	5.799
0.1494	0.0684	8.297	0.6510	0.4261	5.527
0.1999	0.0938	8.030	0.7020	0.4877	5.252
0.2499	0.1197	7.766	0.7527	0.5543	4.981
0.2999	0.1465	7.502	0.8038	0.6266	4.707
0.3502	0.1752	7.238	0.8452	0.6890	4.479
0.4002	0.2060	7.002	0.8993	0.7781	4.182
0.4504	0.2403	6.772	0.9423	0.8590	3.941
0.4511	0.2409	6.741	1.0000	1.0000	3.604
		T = 353.15 K			
0.0000	0.0000	20.643	0.5009	0.2963	14.929
0.0493	0.0235	20.078	0.5512	0.3418	14.267
0.0998	0.0494	19.531	0.5997	0.3906	13.670
0.1499	0.0759	18.974	0.6497	0.4456	13.087
0.2002	0.1027	18.413	0.7002	0.5053	12.507
0.2501	0.1297	17.854	0.7518	0.5699	11.924
0.3002	0.1577	17.311	0.8018	0.6350	11.349

0.3504	0.1874	16.780	0.8514	0.7029	10.769
0.4004	0.2198	16.267	0.8970	0.7707	10.231
0.4505	0.2557	15.771	0.9414	0.8487	9.698
0.4508	0.2559	15.697	1.0000	1.0000	8.695
$T = 393.15$ K					
0.0000	0.0000	79.036	0.5511	0.3547	56.575
0.0478	0.0273	77.525	0.6014	0.4054	54.241
0.1002	0.0562	75.419	0.6511	0.4604	51.990
0.1504	0.0833	73.563	0.7011	0.5202	49.756
0.2005	0.1102	71.799	0.7514	0.5849	47.528
0.2509	0.1378	70.144	0.8010	0.6529	45.364
0.3023	0.1681	67.992	0.8510	0.7260	43.142
0.3507	0.1974	66.035	0.8995	0.8028	41.032
0.4009	0.2303	63.901	0.9510	0.8945	38.681
0.4510	0.2679	61.601	1.0000	1.0000	36.439
0.5011	0.3091	59.014			

[a] Standard uncertainties: $u(x_1) = 0.0005$, $u_r(p) = 5\cdot10^{-4}\cdot$Pa/Pa, $u(T) = 10$ mK.

Tables 6 and 7 summarize the results of data correlation containing the adjustable parameters of the models obtained minimizing the differences between experimental and calculated total pressures, the root mean square of pressure residuals (differences between experimental and calculated pressures) and the maximum value of this residual. For (cyclohexanone + 2-heptanone) system, the calculated azeotrope is also included.

Table 6. VLE data reduction results for the system {Cyclohexanone (1) + 2-Heptanone (2)} at different temperatures: Adjusted parameters, root mean square pressure residual (rms Δp) and the maximum value of the pressure residual (max |Δ*p*|). Δ*p* is defined as the difference between the experimental and calculated pressure) and the subscript "az" means azeotrope.

	Margules	**Wilson**	**NRTL**	**UNIQUAC**
		$T = 313.15$ K		
A_{12}	0.1532	0.6281	-0.0461	1.9409
A_{21}	0.0398	1.3520	0.1629	0.4166
λ_{12}	0.2567			
λ_{21}	-0.1776			
α_{12}			2.0778	
rms Δp/kPa	0.003	0.003	0.004	0.003
max $\|\Delta p\|$/kPa	0.009	0.009	0.009	0.009
$x_{1,\text{az}}$	0.601	0.560	0.0.560	0.574
p_{az}/kPa	1.324	1.323	1.323	1.323
		$T = 333.15$ K		
A_{12}	0.1175	0.4928	-1.7954	2.0158
A_{21}	0.0510	1.5521	2.2306	0.3800
λ_{12}	-0.1393			
λ_{21}	0.0010			
α_{12}			0.0824	
rms Δp/kPa	0.008	0.009	0.009	0.009
max $\|\Delta p\|$/kPa	0.020	0.020	0.020	0.020
$x_{1,\text{az}}$	0.311	0.276	0.283	0.266

p_{az}/kPa	3.754	3.753	3.753	3.753
T = 353.15 K				
A_{12}	0.0441	0.6762	-0.9746	0.6883
A_{21}	0.1508	1.2472	0.7282	1.4534
λ_{12}	-0.5504			
λ_{21}	0.3479			
α_{12}			-0.5064	
rms Δp/kPa	0.019	0.025	0.024	0.024
max $\|\Delta p\|$/kPa	0.060	0.070	0.065	0.066
$x_{1,\ az}$	0.292	0.224	0.238	0.238
p_{az}/kPa	9.356	9.352	9.349	9.346
T = 393.15 K				
A_{12}	0.0687	0.6151	0.5970	0.9391
A_{21}	0.1435	1.3826	0.1156	1.1505
λ_{12}	-0.1978			
λ_{21}	0.4585			
α_{12}			8.1085	
rms Δp/kPa	0.051	0.075	0.061	0.089
max $\|\Delta p\|$/kPa	0.124	0.175	0.124	0.187

Table 7. VLE data reduction results for the system {Cyclohexanone (1) + Hexanal (2)} at different temperatures: Adjusted parameters, root mean square pressure residual (rms Δp) and the maximum value of the pressure residual (max $|\Delta p|$). Δp is defined as the difference between the experimental and calculated pressure.

	Margules	**Wilson**	**NRTL**	**UNIQUAC**
		T = 313.15 K		
A_{12}	-0.2001	2.0127	8.0329	1.5751
A_{21}	0.2296	0.3140	-7.0168	0.6349
λ_{12}	-0.8125			
λ_{21}	0.7227			
α_{12}			0.0175	
rms Δp/kPa	0.010	0.018	0.017	0.019
max $\lvert\Delta p\rvert$/kPa	0.021	0.043	0.037	0.044
		T = 333.15 K		
A_{12}	-0.0270	0.5398	-1.2652	1.9861
A_{21}	0.2126	1.5529	1.5243	0.4070
λ_{12}	-0.4413			
λ_{21}	0.9152			
α_{12}			0.1148	
rms Δp/kPa	0.025	0.035	0.036	0.035
max $\lvert\Delta p\rvert$/kPa	0.056	0.084	0.083	0.085
		T = 353.15 K		
A_{12}	0.05302	0.63482	-0.3966	1.8821
A_{21}	0.39338	1.33941	0.5600	0.4431
λ_{12}	-0.24618			
λ_{21}	1.31833			
α_{12}			0.3100	
rms Δp/kPa	0.049	0.094	0.092	0.099
max $\lvert\Delta p\rvert$/kPa	0.142	0.223	0.222	0.201

$T = 393.15$ K

A_{12}	0.2123	0.2634	-0.6058	2.2363
A_{21}	0.1096	2.0503	1.0903	0.2937
λ_{12}	0.1011			
λ_{21}	0.6242			
α_{12}			0.5425	
rms Δp/kPa	0.133	0.197	0.181	0.165
max $\lvert\Delta p\rvert$/kPa	0.217	0.371	0.280	0.292

Relative pressure residuals obtained using four-parameter Margules model are plotted in Fig. 3 for the two binary systems measured in this work, showing the reliability of the model.

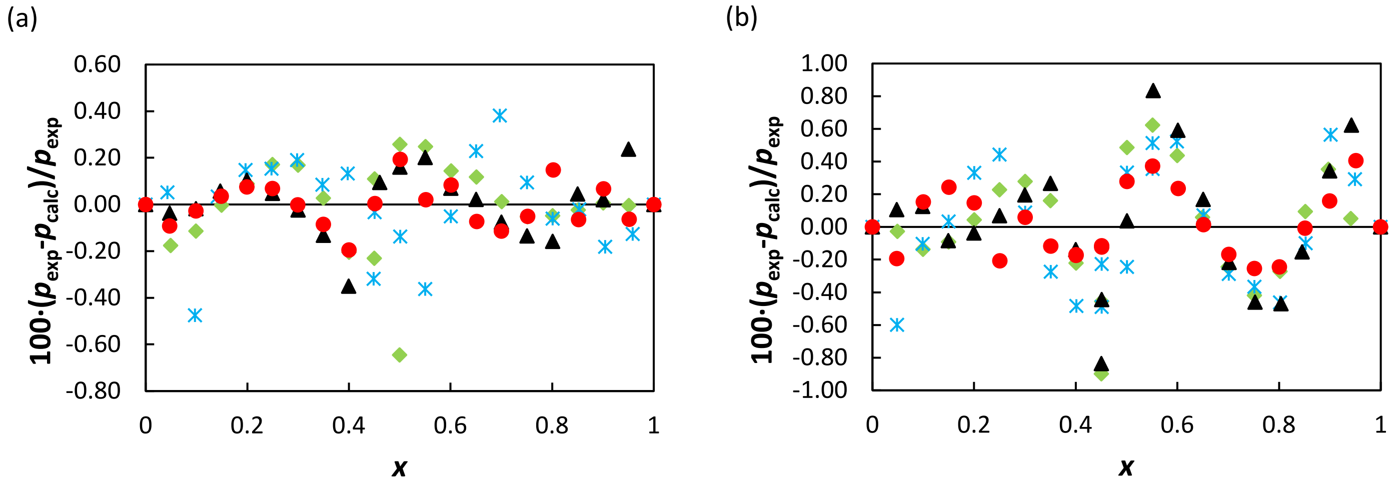

Figure 3. Relative pressure residuals using four-parameter Margules equation at different temperatures: (✳) 313.15 K, (▲) 333.15 K (♦) 353.15 K and (●) 393.15 K, for the systems (a) {Cyclohexanone (1) + 2-Heptanone (2)} and (b) {Cyclohexanone (1) + Hexanal (2)}.

Finally, VLE data are shown graphically in Figs. 4 and 5 where pressure is plotted as a function of the composition for both binary mixtures at two different temperatures to present the effect of temperature in the phase behaviour.

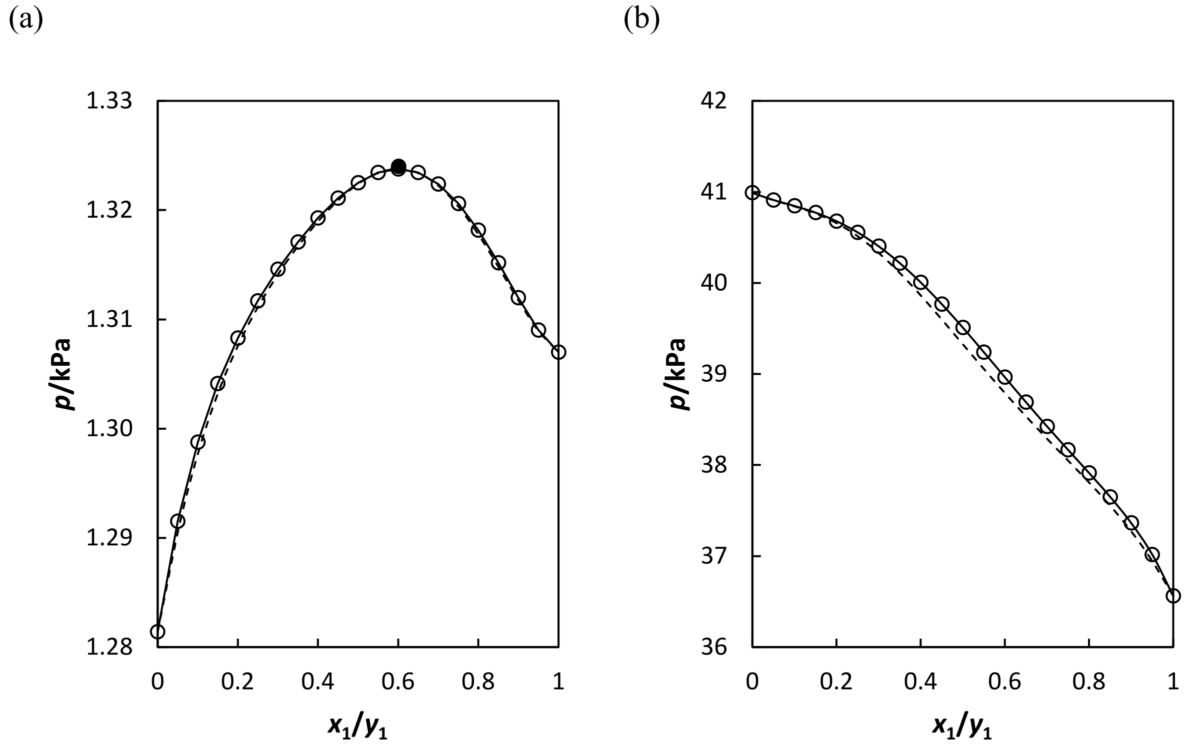

Figure 4. VLE data for the system Cyclohexanone (1) + 2-Heptanone (2) at $T = 313.15$ K (a) and $T = 393.15$ K (b). Lines represent calculated values using Margules equation with the parameters given in Table 6. The black point on the left graph represents the azeotrope.

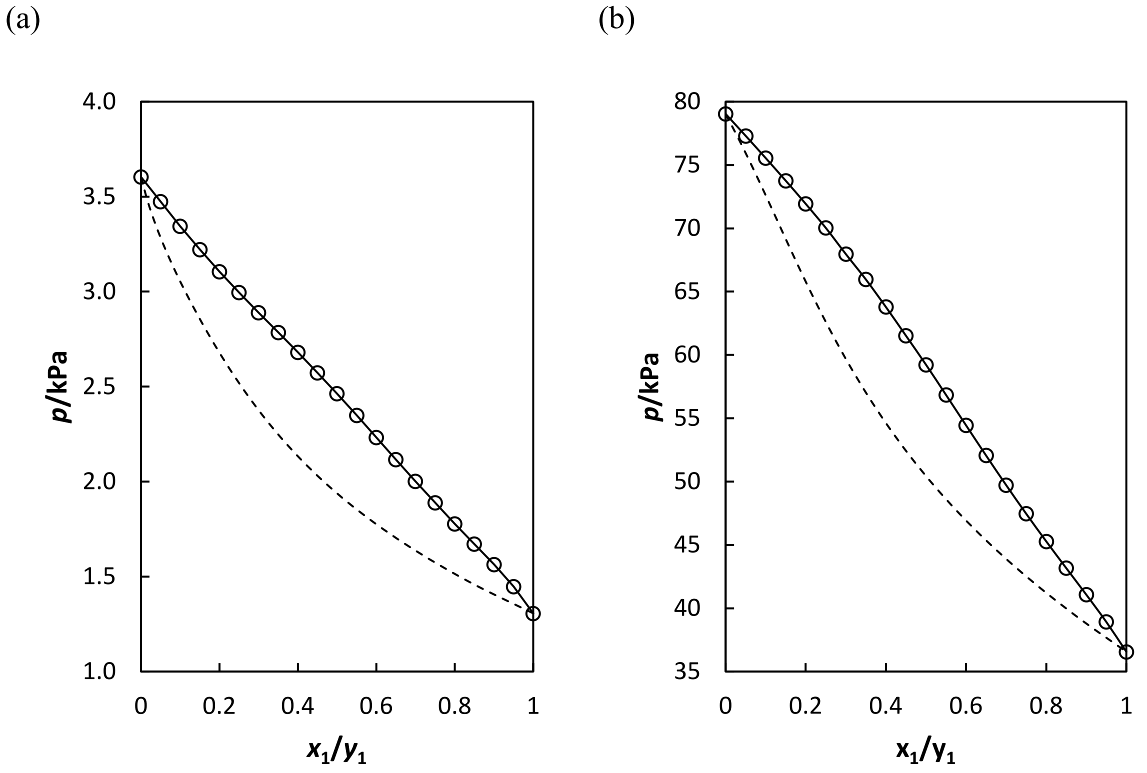

Figure 5. VLE data for the system Cyclohexanone (1) + Hexanal (2) at $T = 313.15$ K (a) and $T = 393.15$ K (b). Lines represent calculated values using Margules equation with the parameters given in Table 7.

4. Discussion

As regards cyclohexanone + 2-heptanone mixture, it presents positive deviations from Raoult's law with a maximum pressure azeotrope at the measured temperatures except for T=393.15 K. The azeotropic composition changes to lower mole fractions of cyclohexanone when temperature is increased in such a way that disappears at 393.15 K.

Analyzing VLE data reduction for this system, all the models give good and similar results in terms of root mean square pressure residuals (rms Δp) which ranges from 3 Pa at 313.15K to 89 Pa at 393.15 K representing relative values of 0.45% and 0.22%, respectively. Four-parameter Margules equation gives the best results at all the temperatures being the rms Δp 3 Pa, 8 Pa, 19 Pa and 51 Pa, for T = 313.15, 333.15, 353.15, 393.15 K, respectively.

The azeotropic behavior was also calculated using the same models, obtaining slight differences in the composition of the azeotrope between them. As can be seen in Table 5, the azeotrope, at T=313.15 K, is found at p_{az}=1.324 kPa and $x_{1,\mathrm{az}}$ = 0.601 when is calculated with four-parameter Margules equation, Wilson and NRTL model give the azeotrope at p_{az} = 1.323 kPa and $x_{1,\mathrm{az}}$ = 0.560 and UNIQUAC results are p_{az} = 1.323 kPa and $x_{1,\mathrm{az}}$ = 0.574. At T = 353.15 K, calculated azeotrope was found at p_{az} = 9.356 kPa and $x_{1,\mathrm{az}}$ = 0.292 using four-parameter Margules equation, at p_{az} = 9.352 kPa and $x_{1,\mathrm{az}}$ = 0.224 using Wilson equation, at p_{az} = 9.349 kPa and $x_{1,\mathrm{az}}$ = 0.238 using NRTL and, finally, at p_{az} = 9.346 kPa and $x_{1,\mathrm{az}}$ = 0.238 using UNIQUAC. In contrast, the mixture does not present an azeotrope at 393.15 K.

In addition, excess Gibbs energy was calculated using four-parameter Margules equation and it is represented in Figure 6 as a function of the liquid phase composition. As can be seen, this system shows positive excess Gibbs energy in all the composition range, being the maximum around x_1 = 0.4, and the highest value is observed at 353.15 K being $G_{\mathrm{m}}^{\mathrm{E}}$ = 93.5 J·mol^{-1}.

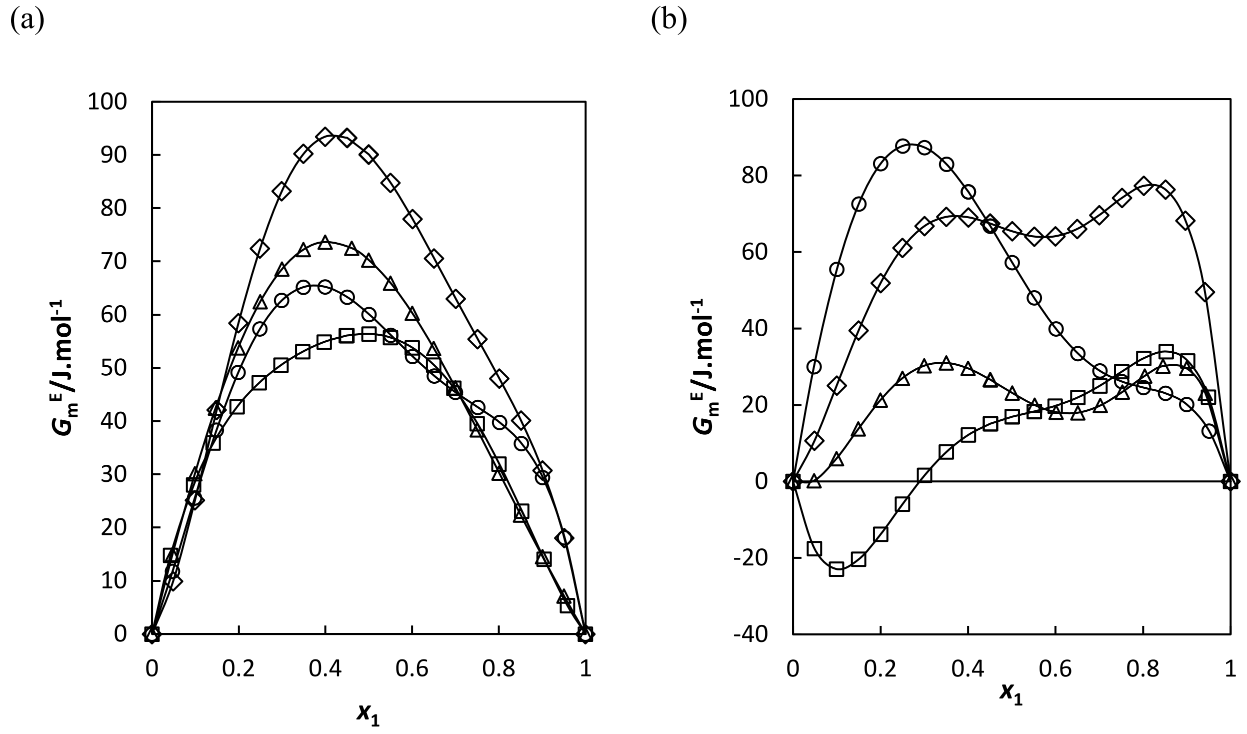

Figure 6. Excess Gibbs energy as a function of liquid phase mole fraction at different temperatures: (□) 313.15 K, (△) 333.15 K (◇) 353.15 K and (○) 393.15 K, for the systems (a) {Cyclohexanone (1) + 2-Heptanone (2)} and (b) {Cyclohexanone (1) + Hexanal (2)}.

Concerning the cyclohexanone + hexanal system, it also exhibits slight positive deviations for the ideality but it does not present an azeotrope. The four models used for data reduction correlate quite well the system obtaining root mean square pressure residuals which vary from 10 Pa using Margules equation to 19 Pa for UNIQUAC at 313.15 K, from 25 Pa for Margules to 36 Pa for NRTL at 333.15 K, from 49 Pa to 99 Pa at 353.15 K, for Margules and UNIQUAC, respectively and, finally at 393.15 K, root mean square pressure residuals range from 133 Pa for four-parameter Margules equation to 197 Pa for Wilson equation.

As shown in Figure 6, excess Gibbs energy for this mixture increases with temperature being the maximum value of 87.8 J·mol^{-1} at x_1 =0.25 and T= 393.15 K. These values are always positive in all the composition range except at T = 313.15 K where G_m^E is negative up x_1 =0.3.

Finally, not only the azeotropic behavior restricts the separation of a mixture in industrials processes, also the relative volatility of the mixture in the whole composition range limits the viability of the processes. When relative volatilities are in the range of 1, separation by distillation process are not possible. For this purpose, a relative volatility chart is shown in figure 7.

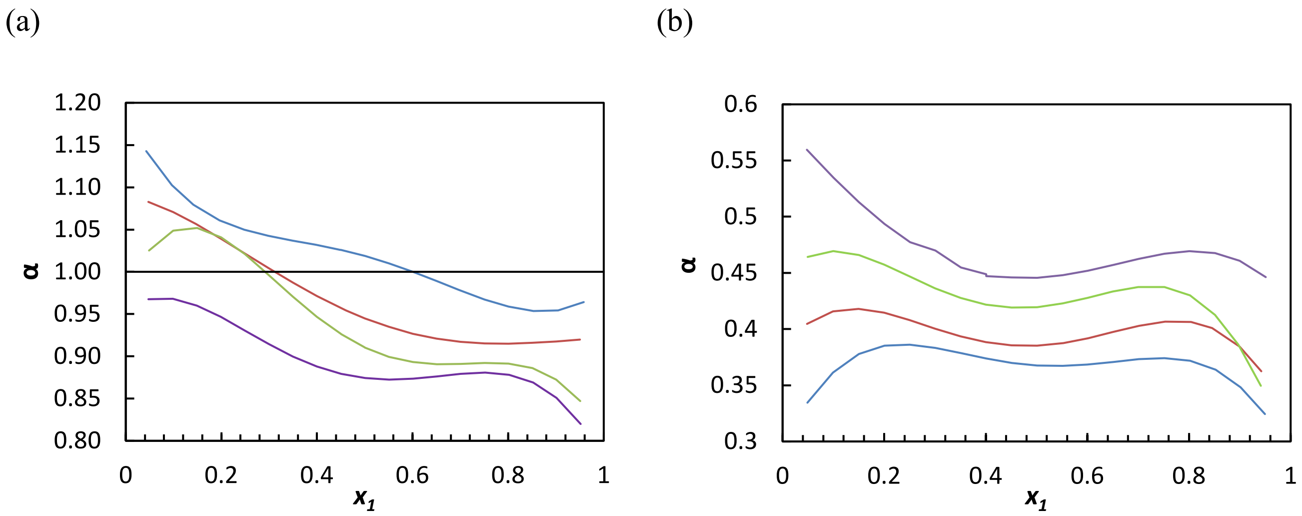

Figure 7. Relative volatility chart for the systems: (a) {Cyclohexanone(1) + 2-Heptanone(2)} and (b) {Cyclohexanone(1) + Hexanal(2)} at different temperatures: (—) 313.15 K; (—) 333.15 K; (—) 353.15 K; (—) 393.15 K.

As can be seen, the system {cyclohexanone + 2-heptanone} plays closely in the range of α=1, with 3 azeotropes at the lowest temperatures, being a cuasi-ideal mixture in all the composition range. In contrast, the mixture {cyclohexanone + hexanal} the relative volatilities are far from the unity, being possible a distillation process.

5. Conclusions

Four isotherms where measured to determine VLE data for the binary systems (Cyclohexanone + 2-Heptanone) and (Cyclohexanone + Hexanal) by means of an accurate static technique. Barker's method was applied to correlate the experimental data using four different models. The best results were obtained using the four-parameter Margules equation at all the temperatures studied, whereas the other models lead to slightly worse results being similar between them. The azeotrope of the system with 2-heptanone was broken at 393.15 K.

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Nomenclature

A_{ij}, A_{ji}	adjustable parameters of the VLE correlation models, Eqs. (9)-(12)
B_{ii}, B_{ij}, B_{jj}	second virial coefficients
$G^E{}_m$	excess molar Gibbs energy
ij	constituent identification: 1 or 2
lit.	literature value

max	maximum value of the indicated quantity
p	total pressure
$p^S{}_i$	vapour pressure of pure constituent i
R	universal gas constant
rms	root mean square
T	absolute temperature
$V^L{}_i$	molar volume of pure liquid i
x	mole fraction, liquid phase
y	mole fraction, vapour phase

Greek letters

Δ	signifies difference
α_{ij}	adjustable parameter in NRTL model, Eq. (11)
λ_{ij}, λ_{ji}	adjustable parameter in Eq. (9)
η_{ij}, η_{ji}	adjustable parameter in Eq. (9)

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