Vapor−Liquid Equilibrium Measurements and Modeling for Cyclohexane + Cyclohexanone[†]

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The characteristically low conversion in the oxidation of cyclohexane to form cyclohexanol and cyclohexanone requires significant recovery work via distillation. In this study, new isothermal vapor−liquid equilibria (VLE) are presented for the cyclohexane + cyclohexanone binary system. Measurements were performed at temperatures of (423, 444, 464, and 484) K, using an apparatus based on the "static−analytic" method, with two ROLSI pneumatic capillary samplers. The generated data are correlated using two equations of state, namely, the Peng−Robinson coupled with the Wong−Sandler mixing rules and the perturbed-chain statistical associating fluid theory (SAFT) with a dipolar contribution by Jog and Chapman. While both models perform reasonably well in describing the phase equilibria, the Peng−Robinson is slightly better than the perturbed-chain SAFT equation of state and tends to be more easily implemented in industrial process simulators.

Introduction

It is well-known that the commercial synthesis of adipic acid and caprolactum, raw materials in Nylon production, follows two possible reaction routes, namely, the oxidation of cyclohexane or the hydrogenation of phenol. Certainly, at an economic level, the oxidation of cyclohexane is favored, using cobalt naphthenate or stearate catalysts[1] to produce a mixture of cyclohexanol, cyclohexanone, and unreacted cyclohexane. In 1990, over 90 % of the global output of adipic acid was produced using this route.[2]

In spite of this, the conversion of cyclohexane oxidation is characteristically low, reaching 5 % conversion and maximum selectivities of 85 % of the desired products.[3] The recovery of downstream chemicals for recycling are usually carried out by distillation, where knowledge of the relative volatilities of cyclohexane + cyclohexanol and cyclohexane + cyclohexanone are vital. This work focuses on the measurement of vapor−liquid equilibria (VLE) data for cyclohexane (1) + cyclohexanone (2). In this study, new isothermal VLE data for cyclohexane + cyclohexanone are presented at temperatures of (423, 444, 464, and 484) K. Bibliographic studies have confirmed that previous experimental VLE work on this system was carried out at temperatures up to only 433 K.[4−9] Susarev and Lyzlova measured the only ternary cyclohexane + cyclohexanol + cyclohexanone system at atmospheric pressure.[4]

The measured data are first treated using the Peng−Robinson[10] (PR) equation of state with the Mathias−Copeman[11] α function. The mixing rule employed herein is that of Wong−Sandler[12] (WS), involving the nonrandom two-liquid

(NRTL) Gibbs free energy model.[13] In view of the rapid rise of the theoretically sound statistical associating fluid theory (SAFT) models, we have tested the perturbed-chain[14] (PC) modification of the SAFT equation, including the dipolar contribution proposed by Jog and Chapman[15] (JC) and Jog et al.[16]

Experimental Section

Materials. Cyclohexane (C_6H_{12}, CAS number: 110-82-7) was supplied by Fluka. Cyclohexanone ($C_6H_{10}O$, CAS number: 108-94-1) was obtained from Sigma Aldrich. Both compounds have a certified mass fraction purity of > 0.998 as determined by GC. The compounds, both being liquids at room temperature, were carefully degassed prior to measurements using a vacuum pump.

Apparatus. The apparatus used in this work is based on a "static−analytic" method with liquid and vapor phase samplings. This apparatus is similar to that described by Valtz et al.[17]

The equilibrium cell is contained in a thermostatted liquid bath. Temperatures are measured thanks to two platinum resistance thermometer probes (Pt100) inserted inside the walls of the equilibrium cell. These Pt100 probes are calibrated against a 25 Ω reference probe (Tinsley Precision Instrument) calibrated by the Laboratoire National d'Essais (Paris) following the 1990 International Temperature Scale protocol.

Pressures are measured using a pressure transducer (Druck, type PTX611, range: (0 to 6) MPa). This pressure sensor was calibrated against a dead weight pressure balance (5202S model from Desgranges and Huot). Pressure and temperature data acquisitions are performed with a computer linked to a Hewlett-Packard unit (HP34970A). The uncertainties in this work, combining both the errors from calibration and repeatability of the measurements, are not higher than ± 0.06 K and ± 0.001 MPa.

The analytical work was carried out using a gas chromatograph (Varian model CP-3800) equipped with a thermal

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Table 1. Pure Component Parameters for Cyclohexane[14,18] (1) and Cyclohexanone[18] (2) in the PR-WS-NRTL and PC-SAFT-JC EoS

	cyclohexane	cyclohexanone
	PR-WS-NRTL	
T_c/K	553.8	653.0
P_c/MPa	4.080	4.000
c_1	0.68359	0.887073
c_2	−0.0887233	−0.598714
c_3	0.549514	1.20276
	PC-SAFT-JC	
m	2.5303	2.3837
σ/nm	0.38499	0.39908
ε_i/k/K	278.11	335.94
x_p	0	0.2098
μ/D	0	3.1
AAD_P/%	0.53	1.4
AAD_ρ/%	3.1	3.2
T_{range}/K	279 to 553	315 to 650

conductivity detector (TCD) connected to a data acquisition system using the Borwin version 1.5 software, from JMBS, France. The analytical packed column (Restek, France) is Apiezon L PAW (80/100 mesh, 2 m X 1/8 Silcosteel). The TCD was repeatedly calibrated by introducing known amounts of each pure compound through a syringe into the injector of the gas chromatograph. Taking into account the uncertainties due to calibrations and dispersions of analyses (five at least for each sample), the resulting uncertainties on vapor and liquid mole fractions are estimated to be less than ± 1.5 %.

Procedure. At room temperature, the equilibrium cell and its loading lines are evacuated down to 0.1 Pa. The cell is first loaded under a vacuum with liquid (about 5 cm³) corresponding to the heavier component. Equilibrium temperature is assumed to be reached when the two Pt100 probes give equivalent temperature values within their temperature uncertainties for at least 10 min. The first equilibrium condition is compared to values of pure component vapor pressures from literature.[18] The lighter component is thereafter introduced step by step, leading to successive equilibrium mixtures of increasing overall global composition. Equilibrium is assumed when the total pressure remains unchanged within ± 0.1 kPa during a period of 10 min under efficient stirring. The two-phase isothermal envelopes are described with about eight *P*, *x*, *y* points (liquid and vapor).

For each equilibrium condition, at least five samples of both vapor and liquid phases are withdrawn using the pneumatic ROLSI samplers,[19] with each measured sample analyzed to check for the measurement repeatability.

Correlations. Peng−Robinson. The aforementioned form of the Peng−Robinson equation (PR-WS-NRTL) contains four interaction parameters adjustable to experimental data. These parameters are distributed among the mixing (α, τ_{12}, τ_{21}) and combining rules (k_{12}). The nonrandomness parameter α within the NRTL model is temperature-independent and fixed at 0.3 in treating the data. The relevant model parameters are listed in Table 1, where constants c_1 to c_3 are obtained from the DIPPR database.[18]

PC-SAFT-JC. The pure component parameters are available for cyclohexane from Gross and Sadowski.[14] No parameter values were found for cyclohexanone. In this work, we treat cyclohexanone molecules as nonassociating chains with discrete dipolar segments, in accordance with the segment approach of Jog and Chapman.[15] The pure component parameters are then adjusted simultaneously to vapor pressures and liquid densities by optimizing the following objective function F,

$$F = \frac{100}{N}\left[\sum_1^N \frac{|P_{exp} - P_{cal}|}{P_{exp}} + \sum_1^N \frac{|\rho_{exp} - \rho_{cal}|}{\rho_{exp}} \right] \quad (1)$$

where N is the number of experimental points taken from the DIPPR database;[18] P the saturation pressure, ρ the saturated liquid density, with exp and cal dealing with the experimental and calculated properties, respectively. We impose two restrictions in the optimization to preserve the physical significance of the model. First, a constant dipole moment μ equal to the experimental value of 3.1 is used,[18] as cyclohexanone contains only a single polar site.[20] Second, we use a constant $m \cdot x_p$ product of 0.5, characteristic of the ketone homologous group for the Jog and Chapman term.[20] This leaves three adjustable pure component parameters, m, σ, and ε/k, which were optimized using eq 1 over a range of reduced temperatures between 0.48 and 0.99. The values for the relevant model parameters are listed in Table 1.

In this work, the PC-SAFT-JC is extended to mixtures by using the Berthelot−Lorentz combining rule, with a single adjustable interaction parameter k_{12}.

Data Treatment. The system temperature and pressure are chosen as independent variables in the data treatment, as these have the smallest experimental uncertainties. The following flash-type objective function is used:

$$F = \frac{100}{N}\left[\sum_1^N \left(\frac{x_{exp} - x_{cal}}{x_{exp}}\right)^2 + \sum_1^N \left(\frac{y_{exp} - y_{cal}}{y_{exp}}\right)^2 \right] \quad (2)$$

where N is the number of data points, x_{exp} and x_{cal} are respectively the measured and calculated liquid compositions, and y_{exp} and y_{cal} are respectively the measured and calculated vapor compositions. The quality of the fit of the data is assessed through two indicators, the average absolute deviation (AAD) and the bias:

$$AAD_U = \frac{100}{N} \sum \frac{|U_{exp} - U_{cal}|}{U_{exp}} \quad (3)$$

$$bias_U = \frac{100}{N} \sum \frac{U_{exp} - U_{cal}}{U_{exp}} \quad (4)$$

where U can be the dependent composition variables x and y, or any other calculated variables arising from an optimization procedure.

Discussion

The experimental isothermal *P*−*x*−*y* measurements for isotherms at (423, 444, 464, and 484) K are reported in Table 2 and presented in Figure 1. There are clear disagreements between our data and the only available literature data at 423 K, from Li et al.[9] The maximum relative errors are 5 % for x_1 and 4 % for y_1. We do note however that the apparatus presented by Li et al.[9] has reported similar errors when compared with other systems in existing literature.

While treating each isotherm individually, it was observed that, for both models, the binary interaction parameters were only weak to moderate functions of temperature. By treating each individual isotherm, it was found that values of the interaction parameters were scattered evenly about a mean value,

Table 2. Vapor−Liquid Equilibrium Pressures and Phase Compositions for the Cyclohexane (1) + Cyclohexanone (2) System at Various Temperatures

T = 423.44 K			T = 443.55 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.319	0.338	0.787	0.309	0.151	0.566
0.342	0.388	0.812	0.358	0.209	0.642
0.367	0.449	0.835	0.413	0.269	0.707
0.394	0.504	0.860	0.464	0.337	0.755
0.419	0.568	0.879	0.518	0.419	0.799
0.441	0.635	0.896	0.569	0.504	0.833
0.466	0.717	0.915	0.621	0.601	0.866
0.492	0.793	0.933	0.678	0.723	0.903
0.510	0.852	0.949	0.723	0.808	0.933
0.534	0.921	0.970	0.779	0.917	0.967

| T = 463.64 K			T = 483.67 K		
P/MPa	x_1	y_1	P/MPa	x_1	y_1
0.323	0.056	0.293	0.462	0.055	0.256
0.400	0.110	0.449	0.580	0.121	0.431
0.481	0.173	0.561	0.689	0.187	0.540
0.565	0.244	0.648	0.798	0.259	0.622
0.648	0.321	0.717	0.912	0.341	0.690
0.732	0.411	0.772	1.019	0.427	0.742
0.817	0.512	0.816	1.132	0.531	0.793
0.900	0.626	0.854	1.242	0.633	0.839
0.987	0.744	0.896	1.355	0.740	0.883
1.070	0.857	0.938	1.462	0.850	0.929

with standard deviations of 30 % or less from the mean. This suggested that the temperature dependency could possibly be abandoned and replaced with a single transferable value for each of the adjustable parameters presented. Any losses in accuracy were confirmed to be minimal. A maximum increase of 1.0 % and 0.3 % in the errors of the compositions, for the PR-WS-NRTL and the PC-SAFT-JC EoS, respectively, were introduced when a single interaction parameter was employed. The interaction parameters for the PR-WS-NRTL and the PC-SAFT-JC EoS are presented in Table 3. Interestingly, the same set of parameters obtained in this work is capable of giving qualitative representations even at significantly lower temperatures,[5] as shown in Figure 2. This is a noteworthy result for separation design purposes.

The performances of the two EoS are similar, although the PR-WS-NRTL EoS is arguably more effective in describing the liquid-phase behavior. This is apparent in its low AAD_x values, as indicated in Table 4. While the PC-SAFT-JC is equally
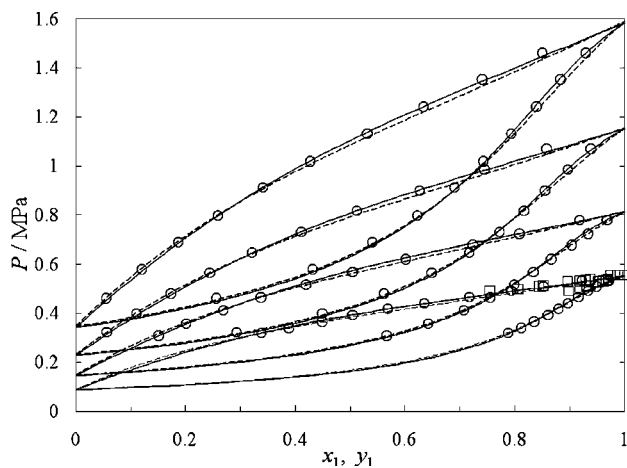
Figure 1. Experimental VLE data and modeling results for the cyclohexane (1) + cyclohexanone (2) system at, from bottom to top, (423, 444, 464, and 484) K. ○, our experimental data; □, Li et al.;[9] −, PR-WS-NRTL EoS; --, PC-SAFT-JC EoS.

Table 3. Global Binary Interaction Parameters for the Cyclohexane (1) + Cyclohexanone (2) System Fitted on Our Experimental VLE Data

model	α^a	τ_{12}/K	τ_{21}/K	k_{12}
PR-WS-NRTL	0.3	703.03	−136.16	0.09329
PC-SAFT-JC				0.01526

[a] This value is not adjusted.
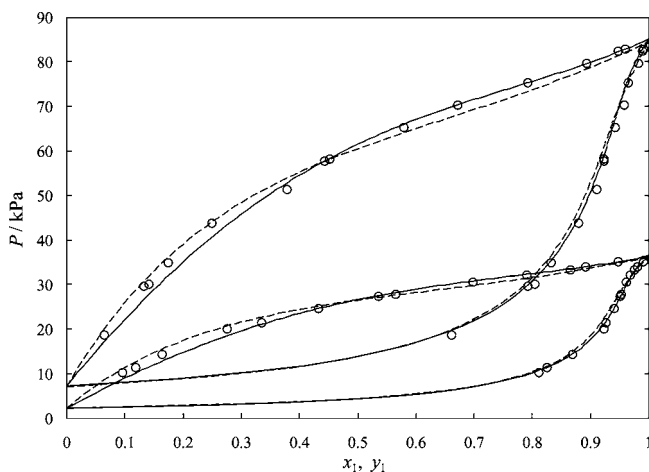
Figure 2. Experimental VLE data and modeling results for the cyclohexane (1) + cyclohexanone (2) system, at (323 and 348) K. ○, Boublik and Lu;[5] −, PR-WS-NRTL EoS; --, PC-SAFT-JC EoS.

Table 4. Average Absolute Deviation (AAD) and Bias Obtained in Fitting Experimental VLE Data[a]

	PR-WS-NRTL				PC-SAFT-JC			
T/K	AAD_x	AAD_y	$bias_x$	$bias_y$	AAD_x	AAD_y	$bias_x$	$bias_y$
423.44	0.9	0.3	−0.2	0.1	3.3	0.4	3.3	0.1
443.55	1.3	0.7	0.7	−0.1	2.3	0.3	−0.03	−0.1
463.64	2.5	1.9	−2.4	−1.7	2.4	1.3	1.4	1.1
483.67	2.1	1.8	−1.8	−1.7	2.3	1.4	1.1	1.4

[a] All values are reported as percentages.

applicable, the absence of any association phenomenon in the system may not provide further justification for its use. We do, however, need to stress that the PR-WS-NRTL is not without shortcomings. A plot of relative volatilities against composition (Figure 3) shows clearly that where data are not present for the 423 K isotherm at the cyclohexane-lean region, the curvature of the PR-WS-NRTL prediction becomes inconsistent compared to the other isotherms. This is due to the optimization of the interaction parameters on a localized region of the phase envelope. Parameters determined in this way represent closely the regressed data, but not necessarily the remaining parts of the phase diagram which would not have been featured in the calculation. This is further illustrated in Figure 4, where the relative volatilities for the low temperature isotherms, none of which were used in the data treatment, are predicted by both models. The predictions by the PR-WS-NRTL follow the same irregular shape as that of the 423 K isotherm, despite showing good agreements in the phase diagrams. Nevertheless, from a separation point of view, where a global representation of the phase equilibria is required, the PR-WS-NRTL EoS remains favorable.

Conclusion

In this work, new VLE data have been obtained for the cyclohexane (1) + cyclohexanone (2) binary system at four temperatures of (423, 444, 464, and 484) K. The measurements
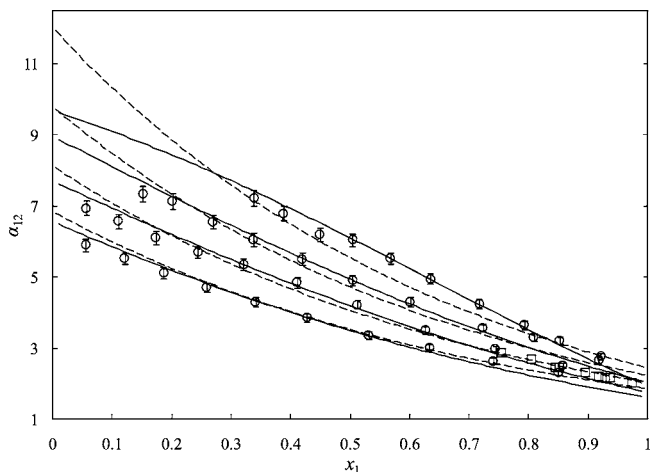
Figure 3. Experimental relative volatilities and modeling results for the cyclohexane (1) + cyclohexanone (2) system at, from top to bottom, (423, 444, 464, and 484) K. ○, our experimental data; □, data at 423 K from Li et al.;[9] —, PR-WS-NRTL EoS and; --, PC-SAFT-JC EoS. Error bars: ± 3 %.
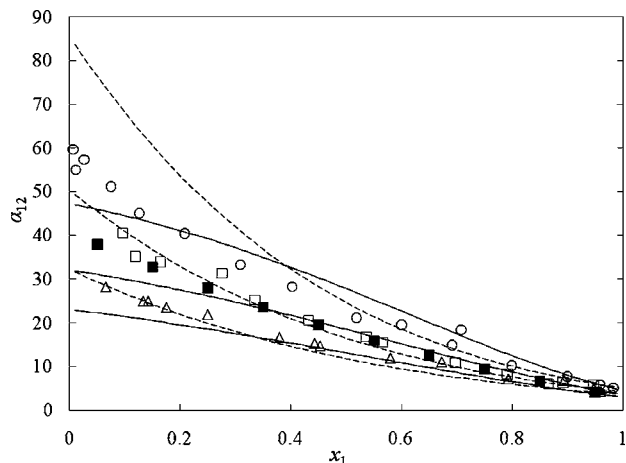

Figure 4. Experimental relative volatilities and modeling results for the cyclohexane (1) + cyclohexanone (2) system, at various temperatures. ○, 298 K;[6] □, 323 K from Boublik and Lou;[5] ■, 323 K from Oveckova et al;[7] ◇, 348 K;[5] —, PR-WS-NRTL EoS; --, PC-SAFT-JC EoS.

were carried out using an apparatus based on the "static−analytic" method with two ROLSI pneumatic capillary samplers, with the following uncertainties: ± 0.06 K and ± 1.0 kPa for temperatures and pressures, respectively, and ± 1.5 % for vapor and liquid mole fractions. Using a flash-type objective function, relevant binary interaction parameters were determined for two models: the PR-WS-NRTL and the PC-SAFT-JC EoS. Only a single set of parameters is required for each model to describe the entire temperature working range, that is, no temperature dependency of the parameters is required. As no association effects were present in the system, the PR-WS-NRTL EoS better represents the phase equilibria and should be the preferred model in process simulations.

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