



## “Vapor–liquid” equilibrium measurements and modeling for the cyclohexane + cyclohexanol binary system

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### ABSTRACT

To simulate cyclohexane oxidation reactors using a dynamic model linking kinetics, thermodynamics and hydrodynamics, the acquisition and modeling of vapor–liquid equilibria of the key components, under the process conditions, are essential. In this work, the vapor–liquid equilibria of the cyclohexane + cyclohexanol system were determined at temperatures 424, 444, 464 and 484 K. The measurements were carried out using an apparatus based on the “static-analytic” method, with two ROLSI™ pneumatic capillary samplers. The generated data are successfully correlated using two equations of state, the Peng–Robinson (PR) and the Perturbed-Chain Statistical Association Fluid Theory (PC-SAFT). A comparison of model performances reveals the former being better in data representation, while the latter has a broader applicability over larger range of temperatures.

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### 1. Introduction

The oxidation of cyclohexane is a significant process in the chemical industry, not only for the production of nylon intermediates: cyclohexanol and cyclohexanone, but also it has been the focus of catalysis research for several decades [1]. The conventional technology, using cobalt-based catalysts, is known to be low in efficiency, with a conversion of cyclohexane of less than 5%, and selectivities of cyclohexanol and cyclohexanone between 70% and 85% [2]. Careful control of reaction temperature, around 423 K, needs to be maintained to avoid the formation of byproducts [2]. Over the years, considerable research on catalysts have been carried out to balance the conversion and selectivity, without losing focus on environmental feasibility. Numerous possible catalysts have been reported in open literature, but with the exception of gold [3], most processes are nevertheless carried out at 400–430 K, and separated downstream.

For unit operations and process design, experimental equilibrium data at such high temperatures are necessary. In this study, the vapor–liquid equilibrium (VLE) data for the cyclohexane + cyclohexanol binary system are presented at 424, 444, 464 and 484 K. Careful bibliographic studies have shown that previous experimental VLE work on the cyclohexane + cyclohexanol system were carried out predominantly at low temperatures up to 433 K [4–7]. Susarev and Lyzlova measured the ternary system cyclohexane + cyclohexanol + cyclohexanone at atmospheric pressure [8]. At low temperatures and pressures, the system exhibits large relative volatilities, often exceeding 100 or more for cyclohexanol-rich regions. No data on liquid–liquid equilibrium have been reported for this system, while solid–liquid equilibrium has been reported for temperatures between 280 and 298 K [9]. Good VLE representations of the system have been achieved in the past using the NRTL local composition model [5,6], and treating the vapor as an ideal phase [6]. In this work, we have tested modeling of our new measured data using cubic and non-cubic equation of states (EoS). The former is based on the Peng–Robinson (PR) cubic equation [10], using the Wong–Sandler (WS) mixing rule [11], and the NRTL Gibbs free energy model [12]. The latter model is the Perturbed-Chain (PC) modification of the SAFT equation [13,14], which we have enhanced for this application through an additional dipolar contribution proposed by Jog and Chapman (JC) [15] and Jog et al. [16].

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## 2. Experimental

### 2.1. Materials

Cyclohexane (C<sub>6</sub>H<sub>12</sub>, CAS No.: 110-82-7) and cyclohexanol (C<sub>6</sub>H<sub>12</sub>O, CAS No.: 108-93-0) were both purchased from Fluka. Their GC certified purities are at least 99.8% and 99%, respectively. Both compounds were used after careful degassing.

### 2.2. 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 thermostated 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: 0–6 MPa). This pressure sensor is calibrated against a dead weight pressure balance (5202S model from Desgranges & 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 conductivity detector (TCD) connected to a data acquisition system using the BORWIN ver. 1.5 software, from JMBS, France. The analytical packed column (RESTEK, France) is Apiezon L PAW (80/100 mesh, 2 m × 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), resulting uncertainties on vapor and liquid mole fractions are estimated to be less than ±1.5%.

### 2.3. Experimental 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 cm<sup>3</sup>) corresponding to the heaviest 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 lighter component is thereafter introduced step by step, leading to successive equilibrium mixtures of increasing overall global compositions. 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 [18], with each measured sample analyzed to check for the measurement repeatability.

## 3. Modeling approach

For this work, a symmetric ( $\psi$ - $\psi$ ) approach is followed to calculate both liquid and vapor phase fugacities.

**Table 1**

Pure component parameters for cyclohexane (1) and cyclohexanol (2) in the PR-WS-NRTL and PC-SAFT-JC EoS [13,21].

	Cyclohexane	Cyclohexanol	
PR-WS-NRTL			
$T_c$ /K	553.8	650.0	
$P_c$ /MPa	4.080	4.260	
$c_1$	0.68359	0.857844	
$c_2$	-0.0887233	-0.341256	
$c_3$	0.549514	4.24572	
PC-SAFT-JC			
Bonding scheme	-	2B	3B
$m$	2.5303	2.5278	2.4714
$\sigma/\text{Å}$	3.8499	3.9355	3.9736
$\varepsilon_i/k$ /K	278.11	326.28	328.70
$\kappa^{ABi}$	0	0.0006735	0.0001798
$\varepsilon^{ABi}/k$ /K	0	3010.54	2679.97
$x_p$	0	0.2769	0.2832
$\mu/D$	0	1.7	1.7
AAD <sub>p</sub> /%	0.53	0.68	0.69
AAD <sub><math>\rho</math></sub> /%	3.12	0.74	0.75
$T_{\text{range}}$ /K	279–553	315–645	315–645

### 3.1. Peng–Robinson equation of state

One of the reasons for the success of the PR EoS to VLE mixtures, is its versatile nature allowing it to adapt to various systems through interchangeable mixing and combining rules. In this work, the Mathias–Copeman expression [19] corrects the alpha function in the attractive term, *a*. The EoS is coupled to the Wong–Sandler mixing rules for extension to mixtures, the latter of which is particular suitable to symmetric, polar–apolar systems [20]. In addition, the excess Gibbs energy  $g^E(T, x)$  function is based on the NRTL local composition model, as a consequence to its high success in literature. The relevant model parameters are listed in Table 1, where constants  $c_1$ – $c_3$  are obtained from the DIPPR correlation [21].

### 3.2. PC-SAFT-JC equation of state

The pure component parameters are available for cyclohexane from Gross and Sadowski [13]. No parameter values have been found for cyclohexanol. As with associating components, the first five of the pure parameters  $m$ ,  $\sigma$ ,  $\varepsilon/k$ ,  $\kappa^{ABi}$ ,  $\varepsilon^{ABi}/k$ ,  $x_p$  and  $\mu$ , are adjusted simultaneously to vapor pressures and liquid densities by optimizing the following objective function:

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

where *N* is the number of experimental points taken from the DIPPR correlation [21]; *P* the saturation pressure,  $\rho$  the saturated liquid density, with exp and cal dealing with the experimental and calculated properties, respectively. The optimization was carried over a 0.49–0.99 reduced temperature range. The dipole moment  $\mu$  is kept constant during the regression. In addition, we assume that cyclohexanol, having a similar dipole moment as aliphatic alcohols ranging from methanol to 1-decanol [22], will result in it having the same fixed  $m \cdot x_p$  product as the (R–C–OH) functional group, i.e. 0.7 [23].

We have modeled first the hydroxyl group using the 2B scheme of Huang and Radosz [24], having a single proton donor and a single proton acceptor. This is as suggested by Van Solms et al. based on steric hindrance [25]. Nevertheless, the 3B bonding (two donors and one acceptor) has also been tested to provide good pure component correlation. Since it is not possible to determine the correct bonding scheme without spectroscopic data, we have tested both schemes on our mixture data. Both bonding schemes yield similar results, with similar binary interaction parameters (BIP) upon

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