

# Isobaric vapor–liquid and vapor–liquid–liquid equilibrium data for the system water + ethanol + cyclohexane

V. Gomis\*, A. Font, R. Pedraza, M.D. Saquete

*Departamento de Ingeniería Química, Universidad de Alicante, Apartado 99,  
E-03080, Alicante, Spain*

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## Abstract

Isobaric vapor–liquid (VLE) and vapor–liquid–liquid equilibria (VLLE) were measured for the ternary system water + ethanol + cyclohexane at 101.3 kPa. The experimental determination was carried out in a dynamic equilibrium still with circulation of both the vapor and liquid phases, equipped with an ultrasonic homogenizer. The experimental data demonstrated the existence of a ternary heterogeneous azeotrope at 335.6 K with a composition of 0.188, 0.292, 0.520 mole fraction of water, ethanol and cyclohexane, respectively. The experimental data were compared with those obtained using UNIFAC and NRTL models with parameters taken from literature.

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## 1. Introduction

For many years, the traditional process to obtain pure ethanol from a water + ethanol mixture has been heterogeneous azeotropic distillation using benzene as the entrainer. In the last few years, because of the carcinogenic effect of benzene, this entrainer has been substituted by other compounds. Currently, cyclohexane is one of the most used entrainers to carry out this separation and there are numerous plants around the world using this compound.

Different researchers have paid attention to the study of the ternary system water + ethanol + cyclohexane and several papers about the vapor–liquid–liquid equilibrium (VLLE) and liquid–liquid equilibrium (LLE) of this system have been published:

- Karrer and Gaube [1] and Connemann et al. [2] presented isothermal vapor–liquid equilibrium (VLE) data at temperatures between 333 and 338 K and pressures between

44 and 92 kPa and LLE data between 303 and 335 K and atmospheric pressure,

- Cui et al. [3] and Antosik et al. [4] worked isothermally at different temperatures in the range 308–340 K and pressures in the range 30–102 kPa,
- and finally Gramajo et al. [5] and Plackov and Stern [6] on LLE at 303 and 298 K, respectively.

However, it is not possible to find a complete experimental study of the isobaric VLLE and VLE equilibrium of the system water + ethanol + cyclohexane at atmospheric pressure in literature. Usually, the equilibrium data for this system, which are necessary for the design and simulation of the heterogeneous azeotropic distillation process are substituted by predictions of these data using activity coefficient models as group contribution models like UNIFAC or by the UNIQUAC or NRTL model with parameters based on the correlation of binary VLE and LLE data.

The objective of this paper is to present the vapor–liquid equilibrium and vapor–liquid–liquid equilibrium for the system water + ethanol + cyclohexane at a constant pressure of 101.3 kPa. The results obtained will permit the reliability of the estimations with different models to be analyzed.

\* Corresponding author. Tel.: +34 965 90 38 67; fax: +34 965 90 38 26.  
E-mail address: [vgomis@ua.es](mailto:vgomis@ua.es) (V. Gomis).

## 2. Experimental

### 2.1. Chemicals

All chemicals were used as supplied after gas chromatography failed to show measurable amounts of organic impurities. The nominal purities of ethanol and cyclohexane obtained from Merck were 99.8 and 99.5 mass%. For the 1-propanol, which was used as the internal standard for chromatographic analysis, the nominal purity was 99.5 mass%. The Karl Fischer titration method was used to determine the water content in mass% for cyclohexane, ethanol and 1-propanol that is 0.004, 0.04, and 0.07, respectively. Ultrapure water was purified using a Milli Q-Plus system.

### 2.2. Apparatus and procedures

The equipment used for the determination of VLE data was a commercial unit (Labodest model 602) built in Germany by Fischer Labor und Verfahrenstechnik, that was modified by Gomis et al. [7] by coupling an ultrasonic homogenizer to the boiling flask. The still allows good mixing of the vapor and liquid phases and good separation of the phases once they reach equilibrium. The ultrasound system ensures a good dispersion of partly miscible liquid phases, and consequently this equipment works perfectly for the determination of VLE data. For VLE determinations, the same equipment without modifications was used.

The temperature in the still was measured with a Pt-100 thermometer connected to an ERTCO-Hart, with an uncertainty of 0.006 °C according to the certificate of calibration (on the ITS 90 [8]). A Fischer M101 phase equilibrium control system was used to measure and control the pressure and the heating power. The pressure in the still was 101.3 kPa, measured and controlled with an accuracy of 0.1 kPa. To guarantee the correct operation of the equipment, the boiling points of pure water and the binary azeotrope water–methyl ethyl ketone (MEK) were measured and compared with the accepted value.

All analytical work was carried out by gas chromatography on a Shimadzu GC-14B coupled with a personal computer by using the Shimadzu CLASS-VP Chromatography Data System. Separation of the components was obtained on a 2 m × 3 mm column packed with Porapak Q 80/100. The oven temperature was 210 °C, and the helium flow rate was 43 mL min<sup>-1</sup>.

Sampling was carried out using different methods depending on the phase treated:

- The sampling of the gaseous phase was carried out using a UW Type, 6-port valve from Valco Instruments Co., which injected the samples automatically into the GC.
- For the sampling of the liquid phase in the heterogeneous region, a small amount of the liquid coming from the separation chamber of the instrument was diverted to a tube using a solenoid valve. In this tube, the dispersed

liquid phases enter and separate into two layers at their bubble point, since the tube is placed in a thermostatic bath at the boiling point temperature of the mixture. A sample of each layer was taken and placed in a vial with a small amount of an internal standard.

- Liquid samples in the homogeneous region were withdrawn with a syringe of the liquid coming from the separator chamber and put into a vial.

To obtain quantitative results in the analysis of the liquid phases, an internal standard method was used. For this reason, 1-propanol (which is completely miscible in water, ethanol, and cyclohexane) was also added to the sample vials. Furthermore, the addition of the standard prevents phase-separation effects when changing the temperature after the separation of the phases. A further description of the sample take off is given in a previous paper [7].

Depending on the composition of the samples, detection was carried out by two different techniques: thermal conductivity detector (TCD) for organic-rich samples (analyzing water, ethanol, and cyclohexane) and flame ionization detector (FID) for water-rich samples (analyzing ethanol and cyclohexane). The temperature of the detector was 220 °C, and the current for the TCD was 100 mA.

The accuracy of the mole fraction measurements was estimated at ±0.002 for all the compounds except for the water in the liquid organic phase and cyclohexane in the aqueous phase, where the accuracy was approximately ±0.005.

## 3. Results

The experimental VLE data of the ternary system studied are summarized in Table 1. VLE data for the homogeneous region are shown in Table 2. In these tables, the bubble point ( $t_b$ , K) and the composition (mole fraction) of the liquid phases ( $x_i$ ) and the vapor phase ( $y_i$ ) are presented.

The experimental ternary VLE and VLE data were tested by the point-to-point L/W Wisniak [9] consistency test and were found to be thermodynamically consistent. All the values of L/W are between 0.98 and 1.00. Vapor pressures were calculated with the Antoine equation, whose parameters  $A_i$ ,  $B_i$ , and  $C_i$  for water, ethanol, and cyclohexane were taken from literature [10] and are given in Table 3. This test does not reveal any substantial inconsistency in the data.

Fig. 1 represents some of the VLE data and includes the nonisothermal binodal curve and the vapor line. This figure shows the presence of a ternary azeotrope in the heterogeneous region. The points of the vapor line corresponding to the liquid–liquid equilibrium lines 1–9 are under the tie line. However, the point corresponding to line 10 is above the tie line. Therefore, there is a point between lines 9 and 10 where the composition of the vapor coincides with that of a liquid heterogeneous mixture. The composition of the ternary azeotrope determined by numerical interpolation is  $x_1 = 0.188$ ,  $x_2 = 0.292$ , and  $x_3 = 0.520$  mole fraction

Table 1  
Vapor–liquid–liquid equilibrium data (mole fraction) for the ternary system water (1) + ethanol (2) + cyclohexane (3) at 101.3 kPa

	Organic phase			Aqueous phase			Vapor phase			$t_b$ (K)
	$x_1$	$x_2$	$x_3$	$x_1$	$x_2$	$x_3$	$y_1$	$y_2$	$y_3$	
1	0.002	0.011	0.986	0.931	0.068	0.0005	0.258	0.162	0.579	338.20
2	0.004	0.018	0.978	0.900	0.099	0.001	0.243	0.193	0.564	337.46
3	0.004	0.031	0.965	0.835	0.164	0.001	0.225	0.232	0.543	336.55
4	0.004	0.035	0.961	0.806	0.193	0.001	0.224	0.240	0.535	336.34
5	0.005	0.051	0.943	0.724	0.272	0.004	0.208	0.256	0.535	335.97
6	0.011	0.076	0.913	0.625	0.363	0.012	0.203	0.272	0.526	335.84
7	0.013	0.094	0.893	0.557	0.425	0.018	0.193	0.280	0.527	335.70
8	0.013	0.105	0.882	0.509	0.463	0.028	0.190	0.286	0.524	335.63
9	0.017	0.127	0.856	0.450	0.508	0.042	0.189	0.290	0.521	335.55
10	0.020	0.151	0.829	0.386	0.555	0.059	0.184	0.298	0.519	335.54
11	0.020	0.157	0.823	0.357	0.569	0.074	0.181	0.301	0.519	335.54

Table 2  
Vapor–liquid equilibrium data (mole fraction) for the ternary system water (1) + ethanol (2) + cyclohexane (3) at 101.3 kPa

Liquid phase			Vapor phase			$t_b$ (K)
$x_1$	$x_2$	$x_3$	$y_1$	$y_2$	$y_3$	
0.053	0.915	0.032	0.050	0.752	0.198	346.06
0.111	0.851	0.037	0.111	0.776	0.113	345.95
0.156	0.813	0.031	0.127	0.650	0.224	344.77
0.204	0.770	0.026	0.163	0.649	0.188	344.67
0.258	0.724	0.018	0.185	0.631	0.185	344.93
0.301	0.683	0.016	0.209	0.609	0.181	344.83
0.357	0.623	0.019	0.194	0.525	0.282	344.00
0.075	0.819	0.106	0.035	0.556	0.409	340.98
0.113	0.785	0.101	0.089	0.498	0.413	340.24
0.162	0.738	0.100	0.106	0.446	0.448	339.47
0.205	0.672	0.124	0.119	0.432	0.449	338.76
0.263	0.662	0.076	0.127	0.355	0.518	337.81
0.066	0.741	0.192	0.061	0.456	0.483	338.25
0.116	0.700	0.184	0.091	0.412	0.497	337.37
0.155	0.655	0.190	0.132	0.480	0.389	336.63
0.063	0.715	0.223	0.061	0.448	0.491	337.80
0.111	0.647	0.242	0.090	0.383	0.527	337.00
0.062	0.673	0.265	0.064	0.429	0.506	337.43
0.227	0.590	0.183	0.166	0.320	0.514	335.78
0.164	0.489	0.347	0.168	0.317	0.515	335.60
0.156	0.470	0.374	0.168	0.318	0.514	335.56
0.134	0.567	0.299	0.144	0.348	0.508	335.93
0.120	0.593	0.287	0.133	0.362	0.505	336.28
0.161	0.589	0.249	0.149	0.347	0.505	336.04
0.004	0.010	0.986	0.258	0.129	0.614	339.37
0.005	0.031	0.965	0.220	0.235	0.546	336.65
0.002	0.004	0.994	0.319	0.130	0.551	339.64

Table 3  
Antoine equation parameters<sup>a</sup> of the pure substances

Compound	A	B	C	Temperature range (°C)
Water	8.07131	1730.630	233.426	+1/+100
Ethanol	8.11220	1592.864	226.184	+20/+93
Cyclohexane	6.85146	1206.470	223.136	+7/+81

<sup>a</sup> Antoine equation:  $\log(P) = A - B/[t + C]$ , with  $P$  (mm Hg) and  $t$  (°C).

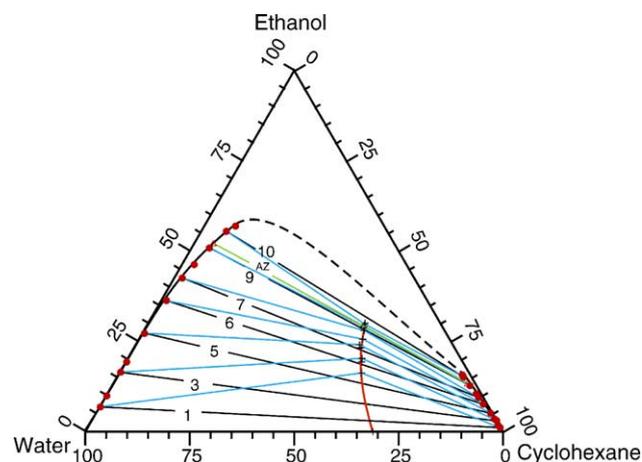


Fig. 1. VLE diagram for the ternary system water (1) + ethanol (2) + cyclohexane (3) at 101.3 kPa: (●) liquid phase; (+) vapor phase, (Δ) azeotrope.

of water (1), ethanol (2), and cyclohexane (3), respectively, and the temperature is 335.54 K. This composition is similar to that reported by Pivovarov et al. (azeotropic composition:  $x_1 = 0.176$ ,  $x_2 = 0.302$ ,  $x_3 = 0.522$ ,  $t = 335.7$  K) and compiled by Gmehling et al. [11]. The composition of the two liquid phases in equilibrium is  $x_1 = 0.433$ ,  $x_2 = 0.521$ , and  $x_3 = 0.046$  in the aqueous phase, and  $x_1 = 0.018$ ,  $x_2 = 0.133$ , and  $x_3 = 0.849$  in the organic-rich phase.

In Fig. 2, the VLE data of liquid mixtures of the homogeneous region have been represented. The figure shows that the equilibrium lines drawn between the liquid and the vapor tend towards the ternary azeotrope. Similarly, several homogeneous points have vapors in equilibrium that belong to the heterogeneous region. These vapors split into two liquid phases after being condensed.

#### 4. Discussion and conclusion

The VLE and VLLE of the ternary system water + ethanol + cyclohexane have been used extensively to describe and solve problems related to the design, analysis and control

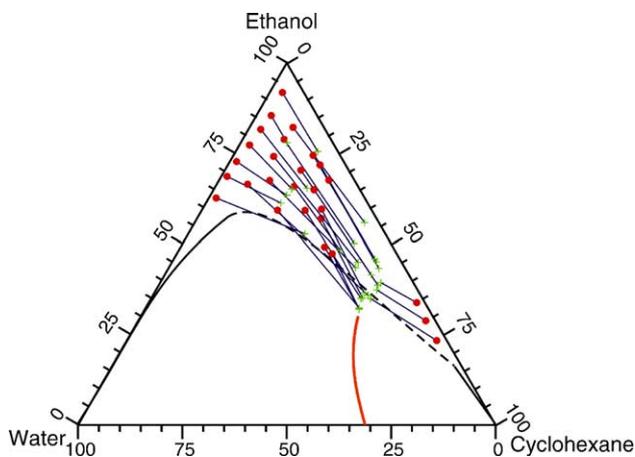


Fig. 2. VLE diagram for the ternary system water (1)+ethanol (2)+cyclohexane (3) at 101.3 kPa: (●) liquid phase; (+) vapor phase.

of separation sequences involving heterogeneous azeotropic distillation towers: residue curve maps and distillation lines [12], method for the synthesis and design of separation sequences [13], dynamic analysis of heterogeneous towers [14] or the analysis of the existence of multiple steady states in heterogeneous azeotropic distillation [15].

However, the authors of these works had to predict the equilibrium data using activity coefficient models such as UNIFAC, UNIQUAC or NRTL. The experimental VLE and VLLE data obtained in this work allow the reliability of the estimations with different models to be analyzed, as can be seen in Fig. 3. This figure shows the comparison between experimental and calculated data with UNIFAC (original)

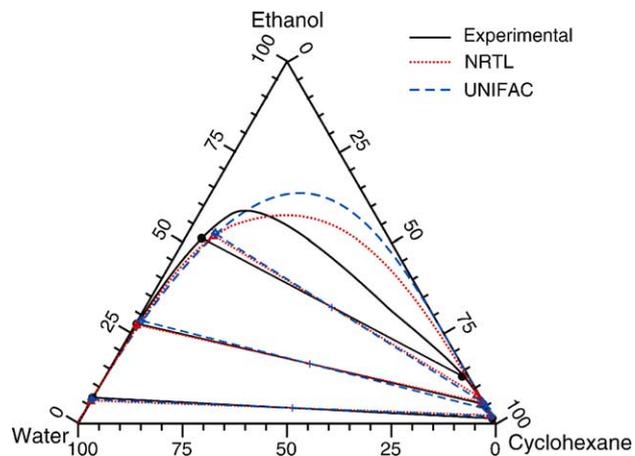


Fig. 3. Comparison between the experimental nonisothermal binodal curve and those determined by the UNIFAC and NRTL models.

and NRTL using binary parameters taken from literature [16]. These VLLE and VLE data have been obtained using the simulation program CHEMCAD V [17]. The experimental VLE data do not differ significantly from that predicted by these models. In fact, the quadratic mean deviation between experimental and calculated mole fraction vapor compositions for all the components is 0.003, while for the temperature it is about 1 °C. However, in both cases it can be observed that the experimental heterogeneous region is smaller than the calculated ones. Consequently, some experimental homogeneous VLE points are included inside of the predicted heterogeneous regions.

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### References

- [1] L. Karrer, J. Gaube, *Fluid Phase Equilib.* 42 (1988) 195–207.
- [2] M. Connemann, J. Gaube, L. Karrer, A. Pfennig, U. Reuter, *Fluid Phase Equilib.* 60 (1990) 99–118.
- [3] Z. Cui, R. Qian, Z. Yun, M. Shi, *J. Chem. Eng. Data* 49 (2004) 212–217.
- [4] M. Antosik, M. Galka, S. Malanowski, *J. Chem. Eng. Data* 49 (2004) 7–10.
- [5] M.B. Gramajo, C.M. Bonatti, H.N. Sólamo, *J. Chem. Thermodyn.* 34 (2003) 2055–2065.
- [6] D. Plackov, I. Stern, *Fluid Phase Equilib.* 71 (1992) 189–202.
- [7] V. Gomis, F. Ruiz, J.C. Asensi, *Fluid Phase Equilib.* 172 (2000) 245–259.
- [8] B.W. Mangum, G.T. Furukawa, U.S. Department of Commerce, National Institute of Standards and Technology, Springfield, 1990.
- [9] J. Wisniak, *Ind. Eng. Chem. Res.* 32 (1993) 1531–1533.
- [10] C.L. Yaws, *Chemical Properties Handbook*, McGraw Hill, New York, 1999.
- [11] J. Gmehling, J. Menken, J. Krafczyk, K. Fischer, *Azeotropic Data*, VCH, Weinheim, 1994.
- [12] W.E. de Villiers, R.N. French, G.J. Koplos, *CEP Magazine* (2002) 66–71.
- [13] I.A. Furzer, *Ind. Eng. Chem. Process Des. Dev.* 23 (1984) 387–391.
- [14] D. Müller, W. Marquardt, *Ind. Eng. Chem. Res.* 36 (1997) 5410–5418.
- [15] J.U. Repke, G. Wozny, *Chem. Eng. Technol.* 25 (2002) 513–519.
- [16] P.A.M. Springer, R. Krishna, *Int. Commun. Heat Mass Transfer* 28 (2001) 347–356.
- [17] CHEMCAD V, Process Flow Sheet Simulator, Chemstations Inc, Houston, 2002.