

MEASUREMENT AND CORRELATION OF ISOBARIC VAPOR-LIQUID EQUILIBRIUM FOR THE BINARY SYSTEM OF CYCLOPENTANE AND TETRAHYDROFURAN

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Abstract - Isobaric vapor-liquid equilibrium (VLE) data for the cyclopentane and tetrahydrofuran (THF) system were measured at 101.3 kPa by using an equilibrium still. Thermodynamic consistency of the experimental data was confirmed by means of the Herington method. The experimental data were correlated and calculated by the Margules, Van Laar and Wilson activity-coefficient models, respectively. The Wilson and Van Laar activity-coefficient models are better than the Margules activity-coefficient model based on the average absolute deviations of temperature and the vapor-phase composition. For the Wilson and Van Laar activity-coefficient models the average absolute deviations between the experimental and the calculated values were 0.24 K and 0.23 K for the boiling point, and 0.0040 for vapor-phase composition, respectively. These agree well with the experimental data. Therefore, it was shown that the Wilson and Van Laar activity-coefficient models satisfactorily correlate the experimental results of the cyclopentane and tetrahydrofuran system.

Keywords: Cyclopentane; Tetrahydrofuran; Vapor-liquid equilibrium.

INTRODUCTION

In industrial production processes, solvent recovery is one of the problems that needs to be solved urgently due to environmental protection and production costs (Slater *et al.*, 2012). Currently, distillation is extensively used for the separation of a great number of liquid mixtures and clearly dominates separation processes, accounting for more applications than all of the other solvent separation processes such as extraction, adsorption, filtration and membrane technologies (Humphrey, 1995; Ramzan *et al.*, 2008; Mohsen-Nia and Memarzadeh, 2010). For the correct design of separation processes, it is essential to obtain accurate and quantitative informa-

tion on the phase equilibrium of binary or multicomponent mixtures (Aucejo *et al.*, 2006; Ovejero *et al.*, 2007).

Cyclopentane and tetrahydrofuran are solvents employed in many processes. Several processes in chemical industries produce mixtures of cyclopentane and tetrahydrofuran, so vapor-liquid equilibrium data of cyclopentane and tetrahydrofuran are indispensable for separation of them. However, so far, no relevant isobaric VLE data are available for cyclopentane and tetrahydrofuran in the open literature. In this paper, we present isobaric vapor-liquid equilibrium measurements for the mixture of cyclopentane and tetrahydrofuran at 101.3 kPa. The vapor-liquid equilibrium data have been correlated

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with the Margules (Margules, 1895), Van Laar (Van Laar, 1910) and Wilson (Wilson, 1964) activity-coefficient models.

MATERIALS AND METHODS

Materials

Chemicals used: all the reagents were analytical purity grade. Cyclopentane was purchased from Tianjin University Ke Wei Company and tetrahydrofuran was purchased from Tianjin Chemical Reagent Third Plant. The purity of the chemicals was checked by gas chromatography (>0.997 mass %), so no further purification was needed. The water content in the chemicals was determined using a Karl-Fischer titration method (<0.03 mass %). The purity of the chemicals was further confirmed by comparing the experimental densities, the refractive indexes and the normal boiling points with those reported (Ma, 2005; Cheng, 2007), as listed in Table 1. The accuracies in

density, and refractive index measurements are $\pm 2.0 \times 10^{-5}$ g/cm³ and ± 0.00001 , respectively.

Apparatus and Procedure

An equilibrium still, the same as in the previous work (Li and Bai, 2012; Li *et al.*, 2013), was employed to measure isobaric VLE data at 101.3 kPa and is shown in Figure 1. The temperature was controlled by a small voltage adjuster. A mercury thermometer calibrated by Shanghai Metrology Institution was used for temperature measurement within an accuracy of ± 0.01 °C.

The temperature uncertainties in this work, combining both the errors from calibration and repeatability of the measurements, are not higher than ± 0.06 K. The actual atmospheric pressure was measured by a mercury barometer with an accuracy of ± 0.1 kPa. Since the atmospheric pressure changed slightly during the experiments, the boiling temperatures at the actual pressure were corrected to 101.3 kPa according to the literature (Hiaki and Kawai, 1999).

Table 1: Density ρ , normal boiling point T_b , and refractive index n_D of the pure components

Component	ρ (293.15K)/(g·cm ⁻³)		T_b (101.3KPa)/°C		n_D (293.15K)	
	Experimental	Literature ^a	Experimental	Literature ^b	Experimental	Literature ^a
Cyclopentane	0.74497	0.74536	49.15	49.26	1.40613	1.40645
tetrahydrofuran	0.88975	0.8892	66.47	67	1.40706	1.4073

^aTaken from Ref. (Cheng, 2007).

^bTaken from Ref. (Ma, 2005).

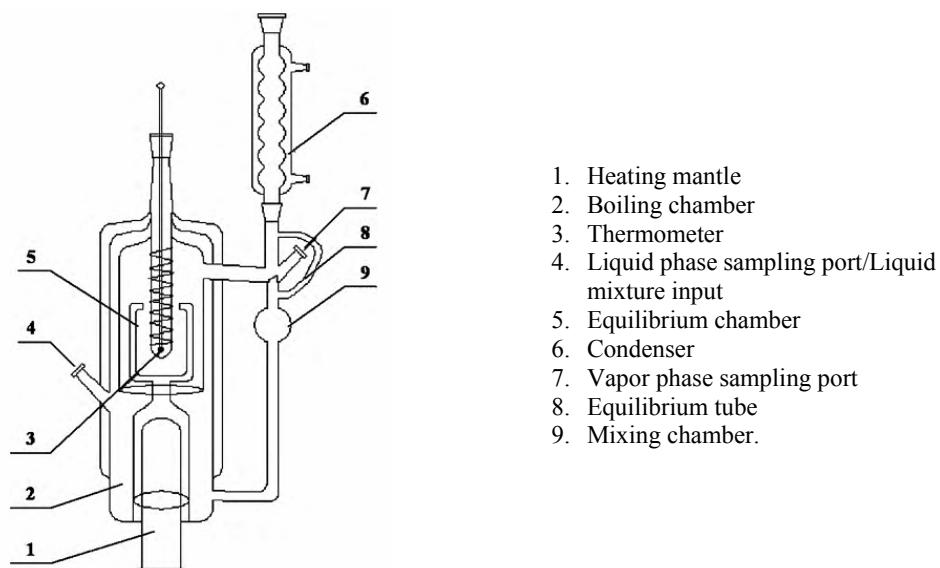


Figure 1: Diagrammatic sketch of the equilibrium still.

The analytical work was carried out using a gas chromatograph (SP-6890) equipped with a thermal conductivity detector (TCD) connected to a data acquisition system. 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 the analyses (at least five for each sample), the resulting uncertainties in vapor and liquid mole fractions are estimated to be 0.0001 in mole fraction.

The still was operated at constant pressure until equilibrium was reached. When constant temperature and pressure were obtained for 30 min or longer, it was assumed that the vapor and liquid phases had achieved balance. To verify the equilibrium conditions, we analyzed the vapor until the variation of the mole fraction of the vapor phase composition was less than 0.0001. Then, samples of liquid and condensate were taken for analysis.

Verification of the Apparatus

In order to verify the reliability of the device, the atmospheric VLE data of the cyclohexane + ethanol binary system were measured by this device and compared with literature data (Yuan *et al.*, 1963) as shown in Figure 2. As can be seen from Figure 2, the measured VLE data were in good agreement with the literature data, so the device can be used to measure the VLE of the binary system cyclopentane and tetrahydrofuran at 101.3 kPa.

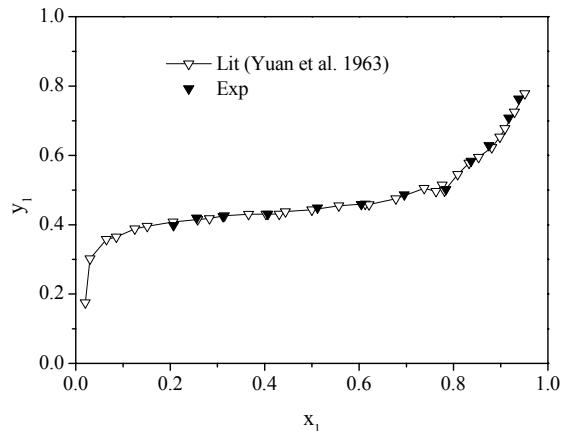


Figure 2: Isobaric VLE diagram for the binary system of ethanol(1) + cyclohexane(2) at 101.3 kPa.

RESULTS AND DISCUSSION

Experimental Data

Table 2 shows the values of the quantities that characterize the equilibrium states of the liquid and vapor phases, x_i , y_i and T at a pressure of $p = 101.3$ kPa. The corresponding phase diagram is shown in Figure 3 and Figure 4. As can be seen from Figure 3, there is no intercrossing point between the bubble point curve and the dew point curve over the entire composition range, which reveals that no azeotrope exists in the cyclopentane + THF binary system.

Table 2: VLE data and correlation results for the cyclopentane+THF system at 101.3 kPa.

x_1	y_1	T / K	Margules		Van Laar		Wilson	
			$ \Delta T $	$ \Delta y $	$ \Delta T $	$ \Delta y $	$ \Delta T $	$ \Delta y $
1	1	322.30	0.07	0	0.07	0	0.07	0
0.9493	0.9598	322.71	0.08	0.0014	0.04	0.0017	0.04	0.0017
0.9065	0.9296	323.05	0.25	0.0043	0.08	0.0007	0.08	0.0007
0.8325	0.8776	323.78	0.33	0.0061	0.11	0.0051	0.11	0.0051
0.7944	0.8408	324.19	0.42	0.0041	0.20	0.0027	0.21	0.0026
0.7382	0.8008	324.73	0.46	0.0056	0.25	0.0003	0.26	0.0004
0.6858	0.7638	325.06	0.29	0.0070	0.10	0.0035	0.11	0.0035
0.6446	0.7344	325.58	0.39	0.0085	0.22	0.0058	0.23	0.0058
0.6036	0.7025	325.91	0.29	0.0122	0.15	0.0055	0.15	0.0055
0.5659	0.6727	326.18	0.15	0.0158	0.03	0.0050	0.03	0.0049
0.5113	0.6347	326.55	0.12	0.0147	0.20	0.0097	0.20	0.0095
0.4635	0.5932	327.04	0.23	0.0205	0.27	0.0060	0.27	0.0058
0.4033	0.5439	327.48	0.61	0.0220	0.60	0.0054	0.59	0.0051
0.3653	0.5119	328.26	0.40	0.0221	0.34	0.0049	0.33	0.0046
0.3024	0.4571	329.32	0.39	0.0192	0.22	0.0044	0.22	0.0041
0.2492	0.3996	330.21	0.52	0.0220	0.24	0.0040	0.24	0.0042
0.1979	0.3419	331.08	0.81	0.0199	0.39	0.0097	0.40	0.0097
0.1469	0.2888	332.45	0.80	0.0041	0.24	0.0036	0.25	0.0036
0.0652	0.1697	335.02	1.03	0.0163	0.40	0.0029	0.40	0.0031
0	0	339.62	0.51	0	0.51	0	0.51	0

$$^a |\Delta y| = |y^{\text{exp}} - y^{\text{cal}}|, \quad ^b |\Delta T| = |T^{\text{exp}} - T^{\text{cal}}|.$$

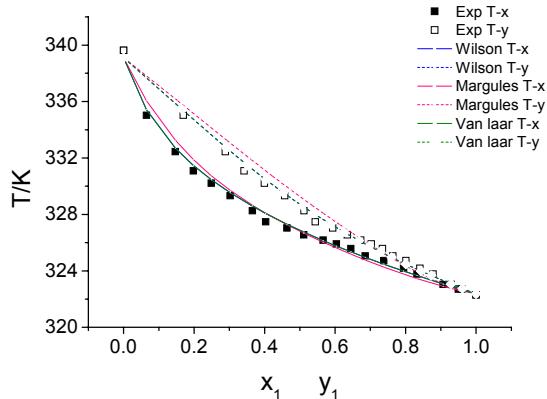


Figure 3: Vapor-liquid equilibrium phase diagram for the cyclopentane+THF system at 101.3 kPa

Thermodynamic Consistency Verification

Thermodynamic consistency of the experimental results was checked by means of two tests: (1) the point-to-point van Ness method (Van Ness *et al.*, 1973) and (2) the Herington method (Herington, 1951).

The thermodynamic consistency of the experimental results was checked using the van Ness method, described by Fredenslund *et al.* (1977) using a third-order Legendre polynomial for the excess free energies. According to this test, experimental data are considered to be consistent if the average deviation in y (Δy) is smaller than 0.01. All the experimental data are consistent, as one can see in Table 3.

Table 3: Results of the thermodynamic consistency test. Average deviations of ΔP and Δy .

System	Δy^a	ΔP^b (kPa)
cyclopentane+ THF	0.0063	0.43

^aMean absolute deviation in the vapor phase composition.

^bMean absolute deviation in pressure.

Experimental errors may cause deviations of the activity coefficients obtained from the experimental VLE data via the Gibbs-Duhem equation (Smith *et al.*, 2001). Therefore, the Herington method was used to check the thermodynamic consistency.

$$D = \frac{|I|}{\sum} \times 100, J = 150 \times \frac{\theta}{T_{\min}}$$

where $I = \int_0^1 \ln(\gamma_1 / \gamma_2) dx_1, \sum = \int_0^1 |\ln(\gamma_1 / \gamma_2)| dx_1$.

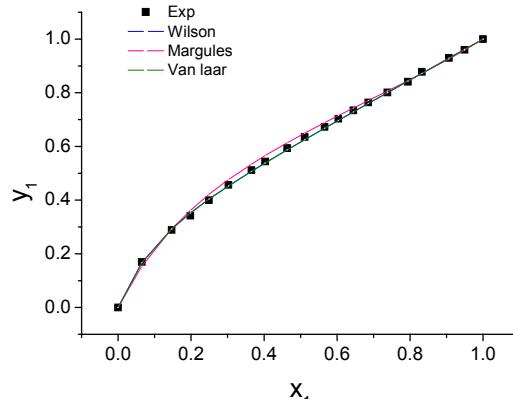


Figure 4: $y - x$ diagram for the cyclopentane+THF system at 101.3 kPa

$\theta = T_{\max} - T_{\min}$, T_{\max} and T_{\min} were the highest and the lowest boiling point in the system, respectively, in K. According to the Herington method, the experimental data are consistent if Herington's ($D - J$) was less than 10. The calculation result was that $|D - J| = 4.81 < 10$, which indicated that all experimental data were in accordance with thermodynamic consistency.

Correlation of the Binary Vapor-Liquid Equilibrium

The activity coefficients were calculated from the equation

$$\gamma_i = \frac{y_i \phi_i p}{x_i \phi_i^s p_i^s} \quad (1)$$

At low pressure, the assumption of ideal behavior is adopted for the vapor (Chen, *et al.* 1993). The fugacity coefficients ϕ_i and ϕ_i^s are equal to unity. Therefore, Eq. (1) can be simplified to

$$p y_i = p_i^s \gamma_i x_i \quad (2)$$

where γ_i is the activity coefficient of component i . p , x_i and y_i are total pressure of the system and the liquid and vapor phase mole fractions in the equilibrium. ϕ_i , ϕ_i^s are the fugacity coefficients of component i in the vapor mixtures and at saturation, respectively. p_i^s is the saturated vapor pressure of pure component i at the system temperature, calculated with the Antoine equation

$$\log p_i^{sat}(kPa) = A - \frac{B}{T(K) + C} \quad (3)$$

where A , B , and C are Antoine constants and T is the temperature in Kelvin. The Antoine constants for cyclopentane and THF were obtained from the literature (Ma, 2005), and are presented in Table 4.

Table 4: Basic properties of pure substances.

Component	Antoine constants			Temperature range/T
	A	B	C	
THF	6.12023	1202.394	-46.883	296-373
cyclopentane	6.06783	1152.57	-38.64	236-348

Because the experiment was carried out at 101.3 kPa, the vapor phase could be regarded as an ideal gas, and the boiling point difference between cyclopentane and THF was not more than 30 K, so the parameters of the activity-coefficient models could be regarded as constant values. In order to find parameters of the equations, the activity coefficients were correlated with the Margules, Van Laar and Wilson equations. Estimation of the parameters of the equations was based on minimization of the following objective function (OF):

$$OF = \sum_k \sum_i (\ln \gamma_i^{cal} - \ln \gamma_i^{exp})_k^2 \quad (4)$$

where k is the number of data points and i the number of components in the mixture. The experimental and calculated values are denoted by the superscripts ‘exp’ and ‘cal’, respectively. γ_i^{exp} is calculated with Equation (1) and γ_i^{cal} is calculated with the Margules, Van Laar and Wilson equations. The parameters of the activity-coefficient models obtained through a simplex search are shown in Table 4. These were then used to calculate y_1^{cal} and t^{cal} under the corresponding liquid compositions and pressure (101.3 kPa). The temperatures and vapor-phase compositions obtained from the theoretical calculations using the three activity-coefficient models were compared with the experimental data. The comparative results are shown in Table 2. The average absolute deviations of temperature and the vapor-phase compositions between the experimental and the calculated values obtained from the Margules, Van Laar and Wilson models, together

with the correlated interaction parameters, are shown in Table 5.

It can be seen from Table 5 that the average absolute deviations between the experimental and the calculated values using the Wilson and Van Laar activity-coefficient models were 0.24 K and 0.23 K for the boiling point and 0.0040 for vapor-phase composition, respectively. However, by the Margules activity-coefficient models the average absolute deviations of temperature and the vapor-phase compositions were 0.41 and 0.0113. When these results are compared, it can be seen that the Wilson and Van Laar activity-coefficient model is better than the Margules activity-coefficient model based on the average absolute deviations of $|\Delta y|$ and $|\Delta T|$.

Table 5: Margules, Van Laar, Wilson and NRTL parameters and mean deviations for the binary system.

Model	Parameters		$ \Delta T $	$ \Delta y $
cyclopentane (1)+ THF (2) at 101.3KPa				
Margules	$A_{12} = 0.497$	$A_{21} = 0.418$	0.41	0.0113
Van Laar	$A_{12} = 0.719$	$A_{21} = 0.300$	0.23	0.0040
Wilson	$\Lambda_{12} = 0.297$	$\Lambda_{21} = 1.495$	0.24	0.0040

Note: $|\Delta T| = \sum |T_{exp} - T_{cal}| / k$; $|\Delta y| = \sum |y_{exp} - y_{cal}| / k$

k : number of data points

CONCLUSIONS

The VLE data for the binary system cyclopentane and tetrahydrofuran at 101.3 kPa are reported in this article. No azeotrope was found in the binary system. The VLE data were verified and were in accordance with the consistency of thermodynamics. They were correlated by the Margules, Van Laar and Wilson activity-coefficient models and the corresponding binary interaction parameters of the three activity-coefficient models were obtained. The average absolute deviations of temperature and the vapor-phase compositions between the experimental and the calculated values using the Wilson and Van Laar activity-coefficient models were 0.24 K and 0.23 K for the boiling point and 0.0040 for the vapor-phase composition, which are better than those obtained by the Margules activity-coefficient model. Therefore, the Wilson and Van Laar activity-coefficient models correlate the experimental results of cyclopentane and tetrahydrofuran system satisfactorily.

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