

## Phase Equilibrium of Binary Mixture for the (propylene oxide + 1-pentanol) System at Several Temperatures

Jeong-lae Kim, Hakmin Kim\*, Su In Park\*, Gyu Min An\*, Min Gi Kim\* and Moon Sam Shin\*<sup>†</sup>

Department of Biomedical Engineering, Eulji University, 553, Sanseong-daero, Sujeong-gu, Seongnam-si, Gyeonggi-do, 13135, Korea

\*Department of Senior Health Care, Eulji University, 553, Sanseong-daero, Sujeong-gu, Seongnam-si, Gyeonggi-do, 13135, Korea

(Received 15 October 2018; Received in revised form 25 November 2018; accepted 27 November 2018)

**Abstract** – Isothermal (vapor + liquid) equilibrium data measurements were undertaken for the binary mixtures of (propylene oxide + 1-pentanol) system at three different temperatures (303.15, 318.15, and 333.15) K. The Peng-Robinson-Stryjek-Vera equation of state (PRSV EOS) was used to correlate the experimental data. The van der Waals one-fluid mixing rule was used for the vapor phase and the Wong-Sandler mixing rule, which incorporates the non-random two liquid (NRTL) model, the universal quasi-chemical (UNIQUAC) model and the Wilson model, was used for the liquid phase. The experimental data were in good agreement with the correlation results.

Key words: Phase equilibrium, Propylene oxide, 1-Pentanol, Vapor, Liquid

### 1. Introduction

Glycol ethers are a group of solvents based on alkyl ethers of ethylene glycol or propylene glycol commonly used in pharmaceuticals, cosmetics and paints. These solvents typically have a higher boiling point, together with the favorable solvent properties of lower-molecular weight ethers and alcohols. Glycol ethers are classified into ethylene glycol ethers and propylene glycol ethers, depending on whether the raw material used in the synthesis is ethylene oxide or propylene oxide [1]. The negligible toxicity of propylene glycol ether supports its use as a safe alternative to toxic ethylene glycol ether [2]. Propylene glycol ethers are based on reacting propylene oxide with varying chain alcohols [1]. The (vapor + liquid) equilibrium information about the mixtures of propylene oxide with alcohols is significant in the design and operation of separation processes. Previously, we measured (vapor + liquid) equilibrium data for (propylene oxide + ethanol) and (propylene oxide + 1-propanol) [3]. In this work, isothermal (vapor + liquid) equilibrium data for the binary mixtures of (propylene oxide + 1-pentanol) system were measured at temperatures between 303.15 and 333.15 K. The experimental data were correlated using the Peng-Robinson-Stryjek-Vera equation of state (PRSV EOS) [4]. The van der Waals one-fluid mixing rule was used for the vapor phase and the Wong-Sandler mixing rule [5], which incorporates the non-random two liquid (NRTL) model [6], the universal quasi-chemical (UNIQUAC) model [7] and the Wilson model [8], was used for the liquid phase.

### 2. Experimental section

#### 2-1. Materials

Propylene oxide and 1-pentanol were supplied by Sigma Aldrich (St. Louis, MO, USA). All chemicals were used without further purification. The supplier and purity of the chemicals are reported in Table 1.

#### 2-2. Apparatus and procedures

A static (vapor + liquid) equilibrium apparatus was used to measure the isothermal (vapor + liquid) equilibrium of binary mixtures. A schematic diagram of the apparatus is shown in Fig. 1. The details of the experimental apparatus and procedures can be found in previous work [3], so only the most salient information is offered here. The experimental pressure was determined using a pressure transducer (Honeywell, Model STJE) with an accuracy of  $\pm 0.01$  kPa, and the experimental temperature was determined using a digital thermometer (Hart Scientific, Model 5618B) with an accuracy of  $\pm 0.008$  K. For each experiment, a small amount of liquid-phase sample was extracted and analyzed by gas chromatography.

#### 2-3. Sample analysis

The composition of the extracted liquid was determined by a DS 6200 gas chromatograph equipped with a thermal conductivity detector. A 10% Carbowax 20M Chrom W-AW packed column (length, 2.438 m; o.d., 3.175 mm; i.d., 2.159 mm) and a 10% OV-101 CHROM W-HP packed column (length, 3.048 m; o.d., 3.175 mm; i.d., 2.159 mm) were used for the (propylene oxide + 1-pentanol) system. For the (propylene oxide + 1-pentanol) system, the oven and detector temperatures were both kept at 373 K, the injector temperature was kept at 423 K and the current of thermal conductivity detector was 60 mA. A cooled syringe was used to inject a liquid

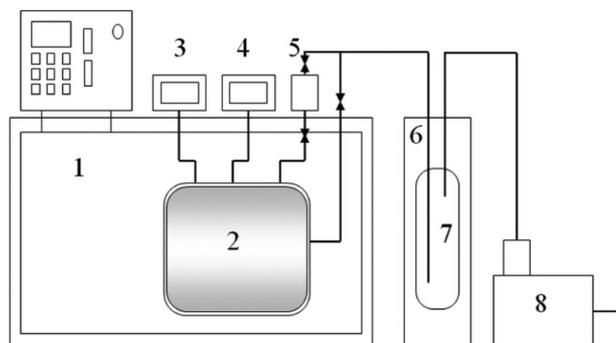
<sup>†</sup>To whom correspondence should be addressed.

E-mail: msshin@eulji.ac.kr

This is an Open-Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

**Table 1. Specifications of the chemicals used for measurements**

Chemical name	IUPAC name	CAS NO.	Supplier	Mass fraction purity
Propylene oxide	Epoxypropane	75-56-9	Sigma-Aldrich	≥0.995
1-Pentanol	Pentan-1-ol	74-41-0	Sigma-Aldrich	≥0.99

**Fig. 1. Schematic diagram of experimental apparatus.**

- |                          |                            |
|--------------------------|----------------------------|
| 1. Isothermal water bath | 5. Feed container          |
| 2. Equilibrium cell      | 6. Cooling bath circulator |
| 3. Temperature indicator | 7. Trap                    |
| 4. Pressure indicator    | 8. Vacuum pump             |

sample into gas chromatography. In each analysis, 1.5  $\mu\text{L}$  of sample was analyzed. High purity helium gas (purity  $\geq 99.99\%$ ) was used as a carrier gas.

### 3. Results and Discussion

Phase equilibrium data for the (propylene oxide + 1-pentanol) were measured and the experimental uncertainty [9] was estimated to be 0.1 K for the temperature and 0.003 for the mole fraction of propylene oxide. Table 2 lists the experimental (propylene oxide + 1-pentanol) equilibrium data with standard uncertainty  $u(p)$  [9] at three different temperatures (303.15, 318.15, and 333.15) K.

PRSV EOS was used for correlating the experimental data. The PRSV EOS is represented as follows:

**Table 2. Experimental (vapor + liquid) equilibrium data for temperature  $T$ , pressure  $p$  with standard uncertainty  $u(p)$ , and mole fraction  $x_1$  for the system propylene oxide(1) + 1-pentanol(2)<sup>a</sup>**

$T/\text{K}$	$x_1$	$p/\text{kPa}$	$u(p)/\text{kPa}$	$T/\text{K}$	$x_1$	$p/\text{kPa}$	$u(p)/\text{kPa}$
303.15	0.0324	5.76	0.12	318.15	0.0324	9.38	0.16
303.15	0.0775	12.78	0.13	318.15	0.0775	20.18	0.17
303.15	0.1265	19.29	0.16	318.15	0.1265	30.44	0.18
303.15	0.1800	25.89	0.17	318.15	0.1800	40.83	0.23
303.15	0.2382	32.19	0.19	318.15	0.2382	51.21	0.26
303.15	0.2946	38.04	0.21	318.15	0.2946	60.38	0.30
303.15	0.3678	44.38	0.22	318.15	0.3678	71.25	0.36
303.15	0.4325	49.05	0.25	318.15	0.4325	79.72	0.40
303.15	0.4900	53.28	0.27	318.15	0.4900	87.00	0.44
303.15	0.5681	58.23	0.29	318.15	0.5681	95.92	0.48
303.15	0.6395	62.71	0.31	318.15	0.6395	104.04	0.52
303.15	0.7463	69.40	0.35	318.15	0.7463	115.65	0.58
303.15	0.8344	74.58	0.37	318.15	0.8344	126.00	0.63
303.15	0.9164	80.12	0.40	318.15	0.9164	136.11	0.68
303.15	1.0000	86.90	0.43	318.15	1.0000	147.85	0.74
333.15	0.0000	3.09	0.12				
333.15	0.0324	14.92	0.16				
333.15	0.0775	30.55	0.18				
333.15	0.1265	46.01	0.23				
333.15	0.1800	61.51	0.31				
333.15	0.2382	77.61	0.39				
333.15	0.2946	92.02	0.46				
333.15	0.3678	109.23	0.55				
333.15	0.4325	123.32	0.62				
333.15	0.4900	134.61	0.67				
333.15	0.5681	149.83	0.75				
333.15	0.6395	163.86	0.82				
333.15	0.7463	184.46	0.92				
333.15	0.8344	202.34	1.01				
333.15	0.9164	219.39	1.10				
333.15	1.0000	237.88	1.19				

<sup>a</sup>Standard uncertainties  $u$  are  $u(T) = 0.10\text{K}$  and  $u(x_1) = 0.0030$

$$p = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \quad (1)$$

$$a(T) = 0.45724 \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (2)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (3)$$

$$\alpha(T) = \left[ 1 + \kappa (1 - T_r^{0.5}) + \kappa_1 (1 - T_r) (0.7 - T_r) \right]^2 \quad (4)$$

$$\kappa = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (5)$$

where  $P_c$  is the critical pressure,  $T_c$  the critical temperature,  $T_r$  the reduced temperature,  $\kappa_1$  the adjustable parameter characteristic of each pure compound, and  $\omega$  the acentric factor.

The van der Waals one-fluid mixing rule was used for the vapor phase as follows:

$$a_m = \sum_i \sum_j x_i x_j a_{ij} \quad (6)$$

$$b_m = \sum_i x_i b_i \quad (7)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (8)$$

where  $k_{ij}$  is the binary interaction parameter.

The Wong-Sandler mixing rule was used for the liquid phase as follows:

$$\frac{a_m}{RT} = Q \frac{D}{(1-D)} \quad (9)$$

$$b_m = \frac{Q}{(1-D)} \quad (10)$$

where Q and D are defined as:

$$Q = \sum_i \sum_j x_i x_j \left( b - \frac{a}{RT} \right)_{ij} \quad (11)$$

$$D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A_c^E}{CRT} \quad (12)$$

and where  $(b - a/RT)_{ij}$  and C are defined as:

**Table 3. Comparison of pure component vapor pressures**

Compound	T/K	$p_{\text{vap}}^{\text{exp}}/\text{kPa}$	$u(p)/\text{kPa}$	$p_{\text{vap}}^{\text{lit}}/\text{kPa}$
Propylene oxide	303.15	86.90	0.43	86.75 <sup>a</sup>
	318.15	147.85	0.74	147.43 <sup>a</sup>
	333.15	237.88	1.19	237.12 <sup>a</sup>
1-Pentanol	333.15	3.09	0.12	3.11 <sup>b</sup>

$u(T) = 0.1\text{K}$

<sup>a</sup>Reference [10]

<sup>b</sup>Reference [11]

**Table 4. Parameters used in the correlation**

Compound	$r^a$	$q^b$	$v^c/(\text{cm}^3/\text{mol})$
Propylene oxide	2.266 <sup>d</sup>	1.856 <sup>d</sup>	70.549 <sup>d</sup>
1-Pentanol	4.1287 <sup>d</sup>	3.592 <sup>d</sup>	108.534 <sup>d</sup>

<sup>a</sup>Van der Waals volume of the molecule relative to those of a standard segment, UNIQUAC volume parameter

<sup>b</sup>Van der Waals area of the molecule relative to those of a standard segment, UNIQUAC area parameter

<sup>c</sup>Pure-component liquid molar volume

<sup>d</sup>Reference [12]

$$\left( b - \frac{a}{RT} \right)_{ij} = \frac{\left( b_i - \frac{a_i}{RT} \right) + \left( b_j - \frac{a_j}{RT} \right)}{2} (1 - k_{ij}) \quad (13)$$

$$C = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1) \quad (14)$$

Because excess Gibbs free energy ( $G^E$ ) is approximately equal to excess Helmholtz free energy at infinite pressure ( $A_\infty^E$ ), at low pressure  $G^E$  can be substituted for  $A_\infty^E$ . To obtain  $G^E$ , we used the NRTL model, the UNIQUAC model and the Wilson model. The non-randomness parameter ( $\alpha_{ij}$ ) was fixed at 0.47, and the coordination number ( $z$ ) was fixed at 10. The correlating procedure is the same as in the previous work [3].

The vapor pressures of the pure propylene oxide at three different temperatures (303.15, 318.15, and 333.15) K and of pure 1-pentanol at 333.15 K were measured. The measured vapor pressures and literature values [10,11] are listed in Table 3 they deviated slightly from each other. Pure parameters for PRSV EOS are presented in Table 4, and the correlation results and average absolute deviations

**Table 5. The interaction parameters and average absolute deviations of pressure for propylene oxide + 1-pentanol system**

System	T/K	Model	Parameters <sup>a</sup>		$k_{ij}^b$	$10^2 \text{AAD}_p$
			$A_{12}$	$A_{21}$		
Propylene oxide + 1-Pentanol	303.15	NRTL	586.789	92.062	-0.089	0.314
		UNIQUAC	-91.655	225.409	0.211	0.316
		Wilson	193.876	38.646	0.185	0.316
	318.15	NRTL	740.107	113.419	-0.168	0.358
		UNIQUAC	-135.226	268.734	0.241	0.397
		Wilson	241.807	-80.527	0.218	0.396
333.15	NRTL	898.066	127.724	-0.216	0.515	
	UNIQUAC	-176.020	314.385	0.262	0.606	
	Wilson	294.979	-163.976	0.225	0.609	

<sup>a</sup>NRTL,  $A_{12} = \Delta g_{12}/R$ ,  $A_{21} = \Delta g_{21}/R$ ; UNIQUAC,  $A_{12} = \Delta u_{12}/R$ ,  $A_{21} = \Delta u_{21}/R$ , Wilson,  $A_{12} = \Delta \gamma_{12}/R$ ,  $A_{21} = \Delta \gamma_{21}/R$

<sup>b</sup>Binary interaction parameter

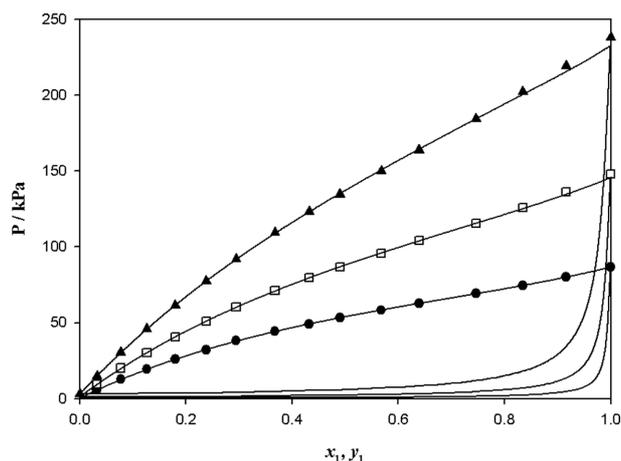


Fig. 2. Experimental (vapor + liquid) equilibrium data and correlated data by the NRTL for propylene oxide (1) + 1-pentanol (2) at temperatures from (303.15 to 333.15) K: ●, 303.15 K; □, 318.15 K; ▲, 333.15 K; solid lines, NRTL.

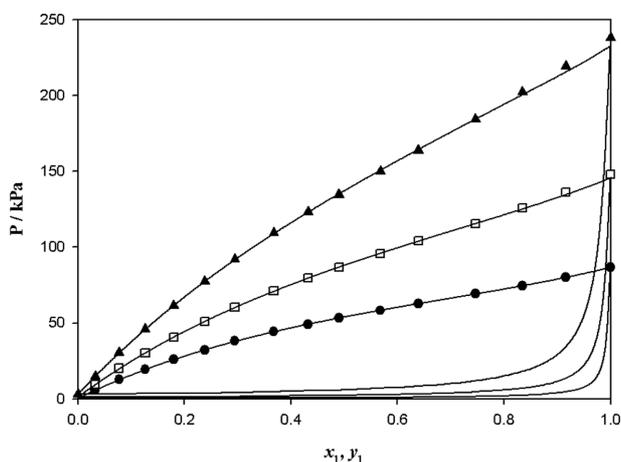


Fig. 3. Experimental (vapor + liquid) equilibrium data and correlated data by the UNIQUAC for propylene oxide (1) + 1-pentanol (2) at temperatures from (303.15 to 333.15) K: ●, 303.15 K; □, 318.15 K; ▲, 333.15 K; solid lines, UNIQUAC.

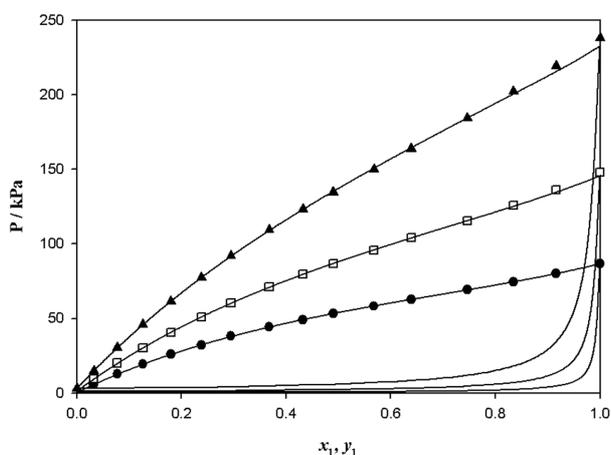


Fig. 4. Experimental (vapor + liquid) equilibrium data and correlated data by the Wilson for propylene oxide (1) + 1-pentanol (2) at temperatures from (303.15 to 333.15) K: ●, 303.15 K; □, 318.15 K; ▲, 333.15 K; solid lines, Wilson.

of pressure ( $AADp$ ) are presented in Table 5.

The interaction parameters were regressed by minimizing the objective function,  $AADp$ , using a simplex algorithm. The  $AADp$  is defined as follows:

$$AADp = \frac{1}{N} \sum_i \left| \frac{p_i^{\text{exp}} - p_i^{\text{cal}}}{p_i^{\text{exp}}} \right| \quad (15)$$

where  $N$  is the number of experimental data points,  $p_i^{\text{exp}}$  the experimental pressure, and  $p_i^{\text{cal}}$  the calculated pressure.

As shown in Table 5, the experimental (propylene oxide + 1-pentanol) equilibrium data were correlated within 0.515%, 0.606%, and 0.609%  $AADp$  for the NRTL, UNIQUAC, and Wilson models, respectively. In all cases, the NRTL model showed the best correlated results among the three models. Therefore, the NRTL model is appropriate for the systems studied in this work, and the UNIQUAC and Wilson models showed similar correlation results. Figs. 2, 3, 4 show the experimental data and correlated values for the (propylene oxide + 1-pentanol) system, by NRTL, UNIQUAC, Wilson, respectively.

#### 4. Conclusions

Isothermal (vapor + liquid) equilibrium data measurements were undertaken for the binary mixtures of (propylene oxide + 1-pentanol) system at three different temperatures (303.15, 318.15, and 333.15) K. The correlation results were obtained from PRSV EOS with the van der Waals one-fluid mixing rule for the vapor phase and with the Wong-Sandler mixing rule for the liquid phase. The NRTL, UNIQUAC, and Wilson models were used to calculate the excess Gibbs free energy. The experimental data were in good agreement with the correlation results obtained by all three models within less than 1%  $AADp$ . The NRTL model is more suitable than the UNIQUAC and Wilson models for the systems studied in this work.

#### Acknowledgments

This research was supported by the Bio & Medical Technology Development Program of the National Research Foundation (NRF) funded of the Ministry of Science & ICT(2017M3A9D8048416).

#### References

1. Russo, V., Tesser R., Santacesaria E. and Serio M., "Chemical and Technical Aspects of Propene Oxide Production via Hydrogen Peroxide (HPPO Process)," *Ind. Eng. Chem. Res.*, **52**, 1168-1178(2013).
2. Zhang, W., Wang, H., Wei, W. and Sun, Y., "Solid Base and Their Performance in Synthesis of Propylene Glycol Methyl Ether," *J. Mol. Catal. A. Chem.*, **231**, 83-88(2005).
3. Kim, H., Hyeong, S., Hong, J. H., Kim, A. R., Shin, M. S. and Kim, H., "Isothermal (Vapor + liquid) Equilibria for the Binary Mixtures of (Propylene oxide + ethanol) and (Propylene oxide + 1-propanol) at Several Temperatures," *J. Chem. Thermodyn.*, **86**,

- 1-5(2015).
4. Stryjek, R. and Vera, J. H., "PRSV: An Improved Peng-Robinson Equation of State for Pure Compounds and Mixtures," *Can. J. Chem. Eng.*, **64**, 323-333(1986).
  5. Wong, D. S. H. and Sandler, S. I., "A Theoretically Correct Mixing Rule for Cubic Equations of State," *AIChE J.* **38**, 671-680(1992).
  6. Renon, H. and Prausnitz, J. M., "Local Compositions in Thermodynamic Excess Function for Liquid Mixtures," *AIChE J.*, **14**, 135-144(1968).
  7. Abrams, D. S. and Prausnitz, J. M., "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems," *AIChE J.*, **21**, 116-128(1975).
  8. Wilson, G. M., "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing," *J. Am. Chem. Soc.*, **86**, 127-130(1964).
  9. "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, 1994 Edition.
  10. Horstmann, S., Gardeler, H., Fischer, K., Köster, F. and Gmehling, J., "Vapor Pressure, Vapor-liquid Equilibrium, and Excess Enthalpy Data for Compounds and Binary Subsystems of the Chlorohydrin Process for Propylene Oxide Production," *J. Chem. Eng. Data*, **46**, 337-345(2001).
  11. NIST Chemistry Webbook Home Page. <http://webbook.nist.gov/chemistry/>(accessed Oct 15, 2018).
  12. DIPPR 801 Database, Design Institute for Physical Property Data, American Institute of Chemical Engineers (2002).