

Isothermal Vapor-Liquid Equilibrium of Methanol + Glycerol and 1-Propanol + Glycerol

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ABSTRACT

Isothermal vapor-liquid equilibrium (VLE) data for two binary mixtures of methanol + glycerol and 1-propanol + glycerol were determined at the temperature range from (313.15 to 363.15) K using a simple quasi-static ebulliometer. All systems showed that the vapor pressures increased with increasing alcohols (methanol or 1-propanol) concentrations at corresponding system. The Wilson, Non-Random Two-Liquid (NRTL) and Universal Quasi-Chemical (UNIQUAC) activity coefficient models were used to correlate the experimental data. Both systems showed slightly deviations from the ideal liquid phase behavior.

Keywords: vapor-liquid equilibrium; binary mixtures; methanol; 1-propanol; glycerol

ABSTRAK

Data kesetimbangan uap-cair isothermal untuk dua campuran biner metanol + gliserol dan 1-propanol + gliserol diukur pada rentang suhu 313,15 sampai 363,15 K dengan menggunakan "simple quasi-static ebulliometer". Semua sistem menunjukkan bahwa tekanan uap meningkat seiring dengan meningkatnya konsentrasi alkohol (metanol atau 1-propanol) pada sistem yang bersangkutan. Model koefisien aktivitas Wilson, Non-Random Two-Liquid (NRTL) dan Universal Quasi-Chemical (UNIQUAC) digunakan untuk mengkorelasi data eksperimen. Kedua sistem menunjukkan deviasi yang kecil terhadap perilaku larutan ideal.

Kata Kunci: kesetimbangan uap-cair; campuran biner; metanol; 1-propanol; gliserol

INTRODUCTION

The depletion of fossil fuel caused by high energy demand in the industrialized world has been attracting much attention especially on alternative energy development. Biodiesel is an alternative energy (fuel) produced from renewable resources. It is a mixture of fatty acid alkyl esters that can be used in conventional diesel engines without major modifications [1-2]. It has no toxicity, no sulfur content and low emission of carbon monoxide and particulate matter which less pollutes than diesel fuel [1,3]. Vegetable oils (palm oil [3], corn oil [4]), animal fats (chicken fat [4-5], mutton fat [5]) and microalgae oil [2,6] can be potential feedstock for biodiesel production. In the biodiesel production, process of transesterification, hydroesterification, enzymatic transesterification and supercritical transesterification process have been applied. However, transesterification is the most utilized process [3,5]. Transesterification refers to a chemical reaction of oil or fat with an excess of alcohols in the presence of a homogeneous or heterogeneous catalyst to yield biodiesel and glycerol [1,3]. After cooling to room temperature, the glycerol layer settles to the bottom and the ester-rich phase

(FAME) forms the upper layer [7]. Then, biodiesel separation and purification are required to avoid diesel engines problems during biodiesel usage [2]. Separation of glycerol and unreacted alcohol is carried out to recover alcohol that can be recycled to transesterification reactor [7]. The glycerol-rich phase will be further processed to produce crude glycerol [3,7]. In the transesterification reaction, the glycerol is considered as commercial byproduct that can be used in food, pharmacy and cosmetics industry [8]. By applying suitable biodiesel production, high-quality and low cost biodiesel can be achieved [2]. In order to optimize the biodiesel production, the vapor-liquid equilibrium (VLE) data for the binary system of alcohol + glycerol are required, especially to design and optimize the glycerol recovery section.

Many researchers have published the VLE data of alcohols + glycerol. The isobaric binary VLE data of methanol + glycerol system have been published by several researchers [9-11]. The VLE data for this system at high temperature of 493–573 K were measured isothermally by Shimoyama et al. [12]. For higher chain alcohols, Oliveira et al. [9] also measured the VLE data of 1-propanol + glycerol at atmospheric

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Table 1. Properties of pure components

Component	Mass fraction purity	MW (g·mol ⁻¹)	Boiling point (K)	Density ^a (g·cm ⁻³)
methanol	0.999	32.042	337.69 ^a	0.78659 ^c
1-propanol	0.997	60.096	370.93 ^b	0.79962 ^d
glycerol	0.995	92.095	563.00 ^e	1.25780 ^f

^a $T = 298.15$ K. ^b ref [24]. ^c ref [25]. ^d ref [26]. ^e ref [27]. ^f ref [28].

Table 2. Parameters of the Antoine equation for pure compounds

Component	A	B	C
methanol ^a	5.20277	1580.080	239.500
1-propanol ^a	4.99991	1512.940	205.807
glycerol ^b	10.6190	4487.040	-140.200

^a ref [24], $\log(P^s) = A - B/(T + C - 273.15)$, where P^s is in bar and T is in K.

^b ref [27], $\ln(P^s) = A - B/(T + C)$, where P^s is in bar and T is in K.

pressure with limited mol fractions ranges of (0.0418 to 0.4410). In our previous work [13], the VLE data for two binary systems of ethanol + glycerol and 2-propanol + glycerol have been measured at the temperatures of (323.15 and 333.15) K and (333.15 and 343.15) K, respectively. To the best of our knowledge, the isothermal VLE data for this system still remain scarce. On the other hand, glycerol has high-boiling points, so that the separation at low pressure is preferred because of low energy consumption than others processes [14-17]. Therefore, in this work, the VLE data (P - x) were measured using a simple quasi-static ebulliometer for two binary systems of methanol + glycerol and 1-propanol + glycerol over the entire composition range at the constant low temperatures of (313.15 and 323.15) K and (343.15, 353.15 and 363.15) K, respectively. The experimental data were correlated with the Wilson [18], nonrandom two-liquid (NRTL) [19] and universal quasi-chemical (UNIQUAC) [20] models.

EXPERIMENTAL SECTION

Materials

All materials used in this work (methanol, 1-propanol and glycerol) were supplied by Merck (Germany) and used without additional purification. The properties of each material are presented in Table 1.

Instrumentation

The apparatus used in this study consist of simple quasi-static ebulliometer equipped with stirrer, electric heater and thermocouple (RTD Pt 100). The schematic diagram and the details of the experimental apparatus were described in our previous work [21]. Ohaus balance with an accuracy of ± 0.0001 g was used to weigh the sample. The temperature of the system was controlled by using ANLY AT 502 (accuracy of ± 0.1 K). The vapor pressures at various temperatures and

compositions were measured using a mercury manometer with a precision of ± 0.1 mm Hg [21].

Procedure

In this study, the simple quasi-static ebulliometer is used to measure the vapor pressure. Revalidation of ebulliometer was carried out by measuring the vapor pressure of pure methanol at the temperatures of (304.35, 308.55, 313.15, 318.15, 323.15 and 333.15) K and the binary system of methanol + water at 318.15 K. After verification of its reliability, the VLE measurement for binary system of methanol or 1-propanol + glycerol was started.

The certain composition of sample is prepared gravimetrically, and then the sample was introduced into ebulliometer. The vacuum pump was turned on to remove air and impurities in the equilibrium cell. After the system achieved vacuum condition that shown by constant pressure, the pump was turned off. To reach desired temperature, the electric heater was activated which followed by mixing using a magnetic stirrer to create homogenous mixtures. The equilibrium was reached when the pressure achieved constant value. The value was recorded as the vapor pressure of the sample at the desired temperature. The experimental procedure was repeated for other temperatures and compositions. The liquid phase composition at equilibrium condition was estimated similar with initial composition [21].

RESULT AND DISCUSSION

Vapor pressure of methanol was measured to verify the reliability of our simple quasi-static ebulliometer. The experimental data were compared with the calculated values from Antoine equation where the constants obtained from the Thermodynamics Research Center (TRC) data bank, College Station, TX, USA as listed in Table 2. For further test, the apparatus was subsequently used to measure the vapor

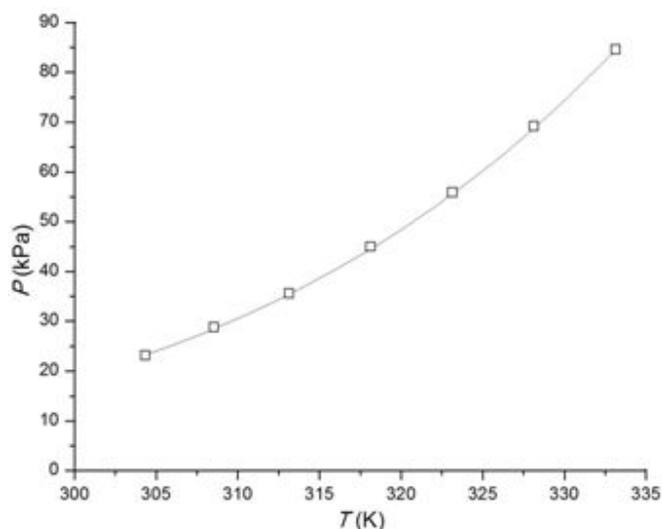


Fig 1. Vapor pressures data of methanol: (□) experimental; and (—) calculation

Table 3. Vapor-liquid equilibrium data for binary system of methanol (1) + glycerol (2) from $T = (313.15 \text{ to } 323.15) \text{ K}^a$

x_1	$P \text{ (kPa)}$	
	$T = 313.15 \text{ K}$	$T = 323.15 \text{ K}$
0.0979	3.31	6.10
0.1954	6.76	11.00
0.2989	11.27	18.04
0.3987	14.19	23.74
0.4980	16.84	27.98
0.5977	22.28	35.68
0.6977	23.47	39.92
0.7981	27.59	45.37
0.8976	31.97	50.54
1.0000	35.55	55.87

^a $u(T) = 0.1 \text{ K}$, $u(P) = 0.05 \text{ kPa}$, and $u(x_1) = 0.001$.

Table 5. Physical properties and parameters of pure components used in the activity coefficients correlation

Component	Molar volume ($\text{cm}^3 \cdot \text{mol}^{-1}$)	r^a	q^a
methanol	40.73 ^b	1.4311	1.432
1-propanol	75.14 ^b	3.2499	3.128
glycerol	73.03 ^c	4.7957	4.908

^a ref [29]. ^b ref [24]. ^c ref [27].

pressure of methanol (1) + water (2) at 318.15 K. The experimental data of these binary system were compared with those reported by Zharov and Pervukhin [22]. The comparison of the experimental data and the literature values were shown in Fig. 1 and 2 for pure methanol and binary mixtures of methanol (1) + water (2), respectively. As presented in these figures, our data agreed well with the literature values as average absolute deviations between experimental and literature data for pure methanol and methanol + water mixtures in the vapor pressures of 0.5% and 0.7%, respectively.

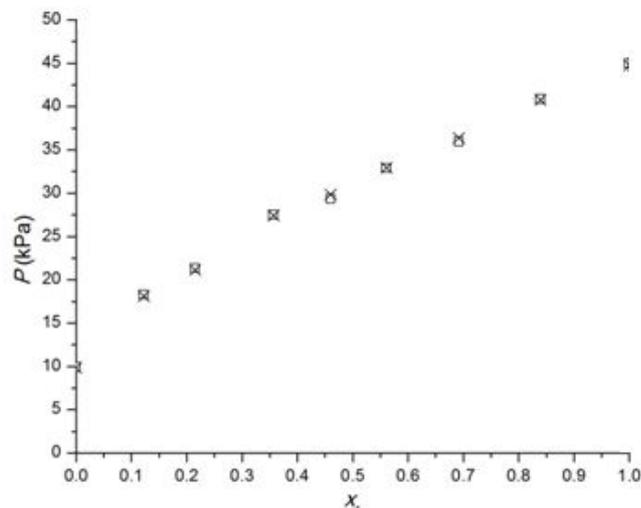


Fig 2. Total vapor pressures data for binary system of methanol (1) + water (2) at $T = 318.15 \text{ K}$: (□) this work; and (×) literature data [22]

Table 4. Vapor-liquid equilibrium data for binary system of 1-propanol (1) + glycerol (2) from $T = (343.15 \text{ to } 363.15) \text{ K}^a$

x_1	$P \text{ (kPa)}$		
	$T = 343.15 \text{ K}$	$T = 353.15 \text{ K}$	$T = 363.15 \text{ K}$
0.1223	3.97	6.50	8.35
0.2170	6.89	10.61	17.51
0.3139	9.41	16.58	23.61
0.4051	13.59	21.22	29.97
0.5024	16.57	26.19	39.53
0.6009	19.63	31.17	47.09
0.7013	22.55	36.34	52.93
0.8005	27.72	41.92	61.15
0.8995	28.91	47.22	68.19

^a $u(T) = 0.1 \text{ K}$, $u(P) = 0.05 \text{ kPa}$, and $u(x_1) = 0.001$.

From these results, the ebulliometer used in this work is reliable to measure the vapor pressures accurately.

The experimental VLE data (P - x_i) for two binary systems of methanol + glycerol and 1-propanol + glycerol were obtained at the temperatures of (313.15 and 323.15) K and (343.15 to 363.15) K, respectively. The experimental data obtained in this work were presented in Tables 3 and 4. Both systems indicated that the vapor pressures increased with the increasing of alcohols (methanol or 1-propanol) mole fractions at corresponding system.

The experimental data for those binary systems were correlated with the Wilson, NRTL and UNIQUAC equations, the mixture nonrandomness parameter α_{12} in the NRTL equation was fixed at 0.25. The physical properties of each component required in the calculation of the activity coefficients correlations were given in Table 5. Barker's method [23] was used to obtain the optimal values of the binary interaction

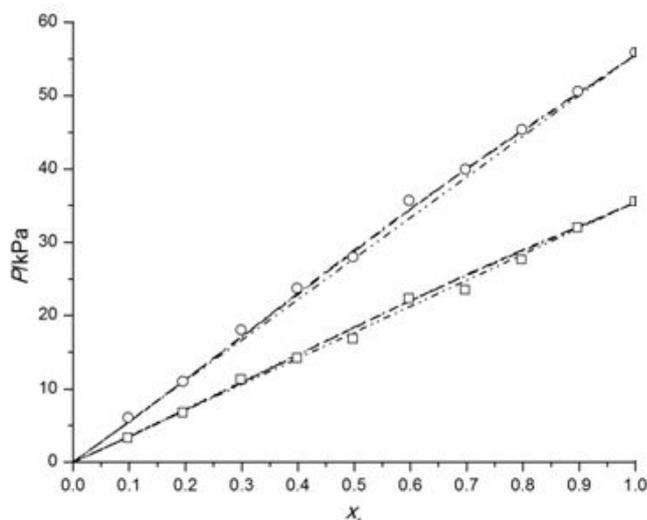


Fig 3. VLE phase ($P-x_1$) diagram for binary system of methanol (1) + glycerol (2): (\square) experimental data at 313.15 K; (\circ) experimental data at 323.15 K; (----) calculated values from the Wilson model; (-.-) calculated values from the NRTL model; (••••) calculated values from the UNIQUAC model; and (-•-•) calculated values from Raoult's law

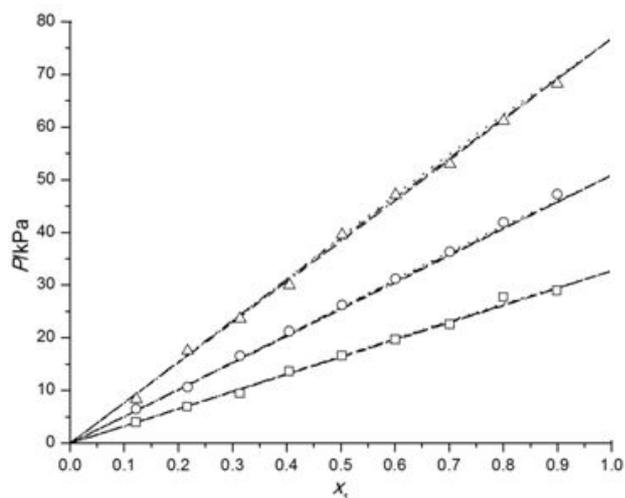


Fig 4. VLE phase ($P-x_1$) diagram for binary system of 1-propanol (1) + glycerol (2): (\square) experimental data at 343.15 K; (\circ) experimental data at 353.15 K; (Δ) experimental data at 363.15 K; (----) calculated values from the Wilson model; (-.-) calculated values from the NRTL model; (••••) calculated values from the UNIQUAC model; and (-•-•) calculated values from Raoult's law

Table 6. Fitted binary interaction parameters of activity coefficient models and average absolute deviations (AAD)

model	parameters		AAD ^a (%)
	A_{12} ($\text{J}\cdot\text{mol}^{-1}$)	A_{21} ($\text{J}\cdot\text{mol}^{-1}$)	
methanol (1) + glycerol (2), $T = (313.15 \text{ to } 323.15) \text{ K}$			
Wilson ^b	-515.7	2329.3	3.4
NRTL ^c	4880.2	-3191.9	3.2
UNIQUAC ^d	-66.3	996.2	3.5
Raoult's law			3.7
1-propanol (1) + glycerol (2), $T = (343.15 \text{ to } 363.15) \text{ K}$			
Wilson	310.0	-306.7	3.1
NRTL	3147.1	-2440.6	3.0
UNIQUAC	2002.6	-1450.1	2.9
Raoult's law			3.1

^a $AAD = (1/n) \sum_{i=1}^n |(P_{cal} - P_{exp})/P_{exp}| \cdot 100\%$, where n is the number of data points.

^b $A_{ji} = \lambda_{ji} - \lambda_{ii}$

^c $A_{ji} = g_{ji} - g_{ii}$

^d $A_{ji} = u_{ji} - u_{ii}$

parameters for the mixtures studied in this work by minimizing the following objective function (OF):

$$OF = \sum_{i=1}^n (P_{i,cal} - P_{i,exp})^2 \quad (1)$$

where n is the number of data points and the subscripts "cal" and "exp" refer to calculated and experimental values, respectively. The calculated pressures were

obtained using the following equation by assuming the vapor phase close to ideal gas behavior at low pressure,

$$P_{cal} = \sum_{i=1}^m x_i \gamma_i P_i^s \quad (2)$$

where x_i are the mole fractions of the liquid phase, γ_i are the activity coefficients of the components, and m are the number of the component in the mixtures. P_i^s are the vapor pressures of the pure components that were calculated by the Antoine equation with the constants obtained from Table 2.

The best fitted binary interaction parameters (A_{12} and A_{21}) obtained in this work and the average absolute deviations (AAD) between the experimental and the calculated vapor pressures are listed in Table 6. This table showed that the experimental data were well correlated with the Wilson, NRTL and UNIQUAC equations. The comparison between experimental data and calculated vapor pressures with the Wilson, NRTL and UNIQUAC activity coefficient models are presented in Fig. 3 and 4. In these figures, solid points represent experimental data, dash lines represent calculated values by Wilson model, dash dot lines represent the calculated values by NRTL model, while dot lines represent the calculated values by UNIQUAC model.

The binary systems of methanol (1) + glycerol (2) and 1-propanol (1) + glycerol (2) in this work behaves almost ideally, thus the vapor pressures were also

correlated using Raoult's law by assuming the liquid phase exhibited ideal solution and the activity coefficients were set to one ($\gamma_i = 1$). The correlations show that the experimental data have slightly deviations from the ideal liquid phase behavior as average absolute deviations between experimental data and calculated values for methanol (1) + glycerol (2) and 1-propanol (1) + glycerol (2) in the vapor pressures of 3.7% and 3.1%, respectively. The comparisons are also presented in Fig. 3 and 4 (Raoult's law; dash dot dot lines). The deviations concluded that Raoult's law sufficiently modeled the vapor pressures of both binary systems. Even though the application of Raoult's law was sufficient to present the VLE behavior of the studied system, the binary interaction parameters of activity coefficients models were required to extend presentation of the VLE multicomponent with the prediction using binary interaction parameters of activity coefficient model.

The vapor phase compositions (y_i) were determined and the results showed that the vapor phase was made up of pure alcohols ($y_1 = 1$) because the vapor pressure of glycerol is close to zero in the range of studied temperatures.

CONCLUSION

In the present study, isothermal VLE data for two binary systems of (methanol or 1-propanol) + glycerol have been measured using a simple quasi-static ebulliometer at different temperatures. The experimental data were well correlated using the Wilson, NRTL and UNIQUAC models. In the methanol + glycerol mixture, the AAD values in the vapor pressures are 3.4, 3.2 and 3.5% for the Wilson, NRTL and UNIQUAC models, respectively. For the binary system of 1-propanol + glycerol, the AAD values in the vapor pressures are 3.1, 3.0 and 2.9% for the Wilson, NRTL and UNIQUAC models, respectively. Both of systems exhibit slight deviations from the Raoult's law with the AAD values in the vapor pressures are 3.7 and 3.1% for the binary system of methanol + glycerol and 1-propanol + glycerol, respectively. Based on the calculation, the mole fraction of the alcohols in the vapor phase at studied temperature range is close to unity indicating alcohol can be completely separated from glycerol stream in the biodiesel production.

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REFERENCES

1. Veljković, V.B., Banković-Ilić, I.B., and Stamenković, O.S., 2015, *Renewable Sustainable Energy Rev.*, 49, 500–516.
2. Atadashi, I.M., Aroua, M.K., and Aziz, A.A., 2011, *Renewable Energy*, 36 (2), 437–443.
3. Kuss, V.V., Kuss, A.V., da Rosa, R.G., Aranda, D.A.G., and Cruz, Y.R., 2015, *Renewable Sustainable Energy Rev.*, 50, 1013–1020.
4. Alptekin, E., Canakci, M., and Sanli, H., 2014, *Waste Manage.*, 34 (11), 2146–2154.
5. Bhatti, H.N., Hanif, M.A., Qasim, M., and Ata-ur-Rehman, 2008, *Fuel*, 87 (13-14), 2961–2966.
6. López, B.C., Cerdán, L.E., Medina, A.R., López, E.N., Valverde, L.M., Peña, E.H., Moreno, P.A.G., Grima, E.M., 2015, *J. Biosci. Bioeng.*, 119 (6), 706–711.
7. Saleh, J., Tremblay, A.Y., and Dubé, M.A., 2010, *Fuel*, 89 (9), 2260–2266.
8. Qadariah, L., Mahfud, Sumarno, Machmudah, S., Wahyudiono, Sasaki, M., and Goto, M., 2011, *Bioresour. Technol.*, 102 (19), 9267–9271.
9. Oliveira, M.B., Teles, A.R.R., Queimada, A.J., and Coutinho, J.A.P., 2009, *Fluid Phase Equilib.*, 280 (1-2), 22–29.
10. Soujanya, J., Satyavathi, B., and Prasad, T.E.V., 2010, *J. Chem. Thermodyn.*, 42 (5), 621–624.
11. Veneral, J.G., Benazzi, T., Mazutti, M.A., Voll, F.A.P., Cardozo-Filho, L., Corazza, M.L., Guirardello, R., and Oliveira, J.V., 2013, *J. Chem. Thermodyn.*, 58, 398–404.
12. Shimoyama, Y., Abeta, T., Zhao, L., and Iwai, Y., 2009, *Fluid Phase Equilib.*, 284 (1), 64–69.
13. Wibawa, G., Mustain, A., Akbarina, M.F., and Ruslim, R.M., 2015, *J. Chem. Eng. Data*, 60 (3), 955–959.
14. Chen, R., Ding, H., Liu, M., Qi, J., Zhou, H., and Chen, N., 2014, *Fluid Phase Equilib.*, 382, 133–138.
15. Yang, Z., Xia, S., Shang, Q., Yan, F., and Ma, P., 2014, *J. Chem. Eng. Data*, 59 (3), 825–831.
16. Yang, C., Sun, Y., Qin, Z., Feng, Y., Zhang, P., and Feng, X., 2014, *J. Chem. Eng. Data*, 59 (4), 1273–1280.
17. Zhang, L., Wu, W., Sun, Y., Li, L., Jiang, B., Li, X., Yang, N., and Ding, H., 2013, *J. Chem. Eng. Data*, 58 (5), 1308–1315.
18. Wilson, G.M., 1964, *J. Am. Chem. Soc.*, 86 (2), 127–130.
19. Renon, H., and Prausnitz, J.M., 1968, *AIChE J.*, 14 (1), 135–144.
20. Abrams, D.S., and Prausnitz, J.M., 1975, *AIChE J.*, 21, 1, 116-128.

21. Oktavian, R., Amidelsi, V., Rasmito, A., and Wibawa, G., 2013, *Fuel*, 107, 47–51.
22. Zharov, V.T., and Pervukhin, O.K., 1972, *Zh. Fiz. Khim.*, 46, 1970–1973.
23. Barker, J.A., 1953, *Aust. J. Chem.*, 6 (3), 207–210.
24. Poling, B.E., Prausnitz, J.M., and O'Connell, J.P., 2001, *The Properties of Gases and Liquids*, 5th Ed., McGraw-Hill, New York.
25. Gómez, E., Calvar, N., Macedo, E.A., and Domínguez, Á., 2012, *J. Chem. Thermodyn.*, 45 (1), 9–15.
26. Segade, L., de Llano, J.J., Domínguez-Pérez, M., Cabeza, Ó., Cabanas, M., and Jiménez, E., 2003, *J. Chem. Eng. Data*, 48 (5), 1251–1255.
27. Reid, R.C., Prausnitz, J.M., and Poling, B.E., 1987, *The Properties of Gases and Liquids*, 4th Ed., McGraw-Hill, New York.
28. Ge, M-L., Ma, J-L., and Chu, B., 2010, *J. Chem. Eng. Data*, 55 (7), 2649–2651.
29. Hansen, H.K., Rasmussen, P., Fredenslund, A., Schiller, M., and Gmehling, J., 1991, *Ind. Eng. Chem. Res.*, 30 (10), 2352–2355.