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Vapor-Liquid Equilibrium Experiments for Di-*n*-propyl Ether and 1-Propanol Binary System at 1,013 and 300 mbar and Prediction of Equilibrium Experimental Data using Wilson, UNIQUAC and NRTL Models

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Herein, isobaric vapor-liquid phase equilibrium experiments for the binary mixture of di-*n*-propyl ether and 1-propanol were performed at 1,013 and 300 mbar, respectively. At 1,013 mbar, an azeotrope was formed where the mole composition of di-*n*-propyl ether is 0.6472 with azeotropic temperature of 90.18 °C. On the other hand, at 300 mbar, an azeotrope was formed with a mole composition of 0.7682 mole fraction of di-*n*-propyl ether and an azeotropic temperature of 52.61 °C. Throughout these vapor-liquid phase equilibrium experiments, it was observed that the azeotropic point of the di-*n*-propyl ether/1-propanol binary system changes with the system pressure. By conducting a regression analysis of the binary vapor-liquid phase equilibrium experimental data using liquid activity coefficients thermodynamics (LACT) models, such as UNIQUAC, NRTL and Wilson embedded in PRO/II with PROVISION 9.1, a commercial chemical process simulator from Invensys, Inc., optimum binary interaction parameters for the individual model equations were determined. This work lead to the generation of binary interaction parameters that better fit the experimental data parameters embedded in the PRO/II simulator.

Keywords: Vapor-liquid equilibrium experiments, Di-*n*-propyl ether, 1-Propanol.

INTRODUCTION

Di-*n*-propyl ether is manufactured by reacting alcohols with sulfuric acid, as shown in eqn. 1, where X signifies halogen.

$$CH_3CH_2CH_2CO^- + CH_3CH_2CH_2X \rightarrow CH_3CH_2CH_2OCH_2CH_2CH_3 + X \quad (1)$$

Di-*n*-propyl ether is widely used as a solvent because it dissolves most organic materials; it is also utilized as a soil insecticide and medical anesthetic[1]. Propanol can exists as either 1-propanol or 2-propanol isomers, according to the position of the hydroxyl functional group. 1-Propanol is prepared by the oxo reaction shown in eqn. 2. 1-Propanol produced in this manner is mainly used for manufacturing cosmetics, dental lotion and insecticides[2].

$$2HC = CH_2 + CO + H_2 \rightarrow CH_3CH_2HC = O$$
$$CH_3CH_2HC = O + H_2 \rightarrow CH_3CH_2CH_2OH \quad (2)$$

As the di-*n*-propyl ether/1-propanol binary system forms an azeotrope at 66.47 mol % at atmospheric pressure, it is very difficult to separate them into high-purity components by using a single-distillation column. Typical procedures to separate azeotropic mixtures using more than 2 distillation columns are pressure swing distillation, azeotropic distillation and extraction distillation processes[3]. To perform computer simulations on these processes, the vapor-liquid phase equilibrium should be studied before hand. The database of physical properties in the PRO/II simulator with PROVISION 9.1[4] software (a commercial chemical process simulator of Invensys, Inc.) is equipped with binary interaction parameters of thermodynamic model equations for the di-*n*-propyl ether/1-propanol binary system. In Fig. 1, the experimental data[5] for the vapor-liquid phase equilibrium of the di-*n*-propyl ether/1- propanol system at atmospheric pressure are compared with the calculated values obtained by using the NRTL liquid activity coefficient model equation embedded in PRO/II with PROVISION 9.1. Unfortunately, the data embedded in the simulator leads to somewhat inconsistent results. Thus, in this study, vapor-liquid phase equilibrium experiments for the di-*n*-propyl ether/1-propanol binary system were conducted at 1,013 and 300 mbar, respectively, to determine the exact coefficient parameters which fit in well with the experimental data. Experimental pressures were chosen as 1,013 mbar and 300 mbar of reduced pressure to match the operating pressure of a pressure swing distillation column. UNIQUAC, NRTL and Wilson equations of the LACT (liquid activity coefficients thermodynamics) model were used for the regression analysis of the vapor-liquid phase equilibrium and the accuracies among the model equations were compared[6,7].

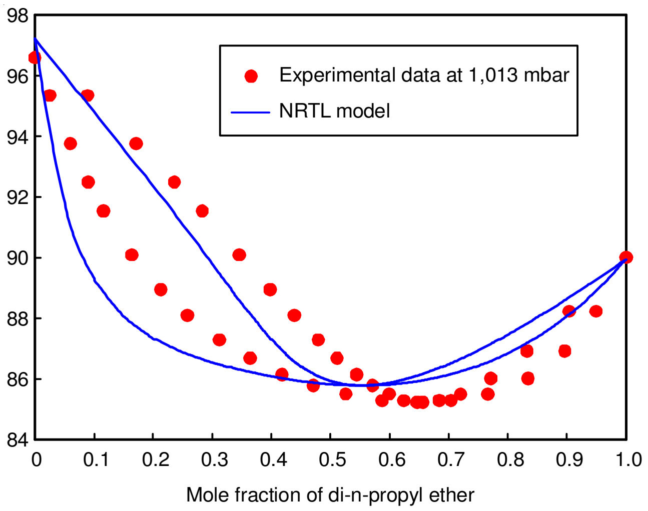
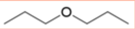
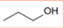


Fig. 1. Binary experimental data for di-*n*-propyl ether and 1-propanol at 1,013 mbar and its prediction

EXPERIMENTAL

Di-*n*-propyl ether (Tokyo Chemical Industry Co.) with a purity of higher than 98 wt.% was used. 1-Propanol was obtained from the SIGMA-ALDRICH Co. with a purity greater than 99.9 wt.%. By measuring the boiling points of the pure components, it was confirmed that di-*n*-propyl ether was boiling at 90.18 °C and 1-propanol at 97.30 °C. Accuracy in the temperature measurements was ± 0.02 °C. Their boiling points and physical properties obtained from the literatures are shown in Table-1.

TABLE-1
PHYSICAL PROPERTY OF DI-*n*-PROPYL ETHER AND 1-PROPANOL

Property	Di-*n*-propyl ether	1-Propanol
Structure		
Formula	$C_6H_{14}O$	C_3H_8O
Molecular weight	102.17	60.10
Density (g/cm^3)	0.75	0.80
Melting point (ºC)	-122	-126
Boiling point (ºC)	90	97-98
Experimental boiling point (ºC)	90.18	97.30
Flash point (ºC)	-18	15

Procedure: Vapor-liquid phase equilibrium experiments were conducted using a VLE 602 apparatus (Fischer Engineering GmbH), as shown in Fig. 2. Descriptions of its parts are summarized in Table-2. In this apparatus, heat was provided from the immersion heater (No. 1), which rapidly increased the temperature of the mixture and generated vapor while the liquid was circulating.

The system pressure can be adjusted in 0.01 mbar increments using a separate control box. The temperature of the system can be increased in 0.01 °C increments using a digital thermometer, which was installed at no. 8 and no. 9 (Fig. 2). The thermometer can measure a wide temperature range varying between -200 and 845 °C with an accuracy of ± 0.02 °C. In case of 1,013 mbar, experiments were carried out by opening valves no. 17, 18, 19 and 20 (Fig. 2) to ensure a passage way to the atmosphere. For low-pressure experiments, the pressure was controlled by using a vacuum pump installed separately. In this work, a vacuum was maintained between no. 15 and 16 in order to take samples by closing valves no. 19 and 20 and opening valves no. 17 and 18 (Fig. 2). In this study, experiments were performed after confirming that each set pressure was maintained for longer than 0.5 h.

TABLE-2
DETAILS OF THE VAPOR-LIQUID EQUILIBRIUM EXPERIMENTAL EQUIPMENT

No.	Name	No.	Name
1	Heater	14	Solenoid: vapor
2	Cottrell-pump	15	Receiver: liquid
3	Separation chamber	16	Receiver: vapor
4	Condenser	17	Valve
5	Cooler vapor phase	18	Valve
6	Cooler liquid phase	19	Ventilation valve
7	Mixing chamber	20	Ventilation valve
8	Thermometer: vapor	21	Sample valve
9	Thermometer: liquid	22	Sample valve
10	Septum: liquid	23	Discharge valve
11	Septum: vapor	24	Isolation tube
12	Septum: vapor	25	Isolation jacket
13	Solenoid: liquid	26	Connection to vessel

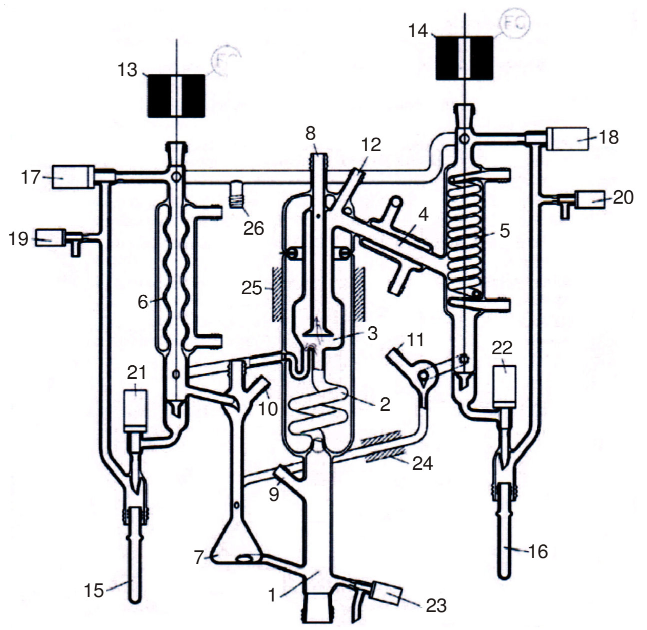


Fig. 2. Apparatus for vapor-liquid equilibrium experimental equipment

The samples obtained from experiments were analyzed by aYL6100 Gas chromatograph (GC, Younglin instrument Co., Ltd). A capillary column was installed to ensure facile high-concentration analysis. In addition, an autosampler of HT300A type was used for the GC analysis. The autosampler was useful in obtaining more accurate analysis results by controlling the sample feeding rate. The detailed conditions used in the GC analysis are represented in Table-3.

TABLE-3
CONDITIONS FOR THE GAS CHROMATOGRAPHIC ANALYSIS OF SAMPLE

Contents	Setting values
GC	YL 6100 GC
Autosampler	HT300A
Carrier gas	Helium, 1.3 mL/min
Column	Carbowax capillary (30 m × 0.32 mm × 0.25 μm)
Injector	Temperature 200 °C Flow rate 5 mL/min Split ratio 100:1 Split flow 495.0 mL/min Total flow 503.0 mL/min Pressure: 5.1 psi
Oven	Initial: 60 °C, 2 min hold
Detector	Flame ionization detector (FID) Temperature: 230 °C H_2: 30 mL/min Air: 300 mL/min

Calibration curve preparation: It is essential to prepare a calibration curve for the concentration analysis of samples obtained from vapor-liquid phase equilibrium experiments. In this study, GC analysis was performed using a total of 11 standard samples prepared based on the weight percentage of di-*n*-propyl ether. Weights and weight percentages of di-*n*-propyl ether measured during standard sample preparation are shown in Table-4.

TABLE-4
CALCULATED WEIGHT PERCENTAGES OF DI-*n*-PROPYL ETHER

No.	Weight of di-*n*-propyl ether (g)	Total weight (g)	wt.%
1	1.97	20.00	9.85
2	3.93	20.01	19.64
3	5.88	20.00	29.40
4	7.84	20.00	39.20
5	9.80	20.01	48.98
6	11.76	20.00	58.80
7	13.72	20.08	68.33
8	15.68	20.01	78.36
9	17.64	20.00	88.20

For highly accurate calibration curve preparation, GC analysis was carried out five times at each standard sample concentration; calibration curves and their equations are shown in Fig. 3 and Table-5. The x-axis of Fig. 3 is an area ratio of di-*n*-propyl ether based on the total area measured from GC analysis as 100 %, while the y-axis corresponds to the real weight percentage of di-*n*-propyl ether. Our result has high accuracy because the value of the correlation coefficient (R^2) of the calibration curve was calculated to be greater than 0.999.

RESULTS AND DISCUSSION

Vapor-liquid phase equilibrium experiments at 1,013 mbar: In this study, vapor and liquid samples were collected 21 times during the vapor-liquid phase equilibrium experiments at 1,013 mbar. The samples collected were analyzed three times per sample using GC and an arithmetic average of the calculated area ratios was taken. The weight concentration based of di-*n*-propyl ether was calculated by applying the arithmetic average value to the calibration curve.

TABLE-5
PHYSICAL PROPERTY OF DI-*n*-PROPYL ETHER AND 1-PROPANOL

Component	Equation	R^2
Di-*n*-propyl ether	$y = 0.0026 x^2 + 0.7477x$	0.9996

x. Area ratio of di-*n*-propyl ether,
y. Real weight percent of di-*n*-propyl ether

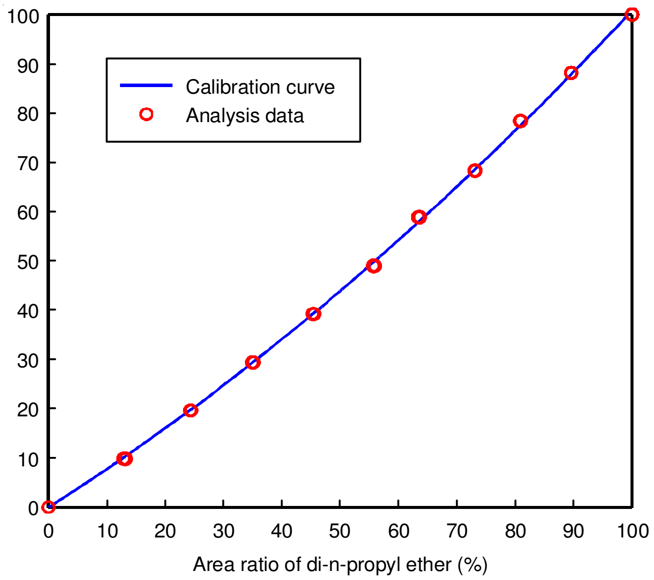


Fig. 3. Calibration curve for the experimental results

The weight concentrations were converted to mole concentrations by using calculated weight concentrations and the molecular weight of each component. The experimental results at 1,013 mbar are shown in Table-6 and TXY phase equilibrium experimental data of the di-*n*-propyl ether/1-propanol binary system are shown in Fig. 4.

TABLE-6
EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM DATA FOR THE DI-*n*-PROPYL ETHER (1) AND 1-PROPANOL (2) SYSTEM AT 1,013 mbar

No.	Temperature (°C)	x_1	y_1
1	97.30	0.0000	0.0000
2	97.14	0.0032	0.0090
3	96.50	0.0120	0.0354
4	95.89	0.0229	0.0664
5	95.06	0.0363	0.1020
6	94.42	0.0462	0.1314
7	93.43	0.0672	0.1799
8	92.56	0.0874	0.2150
9	91.13	0.1248	0.2895
10	89.89	0.1681	0.3432
11	89.08	0.2007	0.3784
12	86.88	0.3350	0.4815
13	85.74	0.5035	0.5765
14	85.62	0.5258	0.5957
15	85.54	0.5618	0.6069
16	85.46	0.5953	0.6257
17	85.44	0.6645	0.6544
18	85.72	0.7986	0.7398
19	87.15	0.9066	0.8475
20	88.93	0.9693	0.9334
21	90.18	1.0000	1.0000

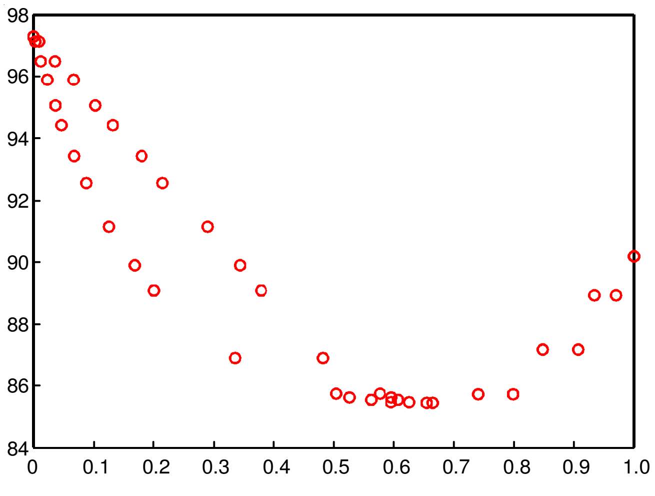


Fig. 4. TXY plot for experimental VLE data at 1,013 mbar

Studies have been carried out on the vapor-liquid phase equilibrium experiments in the di-*n*-propyl ether/1-propanol binary system at atmospheric pressure[8]. Furthermore, accurate literature data for boiling points of their pure components also exist. The results obtained from these experiments were compared with those of the preceding work in Table-7. It was demonstrated during the course of this work that the experimental results in this study are similar to those of the preceding work in terms of azeotropic composition and temperature. In addition, the boiling points of pure components showed less deviation than those of the previous work. Thus, it was confirmed that this study exhibited a relatively high level of accuracy.

TABLE-7
COMPARISON OF EXPERIMENTAL DATA AT
1,013 MBAR WITH PRESENT AND PREVIOUS DATA

Contents	Present data	Previous data	Experimental data
Boiling point of 1-propanol (℃)	97.22	96.60	97.30
Azeotropic temperature (°C)	-	85.16	85.45
Azeotropic composition	-	0.6647	0.6472
Boiling point of di-*n*-propyl ether (°C)	90.08	90.01	90.18

Vapor-liquid phase equilibrium experiments at 300 mbar: Based on the experimental findings at 1,013 mbar, a set of experiments were carried out at a low pressure of 300 mbar. Analogous to the experiments at atmospheric pressure, vapor and liquid samples were collected 21 times and the GC analysis was performed three times per sample. The experimental results at 300 mbar are shown in Table-8 and TXY phase equili-brium experimental data of di-*n*-propyl ether/1-propanol binary system are shown in Fig. 5.

The experimental results determined that the azeotropic composition at 300 mbar was 0.7682 and the azeotropic temperature was 52.61 °C. By comparing theses results with the results at 1,013 mbar, it was found that the azeotropic temperature decreased and the azeotropic composition increased when the system pressure was decreased. Accordingly, it was identified that the azeotropic point of di-*n*-propyl ether/1-propanol binary pair changes according to the pressure level.

TABLE-8
EXPERIMENTAL VAPOR-LIQUID EQUILIBRIUM
DATA FOR THE DI-*n*-PROPYL ETHER (1) AND
1-PROPANOL (2) SYSTEM AT 300 MBAR

No.	Temperature (°C)	x_1	y_1
1	68.45	0.0000	0.0000
2	68.36	0.0031	0.0096
3	66.38	0.0226	0.0964
4	63.91	0.0529	0.2134
5	61.75	0.0888	0.3133
6	60.80	0.1075	0.3596
7	58.94	0.1527	0.4438
8	56.93	0.2195	0.5319
9	55.58	0.2978	0.5883
10	54.88	0.3473	0.6167
11	54.35	0.3892	0.6377
12	53.89	0.4344	0.6595
13	53.32	0.5151	0.6873
14	52.93	0.5951	0.7126
15	52.79	0.6319	0.7245
16	52.73	0.6636	0.7362
17	52.63	0.7201	0.7561
18	52.60	0.8145	0.7798
19	52.72	0.8859	0.8299
20	53.28	0.9463	0.9032
21	54.54	1.0000	1.0000

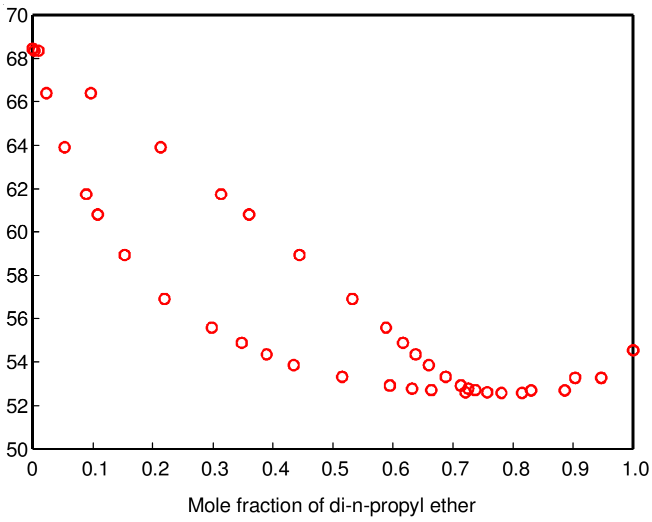


Fig. 5. TXY plot for experimental VLE data at 300 mbar

Thermodynamic data regression: In this study, the commercial chemical process simulator PRO/II with the PROVISION 9.1 program was utilized for the regression analysis of the experimental data. Liquid activity coefficient models such as UNIQUAC, NRTL and Wilson equations were adopted for the analysis. In PRO/II with PROVISION 9.1, binary interaction parameters for each LACT model are built-in, as shown in Table-9. Unfortunately, the embedded parameters led to poor vapor-liquid phase equilibrium calculations. A significant deviation between the results calculated from the built-in parameters and the experimental data obtained in this study was revealed, as shown in Fig. 6.

By performing the regression analysis using vapor-liquid phase equilibrium experimental data produced at 1,013 and 300 mbar, the binary interaction parameters of thermodynamic model equations were determined. The optimized parameters were obtained in such a way to minimize the object function

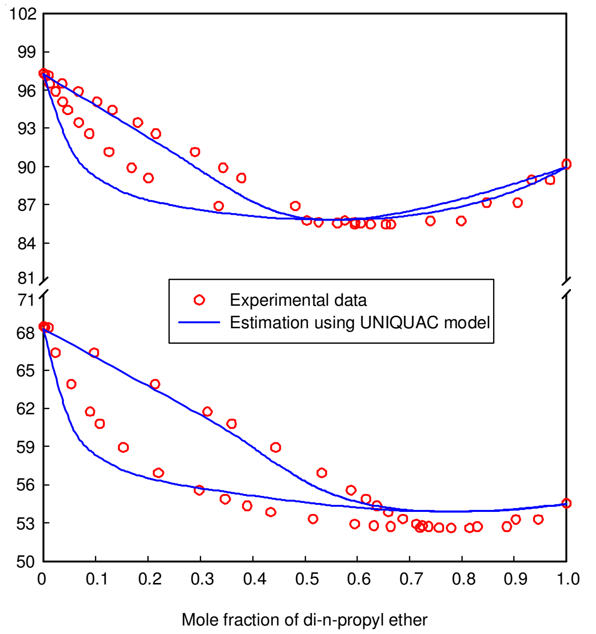


Fig. 6. Comparison of experimental data with calculated data using existing UNIQUAC parameter

TABLE-9
BINARY PARAMETERS BUILT IN PRO/II FOR DI-*n*-PROPYL ETHER(1) AND 1-PROPANOL(2) SYSTEM

Thermodynamic model	Parameters built in PRO/II
UNIQUAC	A_{12} = -21.0865 A_{21} = 200.4666
NRTL	B_{12} = -114.0849 B_{21} = 769.8521 α_{12} = 0.3
WILSON	A_{12} = 670.4239 A_{21} = 189.7614

(OF) defined in eqn. 3 as a form of relative deviation between the experimental K-values and the calculated K-values.

$$\text{Object function (OF)} = \sum_{i=1}^{2}\sum_{j=1}^{N}\left[\frac{K_{i,j,exp}-K_{i,j,cal}}{K_{i,j,exp}}\right]^2 \quad (3)$$

The binary parameters of each model obtained from the regression analysis are presented in Table-10. In addition, the azeotropic composition and temperature of each model were calculated through flash calculation using PRO/II; their results are summarized in Table-11 along with the experimental results. The UNIQUAC model is shown to estimate the azeotropic composition and temperature that are similar to the experimental results.

TABLE-10
REGRESSED BINARY PARAMETERS FOR DI-*n*-PROPYL ETHER(1) AND 1-PROPANOL(2) SYSTEM

Thermodynamic model	Regressed binary parameters
UNIQUAC	A_{12} = 886.1091 A_{21} = -353.618 B_{12} =- 1.76182 B_{21} = 0.784816
NRTL	B_{12} = 301.4776 B_{21} = 152.3047 α_{12} = 0.3
WILSON	A_{12} = -12.0442 A_{21} = 503.022

TABLE-11
AZEOTROPIC TEMPERATURE AND MOLE COMPOSITION OF DI-*n*-PROPYL ETHER

Pressure (mbar)	Thermodynamic model	Azeotropic temp. (°C)	Azeotropic comp.
1,013	Experimental	85.45	0.6472
	UNIQUAC	85.53	0.6496
	NRTL	85.15	0.6569
	WILSON	85.16	0.6573
300	Experimental	52.61	0.7682
	UNIQUAC	52.58	0.7813
	NRTL	52.79	0.7843
	WILSON	52.80	0.7917

For a more precise comparison, RMSD (root mean square deviation) and AAD % (average absolute deviation %) were calculated by using the experimental and calculated data. RMSD and AAD % are defined as in eqn. 4 and 5, respectively, where N and y_i represents the number of data and vapor mole fraction of component *i*. Results of RMSD and AAD % are summarized in Tables 12 and 13, respectively along with their existing embedded parameters.

$$\text{RMSD} = \sqrt{\frac{1}{N}\Sigma(y_i^{exp} - y_i^{cal})^2} \quad (4)$$

$$\text{AAD \%} = \frac{100}{N}\,|\,y_i^{exp} - y_i^{cal}\,| \quad (5)$$

TABLE-12
RESULTS OF RMSD CALCULATION

Pressure (mbar)	Thermodynamic model	RMSD (Existing)	RMSD (New)
1,013	UNIQUAC	0.06369	0.00877
	NRTL	0.06111	0.01171
	WILSON	0.07651	0.01218
300	UNIQUAC	0.08165	0.00858
	NRTL	0.08009	0.01433
	WILSON	0.09200	0.02878

TABLE-13
RESULTS OF AAD % CALCULATION

Pressure (mbar)	Thermodynamic model	AAD % (Existing)	AAD % (New)
1,013	UNIQUAC	5.137	0.748
	NRTL	4.969	0.997
	WILSON	5.923	0.873
300	UNIQUAC	6.690	0.621
	NRTL	6.662	1.233
	WILSON	7.374	2.134

It was clear that the accuracy of the calculated results was significantly enhanced when new parameters were used instead of the existing built-in parameters. Similar to the instance of the calculation of azeotropic composition and temperature, the UNIQUAC model also exhibited the smallest RMSD and AAD % values with the experimental results. The calculated results obtained using new parameters of the UNIQUAC model are compared with the experimental results in Fig. 7.

Conclusion

Herein, vapor-liquid phase equilibrium experiments for the di-*n*-propyl ether/1-propanol binary system were carried out at 1,013 and 300 mbar, respectively. The results showed

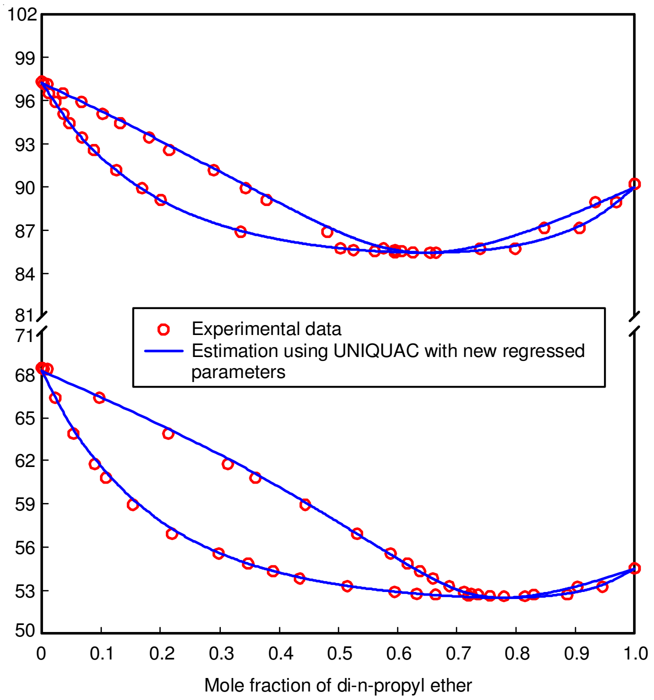


Fig. 7. Comparison of experimental data with calculated data using new parameters regressed by UNIQUAC model

that the azeotropic composition increased from 0.6472 to 0.7682 when the system pressure was reduced from 1,013 to 300 mbar. By performing regression analysis of the experimental results at atmospheric pressure and lower pressure, the interaction parameters of UNIQUAC, NRTL and WILSON models (based on the LACT method) were obtained. By calculating the vapor-liquid phase equilibrium using the new sets of parameters, higher accuracy results could be obtained compared with those using the parameters embedded in the PRO/II simulator. It was found that the UNIQUAC model provides the highest accuracy among various LACT models.

More accurate results can be obtained if the new interaction parameters achieved from this study are applied in the simulation of the di-*n*-propyl ether/1-propanol binary system. It would be very useful to obtain parameters of high accuracy by extending the application of the methodology reported here to other various binary systems.

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