Isobaric Vapor–liquid equilibrium for the binary system Diisopropylether + Isopropanol at 95 kPa

Ahmad T. Shawaqfeh
Chemical Engineering Department, Mutah University, Mutah Box 7, Karak 61710 JORDAN

Equilibrio isobárico líquido-vapor para el sistema binario Diisopropileter + isopropanol a 95 kPa.

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RESUMEN

Se han determinado los datos sobre el equilibrio isobárico líquido – vapor para el sistema binario compuesto por Diisopropil éter (1) y Isopropanol (2) a 95 kPa. Para ello se ha utilizado un aparato de destilación totalmente de vidrio, equipado con una bomba de circulación Cottrell. Este sistema se caracteriza por la formación de un azeótropo a $x_1 = 0.796$ al mínimo punto de ebullición. Datos VLE termodinámicamente coherentes correlacionan satisfactoriamente con el coeficiente de actividad de la fase líquida, utilizando los modelos NRTL, Wilson y UNIQUAC. Las predicciones del punto de burbuja y la composición de la fase vapor utilizando estos modelos fueron consistentes con las determinaciones experimentales. La desviación cuadrática media para el punto de burbuja y la fracción molar del vapor, utilizando los modelos NRTL, Wilson y UNIQUAC, fueron (0.6 K, 0.030), (0.5 K, 0.030), y (0.6 K, 0.028) respectivamente

Palabras clave: mezcla binaria, diisopropil éter (DIPE); datos VLE isobáricos; Isopropanol.

SUMMARY

Isobaric vapor–liquid equilibrium data have been measured for the binary system involved {Di-isopropyl Ether (1) + Isopropanol (2)} at 95 kPa. An all-glass re-circulating still equipped with a Cottrell circulation pump was used. The formation of an azeotrope was characteristic for this system at $x_1 = 0.796$ at the minimum boiling point. Thermodynamically consistent VLE data have been satisfactorily correlated using the NRTL, Wilson and UNIQUAC models for the activity coefficient of the liquid phase. The predictions of bubble point and vapor phase compositions using these models were close to experimental measurements. Root-Mean-Square-Deviation for bubble point and vapor mole fraction predictions were (0.6 K, 0.030), (0.5 K, 0.030), and (0.6 K, 0.028) when using NRTL, Wilson and UNIQUAC models, respectively.

Keywords: Binary mixture; Di-isopropyl ether (DIPE); Isobaric VLE data; Isopropanol

RESUM

S'han determinat les dades sobre l'equilibri isobàric líquid-vapor per al sistema binari format per Diisopropil èter (1) i Isopropanol (2) a 95 kPa. Per fer això s'ha utilitzat un aparell de destil·lació totalment de vidre, equipat amb una bomba de circulació Cottrell. Aquest sistema es caracteritza per la formació d'un azeòtrop a $x_1 = 0.796$ al mínim punt d'ebullició. Dades VLE termodinàmicament coherents correlacionen satisfactòriament amb el coeficient d'activitat de la fase líquida, utilitzant els models NRTL, Wilson i UNIQUAC. Les prediccions del punt de bombolla i la composició de la fase vapor utilitzant aquests models van ser consistents amb les determinacions experimentals. La desviació quadràtica mitjana per al punt de bombolla i la fracció molar del vapor, utilitzant els models NRTL, Wilson i UNIQUAC, van ser (0.6 K, 0.030), (0.5 K, 0.030), i (0.6 K, 0.028) respectivament.

Paraules clau: mescla binària, diisopropil èter (DIPE); dades VLE isobàriques; Isopropanol.

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*Corresponding author: Tel: (+962)323-72380(x-6113); Fax: (+962)323-72384; shawaqat@mutah.edu.jo

INTRODUCTION

Tertiary ethers with 5 or 6 carbons, like diisopropyl ether (DIPE), show excellent antiknock properties besides their less polluting effects. These compounds are becoming the preferred oxygenates for use in gasoline in order to improve its octane rating (Heese et al., 1999; Kinfton and Dai, 1999). DIPE is obtained by a reaction of propylene with isopropyl alcohol, which is initially produced by hydration of propylene. The ether purification involves extraction of alcohol with water. Information on the vapor–liquid equilibrium (VLE) is essential for development and design of equipment for separation processes. Therefore, phase equilibrium data of oxygenated mixtures are important for predicting the vapor phase composition in equilibrium with hydrocarbon mixtures. In many cases, the system formed by the ether and the homologous alcohol resulted in an azeotropic mixture (Gmehling and Blts, 1996; Lladosa et al., 2007). Experimental determination of VLE data involves temperature, pressure, and phase compositions. Correlation and prediction of VLE data refer to the relationship between compositions of each component in the coexisting phases.

Isothermal as well as isobaric vapor–liquid equilibrium data were reported in literature for binary and ternary systems involving DIPE and 2-propanol (Lladosa et al., 2007; Miller and Bliss, 1940; Verhoeye, 1970; Chamorro et al., 2002; Arce et al., 2003; Villamañán et al., 2006; Lladosa et al., 2006; Ku and Tu, 2006). Most of the isobaric VLE data of this system were reported at an adjusted standard pressure of 101.32 kPa. Different equations of state were used to calculate the nonideality of the vapor-phase. The thermodynamic consistency of the binary VLE data was examined by the direct test of Van Ness (Van Ness, 1995) and the method of Kojima et al. (Kojima et al., 1990). The VLE data of the ternary system passed the thermodynamic consistency test of the McDermott–Ellis method as modified by Wisniak and Tamir (McDermott and Ellis, 1965; Wisniak and Tamir, 1977). Activity coefficients of both the binary and the ternary systems were satisfactorily correlated by Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) models.

The objective of the present study is to measure experimentally the VLE behavior of the DIPE + Isopropanol binary system; at an ambient pressure of 95 kPa. The experimental data will then be analyzed and correlated using Wilson, NRTL and UNIQUAC models. Predictions will then be compared with the experimental data.

EXPERIMENTAL

Chemicals

All chemicals used in this study were of high-purity grade purchased from Aldrich. The purity of all chemicals was greater than 99.8% as validated for each one by using gas chromatograph. These chemicals were used without further purification.

Apparatus and Procedure

The vapor–liquid equilibrium apparatus used in this work is depicted in Figure 1. It is mainly an all-glass re-circulating still in which both liquid and vapor phase are continuously re-circulated. It was equipped with Cottrell circulation pump to ensure continuous and intimate contact between liquid and vapor phases during boiling as well as their contact with the temperature sensing element. The equilibrium temperature was measured with a Beckman thermometer with uncertainty of ±0.02 K. The ambient pressure was measured using a manometer with uncertainty of ±0.3 kPa. The experimental procedure was described elsewhere (Darwish and Al-Anbar, 1997). When equilibrium was reached, liquid and vapor-condensed phase were sampled and their compositions were analyzed using gas chromatograph (Varian® CP-3800, column temperature 333.2 K, injector temperature 493.2 K, detector temperature 503.2 K, flow rate 30 ml.min^{-1}). Experimental uncertainties in liquid and vapor mole fractions were estimated as ±0.001.

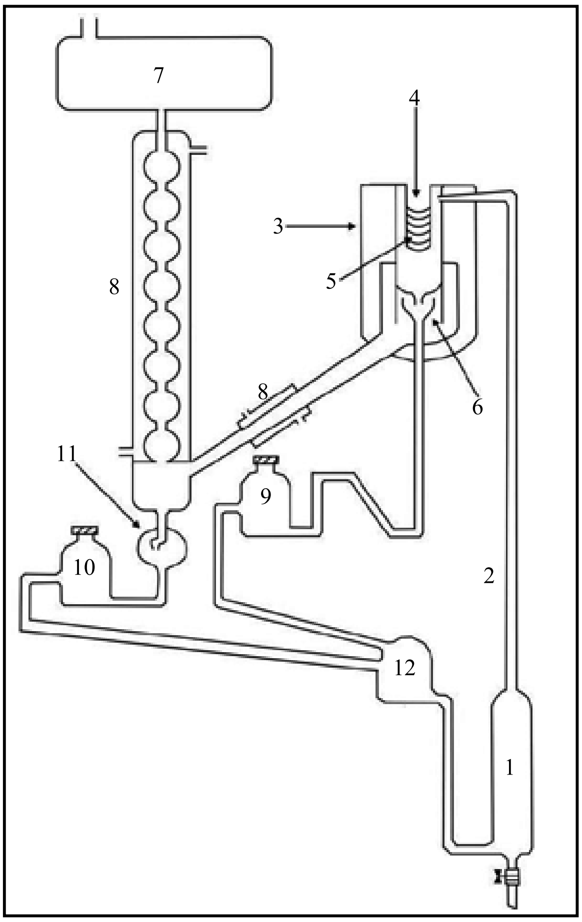

Figure 1: Scheme of the experimental setup for the measurement of vapor-liquid equilibrium. 1, boiler; 2, Cottrell pump; 3, separation still; 4, thermowell; 5, spiral; 6, separation cup; 7, pressure damper; 8, heat exchanger; 9, liquid sampling; 10, vapor sampling; 11, drop counter; 12, mixing chamber.

RESULTS AND DISCUSSION

The following equation was used to calculate activity coefficient for each component using the experimental VLE data. The nonideality of vapor phase was calculated using the virial equation of state

$$\gamma_i = \frac{Py_i}{P_i^s x_i} \quad \left[\frac{(B_{ii} - v_i^L)(P - P_i^s) + (1 - y_i)^2 P\delta_{ij}}{RT} \right] \tag{1}$$

where γ_i is the liquid-phase activity coefficient of component *i*, x_i and y_i are the experimental values of the liquid and vapor-phase compositions, *P* is the total pressure, and $\delta_{ij} = 2B_{ij} - B_{ii} - B_{jj}$ .The pure liquid molar volume v_i^L was calculated using the modified Rackett equation (Spencer and Danner, 1972). The vapor pressures P_i^s of pure compounds were calculated using Antoine's equation. The second virial coefficient of pure materials B_{ii} and cross second virial coefficients B_{ij} were calculated according to the method of Hayden and O'Connell (Hayden and O'Connell, 1975).

The experimental values of liquid and vapor phases compositions, x_i and y_i, and equilibrium temperatures, *T*, for the binary system DIPE (1) + Isopropanol (2) are presented in Table 1. The same table shows values of activity coefficients as were calculated using Eq. (1) with the experimental values of temperatures and mole fractions.

Table 1: Experimental VLE data for Diisopropyl Ether (1) + Isopropanol (2) system at *P*=95 kPa.

x_1	y_1	T (K)	γ_1	γ_2
0.000	0.000	352.8	-	1.042
0.0263	0.0483	351.6	1.298	1.068
0.0584	0.100	350.6	1.246	1.086
0.122	0.249	347.4	1.615	1.106
0.146	0.376	345.6	2.156	1.017
0.193	0.445	343.8	2.034	1.031
0.208	0.465	342.8	2.028	1.056
0.233	0.523	342.2	2.073	0.997
0.277	0.538	341.4	1.836	1.060
0.366	0.617	339.3	1.696	1.098
0.506	0.695	338.7	1.411	1.148
0.651	0.749	337.6	1.221	1.406
0.716	0.772	337.2	1.159	1.595
0.776	0.782	336.8	1.096	1.972
0.823	0.799	336.8	1.056	2.299
0.922	0.892	337.0	1.046	2.769
0.986	0.971	337.6	1.046	3.878
1.000	1.000	338.6	1.029	-

The azeotropic composition was determined by finding the value of x_1 that make the function $f(x_1) = (y_1 - x_1)$ equal to zero. The composition and boiling temperature of the azeotrope are summarized in Table 2, together with the corresponding literature values (Lladosa et al., 2007). Azeotropic temperature was obtained from the best polynomial fit for $T=f(x_1)$, using the x_1 values previously determined. One can observe from Table 2 the strong dependency of azeotropic composition and temperature on pressure as well the consistency of our results with those reported in the literature.

Table 2: *Azeotropic compositions and temperatures for the system Diisopropyl Ether (1) + Isopropanol (2) at different pressures.*

P (kPa)	*T* (K)		x_1	
	This work	(Lladosa et al., 2007)	This work	(Lladosa et al., 2007)
30		307.3		0.906
95	336.9		0.796	
101.3		339.1		0782

The experimental data were analyzed and assessed for thermodynamic consistency by applying the Herington area test (Herington, 1951). According to this test the ratio of the experimental activity coefficients was plotted against the liquid mole fraction of DIPE, x_1, on a semi-logarithmic scale. The following parameters were defined as

$$D = \frac{I - II}{I + II} \times 100 \qquad (2)$$

$$J = \frac{T_2 - T_1}{T_{\min}} \times 150 \qquad (3)$$

where I and II are the areas above and below the zero axis, respectively. T_1, T_2, and T_{min} are the boiling points of pure 1 and 2, and the lowest boiling point observed in the entire composition range, respectively (all in Kelvin). Figure 2 shows the plot of (γ_1/γ_2) versus x_1, where D is calculated as -3.45 and J was 6.32. Herington showed that if |D| -J < 10, the data will be consistent. Numerically, this difference equal to -2.87 which confirms the thermodynamic consistency of the experimental data.

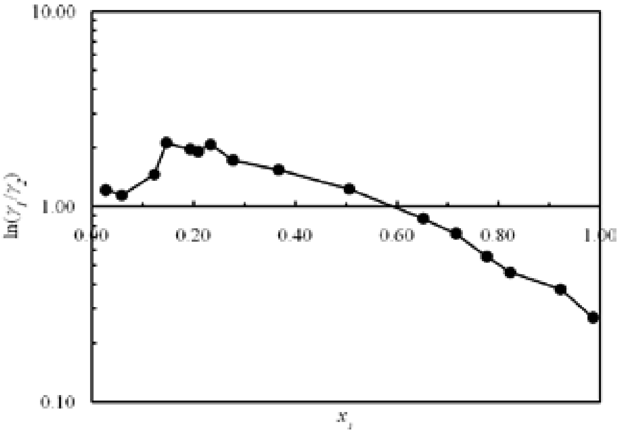

Figure 2: *Thermodynamic consistency area test of VLE data for the diisopropyl ether (1) + isopropanol (2) system at P= 95 kPa as proposed Herington (Herington, 1951).*

The VLE data presented by this work at 95 kPa were compared with those in the literature at atmospheric pressure for the same system. Figures 3 and 4 show these comparisons for equilibrium compositions, and temperatures, respectively. Both figures show similar trend for the variation with mole fraction. However, the comparison showed that the effect of pressure was evident in lowering the equilibrium temperature and increasing the azeotropic composition. This effect was confirmed by the results presented in Table 2.

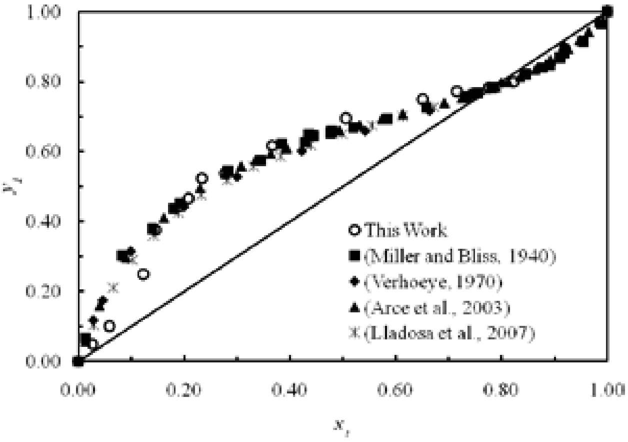

Figure 3: *Comparison of experimental x,y equilibrium data for diisopropyl ether (1) in the diisopropyl ether (1) + isopropanol (2) solution. Measurements of this work were at P= 95 kPa, while the literature data were at P= 101.3 kPa*

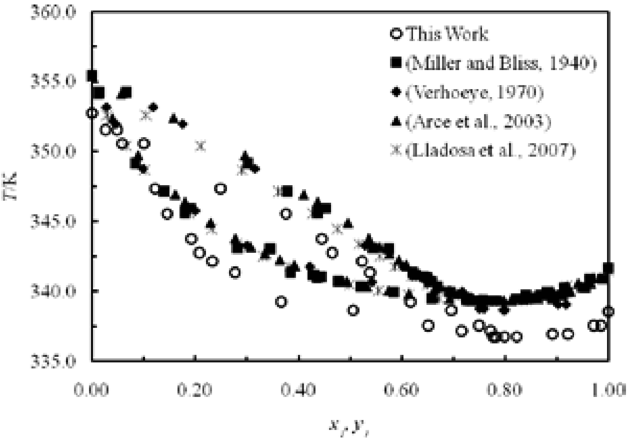

Figure 4: *Comparison of experimental (T, x, y) equilibrium data for diisopropyl ether (1) in the diisopropyl ether (1) + isopropanol (2) solution. Measurements of this work were at P= 95 kPa, while the literature data were at P= 101.3 kPa.*

The activity coefficients were correlated with the NRTL, Wilson and UNIQUAC models. Estimation of parameters for each model was based on maximum likelihood principles as developed by Prausnitz (Prausnitz, 1969). Regression based on this principle requires the estimated uncertainties, σ^2, in each measured variables. In this study, the following uncertainties were used: 0.3 kPa in pressure, 0.1 K in temperature, 0.001 in liquid mole fraction, and 0.003 in vapor mole fraction (Walas, 1985). The effective binary interaction parameter A_{ij} for the models NRTL, Wilson, and UNIQUAC are defined by $A_{ij} = (g_{ij} - g_{jj})$, $A_{ij} = (a_{ij} - a_{ii})$ and $A_{ij} = (u_{ij} - u_{jj})$, respectively. The relevant parameters obtained from the correlation of experimental data using model equations were presented in Table 3 for each model. These regressed parameters were used in predicting activity coefficients. Then, the equilibrium vapor phase composition and temperature were calculated corresponding to the measured pressure and liquid phase compositions.

Table 3: *Estimated values of binary interaction parameters A_{12} and A_{21} in the NRTL (α_{12}=0.30), Wilson, and UNIQUAC models for the system Diisopropyl Ether (1) + Isopropanol (2) at P=95 kPa.*

Model	A_{12} (J•mol^{-1})	A_{21} (J•mol^{-1})
NRTL, α_{12}= 0.30	1682.5	-192.2
Wilson	-415.1	2474.4
UNIQUAC	3136.7	-533.8

Figures 5 and 6 show the predicted values versus the experimentally measured values of temperature and vapor phase composition of DIPE, respectively. The results presented in these figures indicate the ability of the three models in describing the phase behavior of DIPE + Isopropanol system. The good agreement of the predicted results with the experimental ones was evident from Figures 7 and 8. These figures show the temperature and vapor phase composition deviations for the three models from the experimental ones.

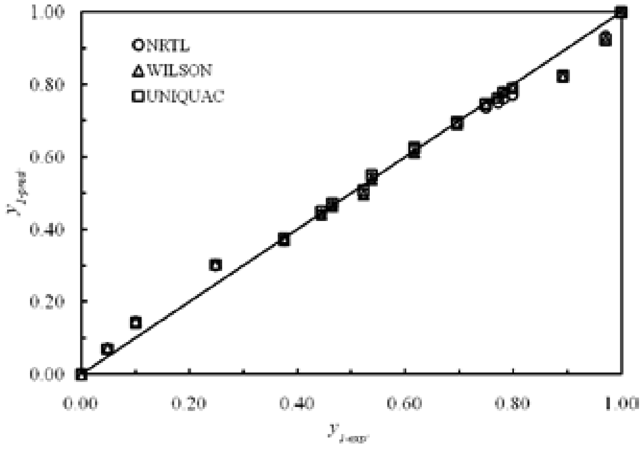

Figure 5: *Comparison between the calculated and measured mole fractions of diisopropyl ether in the vapor phase for the system diisopropyl Ether (1) + isopropanol (2) at P=95 kPa.*

The root mean square deviations (RMSD) were calculated from the difference between the experimental data and the calculated values for each model according to the following equation:

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

where N is the number of experimental data points, $y_i^{\exp}$ and y_i^{cal} are the experimental and calculated vapor-phase mole fractions, respectively. The RMSD values for the DIPE (1) + Isopropanol (2) binary system are tabulated in Table 4. These results show that the deviations in vapor phase compositions and equilibrium temperatures are reasonably small, and it is indicated that the activity coefficient for all three models are suitable to represent the binary experimental data.

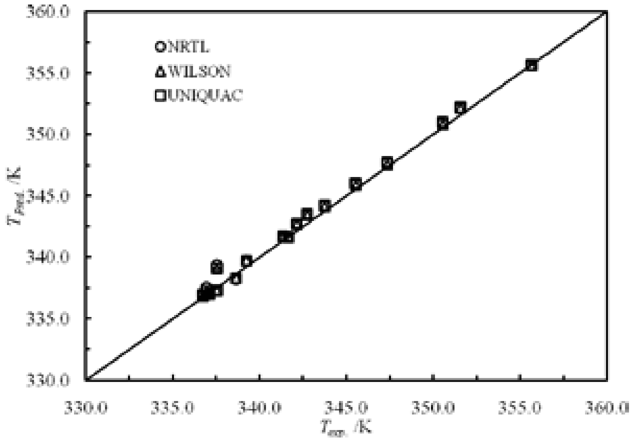

Figure 6*: Comparison between the calculated and measured bubble point temperatures for the system diisopropyl ether (1) + isopropanol (2) at P=95 kPa.*

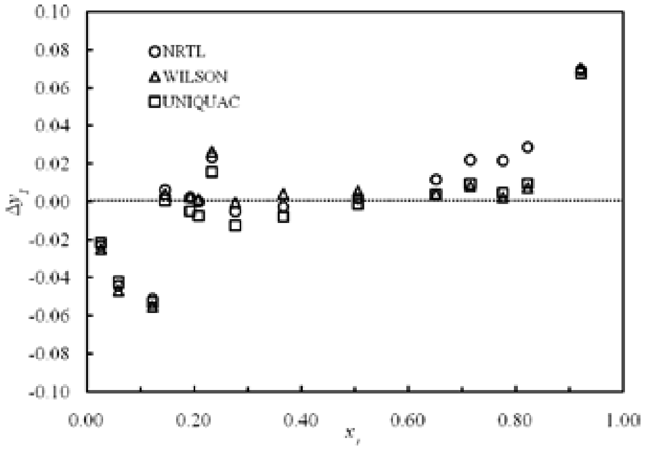

Figure 7*: Deviation Δy1 =y(exptl.) - y(calcd.) between the calculated and measured mole fractions of diisopropyl ether in the vapor phase for the system diisopropyl ether (1) + isopropanol (2) at P=95 kPa.*

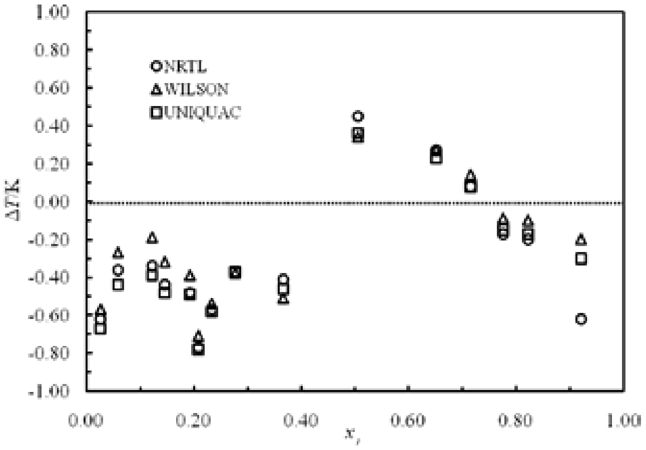

Figure 8*: Deviation ΔT/K =T(exptl.)/K - T(calcd.)/K between the calculated and measured bubble point temperatures for the binary system diisopropyl ether (1) + isopropanol (2) at P=95 kPa.*

Table 4: *Root mean square deviation (RMSD) for vapor phase composition and bubble point temperature predictions by the NRTL (α_{12}=0.30), Wilson, and UNIQUAC models for the system Diisopropyl Ether (1) + Isopropanol (2) at P=95 kPa.*

Models	y_{RMSD}	T_{RMSD} (K)
NRTL, α12= 0.30	0.030	0.63
Wilson	0.030	0.53
UNIQUAC	0.028	0.58

CONCLUSIONS

The experimentally measured VLE data for {DIPE (1) + Isopropanol (2)} binary system were successfully correlated using NRTL, Wilson, and UNIQUAC model equations. Results showed that the calculated parameters were fitted adequately by these models. Deviations of predictions of these equations were reasonably small and of similar order of magnitude. Azeotropic conditions were consistent with the literature findings and confirm sensitivity of these conditions to the pressure of the system. Based on these results, these models could be used equivalently to describe the VLE for the {DIPE (1) + Isopropanol (2)} system. They meet the need for the design and operation of separation processes.

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List of Symbols

B_{ii}	second virial coefficient of component *i* (m^3/mol)
B_{ij}	cross virial coefficient of components *i* and *j* (m^3/mol)
D	area ratio in Herington area test method
g	characteristic energy (J mol^{-1})
J	boiling temperature ratio defined by Herington area test method
P	system total pressure (kPa)
P_i^s	saturation vapor pressure of the pure liquid *i* (kPa)
R	gas constant (8.314 J mol^{-1} K^{-1})
T	equilibrium boiling temperature (K)
x_i	mole fraction of component *i* in the liquid phases
y_i	mole fraction of component *i* in vapor phases

Greek symbols

α	adjustable parameter in NRTL model
γ_i	activity coefficient of component *i* in the liquid phase
v_i^L	molar volume of pure liquid component *i* (m^3/mol)

Superscripts

cal	calculated results
exp	experimental results
L	Liquid
s	saturated
Subscripts	
i, j	component

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