Prediction of Liquid-Liquid Equilibria of Binary Systems Containing Alcohols Using EoS-G^E Models

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Abstract

In this work, the equation of state-excess Gibbs energy (EoS-G^E) model has been employed to predict Liquid-Liquid Equilibria (LLE) of some binary mixtures at 0.1 MPa. Three binary systems containing Decane+Methanol, Cyclohexane+Methanol and Cyclohexane+2,2,2-Trifluoroethanol (TFE) have been tested using Peng–Robinson EoS modified by Stryjek and Vera (PRSV), along with the excess Gibbs mixing rules MHV1 and MHV2 and two excess Gibbs models: Wilson equation modified by Tsuboka and Katayama (T–K–Wilson) and UNIQUAC equation. The interaction parameters of T-K-Wilson and UNIQUAC G^E models for three binary systems have been determined from LLE data points at 0.1 MPa. The prediction ability of the models has been evaluated by comparison of the results with experimental data. Average Absolute Error (AAE) of 0.047 for MHV1 and T–K–Wilson model, 0.0117 for MHV2 and T–K–Wilson model, 0.0317 for MHV1 and UNIQUAC model and 0.0109 for MHV2 and UNIQUAC model have been obtained. As it is clear, the combination of MHV2 excess Gibbs mixing rule with UNIQUAC equation shows a satisfactory agreement with experimental data.

Keywords: *EoS, Mixing Rule, Liquid–Liquid Equilibria, Excess Gibbs Energy*

1- Introduction

Nowadays scientists are keenly devoted to providing new solvent mixtures and energetic fluids with clean and safe characteristics. 2,2,2-Trifluoroethanol (TFE) is an environmentally friendly, novel and clean energetic fluid source with good chemical and thermal stability which shows characteristics of solvation [1]. TFE (commercially called fluorinol) and its solvent mixtures have been proposed and tested as organic working fluids in high-temperature absorption heat pumps and heat transformers [2]. Cyclohexane, partially soluble in TFE, occurs naturally in crude oil and has large industrial applications: nylon and rubber manufacturing, varnish and paint remover and a dehydrating solvent for alcohols, whether obtained from fermentation or synthetic processes [1].

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Due to the rising cost of energy, new separation processes based on extraction are becoming attractive. Many pairs of liquids of industrial importance have limited mutual solubility. Liquid–Liquid Equilibrium (LLE) data are essential when considering separation processes. Recently, LLE data for wide pressure and temperature ranges have become necessary because of the diversification of separation processes. One of the common approaches for modeling LLE is to use the equation of state-excess Gibbs energy (EoS-G^E) model that combines the EoS with the excess Gibbs energy (G^E) at a particular standard state. A particularly useful equation for G^E, applicable to a wide variety of liquid mixtures, has been given by Abrams and Prausnitz [3], named UNIQUAC. The combination of EoS, mainly cubic ones, with excess Gibbs free energy (G^E) models originated from the pioneering work of the late Vidal [4], represents a major development in the field of chemical engineering thermodynamics, for it expands the successful performance of cubic EoS in the field of the non-polar systems to that of polar ones. Vidal's work is followed by the Huron and Vidal model [5], which coupled the SRK EoS with the NRTL model at infinite reference pressure.

The attempt of this work is to use MHV1 and MHV2 mixing rules and modified Peng-Robinson (PR) EoS coupled with two excess Gibbs energy models: modified Wilson equation (T–K–Wilson) proposed by Tsuboka and Katayama [6] and UNIQUAC equation for calculating LLE in Decane + Methanol, Cyclohexane + Methanol and Cyclohexane + TFE systems at 0.1 MPa.

2- Thermodynamic model

In this study, we have used PR EoS modified by Stryjek and Vera (PRSV) [7]:

$$P = \frac{RT}{V-b} - \frac{a}{V^2 - 2bCV - b} \tag{1}$$

with:

$$a(T) = 0.457235 (\frac{R^2 T_c^2}{P_c}) \alpha(T) \tag{2}$$

$$b = 0.077796 (\frac{RT_C}{P_C}) \tag{3}$$

$$\alpha(T) = (1 + k(1 - T_r)^{0.5})^2 \tag{4}$$

$$k = k_0 + k_1(1 - T_r^{0.5})(0.7 - T_r) \tag{5}$$

$$k_0 = 0.378893 + 1.489715\,\omega - 0.17131\,\omega^2 + 0.01965\,\omega^3 \tag{6}$$

where ω is the acentric factor, and k_1 is a specific parameter for each compound used to accurately fit its low temperature saturation pressures. The parameters $T_{c,i}$, $P_{c,i}$ and ω_i, necessary for calculating pure component parameters, and a_{ii} and b_i of PRSV EoS, have been shown in Table 1. Two EoS-G^E models, the MHV1 and MHV2 by Michelsen [8] have been applied for calculating the mixture parameters a and b which are defined as follows:

$$q_1 (\alpha_{mix} - \sum_{i=1}^{C} Z_i \alpha_i) = \frac{g_0^E}{RT} + \sum_{i=1}^{C} Z_i \ln(\frac{b}{b_i}) \tag{7}$$

$$q_1 \left(\alpha_{mix} - \sum_{i=1}^{C} Z_i \alpha_i \right) + q_2 \left(\alpha_{mix}^2 - \sum_{i=1}^{C} Z_i \alpha_i^2 \right)$$

$$= \frac{g_0^E}{RT} + \sum_{i=1}^{C} Z_i \ln(\frac{b}{b_i}) \tag{8}$$

$$b = \sum_i x_i b_i \tag{9}$$

Equations 7 and 8 show MHV1 and MHV2 mixing rules, respectively. In these equations the parameter α is defined as:

$$\alpha = \frac{a}{bRT} \tag{10}$$

The partial derivatives of na, nb and nG^E with respect to composition and fugacity coefficient have been given in the Appendix. In the MHV1 model, a value of $q_1 = -0.53$ has been used as suggested by Michelsen [8] for PR EoS. The values of $q_1 = -0.4347$ and $q_2 = -0.003654$ suggested by Huang and Sandler [9] have been employed in the MHV2 model. The MHV1 and MHV2 models include excess Gibbs energy at zero pressure, g_0^E. One of the G^E models is the modified Wilson equation proposed by Tsuboka and Katayama (T–K–Wilson) [6]:

$$\frac{G^E}{RT} = \sum_i x_i \ln \frac{\sum_j (v_j^L / v_i^L) x_j}{\sum_k x_k \Lambda_{ik}} \tag{11}$$

where

$$\Lambda_{ij} = \frac{v_j^L}{v_i^L} \exp\left[-\frac{\lambda_{ij} - \lambda_{ii}}{RT} \right] \tag{12}$$

In these equations, v_i^L is the liquid molar volume of the pure component i calculated by means of the modified Rackett equation [16]:

$$v_i^L = \frac{RT_{c,i}}{P_{c,i}} Z_{RA,i}^{\left[1 + (1 - T_{r,i})^{2/7}\right]} \tag{13}$$

The parameter $Z_{RA,i}$ has been given in Table 1. In the UNIQUAC model, G^E is split into the combinatorial and residual terms [18]:

$$\frac{G^E}{RT} = \frac{G^E(combinatorial)}{RT} + \frac{G^E(residual)}{RT} \tag{14}$$

Where

$$\frac{G^E(combinatorial)}{RT} = x_1 \ln \frac{\varphi_1}{x_1} + x_2 \ln \frac{\varphi_2}{x_2}$$

$$+ (\frac{Z}{2})(q_1 x_1 \ln(\frac{\theta_1}{\varphi_1}) + q_2 x_2 \ln(\frac{\theta_2}{\varphi_2})) \tag{15}$$

Table 1. Pure component critical data, acentric factor ω, Z_{RA} and PRSV k_1 used in the calculations.

Component	Tc(K)	Pc (KPa)	ω	k_1	Z_{RA}
Methanol	512.6[a]	8090[a]	0.556[a]	-0.1682[c]	0.2318[e]
Cyclohexane	553.5[a]	4070[a]	0.212[a]	0.0702[c]	0.2729[e]
2,2,2Trifluoroethanol	499.3[b]	4870[b]	0.635[b]	0.1209[d]	0.2348[f]
Decane	617.5[g]	2110[g]	0.490[g]	0.0451[g]	0.2507[h]

[a]Reid et al. [10], [b]Z. Atik [2], [c]Stryjek and Vera [7], [d]Orbey and Sandler [11], [e]Spencer and Danner [12], [f]$Z_{RA} = 0.29056 - 0.08775\omega$, Yamada and Gunn [13], [g]J. A. Lopez, C. A. Cardona [14], [h]H. Matsuda, K. Ochi [15].

and

$$\frac{G^E\,(\,residual\,)}{RT} = -q_1 x_1\, ln[\,\theta_1 + \theta_2 \tau_{21}] \qquad (16)$$
$$-q_2 x_2\, ln[\,\theta_2 + \theta_1 \tau_{12}]$$

The binary interaction parameter, τ_{ij}, is given by the following expression:

$$\tau_{ij} = \exp\left\{-\left[\frac{u_{ij} - u_{jj}}{RT}\right]\right\} \qquad (17)$$

The average area fraction, θ, and the average segment fraction, ϕ, is given by [3]:

$$\theta_1 = \frac{x_1 q_1}{x_1 q_1 + x_2 q_2} \qquad (18)$$

and

$$\phi_1 = \frac{x_1 r_1}{x_1 r_1 + x_2 r_2} \qquad (19)$$

where r and q, shown in Table 2, are the van der Waals volume and area parameters of molecule i calculated through group contribution increments and x is the mole fraction of component i. The first derivative of G^E is needed for calculation of the fugacity coefficient, and so for PRSV the equation of state has been given in the Appendix. The temperature dependence of binary interaction parameters $\lambda_{ij} - \lambda_{ii}$ and $u_{ij} - u_{jj}$, can be expressed by the following equations suggested by Escobedo-Alvarado and Sandler [17]:

$$u_{ij} - u_{jj} = A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \qquad (20)$$

and

$$\lambda_{ij} - \lambda_{ii} = A_{ij} + B_{ij}T + \frac{C_{ij}}{T} \qquad (21)$$

Table 2. The van der Waals volume and area parameters

Component	UNIQUAC Parameters		Reference
	r	q	
Methanol	1.431	1.430	[18]
Cyclohexane	4.046	3.240	[1]
TFE	2.610	2.504	[1]
Decane	7.197	6.016	[19]

3- Results and discussion

In this work, the LLE data at 0.1 MPa have been directly correlated using the T–K–Wilson and UNIQUAC equation with flash calculations between two liquid phases. Compositions at liquid–liquid equilibrium have been employed from various references to determine A_{ij}, B_{ij}, and C_{ij} in Eqs. (20) and (21). These binary parameters are directly fitted so that the objectives function:

$$F_{obj} = \sum_{k=1}^{NDP}\left[(x^{\mathrm{I}}_{1,exp} - x^{\mathrm{I}}_{1,calc})_k^2\right.$$
$$\left. + (x^{\mathrm{II}}_{1,exp} - x^{\mathrm{II}}_{1,calc})_k^2\right] \qquad (22)$$

has been minimized for each binary system at 0.1 MPa. In this equation, x^{I} and x^{II} are mole fractions of two phases. The estimated values of A_{ij}, B_{ij} and C_{ij} for the calculation of $\lambda_{ij} - \lambda_i$ in T–K–Wilson, and $u_{ij} - u_{jj}$ in UNIQUAC equations, have been listed in Table 3.

Table 3. Fitted T-K-Wilson and UNIQUAC parameters for three binary systems.

| System	Parameters	T-K-Wilson		UNIQUAC	
		ij=12	ij=21	ij=12	ij=21
Cyclohexane (1)-Methanol (2)	$A_{ij}(Jmol^{-1})$	$3.511403×10^4$	$-5.910371×10^4$	$1.195376×10^4$	$-1.250617×10^4$
	$B_{ij}(Jmol^{-1}K^{-1})$	$-6.9812043×10$	$9.0511213×10$	$-2.4774876×10$	$1.8337865×10$
	$C_{ij}(Jmol^{-1}K)$	$-4.1876199×10^6$	$1.2016354×10^7$	$2.156704×10^5$	$2.118772×10^6$
Cyclohexane (1)-TFE(2)	$A_{ij}(Jmol^{-1})$	$-6.319678×10^4$	$-6.647862×10^4$	$1.462271×10^4$	$-1.122927×10^4$
	$B_{ij}(Jmol^{-1}K^{-1})$	$8.7997614×10$	$1.082553×10^2$	$-2.2263885×10$	$1.7289490×10$
	$C_{ij}(Jmol^{-1}K)$	$1.282609×10^7$	$1.250454×10^7$	$-2.620608×10^6$	$1.388552×10^6$
Methanol (1)-Decane (2)	$A_{ij}(Jmol^{-1})$	$-1.410595×10^5$	$4.746543×10^4$	$2.0305878×10^4$	$-5.701979×10^4$
	$B_{ij}(Jmol^{-1}K^{-1})$	$2.093436×100$	$-8.657072×10$	$-3.117918×10$	$7.752136×10$
	$C_{ij}(Jmol^{-1}K)$	$2.623824×10^7$	$-7.075005×10^6$	$-3.260619×10^7$	$1.2201739×10^7$

Predictions of the LLE at 0.1 MPa for three binary systems are made in order to examine two mixing rules, MHV1 and MHV2 combined with two G^E models, T-K-Wilson and UNIQUAC. Liquid-liquid flash calculations are performed for these calculations. The values of Table 3 are applied directly to the binary interaction parameters of T–K–Wilson and UNIQUAC equations.

The activity of cyclohexane in the binary system of cyclohexane-methanol calculated using T-K-Wilson and UNIQUAC equations has been plotted versus composition in Fig. 1. As it is clear in this figure, the activity of cyclohexane approaches unity with the increase of its mole fraction, which demonstrates the validity of the calculations.

In Fig. 2, the results of the predicting model for liquid-liquid equilibria in Methanol-Decane binary system at 0.1 MPa has been compared with the experimental data of Higashiuchi [21] and Matsuda [15]. As shown in Fig. 2, a reasonable agreement has been observed between the model prediction

and the literature experimental data.
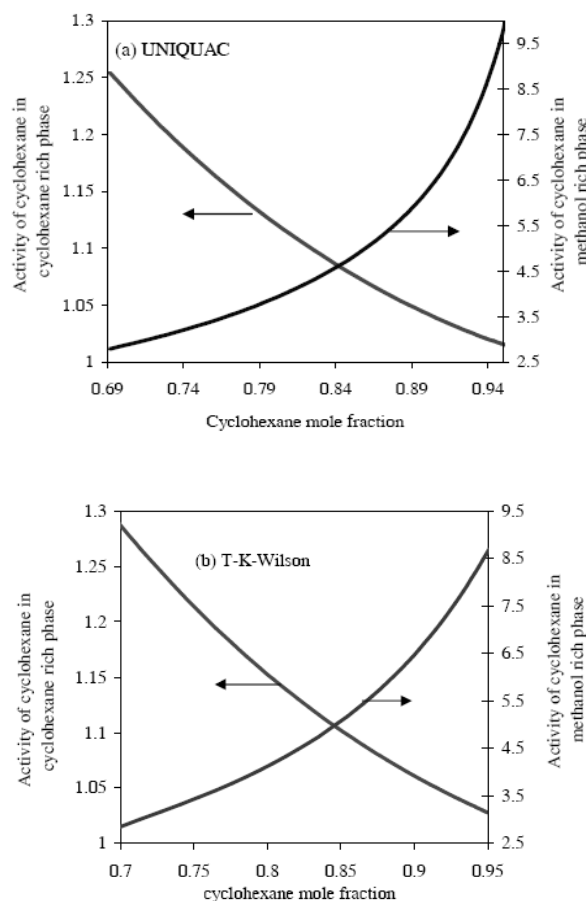
Figure 1. The activity of cyclohexane in system of cyclohexane(1) + methanol(2) phase (a) UNIQUAC equation (b) T-K-Wilson equation.
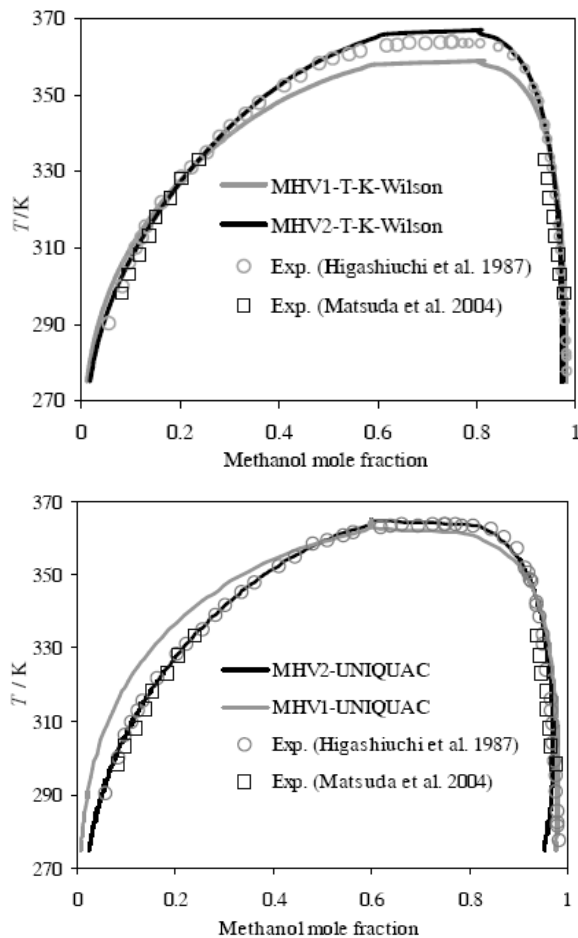
Figure 2. The predicted results for liquid-liquid equilibria at 0.1 MPa for Methanol (1)+ Decane(2). (—) MHV1 mixing rule, (—) MHV2 mixing rule,(□) exp. from Ref. [15], (O) exp. from Ref. [21].

In Fig. 3, the results of the predicting model for liquid-liquid equilibria of Cyclohexane-Methanol binary system have been compared with the experimental data of Atik [20] and Matsuda [22]. A reasonable agreement between the model prediction and the literature experimental can be observed.

Fig. 4 presents the results of the predicting model for liquid-liquid equilibria of the Cyclohexane-TFE binary system and their comparison with the experimental data of Atik [20].
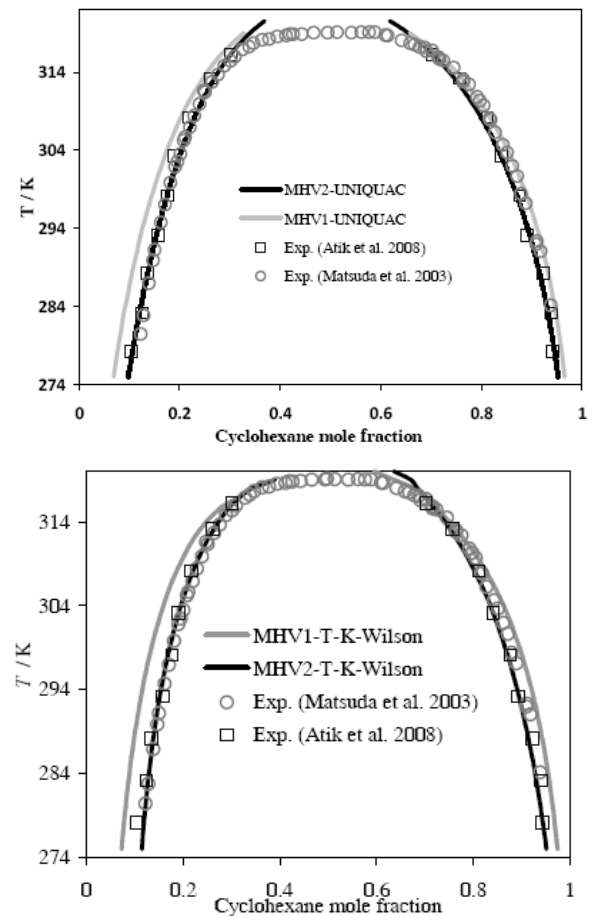
Figure 3. The predicted results of liquid–liquid equilibria at 0.1 MPa for Cyclohexane (1) + Methanol (2). (—) MHV1 mixing rule, (—) MHV2 mixing rule, (O) exp. from Ref. [22], (□) exp. from Ref. [20].

Table 4 shows the absolute average error between LLE experimental data for three binary systems and the prediction of four models containing MHV1 and T–K–Wilson, MHV2 and T–K–Wilson, MHV1 and UNIQUAC, and MHV2 and UNIQUAC models in specified temperature ranges. As it is clear, a reasonable agreement between the model prediction and the literature experimental data has been observed and the MHV2 excess Gibbs mixing rule with UNIQUAC equation Gibbs models have shown a satisfactory agreement with the experimental data.
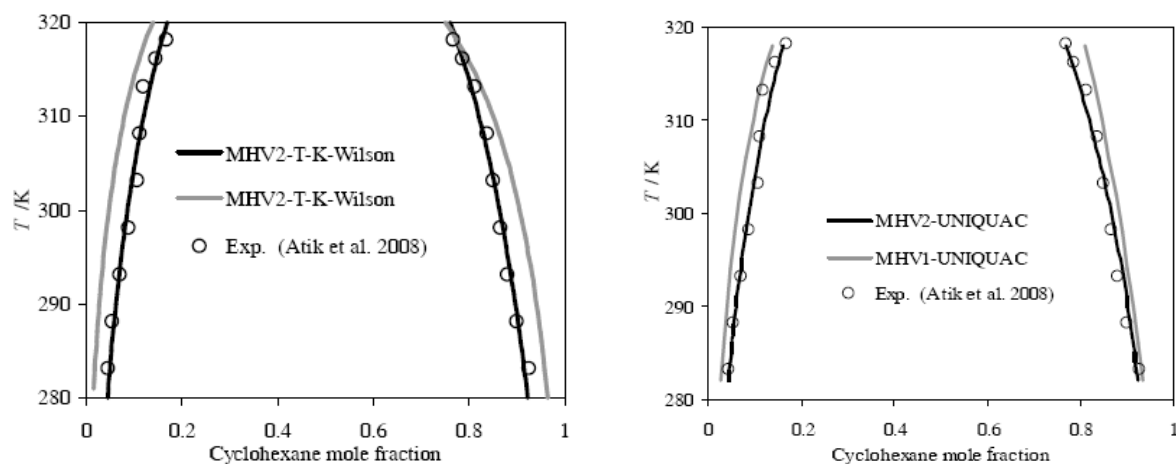
Figure 4. The predicted results of liquid–liquid equilibria at 0.1 MPa for Cyclohexane (1) + TFE (2). (——) MHV1 mixing rule, (——) MHV2 mixing rule, (O) exp. from Ref. [20].

Table 4. The predicted results of liquid–liquid equilibria at 0.1 MPa using MHV1, MHV2.

System	T-range/K	$\|\Delta x_1\|_{ave}$ [a]				Data source	[b]NDP
		MHV1 T-K-Wilson	MHV2 T-K-Wilson	MHV1 UNIQUAC	MHV2 UNIQUAC		
Cyclohexane (1)-Methanol (2)	278.15-316.15[c]	0.0262	0 .0053	0.0194	0.0054	[20]	9
	280.45-318.18 & 284.14-317.65[d]	0.0237	0.0094	0.0194	0.0104	[22]	28
Cyclohexane(1)-TFE(2)	283.15-318.15[c]	0 .0487	0.0058	0.0155	0.0012	[20]	9
Methanol(1)-Decane(2)	290.24-363.16 & 277.74-357[d]	0.0498	0 .0093	0.0246	0 .0075	[15]	22
	298.15-333.15[c]	0.0134	0.008	0.0390	0.0090	[21]	8

$$^a\left|\Delta x_1\right|_{ave} = \frac{1}{2NDP}\sum_{k=1}^{NDP}\left(\left|x^I_{1,calc.} - x^I_{1,exp.}\right|_k + \left|x^{II}_{1,calc.} - x^{II}_{1,exp.}\right|_k\right)$$

x_1^I =mole fraction in phase 1.

x_1^{II} = mole fraction in phase 2.

[b]Number of Data Points.

[c]This temperature range is for both phases

[d]These temperature ranges are for two separate phases.

4- Conclusions

In this study, the interaction parameters A_{ij}, B_{ij} and C_{ij} of T-K-Wilson and UNIQUAC G^E models for three binary systems, Decane+Methanol, Cyclohexane+Methanol and Cyclohexane+2,2,2-Trifluoroethanol (TFE), have been obtained from LLE data. Then the activity of cyclohexane in the binary system of cyclohexane-methanole has been calculated using T-K-Wilson and UNIQUAC equations. The activity of cyclohexane approaches to unity by increasing its mole fraction, which demonstrates the validity of the calculations. Using two MHV1 and MHV2 mixing rules and T-K-Wilson and UNIQUAC G^E models, Liquid-Liquid equilibria for three binary systems has been predicted. The good agreement obtained between the LLE experimental data and the predictions indicates the reliability of the developed model. As evident in Figs. 2 to 4, the results are not satisfactory near the critical points. Thus, in the calculations of the average errors in Table 4 these points have not been taken into account. In comparison to the two EoS-G^E mixing rules, the MHV2 mixing rule with the UNIQUAC model has shown better agreement with the LLE data than the other ones. The MHV1 model is also able to reproduce LLE data at 0.1 MPa; however, the accuracy of the predictions is not high.

5- Appendix

The partial derivative of $n\alpha$, nb and activity coefficient with respect to composition at constant temperature and total volume:

$$x_i = \frac{n_i}{\sum n_j} = \frac{n_i}{n} \tag{A-1}$$

$$\frac{\partial(nb_{mix})}{\partial n_i} = b_i \tag{A-2}$$

$$\frac{1}{n}\frac{\partial(n^2 a)}{\partial ni} = \alpha b_i RT + \frac{\partial(n\alpha)}{\partial(n_i)}b_{mix}RT \tag{A-3}$$

A.1. For T-K-Wilson equation activity coefficient is equal to:

$$ln\,\gamma_i = \left[\frac{\partial(nG^E)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = ln\left(\frac{\displaystyle\sum_{j=1}^{n}x_j V_{ij}}{\displaystyle\sum_{j=1}^{n}x_j \Lambda_{ij}}\right)$$

$$+\sum_{k=1}^{n}x_k\left(\frac{V_{ki}}{\displaystyle\sum_{j=1}^{n}x_j V_{kj}} - \frac{\Lambda_{ki}}{\displaystyle\sum_{j=1}^{n}x_j \Lambda_{kj}}\right) \tag{A-4}$$

and for UNIQUAC equation this equation is defined as follows:

$$ln\,\gamma_i = \left[\frac{\partial(nG^E)}{\partial n_i}\right]_{T,P,n_{j\neq i}} = ln\frac{\phi_i}{x_i} + \left(\frac{z}{2}\right)q_i\,ln\frac{\theta_i}{\phi_i}$$

$$+l_i - \frac{\phi_i}{x_i}\sum_j x_j l_j - q_i\,ln\left(\sum_j \theta_j \tau_{ji}\right) + q_i$$

$$-q_i\sum_j\frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \tag{A-5}$$

$$l_j = \left(\frac{z}{2}\right)(r_j - q_j) - (r_j - 1) \tag{A-6}$$

A.2. The partial derivative equation required for the MHV1 mixing rule:

$$\frac{\partial(n\alpha)}{\partial n_i} = \alpha_i + \frac{1}{q_1}\left(ln\,\gamma_i + ln\frac{b_{mix}}{b_i} + \frac{b_i}{b_{mix}} - 1\right) \tag{A-7}$$

A.3. The partial derivative equation required for the MHV2 mixing rule:

$$\frac{\partial(n\alpha)}{\partial n_i} = \frac{1}{(q_1 + \alpha q_2)}$$

$$\left(q_1\alpha_i + ln\,\gamma_i + q_2(\alpha_i^2 + \alpha^2) + ln\frac{b_{mix}}{b_i} + \frac{b_i}{b_{mix}} - 1 \right)$$

(A-8)

A.4. Fugacity coefficient for PRSV equation of state is defined as follows:

$$ln\,\phi_i = \frac{b_i}{b_{mix}}(Z-1) - ln(Z-B) - \frac{\alpha}{2\sqrt{2}}$$

$$\left(\frac{1}{n}\frac{\partial n^2 a}{\partial n_i} - \frac{b_i}{b_m} \right) ln\left(\frac{Z+2.414B)}{Z-0.414B} \right)$$

(A-9)

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