VLE Predictions of Strongly Non-Ideal Binary Mixtures by Modifying Van Der Waals and Orbey-Sandler Mixing Rules

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ABSTRACT: *By proposing a predictive method with no adjustable parameter and by using infinite dilution activity coefficients of components in binary mixtures obtained from UNIFAC model, the binary interaction parameters (k_{12}) in van der Waals mixing rule (vdWMR) and Orbey-Sandler mixing rule (OSMR) have been evaluated. The predicted binary interaction parameters are used in Peng-Robinson-Stryjek-Vera equation of state (PRSV-EoS) to obtain the vapor-liquid equilibrium (VLE) for six strongly polar and asymmetric binary mixtures. The binary interaction parameters evaluated by correlation of VLE experimental data and by PRSV EoS are also used in VLE calculations of the same binary mixtures. The average absolute deviations (AADs%) of the calculated results by both predictive and correlative methods are reported. The results indicate that although the correlative method has a more flexibility to fit the VLE experimental data, the AAD% of the predictive method is comparable and in some cases even better than that of correlative method.*

KEY WORDS: *Vapor-liquid equilibrium, Predictive method, Binary interaction parameter, PRSV-EoS, PR-EoS, Mixing rule.*

INTRODUCTION

Vapor-liquid equilibrium (VLE) at high pressures are important for chemical process such as supercritical extraction. In practice, VLE data are provided by measurement [1-3] or thermodynamic modeling. Experimental determination of the phase equilibrium over the whole temperature, pressure and concentration range is expensive and time consuming. Therefore the thermodynamic modeling is used to draw an exact conclusion concerning the proper choice of operating conditions, equipment size and extraction yield. Of course, sufficient and reliable experimental data are needed to test the thermodynamic model.

Cubic equations of state (EoS) have been used widely in chemical process industries for calculation of vapor-

liquid equilibrium (VLE). The alpha function developed in the *Peng-Robinson-Stryjek-Vera* (PRSV) [4] equation of state facilitates VLE calculations. However to apply PRSV EoS to VLE calculations of complexmixtures,an effective mixing rule is required. One of the famous and widely used mixing rules for non-polar and slightly polar mixtures is the *van der Waals* mixing rule (vdWMR).

In the recent years, several mixing rules have been proposed by combining the excess *Gibbs* free energy models and equation of state. In this respect the following mixing rules can be mentioned, *Huron* and *Vidal* [5], *Dahl* and *Michelsen* [6], *Heidemann* and *Kokal* [7], *Holderbaum* and *Gmehling* [8], *Wong* and *Sandler* (WSMR)[9], *Orbey* and *Sandler* (OSMR) [10] and *Twu* and *Coon* (TCMR) [11].

Wong and *Sandler* [9] proposed a mixing rule that provided a connection between equations of state and the excess *Gibbs* free energy models. In the WSMR it is assumed that the cross second virial coefficient B_{ij} can be presented in terms of the second virial coefficient of pure components i and j in the following form:

$$B_{ij} = \frac{1}{2}\left[B_i + B_j\right](1 - k_{ij}) \qquad (1)$$

where k_{ij} is the binary interaction parameter. According to the *van der Waals* equation of state (vdW EoS) for a pure component, the second virial coefficient B is obtained in terms of parameters a and b of vdW EoS as: $B = (b - a/RT)$, therefor Eq. (1) can be presented as :

$$B_{ij} = (b - \frac{a}{RT})_{ij} = \frac{1}{2}\left[(b - \frac{a}{RT})_i + (b - \frac{a}{RT})_j\right](1 - k_{ij}) \qquad (2)$$

Application of the WSMR without using the binary interaction parameters shows a large deviation from VLE experimental data.

Orbery and *sandler* [10] slightly reformulated the WSMR by rewriting the cross second virial coefficient in the following from:

$$B_{ij} = (b - \frac{a}{RT})_{ij} = \frac{1}{2}\left[b_i + b_j\right] - \frac{\sqrt{a_i a_j}}{RT}(1 - k_{ij}) \qquad (3)$$

The *Orbey-Sandler* mixing rule (OSMR) can give accurate results in VLE calculations if the interaction parameter k_{ij} is used as a correcting term. The WSMR and the OSMR require an excess *Gibbs* free energy term which can be obtained from other models such as NRTL, *Van laar*, UNIFAC and UNIQUAC models [12-15].

In our previous work [16], VLE for 7 strongly non-ideal binary and 5 ternary mixtures at high pressure were calculated using the PRSV-EoS with mixing rules WSMR, OSMR and TCMR (the *Twu-Coon* mixing rule [11]). The calculated results indicated that the PRSV-EoS is suitable for high pressure VLE calculations. By comparing the absolute average deviation percent (AAD%) for the WSMR, OSMR and TCMR for both binary and ternary mixtures, it was seen that, in most of the cases the WSMR has slightly less AAD% than other mixing rules.

Rui Ruivo et al., [17] correlated VLE data for the ternary system methyl oleate-squalene-carbon dioxide in the temperature range of 313-343 K and in the pressure range of 11-21 Mpa using SRK-EoS with the *Mathias-Koltz-Prausnitz* mixing rule.

Rudolph et al., [18] presented phase behaviour of water-nonionic surfactant systems experimentally. They also modelled the systems applying the *Peng-Robinson* EoS with the *Wong-Sandler* mixing rule and the UNIQUAC g^E-model. They adjusted the model parameters to experimental phase equilibrium data at 0.1 Mpa and used the resulting parameter sets for the prediction of the phase behaviour at high pressures. However, the pressure influence on the phase behaviours of these systems could only be described qualitatively.

Keshtkar et al., [19] used the UNIQUAC-based HURON-Vidal mixing rule in SRK-EoS to evaluate VLE of CO_2 binary systems. They determined the interaction parameters through the regression of experimental VLE data. This type of calculations are considered as correlative ones since they depend on adjusted k_{ij} values based on experimental VLE data.

In this work the binary interaction parameters (k_{ij}) in *van der Waals* mixing rule (vdWMR) and *Orbey-Sandler* mixing rule (OSMR) have been evaluated in terms of the thermodynamic properties of components i and j and infinite dilution activity coefficients of components i and j in binary mixtures obtained from UNIFAC model. This predictive models are used in VLE calculations of six highly polar and asymmetric mixtures.

THEORY

The fugacity coefficient of pure component i (ϕ_l°) is obtained by using the following equation:

$$\ln \phi_1^\circ = Z_i - 1 - \ln \frac{(V_i - b_i)Z_i}{V_i} + \tag{4}$$

$$\frac{a_i/b_i RT}{w-u} \ln\left(\frac{V_i + ub_i}{V_i + wb_i}\right)$$

where Z_i is compresibility factor of component i and is given by an EoS of the following general form:

$$P_i = \frac{RT}{V_i - b_i} - \frac{a_i}{(V_i + ub_i)(V_i + wb_i)} \tag{5}$$

In the above EoS, V_i is the molar volume of component i and a_i and b_i are the parameters of the EoS. u and w are the constants of equation (for *Peng-Robinson-Stryjek-era-EoS* [4]: $w = 1 - \sqrt{2}$, $u = 1 + \sqrt{2}$). Also ϕ_l the fugacity coefficient of component i at composition x_i in the mixture is expressed as:

$$\ln \phi_i = \frac{1}{b_m}\left[\frac{\partial(nb_m)}{\partial n_i}\right]_{T.n_j} (Z-1) - \ln\frac{V-b_m)Z}{V} \tag{6}$$

$$\frac{a_m/b_m RT}{w-u}\left(\frac{1}{a_m}\left[\frac{1}{n}\left[\frac{\partial(n^2 a_m)}{\partial n_i}\right]_{T.n_j}\right]\right.$$

$$\left.\frac{1}{b_m}\left[\frac{\partial(nb_m)}{\partial n_i}\right]_{T.n_j}\right)\ln\left(\frac{V+ub_m}{V+wb_m}\right)$$

The parameters a_m and b_m for the mixture can be obtained using appropriate mixing rules. In this work two mixing rules are used: (i) *van der Waals* and (ii) *Orbey-Sandler.*

i) van der Waals mixing rule

The *van der Waals* mixing rule for parameters a_m and b_m can be presented as:

$$a_m = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \quad ; \quad a_{12} = (a_1 a_2)^{1/2}(1-k_{12}) \tag{7}$$

$$b_m = \sum_{i=1}^{n} x_i b_i$$

where k_{12} is the interaction parameter.

For a binary mixture using Eq. (7) we have:

$$\left[\frac{1}{n}\left[\frac{\partial(n^2 a_m)}{\partial n_i}\right]_{T.n_j}\right] = 2x_1 a_{12} + 2x_2 a_2 ; \tag{8}$$

$$\left[\frac{\partial(nb_m)}{\partial n_i}\right]_{T.n_j} = b_2$$

Since the mixing rule expressed by Eq. (7) for a_m is valid for simple molecules and only for binary interactions between the molecules, this equation should be corrected for its shortcomings by assigning an appropriate mole fraction functionality to the binary interaction parameter k_{12} [20-22]. By considering the existing functionalities, we propose the following symple equation for k_{12} of a binary mixtures in terms of mole fractions of components (x_1 and x_2) in the following form:

$$k_{12} = x_1 k_2^\infty + x_2 k_1^\infty \tag{9}$$

where k_1^∞ and k_2^∞ are the constants of equation and correspond to infinite dilution, that is; as $x_2 \to 0$ then $k_{12} \to k_2^\infty$ or as $x_1 \to 0$ then $k_{12} \to k_1^\infty$. At infinite dilution of component 2 ($x_2 \to 0$) Eq. (8) becomes:

$$\left[\frac{1}{n}\left[\frac{\partial(n^2 a_m)}{\partial n_i}\right]_{T.n_j}\right] = 2a_{12} ; \tag{10}$$

$$\left[\frac{\partial(nb_m)}{\partial n_i}\right]_{T.n_j} = b_2$$

and also from Eq. (7) at ($x_2 \to 0$) we have:

$$a_m = a_1 \quad ; \quad b_m = b_1 \tag{11}$$

At ($x_2 \to 0$), using Eqs. 10, 11 and 7 and $k_{12} = k_2^\infty$, Eq. (6) for binary mixture will be written as:

$$\ln \phi_2^\infty = \frac{b_2}{b_1}(Z_1 - 1) - \ln\frac{(V_1 - b_1)Z_1}{V_1} + \frac{a_1/b_1 RT}{w-u} \tag{12}$$

$$\left[2(1-k_2^\infty)(a_2/a_1)^{1/2} - \frac{b_2}{b_1}\right]\ln\left(\frac{V_1 + ub_1}{V_1 + wb_1}\right)$$

The fugacity coefficient of pure component 2 (ϕ_2°) is obtained by using Eq. (4) and then by substituting for ϕ_2^∞ and ϕ_2° in the well-known equation ($\ln \gamma_2^\infty = \ln \phi_2^\infty - \ln \phi_2^\circ$) [23] and solving the equation for k_2^∞, the following equation is derived:

$$k_2^\infty = 1 - \frac{S_2 + b_2/b_1}{2(a_2/a_1)^{1/2}} \tag{13}$$

where

$$S_2 = \frac{\ln\phi_2^\circ + \ln\gamma_2^\infty - \dfrac{b_2}{b_1}(Z_1-1) + \ln\dfrac{(V_1-b_1)Z_1}{V_1}}{\dfrac{a_1/b_1RT}{w-u}\ln\left(\dfrac{V_2+ub_2}{V_2+wb_2}\right)} \qquad (14)$$

Similarly as $x_1 \to 0$ for k_1^∞.

$$k_1^\infty = 1 - \frac{S_1+b_1/b_2}{2(a_1/a_2)^{1/2}} \qquad (15)$$

where:

$$S_1 = \frac{\ln\phi_1^\circ + \ln\gamma_1^\infty - \dfrac{b_1}{b_2}(Z_1-1) + \ln\dfrac{(V_2-b_2)Z_2}{V_2}}{\dfrac{a_2/b_2RT}{w-u}\ln\left(\dfrac{V_2+ub_2}{V_2+wb_2}\right)} \qquad (16)$$

ii) Orbey-Sandler mixing rule

The parameters a_m and b_m by *Orbey-Sandler* [10] mixing rule can be presented as:

$$a_m = bRT\left[\frac{G^{ex}}{C^*RT} + \sum_{i=1}^{n} x_i\frac{a_i}{b_iRT}\right] \qquad (17)$$

$$b_m = \frac{RT\sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j\left(b-\dfrac{a}{RT}\right)_{ij}}{RT - \left[\sum_{i=1}^{n} x_i\dfrac{a_i}{b_i} + \dfrac{G^{ex}}{C^*}\right]} \qquad (18)$$

where G^{ex} is the *Gibbs* excess function, $\left(b-\dfrac{a}{RT}\right)_{12} = \dfrac{1}{2}[b_1+b_2] - \dfrac{\sqrt{a_1a_2}}{RT}(1-k_{12})$ is given by Eq. (3) and C^* has the values of -0.62323 for PRSV EoS [4].

For a binary mixture using Eqs. (17) and (18) we have:

$$\left[\frac{1}{n}\left[\frac{\partial(n^2a_m)}{\partial n_2}\right]_{T.n_1}\right] = \left[\frac{\partial(nb_m)}{\partial n_2}\right]\times \qquad (19)$$

$$\left(\frac{G^{ex}}{C^*RT} + \sum_{i=1}^{n} x_i\frac{a_i}{b_iRT}\right) + b_m\left(RT\frac{\ln\gamma_2}{C^*} + \frac{a_2}{b_2}\right)$$

$$\left[\frac{\partial(nb_m)}{\partial n_2}\right]_{T.n_1} = \frac{2\sum_{j=1}^{n} x_j\left(b-\dfrac{a}{RT}\right)_{2j}}{1 - \left(\sum_{i=1}^{n} x_i\dfrac{a_i}{b_iRT} + \dfrac{G^{ex}}{C^*RT}\right)} \qquad (20)$$

$$\frac{\left(\sum_{j=1}^{n} x_i x_j\left(b-\dfrac{a}{RT}\right)_{ij}\right)\left(1-\dfrac{\ln\gamma_2}{C^*}-\dfrac{a_2}{b_2RT}\right)}{\left[1-\left(\sum_{i=1}^{n} x_i\dfrac{a_i}{b_iRT} + \dfrac{G^{ex}}{C^*RT}\right)\right]^2}$$

where $k_{ii}=0$ and k_{12} is evaluated from the values of k_1^∞ and k_2^∞ by Eq. (9). Then at infinite dilution of component 2, $(x_2 \to 0)$ it can be shown that:

$$\frac{1}{a_m}\left[\frac{1}{n}\left[\frac{\partial(n^2a_m)}{\partial n_2}\right]_{T.n_1}\right] - \frac{1}{b_m}\left[\frac{\partial(nb_m)}{\partial n_2}\right]_{T.n_1} = \qquad (21)$$

$$\frac{b_1}{a_1}\left(\frac{a_2}{b_2} + RT\frac{\ln\gamma_2^\infty}{C^*}\right)$$

$$\frac{1}{b_1}\left[\frac{\partial(nb_m)}{\partial n_2}\right]_{T.n_1} = \qquad (22)$$

$$\frac{2\left(b-\dfrac{a}{RT}\right) - b_1\left(1-\dfrac{a_2}{b_2RT} + \dfrac{\ln\gamma_2^\infty}{C^*}\right)}{\left(b_1-\dfrac{a_1}{RT}\right)}$$

and also from Eqs. (17) and (18) at $(x_2\to0)$ we have:

$$a_m = a_1 \quad ; \quad b_m = b_1 \qquad (23)$$

and using Eqs. (17), (18), (21), (22) and (23) and $k_{12} = k_2^\infty$, Eq. (6) for binary mixture will be written as:

$$\ln\phi_2^\infty = \left[\left[2\left(b-\frac{a}{RT}\right)_{12} - b_1\left(1-\frac{a_2}{b_2RT} + \frac{\ln\gamma_2^\infty}{C^*}\right)\right]\right] \qquad (24)$$

$$\bigg/\left(b_1-\frac{a_1}{RT}\right)\right](Z_1-1) - \ln\frac{(V_1-b_1)Z_1}{V_1} +$$

$$\frac{a_1/b_1RT}{w-u}\left[\frac{b_1}{a_1}\left(\frac{a_2}{b_2} + RT\frac{\ln\gamma_2^\infty}{C^*}\right)\right]\ln\left(\frac{V_1+ub_1}{V_1+wb_1}\right)$$

The fugacity coefficient of pure component 2, ϕ_2°, is also obtained by using Eq. (4) and then by substituting for ϕ_2^∞ and ϕ_2° in $\ln\gamma_2^\infty = \ln\phi_2^\infty - \ln\phi_2^\circ$ and solving the obtained equation for k_2^∞, the following equation for OSMR is derived:

$$k_2^\infty = 1 + \frac{S_2-(b_1+b_2)}{\sqrt{a_1a_2}/RT} \qquad (25)$$

$$S_2 = \left(\frac{\ln \gamma_2^\infty + \ln \phi_{2_2}^\circ - Q_2}{Z_1 - 1} \right)\left(b_1 - \frac{a_1}{RT} \right) + \qquad (26)$$

$$b_1 \left(1 + \frac{\ln \gamma_2^\infty}{C^*} - \frac{a_2}{b_2 RT} \right)$$

$$Q_2 = -\ln \frac{(V_1 - b_1)Z_1}{V_1} + \qquad (27)$$

$$\frac{1}{w - u} \left(\frac{a_2}{b_2 RT} - \frac{\ln \gamma_2^\infty}{C^*} \right) \ln \frac{V_1 + ub_1}{V_1 + wb_1}$$

Similarly as $x_1 \rightarrow 0$ for k_1^∞.

$$k_1^\infty = 1 + \frac{S_1 - (b_1 + b_2)}{\sqrt{a_1 a_2}/RT} \qquad (28)$$

$$S_1 = \left(\frac{\ln \gamma_1^\infty + \ln \phi_1^\circ - Q_2}{Z_2 - 1} \right)\left(b_2 - \frac{a_2}{RT} \right) + \qquad (29)$$

$$b_2 \left(1 + \frac{\ln \gamma_1^\infty}{C^*} - \frac{a_1}{b_1 RT} \right)$$

$$Q_1 = -\ln \frac{(V_2 - b_2)Z_2}{V_2} + \qquad (30)$$

$$\frac{1}{w - u} \left(\frac{a_1}{b_1 RT} - \frac{\ln \gamma_1^\infty}{C^*} \right) \ln \frac{V_2 + ub_2}{V_2 + wb_2}$$

RESULTS AND DISCUSSION

In this work the binary interaction parameters (k_{12}) in *van der Waals* mixing rule (vdWMR) and *Orbey-Sandler* mixing rule (OSMR) have been evaluated in terms of the thermodynamic properties of components 1 and 2 using Eq. (9) ($k_{12} = x_1 k_2^\infty + x_2 k_1^\infty$). The values of k_1^∞ and k_2^∞ have been predicted for PR EOS with vdWMR from Eqs. (13) to (16) and for PRSV EOS with OSMR from Eqs. (25) to (30). In these equations, the activity coefficients at infinite dilution (γ_i^∞) are caculated for the studied mixtures by UNIFAC model [14]. This method is refered to as predictive method with no adjustable parameters that is $k_{12} = x_1 k_2^\infty + x_2 k_1^\infty$. By using the predictive binary interaction parameters in *Peng-Robinson-Stryjek-Vera* equation of state (PRSV-EoS) the vapor-liquid equilibrium (VLE) for the highly polar and asymmetric mixtures are calculated. The

average absolute deviation (AAD%) of the calculated results compared with the experimental data of 6 binary systems (obtained from references [24-26]) for vapor pressure and vapor composition are listed in tables 1 and 2 for vdWMR and OSMR respectively. The values of k_1^∞ and k_2^∞ are also reported in these tables.

The binary interaction parameters (k_{12}) are also evaluated by correlating with the VLE experimental data for the same mixtures. The results of correlation for PR EOS with vdWMR are reported in table 1. The results of correlation for PRSV EOS with OSMR are reported in table 2. The method of determination of interaction parameter through the regression of experimental VLE data is refered to as cerrelative method (with k_{12} as adjustable parameter). The values of k_{12} obtained through the regression of experimental VLE data are also reported in tables 1 and 2.

In table 1 the AAD% of predictive method for ethanol-water, methanol-acetone and 2-propanol-water systems is less than the AAD% of correlative method. The calculated average absolute deviations (AADs%) in vapor mole fractions and total pressures by using the predictive and correlative interaction parameters are in close agreement (for some systems the results of predictive method are better than the results of correlative method) and indicate the effectiveness of the predictive method proposed in this work.

Fig. 1 shows the vapor-liquid equilibrium (VLE) results for ethanol-water system with the PRSV-EoS and *Orbey-Sandler* mixing rule (OSMR) compared with the experimental measurements. In this figure the solid line indicates the obtained results by the predictive method and the dotted line indicates the obtained results by the correlative method. Fig. 2 is the same as Fig. 1 but the calculated results are obtained with the PRSV-EoS and *van der Waals* mixing rule (vdWMR). In both figures a reasonably good representation of VLE behaviour is found by the predictive method.

CONCLUSIONS

In this work we have formulated the binary interaction parameter in *van der Waals* mixing rule (vdWMR) and *Orbey-Sandler* mixing rule (OSMR) in terms of pure components thermodynamic properties and their infinite dilution activity coefficients in the binary mixtures.

Table 1: Average absolute deviation in P and y_1 with PR EOS and vdWSMR for both the predictive and correlative methods.

system	T(k)	Correlative method			Predictive method			
		k_{12}	AAD% in P	AAD% in y_1	k_1	k_2	AAD% in P	AAD% in y_1
Ethanol-Water	363.15	-0.096	2.673	3.333	-0.1162	-0.0587	2.449	2.464
Methanol-Acetone	298.15	-0.042	13.648	18.114	-0.0044	0.0253	1.864	4.687
2-Propanol-Water	298.15	-0.180	10.436	16.827	-0.1981	-0.1437	7.897	9.551
Ethanol-Heptane	333.15	0.017	10.839	11.584	0.2090	-0.0313	12.642	16.076
Benzene- 1-propanol	348.15	0.057	9.254	15.980	0.1381	0.0799	24.985	15.485

Note that k_{12} is evaluated by correlation of the binary experimental data and k_1 and k_2 are calculated from Eqs. (13) to (16).

Table 2: Average absolute deviation in P and y_1 with PRSV EOS and OSMR for both the predictive and correlative methods.

system	T(k)	Correlative method			Predictive method			
		k_{12}	AAD% in P	AAD% in y_1	k_1	k_2	AAD% in P	AAD% in y_1
Ethanol-Water	363.15	-0.656	0.9000	1.242	-0.6768	-0.5208	0.914	2.464
Methanol-Acetone	298.15	-1.260	4.205	10.208	-0.8165	-0.7159	4.491	4.030
2-Propanol-Water	298.15	-0.840	10.731	8.453	-0.6053	-0.3314	19.994	9.080
Benzene-1-Propanol	348.15	-0.760	6.758	14.990	-0.5025	-0.7117	9.391	14.629
Carbon dioxide-Ethanol	333.45	-0.570	1.962	0.223	-1.062	-0.8912	20.482	0.583

Note that k_{12} is evaluated by correlation of the binary experimental data and k_1 and k_2 are calculated from Eqs. (25) to (30).
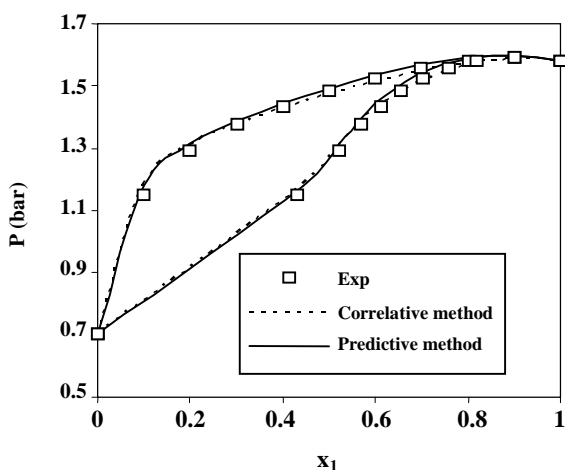

Fig. 1: The vapor-liquid equilibrium (VLE) results for ethanol-water system with the PRSV-EoS and Orbey-Sandler mixing rule (OSMR) compared with the experimental measurements [25]. The solid line results from determining the interaction parameter by the predictive method. The dotted line results from determining the interaction parameter by the correlative method.
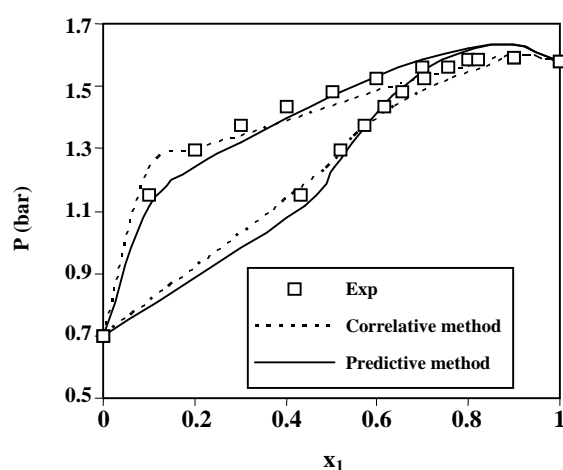

Fig. 2: The same as Fig. 1 but the calculated results are obtained with the PRSV-EoS and van der Waals mixing rule (vdWMR) [25].

The infinite dilution activity coefficients of components 1 and 2 were obtained by using UNIFAC model. It is shown that by the proposed predictive method, the binary interaction parameter (k_{12}) can be evaluated directly without recourse to the VLE data.

The obtained results for the mixtures of [ethanol-heptane], [1-propanol - benzene] and [carbon dioxide-ethanol] indicated that the average absolute deviations of proposed method are near to those of correlative method but for the mixtures of [ethanol-water], [methanol-acetone] and [2-propanol-water], the results of predictive method even are better than the correlative method.

Nomenclatures

a	Attraction parameter in equation of state
b	Covolume parameter in equation of state
C	Equation of state dependent constant in Wong-Sandler mixing rule
f	Fugacity
G^E	Excess Gibbs free energy
k_{ij}	Binary interaction parameter
P	Pressure
R	Ggas constant
T	Ttemperature
v	Mmolar volume
x	Liquid mole fraction
y	Gas mole fraction
u,w	Constants of equation of state

Greek symbols

γ	Activity coefficient
ϕ	Fugacity coefficient
ω	Acentric factore

Subscript/supercript

c	Critical property
ex	Excess property
exp	Experimental
i, j	Component in a mixture
m	Mixture
l	Liquid
v	Vapor

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