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Combining the CORGC and UNIFAC Models for Prediction of Multicomponent VLE Behavior for Polar Systems

Z. Arab-Abousadi[1] **and M. Moshfeghian***

In this paper, the CORGC EOS is combined with an Excess-Gibbs-Energy model such as UNIFAC in order to extend the capabilities and improve the accuracy of the CORGC EOS in predicting the vapor-liquid equilibrium behavior of mixtures containing polar components. The CORGC EOS is used together with the PSRK mixing rule and the original UNIFAC is applied as Excess-Gibbs-Energy model in the proposed approach. Comparison between this work (CORGC/UNIFAC) and the original CORGC with experimental data of several polar mixtures are presented. The outcomes indicate that CORGC/UNIFAC provides better vapor-liquid equilibria results than the original CORGC and the accuracy of binary polar systems is nearly twice that of the original CORGC. The required missing interaction parameters of the original UNIFAC model are fitted with experimental data and the missing interaction parameters for unlike pairs of groups in the original CORGC EOS are also determined. The model parameters are determined from VLE of binary mixtures and are reported. These parameters are, then, used without any further adjustment to predict VLE of multicomponent mixtures, for which more accurate results in comparison to the original CORGC are observed.

INTRODUCTION

The accuracy and reliability of a process simulation usually depend on the accuracy of the Equation Of State (EOS) used for calculating vapor-liquid equilibrium and other thermodynamic properties.

Due to the importance of EOS for calculation of equilibrium and thermodynamic properties in chemical engineering, extensive research has been conducted to develop new EOS and also to improve the existing ones.

The literature on this subject is comprehensive; therefore, only a few examples are cited here, such as Soave [1], Cunningham and Wilson [2], Peng and Robinson [3] and Pults, et al. [4]. In spite of this large volume of research, there is still a wide range of components and mixtures as well as conditions and properties that existing EOS cannot predict satisfactorily. Also, most EOS contain parameters that must be obtained from experimental VLE data in order to satisfactorily predict VLE and thermodynamic properties accurately. Polar components and mixtures containing polar constituents are difficult to be handled properly by all EOS.

Classical mixing rules imply a quasi-regular behavior [5] and, unless a thorough revision is made, the method cannot be applied to polar mixtures. However, the close relation between excess Gibbs energy and mixing rules leads to the problem of evaluating mixture parameters. Consequently this work is devoted to mixing rules.

The idea of combining simple EOS with excess-Gibbs-energy models, for the first time was presented by Huron and Vidal [6]. They assumed that no excess volume exists at an infinite pressure limit and determined the energy parameter by equating the Gibbs free energy calculated by the EOS to that of a liquid model. The resulting model was capable of correlating high temperature phase equilibrium but could not directly utilize parameter tables for existing G^E models, correlated from low temperature data. Since then for solving this problem, numerous publications have appeared with more or less similar approaches [1,7-12]. For example, Michelsen and Holderbaum-Gmehling [8,9] de-

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[1] *Department of Chemical Engineering, Shiraz University, Shiraz, I.R. Iran.*

* *Corresponding Author, Department of Chemical Engineering, Shiraz University, Shiraz, I.R. Iran.*

veloped the idea of applying the Soave-Redlich-Kwong (SRK) EOS combined with the G^E model at zero or low pressures, as originally suggested by Mollerup [13], and obtained new mixing rules for attractive energy parameters of the EOS. These mixing rules are known as MHV1, MHV2 (proposed by Michelsen) and PSRK (proposed by Holderbaum-Gmehling), in which any G^E model like UNIQUAC or UNIFAC can be used.

The objective of this work is to combine CORGC equation of state with UNIFAC model (for estimation of excess Gibbs energy) in order to improve the capability of CORGC equation of state for calculation of vapor-liquid equilibrium constants of multicomponent polar systems. In this paper, the missing interaction parameters of the original UNIFAC model are obtained with very good accuracy and the missing interaction parameters for unlike pairs of groups in the original CORGC EOS are also determined. The model parameters are determined from VLE of binary mixtures and reported. These parameters are then used, without any adjustment, to predict VLE of multicomponent mixtures.

CORGC/UNIFAC EOS

In this study, the CORGC [4] equation of state, which yields good results for vapor-liquid equilibrium of non polar or slightly polar mixtures, is used,

$$z = \frac{1+y+y^2-y^3}{(1-y)^3} + \frac{c(\alpha-1)}{2}\frac{3y+3\alpha y^2-(\alpha+1)y^3}{(1-y)^3} - \frac{a}{RT(v+b)}, \tag{1}$$

where $y = b(T)/4v$ is the reduced density and $b(T)$ is the molecular co-volume, which is proportional to the hard core volume of the fluid. The parameter c is the degree of freedom and α is the rotator parameter for the single bond between two carbon atoms, which is equal to 1.078. Both $a(T)$ and $b(T)$ are functions of temperature.

The equation of state parameters a, b and c are made up of group contributions according to the following equations:

$$a_{ij} = \sum_m^{NG}\sum_n^{NG} \nu_{im}.\nu_{jn}.q_m.q_n.a_{mn}(T), \tag{2}$$

$$a(T) = \sum_i^{NC}\sum_j^{NC} x_i.x_j.a_{ij}, \tag{3}$$

$$b_i(T) = \sum_m^{NG} \nu_{im} b_m(T), \tag{4}$$

$$b(T) = \sum_i^{NC} x_i b_i(T), \tag{5}$$

$$c_i = \sum_m^{NG} \nu_{im} c_m, \tag{6}$$

$$c = \sum_i^{NC} x_i c_i. \tag{7}$$

In these equations, ν_{im} is the number of groups m in molecule i. The index NG is the number of groups in the system, and NC represents the number of components in the mixture. q_m is the normalized surface area of group m.

The temperature dependence of group constants $a_{mn}(T)$ and $b_m(T)$ is similar to equations derived by Pults et al. [4]:

$$a_{mn}(T) = a^+_{mn}(T/T^+_{mn})^{-0.18135}\exp(-T/T^+_{mn}), \tag{8}$$

$$b_m(T) = b^*_m \exp(-T/T^*_m). \tag{9}$$

In order to extend the capabilities and improve the accuracy of the CORGC equation of state in predicting the VLE behavior of mixtures containing polar components specially at high temperatures and pressures, the following modification is proposed.

The proposed modification concerns the mixing rule for the parameter a that can also be easily derived for this equation of state. The common linear mixing rules are used for the parameters b and c.

The PSRK mixing rule [9] for parameter a of EOS is:

$$\theta - \sum \theta_i x_i = \frac{1}{q_1}\left[\frac{G_0^E}{RT} + \sum x_i \ln\frac{b}{b_i}\right], \tag{10}$$

where q_1 is constant and equal to -0.64663 and:

$$\theta = \frac{a}{bRT}, \tag{11}$$

$$\theta_i = \frac{a_i}{b_i RT}, \tag{12}$$

$$\frac{G_0^E}{RT} = \sum x_i \ln \gamma_i. \tag{13}$$

In this work, PSRK mixing rule is used for the parameter a of the CORGC equation of state. Considering these mixing rules for a, b and c, the fugacity coefficient of component i in a mixture and enthalpy and entropy departure functions can be expressed, respectively, as:

$$\begin{aligned}\ln\varphi_i =&\frac{y(4-3y)}{(1-y)^2}+\frac{b_i}{b}(Z-1)-\ln Z\\&+\frac{c_i(a-1)}{2}\left[\frac{4y+ay-3y^2}{(1-y)^2}(a+1)\ln(1-y)\right],\\&-\bar{\theta}_i\ln(1+4y),\end{aligned}\tag{14}$$

where,

$$\bar{\theta}_i=\frac{\partial(n\theta)}{\partial n_i}=\frac{1}{q_1}\left[q_1\theta_i+\ln\gamma_i+\ln\frac{b}{b_i}+\frac{b_i}{b}-1\right],\tag{15}$$

$$\begin{aligned}H-H^0=RT\Big[&(Z-1)\left(1-\frac{T(\partial b/\partial T)}{b}\right)\\&+\frac{1}{bRT}\left(-a+\frac{T\partial a}{\partial T}-\frac{aT(\partial b/\partial T)}{b}\right)\ln(1+4y),\end{aligned}\tag{16}$$

$$\begin{aligned}S-S^0=R\Big[&(Z-1)\left(1-\frac{T(\partial b/\partial T)}{b}\right)\\&+\frac{1}{bRT}\left(-a+\frac{T\partial a}{\partial T}-\frac{aT(\partial b/\partial T)}{b}\right)\\&\times\ln(1+4y)-R\ln\varphi\end{aligned}\tag{17}$$

Any appropriate model for the excess Gibbs energy can be used in connection with the present mixing rules. In this study, original UNIFAC [14,15] is used. As recommended by Holderbaum and Gmehling [9], the temperature-dependent parameter, Ψ_{nm} in G^E models is introduced as a function of temperature:

$$\Psi_{nm}=\exp\left(-\frac{au_{nm}+bu_{nm}T+cu_{nm}T^2}{T}\right),\tag{18}$$

where au_{nm}, bu_{nm} and cu_{nm} are interaction parameters between each two groups of n and m in the UNIFAC model.

The molecular parameters R and Q in the original UNIFAC are determined from structural parameters R and Q that are provided by Fredenslund et al. [16] and Holderbaum-Gmehling [9] for organic group structure and several gases, respectively.

DATA REDUCTION FOR GROUP PARAMETERS

The CORGC EOS has six parameters for each group m, a^+_{mm}, T^+_{mm}, b^*_m, T^*_m, c_m and q_m. These parameters must be determined from experimental PVT data. In addition, for each pair of groups m and n, two group interaction parameters are needed, a^+_{mn} and T^+_{mn}. These binary group parameters could be obtained based on the vapor-liquid equilibrium properties of binary mixtures. For several groups, parameters are reported by Shariat et al. [17].

In the modified CORGC EOS (CORGC/UNIFAC), there is no need for interaction parameters (a^+_{mn} and T^+_{mn}) between each pair groups m and n that are not in the same molecule, therefore, the number of needed parameters for CORGC are decreased.

As mentioned previously, the original UNIFAC has two parameters for each group, the Van der Waals volume and surface area (R_k and Q_k), as well as six interaction parameters au_{nm}, au_{mn}, bu_{nm}, bu_{mn}, cu_{nm}, cu_{mn} between each two groups n and m that must be obtained from VLE data and which will be described in detail, in the next section

DETERMINATION OF REQUIRED PARAMETERS

The generation of reliable group interaction parameters for UNIFAC model requires a reliable data base for fitting the required parameters. For any desired system, the data base should contain vapor-liquid experimental data ($T-P-x-y$), CORGC group parameters, Van der Waals volume and surface parameters (R_k and Q_k) and, finally, six interaction parameters of UNIFAC model (au_{nm}, au_{mn}, bu_{nm}, bu_{mn}, cu_{nm}, cu_{mn}). For this purpose, the group parameters of CORGC, reported by Shariat et al. are being used [17] and, consequently, there is no need for interaction parameters (a^+_{mn} and T^+_{mn}) between each pair groups m and n that are not in the same molecule.

The computer package, developed here for finding these parameters, consists of two major parts:

a) The first part is based on CORGC/UNIFAC basic equations, which permits the prediction of derived properties for a specified system;

b) The second part is a nonlinear regression program which is based on Marquardt method for optimization of the parameters [18].

The following procedure is considered for obtaining the group interaction parameters of UNIFAC model in the CORGC/UNIFAC equation of state:

1. Guess an initial value for group interaction parameters;
2. Maximum and minimum possible values for these parameters and weighting factor for each property should be set;
3. Guess an initial value for liquid and vapor mole fraction (experimental values can be used as initial estimate);
4. Calculate mixture parameters b and c from Equations 4 to 7;

5. Calculate the excess Gibbs energy and activity coefficients from the UNIFAC model;
6. Calculate the mixture parameter and composition derivative of a from Equations 10 to 13 and 15;
7. Solve the equation of state, for compressibility factors of liquid and vapor phases, separately;
8. Calculate the fugacity coefficients from Equation 14 and then the K-values;
9. By performing a flash calculation at a specified temperature and pressure, the Objective Function (OF) is calculated as follows:

$$OF=\sum_{i}^{NP}\left[A\left(\frac{EK_1-CK_1}{EK_1}\right)^2+B\left(\frac{EK_2-CK_2}{EK_2}\right)^2+C\left(\frac{EX_1-CX_1}{EX_1}\right)^2+D\left(\frac{EY_1-CY_1}{EY_1}\right)^2\right]_i, \tag{19}$$

10. Use the Marquardt [18] nonlinear regression program developed by Chandler [19] for minimizing the objective function and obtaining a new set of values for group interaction parameters of Equation 18;
11. Repeat Steps 2 to 10 for obtaining optimal group interaction parameters of UNIFAC model.

RESULTS

The missing interaction parameters of CORGC/UNIFAC for 14 groups are fitted in this work and the results are shown in Table 1. As mentioned in the previous section, for each experimental data, a flash calculation is performed. Vaporization equilibrium ratios and composition of each component in the binary mixture are predicted and the Objective Function (OF) is minimized to obtain the best parameters. These parameters are then used without any adjustment to predict the VLE behavior of multicomponent polar mixture

For comparison of the VLE results of the two EOS, it is necessary to determine the missing interaction parameters for unlike pairs of groups in the original CORGC. Similar to the modified CORGC, for each experimental data, a flash calculation is performed. Vaporization equilibrium ratios and phase composition of each component in the binary mixture are predicted and the OF is minimized to obtain the best parameters. These parameters are then used without any adjustment to predict VLE behavior of multicomponent polar mixtures, for which the results are shown in Table 2.

Comparison of VLE results for polar binary systems obtained from the original CORGC and the modified CORGC (CORGC/UNIFAC) using the group parameters, is shown in Table 3. Good agreement between all results and experimental data is observed in the modified CORGC EOS. Furthermore, It is observed that the Average Absolute Percent Deviation (AAPD) in obtaining vaporization equilibrium ratios ($K_i = y_i/x_i$) of the original CORGC is larger than the modified CORGC and the accuracy of the modified

Table 1. Binary group interaction parameters for unlike pairs of groups in the CORGC/UNIFAC (modified CORGC) equation of state.

n	m	au_{nm}(K)	au_{mn}(K)	bu_{nm}	bu_{mn}	cu_{nm} (×100)(K^{-1})	cu_{mn} (×100)(K^{-1})	Temperature Range (K)
CO_2	CH_2	22.1578	714.5986	0.6526	-4.5086	-0.26	0.93	116.7 - 283.3
CO_2	CCOH	-331.8352	400.2017	0.1702	-0.1301	0.02	-0.1	304.2 - 337.2
CO_2	H_2O	-587.3681	-1726.319	1.32422333	11.11243628	-0.29206489	-1.37393443	288.9 - 394.4
CO_2	CH_3OH	-409.6271	374.5312	0.0	0.0	0.0	0.0	250 - 477.6
CH_4	CH_2	26.1015	2.2308	-0.4877	0.0424	-0.08	0.24	130 - 283.3
CH_4	CCOH	-171.2049	-146.989	-0.05648195	0.12409412	-0.0394774	0.01135837	313.6 - 333.6
CH_4	CH_3OH	-393.0639	428.9596	-0.14030396	-0.29089959	-0.01818808	0.0343487	273.2 - 330
CH_4	H_2O	-595.3486	1471.2419	0.10087754	-1.32459761	0.00164596	-0.03130936	323.3 - 588.9
CH_2	CH_3CH_2OH	755.7	-77.7	9.7926	-2.2601	-2.88	0.44	313.6 - 333.6
CH_2	CH_2CH_2OH	737.5	-87.93	-7.0308	-0.5408	3.11	-0.16	313.4 - 333.4
CH_2	CH_3OH	1820.3319	-121.4327	3.6071103	-0.29735782	1.33974091	-0.1168365	310.7 - 472.3
CH_3OH	CCOH	-80.78	127.4	-0.01619588	-0.02108405	-0.0072782	-0.00960746	338.4 - 350.3
CH_3OH	H_2O	-181.0	289.6	0.50219	-1.36303051	-0.1100887	0.22334954	369.7 - 454.6
CH_3CH_2OH	H_2O	294.7	-191.6	-1.9428723	-0.99019894	-0.00811366	0.80129746	323.2 - 351.3

Table 2. Interaction parameters a_{mn}^{+} and T_{mn}^{+} for unlike pairs of groups: value above the diagonal are $a_{mn}^{+} \times 10^{-2}$ (cm^6 bar mol^{-2}); those below the diagonal are $T_{mn}^{+}(K)^a$.

Group	CH_4	C_2H_6	al-CH_3	al-CH_2-al	CO_2	H_2S	H_2O	CH_3OH	$(CH)_{ar}$	OH^1
CH_4	-	546.12	680.66	405.47	737.67	NA	5262.36	1310.33	NA	1530.19
C_2H_6	305.22	-	619.83	653.94	682.0	777.79	1120.46	1146.75	NA	1307.51
al-CH_3	239.11	367.39	-	609.16	543.87	NA	1914.98	1098.07	652.42	1657.9
al-CH_2-al	798.61	493.89	561.85	-	998.33	NA	2173.3	1100.38	740.49	1034.9
CO_2	216.49	307.43	332.34	339.12	-	NA	2967.83	2576.29	NA	1713.97
H_2S	NA	356.68	NA	NA	NA	-	NA	NA	NA	NA
H_2O	152.421	528.747	1037.0999	655.8374	234.9199	NA	-	3185.2	NA	-221.21
CH_3OH	450.2917	458.6052	206.2828	228.5329	265.9666	NA	444.46	-	NA	2873.01
$(CH)_{ar}$	NA	NA	754.1634	792.0679	NA	NA	NA	NA	-	NA
OH^1	235.7512	233.983	298.22	336.96	227.4881	NA	135.4614	424.0574	NA	-

NA, not available,
OH^1 appears in primary alcohols, -CH_2-OH

Table 3. Ability of the CORGC/UNIFAC (modified CORGC) and the original CORGC equation of states to predict VLE ratios of binary systems.

Mixture Components (1-2)	No. of Pints	Temperature Range (K)	Pressure Range (MPa)	Original CORGC AAPD		Modified CORGC AAPD		Reference Number
				K_1	K_2	$K_1$1	K_2	
CO_2 + CH_3OH	104	230 - 477.6	0.44 - 16.3	37.12	103.53	18.84	64.63	[8]
CO_2 + C_3H_7OH	47	313.4 - 337.1	0.52 - 10.8	19.61	51.8	10.67	15.14	[17]
CO_2 + H_2O	21	288.9 - 394.4	0.69 - 20.3	21.25	64.35	12.18	40.62	[20]
CH_4 + C_2H_5OH	10	313.6 - 333.6	1.8 - 10.4	14.35	20.03	0.64	8.83	[17]
CH_4 + C_3H_7OH	10	313.6 -333.6	1.4 -10.2	101.27	36.89	6.74	11.21	[17]
C_2H_6 + C_2H_5OH	14	313.6 - 333.6	1.3 - 7.9	110.63	14.73	7.27	8.81	[17]
C_2H_6 + C_3H_7OH	11	313.4 - 333.4	1.3 - 6.7	50.86	172.97	25.92	11.45	[17]

CORGC in these systems is nearly twice that of the original CORGC.

For a number of selected binary systems, the vaporization equilibrium ratio is illustrated in Figures 1 to 7 as a function of pressure, obtained from the original CORGC and the CORGC/UNIFAC with respect to experimental data.

In Figure 1, vaporization equilibrium ratio (K-value) for the binary mixture of CO_2+CH_3OH at a constant temperature is shown for different pressures. In this system, carbon dioxide is a supercritical component. The results demonstrate that the accuracy of the original CORGC decreases with increasing the pressure for both components.

Figure 2 represents VLE for CO_2+C_3H_7OH at 337.1 K (carbon dioxide is a supercritical component in the mixture). The capabilities of the modified CORGC at pressures greater than 6 MPa are also shown. Finally Figure 3 is for CO_2+H_2O at 394.4 K. These figures and the results in Table 3 indicate that the prediction of the modified CORGC for binary mixtures containing carbon dioxide is satisfactory.

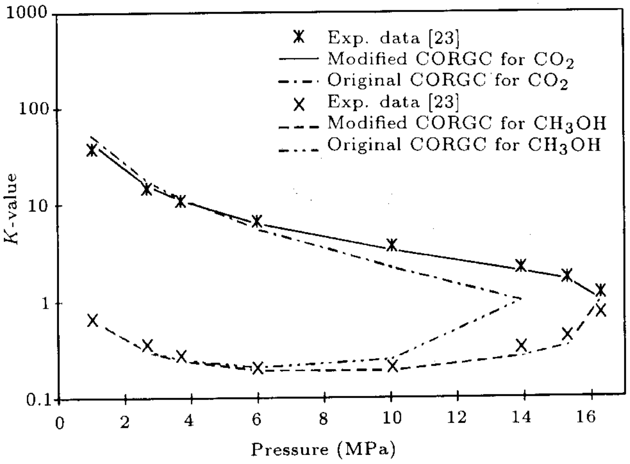

Figure 1. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CO_2 + CH_3OH mixture at 394.2 K.

Figures 4 and 5 illustrate the vaporization equilibrium ratio of methane (methane is a supercritical component in the mixtures) binary systems with ethanol and propanol at 333.6 K. These figures show that the accuracy of the modified CORGC for methane/alcohol systems are good.

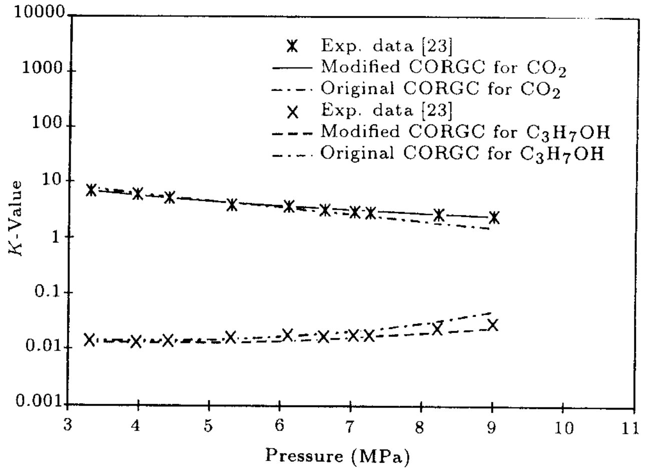

Figure 2. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CO_2 + C_3H_7OH mixture at 337.1 K.

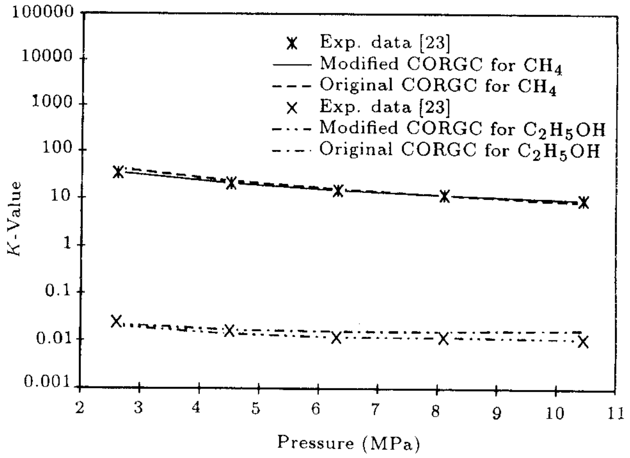

Figure 4. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CH_4 + C_2H_5OH mixture at 333.6 K.

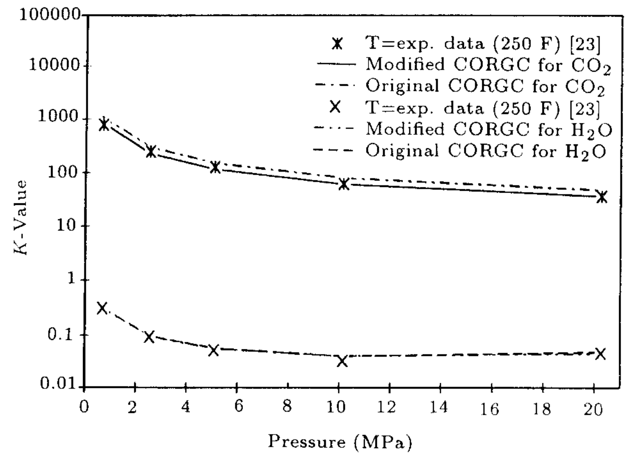

Figure 3. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CO_2 + H_2O mixture at 394.4 K.

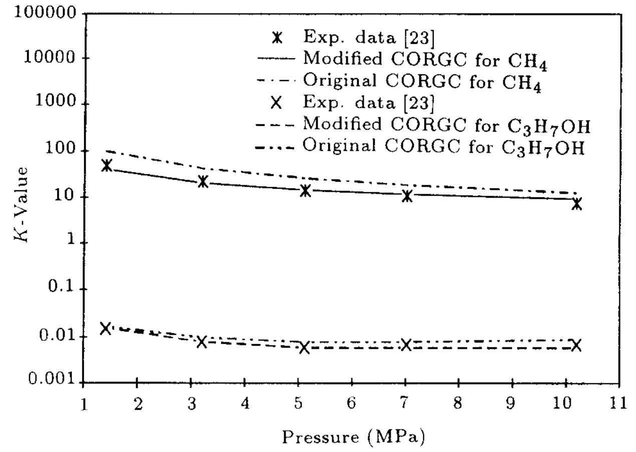

Figure 5. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CH_4 + C_3H_7OH mixture at 333.6 K.

The VLE results of CORGC/UNIFAC and the original CORGC equations of state for C_2H_6+C_3H_7OH and C_2H_6+C_2H_5OH (ethane is a supercritical component) are illustrated in Figures 6 and 7.

TESTING THE MODELS

For most EOS, accurate representation of binary mixture K-values provides a good indication. However, in order to demonstrate the performance and accuracy of the CORGC/UNIFAC equation of state compared to the original CORGC in predicting the VLE behavior of polar ternary mixtures, Table 4 is provided. Although, the parameters obtained from binary mixtures have been used, the AAPD for multicomponent is relatively good.

Figure 8 shows vaporization equilibrium ratio for the multicomponent mixture of CO_2 + CH_3OH + C_2H_5OH at 313.2 K. As shown in this figure, the accuracy of the modified CORGC is very good for this polar mixture.

Figures 9 and 10 represent VLE for H_2O + C_2H_5OH + CO_2 at 308.3 K and 323.3 K. The results obtained by the modified CORGC are very good relative to the original CORGC. The parameters are used without any adjustment to predict VLE behavior of ternary polar mixtures. The AAPD for multicomponent is relatively satisfactory, although the parameters obtained from binary mixtures have been used.

Figures 8 to 10 illustrate the performance of the CORGC/UNIFAC EOS compared to the original CORGC EOS in predicting the K-values for a few multicomponent polar mixtures. It can be seen that the values predicted by the modified CORGC are in good agreement with the experimental data.

VLE for non-polar multicomponent mixture of

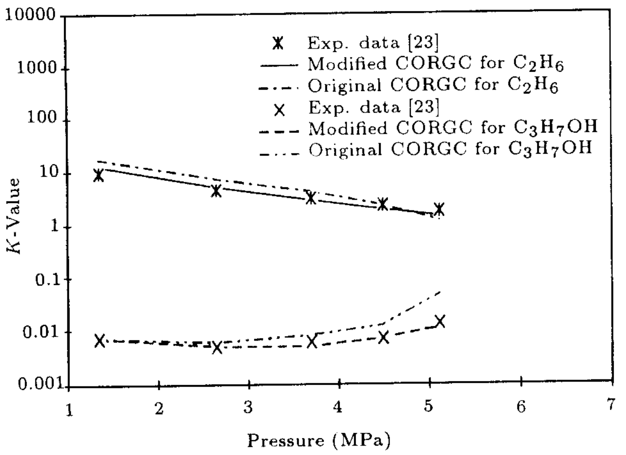

Figure 6. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of C_2H_6 + C_3H_7OH mixture at 313.4 K.

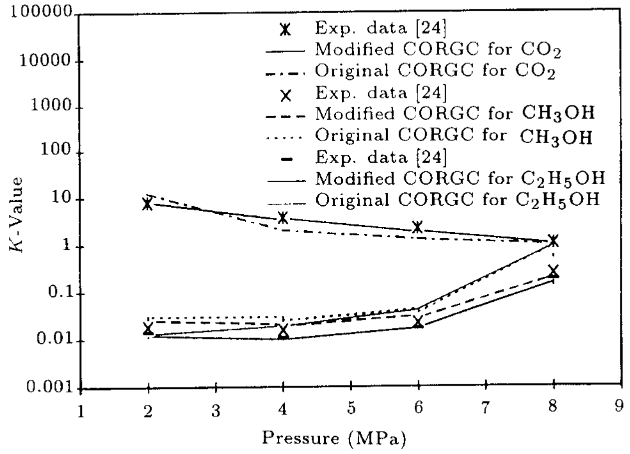

Figure 8. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CO_2 + CH_3OH + C_2H_5OH mixture at 313.2 K.

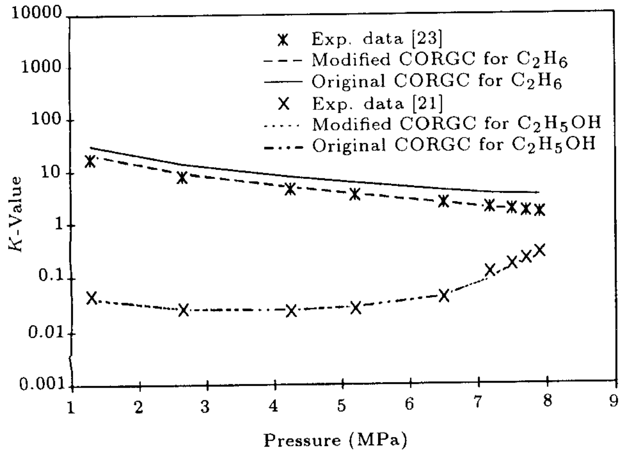

Figure 7. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of C_2H_6 + C_2H_5OH mixture at 333.6 K.

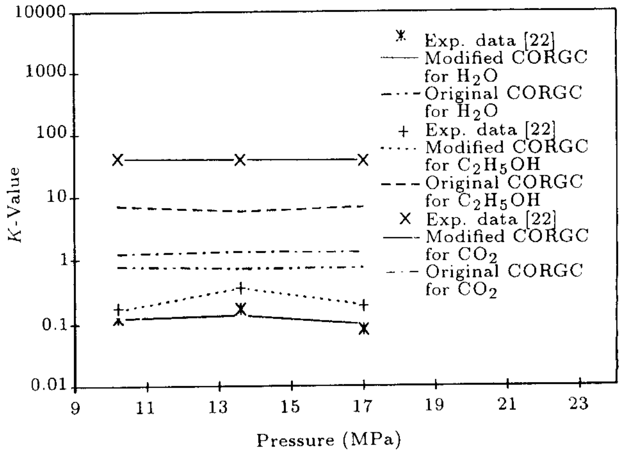

Figure 9. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium rtios of H_2O + C_2H_5OH + CO_2 mixture at 308.3 K.

CO_2 + C_3H_8 +C_5H_{12} + C_8H_{18} at 310.93 K is shown in Figure 11. The results demonstrate that the modified CORGC has the same accuracy of the original CORGC for non-polar multicomponent mixtures, indicating that the modified CORGC not only improves the accuracy of CORGC for polar systems, but also provides the same accuracy for non-polar systems. Thus, another advantage of this new EOS is shown.

CONCLUSIONS

The objective of this study was to improve the performance and accuracy of the CORGC equation of state

Table 4. Ability of the CORGC/UNIFAC (modified CORGC) and original CORGC equations of state to predict VLE ratios of multi-component systems.

Mixture Components (1-2-3)	No. of Points	Temperature Range (K)	Pressure Range (MPa)	Original CORGC AAPD			Modified CORGC AAPD			Reference Number
				K_1	K_2	K_3	K_1	K_2	K_3	
CO_2 + CH_3OH + C_2H_5OH	16	313.2	2 - 8	0.38	52.79	22.84	0.26	42.95	34.26	[8]
CO_2 + CH_3OH + H_2O	14	313.2	7 - 12	32.21	577.42	2813.81	11.15	551.1	1084.77	[21]
H_2O + C_2H_5OH + CO_2	13	308 - 338	10.2 - 17	2194.01	351	71.4	640.3	97.22	320.74	[14]

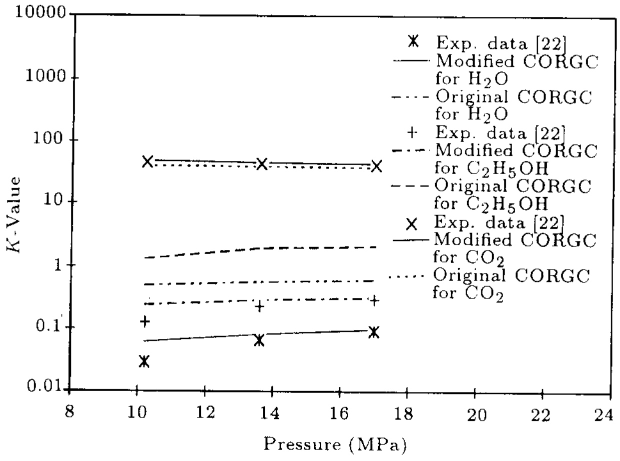

Figure 10. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of H_2O + C_2H_5OH + CO_2 mixture at 323.3 K.

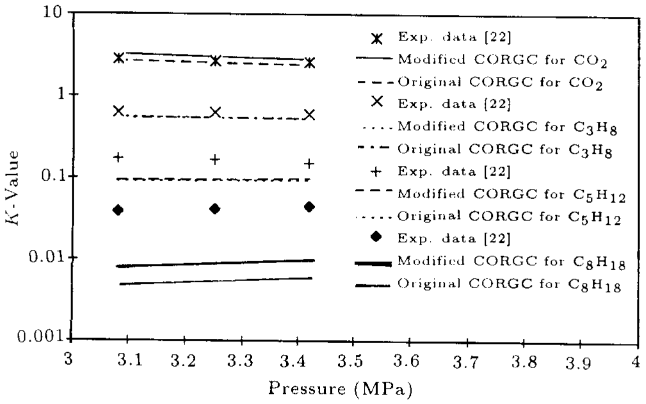

Figure 11. Comparison of CORGC/UNIFAC and CORGC in predicting vaporization equilibrium ratios of CO_2 + C_3H_8 + C_5H_{12} + C_8H_{18} mixture at 310.93 K.

for vapor-liquid equilibria of polar multicomponent mixtures. Therefore, the CORGC equation of state together with PSRK mixing rule was used and the original UNIFAC was applied as G^E model in this approach. The accuracy of the original CORGC and the modified CORGC (CORGC/UNIFAC) equations of state were compared. The required parameters of the UNIFAC model for this investigation were fitted to binary experimental vapor-liquid equilibrium data.

The missing interaction parameters for several unlike pairs of groups in the original CORGC were also determined and reported.

One of the main advantages of the modified CORGC EOS (CORGC/UNIFAC) is that there is no need for interaction parameters (a^+_{mn} and T^+_{mn}) between each pairs of groups m and n that are not in the same molecules; therefore, the required parameters for CORGC are decreased.

The outcomes demonstrate that CORGC/UNIFAC provides better VLE calculation results for polar mixtures than CORGC, especially at high temperatures and pressures. Another advantage of this work is that the same accuracy for VLE calculation of non-polar mixtures is obtained. This improved accuracy has been achieved by introducing 4 extra parameters.

NOMENCLATURE

a	attraction energy parameter of CORGC EOS, (cm^6.bar/mol^2)
a_{mn}	attraction energy between groups m and n (cm^6.bar/mol/K)
au_{nm}	interaction parameter for groups or components n and m in UNIFAC model (K)
A, B, C, D	weighting factors for the error objective functions
b	molecular co-volume (cm^3/mol)
b_m	co-volume of group m (cm^3.bar/mol)
bu_{nm}	interaction parameter for groups or components n and m in UNIFAC model
c	equivalent degree of freedom
c_m	equivalent degree of freedom of group m
cu_{nm}	interaction parameter for groups or components n and m in UNIFAC model, (K^{-1})
CK_j	calculated vaporization equilibrium ratio of component j
CX_j	calculated liquid mole fraction of component j
CY_j	calculated vapor mole fraction of component j
EK_j	experimental vaporization equilibrium ratio of component j
EX_j	experimental liquid mole fraction of component j
EY_j	experimental vapor mole fraction of component j
G_0^E	excess molar Gibbs energy at zero pressure or at normal pressure
G^E	excess Gibbs energy
NC	number of components
NG	number of groups
NP	number of data points
P	pressure (MPa)
q_m	normalized surface area of group m
q_1	mixing rule constants defined in Equation 10

R	universal gas constant, 83.14 (cm^3.bar/mol.K)
T	temperature (K)
T_m	co-volume parameter temperature dependency (K)
T_{mn}	energy parameter temperature dependency (K)
v	molar volume
x	phase composition
y	b/4v
z	phase composition
Z	compressibility factor

Greek Symbols

α	constant equal to 1.078
θ	equation of state mixture parameter defined in Equation 11
γ	activity coefficient
φ	fugacity coefficient
ν_{im}	number of group m in the molecule i
ν	group composition variable
Ψ_{nm}	parameter defined in Equation 8

Subscripts

i	parameter for pure component i
ij	characteristic of components i and j interaction
0	reference fluid or zero pressure

Superscripts

E	excess property
$*$	group co-volume parameter in the CORGC equation of state
$+$	group energy parameter in the CORGC equation of state

ABBREVIATIONS

AAD	average absolute deviation
AAD%	average absolute deviation percent
CORGC	chain of rotator group contribution equation of state
EOS	equation of state
UNIFAC	universal functional group activity coefficients
VLE	vapor liquid equilibria

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