

VLE calculation of carbon dioxide+n-alkanes binary mixtures with MHV2 mixing rule

Behzad Khodakarami[†] and Abbas Naderifar

Department of Chemical Engineering, Amir Kabir University of Technology, Tehran, Iran
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Abstract—Vapor-liquid equilibria for binary and asymmetric systems include carbon dioxide+C₁-C₈, C₁₀ are calculated by using the Peng-Robinson-Stryjek-Vera equation of state coupled with the modified MHV2 mixing rule. The modified UNIFAC model is used for determining activity coefficient and excess Gibbs free energy. Calculated equilibrium pressures and mole fractions in vapor phase are compared with the experimental data. The average absolute deviation percent (AAD%)s indicates that the error involved in the application of the MHV2 mixing rule by optimized q_1 and q_2 is less than WS and PRSK mixing rules in most cases.

Key words: Mixing Rule, Equation of State, Supercritical, Equilibrium

INTRODUCTION

In the recent years several mixing rules, combining excess Gibbs free energy models and equations of state, have been proposed and used to correlate and/or predict phase equilibria of non-ideal mixtures. Huron and Vidal give one approach that is the infinite-pressure bases [1]. The other is the zero-pressure approach as developed by Heidemann and Kokal [2] and Michelsen [3]. Huron and Vidal approach was proposed 30 years ago but their mixing rule has not been widely used. The primary reason for that is due to the lack of parameters for excess Gibbs free energy at infinite pressure in the literature. To make the Huron-Vidal mixing rule useful in practical application, Soave [4] proposed an elaborate procedure to numerically calculate the excess Gibbs energy at infinite pressure from the values of the activity coefficients in the liquid phase. However, the application of his procedure to the HV mixing rule is not straightforward, so the procedure has rarely been applied. Therefore, for all practical purposes, the Huron-Vidal mixing rule still remains unappreciated.

Currently, the MHV1 mixing rule is one of the few mixing rules working quite successfully in phase equilibrium calculations for a large number of systems without the need of introducing new binary interaction parameters. In view of the success of MHV1, some modifications of the MHV1 mixing rule have been proposed. For example, Michelsen obtained MHV1 from fitting his definition of the $q(\alpha)$ function to a linear function of α in the range of 10 to 13. Holderbaum and Gmehling [5] modified Michelsen's procedure to get their PSRK mixing rule by fitting the same $q(\alpha)$ function to a much higher range of α than Michelsen's. Dahl and Michelsen [6] proposed the MHV2 model by approximating $q(\alpha)$ with a second order polynomial.

Wong and Sandler [7] proposed a mixing rule that is one of the very few mixing rules effective in predicting high-temperature and high-pressure phase behavior by using available activity coefficient parameters at low temperatures.

Orbey and Sandler [8] slightly reformulated the WSMR by rewriting the cross second virial term. This mixing rule is accurate and useful for predictions of multi-component vapor-liquid equilibria.

Twu and Coon [9] also developed another mixing rule for application to strongly non-ideal chemical mixtures. The Twu and Coon mixing rule (TCMR) could be reduced to the vdWMR when the parameters in the non-random excess Helmholtz free energy are set zero.

Systems of light components and heavy hydrocarbons are highly asymmetric and industrially important. A number of investigations over the last years have shown that most EOS/ G^E models (MHV2, PSRK, Wong-Sandler) fail to represent these asymmetric systems [10,11].

Comparison and evaluation of various mixing rules can be found in the works of Kwak et al. [12], LEE et al. [13], Mulero et al. [14].

In this work vapor-liquid equilibria for nine asymmetric binary mixtures are calculated by using the PRSV EOS with MHV2 mixing rule by optimized q_1 and q_2 , Wong-Sandler and PSRK mixing rules and modified UNIFAC model.

THERMODYNAMIC MODEL

The condition for vapor-liquid equilibrium is

$$f_i^l = f_i^v \text{ or } \phi_i^l x_i = \phi_i^v y_i \quad (1)$$

In order to use Eq. (1) to model VLE and to obtain predictions in regions where no experimental data exist, the fugacity coefficients must be calculated from an appropriate equation of state.

The Peng-Robinson-Stryjek-Vera (PRSV) [15] equation of state is suitable for high-pressure vapor-liquid equilibrium calculations. This EOS is as follows:

$$P = \frac{RT}{v-b} - \frac{a}{(v+ub)(v+wb)} \quad (2)$$

In the above equation, $u=1+\sqrt{2}$, $w=1-\sqrt{2}$ and

$$a = \left(0.457235 \frac{R^2 T^2}{P}\right) \alpha(T) \quad (3)$$

[†]To whom correspondence should be addressed.

E-mail: b_khodakarami@yahoo.com

Table 1. Vapor-liquid equilibria using the PRSV EOS with MHV2*, PSRK and WS mixing rules

Binary system	Temperature range (K)	No. of data point	P/P _A × 100			Δy × 100			Data Ref.
			MHV2*	PSRK	WS	MHV2*	PSRK	WS	
CO ₂ +C ₁	230.00-270.00	52	2.0	2.2	2.8	0.86	1.04	1.45	[17]
CO ₂ +C ₂	207.00-270.00	84	0.9	0.8	0.4	1.98	0.70	2.82	[17]
CO ₂ +C ₃	311.05-361.15	59	2.7	1.7	3.5	0.90	1.88	1.81	[18]
CO ₂ +n-C ₄	277.90-418.48	96	1.1	2.2	1.8	1.98	3.95	2.35	[19]
CO ₂ +n-C ₅	252.67-458.54	108	2.5	2.8	3.8	0.62	2.65	0.35	[20]
CO ₂ +n-C ₆	298.15-313.15	20	3.2	4.7	3.9	0.51	0.81	0.65	[21]
CO ₂ +n-C ₇	310.65-477.21	51	4.0	3.9	4.2	1.00	0.64	1.95	[22]
CO ₂ +n-C ₈	313.15-348.15	20	4.2	4.9	7.5	1.12	0.57	0.92	[23]
CO ₂ +n-C ₁₀	462.55-583.65	16	6.5	18.1	8.9	1.92	2.44	1.75	[24]
Average			3.0	4.6	4.1	1.21	1.63	1.56	

*MHV2 mixing rule by optimized q_1 and q_2

Table 2. Coefficients for the generalized correlations for the parameters q_1 and q_2

	i=1	i=2	i=3	i=4	i=5	i=6
m_i	-0.44812	0.01331	-0.16602	-0.00321	-0.00125	-0.00134
n_i	-0.000073	-0.000051	0.000204	0.000002	-0.000001	0.001092

$$b = 0.077796 \frac{RT_c}{P_c} \quad (4)$$

$$\alpha(T) = \{1 + \kappa[1 - (T/T_c)^{1/2}]\}^2 \quad (5)$$

where

$$\kappa = \kappa_0 + \kappa_1[1 + (T/T_c)^{1/2}](0.7 - T/T_c) \quad (6)$$

and

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (7)$$

and the constant κ_1 is a characteristic of each pure component.

In the MHV2 mixing rule the parameter b of EOS for a mixture are calculated by:

$$b = \sum_i x_i b_i \quad (8)$$

And the parameter a of EOS calculated from solving the following second order equation for ε (higher real root):

$$q_2 \varepsilon^2 + q_1 \varepsilon + \left[-q_1 \sum_i x_i \varepsilon_i - q_2 \sum_i x_i \varepsilon_i^2 - \frac{G^E}{RT} - \sum_i x_i \ln\left(\frac{b_i}{b}\right) \right] = 0 \quad (9)$$

$$\varepsilon = a/(bRT) \quad (10)$$

The recommended values of q_1 and q_2 for the MHV2 mixing rule are -0.478 and -0.0047 for RK EOS, respectively [6] and -0.4347 and -0.003654 for PR EOS, respectively [16].

RESULTS AND DISCUSSION

The VLE for nine binary asymmetric mixtures under isothermal conditions at several temperature have been studied. To calculate the excess Gibbs free energy, the modified UNIFAC activity coefficient model is used. The selected asymmetric systems are carbon dioxide - C₁-C₈, C₁₀. Calculated equilibrium pressures and vapor mole fraction are compared with the experimental data, and the average

absolute deviation percent (AAD%) in equilibrium pressures and vapor mol fraction are listed in Table 1. The two parameters q_1 and q_2 included in the MHV2 mixing rule may be calculated from vapor-liquid equilibrium data. These were presented with a good approximation in terms of $T_f = T/(T_c + T_{c1})$ and $\psi = b_2/b_1$ ($b_2 < b_1$), as follows:

$$q_1 = a_1 + a_2 \psi + a_3 \psi^2$$

$$q_2 = a_4 + a_5 \psi + a_6 \psi^2$$

$$a_i = m_i + \frac{n_i}{T_f}$$

n_i and m_i are reported in Table 2.

NOMENCLATURE

a	: attraction parameter in equation of state
b	: covolume parameter in equation of state
f	: fugacity
G^E	: excess Gibbs free energy
P	: pressure
P_c	: critical pressure
R	: gas constant
T	: temperature
T_c	: critical temperature
v	: molar volume
x	: liquid mole fraction
y	: vapor mole fraction
u, w	: constant of equation of state

Greek Letters

α	: temperature correction of the equation of state attraction-term parameter 'a'
κ, κ_0	: parameters in PRSV equation of state
κ_1	: characteristic parameter in PRSV equation of state depending upon the physical properties of the pure component

ε : equation of state mixture parameter
 ϕ : fugacity coefficient
 ω : acentric factor

Subscripts/Superscripts

c : critical property
 E : excess property
 exp : experimental
 i, j : in a mixture
 m : mixture
 l : liquid
 v : vapor

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