

# Phase Equilibrium of Asymmetric Systems by Predictive Equations of State Models

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In this study the modified Wong–Sandler (WS), the modified Huron–Vidal second-order (MHV2), and the Orbey–Sandler (HVOs) mixing rules were used for phase equilibrium correlation of carbon dioxide in *n*-alkanes, alcohols and water systems. Their correlative and predictive capabilities were compared. In all of these calculations, the Peng–Robinson–Stryjek–Vera (PRSV) equation of state (EOS) was used. It was found that the correlation capacity of the WS mixing rule is better than the HVOs mixing rule. The MHV2 mixing rule failed for highly asymmetric systems, especially in the critical region. The prediction capacities of the WS and HVOs mixing rules, based on the extrapolation of model parameters obtained at the lowest available temperature and pressure to higher values, were found to be acceptable. Also, for carbon dioxide–alkane binaries model parameters were expressed successfully as a function of temperature and the number of carbon atoms in the solvent using the WS mixing rule.

## Introduction

Cubic equations of state (EOS) are widely used for the description of vapor–liquid equilibrium (VLE) with the proper choice of a mixing rule. Although the van der Waals one-fluid mixing rule is used for relatively simple mixtures, even with two binary interaction parameters,  $k_{ij}$  and  $l_{ij}$ ; it cannot accurately represent complex mixtures. A number of ad hoc modifications have been proposed for such systems.<sup>1–3</sup> Another group of mixing rules is based on equating the excess free energy from a liquid-phase activity coefficient model with the corresponding term from an EOS,<sup>4</sup> and those that make this link at infinite pressure are free of ad hoc assumptions. The first successful attempt is that of Huron and Vidal<sup>5</sup> which requires a complete refitting of data and cannot be used to accurately extrapolate over temperature with temperature-independent parameters. The WS mixing rule<sup>6</sup> makes use of excess Helmholtz free energy at infinite pressure, providing a number of advantages, and has the correct low-density composition dependence. The modified Huron–Vidal mixing rule of Michelsen (MHV1)<sup>7,8</sup> and that of Dahl and Michelsen (MHV2)<sup>9</sup> are the most used ones of the low pressure class. Although MHV1 and MHV2 do not satisfy the second virial coefficient boundary condition and include an ad hoc extrapolation procedure, they have been found to give quite reasonable correlations and predictions of experimental data for highly nonideal systems. The modification introduced by Orbey and Sandler<sup>10</sup> for the HVOs mixing rule is based on the assumption of a universal linear algebraic function,  $u$ , that relates the liquid molar volumes and their hard core volumes. A detailed summary of these can be found elsewhere.<sup>11–13</sup>

In this work, vapor liquid equilibrium (VLE) of asymmetric systems of CO<sub>2</sub> with alcohols, heavy alkanes and water were studied with the PRSV equation of

state<sup>14</sup> coupled with WS, MHV2, and HVOs mixing rules. Prediction capacity of the models are investigated by two approaches. In the first approach, the prediction method was used to extend the experimental information available at the milder temperature and pressure (such as room temperature and pressure) to design conditions. In the second approach, it was attempted to make all model parameters of the WS mixing rule a function of temperature and the number of carbon atoms in the solvent to analyze the predictive capacity of the mixing rules.

## Phase Equilibrium Using Equations of State Approach

Many cubic equations of state are available in the literature; some recent and comprehensive reviews are available.<sup>15</sup> For the case of PRSV EOS

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (1)$$

where

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

and

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

These relations ensure that the critical point is obtained from the EOS. The term  $\alpha(T)$  in eq 2 is temperature dependent, is unity at the critical temperature, and has been chosen to ensure that the vapor pressure calculated from the EOS at other temperatures is acceptably accurate. One such representation is

$$\alpha(T) = [1 + \kappa(1 - \sqrt{T/T_c})]^2 \quad (4)$$

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**Table 1. Model Parameters for WS, HVOS and MHV2 Mixing Rules**

mixing rules	WS	HVOS	MHV2
equation of state	PRSV		
	$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}$		
activity coeff model	NRTL		van Laar
	$\frac{A^{\text{ex}}}{RT} = x_1 x_2 \left[ \frac{\tau_{21} G_{21}}{x_1 + x_2 G_{21}} + \frac{\tau_{12} G_{12}}{x_2 + x_1 G_{12}} \right]$ $G_{ij} = b_{ij} \exp(-\alpha_{ij} \tau_{ij})$		$\frac{G^{\text{ex}}}{RT} = \frac{2a_{12}x_1k_1x_2k_2}{x_1k_1 + x_2k_2}$
model parameters	$\alpha_{ij}, k_{ij}, \tau_{ij}$		$k_1, k_2$

**Table 2. Binaries Studied in the Analysis of the Mixing Rules and Pure Component Parameters<sup>15</sup>**

solute; $T_c$ (K), $P_c$ (bar), $\omega$ , $\kappa_1$	solvent; $T_c$ (K), $P_c$ (bar), $\omega$ , $\kappa_1$	temp range (K)
CO <sub>2</sub> 304.21, 73.82, 0.22500, 0.04285	<i>n</i> -decane 617.50, 21.03, 0.49052, 0.04510	277–583
	<i>n</i> -heptane 540.10, 27.36, 0.35022, 0.04648	310–477
	<i>n</i> -pentane 469.70, 33.69, 0.25143, 0.03946	252–458
	methanol 512.58, 80.96, 0.56533, -0.16816	213–313
	ethanol 513.92, 61.48, 0.64439, -0.03374	313–337
	butanol 562.98, 44.13, 0.59022, 0.33431	314–337
	1-pentanol 588.15, 39.09, 0.57839, 0.36781	314–337
	water 647.29, 220.90, 0.34380, -0.06635	383–623

In this work the temperature dependence of the  $\alpha$  term proposed by Stryjek and Vera<sup>14</sup> is used

$$\kappa = \kappa_0 + \kappa_1(1 + T_r^{0.5})(0.7 - T_r) \quad (5)$$

with

$$\kappa_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (6)$$

and where the constant  $\kappa_1$  is specific for each pure compound and is used to fit low-temperature saturation pressures accurately. Both vapor and liquid phase can be described by the same EOS model. However, for the success of EOS models, they must accurately predict the saturation pressure of the pure components, and proper mixing rules must be available to extend their use to multicomponent mixtures.

To test the selected mixing rules, asymmetric binary mixtures were used and isothermal vapor–liquid equilibria of these pairs were calculated by the QBASIC and FORTRAN programs.<sup>16</sup> Required thermodynamic properties such as critical temperature ( $T_c$ ) and pressure ( $P_c$ ), Pitzer's acentric factor ( $\omega$ ), the PRSV equation parameter ( $\kappa_1$ ), experimental liquid and vapor mole fractions and equilibrium pressures, etc. were given as an input to the program. Other inputs are the model parameters of the activity coefficient model used. The model parameters for each mixing rule are summarized in Table 1. These parameters were given as input at the beginning of the program execution as an initial estimate. The program calculates the vapor liquid equilibrium and

tries to minimize the error, which is defined as

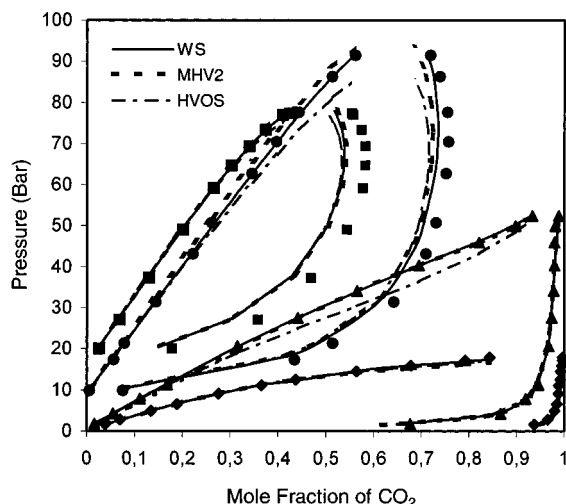
$$\text{error} = \frac{\sum_{i=1}^c |P_{\text{exp}} - P_{\text{cal}}|}{c} \quad (7)$$

In the optimization of model parameters simplex method is used.

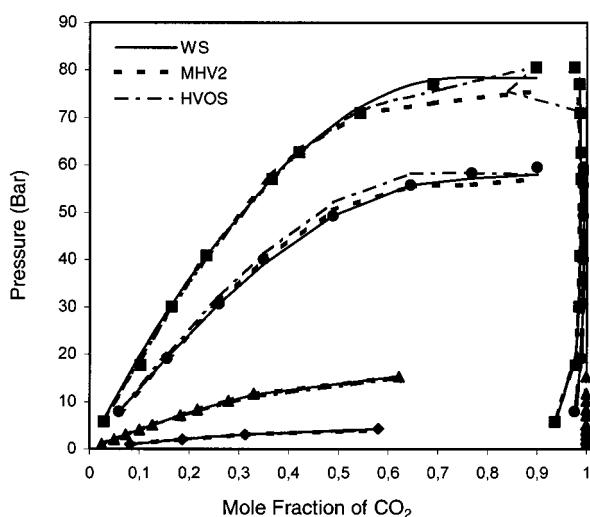
The binaries studied in order to investigate the correlation and prediction capabilities of WS, MHV2, and HVOS mixing rules, the range of temperatures investigated and pure component parameters are shown in Table 2. The light components which are supercritical at most of the times such as methane, nitrogen, carbon dioxide, etc. form asymmetric systems with heavy compounds and/or polar compounds like alcohols, water, etc. The systems in Table 2 are asymmetric and are widely used in industrial applications. The phase behavior of CO<sub>2</sub> mixtures is of technological interest because of the occurrence of CO<sub>2</sub> in natural gas, crude oil, and numerous chemical processes.<sup>17</sup>

## Results and Discussion

The correlation capacities of the mixing rules used in this study are tested<sup>16</sup> and the results for CO<sub>2</sub> systems are presented here. The CO<sub>2</sub> + *n*-pentane system was chosen as a representative binary within the CO<sub>2</sub> + alkane systems studied, and the correlation results are shown in Figure 1. At 252 K, CO<sub>2</sub> is subcritical while at other temperatures it is supercritical. In general good matches were obtained with the



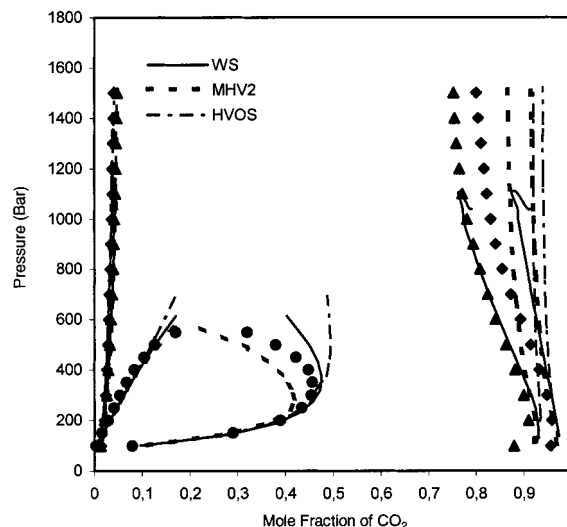
**Figure 1.** VLE correlation of the CO<sub>2</sub>-*n*-pentane system by WS, MHV2, and HVOS mixing rules. The points (♦, ▲, ●, ■) are the experimental data for the temperatures (252, 294, 394, and 423 K), respectively.<sup>21</sup>



**Figure 2.** VLE correlation of the CO<sub>2</sub>-methanol system by WS, MHV2, and HVOS mixing rules. The points (♦, ▲, ●, ■) are the experimental data for the temperatures (213, 247, 293, and 313 K), respectively.<sup>22</sup>

experimental data. With the WS mixing rule as the temperature approaches the critical temperature of *n*-pentane, the vapor phase was found to be richer in *n*-pentane compared to the experimental results. In general, as the asymmetry of the system increases, the MHV2 mixing rule has some shortcomings around the critical region, but as the nonrandomness of the binaries decreases, its results are comparable to those obtained by WS mixing rule. The model parameters of HVOS mixing rule are  $\alpha$ ,  $\tau_{12}$ , and  $\tau_{21}$ . Since  $\alpha$  is an indication of nonrandomness of the system,  $\alpha$  values were taken to be the same as those found by the WS mixing rule. Therefore, only  $\tau_{12}$  and  $\tau_{21}$  are optimized. The results are similar to that obtained by the WS mixing rule although the latter was more accurate at the critical region.

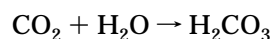
The results for the correlation of CO<sub>2</sub> + methanol system is shown in Figure 2. The WS mixing rule captures the phase equilibrium behavior very well. For the case of the MHV2 mixing rule, the general phase behavior is captured; however, pressures are found to be slightly lower than the experimental measurements.



**Figure 3.** VLE correlation of the CO<sub>2</sub>-water system by WS, MHV2, and HVOS mixing rules. The points (♦, ▲, ●) are the experimental data for the temperatures (383, 423, and 573 K), respectively.<sup>23</sup>

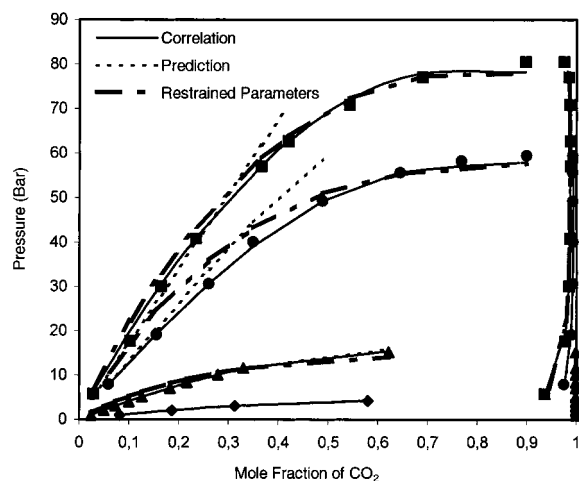
The results of the HVOS mixing rule, except for the temperature at which CO<sub>2</sub> is supercritical, are quite good. At 313 K, the calculated pressure values are somewhat lower than the experimental measurements around the critical region, and the loop closes inaccurately. The model cannot find the correct phase equilibrium behavior at that region.

The CO<sub>2</sub> + water system is highly asymmetric and industrially important so that calculation of the correct phase equilibrium of this system is a good indication of the accuracy and capability of correlation of the mixing rules. The results for the CO<sub>2</sub> + water system are presented in Figure 3. At the temperatures studied CO<sub>2</sub> is supercritical. At temperatures 383 and 423 K, the WS mixing rule fails; however, at a temperature of 573 K, the results are more accurate. This result is arising due to the reversible reaction

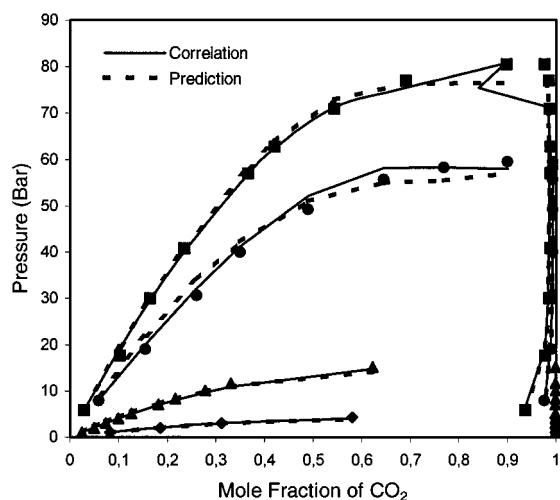


which has been neglected, and it strongly influences the concentration of CO<sub>2</sub> in water. This effect becomes negligible as temperature increases due to the exothermic nature of the reaction. The MHV2 mixing rule encircles the general phase equilibrium behavior of the system, but it systematically calculates the vapor phase to be rich in CO<sub>2</sub> in the reaction dominant temperature range. At 573 K, at which the existence of H<sub>2</sub>CO<sub>3</sub> can be taken as negligible, calculated CO<sub>2</sub> vapor phase compositions are lower than the experimental ones. The HVOS mixing rule finds the vapor phase composition too rich in CO<sub>2</sub> but calculates pressure values very well.

The prediction capacities of the mixing rules were tested by following two approaches. In the first approach, WS and HVOS mixing rules were tested by determining the model parameters by the correlation of the lowest available temperature vapor-liquid equilibrium data set and making predictions at all higher temperatures. For the CO<sub>2</sub>-methanol system, parameters at 213 K, at which CO<sub>2</sub> is subcritical, were used at higher temperatures. The WS mixing rule found a false liquid-liquid phase split, and the computer program did not converge at high temperatures because of the lack of robustness of the model. Consequently,



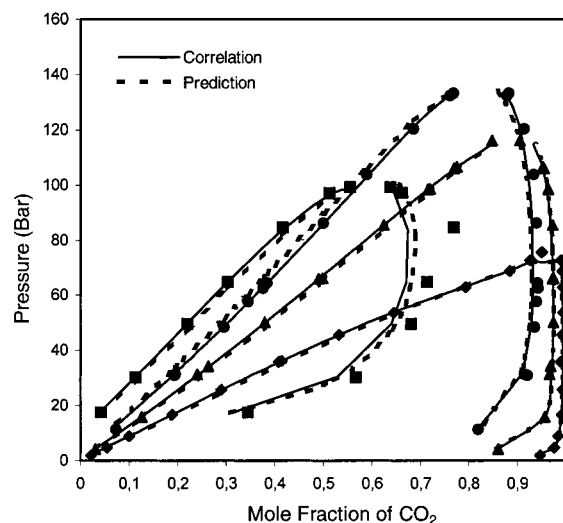
**Figure 4.** VLE correlation and prediction of the CO<sub>2</sub>-methanol system by WS mixing rule. In this prediction, low-temperature parameters are used. The points (♦, ▲, ●, ■) are the experimental data for the temperatures (213, 247, 293, and 313 K), respectively.<sup>22</sup>



**Figure 5.** VLE correlation and prediction of the CO<sub>2</sub>-methanol system by HVOS mixing rule. In prediction, restrained parameters are used. The points (♦, ▲, ●, ■) are the experimental data for the temperatures (213, 247, 293, and 313 K), respectively.<sup>22</sup>

following the suggestion of Englezos et al.,<sup>18</sup> a restrained parameter fit was performed at 213 K. For the WS mixing rule,  $\alpha$  and  $k_{ij}$  parameters were taken as found in the correlation and  $\tau_{12}$  and  $\tau_{21}$  parameters were restrained. It is presented in Figure 4 that the phase behavior with restrained parameters is quite better than the results obtained with the original correlation parameters. The same approach was also used in testing the prediction capacity of the HVOS mixing rule. The parameters found at 213 K can accurately estimate the phase behavior at 247 and 298 K where CO<sub>2</sub> is subcritical; however, liquid split was observed at 313 K at which CO<sub>2</sub> is supercritical. At 213 K, restrained model parameters,  $\tau_{12} = 1.5$  and  $\tau_{21} = 0.3$  were used in order to avoid a phase split. The results found with the restrained parameters are given in Figure 5, and they are very close to experimental values. The phase split was not observed, and the prediction with restrained parameters is better than correlation at 313 K.

In the second approach, a relation between model parameters with temperature and structure of the solvent was sought. In relation to the structure of the



**Figure 6.** VLE correlation and prediction of the CO<sub>2</sub>-nheptane system by WS mixing rule. In prediction, all the model parameters are functions of temperature and number of carbon atoms in the alkane. The points (♦, ▲, ●, ■) are the experimental data for the temperatures (310, 354, 394, and 477 K), respectively.<sup>24</sup>

solvent, extensive models are also available<sup>19,20</sup> for CO<sub>2</sub> and CH<sub>4</sub> with alkanes very different in chain length. In this study, for CO<sub>2</sub> + *n*-alkane systems, all the model parameters,  $\alpha_{ij}$ ,  $k_{ij}$ ,  $\tau_{12}$ , and  $\tau_{21}$ , were related to the number of carbon atoms in the alkane (*C*) and temperature. Then  $\alpha$  and  $k_{ij}$  can be expressed as

$$\alpha_{ij} = 0.0219737(C) + 0.380526 \quad (8)$$

$$k_{ij} = 0.272467 - 0.03256(C) + 0.00181333(C)^2 \quad (9)$$

A linear relationship was found for  $\tau_{21}$  with respect to temperature, the coefficients of which were expressed as a function of carbon in the alkane.

$$a = -0.00011188(C) - 0.00269061 \quad (10)$$

$$b = 3.08348 - 0.39107(C) + 0.0301533(C)^2 \quad (11)$$

Finally  $\tau_{21}$  can be expressed as

$$\tau_{21} = (-11.188 \times 10^{-5}(C) - 0.00269061)T(K) + (3.08348 - 0.39107(C) + 0.0301533(C)^2) \quad (12)$$

Using a similar procedure  $\tau_{12}$  can be expressed as

$$\tau_{12} = (-9.73221(C) + 108.457) + (0.0622857(C) - 0.669738)T(K) + (-9.55728 \times 10^{-5}(C) + 0.0010067)T^2(K) \quad (13)$$

The results for the CO<sub>2</sub> + *n*-heptane system using the predicted values of the parameters are given in Figure 6 in which solid lines show correlation and dash lines are for prediction results. The results indicated that the WS mixing rule is successful in phase equilibrium prediction for asymmetric systems. With the HVOS mixing rule, no direct relationship was found among model parameters, temperature, and number of carbon atoms in the solvent.

## Conclusions

It is difficult to accurately predict, or even correlate, the isothermal vapor-liquid equilibrium of carbon



dioxide systems owing to the asymmetric nature. In this study, the correlation capability of WS and HVOS mixing rules were shown to be successful and comparable, except that near the critical region the former was superior. An examination of the optimized parameters for the WS mixing rule for various mixtures shows that, as the asymmetry of the system increased, values of nonrandomness parameter  $\alpha_{ij}$  increased and those of binary interaction parameters decreased. The MHV2 mixing rule failed for highly asymmetric systems, especially in the critical region. Prediction capacities of WS and HVOS mixing rules were tested by using the model parameters found at the lowest available temperature, and it was found that the WS mixing rule was better than the HVOS mixing rule. It was also shown that the WS mixing rule parameters can be generalized in terms of temperature and the number of carbon atoms in the  $n$ -alkane up to  $n$ -decane so that quite acceptable extrapolations and predictions are possible.

## Nomenclature

$a$  = equation of state energy parameter  
 $A^{\text{ex}}$  = excess Helmholtz free energy  
 $b$  = equation of state excluded volume parameter  
 $G_{ij}$  = NRTL liquid activity model parameter  
 $G^{\text{ex}}$  = excess Gibbs free energy  
 $k_{ij}$  = binary interaction parameter  
 $P$  = pressure  
 $P_c$  = critical pressure  
 $R$  = gas constant  
 $T$  = temperature  
 $T_c$  = critical temperature  
 $V$  = volume

## Greek Letters

$\alpha$  = temperature-dependent equation of state parameter  
 $\alpha_{ij}$  = nonrandomness parameter  
 $\kappa$  = Peng–Robinson equation parameter  
 $\kappa_0$  = PRSV equation parameter  
 $\kappa_1$  = PRSV equation parameter  
 $\tau_{ij}$  = parameter in local composition factor of NRTL model  
 $\omega$  = Pitzer's acentric factor

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