

## **THE ROLE OF MIXING RULES AND THREE-BODY FORCES IN THE PHASE BEHAVIOR OF MIXTURES: SIMULTANEOUS VLE AND VLLE CALCULATIONS**

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### **ABSTRACT**

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It is demonstrated that with the use of proper statistical mechanical mixing rules in empirical equations of state it is possible to predict the vapor–liquid equilibrium (VLE) and vapor–liquid–liquid equilibrium (VLLE) of highly polar multicomponent mixtures. It is also shown that the new mixing rules are capable of predicting the VLE and VLLE data of a given mixture, simultaneously, with the use of only one set of unlike-binary interaction parameters.

In predicting the VLE data of ternary mixtures using equations of state a common problem has been the inaccuracy of prediction around the critical solution point of the mixture. This problem is resolved here through the inclusion of the unlike-three-body intermolecular interaction contribution in formulating the VLE algorithm. A number of sample calculations demonstrating the correcting roles of the new mixing rules and unlike-three-body contribution in VLE and VLLE predictions is presented.

### **INTRODUCTION**

Equations of state in general do not reliably predict the phase behavior of polar systems, particularly multicomponent systems such as acetone–methanol–water. They also fail to describe systems which exhibit more than two phases at equilibrium, such as nitrogen–ethane–methanol and nitrogen–ethene–methanol (Zeck and Knapp, 1986a, b). In addition, the prediction of the vapor–liquid coexistence curves of the nitrogen–methane–carbon dioxide and nitrogen–methane–ethane (Al-Sahlaf et al., 1983; Gupta et al., 1980) systems through equations of state has not been satisfactory in all ranges of pressures and compositions.

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The objective of this paper is to improve the predictive capabilities of existing equations of state by the use of statistical mechanical mixing rules and the implementation of the unlike-three-body effects in the phase behavior calculations.

## THEORY

An empirical pure fluid equation of state or a fundamental thermodynamic property is usually written in the following form:

$$\Psi^e = \Psi^e(v, T, a^{(1)}, \dots, a^{(c)}) \quad (1)$$

where  $\Psi$  is a thermodynamic property (such as pressure, enthalpy, ... etc.),  $v$  is the molar volume,  $T$  is the temperature,  $a^{(i)}$ s are constants of the equation of state and  $c$  is the number of such constants.

To extend the applicability of this equation to mixtures one usually combines it with the mixing rules for the parameters of the equation of state, thus:

$$a_m^{(k)} = a_m^{(k)}(a_{ij}^{(k)}, x_i, x_j) \quad i, j = 1, \dots, n \text{ and } k = 1, \dots, c \quad (2)$$

where  $n$  is the number of components in the mixture,  $a_{ij}^{(k)}$  ( $i = j$ ) is the  $k$ th parameter of pure component  $i$ , while  $a_{ij}^{(k)}$  ( $i \neq j$ ) is the interaction parameter between components  $i$  and  $j$ ,  $a_m^{(k)}$  is called the mixing rule for the  $k$ th parameter of the equation of state.

As a result, thermodynamic properties of a multicomponent mixture can be shown in the following form:

$$\begin{aligned} \Psi_m^e &= \Psi_m^e(v, T, a_m^{(1)}, \dots, a_m^{(c)}) \\ &= \Psi_m^e(v, T, a_{11}^{(1)}, a_{12}^{(1)}, \dots, a_{nn}^{(1)}, \\ &\quad \vdots \quad \quad \quad \vdots \\ &\quad \quad \quad a_{11}^{(c)}, a_{12}^{(c)}, \dots, a_{nn}^{(c)}, x_1, x_2, \dots, x_{n-1}) \end{aligned} \quad (3)$$

To apply eqn. (3) to mixture property calculations the numerical values of  $a_{ij}$  are needed. It is a general practice to derive parameters  $a_{ij}^{(k)}$  ( $i = j$ ) from pure component properties and parameters  $a_{ij}^{(k)}$  ( $i \neq j$ ) from binary mixture data of components  $i$  and  $j$  (such as the excess properties, interaction second virial coefficients, vapor-liquid equilibrium data, etc.). The above formulation is the basic idea behind most of the existing equations of state used for mixture calculations. There exist always problems in prediction and correlation of binary mixtures using existing mixture equations of state. To improve such predictions, a large number of mixing rules have been proposed by different investigators. We have proposed a new version of the van

der Waals mixing rules that are consistent with the conformal solution theory of statistical mechanics (Benmekki and Mansoori, 1987). It has been shown that such conformal solution van der Waals (CSvdW) mixing rules predict and correlate binary mixtures properties more accurately, as will also be illustrated here for the systems which are studied.

It is demonstrated that equations of state which are built on pure component and binary data are sometimes incapable of accurately predicting ternary and multicomponent properties. This problem will exist regardless of the amount of refinement that one can make in the mixing rules (Somait and Kidnay, 1978; Zeck and Knapp, 1986a). This is especially observed for ternary mixtures around their critical point for which there is sufficient experimental data available. For a long time different investigators have been associating this shortcoming of equations of state to the lack of their accuracy around the critical point. Some investigators have also tried to derive pair-interaction parameters from ternary data. As a result, while they have been able to correlate ternary critical region data, the binary mixture predictions were deteriorating. The reason for the deviation of prediction of equation of state around the ternary mixture critical region can be described as follows. In a ternary mixture, in addition to the kinds of interactions which exist between molecules in binary mixtures, there also exists an interaction which we would call the unlike-three-body interaction, which happens when there are three molecules of three different kinds interacting in a mixture. Considering the fact that there exists no such term in an equation of state, such as the cubic equations of state, we would expect that the unlike-three-body interaction contribution to the equation of state will not be accounted for when the equation of state is based on the pure component and binary mixture data. Symbolically we will define the unlike-three-body interaction contribution to  $\Psi$  by  $x_1x_2x_3 \Delta\Psi(T, v, \nu_{123})$ , where  $\nu_{123}$  is a parameter corresponding to the unlike-three-body interaction. As a result the equation of state of a mixture must be written in the following form:

$$\Psi_m = \Psi_m^c(v, T, a_m^{(1)}, \dots, a_m^{(c)}) + \sum_{i>j>k} x_i x_j x_k \Delta\Psi(v, T, \nu_{ijk}) \quad (4)$$

The second term in the right-hand side of this equation includes all the unlike-three-body interactions between every three different molecules in the multicomponent mixture.

For  $n = 3$  the second term of eqn. (4) will be

$$\sum_{i>j>k} x_i x_j x_k \Delta\Psi(v, T, \nu_{ijk}) = x_1 x_2 x_3 \Delta\Psi(v, T, \nu_{123}) \quad (5)$$

while for  $n = 4$  it will be

$$\begin{aligned} & \sum_{i>j>k} x_i x_j x_k \Delta\Psi(v, T, \nu_{ijk}) \\ &= x_1 x_2 x_3 \Delta\Psi(v, T, \nu_{123}) + x_1 x_2 x_4 \Delta\Psi(v, T, \nu_{124}) \\ & \quad + x_1 x_3 x_4 \Delta\Psi(v, T, \nu_{134}) + x_2 x_3 x_4 \Delta\Psi(v, T, \nu_{234}) \end{aligned} \quad (6)$$

The basic question to be answered at this stage is that of how to arrive at an expression for the unlike-three-body interaction term. This problem has been addressed in the statistical mechanical theory of many-body interactions, starting with the work of Axilrod and Teller (1943) and Axilrod (1951) in the development of algebraic expressions for three-body intermolecular interaction energy and finally the development of an analytic expression for the unlike-three-body interaction Helmholtz free energy using the perturbation theory of statistical mechanics (Barker et al., 1968). The final expression for the unlike-three-body interaction Helmholtz free energy,  $A_{ijk}^{3b}$ , is

$$A_{ijk}^{3b} = \frac{N\nu_{ijk}f_1(\eta)}{d^9f_2(\eta)} \quad (7)$$

where  $\nu_{ijk}$  is the triple-dipole constant and

$$f_1(\eta) = 9.87749\eta^2 + 11.76739\eta^3 - 4.20030\eta^4 \quad (8)$$

$$f_2(\eta) = 1 - 1.12789\eta + 0.73166\eta^2 \quad (9)$$

$$\eta = (\pi/6)(nd^3/V) \quad (10)$$

in which  $N$  is the number of molecules in volume  $V$  and  $d$  is the mixture average hard-core molecular diameter.

Knowing the unlike-three-body interaction Helmholtz free energy we can now calculate the contribution of the unlike-three-body interactions to other thermodynamic properties. As a result the correct compressibility factor of a multicomponent mixture will be (Lan and Mansoori, 1977)

$$Z_m = Z_m^e + \sum_{i>j>k=1}^n \sum_{j=1}^n \sum_{k=1}^n x_i x_j x_k \frac{\eta\beta_{ijk}}{b^3v} \left( \frac{f_1'f_2 - f_1f_2'}{f_2^2} \right) \quad (11)$$

where  $Z_m^e$  is the expression for the empirical equation of state and

$$\beta_{ijk} = (8/27)\pi N_0^4 \nu_{ijk} \quad (12)$$

$$f_1' = (\delta f_1 / \delta \eta) = 19.75498\eta + 35.30217\eta^2 - 16.80120\eta^3 \quad (13)$$

$$f_2' = (\delta f_2 / \delta \eta) = -1.12789 + 1.46332\eta \quad (14)$$

The co-volume parameter,  $b$ , is related to  $\eta$  through the following relation:

$$\eta = (b/4v) \quad (15)$$

Equation (11) constitutes the governing equation which will be used for phase equilibrium calculations.

#### PHASE EQUILIBRIUM FORMULATION

In the present calculations we utilize the Peng–Robinson equation of state (PR EOS). For this equation of state we use two different sets of mixing rules, one set is the original PR mixing rules (Peng and Robinson, 1976) and the other set is based on the van der Waals conformal solution theory (CSvdW). The latter mixing rules will produce the following expression for the PR EOS (Benmekki and Mansoori, 1987):

$$Z = \frac{v}{v-b} - \frac{c/RT + d - 2\sqrt{(cd/RT)}}{(v+b) + (b/v)(v-b)} \quad (16)$$

where

$$c = a(T_c)(1 + K)^2 \quad (17)$$

$$d = a(T_c)K^2/RT_c \quad (18)$$

the mixing rules for  $c$ ,  $b$ , and  $d$  are

$$c = \sum_i^n \sum_j^n x_i x_j c_{ij} \quad (19)$$

$$b = \sum_i^n \sum_j^n x_i x_j b_{ij} \quad (20)$$

$$d = \sum_i^n \sum_j^n x_i x_j d_{ij} \quad (21)$$

The combining rules for the unlike interaction parameters  $b$ ,  $c$  and  $d$  that are consistent with the above mixing rules are

$$b_{ij} = (1 - l_{ij})^3 \left( \frac{b_{ii}^{1/3} + b_{jj}^{1/3}}{2} \right)^3 \quad (22)$$

$$d_{ij} = (1 - m_{ij})^3 \left( \frac{d_{ii}^{1/3} + d_{jj}^{1/3}}{2} \right)^3 \quad (23)$$

$$c_{ij} = (1 - k_{ij}) (c_{ii} c_{jj} / b_{ii} b_{jj})^{1/2} b_{ij} \quad (24)$$

In eqns. (22)–(24) parameters  $k_{ij}$ ,  $l_{ij}$  and  $m_{ij}$  are the binary interaction

parameters that can be adjusted to provide the best fit to the experimental data.

A single equation of state is used to describe all the phases at equilibrium with the following equilibrium conditions:

$$\mu_i^I(T, P, \{x\}) = \mu_i^{II}(T, P, \{x\}) = \dots = \mu_i^N(T, P, \{x\}) \quad i = 1, 2, \dots, n \quad (25)$$

which can be expressed by

$$x_i \phi_i^I = x_i \phi_i^{II} = \dots = x_i \phi_i^N \quad i = 1, 2, \dots, n \quad (26)$$

where I, II, ..., N represent the phases at equilibrium. With the use of the CSvdW mixing rules and the implementation of the unlike-three-body interactions the following expression for the fugacity coefficient will be derived:

$$\begin{aligned} \ln \phi_i = & \left( (2 \sum x_j b_{ij} - b) / b \right) (P^e v / RT - 1) - \ln(P(v - b) / RT) \\ & \times (c / 2(2\sqrt{2RTb})) (2 \sum x_j c_{ij} - 2RT \sum x_j d_{ij} - 2\sqrt{(RT)}) \\ & \times (c \sum x_j d_{ij} + d \sum x_j c_{ij}) / \sqrt{(cd)} / c - (2 \sum x_j b_{ij} - b) / b \\ & \times (\ln((v + (1 + \sqrt{2})b) / (v + (1 - \sqrt{2})b))) \\ & + d \left( \sum_{i>j>k} x_i x_j x_k A_{ijk}^{3b} \right) / dn_i \end{aligned} \quad (27)$$

where  $P^e$  is the pressure for the empirical equation of state.

In the present calculations, experimental binary vapor–liquid equilibrium and vapor–liquid–liquid equilibrium data are used in the evaluation of the binary interaction parameters by minimizing an objective function. In the case of VLE calculations, the objective function is in the following form:

$$OF = \sum_{i=1}^{M_1} \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)_i^2 \quad (28)$$

in the case of vapor–liquid–liquid equilibrium calculations the objective function is in the following form:

$$OF = \sum_{i=1}^{M_1} \left( \frac{P_{\text{exp}} - P_{\text{cal}}}{P_{\text{exp}}} \right)_i^2 + \sum_{i=1}^{M_2} \left( \frac{x_{\text{exp}} - x_{\text{cal}}}{x_{\text{exp}}} \right)_i^2 \quad (29)$$

In eqns. (28) and (29),  $M_1$  is the number of experimental VLE bubble point data, pressure ( $P_{\text{exp}}$ ), and  $M_2$  is the number of experimental VLLE bubble point composition ( $x_{\text{exp}}$ ) data (composition of the saturated liquid phase of the VLLE region rich in the heavier component in equilibrium with the

TABLE 1  
Values of binary interaction parameters for the different mixing rules

System	Temperature (K)	Pressure range (bar)	Binary interaction parameters			
			CSvdW mixing rules			Original mixing rules
			$k_{12}$	$l_{12}$	$m_{12}$	$\xi_{12}$
Methane– carbon dioxide	270.00	31– 83	0.1831	0.1280	–0.0124	0.1047
Nitrogen– carbon dioxide	270.00	48–118	–0.0161	–0.0165	–0.0281	–0.0101
Nitrogen– methane	180.00	32– 48	0.1219	0.1304	0.0363	0.0663
Nitrogen– ethane	260.00	25– 75	0.0291	–0.0262	–0.0253	0.0511
Nitrogen– methanol	250.00	24–180	–0.1585	0.0367	–0.0248	–0.1927
Ethane– methanol <sup>a</sup>	260.00	4– 17	–0.2684	–0.1863	–0.0051	–0.0051
Ethane– methanol <sup>b</sup>	260.00	4– 17	–0.3916	–0.2674	–0.0024	–

<sup>a</sup> From vapor–liquid equilibrium data.

<sup>b</sup> From vapor–liquid and vapor–liquid–liquid equilibrium data.

vapor phase). Subscript “cal” stands for the calculated result. A three parameter search routine is used to evaluate the binary interaction parameters of the CSvdW mixing rules. Values of the binary interaction parameters of all the systems studied in this paper are reported in Table 1.

Since the value of the triple-dipole constant  $\nu_{123}$  is obtained from an approximate expression (Maitland et al., 1981), an adjustable parameter,  $\epsilon$ , is introduced here such that

$$\beta_{ijk} = \epsilon(8/27)\pi N_0^4 \nu_{ijk} \quad (30)$$

Parameter  $\epsilon$  is then adjusted to provide the best possible correlation of the ternary system.

## RESULTS AND CONCLUSIONS

Correlation and prediction of the phase equilibrium properties of three-component multiphase systems are a challenge for equations of state. Actually there are no correlations available that could describe the phase behavior of three-component multiphase systems with the kind of accuracy required in chemical process design (Zeck and Knapp, 1986a).

TABLE 2

Vapor-liquid equilibrium calculations for acetone (1)-methanol (2)-water (3) at 373 K

Liquid phase		Equilibrium Pressure (psia)		Vapor phase			
$x_1$	$x_2$	$P_{exp}$	$P_{cal}$	$y_{1cal}$	$Dy_1$	$y_{2cal}$	$Dy_2$
0.2700	0.6790	55.4	54.18	0.3308	-0.0078	0.6508	-0.0028
0.9160	0.0500	54.6	54.44	0.9037	-0.0027	0.0661	0.0029
0.6070	0.3300	56.9	56.43	0.6409	-0.0199	0.3279	0.0111
0.3810	0.5490	56.5	55.04	0.4571	-0.0271	0.5163	0.0087
0.2570	0.6400	54.4	52.24	0.3304	-0.0064	0.6311	-0.0101
0.2310	0.6390	52.9	50.92	0.3046	0.0063	0.6456	-0.0216
0.3850	0.4790	54.6	53.11	0.4919	-0.0369	0.4535	0.0205
0.1770	0.6540	51.0	48.73	0.2393	0.0197	0.6936	-0.0366
0.1820	0.6160	50.5	47.70	0.2545	0.0175	0.6635	-0.0345
0.4940	0.2940	53.4	52.28	0.6336	-0.0406	0.2669	0.0281

$$Dy = y_{cal} - y_{exp}$$

In a recent publication the authors (Benmekki and Mansoori, 1987) demonstrated the superiority of the CSvdW mixing rules in correlating the VLE properties of highly polar binary mixtures. Furthermore, Table 2 is produced to demonstrate the predictive capabilities of these mixing rules for ternary mixtures (in this case the acetone-methanol-water system, which is also considered as a highly polar mixture). The binary interaction parameters used in this calculation were reported earlier (Benmekki and Mansoori, 1987). According to this table the predictions based on the CSvdW are in excellent agreement with the experimental (Griswold and Wong, 1952) data. It should be pointed out that the other existing empirical mixing rules, including the PR mixing rules, are incapable of predicting such VLE system.

To demonstrate the utility of CSvdW mixing rules in the simultaneous correlation and prediction of VLE and VLLE properties of multicomponent multiphase systems Figs. 1-6 are reported here. In these figures the binary and ternary mixtures of supercritical nitrogen, ethane and methanol are considered. According to the experimental data of these compounds (Zeck and Knapp, 1986a; Grauso et al., 1977) mixtures of supercritical nitrogen-methanol and supercritical nitrogen-ethane exhibit vapor-liquid equilibria, mixtures of ethane-methanol exhibit both vapor-liquid and vapor-liquid-liquid equilibria, and the ternary mixtures of supercritical nitrogen-ethane-methanol also exhibit both vapor-liquid and vapor-liquid-liquid equilibria. Figures 1 and 2 consist of binary mixture VLE data, correlations using the CSvdW mixing rules, and the original PR mixing rules, both using PR equation of state. According to these figures, calculations using CSvdW are much closer to the experimental data than the

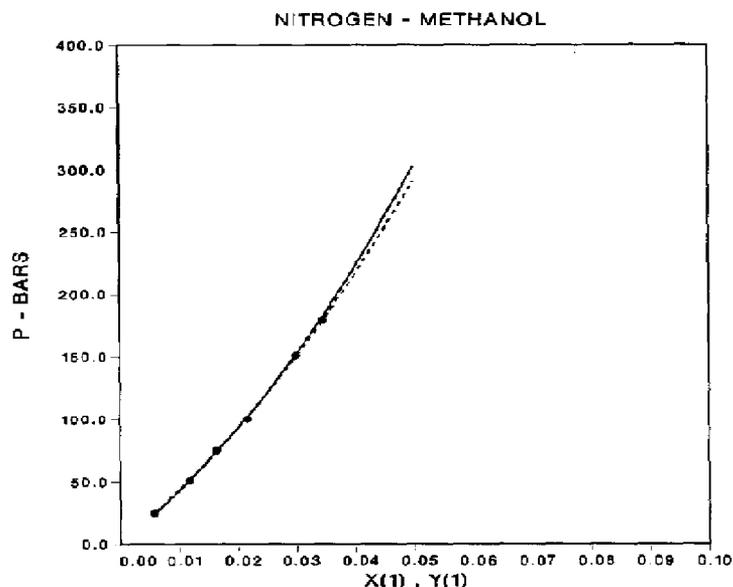


Fig. 1. Equilibrium pressure–composition diagram for nitrogen–methanol system. Solid line, correlation of the VLE data with the PR EOS and the CSvdW mixing rules; dashed line, PR EOS and the original mixing rules; dots, experimental VLE data (Zeck and Knapp, 1986a).

original PR mixing rules. For the system ethane–methanol (reported in Fig. 3) the PR mixing rule is incapable of correlating the VLE data and predicting the VLLE data while the CSvdW can correlate the VLE data quite satisfactorily and it simultaneously can predict the VLLE data rather well. The binary interactions parameters used for the simultaneous prediction of VLE and VLLE ternary data in Fig. 4 are evaluated using the VLE data reported in Figs. 1–3. According to this figure, simultaneous predictions of VLE and VLLE ternary data are good. The PR mixing rules (and other existing empirical mixing rules) are incapable of predicting such a phase behavior.

In order to improve the simultaneous prediction of VLE and VLLE data in the ternary mixture the VLLE data of ethane–methanol binary data are included in the optimization of its pair interaction parameters. Figure 5 consists of the reported simultaneous correlation of binary VLE and VLLE data of ethane–methanol, while Fig. 6 consists of the simultaneous prediction of ternary VLE and VLLE data of supercritical nitrogen–ethane–methanol. The correlation reported in Fig. 5 is not of much improvement over the correlation reported in Fig. 3. However, the ternary predictions reported in Fig. 6 are much superior to the ternary predictions reported in Fig. 4. In

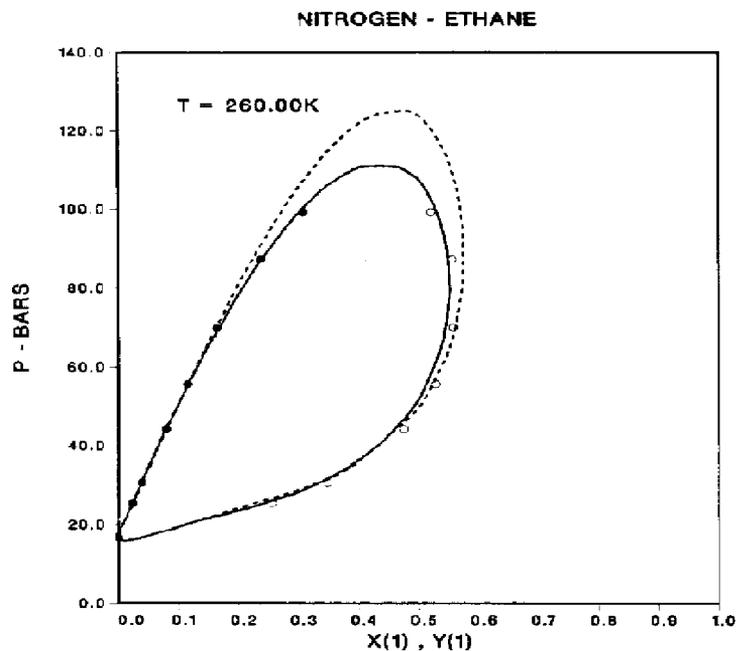


Fig. 2. Equilibrium pressure-composition diagram for nitrogen-ethane system. Solid line, correlation of the VLE data with the PR EOS and the CSvdW mixing rules; dashed line, PR EOS and original mixing rules; dots and circles, experimental VLE data (Grauso et al., 1977).

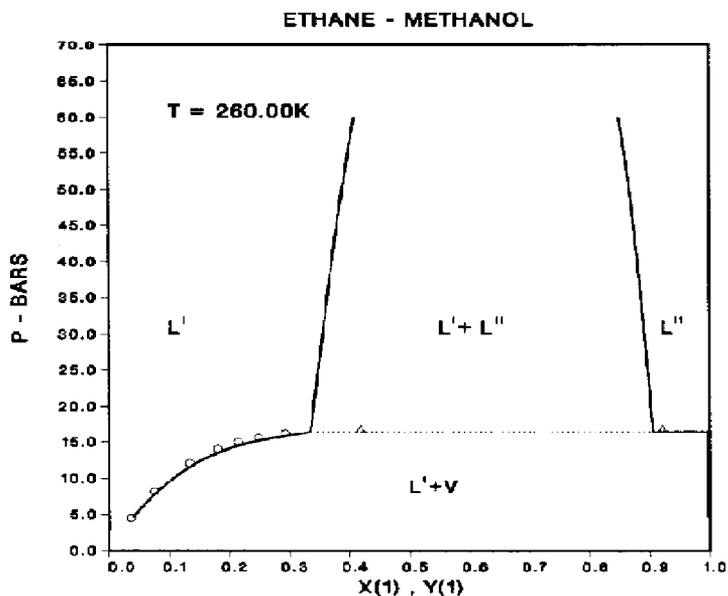


Fig. 3. Equilibrium pressure-composition diagram for ethane-methanol system. Solid lines, correlation of the VLE data with the PR EOS and the CSvdW mixing rules; circles, experimental VLE data; triangles, experimental VLLE data (Zeck and Knapp, 1986a).

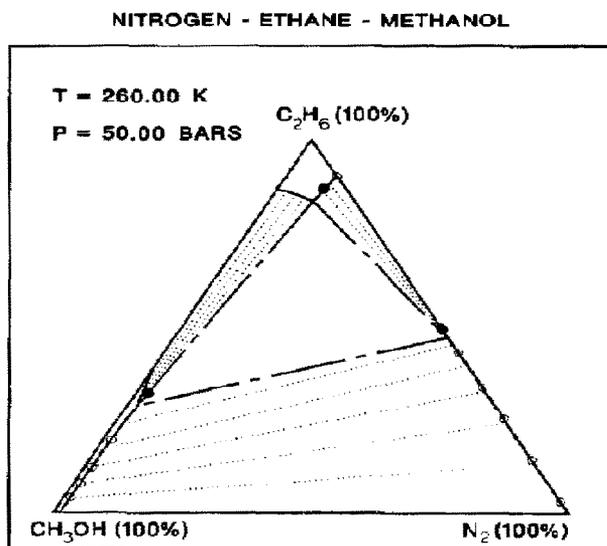


Fig. 4. Prediction of the phase behavior of nitrogen-ethane-methanol system with the PR EOS and the CSvdW mixing rules from binary VLE data. Dots and circles, experimental data (Zeck and Knapp, 1986a).

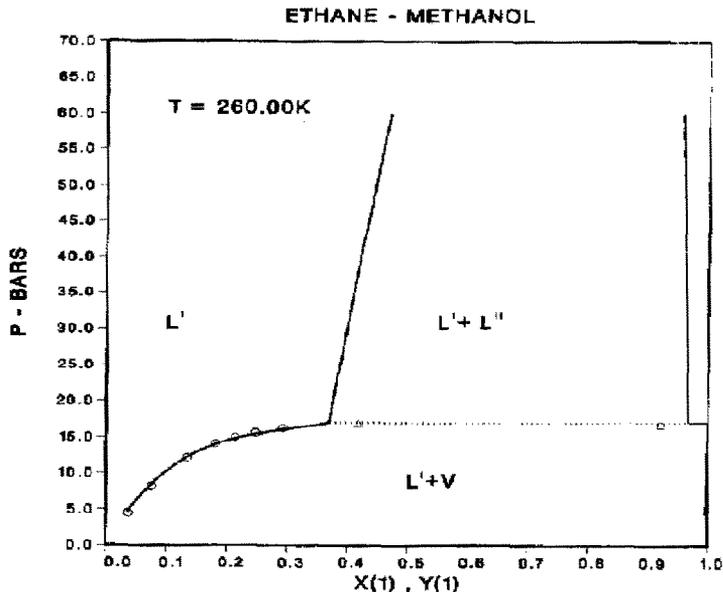


Fig. 5. Equilibrium pressure-composition diagram for ethane-methanol system. Solid lines, correlation of the VLE and VLLE data with the PR EOS and the CSvdW mixing rules; circles, experimental VLE data; triangles, experimental VLLE data (Zeck and Knapp, 1986a).

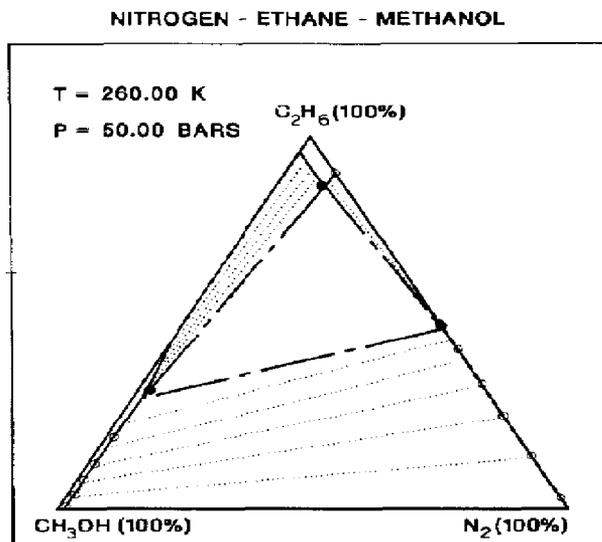


Fig. 6. Prediction of the phase behavior of nitrogen-ethane-methanol system with the PR EOS and the CSvdW mixing rules from binary VLE and VLLE data; dots and circles, experimental data (Zeck and Knapp, 1986a).

these ternary mixture predictions we have not included the unlike-three-body interaction contribution to the equation of state. This is because, for the data reported in Figs. 4 and 6, the composition of one of the components is always much smaller than the other two components. As a result the term  $x_1 x_2 x_3 A_{123}^{3b}$  is negligible.

In order to demonstrate the role of both mixing rules and unlike-three-body interactions in the prediction of ternary mixture phase behavior Fig. 7(a)-(d) are reported. Figure 7(a)-(c) are binary VLE phase diagrams of nitrogen-methane, nitrogen-carbon dioxide, and methane-carbon dioxide systems, respectively, while Fig. 7(d) is the ternary VLE phase diagram of nitrogen-carbon dioxide-methane. According to Fig. 7(a)-(c) correlations of the binary data using the CSvdW mixing rules are clearly superior to the PR mixing rules. Also, according to Fig. 7(d), prediction of the ternary phase diagram using the CSvdW mixing rules is far superior to the PR mixing rules. However, such predictions deviate considerably from the experimental data at and around the critical point. In order to improve the predictions in this region the unlike-three-body interaction contribution to the equation of state is included in the calculation (with  $\epsilon = 0.2$ ) and the result is also reported in Fig. 7(d) (chain-dotted line). According to this figure, inclusion of the unlike-three-body interaction contribution in the phase behavior calculation improves the predictions appreciably. There is

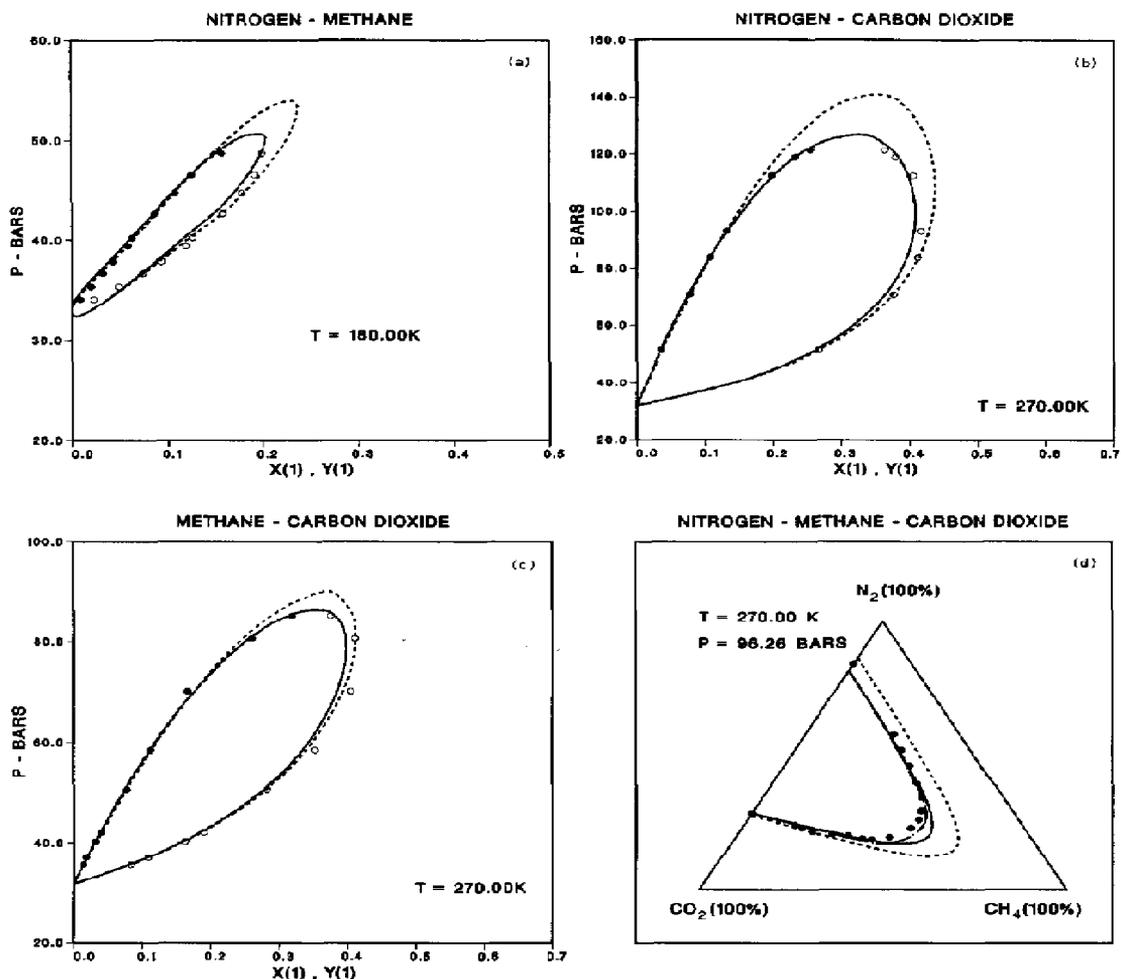


Fig. 7. (a) Equilibrium pressure-composition diagram for nitrogen-methane system. Solid line, correlation of the VLE data with the PR EOS and the CSvdW mixing rules; dashed line, PR EOS and original mixing rules; dots and circles, experimental VLE data (Kidnay et al., 1975). (b) Equilibrium pressure-composition diagram for nitrogen-carbon dioxide system. Solid line, correlation of the VLE data with the PR EOS and the CSvdW mixing rules; dashed line, PR EOS and original mixing rules; dots and circles, experimental VLE data (Somait and Kidnay, 1978). (c) Equilibrium pressure-composition diagram for methane-carbon dioxide system. Solid line, correlation of the VLE data with the PR EOS and CSvdW mixing rules; dashed line, PR EOS and original mixing rules; dots and circles, experimental VLE data (Somait and Kidnay, 1978). (d) Equilibrium vapor-liquid composition diagram for nitrogen-methane-carbon dioxide. Dashed line, PR equation of state with original mixing rules; solid line, PR EOS with the CSvdW mixing rules; chain-dotted line (— · — · —), PR EOS with the CSvdW mixing rules and including the three-body effects; dots, experimental data (Somait and Kidnay, 1978).

still some deviation of the predictions from the experimental data around the critical region, which may be associated to the mean-field nature of the classical equations of state of mixtures used in this report.

For the first time, through the proposed equation of state technique, it has become possible to predict simultaneously the VLE and VLLE data of ternary systems. Mixing rules and an analytical expression that accounts for the contribution of the unlike-three-body interactions derived from theoretical considerations are joined with an empirical equation of state to improve its performance in phase behavior calculations.

#### ACKNOWLEDGEMENT

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#### LIST OF SYMBOLS

$k, l, m$	Binary interaction parameters of the CSdvW mixing rules
$N$	number of molecules
$n$	number of moles
$N_0$	Avogadro constant
$P$	pressure
$R$	universal gas constant
$T$	temperature
$v$	molar volume
$x, y$	mole fraction in liquid and vapor phase, respectively
$Z$	compressibility factor

#### *Greek letters*

$\phi$	fugacity coefficient
$\eta$	reduced density
$\omega$	acentric factor
$\xi$	binary interaction parameter of the original mixing rules

#### *Superscripts and subscripts*

$c$	critical state
$e$	property used in the empirical equation of state
$i$	component identification
$m$	mixture property

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