

## A NON-CUBIC HARD-SPHERE PERTURBED EQUATION OF STATE FOR REPRESENTING PHASE EQUILIBRIA BEHAVIOR OF FLUID MIXTURES\*

DAN GEANĂ

Department of Applied Physical Chemistry, "Politehnica" University Bucharest,  
Spl. Independentei 313, Bucharest, Romania, e-mail: d\_geana@chim.upb.ro

Received, January 17<sup>th</sup>, 2005

In a recent paper (*Proc. Rom. Acad., Series B, 2003, 1-2, p. 3-10*), a new equation of state was proposed, combining a hard-sphere reference model with a general inverse quadratic attractive term, used previously by the author, in a general cubic equation of state (GEOS). The procedure can be generalized for many reference hard-sphere or chain-hard-sphere forms proposed in literature. The main result was the good representation of *PVT* and phase behaviour of pure fluids. In this work, the equation is extended to mixtures using the Boublik-Mansoori scaled-particle theory and the one-fluid theory. Some examples of applications to vapor-liquid equilibria of binary mixtures are presented.

Key words: Equation of state; Perturbed hard sphere; Phase equilibria; VLE of mixtures.

### INTRODUCTION

Equations of state are commonly used in thermodynamic and phase equilibrium calculations. For standard chemical engineering applications the most used equations of state are the simple cubic van der Waals forms. On the other hand much attention has been given to the development of semi-theoretical equations of state. For correlation and prediction of pressure-volume-temperature (*PVT*) and phase equilibria behaviour, a useful reference system is a hard-sphere model.

In a previous work<sup>1</sup>, a new equation of state was proposed by combining a hard-sphere reference model with a general inverse quadratic attractive term, previously used by the author<sup>2-6</sup> in a general cubic equation of state (GEOS). Similarly to the GEOS, a parameterization based on four critical conditions is applied to the hard-sphere perturbed equation of state. The Carnahan-Starling equation of state for hard spheres was used together with a van der Waals hard-sphere term as a reference form. For pure fluids both vapor pressure and liquid density are accurately represented for an extensive range of temperature and a diversity of substances, by using a temperature dependence of the attractive term. The

temperature function has three parameters ( $C_1$ ,  $C_2$ ,  $C_3$ ) estimated by matching points on the saturation curve (vapor pressure and the corresponding liquid volumes).

In this work, the equation of state<sup>1</sup> is extended to mixtures using the Boublik-Mansoori scaled-particle theory<sup>7,8</sup> and the one-fluid theory. Some examples of application to vapor-liquid equilibria of binary mixtures are presented.

### THE PERTURBED HARD-SPHERE EQUATION OF STATE

In a recent paper the cubic equation of state has been generalized to the hard-sphere equation combined with a general inverse quadratic perturbation term (PHSGEOS):<sup>1</sup>

$$Z = Y - \frac{4a(T_r)}{RTb} \eta \frac{1}{(1 - 4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \quad (1)$$

where  $Y$  is a short notation for any kind of hard-sphere reference function  $Y(\eta)$ , where  $\eta = b\rho/4$  is the reduced density.

The following notation is introduced:

\* Paper presented by Mircea Banciu

$$a_c = \Omega_a \frac{R^2 T_c^2}{P_c} \quad b = \Omega_b \frac{RT_c}{P_c} \quad (2)$$

$$c = \Omega_c \frac{R^2 T_c^2}{P_c^2} \quad d = \Omega_d \frac{RT_c}{P_c} \quad (3)$$

by using the critical temperature and pressure ( $T_c, P_c$ ).  $R$  is the universal gas constant, and  $\Omega_a, \Omega_b, \Omega_c, \Omega_d$  are nondimensional parameters. The function:

$$a(T_r) = a_c \beta^2(T_r) \quad (4)$$

and

$$\beta(T_r) = 1 + C_1 y + C_2 y^2 + C_3 y^3 \quad \text{for } T_r \leq 1 \quad (5)$$

$$\beta(T_r) = 1 + C_1 y \quad \text{for } T_r > 1 \quad (6)$$

$$y = 1 - \sqrt{T_r} \quad (7)$$

with  $T_r$  - the reduced temperature by its critical value ( $T/T_c$ ) and  $C_1, C_2, C_3$  - constants. Then the PHSGEOS equation (1) becomes:

$$Z = Y - \frac{4\Omega_a \beta(T_r)}{\Omega_b T_r} \eta \frac{1}{(1 - 4\frac{\Omega_d}{\Omega_b} \eta)^2 + 16\frac{\Omega_c}{\Omega_b^2} \eta^2} \quad (8)$$

In reduced variables the equation of state (8) takes the form:

$$P_r = \frac{T_r}{Z_c V_r} Y - \frac{\Omega_a \beta(T_r)}{(Z_c V_r - \Omega_d)^2 + \Omega_c} \quad (9)$$

with  $T_r = T/T_c$ ,  $P_r = P/P_c$ ,  $V_r = V/V_c$ , and the critical compressibility factor  $Z_c = P_c V_c / RT_c$ .  $V_c$  is the critical molar volume.

Taking into consideration the relative good representation of  $PVT$  and phase equilibrium behaviour achieved by the cubic equation of state, it is interesting to study the following equation of state:<sup>1</sup>

$$Z = 1 + c_0 \frac{4\eta - 2\eta^2}{(1 - \eta)^3} + f \frac{4\eta}{1 - 4\eta} - \frac{4a(T_r)}{RTb} \eta \frac{1}{(1 - 4\frac{d}{b} \eta)^2 + 16\frac{c}{b^2} \eta^2} \quad (10)$$

The reference term is a combination of a hard sphere Carnahan-Starling expression with a van der Waals form:

$$Y = 1 + c_0 \frac{4\eta - 2\eta^2}{(1 - \eta)^3} + f \frac{4\eta}{1 - 4\eta} \quad (11)$$

The parameters  $c_0$  and  $f$  enable the transition between the limiting cases:  $c_0 = 0$  and  $f = 1$  (the cubic GEOS equation) and  $c_0 = 1$  and  $f = 0$  (the CS + inverse quadratic equation). The results show that an appropriate combination is with the values  $c_0 = 1$  and  $f = 0.6$ . The new equation is:

$$Z = 1 + \frac{4\eta - 2\eta^2}{(1 - \eta)^3} + \frac{2.4\eta}{1 - 4\eta} - \frac{4a(T_r)}{RTb} \eta \frac{1}{(1 - 4\frac{d}{b} \eta)^2 + 16\frac{c}{b^2} \eta^2} \quad (12)$$

A common method for extension the Carnahan-Starling equation to a mixture of hard spheres is provided by the mixing rules based on the one-fluid theory. In this case, equation (12) is used with the parameter  $b$  in the reduced density  $\eta$  given by:

$$b = \sum_{i=1}^N \sum_{j=1}^N X_i X_j b_{ij} \quad (13)$$

where  $N$  is the number of components in the mixtures and  $X$  is the mole fraction. For the cross-parameter  $b_{ij}$  a suitable combining rule was used, e.g. an arithmetic mean or a cube-root combining rule.<sup>9</sup>

Another approach is that proposed independently by Boublik<sup>7</sup> and Mansoori et al.,<sup>8</sup> based on scaled-particle and on Percus-Yevick theory. The following expression is obtained for the compressibility factor of mixtures of hard spheres:

$$Z^{BM} = 1 + [(3DE/F + 1)\eta + (3E^3/F^2 - 3DE/F - 2)\eta^2 - (E^3/F^2 - 1)\eta^3]/(1 - \eta)^3 \quad (14)$$

where superscript BM denotes Boublik-Mansoori and:

$$D = \sum_{i=1}^N X_i \sigma_i \quad (15)$$

$$E = \sum_{i=1}^N X_i \sigma_i^2 \quad (16)$$

$$F = \sum_{i=1}^N X_i \sigma_i^3 \quad (17)$$

where  $\sigma$  is the hard-sphere diameter.

The reduced density,  $\eta = b\rho/4$ , involves the covolume parameter of the mixture:

$$b = \frac{2}{3} \pi N_A F \quad (18)$$

Considering the covolume parameter of the pure component:

$$b_i = \frac{2}{3} \pi N_A \sigma_i^3 \quad (19)$$

it results that a linear mixing rule is applied for the covolume parameter:

$$b = \sum_{i=1}^N X_i b_i \quad (20)$$

The equation of state for mixtures (called CSBM GEOS) is:

$$Z = Z^{BM} + f \frac{4\eta}{1-4\eta} - \frac{4a(T_r)}{RTb} \eta \frac{1}{(1-4\frac{d}{b}\eta)^2 + 16\frac{c}{b^2}\eta^2} \quad (21)$$

with  $f = 0.6$ .

For the other parameters of the equation of state (21), similarly to the cubic equation of state (GEOS), the following one-fluid mixing rules were used:<sup>3,6</sup>

$$a = \sum_{i=1}^N \sum_{j=1}^N X_i X_j a_{ij} \quad (22)$$

$$c = \sum_{i=1}^N \sum_{j=1}^N X_i X_j c_{ij} \quad (23)$$

$$d = \sum_{i=1}^N X_i d_i \quad (24)$$

A binary interaction parameter  $k_{ij}$  is introduced in the usual way, to correct for small deviations from the geometric mean combining rule, for the attractive force cross parameter:

$$a_{ij} = (a_i a_j)^{1/2} (1 - k_{ij}) \quad (25)$$

Also a geometric mean combining rule was used for the cross parameter  $c_{ij}$ :

$$c_{ij} = -\sqrt{-c_i} \sqrt{-c_j} \quad (26)$$

for both  $c_i, c_j < 0$ . It must be mentioned that for all studied pure substances the  $c$  parameter is negative. The parameter  $k_{12}$  was adjusted in a bubble pressure calculation to the experimental equilibrium pressure.

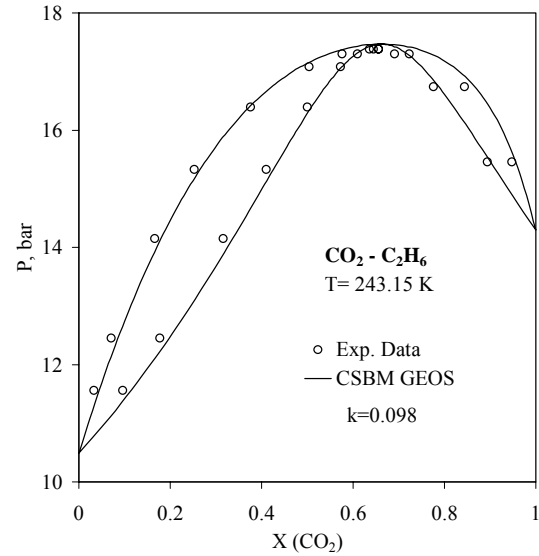


Fig. 1. Experimental<sup>10</sup> and calculated vapor-liquid equilibria for the carbon dioxide + ethane system, at 243.15 K.

## RESULTS AND DISCUSSION

The equation of state (21) was applied to calculate the phase equilibria of several fluid mixtures. The parameter  $k_{12}$  was adjusted in a bubble pressure calculation to the experimental equilibrium pressure. Figure 1 shows calculated and experimental<sup>10</sup> phase equilibria for the  $\text{CO}_2$  + ethane system at 243.15 K. The agreement between calculated and experimental phase diagrams is good for this azeotropic system. The phase diagram, calculated by the cubic equation of state (GEOS), is almost the same and was not displayed in the figure. For this system, which contains molecules of similar size, it appears to be no essential difference between the two reference systems.

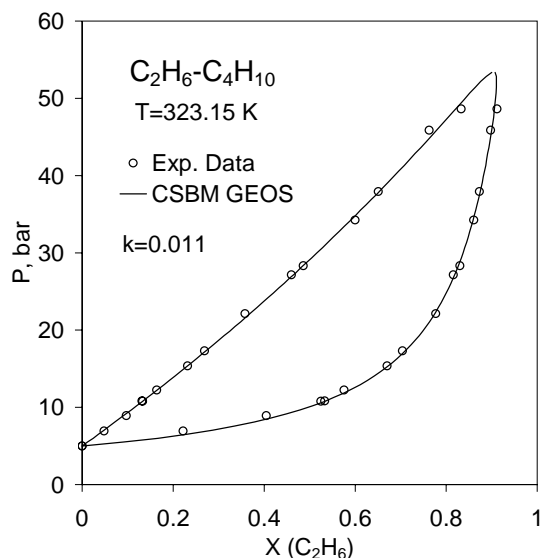


Fig. 2. Experimental<sup>11</sup> and calculated vapor-liquid equilibria for the ethane + n-butane system, at 323.15 K.

Figure 2 shows calculated and experimental<sup>11</sup> phase equilibria for the ethane + n-butane system at 323.15 K. The agreement between calculated and experimental phase diagrams is also good for this system. The phase diagram, calculated by the cubic equation of state (GEOS), is almost the same and was not displayed in the figure.

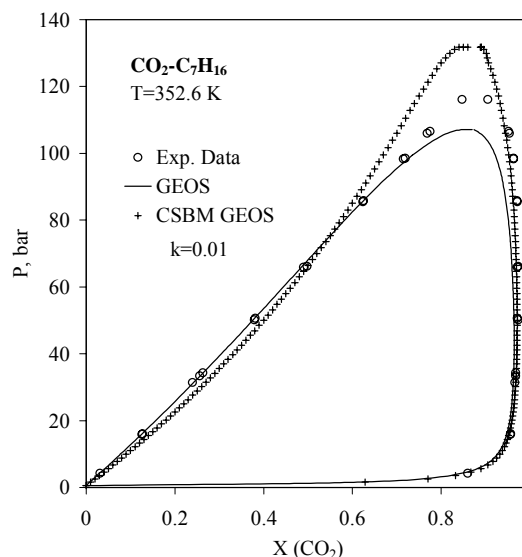


Fig. 3. Experimental<sup>12</sup> and calculated vapor-liquid equilibria for the carbon dioxide + n-heptane system, at 352.6 K.

Figure 3 shows calculated and experimental<sup>12</sup> phase equilibria for the  $\text{CO}_2$  + n-heptane system, at 352.6 K. A comparison is made with the phase diagram calculated by the cubic equation of state (GEOS). For this system containing molecules with a larger size difference, the cubic equation correlates better the liquid curve, but the new equation (21) with the Boublik-Mansoori term (14) reproduces correctly the vapor phase behavior. Both equations do poorly in the critical region, but in different ways. The cubic equation underpredicts the critical point of the mixture, whereas the equation (32) leads to higher critical point pressure than that observed.

Figure 4 shows calculated and experimental<sup>13</sup> phase equilibria for the  $\text{CH}_4$  + n-heptane system, at 310.94 K. Again the vapor phase behaviour is reproduced correctly by equation (21), but the errors are larger in the mixture critical region.

Another example is given in the figure 5, which shows the calculated and experimental<sup>14</sup> vapor-liquid equilibria, for the ethane + n-decane system at 410.94 K. The new equation of state (21) correlates better the vapor-liquid equilibria for this highly asymmetric system.

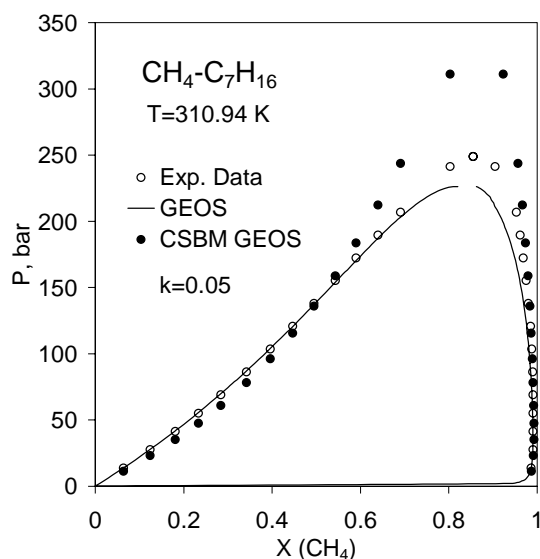


Fig. 4. Experimental<sup>13</sup> and calculated vapor-liquid equilibria for the methane + n-heptane system, at 310.94 K.

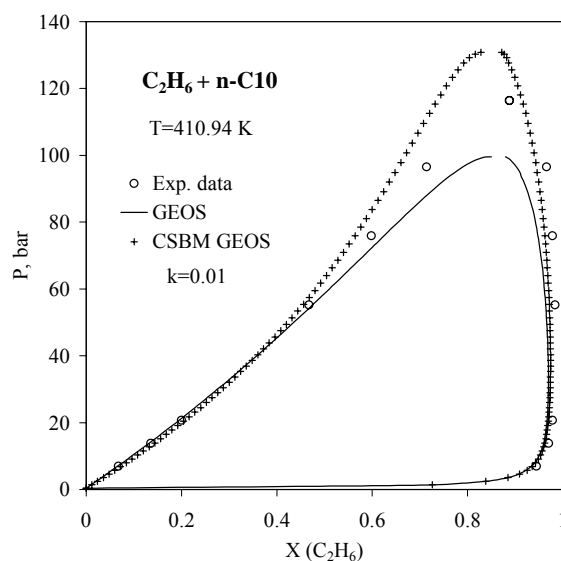


Fig. 5. Experimental<sup>14</sup> and calculated vapor-liquid equilibria for the ethane + n-decane system, at 410.94 K.

Figure 6 shows calculated and experimental<sup>15</sup> phase equilibria for the nitrogen + n-pentane system, at 310.7 K. In this case the new equation of state with the Boublik-Mansoori form (14) reproduces correctly the phase behavior of the mixture.

The calculations presented here suggest that the cubic equation of state and the new equation of state (21) correlate similarly the phase behaviour of binary systems containing molecules of similar size. However, it appears that phase behaviour of binary mixtures with larger size differences can be better correlated with the new reference hard-sphere term equation of state. Surely, an extensive study is required in order to arrive to definite conclusions. The most important result is the possibility to compare the cubic equation of state and the noncubic form, i.e. the different reference hard sphere forms, having a common base of parameterization.

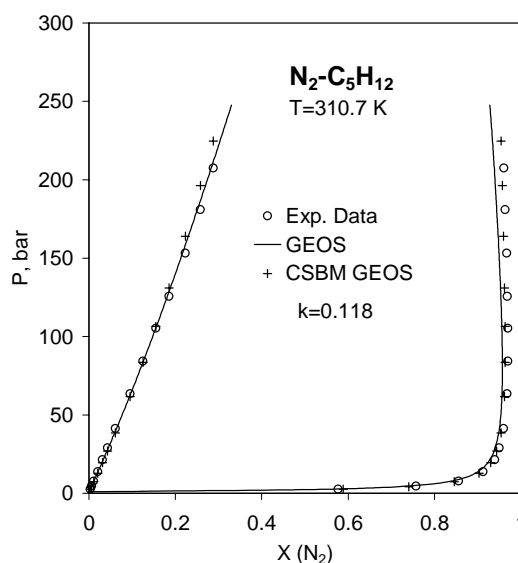


Fig. 6. Experimental<sup>15</sup> and calculated vapor-liquid equilibria for the nitrogen + n-pentane system, at 310.7 K.

## CONCLUSIONS

The generalized equation of state,<sup>1</sup> combining a hard-sphere reference model with a general inverse quadratic attractive term used previously by the author, in a cubic general equation of state has been extended to mixtures. Similarly to the cubic GEOS, a parameterization based on four critical conditions was applied to the hard-sphere perturbed equation of state. The Carnahan-Starling equation of state for hard spheres was used together with a van der Waals hard-sphere term as a reference form. The extension of the equation to mixtures was done using the Boublik-Mansoori scaled-particle theory for the hard sphere reference term and the one-fluid theory for the other parameters in the attractive term of the equation of state.

## APPENDIX

The fugacity coefficient is calculated from the thermodynamic equation:

$$\ln \phi_i = \left( \frac{\partial(n\tilde{A})}{\partial n_i} \right)_{\rho, T, n_{j \neq i}} + (Z - 1) - \ln Z \quad (\text{A1})$$

$\tilde{A}$  is the reduced molar residual Helmholtz energy  $A^r / RT$ ,  $n_i$  is the number of moles of component and  $n$  is the total number of moles in the mixtures. The compressibility factor is given by equation (21). The corresponding expression for  $\tilde{A}$  is:

$$\begin{aligned} \tilde{A} = \tilde{A}^{BM} - f \ln(1 - 4\eta) - \\ - \frac{a}{2\sqrt{-c}RT} \ln \frac{1 - 4\frac{d}{b}\eta + 4\frac{\sqrt{-c}}{b}\eta}{1 - 4\frac{d}{b}\eta - 4\frac{\sqrt{-c}}{b}\eta} \end{aligned} \quad (\text{A2})$$

with

$$\tilde{A}^{BM} = \frac{\frac{3DE}{F}\eta - \frac{E^3}{F^2}}{(1-\eta)} + \frac{\frac{E^3}{F^2}}{(1-\eta)^2} + \left( \frac{E^3}{F^2} - 1 \right) \ln(1-\eta) \quad (\text{A3})$$

The derivative from (A1) is:

$$\begin{aligned} \left( \frac{\partial(n\tilde{A})}{\partial n_i} \right)_{\rho, T, n_{j \neq i}} = \tilde{A} + \left( \frac{D\tilde{A}}{DX_i} \right)_{\rho, T, X_{j \neq i}} - \\ - \sum_{j=1}^N X_j \left( \frac{D\tilde{A}}{DX_j} \right)_{\rho, T, X_{i \neq j}} \end{aligned} \quad (\text{A4})$$

The differential operator  $(D/DX_i)_{X_{j \neq i}}$  is used to indicate differentiation with respect to  $X_i$  where all other  $X_j$  are held constant.

## REFERENCES

1. Geană D., *Proc. Rom. Acad., Series B*, **2003**, 1-2, 3.
2. Geană D., *Rev. Chim.(Bucharest)*, **1986**, 37, 303.
3. Geană D., *Rev. Chim.(Bucharest)*, **1986**, 37, 951.
4. Geană D., *Rev. Chim.(Bucharest)*, **1987**, 38, 975.
5. Geană D., Feroiu V., *Fluid Phase Equilibria*, **2000**, 174, 51.
6. Geană D., Feroiu V., *Equations of State. Applications to Phase Equilibria*, Ed. Tehnică, Bucharest, 2000.
7. Boublik T., *J. Chem. Phys.*, **1970**, 53, 471.
8. Mansoori G. A., Carnahan N.F., Starling K.E., Leland T. W., *J. Chem. Phys.*, **1971**, 54, 1523.
9. Dimitrelis D., Prausnitz J.M., *Fluid Phase Equilibria*, **1986**, 31, 1.
10. Fredeslund A., Mollerup J., *Far. Trans. I*, **1974**, 70, 1653.
11. Lhotak V., Wichterle I., *Fluid Phase Equilibria*, **1981**, 6, 229.
12. Robinson D.B., NGPA, RR-18 August 1976.
13. Reamer H.H., Sage B.H., *J. Chem. Eng. Data*, **1956**, 1, 29.
14. Reamer H.H., Sage B.H., *J. Chem. Eng. Data*, **1963**, 8, 508.
15. Karla H., Robinson D.B., Besserer G.J., *J. Chem. Eng. Data*, **1977**, 22, 215.