



A modified dieterici equation of state for vapor pressures up to the critical point

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ABSTRACT

A modification of the Dieterici equation of state (D-EOS) is proposed: the repulsive term is described by the Guggenheim hard-sphere repulsive term. Further, the temperature dependence of the attractive term is described using an alpha function $\alpha(\text{Tr}, \omega)$ based on the modified Mathias-Copeman correlation; the temperature dependence of the repulsion term is described using a beta function $\beta(\text{Tr}, \omega)$, analog to the Mathias-Copeman function. Vapor pressure of industrially important pure compounds was correlated using the modified Dieterici EOS. Agreement between experimental and calculated values is satisfactory.

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KEYWORDS

Dieterici EOS;
Equation of state;
Generalized alpha and beta functions;
Modeling;
Pure compounds.

INTRODUCTION

An equation of state can be represented mathematically as a sum of a repulsion term and an attraction term; equations of van der Waals^[1], Soave-Redlich-Kwong (SRK)^[2] and Peng-Robinson (PR)^[3] are well-known examples of application of this framework. An alternative format for an EOS was proposed by Dieterici^[4,5], whose repulsion term is multiplied by an exponential term in which the attractive contribution is accounted:

$$p = \frac{RT}{(V-b)} e^{\frac{-a}{RTV}} \quad (1)$$

wherein R is the universal gas constant, b accounts for

the volume occupied by the molecules, a represents the attraction parameter, and p, V and T are pressure, volume and temperature, respectively. In spite of advantages of the Dieterici EOS (D-EOS) documented in^[4-6] it has not contributed significantly to development of new equations of state (as in the case of the van der Waals EOS). Only since 2001 works dedicated to use Dieterici EOS are presented in literature: Sadus^[4] revisited D-EOS and proposed a modification of its repulsive term, consisting to replace it by that proposed by Carnahan-Starling^[7,8], more accurate in representation of the repulsion effects between molecules.

This new EOS was used in the representation of the phase equilibria of the pure compounds; in another

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work^[6], Sadus extended the Dieterici-Carnahan-Starling EOS (DCS-EOS) to predictions of the vapor-liquid data of binary mixtures. The results, in both works, are in excellent agreement with the experimental ones. Polishuk and Vera^[9], searching to improve the predictions of the liquid-liquid equilibrium data in mixtures, combined both van der Waals and Dieterici EOS, since the former overestimates the predicted liquid-liquid equilibrium data in mixtures while the latter, underestimates these data; following the authors, the results obtained are satisfactory.

Our proposal is divided into two parts: first, to substitute the original repulsive term of the Dieterici EOS by the repulsion term developed by Guggenheim^[10] and second, to propose generalized $\alpha(\text{Tr}, \omega)$ and $\beta(\text{Tr}, \omega)$ functions with temperature dependence, based on Mathias-Copeman alpha functions. The predictive capability using this modified D-EOS for vapor pressure^[13-15] is tested and comparisons with results obtained from other equations of state are made.

Equations of state

Based on analysis of the reduced geometric series of virial equation, Guggenheim^[10] developed an equation of state for non-attracting hard-spheres. The form of this equation is,

$$p = \frac{RT}{V(1-y)^4} \quad (2)$$

Replacing the repulsive term of the original Dieterici EOS (equation (1)) by the equation (2) and taking into account the temperature dependence both the attraction parameter (a term) and the molecular volume (b term), the expression resultant is,

$$p = \frac{RT}{V(1-y)^4} e^{\frac{-a(T)}{RTV}} \quad (3)$$

in which $y = b(T)/(4V)$. Equation (3) can be represented as a function of the compressibility factor

$$Z^4 - (B + e^{-A})Z^3 + 0.375B^2Z^2 + 0.0625B^3Z - 0.0039063B^4 = 0 \quad (4)$$

wherein $A = a(T)P / (RT)^2$, $B = b(T)P / (RT)$ and $Z = PV / (RT)$. Using the conventional criteria for critical condition (the first and second derivatives of pressure in relation to volume are equal to zero), it is possible to obtain equation of state parameters in terms of the critical properties of the compounds ($a_c = 0.756(R^2T_c^2)/P_c$ and $b_c = 0.336(RT_c)/P_c$), whose subscripts c indicates critical condition. At temperatures other than the criti-

cal condition,

$$a(T) = a_c \alpha(\text{Tr}) \quad (5)$$

$$b(T) = b_c \beta(\text{Tr}) \quad (6)$$

where $a(T)$ and $b(T)$ are the attraction parameter and molecular volume of the pure compound, respectively, both temperature dependents. $\alpha(\text{Tr})$ and $\beta(\text{Tr})$ are dimensionless functions of reduced temperature (Tr). To represent these functions similar expressions to the Mathias-Copeman (M-C)^[11] equation are proposed:

$$\alpha(\text{Tr}) = (1 + A_1(\omega)(1 - \text{Tr}^{0.5})^{0.5} + A^2(\omega)(1 - \text{Tr}^{0.5}) + A^3(\omega)(1 - \text{Tr}^{0.5})^{1.5})^2 \quad (7)$$

and

$$\beta(\text{Tr}) = (1 + B_1(\omega)(1 - \text{Tr}^{0.5})^{0.5} + B^2(\omega)(1 - \text{Tr}^{0.5}) + B^3(\omega)(1 - \text{Tr}^{0.5})^{1.5})^2 \quad (8)$$

For the range $0.3 < \text{Tr} < 1.0$. Each function has its proper adjustable parameter group (A's and B's) which is structured as a power series in the acentric factor (ω)^[15] truncated at 2nd order,

$$\begin{aligned} A_1(\omega) &= A_{11} + A_{12}\omega + A_{13}\omega^2 \\ A_2(\omega) &= A_{21} + A_{22}\omega + A_{23}\omega^2 \\ A_3(\omega) &= A_{31} + A_{32}\omega + A_{33}\omega^2 \end{aligned} \quad (9)$$

$$\begin{aligned} B_1(\omega) &= B_{11} + B_{12}\omega + B_{13}\omega^2 \\ B_2(\omega) &= B_{21} + B_{22}\omega + B_{23}\omega^2 \\ B_3(\omega) &= B_{31} + B_{32}\omega + B_{33}\omega^2 \end{aligned} \quad (10)$$

From $\alpha(\text{Tr})$ and $\beta(\text{Tr})$ values at each Tr , it is possible to calculate the A and B adjustable parameters of equations (7) and (8), characteristic of each pure compound; in this way, if various pure compounds were used, various A's and B's adjustable parameters groups are obtained. Each pure compound has its particular acentric factor (ω). So, employing these parameters in equations (9) and (10), generalized alpha and beta functions are obtained for all compounds studied in this work.

There are some limiting conditions and general trends which must be satisfied by any equation of state^[30]. The first criterion analyzed is to verify if $\lim_{P \rightarrow 0} PV = RT$ at any temperature. Considering equation (3) multiplied by volume (V).

$$pV = \frac{RT}{(1-y)^4} e^{\frac{-a(T)}{RTV}} \quad (11)$$

The following limit condition is observed at any temperature:

$$\lim_{\substack{V \rightarrow \infty \\ P \rightarrow 0}} PV = RT \quad (12)$$

Since $b/(4V) \rightarrow 0$ and $a/(V + 2b - (b^2)/V) \rightarrow 0$ as $V \rightarrow \infty$. The second criterion analyzed is associated to the inflexion point of the critical isotherm curve. Mathematically,

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \quad (13)$$

Applying the proposed EOS (3) at the critical conditions,

$$P_c = \frac{RT_c}{V_c(1 - b/4V_c)^4} e^{-\frac{a}{RT_c V_c}} \quad (14)$$

Considering $a_c = 0.756(R^2 T_c^2)/P_c$ and $b_c = 0.336(RT_c)/P_c$, we can derive expressions for a, b and R in terms of V_c , P_c and T_c :

$$b = 1.3334V_c, \quad a = 11.903P_c V_c^2, \quad R = 3.9683 \frac{P_c V_c}{T_c} \quad \text{as well as}$$

$$Z_c = \frac{P_c V_c}{RT_c} = 0.252 \quad (15)$$

The third criterion is to verify if (P x T) curves (isometrics) are linear, since this behavior is normally verified except at very high densities. Mathematically,

$$\left(\frac{\partial P}{\partial T}\right)_V = K \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_V = 0 \quad (16)$$

The a and b parameters of the proposed EOS (3) are temperature dependent and the conditions showed in equations (16) are not satisfied. Consequently, equation (3) is unable neither to describe heat capacities near the critical point nor to reproduce isochoric inflection points^[11].

RESULTS AND DISCUSSION

The a(T) and b(T) values in equation (3) of each pure substance were obtained from vapor pressure and volume data[24-26] applying the Newton method of search. Minimum values of the difference between experimental data (P_{ex}) and calculated data of vapor pressure (P_{calc}) from equation (3) are set lower than 10^{-4} bar. A program in FORTRAN language was developed, using the Gauss minimization routine. For the determination of A's and B's adjustable parameters the same Gauss routine is used, now minimizing (to values lower than 10^{-5}) the difference between the alpha and beta values calculated in equations (5) and (6) and those obtained from equations (7) and (8), with $0.3 < Tr <$

TABLE 1 : Parameters of equations (9) and (10)

	A ₁₁	0.00196		B ₁₁	0.10818
A ₁ (ω)	A ₁₂	-0.02644	B ₁ (ω)	B ₁₂	5.92202
	A ₁₃	0.05563		B ₁₃	-19.77905
	A ₂₁	-0.00710		B ₂₁	-0.77292
A ₂ (ω)	A ₂₂	0.10837	B ₂ (ω)	B ₂₂	-23.56042
	A ₂₃	-0.23440		B ₂₃	74.69778
	A ₃₁	0.00418		B ₃₁	3.73965
A ₃ (ω)	A ₃₂	-0.09549	B ₃ (ω)	B ₃₂	-4.67642
	A ₃₃	0.22357		B ₃₃	-11.13534

TABLE 2 : Critical pressure (P_c) and critical temperature (T_c) and AAD between experimental and calculated vapor pressure using various EOS

Compound	P_c (bar)	T_c (K)	SRK ^[2] with M-C	PR ^[3] with M-C	This
			alpha function ^[11]	alpha function ^[11]	work
			AAD*(%)	AAD*(%)	AAD* (%)
Methane	45.90	190.58	0.68	0.77	0.55
Ethane	48.50	305.42	1.54	1.11	0.51
Propane	42.10	369.82	1.69	1.46	0.58
n-Butane	37.70	425.20	0.86	0.40	0.73
n-Pentane	33.60	469.65	1.94	1.28	0.41
n-Hexane	30.40	507.43	1.84	1.78	1.50
n-Heptane	27.20	539.71	2.03	1.45	0.99
n-Octane	24.70	568.70	1.95	1.55	1.07
n-Nonane	23.10	594.60	2.65	2.21	1.30
n-Decane	20.90	617.50	2.46	2.12	1.22
Ethylene	50.30	280.69	2.45	1.85	1.52
Propylene	46.30	364.76	3.22	1.95	1.86
Nitrogen	33.90	126.26	1.26	0.59	0.50
Carbon dioxide	73.90	304.21	1.87	1.01	0.77
Sulfur dioxide	78.60	430.65	3.56	2.62	1.21

$$* \text{AAD} = \frac{N}{i=1} |P_{\text{exp},i} - P_{\text{calc},i}| / P_{\text{exp},i} \cdot 100 / N_p$$

1.0. Using A's and B's parameters and equations (9) and (10), generalized adjustable parameters for the pure substances studied (A_{11} to A_{33} and B_{11} to B_{33}) are calculated and generalized alpha and beta functions are obtained. Parameters values are showed in TABLE 1.

Average absolute deviations (AAD) between experimental and calculated data of vapor pressure of pure compounds using equation (3) are determined and showed in TABLE 2. Observing this Table is possible to establish comparisons between AAD obtained in this work with those obtained using the Mathias-Copeman generalized alpha function^[11] in the original forms of SRK^[2] and PR EOS^[3].

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TABLE 3 : Critical compressibility factor (Z_c) of pure compounds and calculated from equation (3) as well as its deviations (AAD)

Compound	Z_c calculated from critical properties ^[13-15]	Z_c calculated using equation(3)	AAD (%)
Methane	0.2868	0.2874	0.21
Ethane	0.2744	0.2753	0.33
Propane	0.2706	0.2716	0.37
n-Butane	0.2599	0.2611	0.46
n-Pentane	0.2753	0.2734	0.69
n-Hexane	0.2650	0.2637	0.49
n-Heptane	0.2573	0.2592	0.74
n-Octane	0.2508	0.2527	0.76
n-Nonane	0.2401	0.2415	0.58
n-Decane	0.2465	0.2477	0.47
Ethylene	0.2691	0.2690	0.04
Propylene	0.2771	0.2791	0.72
Nitrogen	0.2982	0.2987	0.17
Carbon dioxide	0.2771	0.2770	0.04
Sulfur dioxide	0.2731	0.2735	0.15
Average	0.2681	0.2698	0.42

The critical compressibility factor $Z_c = 0.252$ is in satisfactory agreement with the experimental values reported for the majority of gases; this Z_c value is physically more adequate than that calculated by Carnahan-Starling^[5] using their repulsion term in the van der Waals and RK EOS. Sadus^[6], after changing the repulsive term in the Dieterici EOS by the Carnahan-Starling term^[7,8], found a value for $Z_c = 0.2705$, close to obtained here. However, the Z_c value characteristic of each pure compound is also predicted by equation (3), as showed in TABLE 3.

Observing the average values presented in this table it is possible to verify the ability of the equation (3) to represent the critical conditions of pure compounds. This ability is also observed for prediction of the compressibility coefficients data in the vapor phase (and consequently for vapor volume prediction) for the $0.3 < Tr < 1.0$ range; for liquid volume data, the predictive capability of the equation (3) is not satisfactory.

CONCLUSION

Modifications in the Dieterici equation of state^[4] replacing its repulsive term by the Guggenheim^[10] repulsion term, and the temperature dependence of the at-

tractive and repulsion parameters by equations (7) and (8), are proposed. The results obtained using these modifications are in satisfactory agreement with experimental data of vapor pressure and vapor volume^[13-15] of non-polar pure compounds. The deviations show that the predictive ability of the proposed EOS is better than those showed in the literature^[2,3]. This improvement is probably due to the theoretical consistency of the repulsive term employed in the EOS (3). The calculations show that the introduction of new alpha and beta functions is consistent physically and contributes to improve the predictive capability of the EOS.

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