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CORRELATIONS

α Function for a Series of Hydrocarbons to Peng−Robinson and van der Waals Equations of State

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This paper reports estimated coefficients for the α function based on vapor pressure data to a series of 438 components, mainly hydrocarbons, for both van der Waals and Peng−Robinson equations of state (EoS). The α function utilized for the attractive term is the one proposed by Mathias and Copeman in 1983, and it improves the cubic EoS calculations. Accurate vapor-pressure correlations and critical data required for the estimation of the constants were retrieved from two databases, i.e., AIChE DIPPR and the Reid et al. (*The Properties of Gases and Liquids*; McGraw-Hill: New York, 1987) reference book. The method of calculation is described, and the constants are tested with respect of their representation of thermodynamic properties, mainly in terms of the vapor-pressure deviations. The behavior of density and enthalpy EoS predictions is also evaluated. The estimated coefficients for the α function are reported in the Supporting Information and may be applied as a data bank in a simulator, providing more accurate thermodynamic property calculations in the recommended temperature range, as demonstrated.

Introduction

Cubic equations of state (EoS) are characterized by their capability and simplicity in calculating thermodynamic properties, i.e., phase equilibrium, density, and enthalpy. Having in sight the great potential of applicability of the cubic EoS, many researchers have concentrated their efforts on improving the property representations using these equations.[1] This paper reports coefficients for the α expression, which improves significantly vapor-pressure calculations for both van der Waals (vdW) and Peng−Robinson (PR) EoS. The vapor pressure is a fundamental property, and it is a good indicator of application of the cubic EoS, inclusive for other thermodynamic properties, in the recommended temperature range.

Thermodynamic Models

The first cubic EoS was proposed by van der Waals in 1873.[2] Later, many other modifications were presented, and one usually applied is the PR equation.[3] The vdW and PR EoS are represented by eqs 1 and 2, respectively.

$$P = \frac{RT}{v - b} - \frac{a}{v^2} \tag{1}$$

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

The attractive and repulsive parameters, *a* and *b*, respectively, are obtained from the two restrictions of the critical point. They are shown by eqs 3 and 4 for the two EoS.

$$a_{\mathrm{vdW}} = 0.421875\frac{R^2T_c^{\,2}}{P_c}\alpha; \quad b_{\mathrm{vdW}} = 0.125\frac{RT_c}{P_c} \tag{3}$$

$$a_{\mathrm{PR}} = 0.45724\frac{R^2T_c^{\,2}}{P_c}\alpha; \quad b_{\mathrm{PR}} = 0.07780\frac{RT_c}{P_c} \tag{4}$$

To improve the vapor-pressure representation, many authors presented different expressions for α to calculate the attractive parameter.[1,4−11] In this work, the Mathias and Copeman[4] correlation has been used (see eq 5), which is an expansion of the Soave term.

$$\alpha = [1 + C_1(1 - \sqrt{T_r}) + C_2(1 - \sqrt{T_r})^2 + C_3(1 - \sqrt{T_r})^3]^2; \quad T_r = T/T_c \tag{5}$$

Methods of Calculation

The desired C_1, C_2, and C_3 coefficients were determined using a computational program, which applies a

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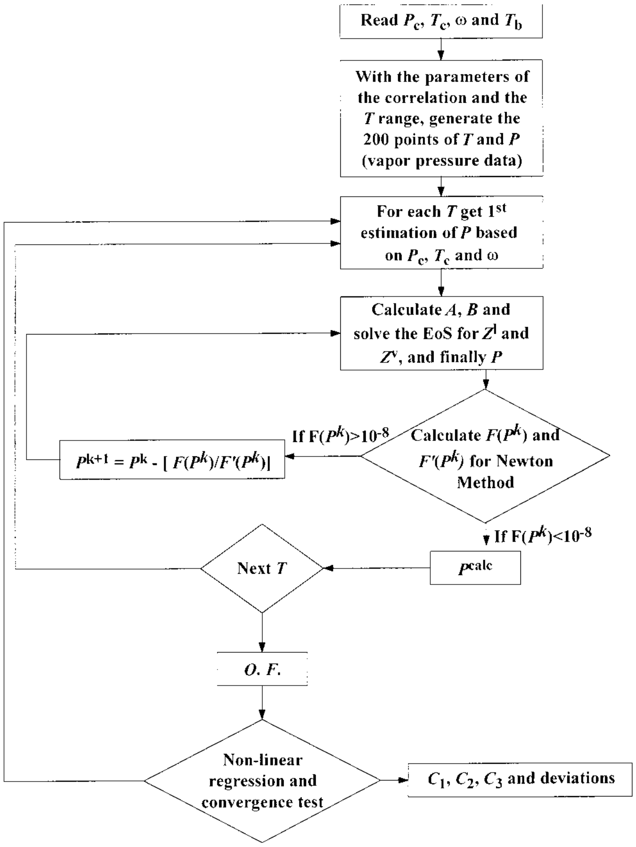

Figure 1. Iterative calculation algorithm for the constants C_1, C_2, and C_3 of the α term.

modified Marquardt method for nonlinear least-squares fitting.[12] The objective function (OF) for minimization was defined in terms of the relative vapor-pressure error (see eq 6).

$$\mathrm{OF} = \mathrm{MIN} = \sum_{i=1}^{N}\left(\frac{P_{\mathrm{calcd},i} - P_{\mathrm{exptl},i}}{P_{\mathrm{exptl},i}}\right)^2 \tag{6}$$

The pseudoexperimental values for vapor pressure as a function of temperature were generated, using the correlations given by Reid et al. (1987) and AIChE DIPPR data compilations, with 200 points for each component.[13,14] It would have been better to use reliable experimental data instead of the vapor-pressure correlation. However, it may be regarded that these databases selected the most reliable data for every component evaluated.[15] Therefore, it is reasonable to assume that the correlations used represent the experimental data within experimental error, for the stated temperature range.

Figure 1 illustrates the iterative algorithm presented by Knudsen[16] for calculation of the constants C_1, C_2, and C_3. The program called VAPP[17,18] that applies this algorithm was modified in this work for the vdW and PR EoS. It is noteworthy that, at each temperature and set of constants, the program calculates the vapor pressure using the isofugacity criterion.

Results and Discussion

The results of all estimated coefficients for the vdW and PR EoS to the selected hydrocarbons are presented in the Supporting Information, together with the critical properties used.

For each set of coefficients determined, i.e., for each component, we evaluated the deviations in order to give the quality of representation. The mean (AAD) and maximum deviations (MD) used are defined by eqs 7 and 8. On the basis of the AAD, we made the global average for the 438 components, and the results are 0.32% for vdW and 0.28% for PR. In terms of the MD, the global averages are 0.90% for vdW and 0.81% for PR. As we can observe, both EoS presented the same good quality of representation, and these pictures may be seen graphically in Figures 2 and 3.

$$\mathrm{AAD} = \frac{100}{N}\sum_{i=1}^{N}\frac{|P_{\mathrm{exptl},i} - P_{\mathrm{calcd},i}|}{P_{\mathrm{exptl},i}} \tag{7}$$

$$\mathrm{MD} = \frac{|P_{\mathrm{exptl}} - P_{\mathrm{calcd}}|}{P_{\mathrm{exptl}}} \times 100 \tag{8}$$

To ensure that the constants used for the vapor-pressure correlations are coherent and precise, the deviation at the normal boiling point (DBP) for each component was evaluated (see eq 9). The global mean

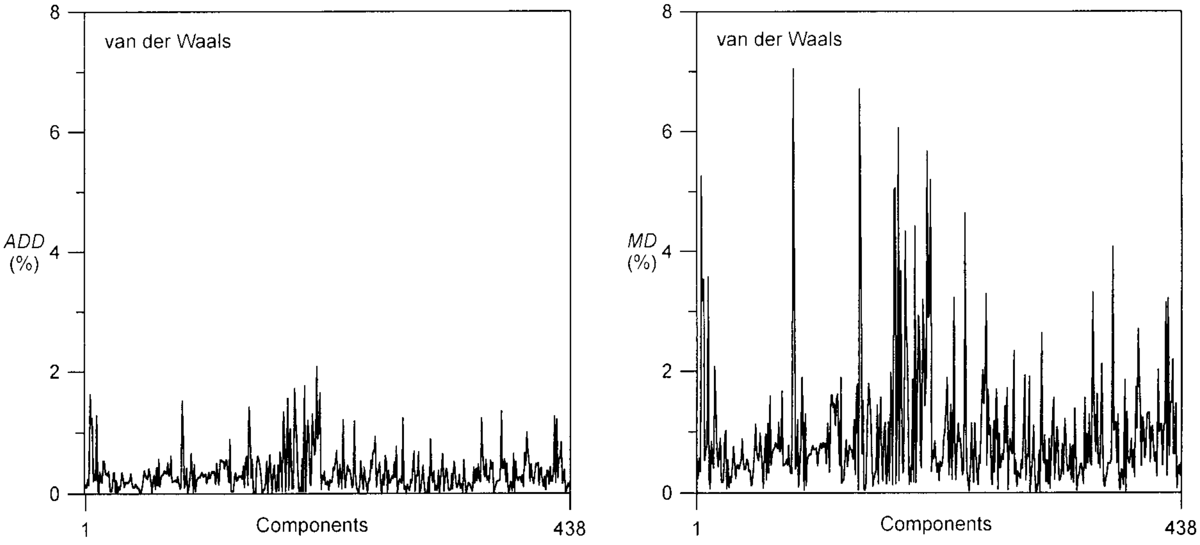

Figure 2. AAD and MD obtained with the fitted constants C_1, C_2, and C_3 for the vdW EoS; see eqs 7 and 8.

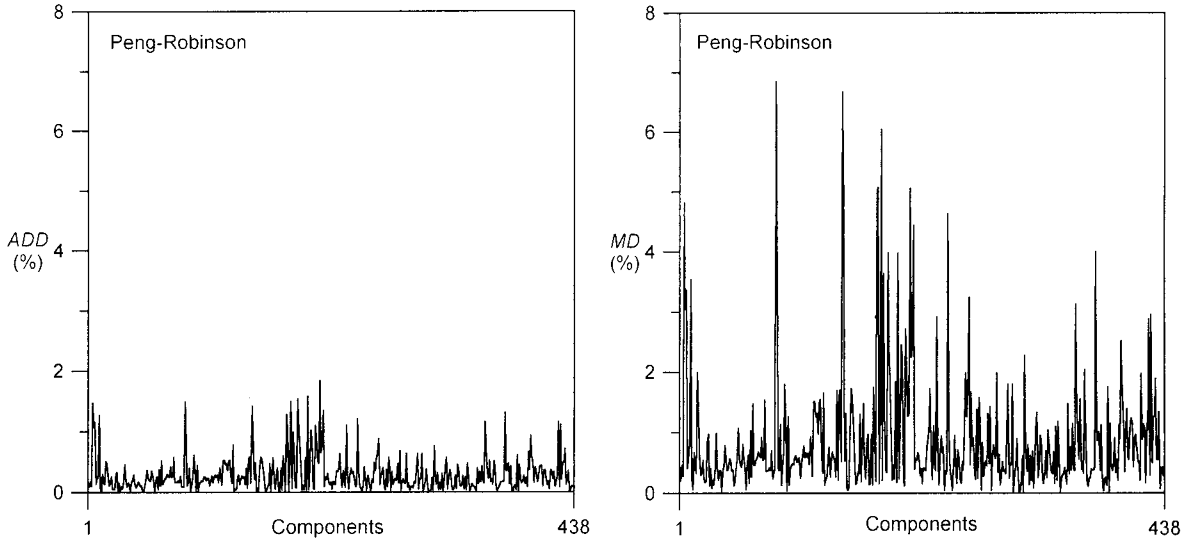

Figure 3. AAD and MD obtained with the fitted constants C_1, C_2, and C_3 for the PR EoS; see eqs 7 and 8.

Table 1. Comparison of the Representation of the Vapor-Pressure Data[a] Using the Mathias and Copeman Attractive Term for the vdW and Original PR EoS

		PR-C_1 (original)		vdW-$C_1C_2C_3$ (this work)	
component	range of T (K)	AAD (%)	MD (%)	AAD (%)	MD (%)
water	273−643	6.56	29.09	0.20	0.54
oxygen	55−153	2.67	5.45	0.16	0.45
nitrogen	64−125	1.77	3.49	0.11	0.28
hydrogen sulfide	273−342	1.53	2.49	0.06	0.35
carbon monoxide	68−132	1.37	2.44	0.12	0.34
carbon dioxide	216−303	1.61	2.85	0.01	0.08
methane	91−189	2.32	7.15	0.14	0.37
ethane	91−302	2.17	3.96	0.32	0.76
propane	117−366	2.33	14.01	0.38	0.93
butane	138−420	2.27	11.09	0.37	0.92
isobutane	135−405	3.01	24.55	0.26	0.55
isopentane	155−457	2.26	11.54	1.06	2.93
pentane	160−468	2.86	21.38	0.37	0.80
3-methylpyridine	255−644	5.80	39.61	0.19	0.39
3,4-xylenol	339−724	4.45	9.93	0.37	1.12
decane	243−613	2.24	15.63	1.61	2.79
pentadecane	305−705	3.05	20.38	0.81	1.23
eicosane	360−760	1.95	11.36	0.20	0.98
pentacosane	400−787	6.00	9.72	1.30	3.19
triacontane	440−840	11.37	18.26	0.89	2.89
dotriacontane	455−845	13.95	20.87	1.04	3.05
hexatriacontane	474−860	23.30	35.24	1.65	5.20

[a] Data obtained from the AIChE DIPPR compilation.[14]

deviation at the normal boiling point for the studied components is 0.50%.

$$\mathrm{DBP} = \frac{|P_{\mathrm{calcd}}(T_{\mathrm{b}}) - 101325|}{101325} \times 100 \qquad (9)$$

Table 1 demonstrates the contribution of the α function for the representation of the vapor-pressure data of a sample of compounds, by comparing the deviations between the vdW-$C_1C_2C_3$ EoS and the original PR. As we could expect, the deviations for the original PR EoS are especially higher than those for vdW-$C_1C_2C_3$ for compounds where polarity and molecular weight are increased. It should be cited that the expression for C_1 as function of the acentric factor, proposed by Watson et al.,[19] was used for the original PR EoS, which is more accurate for hydrocarbons.

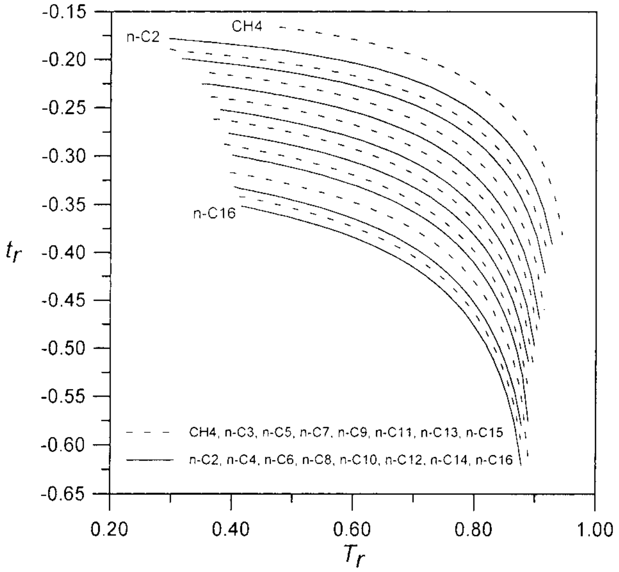

Figure 4. Behavior of the reduced translation term [$t_r \equiv (v_{\mathrm{exptl}} - v_{\mathrm{vdW}})/v_c$], as a function of the reduced temperature, using the estimated C_1, C_2, and C_3 constants, for a series of n-alkanes from methane (CH_4) to n-hexadecane (n-C_{16}).

The volumetric behavior was also investigated with the estimated constants for both equations and especially for the vdW EoS, via a translation function.

$$t \equiv v_{\mathrm{exptl}} - v_{\mathrm{vdW}} \qquad (10)$$

The representation of liquid densities by cubic EoS is one limitation, and thereby it is important to verify that using the estimated coefficients ($C_1C_2C_3$) for a series of n-alkanes presents a uniform behavior (see Figure 4). Furthermore, a correction of Péneloux type[20] using a group contribution is found to be applicable for the series of n-alkanes, in which the dependence was linear with respect to the functional groups and quadratic in terms of the reduced temperature.

Heat of vaporization predictions were made, and it could be observed that the representation using the estimated α coefficients is also improved. The estimated constants were also successfully applied in a simulator for a unit of natural gas absorption, where an enthalpy balance is performed, requiring the derivatives of the α term with respect to the temperature.[21]

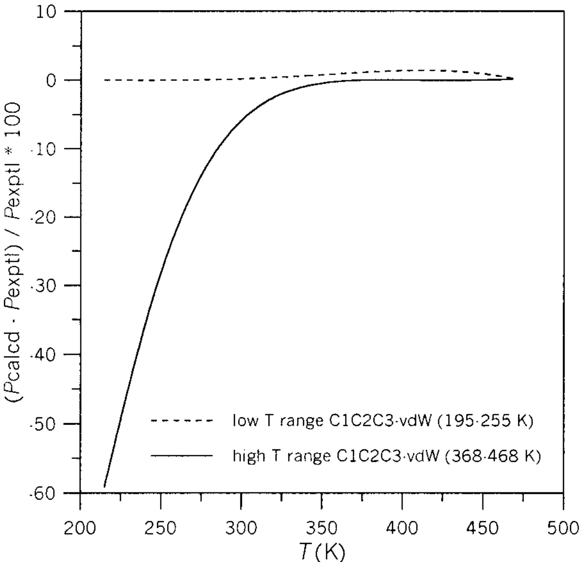

Figure 5. Tests of extrapolation of the estimated low- and high-temperature range ($C_1C_2C_3$) constants for the pentane, using the vdW EoS.

It must be emphasized that the estimated coefficients ($C_1C_2C_3$) are useful for the recommended temperature range and subcritical temperatures. To illustrate what can happen on extrapolation at lower and higher temperatures than the stated temperature range used in the estimation procedure, pentane was taken as an example, together with vdW EoS. Two sets of coefficients were estimated at low (195−255 K) and high (368−468 K) temperature ranges with the proposed procedure, resulting in precise fittings, as usual. Afterward, these estimated coefficients were used for representation of the complete range (195−468 K) studied to evaluate the behavior on extrapolation in terms of vapor-pressure deviations (see Figure 5). It should be pointed out that the extrapolation must not be made, and it is even more deficient at lower temperatures, because the critical point is used as a restriction in the EoS.

Conclusions

The Mathias and Copeman constants C_1, C_2, and C_3 were obtained in a series of 438 hydrocarbons for both vdW and PR EoS. It is demonstrated that representation of the vapor pressure is significantly improved and precise in the temperature range of the experimental data, inclusive at low pressures.

The use of C_2 and C_3 is clearly justified for compounds presenting polarity and high molecular weight. However, for low pressures the complete α term is also significantly useful for apolar compounds. Good vapor-pressure representation of pure compounds reflects directly on the prediction of mixtures.

Particularly for the vdW EoS, the capability of the vapor−liquid equilibrium calculation is being extended with the implementation of the α function on the same level as PR, even though the last presents a better mathematical flexibility. Although the repulsive term of the vdW-type EoS is not correct, these equations are normally used in chemistry and engineering applications, because of their simplicity and efficiency.[22]

The estimated constants are available at the Supporting Information and may be applied in calculation programs for thermodynamic properties as well as in simulators, especially for chemical processes and petroleum reservoirs.

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Supporting Information Available: Table of constants of the Mathias and Copeman attractive term for vdW and PR EoS to a series of 438 components, mainly hydrocarbons. This material is available free of charge via the Internet at http://pubs.acs.org.

Glossary

A = nondimensional attractive parameter, $aP/(RT)^2$
B = nondimensional repulsive parameter, bP/RT
a = attractive parameter of the EoS
b = repulsive parameter of the EoS
C_1, C_2, C_3 = Mathias and Copeman constants for the α term
N = number of data points
OF = objective function
P = pressure (Pa)
R = gas constant [Pa m^3/(mol K)]
T = temperature (K)
t = molar volume translation (m^3/mol)
v = molar volume (m^3/mol)
Z = compressibility factor

Greek Letters

α = function of the reduced temperature, defined in eq 5
Δ = variation

Superscripts and Subscripts

B = boiling point at normal atmospheric pressure (10 1325 Pa)
calcd = calculated
c = critical property
exptl = experimental
l, v = liquid, vapor
r = reduced property
′ = derivative with respect to pressure (the Newton method)

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