

# Vapor liquid equilibrium modeling of alkane systems with Equations of State: “Simplicity versus complexity”

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## Abstract

Two types of Equations of State (EoS), which are characterized here as “simple” and “complex” EoS, are evaluated in this study. The “simple” type involves two versions of the Peng–Robinson (PR) EoS: the traditional one that utilizes the experimental critical properties and the acentric factor and the other, referred to as PR-fitted (PR-f), where these parameters are determined by fitting pure compound vapor pressure and saturated liquid volume data. As “complex” EoS in this study are characterized the EoS derived from statistical mechanics considerations and involve the Sanchez–Lacombe (SL) EoS and two versions of the Statistical Associating Fluid Theory (SAFT) EoS, the original and the Perturbed-Chain SAFT (PC-SAFT).

The evaluation of these two types of EoS is carried out with respect to their performance in the prediction and correlation of vapor liquid equilibria in binary and multicomponent mixtures of methane or ethane with alkanes of various degree of asymmetry. It is concluded that for this kind of systems complexity offers no significant advantages over simplicity. Furthermore, the results obtained with the PR-f EoS, especially those for multicomponent systems that are encountered in practice, even with the use of zero binary interaction parameters, indicate that this EoS may become a powerful tool for reservoir fluid phase equilibria modeling.

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## 1. Introduction

Hydrocarbons are the major components of oil and natural gas. Their optimum recovery from natural deposits as well as their subsequent processing depends to a large extent on the accurate knowledge of the thermodynamic properties of the mixtures involved and, in particular, of the phase equilibrium. Equations of State (EoS) are traditionally used for reservoir fluid phase equilibrium calculations, since they can be applied for the calculation of pure compound and mixture thermodynamic properties in the liquid, gas and supercritical phases [1,2].

A large variety of EoS is available in the literature for phase equilibrium calculations: from the “simple” ones – basically cubic Equations of State – to those obtained from statistical mechanics considerations and are characterized here as “com-

plex”, at least as compared to the cubic EoS. The argument as to which type of EoS should be used in practical applications is an old one. The senior author recalls a heated debate on this issue between two leading figures in thermodynamics, one from academia and the other from industry, in the late 1970s in an AIChE meeting.

In the last decade, the introduction of association in the second type of EoS, utilizing the perturbation theory of Weirtheim [3], led to the development of the SAFT [4,5] and later the PC-SAFT [6] EoS, which generated added interest in this area. At the same time, the inclusion of the SAFT association term in the SRK EoS, resulted to the so-called Cubic-Plus-Association (CPA) EoS [7], which represents an extension of cubic EoS to associating fluids. The CPA parameters – note that CPA is equivalent to SRK for non-associating compounds – are obtained by fitting vapor pressure and liquid volume data, which suggests the estimation of the parameters in a cubic EoS through such data, rather than through the critical properties and the acentric factor.

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Our purpose in this study is to compare the two types of EoS. The “simple” EoS considered are two versions of the Peng–Robinson (PR) EoS [8]: in the one, the parameters are evaluated from the critical temperature ( $T_c$ ), critical pressure ( $P_c$ ) and acentric factor ( $\omega$ ); in the other by fitting vapor pressure ( $P^s$ ) and saturated liquid volume ( $V^l$ ) data. The “complex” EoS are the Sanchez–Lacombe [9,10], the SAFT [5] and the PC-SAFT [6], whose parameters are also obtained by fitting  $P^s$  and  $V^l$  data.

## 2. The Equations of State

### 2.1. The Peng–Robinson and the PR-f EoS

The expression for the PR EoS is the following [8]:

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

Here  $P$  is the pressure,  $V$  the molar volume,  $T$  the temperature,  $\alpha$  the attractive parameter,  $b$  the co-volume parameter of the fluid and  $R$  is the ideal gas constant. The co-volume parameter  $b$  is temperature independent and is calculated using the critical temperature ( $T_c$ ) and the critical pressure ( $P_c$ ) of the fluid as follows:

$$b = 0.0778 \frac{RT_c}{P_c} \quad (2)$$

The temperature dependent attractive parameter, alpha ( $\alpha$ ), is calculated by the Soave-type expression:

$$\alpha = a(T_c, P_c) [1 + m(1 - T_r^{0.5})]^2 \quad (3)$$

where

$$a(T_c, P_c) = 0.45724 \frac{(RT_c)^2}{P_c} \quad (4)$$

Peng and Robinson correlated the parameter  $m$  to the acentric factor  $\omega$  for light non-polar compounds, hydrocarbons up to decane and some aromatics and arrived at the following expression:

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

For mixtures, cubic EoS like PR are widely applied utilizing the van der Waals one fluid (vdW1f) mixing rules:

$$\alpha_{\text{mix}} = \sum_i \sum_j x_i x_j \alpha_{ij} \quad (6)$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \quad (7)$$

where the cross energy,  $\alpha_{ij}$ , and cross co-volume,  $b_{ij}$ , parameters are calculated with the geometric mean and arithmetic mean combining rules, respectively:

$$\alpha_{ij} = (\alpha_i \alpha_j)^{0.5} (1 - k_{ij}) \quad (8)$$

$$b_{ij} = \frac{1}{2} (b_i + b_j) \quad (9)$$

where  $k_{ij}$  is an adjustable parameter, which is determined by fitting binary phase equilibrium data.

Several researchers have examined the performance of the PR EoS in vapor pressure prediction for light and heavy hydrocarbons. Boston and Mathias [11] proposed different equations of the alpha parameter with respect to temperature for subcritical and supercritical conditions. Magoulas and Tassios [12] proposed a new expression for Eq. (5) using experimental vapor pressure data of alkanes up to C20. Twu et al. [13] suggested a new dependence of alpha on the acentric factor of the PR EoS, which is linear rather than a higher order polynomial such as the fourth order one that results from the combination of Eqs. (3) and (5). They proposed a generalized alpha function with respect to temperature and acentric factor, which gives better vapor pressure predictions than that of Eq. (3) for light and heavy hydrocarbons at reduced temperatures between 0.5 and 0.7, while Eq. (3) is more reliable at reduced temperatures greater than 0.7 for light hydrocarbons. Finally, recently Gasem et al. [14] presented improved PR vapor pressure predictions for heavy hydrocarbons – up to C28 – with a new function for the alpha parameter.

Furthermore many researchers have evaluated the accuracy of different modifications of the PR EoS in mixture phase equilibrium calculations. For example, Floter et al. [15] have examined the performance of PR in the correlation and prediction of vapor liquid equilibria (VLE) of mixtures containing methane at supercritical conditions and a heavy hydrocarbon, using the classical quadratic mixing rules combined with eight different functions the alpha parameter. They also obtained good predictions ( $k_{ij}=0$ ) with an alpha function for supercritical methane optimized to IUPAC recommended fugacities. Finally, Gao et al. [16] have applied the PR and SRK EoS to describe VLE of asymmetric binary mixtures of methane, ethane and other light gases with alkanes up to C44, using a new function for the alpha parameter and a different combining rule for the cross co-volume parameter than that of Eq. (9).

Our purpose here is neither to investigate which is the most suitable alpha function for the description of pure alkane properties with the PR EoS nor to conclude on which are the most suitable mixing and combining rules for the description of VLE of alkane mixtures. Rather, we keep on the original PR EoS given by Eqs. (1)–(9), which is the popular formulation of the model, especially in engineering practice. Besides, however, the traditional methodology based on the corresponding states principle where the EoS parameters are estimated through the critical properties and the acentric factor, a different approach for the application of the PR EoS is also examined in this study: the  $T_c$ ,  $P_c$  and  $\omega$  pure compound parameters are treated as adjustable ones, denoted as  $T'_c$ ,  $P'_c$  and  $\omega'$ , which are determined by fitting  $P^s$  and  $V^l$  data in a wide temperature range, from about the melting point temperature up to close to the critical one, as in the case of the complex EoS. This version of PR is hereafter referred to as PR-fitted (PR-f). Such an approach for the PR EoS was also presented by Ting et al. [17], who obtained satisfactory results in binary asymmetric systems containing alkanes.

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