



Prediction of dew points and liquid dropouts of gas condensate mixtures



Nefeli Novak ^a, Vasiliki Louli ^a, Stathis Skouras ^b, Epaminondas Voutsas ^{a,*}

^a Laboratory of Thermodynamics and Transport Phenomena, School of Chemical Engineering, National Technical University of Athens, 9, Heron Polytechniou Str., Zografou Campus, 15780 Athens, Greece

^b Statoil ASA, Research & Technology Center, Trondheim, Norway

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ABSTRACT

Thermodynamic modeling of reservoir fluids behavior is of great importance for the oil and gas industry. For design and safe operation purposes, it is necessary to have an accurate, simple and robust model for the prediction of the phase equilibrium of reservoir fluids. In this work, the UMR-PRU model is applied in the prediction of dew points and liquid dropouts of gas condensate mixtures, and is compared with the widely used cubic equations of state Soave-Redlich-Kwong (SRK) and Peng-Robinson (PR) as well as the non-cubic Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) equation of state. The evaluation of the models was based both on synthetic and real gas condensate mixtures. For real gas condensates, a characterization method for the C₇₊ fraction based on the one proposed by Pedersen is developed for UMR-PRU. The results reveal that UMR-PRU is a sufficiently accurate model for dew point and liquid dropout predictions of gas condensates.

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1. Introduction

Accurate knowledge of the phase behavior of gas condensate mixtures is essential for the unobstructed gas processing and optimization as well as for gas transportation. More specifically, accurate dew point and liquid dropout data are required in order to ensure that the fluid is either transported in single phase, i.e. above the dew point pressure at a specific temperature, or that the liquid produced due to condensation does not drastically change the mixture composition or damage the infrastructure. PVT experiments like saturation points and liquid dropout measurements, otherwise referred to as constant composition expansion experiments (CCE), are effectively used to design an efficient extraction process without operational problems and loss of valuable product. The same data can also be utilized for flow assurance through the pipeline network.

Equations of state (EoSs) are routinely used for the prediction of phase behavior and thermodynamic properties of petroleum fluids. Cubic EoSs, like Peng-Robinson (PR) [1] and Soave-Redlich-Kwong (SRK) [2], are still very popular for such calculations. Many modifications have been proposed creating families of EoSs that

differentiate from one another either in the attractive parameter or the co-volume parameter. Modifications of the attractive term parameter aim to improve vapor pressure predictions of the condensable components [3–8] and supercritical behavior of the light ones [6,9–11] while the modifications of co-volume parameter aim to the improvement of density predictions [7,12]. Towards the improvement of the density predictions, the use of a volume translation is a simple and effective method that does not alter the equilibrium conditions [13–15]. Extension of a cubic EoS to mixtures requires mixing rules for the attractive-term and co-volume parameters. A widely employed method to extend the cubic EoS to multicomponent mixtures is via the Van der Waals one-fluid (vdW1f) mixing rules, i.e. quadratic composition dependency for both parameters coupled with the geometric mean combining rule for the cross attractive-term parameter and the arithmetic mean rule for the cross co-volume parameter. However, it has been shown [16] that cubic EoSs coupled with the vdW1f mixing and combining rules fail for asymmetric -with respect to the size of the molecules involved-mixtures. So, apart from improving the EoS for pure component predictions, the use of advanced mixing rules, such as those derived by combining a cubic EoS and an excess Gibbs energy model, like UNIQUAC, NRTL, Wilson and UNIFAC, has been known to improve EoS predictions, even for mixtures containing non-polar components, such as CCS [17] and natural gas mixtures

* Corresponding author.

E-mail address: evoutsas@chemeng.ntua.gr (E. Voutsas).

[18–21].

Except for the classical two-parameter cubic EoSs, three-parameter cubic EoSs [22–26] have also been used for petroleum fluid modeling, due to their improved density predictions [27,28]. Three-parameter EoSs, like Patel-Teja and Patel-Teja-Valderrama, have shown to be more accurate than PR and SRK for density and compressibility factor predictions [28,29]. Dew point predictions however are not necessarily improved with the addition of a third parameter [28,29].

Another class of equations of state, of non-cubic form, based on the statistical thermodynamic principles of SAFT (Statistical Associating Fluid Theory), has gained popularity in the industry after the integration of the derived EoS in commercial process simulators. For example, the Perturbed-Chain SAFT EoS (PC-SAFT) is widely used for predicting asphaltene precipitation [30–39]. Recently, Yan et al. [39] compared dew point predictions of PC-SAFT with those obtained by PR and SRK and found that while all models are similar for natural gas dew points, for gas condensates PC-SAFT yields better results. Surprisingly, for mixture liquid densities, PC-SAFT was found to yield on average similar results with the untranslated PR, although it is clearly superior for pure components [40].

Gas condensate mixtures consist of numerous different components, which makes a complete component analysis practically impossible. The most common case of compositional analysis of reservoir fluids is to perform detailed analysis up to n-hexane, while the heavy end of the fluid is described by a single plus fraction (C7+). EoS predictions for real gas condensates are greatly influenced by the characterization method of the C7+ fraction, so a good coupling of an EoS with a characterization method is very important for accurate results [28,41–43]. The expected uncertainties of EoSs in gas condensate PVT and saturation point predictions vary from one author to another, depending on the characterization method and the physical properties used for the pseudocomponents. The general conclusion that most researchers agree on is that traditional cubic EoSs do not yield accurate phase equilibrium predictions, unless the fluid is somehow matched to experimental data [29]. These data, such as PVT experiments, saturation points etc., can be used to manipulate the fluid properties, like the MW of the plus fraction [44], or the binary interaction parameters [45] in order to match the model predictions with the experimental data. This has also been done indirectly by calculating EoS dependent pseudo-critical properties for the plus fraction regressed on PVT data [46].

Most characterization methods comprise of three steps: splitting the C7+ fraction into single carbon number (SCN) fractions, assigning physical properties to each SNC according to suitable correlations based on combinations of molecular weight (MW), boiling point (Tb) and density or specific gravity (SG), and, finally, lumping them together again into multiple carbon number (MCN) fractions for computational reasons without losing the information of the SCN approach [47–49]. Detailed review of physical property correlations is available in the literature [50–52]. The selection of a specific correlation for physical properties of the SCN fractions has a significant effect on the EoS predictions but no correlation is consistently better than the others [53]. Several characterization methods have been proposed in the literature for cubic EoSs [51,54–58], the most popular being the ones proposed by Whitson [58] and Pedersen [51]. The same approach has been also proposed for PC-SAFT EoS, however, the determination of the pseudo-components parameters is still under investigation [39,40,59,60].

In previous publications, it has been shown that the UMR-PRU model is superior to SRK, PR and PC-SAFT in dew point predictions of both synthetic and real natural gases [18–20,61]. In this study, the UMR-PRU model is further applied in the prediction of dew points and liquid dropouts of synthetic gas condensates and is

compared with PR, SRK and PC-SAFT. Furthermore, the performance of UMR-PRU model in the prediction of dew points and liquid dropouts of real gas condensates combined with a properly adapted Pedersen characterization method is examined and compared with PR and SRK EoSs.

2. Thermodynamic models

All models considered in this study have been thoroughly presented in the literature. SRK [2] and PR [62] have been applied in this work coupled with the vdW1f mixing and combining rules using temperature independent binary interaction parameters (BIPs) retrieved either from ASPEN-HYSYS process simulator databank or determined in this work. The UMR-PRU model [61,63] has been applied using the UNIFAC interaction parameters presented by Louli et al. [61]. Pure component critical temperatures and pressures as well as acentric factors, needed for SRK, PR and UMR-PRU, were taken from the DIPPR data compilation [64].

For PC-SAFT [65,66], the three pure component parameters for non-associating compounds: the segment number (m), the segment diameter (σ), and the segment energy parameter (ϵ/k), were taken from Gross and Sadowski [66] and Ting et al. [37], except for n-tetracosane and 2,2,4,4,6,8,8- heptamethyl-nonane, which are not available in the literature. The parameters for these components were determined in this study by fitting pure component vapor pressure and saturated liquid density data and are tabulated in Table 1. PC-SAFT has been extended to mixtures by introducing mixture segment diameter and segment energy parameters derived from the van der Waals one fluid theory [66]. Similarly to cubic EoSs, PC-SAFT has been applied using temperature independent binary interaction parameters in the dispersion term of the EoS taken either from the literature or determined in this work.

3. Results and discussion

3.1. Dew point predictions of synthetic gas condensate (SGC) mixtures

The database of synthetic gas condensate (SGC) mixtures that was developed for the evaluation of the models in dew point predictions, consists of eight mixtures that contain hydrocarbon (HC) molecules of diverse chemical structure such as straight chain alkanes, branched alkanes and aromatic hydrocarbons, at various compositions. Moreover, the experimental dew point data cover a wide range of temperatures and pressures. The compositions of the SGCs are given in Table 2.

Initially the effect of the binary interaction parameters (BIPs) in the dew point predictions of gas condensate mixtures was examined. A typical example is presented with PR in Fig. 1, where the effect of using different sets of BIPs is showcased, dividing the HCs into two categories. The first category includes HCs lighter than n-decane, hereby denoted as HCset1, and the second, HCs at least as heavy as n-decane, denoted as HCset2. The following scenarios

Table 1

PC-SAFT pure component parameters regressed in this work. Experimental vapor pressure (P^s) and saturated liquid molar volume (V_l) data were taken from DIPPR [64].

Compound	T-range (K)	m	σ (Å)	ϵ/k (K)	% ΔP^s	% ΔV_l
n-Tetracosane	325–804	9.7400	3.9582	254.36	2.6	3.3
2,2,4,4,6,8,8-heptamethyl-nonane	200–690	5.0666	4.2832	265.35	0.8	2.0

$$\% \Delta P^s = \frac{100}{NDP} \sum_{i=1}^{NDP} \frac{(P_i^{exp} - P_i^{calc})}{P_i^{exp}} \% \Delta V_l = \frac{100}{NDP} \sum_{i=1}^{NDP} \frac{(V_{l,i}^{exp} - V_{l,i}^{calc})}{V_{l,i}^{exp}}$$

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