Oil & Gas Science and Technology – Rev. IFP, Vol. 62 (2007), No. 5, pp. 707-714

DOI: 10.2516/ogst:2007050

Calculation of Phase Equilibrium of Natural Gases with the Peng-Robinson and PC-SAFT Equations of State*

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Résumé — Calcul d'équilibre de phase du gaz naturel avec les équations d'état Peng-Robinson et PC-SAFT — Des équations d'état (EdE) cubiques, comme la EdE de Peng-Robinson, sont régulièrement employées par l'industrie du pétrole et du gaz pour la conception d'opérations de production et de traitement des gaz à hautes pressions. Néanmoins, ces dernières années, on a proposé beaucoup d'équations d'état non-cubiques, dérivées de la thermodynamique statistique et sur des bases théoriques solides. Parmi elles, les EdE de la famille SAFT sont probablement celles à l'acceptation la plus large. Dans ce travail, nous comparons les résultats fournis par les EdE Peng-Robinson et PC-SAFT pour le calcul des points de condensation, points de bulle et points critiques des gaz naturels. Les paramètres binaires d'interaction dans les deux EdE ont été mis égaux à zéro dans tous les calculs pour examiner les possibilités prédictives des modèles. Des calculs ont été exécutés pour 19 gaz naturels synthétiques pour lesquels les données expérimentales sont disponibles en littérature. Pour la plupart des mélanges, les prévisions de la EdE PC-SAFT sont davantage en accord avec les données expérimentales.

Abstract* — *Calculation of Phase Equilibrium of Natural Gases with the Peng-Robinson and PC-SAFT Equations of State — *Cubic equations of state (EOS), such as the Peng-Robinson EOS, are routinely used by the oil and gas industry for the design of recovery and processing operations of gases at high pressures. Nonetheless, many non-cubic equations of state, derived from statistical thermodynamics and with solid theoretical basis, have been proposed in recent years. Among them, EOS of the SAFT-family are possibly those with widest acceptance. In this work, we compare the performance of the Peng-Robinson and PC-SAFT EOS in the calculation of dew points, bubble points, and critical points of natural gases. Binary interaction parameters in both EOS were set equal to zero in all calculations to test the predictive capability of the models. Calculations were performed for 19 synthetic natural gases for which experimental data are available in literature. For most mixtures, predictions of the PC-SAFT EOS are in better agreement with the experimental data.*

* A preliminary version of this work was presented at the Eighth Annual UAE University Research Conference, 2007.

INTRODUCTION

Pressure-temperature (*P-T*) phase diagrams can provide important information for the design of recovery and processing operations of natural gases at high pressures. Three points are of particular interest in this type of diagram: the vapor-liquid critical point, which is the endpoint of the bubble and dew point curves, the cricondenbar and the cricondentherm, which are the saturation points with largest pressure and temperature in the diagram, respectively. Their experimental determination can be difficult and expensive and, therefore, there is motivation to develop and use equations of state (EOS) capable of accurately predicting the phase behavior of natural gases. Cubic EOS are traditionally used to model phase behavior by the oil industry because they provide good results and are mathematically simple (Valderrama, 2003). Some recently proposed non-cubic EOS, derived using statistical thermodynamics, are being increasingly used for many applications by the chemical industry. Compared to cubic EOS, they generally have a sounder theoretical basis even if at the cost of greater mathematical complexity and larger computational effort. Nonetheless, this effort is well within the power of personal computers and no longer represents a major drawback for their usage. A recent review by de Hemptinne *et al.* (2006) ends with a positive view of the potential of these new models and predicts that their use will increase over the next few years. In many cases, however, it remains to be evaluated whether this extra computational effort translates, or not, into significantly better phase behavior predictions.

The evaluation of EOS in predictions of natural gas phase behavior has been the subject of some recent publications. Voulgaris *et al.* (1998) compare the performance of the Peng-Robinson (Peng and Robinson, 1976) and Simplified-Perturbed-Hard-Chain Theory (Kim *et al.*, 1986) EOS in predictions of the condensation behavior of natural gases. Nasrifar and Bolland (2005, 2006) compare cubic EOS in predictions of thermodynamic properties of natural gases. Martinez and Hall (2006) compare three EOS: generalized three-parameter Redlich-Kwong/Peng-Robinson (RK-PR) (Cismondi and Mollerup, 2005), Patel-Teja (1982) and PC-SAFT (Gross and Sadowski, 2001) in the evaluation of thermodynamic properties of synthetic natural gas mixtures. Predictions of the critical points of natural gas mixtures can be found in the work of Huang and Guo (1995).

Our purpose is to compare the quality of predictions of phase equilibrium and critical points calculations in natural gas mixtures using a simple EOS and a complex molecular-based EOS. We use the Peng-Robinson EOS (Peng and Robinson, 1976), which is possibly the cubic EOS most widely used by the oil industry, and the PC-SAFT EOS (Gross and Sadowski, 2001), which is a non-cubic EOS and one of the most recent modifications of the successful SAFT theory (Chapman *et al.*, 1990). We could not identify other contributions in the literature that use the same EOS and the same approach to do this comparison, which is useful to guide the compositional modeling of hydrocarbon reservoirs. Furthermore, EOS based on the SAFT approach have the potential advantage of being capable of modeling polar systems by including an association contribution to the Helmholtz free energy of the system. In this way, an EOS such as PC-SAFT may be useful to model operations such as dehydration of natural gases with glycols and their sweetening with amines. A preliminary step, though, toward this end is to perform a critical evaluation of the PC-SAFT model in predictions of the phase behavior of natural gases.

1 METHODOLOGY

The Peng-Robinson EOS with classical mixing rules and the PC-SAFT EOS were used. Their mathematical expressions can be obtained in the respective original references. The fugacities of each component i in the vapor (f_i^V) and liquid (f_i^L) phases should be equal in the dew and bubble points, i.e.:

$$\ln f_i^L(T, P, \mathbf{x}) - \ln f_i^V(T, P, \mathbf{y}) = 0$$

where x and y are the mole fractions in the liquid and vapor phases, respectively. Construction of the *P-T* diagram requires a series of bubble point and a series of dew point calculations for a mixture of fixed composition. The computational procedure is devised in such a way that it automatically selects whether the pressure or the temperature should be specified, by tracking the value of the derivative pressure with respect to temperature along the saturation line. In this way, impossible specifications such as a temperature larger than the cricondentherm or a pressure larger than the cricondenbar are avoided. We also carried out direct calculations of critical points using a modified version (Castier and Sandler, 1997) of the Hicks and Young (1977) algorithm. At a mixture critical point, the quadratic and the cubic terms of the Helmholtz free energy (A) expansion should be equal to zero. As formulated by Heidemann and Khalil (1980), the quadratic form is:

$$\mathbf{Q} \cdot \Delta\mathbf{n} = \mathbf{0}$$

with

$$\Delta\mathbf{n}^T \cdot \Delta\mathbf{n} = 1$$

The elements of matrix $\mathbf{Q}$ are given by:

$$Q_{ij} = \left(\frac{\partial^2 A}{\partial n_i \partial n_j}\right)_{T,V} = RT\left(\frac{\partial \ln f_i}{\partial n_j}\right)_{T,V,n_{k\neq j}} = RT\left(\frac{\partial \ln f_j}{\partial n_i}\right)_{T,V,n_{k\neq i}}$$

The cubic form is:

$$C = \sum_{i=1}^{c}\sum_{j=1}^{c}\sum_{k=1}^{c}\left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k}\right)_{T,V} \Delta n_i \Delta n_j \Delta n_k = 0$$

The thermodynamic properties and their analytical derivatives required for these calculations were derived from the EOS using computer algebra (Castier, 1999). In all cases, the binary interaction parameters of the EOS were set equal to zero in order to compare the two EOS as *predictive* tools, instead of evaluating their ability to correlate experimental behavior based on fitted parameters. Critical parameters and acentric factors for the Peng-Robinson EOS were taken from Poling *et al.* (2000). Parameters for the PC-SAFT EOS were taken from the work of Gross and Sadowski (2001). The global phase stability of all calculated bubble, dew, and critical points was verified by the tangent plane criterion (Michelsen, 1982).

2 RESULTS AND DISCUSSIONS

We selected 19 synthetic natural gases (SNG) in which all components are well characterized substances, i.e., without lumped heavy fractions such as C6+. This eliminates the effect the lumping procedure might have in the EOS comparison. In their respective original references, these SNG are formulated in such a way that properties such as average

TABLE 1

Composition of SNG1 to SNG10 (% molar).
Sources a: Mørch *et al.* (2006), b: Urlic *et al.* (2003), c: Blanco *et al.* (2000), d: Jarne *et al.* (2004)

	SNG1[a]	SNG2[b]	SNG3[b]	SNG4[c]	SNG5[d]	SNG6[d]	SNG7[a]	SNG8[a]	SNG9[a]	SNG10[a]
N_2					1.559	0.772				
CO_2					25.908	1.700				
C_1	94.085	81.4	60.0	89.0	69.114	84.446	93.505	84.280	96.611	93.600
C_2	4.468			7.0	2.620	8.683	2.972	10.067		2.630
C_3					0.423	3.297	1.008	4.028		
i-C_4				4.0	0.105	0.293	1.050	0.597	1.527	1.490
n-C_4		13.5	31.0		0.104	0.589	1.465	1.028	1.475	1.490
i-C_5	1.4470				0.034	0.084			0.385	0.795
n-C_5					0.023	0.086				
n-C_6					0.110	0.050				
n-C_7										
n-C_8										
n-C_10		5.1	9.0							

TABLE 2

Composition of SNG11 to SNG19 (% molar).
Sources: a: Avila *et al.* (2002a), b: Avila *et al.* (2002b)

	SNG11[a]	SNG12[a]	SNG13[a]	SNG14[a]	SNG15[a]	SNG16[b]	SNG17[b]	SNG18[b]	SNG19[b]
N_2	0.618	0.313	2.80	6.90	5.651				
CO_2	0.187	0.202	0.20	0.51	0.284	0.67	0.48	0.862	0.410
C_1	98.9430	90.4183	96.6159	88.1882	83.3482	89.9584	88.7634	86.4838	96.4654
C_2	0.082	8.038	0.18	2.72	7.526	8.22	8.54	9.832	2.510
C_3	0.065	0.801	0.1029	0.85	2.009	0.90	1.68	2.388	0.213
i-C_4	0.050	0.081	0.0499	0.17	0.305	0.11	0.22	0.183	0.184
n-C_4		0.123	0.0095	0.32	0.520	0.13	0.29	0.231	0.197
i-C_5	0.017	0.010	0.0166	0.0850	0.120	0.0084	0.0182	0.0139	0.0096
n-C_5		0.0079		0.0940	0.144	0.0032	0.0084	0.0063	0.0100
n-C_6	0.032	0.0047	0.0160	0.119	0.068				0.0010
n-C_7	0.0027	0.0011	0.0054	0.0258	0.0138				
n-C_8	0.0033		0.0038	0.0180	0.011				
n-C_10									

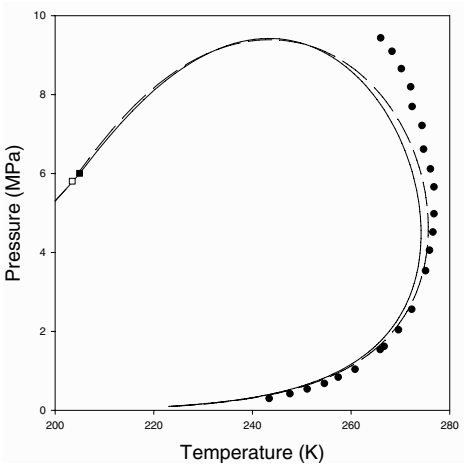
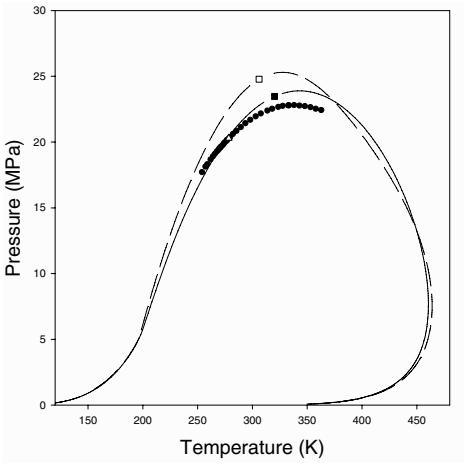


Figure 1
SNG1.



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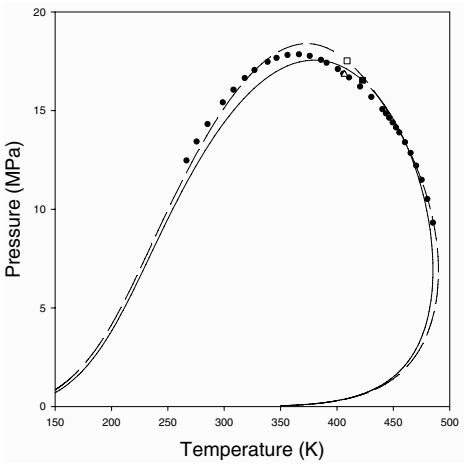
SNG2.



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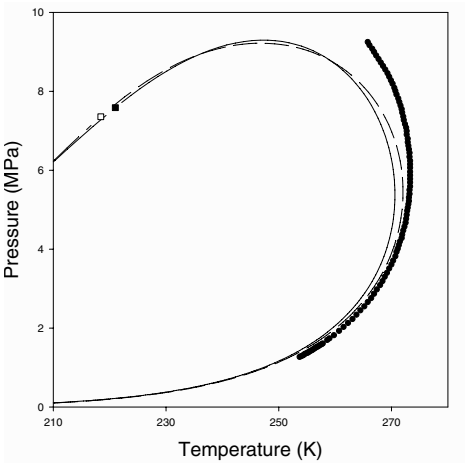
SNG3.



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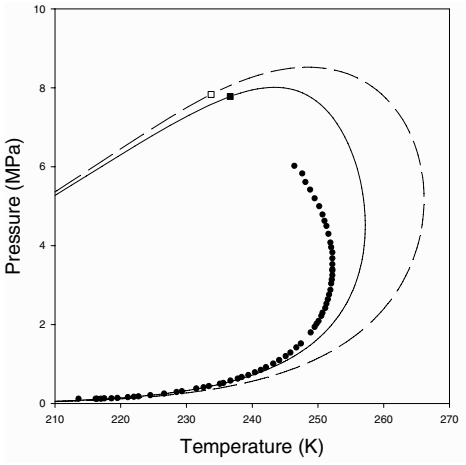
SNG4.



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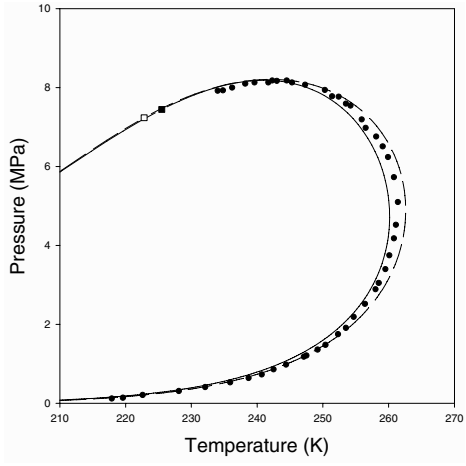
SNG5.



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SNG6.

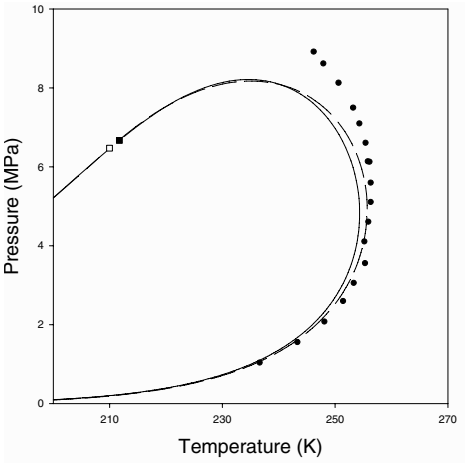


Figure 7

SNG7.

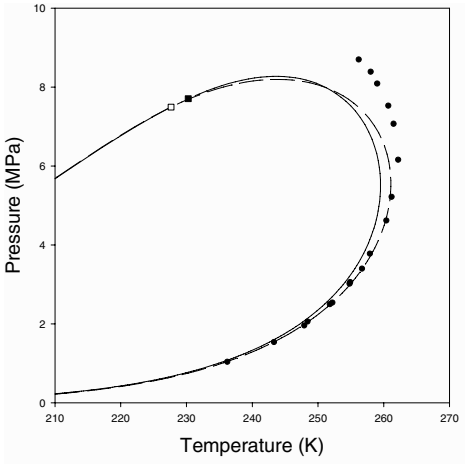


Figure 8

SNG8.

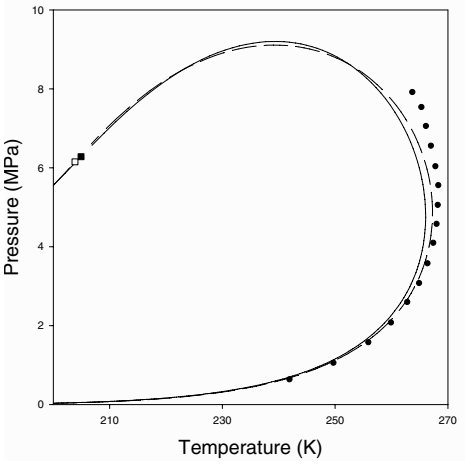


Figure 9

SNG9.

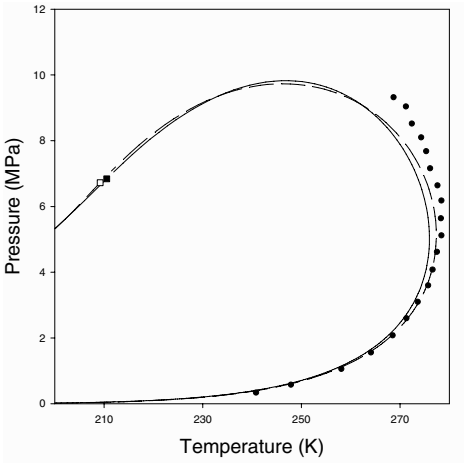


Figure 10

SNG10.

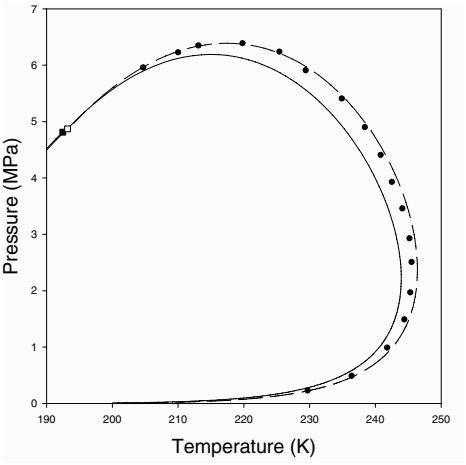


Figure 11

SNG11.

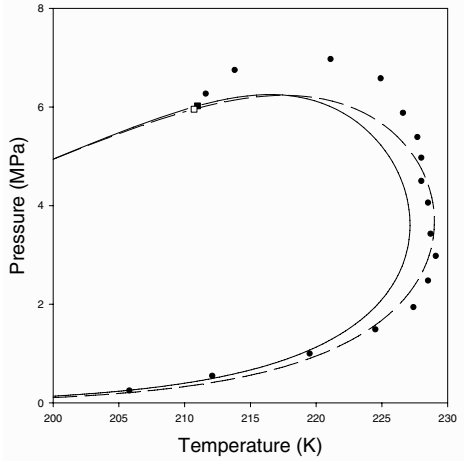
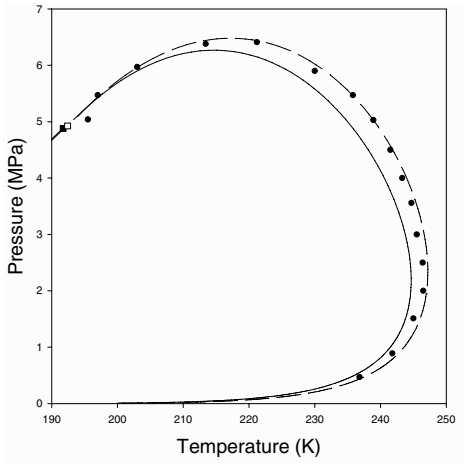


Figure 12

SNG12.



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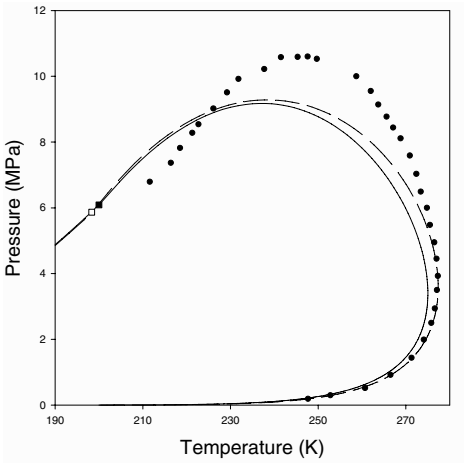
SNG13.



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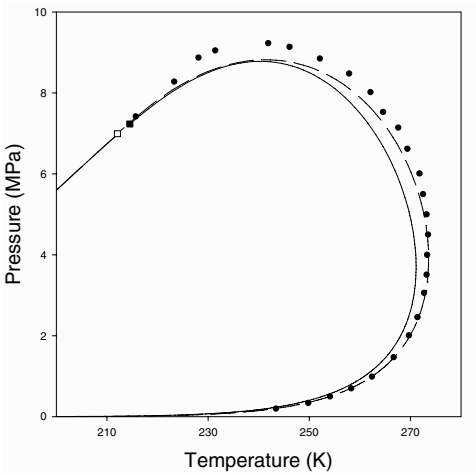
SNG14.



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SNG15.

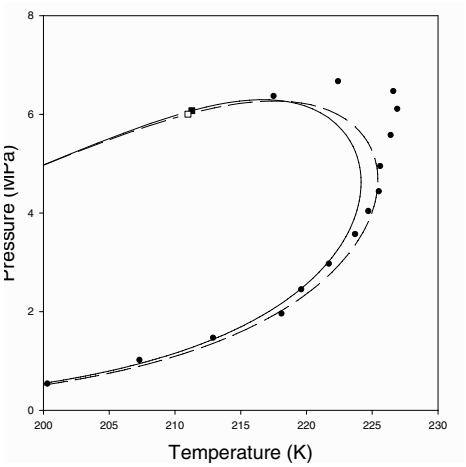

Figure 16
SNG16.

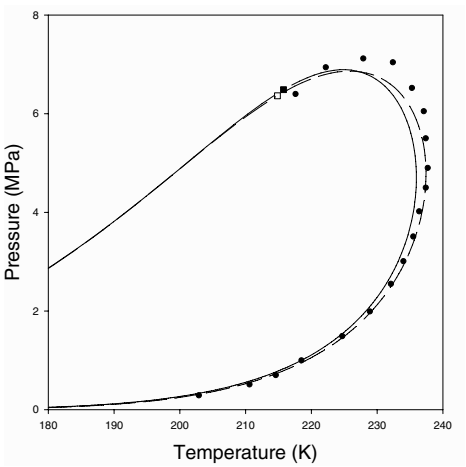

Figure 17
SNG17.

mole mass, density, and composition, are similar to those of actual natural gases. Tables 1 and 2 present the compositions on a molar basis of the SNG used in this work.

Figures 1 to 19 compare model predictions with experimental data. In the figures, the following symbols are used: (—) Peng-Robinson EOS; (−−) PC-SAFT EOS; (•) experimental data; (■) critical point predicted by the Peng-Robinson EOS, (□) critical point predicted by the PC-SAFT EOS, and (△) experimental critical point.

The phase diagram of SNG1 is in good agreement with experimental dew point data from the low pressure region up to the cricondentherm. Deviations become larger as the pressure increases. The PC-SAFT EOS performs better than the Peng-Robinson EOS in SNG1, but the opposite happens in SNG2, with both models giving poor predictions of the

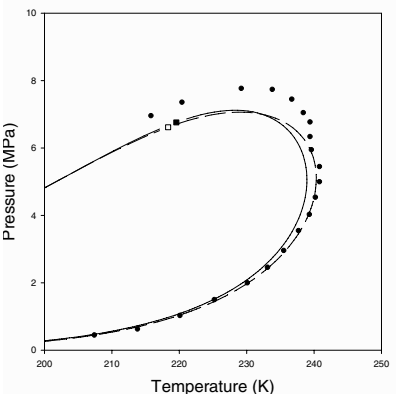

Figure 18
SNG18.

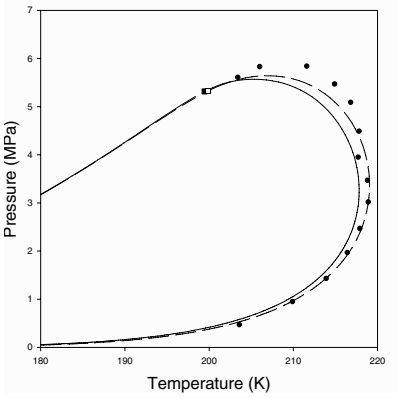

Figure 19
SNG19.

critical coordinates. For SNG3, the PC-SAFT EOS is better than the Peng-Robinson EOS in the range of experimental data. Note that the PC-SAFT EOS shows the smallest percent deviation in critical temperature (0.56%) while the PR EOS presents the smallest percent deviation in critical pressure (1.79%). The phase diagram of SNG4 shows a behavior similar to that of SNG1, i.e., good agreement up to the cricondentherm and larger deviations at larger pressures, with best performance by the PC-SAFT EOS. Predictions for SNG5 by both EOS show large deviations from experimental data. Nasrifar *et al.* (2005) showed that, for the Peng-Robinson EOS, non-zero binary interaction parameters improve results for this fluid, and the same happens with the PC-SAFT EOS, according to Martinez and Hall (2006). Good agreement with experiments is obtained for SNG6 for both EOS, including the cricondentherm and cricondenbar regions.

Both EOS provide a good representation of SNG7 at low pressures, but the PC-SAFT EOS gives a better prediction of the cricondentherm, and the same is observed for SNG8. Gases SNG9, SNG10 have very similar behavior and the PC-SAFT EOS shows better agreement than the Peng-Robinson EOS in the region above the cricondentherm. Figure 11 contains predictions for SNG 11, and the results show that the PC-SAFT EOS gives better agreement with experimental data than the Peng-Robinson EOS, including the cricondentherm and cricondenbar regions. Both EOS give good predictions of the dew point curves from the low pressure region up to the cricondentherm. For SNG12, deviations between the experimental and calculated cricondenbar are large for both models even though the PC-SAFT EOS provides a good representation of the dew point curve up to the cricondentherm.

The behavior of SNG13 is very well predicted by the PC-SAFT EOS. The behavior of SNG14 is similar to that of SNG12, and both EOS predict the cricondenbar poorly. For SNG 15, PC-SAFT EOS results are better than those of the Peng-Robinson EOS. The experimental data show that SNG16 has a peculiar behavior compared to the other systems studied: its cricondenbar and cricondentherm are similar, and none of the two EOS could predict this behavior satisfactorily. Gases SNG17, SNG18, and SNG19 have similar behavior. For these fluids, the PC-SAFT EOS provided better agreement with the experimental data available. Once again, however, large deviations appear at the cricondenbar. For bubble points, predictions of both EOS are almost identical.

As a final comment on our results, the experimental data used for comparison do not present systematic variations in specific variables as, for example, in the mole fraction of some component. Therefore, it is difficult to infer specific trends from the results. However, the overall trends observed in the comparisons are important because they provide an assessment of the EOS abilities to model multicomponent mixtures, which is the typical case in the gas industry.

CONCLUSION

The performances of a cubic (Peng-Robinson) and a non-cubic (PC-SAFT) EOS were compared in phase equilibrium calculations of 19 synthetic natural gases. These calculations were performed with all binary interaction parameters set equal to zero, i.e., no mixture data was used for parameter fitting, with the objective of comparing the *predictive* capability of the two models. The main observations were:

– PC-SAFT EOS results are in better agreement with experimental data than those of the Peng-Robinson EOS in most cases;
– both EOS provide very similar predictions of low-pressure dew points up to the cricondentherm, even

though the results of the PC-SAFT EOS are generally closer to experimental data;
- the cricondenbar was underestimated by both EOS in most cases;
- bubble point curves predicted by both EOS are usually very similar. Experimental bubble points were available only for mixtures SNG2 and SNG3, and both models had similar performance for these mixtures.

Given its good performance in predictions of natural gas phase behavior and its potential ability to model polar systems accurately, the PC-SAFT EOS may be a good model to help design dehydration and sweetening operations, but its ability to do so remains to be investigated.

ACKNOWLEDGEMENTS

The authors acknowledge the discussions with Dr. Papa Matar Ndiaye about the SAFT family EOS in the early stages of this work. This work was financially supported by the following Brazilian agencies and programs: *FINEP*, *PRH-ANP/MCT*, *CNPq*, and *FAPERJ*.

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Final manuscript received in May 2007