

PERFORMANCE OF CUBIC EOS AT HIGH PRESSURES

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PERFORMANCE DES ÉQUATIONS D'ÉTAT CUBIQUES À HAUTES PRESSIONS

Cet article présente une évaluation des performances des équations d'états (EoS) cubiques pour la prévision des comportements de phases des mélanges hyperbares. Il met en évidence un certain nombre de problèmes auxquels il devrait être répondu d'une manière coopérative. Les points relatifs à la définition des paramètres des EoS, tels que les coefficients d'interaction, les propriétés critiques des composants hydrocarbonés et la translation de volume sont examinés. Plusieurs types d'informations ont été pris en compte dans cette étude : les données expérimentales d'équilibre liquide-vapeur (ELV), les données compositionnelles et volumétriques issues d'équilibres isothermes jusqu'à 4 000 bar pour les mélanges binaires, les données PVT jusqu'à 2 000 bar pour des mélanges binaires et des systèmes synthétiques multicomposants.

Des corrélations et des résultats prévisionnels sont présentés à partir de l'équation de Peng-Robinson (t-mPR) traduite et modifiée. Il est montré que l'on rencontre de sérieux problèmes à haute pression dans le cas où l'on utilise des coefficients d'interaction extrapolés. Les prévisions des pressions de saturation des gaz à condensats sont plus satisfaisantes lorsque les paramètres d'interaction binaire sont obtenus à partir d'une corrélation des points de rosée à haute pression. Les prévisions concernant les volumes et les compositions sont remarquables à condition que l'on définisse les paramètres des équations d'état sur la base des données ELV binaires. Des résultats contradictoires sont obtenus avec différentes méthodes dans l'estimation des propriétés critiques des hydrocarbures de poids moléculaires élevés. Les expressions généralisées pour la translation de volume apparaissent comme très efficaces même à très hautes températures et très hautes pressions (jusqu'à 2000 bar).

PERFORMANCE OF CUBIC EOS AT HIGH PRESSURES

This paper presents an evaluation of the performance of cubic equations of state in the prediction of the phase behavior of hyperbaric mixtures. It points out a number of problems that should be resolved in a cooperative way. Items related to EoS parameter definitions such as interaction coefficients, critical properties of hydrocarbon compounds and volume translation are investigated. VLE experimental data, isothermal flash compositional and volumetric data up to 4000 bar as well as PVT data up to 2000 bar for binary mixtures and synthetic multicomponent systems have been considered in this study.

Correlation and prediction results are presented with the translated and modified Peng-Robinson (t-mPR) EoS. It is shown that serious problems are encountered at high pressure, when extrapolated interaction coefficients are used. Prediction of saturation pressures of gas condensates is more satisfactory when binary interaction

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parameters are obtained from high pressure dew point correlations. Compositional and volumetric predictions are remarkable under the assumption that definition of the EoS parameters is based on high pressure VLE binary data. Contradictory results are obtained with different methods for estimating the critical properties of high molecular weight hydrocarbons. Generalized expressions for the volume translation appear to be very efficient even at very high temperatures and pressures (up to 2000 bar).

RESULTADO DE LAS ECUACIONES DE ESTADO CÚBICAS DE ALTAS PRESIONES

Se presenta en este artículo una evaluación de los resultados de las ecuaciones de estado (EoS) cúbicas para la previsión de los comportamientos de fases de mezclas hiperbáricas y se hace resaltar cierto número de problemas a que se debería poder responder de forma cooperativa. Se examinan los puntos relativos a la definición de los parámetros de las EoS, como, por ejemplo, los coeficientes de interacción, las propiedades críticas de los componentes hidrocarbonados y la traslación de volumen. Se han tenido en cuenta y debidamente comentados en el presente estudio, los datos experimentales de ELV, las isoterms flash molares y volumétricas hasta 4000 bar para mezclas binarias, así como los datos PVT hasta 2000 bar para las mezclas binarias y los sistemas sintéticos de componentes múltiples.

Tomando como punto de partida la ecuación de Peng-Robinson (t-mPR) trasladada y modificada se presentan diversas correlaciones y resultados previsionales. Se demuestra que se habrá de tropezar con serios problemas al alcanzar las altas presiones en caso de que se utilicen coeficientes de interacción extrapolados. Las previsiones de las presiones de saturación de los gases de condensados son mayormente satisfactorias cuando los parámetros de interacción binaria se obtienen a partir de una correlación del punto de rocío sobre altas presiones. Las previsiones relativas a los volúmenes y las composiciones son destacadas si se supone que la definición de los parámetros de las ecuaciones de estado se fundan en datos ELV binarios. Se llegan a obtener resultados contradictorios al aplicar distintos métodos para la evaluación de las propiedades críticas de los hidrocarburos de pesos moleculares elevados. Las expresiones generalizadas para la traslación de volumen parecen ser sumamente eficaces al operar a temperaturas muy elevadas y también con presiones muy elevadas (hasta 2000 bar).

INTRODUCTION

Up to now, cubic equations of state (EoS) have been proved to be simple thermodynamic models, with reliable solution algorithms and efficient implementation in reservoir simulators, and to be widely applicable in the petroleum industry. Despite questions that are still open for discussion within the scientific community, EoS, in general, have been successfully used to tackle phase behavior problems for gas, oil and gas condensate fluids under typical reservoir conditions.

In the last few years, as greater depths are explored by drilling, an increasing number of reservoir fields have been discovered at temperatures up to 200°C and at pressures up to 1200 bar. Therefore, cubic EoS must be validated under these severe pressure and temperature conditions, where natural fluids appear to have special characteristics:

- They contain more than 40% mole fraction of methane and relatively high amounts of heavy hydrocarbons;
- They exhibit gas condensate behavior at high temperatures, but can become oils at lower temperatures;
- Three phase (S-L-V) coexistence occurs at moderate temperatures;
- Near-critical phenomena are present.

This work intends to provide a general overview of the performance of cubic EoS under high pressure and temperature conditions. The main goals of the study are to demonstrate the capabilities of EoS to correlate and predict VLE and volumetric behavior of hyperbaric hydrocarbon mixtures, to point out possible problems and to formulate a number of questions that require urgent answers. It is based on the available high pressure (HP) VLE and PVT experimental data, which is limited in the open literature, and on the use of the modified and translated PR EoS (t-mPR) of Magoulas and Tassios (1990) (Appendix).

1 CORRELATION OF HP VLE DATA: WHAT DO WE EXPECT?

The performance of the t-mPR EoS in the correlation of high pressure binary VLE data has been examined, using simple or more complex approaches for the interaction parameters. The following observations arise, and typical results are given in Figures 1 and 2.

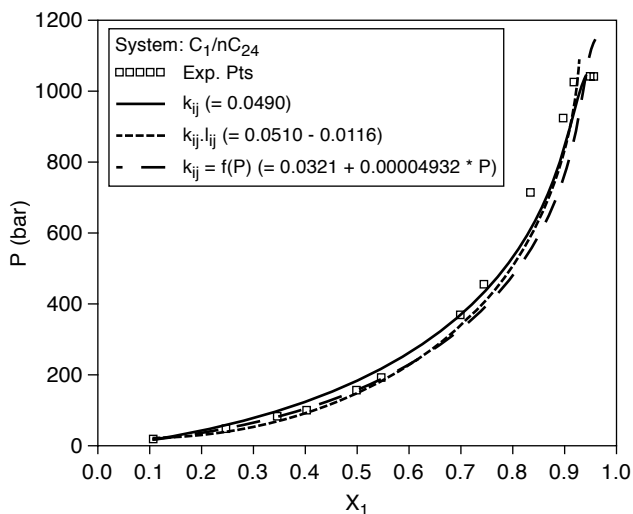


Figure 1

Correlation results of bubble point pressures for the system C_1/nC_{24} at 323 K with t-mPR/ k_{ij} , k_{ij} plus l_{ij} and $k_{ij} = f(P)$ (Floter *et al.*, 1997a).

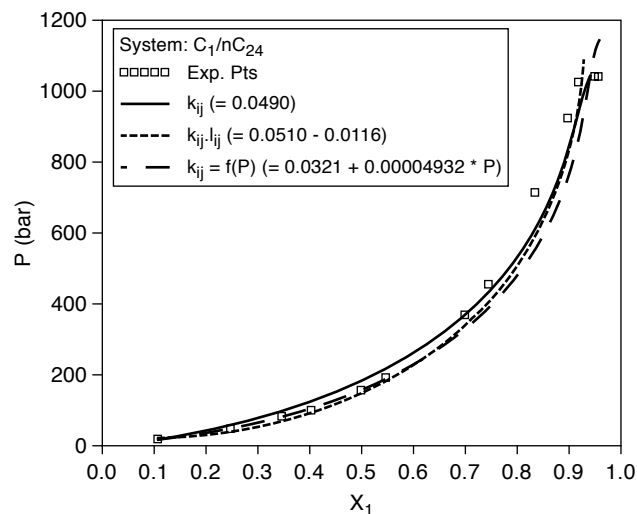


Figure 2

Correlation results of bubble point pressures for the system $C_1/1$ -methylnaphthalene at 373 K with t-mPR/ k_{ij} and $k_{ij} + l_{ij}$ (Marteau *et al.*, 1996).

The one-parameter (k_{ij}) approach provides overall satisfactory performance, even at pressures greater than 1000 bar but, in most cases, suffers in the near-critical region.

The interaction parameter k_{ij} , as a linear function of pressure (following the same approach that Mohamed and Holder (1987) suggested for a density-dependent k_{ij}), does not offer any special improvement.

The two-parameter approach (k_{ij} and l_{ij}) is more advantageous under near-critical conditions. Preliminary calculations of k_{ij} and l_{ij} show wide scattering of these values and their generalization appears to be rather difficult. Therefore, the practical application of this approach to more complex mixtures, and especially to real fluids, is still an issue.

2 COMPOSITIONAL AND VOLUMETRIC PREDICTIONS FROM VLE DATA

The performance of cubic EoS in the prediction of compositional and volumetric behavior for oil-type systems with well-defined compounds is very satisfactory when k_{ij} values are derived from available HP VLE data.

Figure 3 presents the compositional and the volumetric predictions for the system $C_1/1$ -methylnaphthalene. The results, for the concentration of

methane in the liquid and gas phase during an isothermal flash calculation as well as the results for the liquid and the gas phase density, are remarkably good, even at very high pressures up to 2000 bar. The k_{ij} values used in this case were obtained from the HP binary VLE data of Marteau *et al.* (1996).

3 PREDICTION OF HIGH PRESSURE VLE

The evaluation of the ability of the t-mPR EoS to predict high pressure VLE was based on VLE experimental data for binary and multicomponent synthetic mixtures and was performed by investigating the following aspects:

- Is the work so far on generalized expressions of k_{ij} values valid under extreme pressure conditions?
- Are k_{ij} values obtained from bubble point correlation acceptable for dew point predictions?

Concerning the first question, the existing generalized correlations for k_{ij} values are quite satisfactory for systems of alkanes with carbon number (CN) up to 18. Figures 4 and 5 present predictions for the systems N_2/nC_{14} using k_{ij} values from Avlonitis *et al.* (1995) and for the system C_1/nC_{16} using k_{ij} 's from Kordas *et al.* (1995). The results are equivalent to those obtained from correlation even at very high pressures.

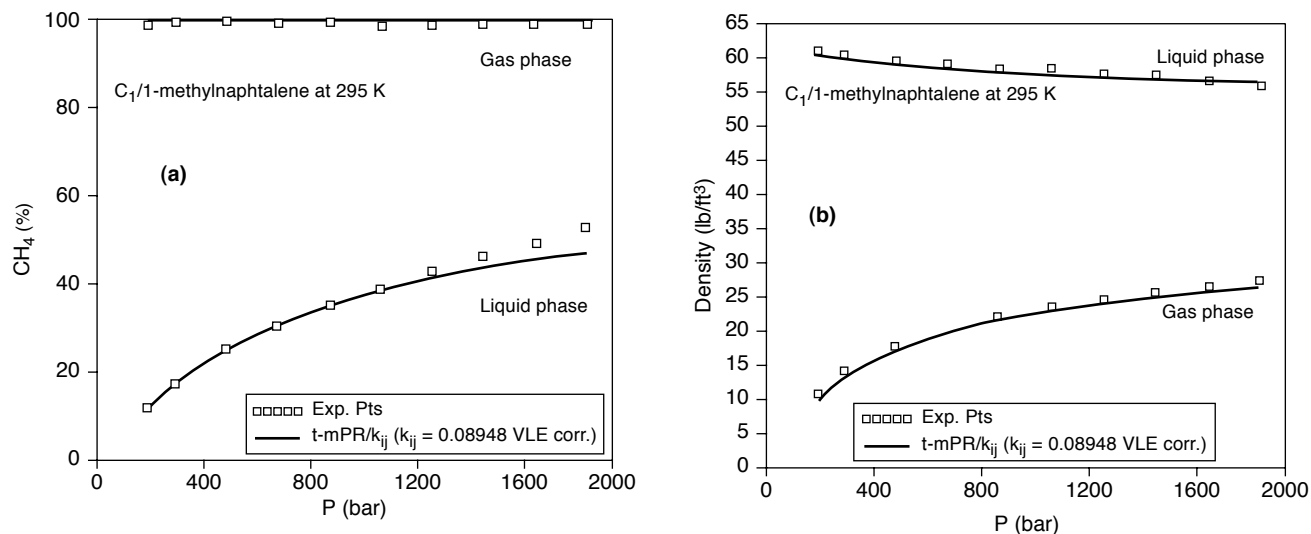


Figure 3

Isothermal flash calculation for $C_1/1$ -methylnaphthalene. Compositional and volumetric predictions with t-mPR, using k_{ij} for $C_1/1$ -methylnaphthalene obtained from HP binary VLE data (Marteau *et al.*, 1996).

a) Predicted concentration of methane in the liquid and gas phase; b) Predicted liquid and gas phase density.

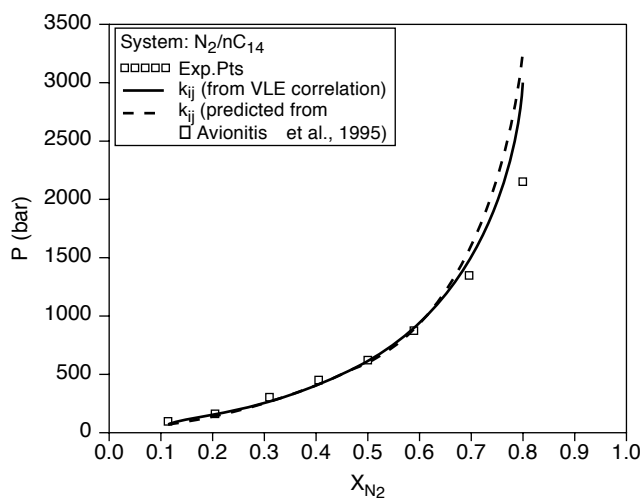


Figure 4

Correlation and prediction results for VLE of the N_2/nC_{14} system at 400 K (de Leeuw *et al.*, 1992).

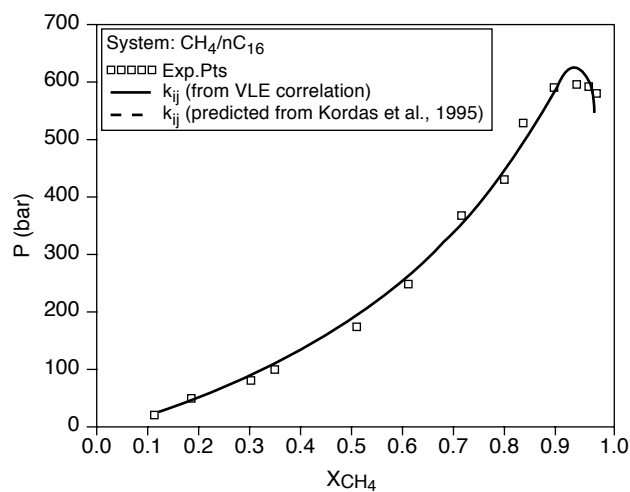


Figure 5

Correlation and prediction results for VLE of the C_1/nC_{16} system at 350 K (Glaser *et al.*, 1985).

As asymmetry increases, however, predicted k_{ij} values become completely useless. Very large errors and convergence problems appear at pressures greater than 350 bar, as the typical results in Figure 6 indicate. This is also the case for the mixture for C_1 /phenanthrene (Fig. 7) where k_{ij} values obtained from the low pressure VLE data of Malone and Kobayashi (1990) and Darwish *et al.* (1994), are totally unacceptable at high pressures.

Therefore, high pressure experimental VLE data are required for asymmetric systems in order to improve the prediction capability of EoS. However, this is very time-consuming and expensive work, and it must be simplified by specifying the minimum number of systems required to establish the trend in k_{ij} values. Additionally, the uncertainty in estimating the critical properties of hydrocarbons with $CN \geq 20$ remains one of the most serious problems.

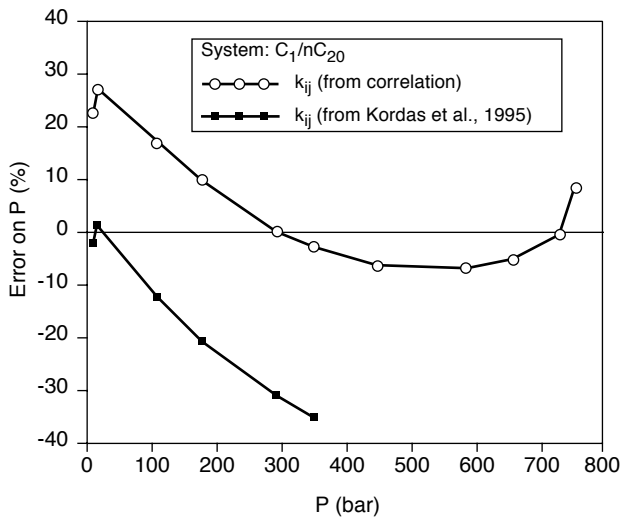


Figure 6
Correlation and prediction results for VLE of the C_1/nC_{20} system at 353 K (van der Kooi *et al.*, 1995). Convergence problems are encountered at high pressures in the case of prediction.

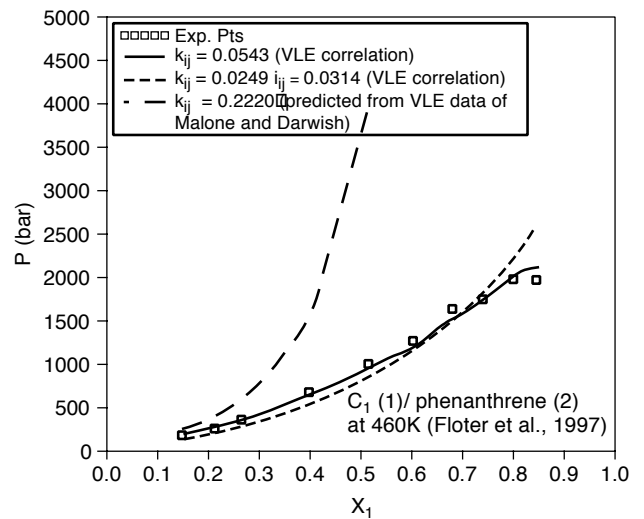


Figure 7
Correlation and prediction results for VLE of the C_1 /phenanthrene system at 460 K (Floter *et al.*, 1997b).

As far as the second question is concerned, Figure 8 presents dew point predictions for the 7-component synthetic mixture of Ungerer *et al.* (1995), whose composition is given in Table 1. In this case, k_{ij} values for all C_1 /HC pairs, except those of C_1 /phenanthrene, are obtained from generalized expressions (Kordas *et al.*, 1995). For the k_{ij} value of C_1 /phenanthrene, three approaches have been followed:

- k_{ij} from bubble point correlation of binary VLE data. In this case, dew point prediction is possible for the far critical region but the solution obtained for the near critical region is trivial.
- k_{ij} from dew point correlation of binary VLE data. Dew point prediction is quite satisfactory (average deviation of 3%).
- k_{ij} from low pressure binary VLE data. Results are totally unacceptable. A trivial solution is obtained for the entire region.

TABLE 1

Composition of the 7-component synthetic mixture	
Component	mole (%)
C_1	75.81
C_2	11.32
nC_4	4.88
Toluene	1.99
nC_8	2.68
nC_{16}	2.30
Phenanthrene	1.02

It appears that, as suggested in Section 3, the generalized correlation for k_{ij} of C_1 /hydrocarbons derived from low P data can be useful if the key binary—in this case C_1 /phenanthrene—is identified. Note that the pressure range, in this case, is up to 500 bar, and, since there are no data available at higher pressures, we can not be certain that the picture will be the same in that region.

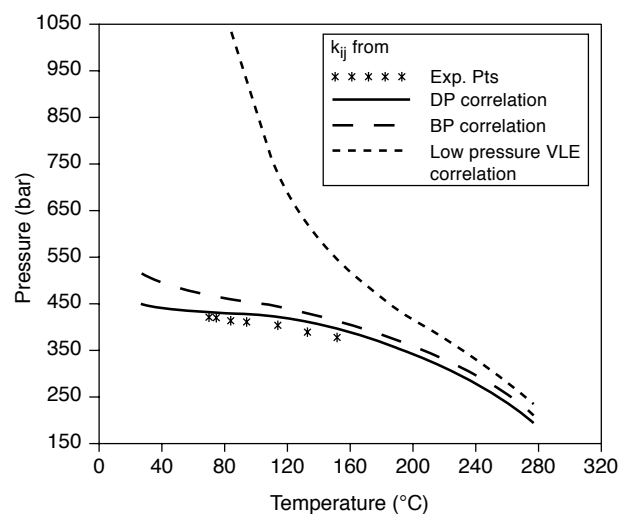


Figure 8
Dew point prediction for the 7-component synthetic mixture (Ungerer *et al.*, 1995).

4 WHAT IS TO BE DONE WITH T_c , P_c AND ω FOR $CN > 20$

The uncertainty in the estimation of the critical properties and the acentric factor is apparent from Figures 9 to 11, where T_c , P_c and ω values are plotted against carbon number, based on different methodologies such as empirical correlations, group contribution and molecular simulation methods. Note that, for the important carbon number range $20 < CN < 40$, the differences among the correlations are more pronounced in P_c values than in T_c values.

These differences have a significant effect on VLE and volumetric predictions as shown in Figures 12 through 14. For the system C_1/nC_{24} (Fig. 12), due to the convergence problems encountered with the use of EoS and k_{ij} values that were predicted from generalized correlations, the EoS/GE model LCVm (Boukouvalas *et al.*, 1994), was used to maintain the predictive type of the results. The different methods applied in the estimation of T_c , P_c and ω of nC_{24} are given in Table 2. According to this table the largest differences occur in the P_c values.

Figure 12 shows the effect of the different P_c values for nC_{24} on VLE prediction results. Estimation methods that provide relatively high P_c values such as that of Del Sordo (1994) and that of Saloustris and

Skouras (work in completion, 1998), appear to be more effective. The other methods fail dramatically at near critical.

TABLE 2
Estimation of T_c , P_c and ω for nC_{24}

Source	T_c (K)	P_c (bar)	ω
Del Sordo	802.5	10.10	1.0488
Saloustris and Skouras	805.3	9.76	1.05
Marano and Holder	807.3	9.2	1.004
Magoulas and Tassios	802.7	8.97	1.039
Twu <i>et al.</i> (ω from K-L)	804.4	9.29	1.0125

Figures 13 and 14 present the prediction of the percent liquid volume for two gas condensates: the system C_1/nC_{24} of Bjorlykke and Firoozabadi (1990) and the 7-component synthetic mixture of Ungerer *et al.* (1995) with the composition given in Table 3.

The methods chosen for the estimation of T_c , P_c and ω of nC_{24} and nC_{36} reflect the two main trends encountered in estimating P_c values according to Figure 10. In the case of the nC_{24} binary the results in Figure 13 suggest that the method of Magoulas and Tassios, that provides lower P_c values, gives better results. On the contrary, the same method in the case of the nC_{36} system (Fig. 14) is not successful, and a higher

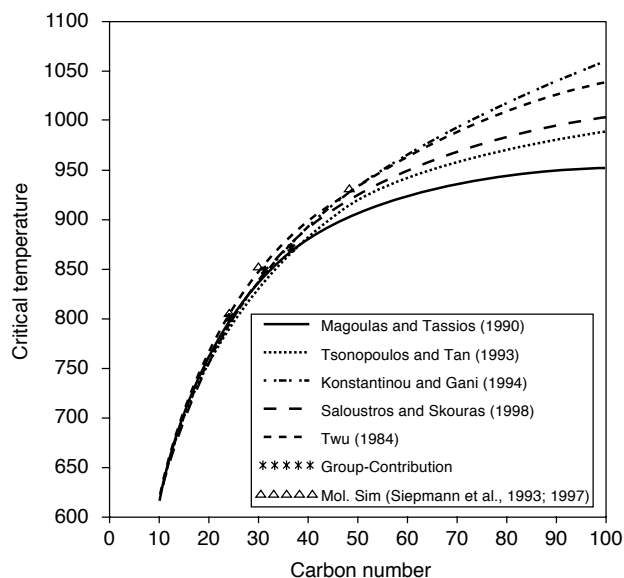


Figure 9
Critical temperature as a function of n -alkane carbon number.

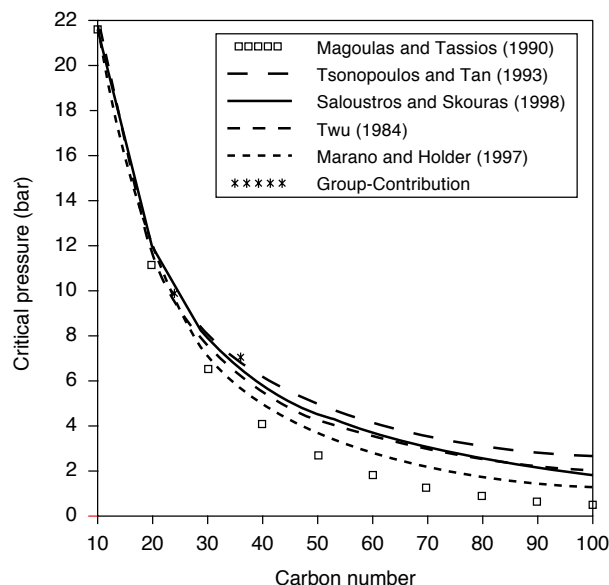


Figure 10
Critical pressure as a function of n -alkane carbon number.

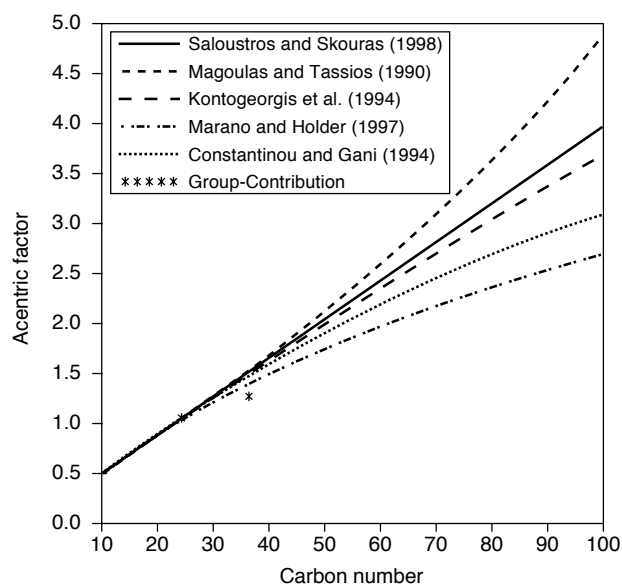


Figure 11

Acentric factor as a function of n -alkane carbon number.

P_c value for nC_{36} is required, as shown by the performance of the group contribution method. For the 7-component system, k_{ij} values are from the generalized correlation of Kordas *et al.* (1995), while for the C_1/nC_{36} , k_{ij} were obtained by fitting the dew

point pressure. For both systems, the liquid drop-out curve is predicted, except for the first point, the dew point pressure, which is fitted.

TABLE 3

Composition of the 7-component synthetic mixture	
Component	mole (%)
C_1	75.6
C_2	11.3
nC_4	4.9
Toluene	2.0
nC_8	2.7
nC_{16}	2.3
nC_{36}	1.2

5 VOLUME TRANSLATION

High temperature (up to 550 K) and high pressure (up to 2000 bar) PVT experimental data of Zoller and Walsh (1995), for pure high molecular weight alkanes, have been used to evaluate the performance of volume translation in volumetric predictions with cubic EoS.

Figures 15 and 16 present the percent error in volume prediction as a function of temperature and of pressure for nC_{24} and nC_{36} . In both cases the modified PR (mPR) EoS has been used, coupled with the

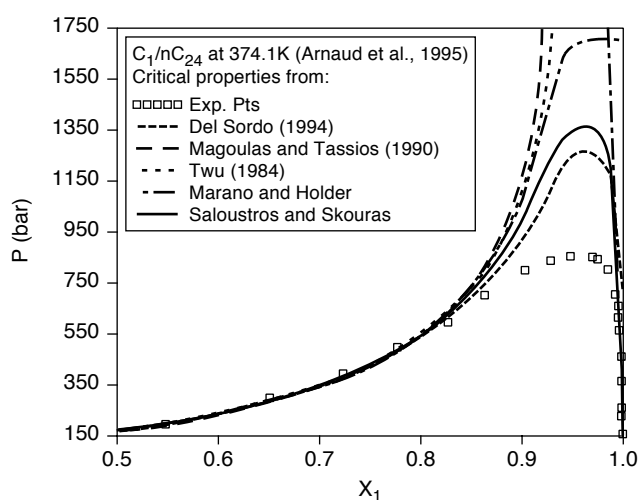


Figure 12

VLE prediction for the system C_1/nC_{24} at 374 K (Arnaud *et al.*, 1995) with the EoS/GE model LCVM.

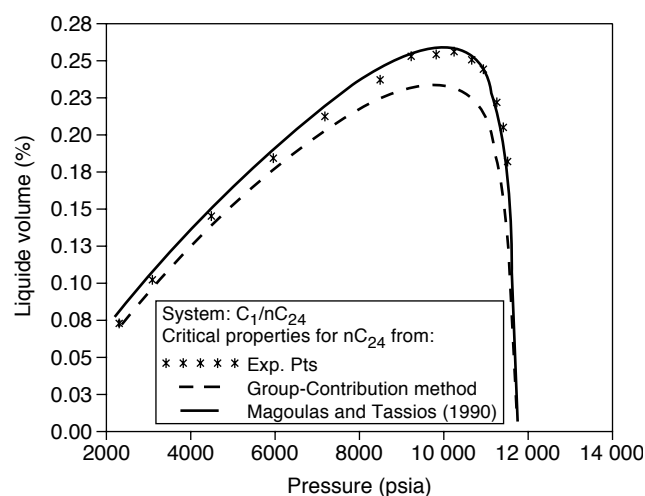


Figure 13

Effect of T_c , P_c and ω on the prediction of the percent liquid volume for the C_1/C_{24} gas condensate at 388 K (Bjorlykke and Firoozabadi, 1990).

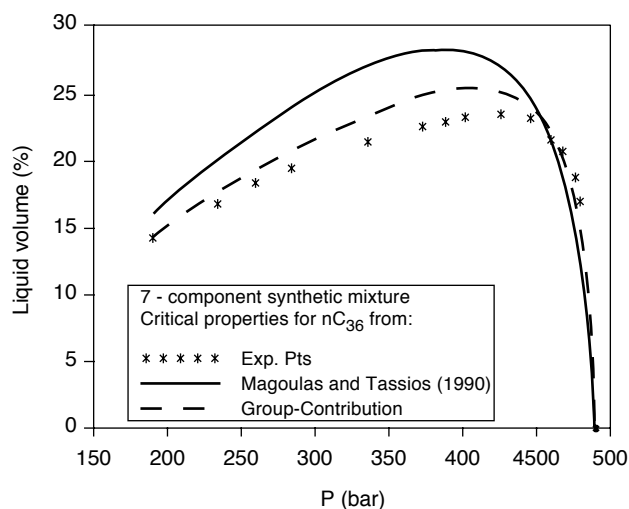


Figure 14

Effect of T_c , P_c and ω on the prediction of the percent liquid volume for the 7-component synthetic gas condensate at 423 K (Ungerer *et al.*, 1995).

temperature independent volume translation of Equation (A.5) of Appendix. The results obtained are quite satisfactory, even at very high pressures and temperatures. Equivalent results are obtained with the PR EoS and the volume translation of Jhaveri and Youngren (1984).

The above remarks indicate that the existing generalized expressions for volume translation, although derived from saturated liquid density data at low and moderate pressures, can be successfully applied to PVT predictions under HP conditions.

CONCLUSIONS

- Using one interaction parameter k_{ij} at high pressures can be considered satisfactory.
- Although it appears that two parameters (k_{ij} and l_{ij}) are more effective in the near critical region, can such an approach be of practical interest for natural fluids?
- Generalized expressions for k_{ij} appear to be adequate for systems with *n*-alkanes up to *n*C₁₈ and for low MW aromatics. As asymmetry increases, however, the results are totally unacceptable.
- When k_{ij} is derived from HP binary VLE data, compositional and volumetric predictions appear to be quite satisfactory for oil-type systems.
- VLE predictions in the high pressure region are very sensitive to the values of critical properties and the acentric factor for compounds with CN > 20, especially that of P_c , where the largest differences among the various predictive schemes are encountered.

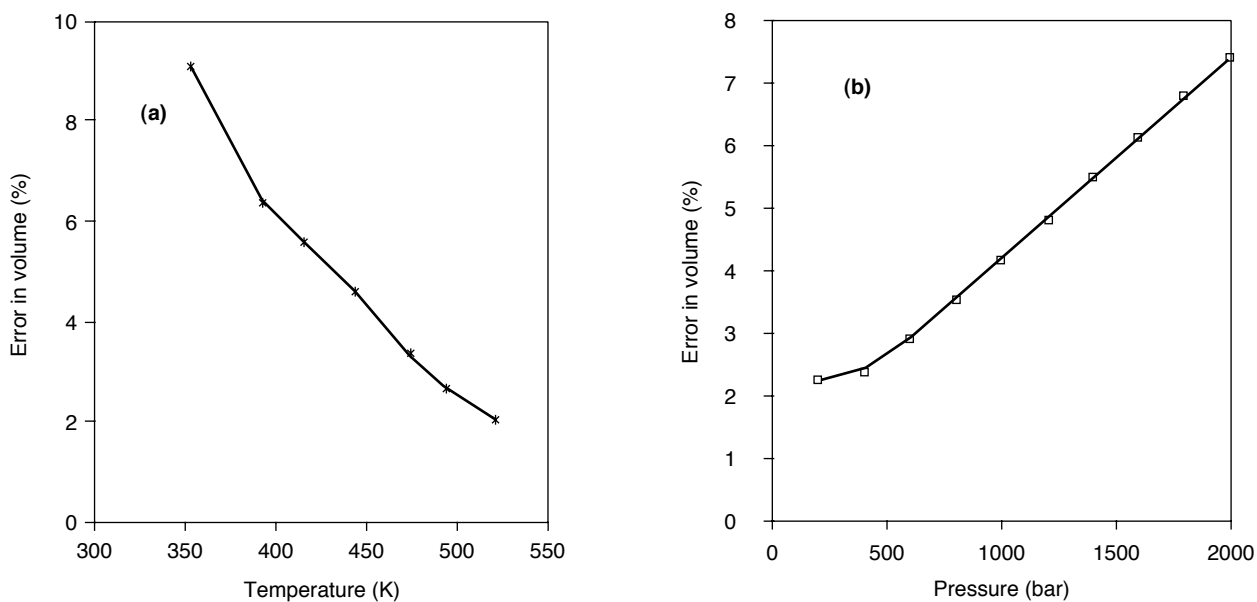


Figure 15

PVT prediction of *n*C₂₄ with t-mPR EoS.

a) Pressure average percent error in volume as a function of temperature; b) Percent error in volume as a function of pressure at 443 K.

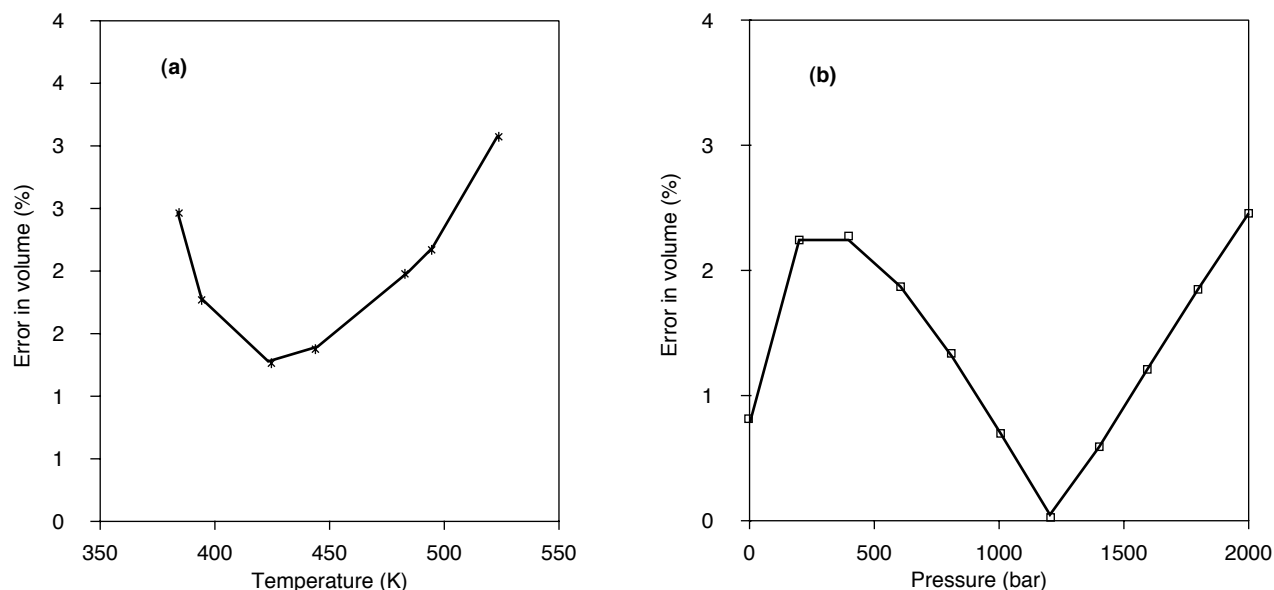


Figure 16

PVT prediction of nC_{36} with t-mPR EoS.

a) Pressure average percent error in volume as a function of temperature; b) Percent error in volume as a function of pressure at 443 K.

- Prediction of VLE suggests the need for higher P_c values. Volumetric predictions give contradictory results. Molecular simulation, unfortunately, only gives T_c estimates, so far. How are we going to arrive at the correct trend for P_c ?
- Generalized correlations for volume translation (t) estimates are very effective over a wide range of temperatures and pressures (up to 2000 bar).

LIST OF SYMBOLS

k_{ij}	interaction parameter
P	pressure
T	temperature
CN	carbon number

Greek symbols

ω	acentric factor
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APPENDIX

The t-mPR EoS has the following form:

$$P = \frac{RT}{V+t-b} - \frac{a_c \alpha}{(V+t)(V+t+b) + (V+t-b)} \quad (\text{A1})$$

where the expressions for its parameters are:

$$\alpha = [1 + m(1 - \sqrt{T_r})]^2 \quad (\text{A2})$$

$$m = 0.384401 + 1.522760 \omega - 0.213808 \omega^2 + 0.034616 \omega^3 - 0.001976 \omega^4 \quad (\text{A3})$$

$$t = t_0 + (t_c - t_0) \exp \beta (|1 - T_r|) \quad (\text{A4})$$

$$t_0 = \frac{RT_c}{P_c} (-0.014471 + 0.067498 \omega + 0.084852 \omega^2 + 0.067298 \omega^3 - 0.017366 \omega^4) \quad (\text{A5})$$

$$\beta = -10.2447 - 28.6312 \omega \quad (\text{A6})$$

$$t_c = \frac{RT_c}{P_c} (0.3074 - Z_c) \quad (\text{A7})$$

The EoS has a cubic form with respect to the compressibility factor as follows:

$$Z^3 - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (\text{A8})$$

where:

$$Z = \frac{PV}{RT} ; A = \frac{aP}{R^2T^2} ; B = \frac{bP}{RT} \quad (\text{A9})$$

To calculate the critical compressibility factor Z_c , the following expression has been assumed (Czerwiński *et al.*, 1988):

$$Z_c = 0.289 - 0.0701 \omega - 0.0207 \omega^2$$

To calculate the parameters a_m , b_m and the translation factor t_m of the t-mPR EoS for binary mixtures, the following mixing rules have been assumed:

– For the a_m parameter:

$$a_m = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 a_{12} \quad (\text{A10})$$

where a_1 and a_2 are the pure component “energy parameters” of the t-mPR EoS and a_{12} is defined by the following expression:

$$a_{12} = \sqrt{a_1 \cdot a_2 (1 - k_{12})} \quad (\text{A11})$$

where k_{12} is the binary interaction coefficient.

– For the b_m parameter the following linear expression is used:

$$b_m = x_1 b_1 + x_2 b_2 \quad (\text{A12})$$

A similar linear expression is also used for the translation factor of the binary mixture, t_m :

$$t_m = x_1 t_1 + x_2 t_2 \quad (\text{A13})$$

l_{12} is defined by:

$$b_{12} = \frac{b_1 + b_2}{2} (1 - l_{12}) \quad (\text{A14})$$