

CORRELATION AND PREDICTION OF PHASE EQUILIBRIA AND VOLUMETRIC BEHAVIOUR OF HYPERBARIC BINARY FLUIDS

S. K. STAMATAKI*, K. G. MAGOULAS,
C. J. BOUKOUVALAS and D. P. TASSIOS

National Technical University of Athens¹

CORRÉLATION ET PRÉDICTION DES ÉQUILIBRES DE PHASES ET DU COMPORTEMENT VOLUMÉTRIQUE DE FLUIDES HYPERBARES BINAIRES.

La capacité des équations d'état (EoS) cubiques pour corrélérer et prédire les équilibres de phases en conditions hyperbares est analysée. Les données PVT de corps purs ainsi que les données d'équilibres liquide-vapeur (VLE) et volumétriques pour des mélanges binaires, jusqu'à 2000 bar sont utilisées. Les résultats des corrélations et des prédictions sont présentés pour l'équation de Peng-Robinson translaturée et modifiée (t-mPR), ainsi que pour les modèles EoS/G^E.

Les performances des EoS cubiques avec un paramètre d'interaction unique (k_{ij}) pour décrire les VLE est remarquable si l'on considère le niveau des pressions pris en compte. Il en va de même pour les résultats PVT, y compris les volumes relatifs liquides pour le système C₁/nC₂₄. Avec des erreurs typiquement de 10 %, des écarts en pression de 100-200 bar sont bien entendu obtenus, ceux-ci pouvant être éliminés par l'utilisation d'un second coefficient d'interaction dans la règle de mélange pour le covolume.

Les valeurs de k_{ij} tirées de corrélations généralisées développées à partir des données VLE à basse pression conduisent à des résultats raisonnables pour les systèmes avec des hydrocarbures jusqu'au nC₁₆, même aux pressions élevées, mais conduisent à des échecs pour les systèmes plus asymétriques.

La translation de volume est essentielle pour la qualité des prédictions PVT. La translation indépendante de la température de l'équation t-mPR, ainsi que celle de Jhaveri et Yougren, donnent de très bons résultats. La méthode LCVM fournit les meilleurs résultats parmi les modèles EoS/G^E étudiés, et donne de très bonnes prédictions pour les systèmes plutôt symétriques, lesquelles deviennent de moindre qualité pour les systèmes asymétriques aux pressions très élevées.

CORRELATION AND PREDICTION OF PHASE EQUILIBRIA AND VOLUMETRIC BEHAVIOUR OF HYPERBARIC BINARY FLUIDS

The capabilities of cubic Equations of State (EoS) in the correlation and the prediction of phase equilibria at hyperbaric conditions is examined. PVT data of pure compounds as well as VLE and volumetric data of binary mixtures up to 2000 bar are used.

(1) Laboratory of Thermodynamics and Transport Phenomena,
Department of Chemical Engineering,
* Department of Mining and Metallurgy,
9, Heroon Polytechniou Str.,
Zographou Campus,
15780 Athens - Greece

Correlation and prediction results are presented with the translated and modified Peng-Robinson (t-mPR) EoS and EoS/G^E models.

The performance of cubic EoS with a single interaction parameter (k_{ij}) in describing VLE is remarkable considering the level of pressures involved. The same is valid for the PVT results including the relative liquid volumes of the C₁/nC₂₄ system. With typical errors of about 10% deviations in pressure of 100-200 bar are, of course, encountered which can be eliminated by the use of second interaction coefficient in the covolume combining rule.

Predicted k_{ij} values obtained from generalized correlations developed from low pressure VLE data provide reasonable results for systems with hydrocarbons up to nC₁₆ even at high pressures, but fail for higher asymmetric ones.

Volume translation is essential for PVT predictions. The temperature independent translation of t-mPR and that of Jhaveri and Yougren give very satisfactory results. LCVM provides the best results of the EoS/G^E models studied and gives very good predictions for rather symmetric systems which become poorer with asymmetric ones at very high pressures.

CORRELACIÓN Y PREDICCIÓN DE LOS EQUILIBRIOS DE FASES Y DEL COMPORTAMIENTO VOLUMÉTRICO DE FLUIDOS HIPERBÁRICOS BINARIOS

Se analiza en este artículo la capacidad de las ecuaciones de estado (EoS) cúbicas para la correlación y predicción de los equilibrios de fase en condiciones hiperbáricas. Se utilizan para ello los datos PVT de cuerpos puros, así como también los datos de los equilibrios líquido-vapor (VLE) y volumétricos para las mezclas binarias, hasta una presión de 2000 bar. Se presentan los resultados de estas correlaciones y predicciones para la ecuación de Peng-Robinson transferida y modificada (t-mPR), así como para los modelos EoS/G^E.

Los resultados de los EoS cúbicos con un parámetro de interacción único (k_{ij}) para describir los VLE son destacados si se considera el nivel de las presiones tenidas en cuenta. Lo mismo ocurre al tratarse de los resultados PVT, e inclusive los volúmenes relativos líquidos para el sistema C₁/nC₂₄. Con errores típicamente expresados de un 10 %, las variaciones de presión de 100-200 bar se obtienen, naturalmente, diferencias que se pueden eliminar por la utilización de un segundo coeficiente de interacción en la regla de mezcla para el covolumen.

Los valores de k_{ij} derivados de correlaciones generalizadas desarrolladas tomando como punto de partida los datos VLE a baja presión, conducen a resultados razonables para los sistemas con hidrocarburos hasta nC₁₆, incluso con presiones elevadas, pero en cambio, conducen a fracasos para los sistemas más asimétricos.

La transferencia de volumen resulta primordial para la calidad de las predicciones PVT. La transferencia independiente de la temperatura de la ecuación t-mPR, así como de aquella de Jhaveri y Yougren, permiten obtener resultados muy correctos. El método LCVM permite conseguir los mejores resultados entre los modelos. EoS/G^E estudiados y da buenos resultados en cuanto a las predicciones para los sistemas más bien asimétricos, los cuales pasan a ser de menor calidad para los sistemas asimétricos que trabajan con presiones más elevadas.

INTRODUCTION

In the last few years as higher depths are explored by drilling (down to approximately 7000 m) wider ranges of temperature (up to 250°C) and pressure (up to 1200 bars) are met in practice.

Arnaud *et al.* (1995) have illustrated the increasing number of oil and gas fields that have been discovered in several regions around the world at such extreme conditions. Especially in the European section high pressure-high temperature gas condensate reservoirs are considered as an important upcoming fossil fuel resource and are anticipated to have a substantial contribution in the future oil and gas production.

Reservoir fluids at such conditions are commonly referred to as hyperbaric fluids. They consist of methane (greater than 40% in mole fraction) and high amounts of heavy hydrocarbons mainly *n*-alkanes. They exhibit gas condensate behavior at high temperatures but they can become oils at moderate ones because of the presence of heavier compounds. Some of these methane-rich fluids are near critical as well. At lower temperatures, 10-30°C, crystallization of heavy hydrocarbons has also been observed.

Experimental data in the open literature are very limited (basically only the C₁/nC₂₄ binary has been fully investigated) and the capabilities of the cubic EoS, used for low pressure reservoir fluids modeling, in the field of hyperbaric fluids are not known.

It is recognized that the generation of consistent, high quality experimental data of simple and complex (real) fluids, combined with the development of versatile thermodynamic models and computational tools for the prediction of their properties, provide the proper approach in the deep understanding of the physical status of these fluids and in the improvement of the technology related to their optimal treatment.

We concentrate in this study on the thermodynamic modeling aspects of this endeavor and consider the traditional tool used in conventional reservoir conditions, i.e. cubic EoS. More specifically we examine:

The capabilities and the limitations of the translated and modified Peng-Robinson (t-mPR EoS) in the:

- Correlation of VLE data with
 - a single interaction parameter (k_{ij});
 - two parameter mixing rules (k_{ij} and l_{ij} as well as linearly pressure-dependent k_{ij}).

TABLE 1
Data base

System	Pressure range (bar)	Temperature range (K)	Type of data	Reference
VLE				
C ₁ /nC ₁₄	27-489	320-432	x,T,P (BP)	de Leeuw <i>et al.</i> , 1992
C ₁ /nC ₁₆	27-706	288-363	x,T,P (BP)	Glaser <i>et al.</i> , 1985
C ₁ /nC ₂₀	4-893	303-370	x,T,P (BP)	Van der Kooi <i>et al.</i> , 1995
C ₁ /nC ₂₄ (1)	20-1040	315-453	x,T,P (BP)	Floter <i>et al.</i> , 1997
C ₁ /nC ₂₄ (2)	164-853	374.1	x,T,P (BP)	Arnaud <i>et al.</i> , 1995
N ₂ /nC ₇	20-998	305-413	x,y,T,P (BP)	Legret <i>et al.</i> , 1981
N ₂ /nC ₁₄	84-2137	321-434	x,T,P (BP)	de Leeuw <i>et al.</i> , 1992
N ₂ /nC ₁₆	49-490	373-423	x,T,P (BP)	IUPAC, 1982
PVT				
C ₁	201-1100	374.1	T,P,V	Arnaud <i>et al.</i> , 1995
nC ₂₄	201-1100	374.1	T,P,V	Arnaud <i>et al.</i> , 1995
C ₁ /nC ₄	86-690	344, 511	x,T,P,V (IF)	Reamer <i>et al.</i> , 1958
C ₁ /cC ₆	159-690	344,455	x,T,P,V (IF)	Reamer <i>et al.</i> , 1958
C ₁ /nC ₁₀	124-690	344,511	x,T,P,V (IF)	Reamer <i>et al.</i> , 1942
C ₂ /nC ₁₀	27-690	344, 511	x,T,P,V (IF)	Reamer <i>et al.</i> , 1942
C ₁ /nC ₂₄ (oil)	201-853.2	374.1	x,T,P,V _{mix} ,V ₁ (IF)	Arnaud <i>et al.</i> , 1995
C ₁ /nC ₂₄ (gas)	163-836	388.5	x,T,P,V _{mix} ,V ₁ (IF)	Bjorlykke and Firoozabadi, 1990

IF: isothermal flash.

BP: bubble point.

- Prediction of the VLE behavior using
 - predicted from generalized correlations k_{ij} 's;
 - three EoS/G^E models (LCVM, MHV2, PSRK).
- Prediction of the PVT behavior of pure compounds and binary mixtures.

The data base used for this purpose is presented in Table 1 and includes pure compounds and binary mixtures. T_c , P_c and ω values for all compounds are obtained from DIPPR (Daubert and Danner, 1985), while the sets of predicted T_c , P_c and ω values for the nC₂₄ considered in this study are presented in Table 2.

TABLE 2

 T_c , P_c and ω values of nC₂₄ estimated by different sources

Source	nC ₂₄		
	T_c (K)	P_c (bar)	ω
Magoulas <i>et al.</i> , 1990	802.7	8.97	1.0390
Del Sordo, 1994	802.5	10.10	1.0488
Teja <i>et al.</i> , 1990 (ω from K-L)	809.9	10.49	1.0029
Twu <i>et al.</i> , 1984 (ω from K-L)	804.4	9.29	1.0125

1 CORRELATION AND PREDICTION RESULTS: VLE

Table 3 presents correlation and prediction results for the systems of this study. Typical ones are presented in Figures 1 to 12. The following comments summarize our observations on the obtained results.

The performance of cubic EoS with a single k_{ij} in the correlation of VLE data is, even at hyperbaric conditions, remarkable taking into account the level of the pressures involved as suggested by the typical phase envelope of Figure 3. In general, for the systems considered in this study, average deviations in pressure less than about 10% have been obtained as shown in Table 3. Furthermore, no failure appeared even at very high pressures or in the cases of asymmetric systems. More specifically:

- For systems at relatively low pressures, say up to 500 bars, (C₁/nC₁₄, N₂/nC₁₆) the results are, as expected, very good (Figs. 1 and 2) with typical average deviation of about 3%.

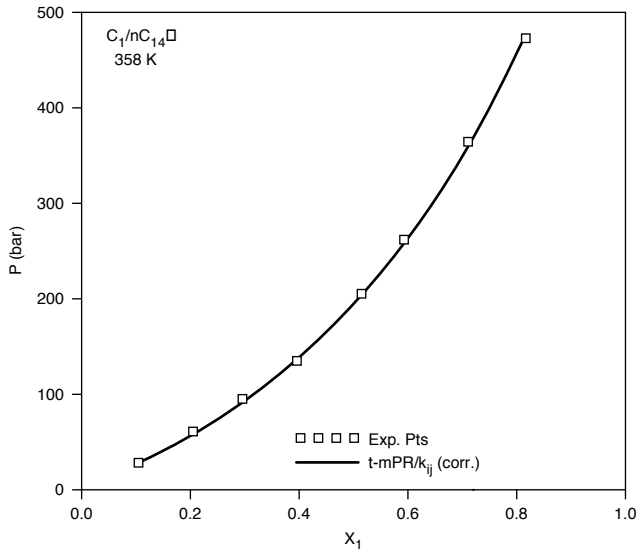


Figure 1

Correlation results for the bubble point pressures of the system C_1/nC_{14} at 358 K (de Leeuw *et al.*, 1992) with t-mPR and k_{ij} .

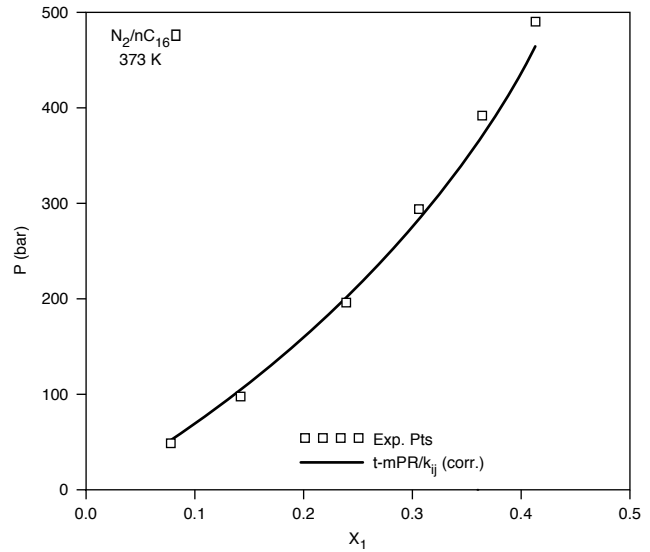


Figure 2

Correlation results for the bubble point pressures of the system N_2/nC_{16} at 373 K (IUPAC, 1982) with t-mPR and k_{ij} .

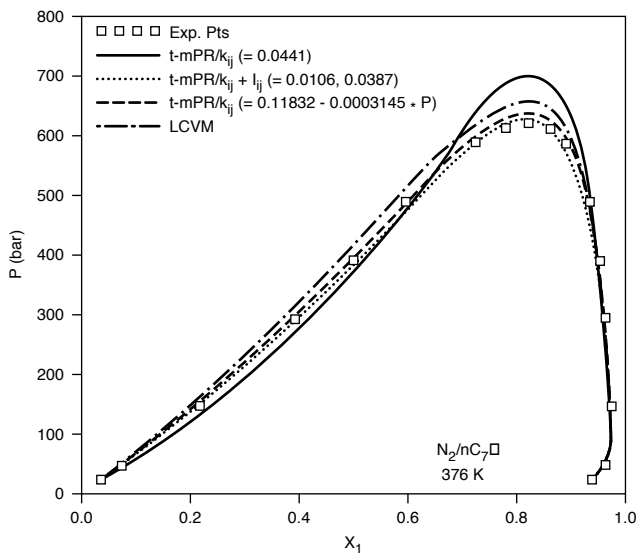


Figure 3

Correlation and prediction of the bubble point pressures of the system N_2/nC_7 at 376 K (Legret *et al.*, 1981). Correlation with t-mPR/ k_{ij} , $k_{ij} + l_{ij}$, $k_{ij} = f(P)$. Prediction with the LCVM model.

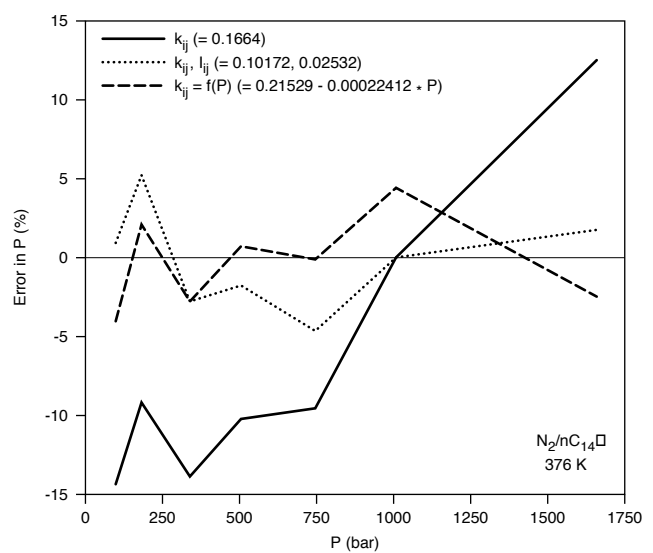


Figure 4

Percent error in the bubble point pressures of the system N_2/nC_{14} at 376 K (de Leeuw *et al.*, 1992). Correlation with t-mPR/ k_{ij} , $k_{ij} + l_{ij}$, $k_{ij} = f(P)$.

- For systems at pressures exceeding the 500 bars larger deviations up to about 20% are observed. Typical error distribution versus pressure are presented in Figures 4 and 5 and indicate that these errors are encountered in both high and low pressure range.

TABLE 3

VLE correlation and prediction results. VLE correlation results with the t-mPR EoS using one interaction parameter (k_{ij}), two interaction parameters ($k_{ij} + l_{ij}$) and one interaction parameter as linear function of pressure ($k_{ij} = f(P)$). VLE prediction results with t-mPR and one interaction parameter (k_{ij}) obtained from Kordas *et al.*, 1995 for C₁/HC and from Avlonitis *et al.*, 1994 for N₂/HC, and LCVM (Boukouvalas *et al.*, 1994).

Results	Correlation			Prediction	
System	AAE in saturation pressure (%)				
	k_{ij}	$k_{ij} + l_{ij}$	$k_{ij} = f(P)$	k_{ij}	LCVM
C ₁ /nC ₁₄	1.2	0.9	0.8	1.2	9.1
C ₁ /nC ₁₆	4.7	3.6	4.2	5.1	4.5
C ₁ /nC ₂₀	10.9	3.8	9.9	14.7*	10.2
C ₁ /nC ₂₄ (Arnaud <i>et al.</i>)	6.7	4.3	6.5	failed	10.9
C ₁ /nC ₂₄ (Floter <i>et al.</i>)	12.6	4.3	9.3	11.6*	16.8
N ₂ /nC ₇	8.5	1.3	2.1	23.7	4.6
N ₂ /nC ₁₄	9.9	2.5	2.4	9.9	8.6
N ₂ /nC ₁₆	5.3	1.0	2.0	5.4	5.0

* 7 points rejected

Use of predicted from generalized correlations k_{ij} values (Kordas *et al.*, 1995) for C₁/HC and Avlonitis *et al.* (1994) for N₂/HC gives reasonable results, equivalent to those obtained from correlation, for systems with hydrocarbons up to nC₁₆ as shown in Table 3. For highly asymmetric ones such as C₁/nC₂₀ and C₁/nC₂₄, however, are totally unacceptable (Table 3 and Fig. 5). For example, the predicted k_{ij} value for C₁/nC₂₀ is -0.04 (Kordas *et al.*, 1995) and the correlated, from high pressure VLE data, one is 0.06.

There is a significant dependency of k_{ij} on pressure for both C₁/HC and N₂/HC mixtures which increases as the asymmetry of the system increases (Figs. 6 and 7). For C₁/HC it appears to increase with P in a polynomial fashion while for the N₂/HC ones a decrease with P in a linear fashion is observed.

Use of a linearly depending on pressure k_{ij} , as suggested by Mohamed and Holder (1987) gives, consequently, good results for N₂/HC but not for C₁/HC (Figs. 3 and 4 and Fig. 5 respectively).

Use, on the other hand, of k_{ij} and l_{ij} leads to very satisfactory results except in the neighborhood of the critical (Fig. 3 to 5).

Arnaud *et al.* (1995) used the following procedure for determining the k_{ij} and l_{ij} values from their VLE and PVT data: k_{ij} from the VLE data and l_{ij} from the excess volume data. It is interesting to note that this set does not sacrifice the description of their VLE data since it is the same as the one obtained here by correlating them (Fig. 8).

Both sets of k_{ij} and l_{ij} give satisfactory predictions of the VLE data for the same system but at temperature 50 K lower (Floter *et al.*, 1997) as shown in Figure 9. This suggests that k_{ij} and l_{ij} for C₁/HC systems may not very sensitive to temperature, at least for reasonable temperature ranges. The same conclusion was reached by Kordas *et al.* (1995) from the correlation of low pressure VLE data, however.

The uncertainty in the predicted T_c , P_c and ω values for nC₂₄ is apparent from Table 2 where values from several correlations are presented. The more pronounced difference among the correlations for P_c as compared to that for T_c is not surprising. Experimental values for P_c are available only up to nC₁₂ while for T_c up to nC₁₈ plus nC₂₄. For the latter Nikitin *et al.* (1994) suggest an uncertainty of 1%. Eventhough such differences are absorbed in the correlation of VLE data, especially the two parameter case, they do effect the prediction results of the vapor pressure as shown in Figure 10 for nC₂₄ and, consequently, they may affect negatively multicomponent predictions.

Of the three commonly used EoS/G^E models: LCVM, MHV2 and PSRK, only the first one provides satisfactory results where T_c , P_c and ω values are available including also the very high pressure data for the N₂/nC₁₄ (Figs. 3, 11 and 12). For more asymmetric systems (Fig. 5), however, increasing errors appear with increasing pressure. The MHV2 and PSRK models fail as shown with the typical results of Figures 11 and 12.

2 PREDICTION RESULTS: PVT

2.1 Pure compounds

Table 4 presents the volumetric predictions with t-mPR for C₁ and nC₂₄ when the different values of the volume translation, also given in Table 4, are used. Notice that:

- The translation is useful not only for the liquid nC₂₄ but also for the gaseous C₁, where it reduces the

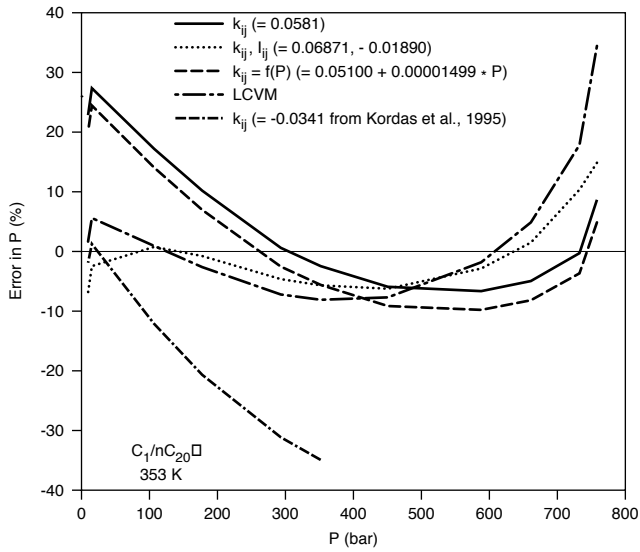


Figure 5

Percent error in the bubble point pressures of the system C_1/nC_{20} at 353 K (van der Kooi *et al.*, 1995). Correlation and prediction results.

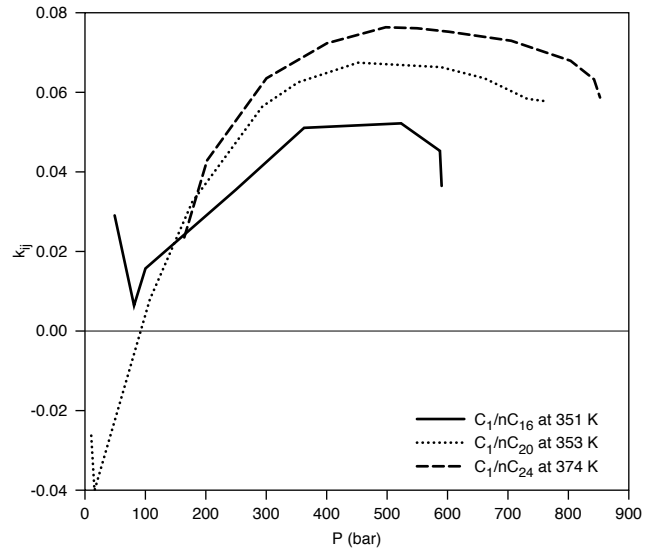


Figure 6

Optimum k_{ij} versus pressure for various C_1/HC systems.

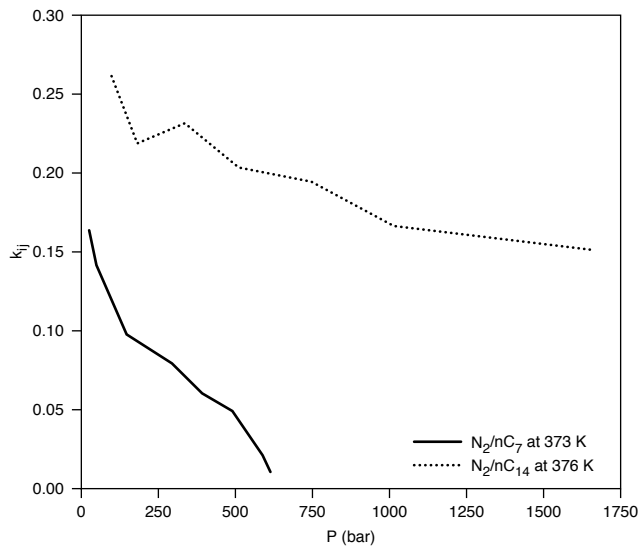


Figure 7

Optimum k_{ij} versus pressure for various N_2/HC systems.

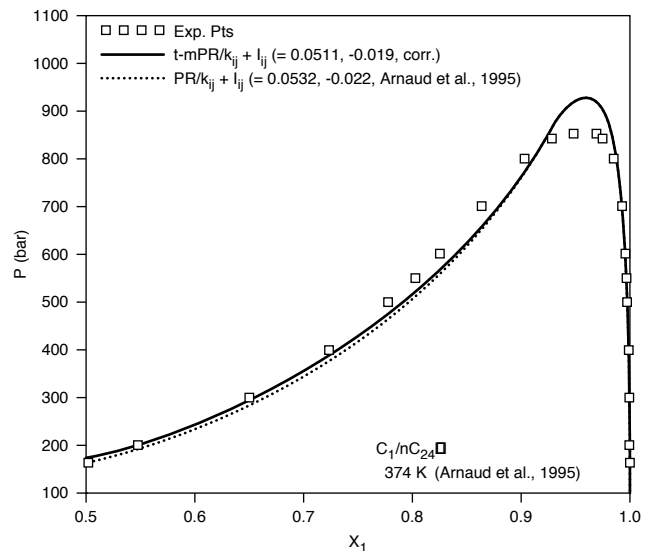


Figure 8

Correlation results for the bubble point pressures of the system C_1/nC_{24} at 374 K (Arnaud *et al.*, 1995).

error from 7% to 0.6% using the generalized correlation for t , or to 0.5% using the t value obtained by fitting the experimental data.

- The t-mPR without translation gives the same results as the PR EoS.
- The T_c , P_c and ω set used for nC_{24} has a significant effect on the obtained results.

TABLE 4

Prediction of the PVT behavior of C_1 and nC_{24} with t-mPR. The volume translation values given by Arnaud *et al.* (1995) have been obtained by fitting their high pressure PVT data with PR EoS and T_c , P_c and ω values obtained from Del Sordo (1994). The other values are obtained from the generalized correlations presented in Appendix, with the different sets of T_c , P_c and ω values.

C_1		nC_{24}				
t (cm ³ /mole)	AAE (%)	T_c , P_c , ω	t (cm ³ /mole)		AAE (%)	
			Method	Value		
C	0.0	7.0	A	–	0.0	40.2
	–4.461	0.7	D	–	0.0	24.8
	–4.965	0.5	A	C	126.77	10.7
B			D	C	112.56	1.5
			D	B	106.84	0.7
A	0.0	6.8	A	–	0.0	40.2
	–4.732	0.6	D	–	0.0	24.8
			A	A	143.61	12.7
			D	A	129.56	0.5

A: Magoulas and Tassios (1990); B: Arnaud *et al.* (1995); C: Jhaveri and Yougren (1985); D: Del Sordo (1994).

2.2 Binary mixtures

Table 5 presents PVT results for several binary systems. Excellent results are obtained through correlation with T-independent k_{ij} as well as prediction using k_{ij} from generalized correlations and LCVM.

Also, satisfactory results are obtained for the more difficult C_1/nC_{24} hyperbaric gas system of Bjorlykke and Firoozabadi (1990) and for the C_1/nC_{24} hyperbaric oil system of Arnaud *et al.* (1995) as shown in Figures 13 and 14 respectively.

The performance of the cubic EoS in the prediction of the relative liquid volumes through an isothermal pressure decrease is very satisfactory for the case of oil system (Fig. 14). It is also remarkable enough for the case of gas condensate system where the obtained maximum deviation of 10% can be considered reasonable (Fig. 13). A single interaction parameter (k_{ij}) obtained from the correlation of the aforementioned VLE data

for C_1/nC_{24} has been used in these calculations. It is expected that the incorporation of a second interaction parameter l_{ij} in the covolume combining mixing rule can improve the obtained predictions.

In both cases, gas and oil system, the effect of translation factor (t) on the prediction of the PVT behavior is examined. To this purpose, t values derived from:

- correlations of V_1^s pure compound data up to nC_{20} such as those of t-mPR (Eq. (A3) of Appendix) and of Jhaveri and Yougren, 1984 (Eq. (A6) and (A7) of Appendix);
- and high pressure PVT data for nC_{24} of Arnaud *et al.* have been utilized and are presented in Table 4.

Prediction results shown in Figures 13 and 14 indicate that although volume translation values for nC_{24} differ by as much as 20% they have a small effect on the prediction of the relative liquid volumes. The generalized expression of t_0 (Eq. (A3) of Appendix) coupled with the t-mPR EoS performs quite well for both gas and oil system as compared to the values derived by fitting high pressure PVT data for nC_{24} and C_1 .

CONCLUSIONS

The performance of cubic EoS with a single interaction parameter (k_{ij}) in describing VLE is remarkable considering the level of pressures involved. However, the extent to which this approach will be sufficient for hyperbaric fluids remains to be seen as more experimental data, especially for synthetic hyperbaric fluids, will become available.

Use of a second interaction parameter l_{ij} in the covolume combining rule, provides overall better results but it still suffers in the neighborhood of critical. Eventhough it appears that a two parameter (k_{ij} and l_{ij}) mixing rule is more effective for the successful correlation of high temperature-high pressure VLE, it is doubtful that this approach will be a practical solution for natural fluids.

VLE prediction results with k_{ij} values from generalized correlations developed from low pressure VLE data are satisfactory at high pressure region for binary systems with hydrocarbons up to nC_{16} . For high asymmetric ones such as C_1/nC_{20} and C_1/nC_{24} predicted k_{ij} values are totally unacceptable and suggest the use of high pressure binary VLE data to derive proper values.

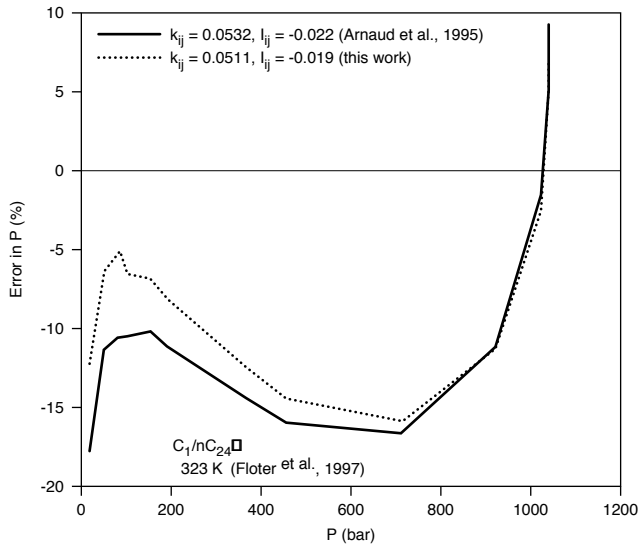


Figure 9

Percent error in the bubble point pressures of the system C_1/nC_{24} at 323 K (Floter *et al.*, 1997). Prediction results.

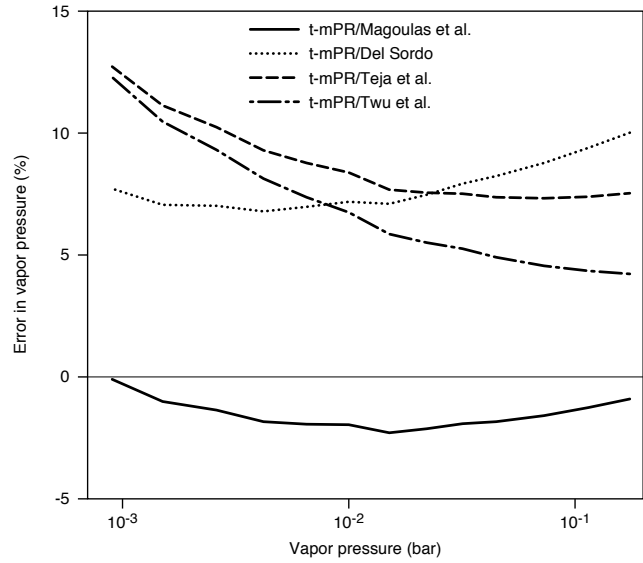


Figure 10

Percent error in predicted vapor pressure values with t-mPR for nC_{24} using the four different sets of T_c , P_c and ω values.

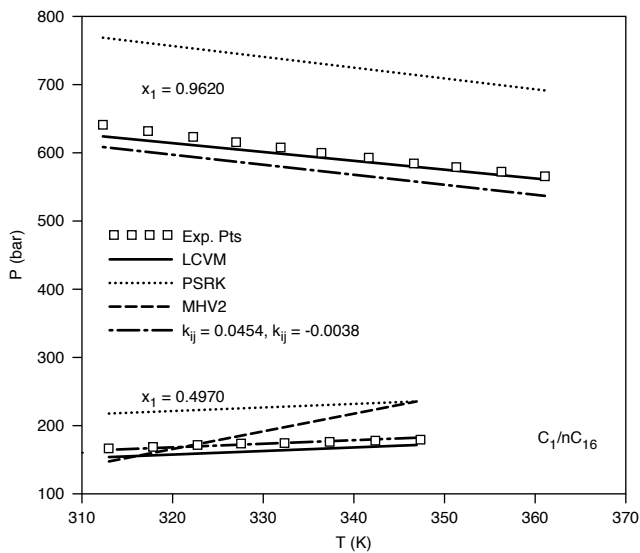


Figure 11

Correlation and prediction of the bubble point pressures of the system C_1/nC_{16} (Glaser *et al.*, 1985). Correlation with t-mPR/ $k_{ij} + l_{ij}$. Prediction with the LCVm, PSRK and MHV2 models.

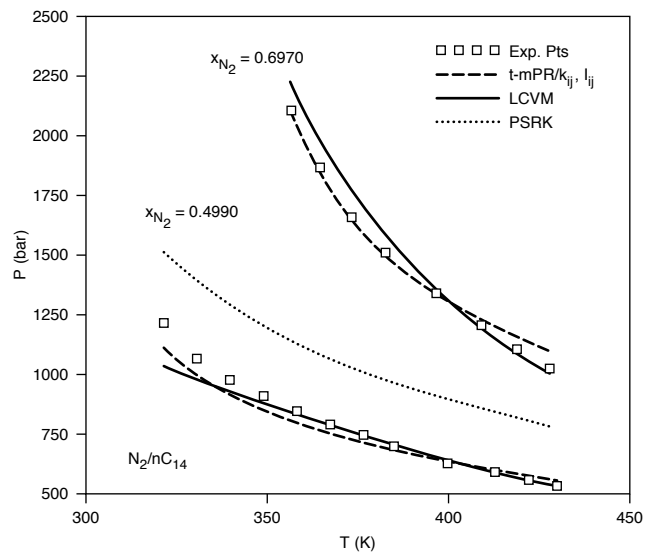


Figure 12

Correlation and prediction of the bubble point pressures of the system N_2/nC_{14} (de Leeuw *et al.*, 1992). Correlation with t-mPR/ $k_{ij} + l_{ij}$. Prediction with the LCVm, and PSRK models. (The prediction results with PSRK for the 0.6970 isopleth are not included due to large deviations).

TABLE 5
Correlation and prediction results of PVT for binary mixtures

(1)/(2)	T (K)	P (bar)	x_1	AE in V (%)		
				t-mPR (corr.)	t-mPR (pred.)	LCVM
C_1/nC_4	344.26	86.2-689.5	0.3960	2.18	2.23	2.21
		139.7-698.5	0.6002	0.89	1.36	1.46
	510.93	13.8-689.5	0.3960	1.26	1.29	1.27
		138.0-689.5	0.6002	0.70	0.74	0.71
C_1/cC_6	344.26	159.1-689.5	0.4000	0.72	1.60	1.69
		239.1-689.5	0.6000	0.56	1.07	1.26
	455.37	166.1-689.5	0.4000	2.17	2.41	2.62
		200.5-689.5	0.6000	1.22	1.42	1.78
C_1/nC_{10}	344.26	124.7-689.5	0.3945	0.24	1.36	1.29
		219.1-689.5	0.5822	0.16	1.81	1.68
	510.93	123.5-689.5	0.3945	1.62	1.63	1.61
		183.0-689.5	0.5822	1.09	1.23	1.06
C_2/nC_{10}	344.26	27.2-689.5	0.4000	0.53	0.72*	0.72
		44.1-689.5	0.6000	0.88	1.03*	1.01
	510.93	65.0-689.5	0.4000	2.40	2.42*	2.40
		97.2-689.5	0.6000	1.91	2.02*	1.93

* $k_{ij} = 0.0$

V: liquid volume

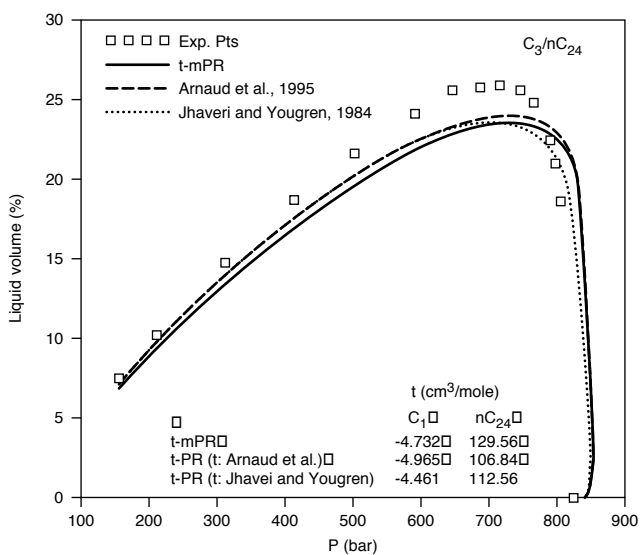


Figure 13

Effect of the volume translation on the prediction of % liquid volume for the C_1/nC_{24} system (Bjorlykke and Firoozabadi, 1990).

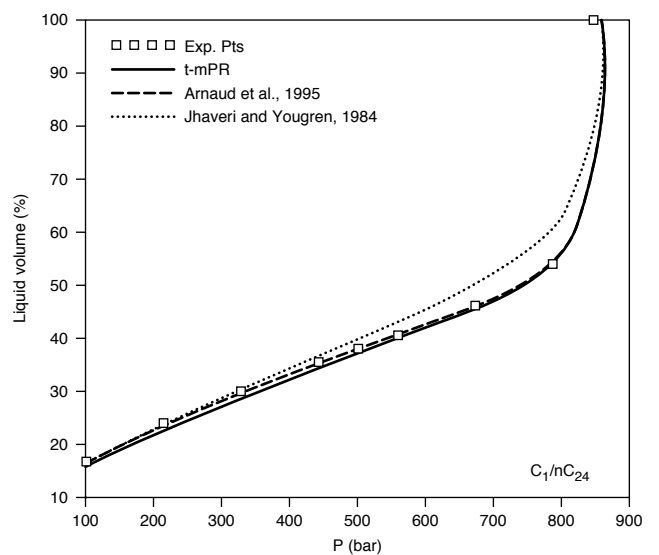


Figure 14

Effect of the volume translation on the prediction of % liquid volume for the C_1/nC_{24} oil system (Arnaud *et al.*, 1995).

Also, remarkable is the performance of the cubic EoS with a single interaction parameter (k_{ij}) in the prediction of the PVT behavior of binary mixtures including the relative liquid volumes of the C_1/nC_{24} system. Volume translation is essential for PVT predictions. It is shown that there is no need for high pressure pure compound PVT data to obtain proper volume translation values generalized expressions for translation factor estimation such as the temperature independent translation of t-mPR and that of Jhaveri and Yougren give very satisfactory results.

Of the EoS/ G^E models considered, LCVm gives very successful predictions for rather symmetric systems which become poorer with asymmetric ones at very high pressures.

LIST OF SYMBOLS

BP	bubble point
Eq. ()	equation number
HC	hydrocarbons
k_{ij}	interaction parameter
l_{ij}	interaction parameter
P	pressure
P_c	critical pressure
T	temperature
t	volume translation
t_0	temperature independent volume translation
T_c	critical temperature.

Greek symbols

ω	acentric factor.
----------	------------------

REFERENCES

- Arnaud J.F., Ungerer P., Behar E., Moracchini G. and Sanchez J. (1995) Improvement of EoS mixing rules from excess volume measurements. Application to the methane+n-tetracosane mixtures at 374 K. Institut français du pétrole, *Report* 42 492.
- Avlonitis G., Mourikas G., Stamataki S. and Tassios D. (1994) A generalized correlation for the interaction coefficients of nitrogen-hydrocarbon binary mixtures. *Fluid Phase Equilibria*, 101, 53-68.
- Bjorlykke O.P and Firoozabadi A. (1990) Measurements and computation of retrograde condensation and near-critical phase behavior. *SPE Paper* 20524.
- Boukouvalas C., Spiliotis N., Coutosikis N., Tsouvaras N. and Tassios D. (1994) Prediction of vapor-liquid equilibrium with the LCVm model: a linear combination of the Vidal and Michelsen mixing rules coupled with the original UNIFAC and the t-mPR Equation of State. *Fluid Phase Equilibria*, 92, 75-106.
- Daubert T.E. and Danner R.P. (1985) *DIPPR Data*, AIChE, New York.
- de Leeuw V.V., de Loos Th.W., Kooijman H.A. and de Swaan Arons J. (1992) The experimental determination and modelling of VLE for binary subsystems of the quaternary system $N_2+CH_4+C_4H_{10}+C_{14}H_{30}$ up to 1000 bar and 440 K. *Fluid Phase Equilibria*, 73, 285-231.
- Del Sordo E. (1994) Étude de l'équation Chain of Rotators. *DEA Report*, École nationale supérieure des industries chimiques de Nancy (in French).
- Floter E., de Loos Th.W. and de Swaan Arons J. (1997) High-pressure solid-fluid and vapour-liquid equilibria in the system (methane-tetracosane). *Fluid Phase Equilibria*, 127, 129-146.
- Glaser M., Peters C.J., van der Kooi H.J. and Lichtenhaler R.N. (1985) Phase equilibria of (methane+n-hexadecane) and (p,Vm, T) of n-hexadecane. *J. Chem. Thermodynamics*, 17, p. 803.
- IUPAC (1982) *Nitrogen and Air, Solubility Data Series*, 10, 1st ed., Pergamon Press, Oxford.
- Jhaveri B.S. and Yougren G.K. (1984) Tree-parameter modification of the Peng-Robinson Equation of State to improve volumetric predictions. *SPE Paper* 13118.
- Kordas A., Magoulas K., Stamataki S. and Tassios D. (1995) Methane-hydrocarbon interaction parameters correlation for the Peng-Robinson and the t-mPR Equation of State. *Fluid Phase Equilibria*, 112, 33-44.
- Legret D., Richon D. and Renon H. (1981) Vapor liquid equilibria up to 100 MPa: A new apparatus. *AIChE Journal*, 27, 2, 203.
- Magoulas K. and Tassios D. (1990) Thermophysical properties of n-alkanes from C_1 to C_{20} and their prediction for higher ones. *Fluid Phase Equilibria*, 56, 119-140.
- Nikitin E.D., Pavlov P.A. and Bessonova N.V. (1994) Critical constants of n-alkanes with 17 and 24 carbon atoms. *J. Chem. Thermodynamics*, 26, 177-182.
- Reamer H.H., Olds R.H., Sage B.H. and Lacey W.N. (1942) Phase equilibria in hydrocarbon systems. Methane-decane system. *Ind. Eng. Chem.*, 34, 12, 1526-1531.
- Reamer H.H., Sage B.H. and Lacey W.N. (1958) Phase equilibria in hydrocarbon systems. Volumetric and phase behavior of the methane-cyclohexane system. *Ind. Eng. Chem.*, 3, 1, 240-245.
- Soreide I. (1989) Improved phase behavior predictions of the petroleum reservoir fluids from a cubic Equation of State. *PhD Thesis*, University of Trondheim.
- Teja A.S., Lee R.J., Rosenthal D. and Anselme M. (1990) Correlation of the critical properties of alkanes and alkanols. *Fluid Phase Equilibria*, 56, 153-169.
- Twu C.H. (1984) An internally consistent correlation for predicting the critical properties and molecular weights of petroleum and coal-tar liquids. *Fluid Phase Equilibria*, 16, 137-150.
- Van der Kooi H.J., Floter E. and de Loos Th.W. (1995) High-pressure phase equilibria of $\{(1-x)CH_4+xCH_3(CH_2)_{18}CH_3\}$. *J. Chem. Thermodynamics*, 27, 847-861.

Final manuscript received in December 1997

APPENDIX

The t-mPR

The t-mPR involves a single expression for $m = f(\omega)$ which covers the whole range of ω values. It provides similar P^s results with a PR EoS but improved ones at low P^s levels.

$$m = 0.384401 + 1.52276\omega - 0.213808\omega^2 + 0.034616\omega^3 - 0.001976\omega^4 \quad (\text{A1})$$

It also provides successful liquid volumes through the following translation expression:

$$t = t_0 + (t_c - t_0) \exp(\beta |1 - T_r|) \quad (\text{A2})$$

where:

$$t = \frac{RT_c}{P_c} (-0.014471 + 0.067498\omega - 0.084852\omega^2 + 0.067298\omega^3 - 0.017366\omega^4) \quad (\text{A3})$$

$$\beta = -10.2447 - 28.6312\omega \quad (\text{A4})$$

$$t_c = \frac{RT_c}{P_c} (0.3074 - Z_c) \quad (\text{A5})$$

The volume translation of Jhaveri-PR

Jhaveri and Yougren (1984), based on PR EoS, suggested a dimensionless correcting factor s , that is

dependent on the component of interest. This factor is determined as $s = c/b$, where b is the covolume parameter of the EoS and c is the correction of the volume that is given by the EoS ($V = V^{\text{EoS}} - c$). The s values up to $n\text{C}_6$ are obtained by matching the experimental molar volumes at $T_r = 0.7$ of the pure compound and they are presented in the next table:

Compound	s	Compound	s
CH ₄	-0.15400	<i>n</i> -C ₄ H ₁₀	-0.06413
C ₂ H ₆	-0.10020	<i>i</i> -C ₅ H ₁₂	-0.04350
C ₃ H ₈	-0.08501	<i>n</i> -C ₅ H ₁₂	-0.04183
<i>i</i> -C ₄ H ₁₀	-0.07935	<i>n</i> -C ₆ H ₁₄	-0.01478

For supercritical CH₄, the proposed by Ingolf Soreide (1989), expression is used:

$$s = -0.037 * T_r - 0.094 \quad (\text{A6})$$

For larger hydrocarbons, the following expression is used:

$$s = 1 - \frac{d}{MW^e} \quad (\text{A7})$$

where MW is the molecular weight. Values for d , e are given in the next table:

Compound	d	e
<i>n</i> -alkanes	2.258	0.1823
naphthenics	3.004	0.2324
aromatics	2.516	0.2008