

Prediction of Phase Equilibria and Volumetric Behavior of Fluids with High Concentration of Hydrogen Sulfide

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Résumé — Prédiction de l'équilibre de phase et du comportement volumétrique des fluides à forte concentration en sulfure d'hydrogène — Cet article expose une étude systématique, à l'aide de l'équation Peng-Robinson modifiée et traduite (t-mPR) et de la même équation traduite selon Jhaveri et Youngren (J-PR), des propriétés du sulfure d'hydrogène et de ses mélanges avec des hydrocarbures. Des prédictions de la pression de vapeur du sulfure d'hydrogène ainsi que du volume liquide saturé sont présentées selon ces deux équations. L'introduction d'un paramètre de correction pour H₂S améliore les prédictions volumétriques par le modèle J-PR.

Une corrélation simple généralisée est présentée pour les paramètres d'interaction des mélanges binaires de H₂S/*n*-alkane en fonction du facteur acentrique des hydrocarbures. Cette corrélation peut également être appliquée aux *i*-alkanes et montre une bonne capacité d'extrapolation aux plus hauts alcanes. Des paramètres d'interaction entre H₂S et d'autres hydrocarbures sont également proposés.

L'application à des mélanges synthétiques multicomposants et aux huiles de réservoir à forte teneur en H₂S donne des résultats très satisfaisants.

Mots-clés : application, équation d'état, équilibre liquide-vapeur, sulfure d'hydrogène, hydrocarbures.

Abstract — Prediction of Phase Equilibria and Volumetric Behavior of Fluids with High Concentration of Hydrogen Sulfide — A systematic study of the properties of hydrogen sulfide and its mixtures with hydrocarbons is presented, using the modified and volume translated (t-mPR) as well as the Jhaveri and Youngren volume translated (J-PR) Peng-Robinson equation of state (EoS). Hydrogen sulfide vapor pressure and saturated liquid volume predictions are presented with both EoS. Volumetric predictions with the J-PR EoS are improved when a shift parameter for H₂S is incorporated.

A simple generalized correlation of the interaction parameters of H₂S/*n*-alkane binary mixtures as a function of the hydrocarbon acentric factor is proposed. The correlation can also be applied to *i*-alkanes and provides good extrapolation capability to larger alkanes. Interaction parameters for H₂S with other hydrocarbons are also given.

Application to synthetic multicomponent mixtures and to reservoir oils with high content of H₂S gives very satisfactory results.

Keywords: application, equation of state, vapor-liquid equilibria, hydrogen sulfide, hydrocarbons.

NOMENCLATURE

% AAD	percent average absolute deviation
a	EoS attractive term (cohesion) parameter
b	EoS covolume parameter
Bo	oil formation volume factor
CN	carbon number
k	interaction parameter in quadratic mixing rule for parameter a
l	interaction parameter in quadratic mixing rule for parameter b
MW	molecular weight
P	pressure
R_s	solution gas/oil ratio
s	shift parameter for the volume in the J-PR EoS
SG	specific gravity
t	translation factor correcting the volume in a cubic EoS
T	temperature, K
V_l	liquid volume

Greek Symbol

ω	acentric factor
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Subscripts

c	critical property
i	component i (H_2S)
j	component j (hydrocarbon)
r	reduced property

Superscripts

calc	calculated value
exp	experimental value
opt	optimum value
s	saturated

INTRODUCTION

Processing of natural fluids with significant amount of hydrogen sulfide is continuously increasing since energy shortage problems impose an integrated and more effective use of energy resources. Some of the following practical problems indicate this upcoming interest:

- the processing of sour natural gas, particularly at low temperatures, to enhance the recovery of ethane and propane;
- the sweetening of the liquefied petroleum gases (LPG) often contaminated with hydrogen sulfide and/or carbon

dioxide (acid gas components must be removed from LPG before any other treatment);

- the recent (renewed) interest in developing oil and gas reserves that have been bypassed in earlier times because of their carbon dioxide and hydrogen sulfide content;
- the number of rich H_2S sour natural gas or oil fields that have been discovered around the world (North China, Canada, Greece, Italy, etc.) and some of them are already under production.

In addition, Swain (1993) underlines the problem of the USA refiners which already face the declining crude oil quality as they will have to process feedstocks that become heavier and sourer than in the past.

The design of any of the above processes is governed by the presence of hydrogen sulfide, which becomes one of the major components of these fluids. It is, therefore, necessary to pay particular attention to the influence of H_2S on mixture behavior. Furthermore, literature data on hydrogen sulfide/hydrocarbon systems are rather limited, since up-to-date research is mainly focused on other non-hydrocarbon/hydrocarbon mixtures such as carbon dioxide or nitrogen.

The purpose of this work is the thorough study of the properties of H_2S and its mixtures with hydrocarbons aiming to provide all the relevant parameters for the existing thermodynamic models in order to enhance their capability in the prediction of vapor-liquid equilibria (VLE) and thermo-physical properties with emphasis on high- H_2S -content hydrocarbon mixtures.

The methodology followed includes:

- prediction of the thermodynamic properties of pure H_2S ;
- use of all the binary VLE data in evaluating the interaction parameters for hydrogen sulfide/hydrocarbon mixtures and in developing generalized correlations for them;
- use of conventional thermodynamic models, cubic equation of state (EoS), to predict the phase behavior and the volumetric properties of synthetic mixtures and natural fluids with high content of hydrogen sulfide.

1 PREDICTION OF VAPOR PRESSURES AND SATURATED LIQUID VOLUMES OF HYDROGEN SULFIDE

Experimental vapor pressures (P^s) and saturated liquid volumes (V_l^s) were available from Clarke and Glew (1970). Similar information was available from the correlation of experimental data of Daubert and Danner (1985, 1989). The comparison of the experimental data with those of the correlation of Daubert and Danner showed a deviation of 2.1 and 0.4% in P^s and V_l^s respectively, values within the uncertainty range of Daubert and Danner equations. The experimental data of Clarke and Glew were adopted for all the following calculations.

The original Peng-Robinson (PR) (Peng and Robinson, 1976), the modified and volume translated PR (t-mPR) of Magoulas and Tassios (1990) and the volume translated PR EoS (J-PR) of Jhaveri and Youngren (1984) were utilized for the prediction of the vapor pressures and saturated liquid volumes of hydrogen sulfide. The t-mPR and J-PR equations used are presented in Appendix.

The results of the prediction of the vapor pressures are shown in Figure 1 and Table 1. There is a slight overall advantage of the t-mPR, with an average deviation of 3.4%, over the PR, with 5.1%. We must note the better performance of the t-mPR at low temperatures.

The J-PR EoS was selected because of its wide application in petroleum industry. The volumetric predictive capability of the J-PR EoS is based on the incorporation of the compound shift parameter (s) that represents the saturated volume correction at $T_r = 0.7$ in the b term of the PR EoS. Authors presented numerical values of the shift parameter for

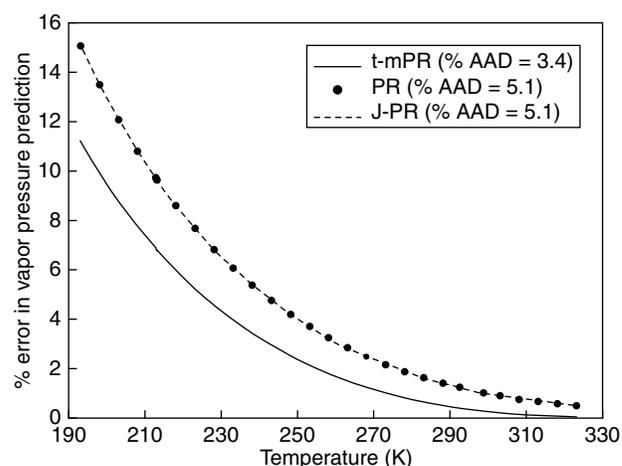


Figure 1
Prediction of the vapor pressure of pure H₂S.

TABLE 1
Prediction results for the vapor pressures and the saturated liquid volumes of H₂S with the t-mPR, PR and J-PR EoS

T (K)	P^s, exp (bar)	V_l^s, exp (ccm/mol)	t-mPR		PR		J-PR	
			% ΔP^s	% ΔV_l^s	% ΔP^s	% ΔV_l^s	% ΔP^s	% ΔV_l^s
193.15	0.3317	34.7	11.2	2.0	15.1	-7.4	15.1	0.9
198.15	0.4508	35.0	9.9	1.8	13.5	-7.4	13.5	0.7
203.15	0.6024	35.3	8.8	1.7	12.1	-7.5	12.1	0.5
208.15	0.7923	35.6	7.7	1.6	10.8	-7.5	10.8	0.4
212.88	1.0130	35.9	6.9	1.5	9.7	-7.5	9.7	0.3
212.97	1.0181	35.9	6.8	1.5	9.7	-7.5	9.7	0.3
213.15	1.0272	35.9	6.8	1.5	9.6	-7.5	9.6	0.3
218.15	1.3141	36.3	6.0	1.2	8.6	-7.7	8.6	0.2
223.15	1.6604	36.6	5.2	1.2	7.7	-7.5	7.7	0.1
228.15	2.0742	37.0	4.6	0.9	6.8	-7.6	6.8	0.0
233.15	2.5639	37.3	4.0	1.0	6.1	-7.5	6.1	0.0
238.15	3.1382	37.7	3.4	0.9	5.4	-7.5	5.4	-0.1
243.15	3.8060	38.1	3.0	0.8	4.8	-7.4	4.8	-0.1
248.15	4.5769	38.5	2.5	0.7	4.2	-7.3	4.2	-0.1
253.15	5.4604	39.0	2.1	0.4	3.7	-7.4	3.7	-0.1
258.15	6.4664	39.4	1.8	0.5	3.3	-7.2	3.2	-0.1
263.15	7.6048	39.9	1.5	0.3	2.9	-7.1	2.8	-0.1
268.15	8.8860	40.4	1.2	0.2	2.5	-7.0	2.5	0.0
273.15	10.3200	40.9	1.0	0.2	2.2	-6.8	2.2	0.2
278.15	11.9190	41.4	0.8	0.2	1.9	-6.5	1.9	0.3
283.15	13.6910	41.9	0.7	0.3	1.6	-6.1	1.6	0.5
288.15	15.6490	42.5	0.5	0.2	1.4	-5.8	1.4	0.8
293.15	17.8020	43.1	0.4	0.3	1.2	-5.5	1.2	1.0
298.15	20.1640	43.8	0.3	0.1	1.1	-5.2	1.0	1.3
303.15	22.7440	44.5	0.2	0.1	0.9	-4.7	0.9	1.7
308.15	25.5530	45.2	0.1	0.2	0.8	-4.1	0.8	2.1
313.15	28.6040	46.0	0.1	0.1	0.7	-3.6	0.7	2.5
318.15	31.9100	46.9	0.1	0.0	0.6	-3.0	0.6	3.0
323.15	35.4790	47.9	0.0	-0.1	0.5	-2.4	0.5	3.5
		% AAD	3.4	0.7	5.1	6.5	5.1	0.7

light components up to *n*-hexane, by using a simple correlation, where *s* is represented as a function of the molecular weight: $s = 1 - d/MW^e$. Values for coefficients *d* and *e* are also proposed for *n*-alkanes, *n*-alkylcyclohexanes and *n*-alkylbenzenes.

For H₂S, the corresponding shift parameter was not available and its evaluation was, therefore, considered worthwhile. The method followed was similar to that suggested by Jhaveri and Youngren in their relevant study (Eqs. (1) to (3)):

$$s = t/b \quad (1)$$

where:

$$t = V_l^{\text{calc}}(T_r=0.7) - V_l^{\text{exp}}(T_r=0.7) \quad (2)$$

$$b = 0.00778 RT_c/P_c \quad (3)$$

The obtained value was $s = -0.10356$.

The negative value of the shift parameter indicates the underprediction of the liquid density from the EoS. Table 1 and Figure 2 present the performance of all the EoS in the prediction of the saturated liquid volumes. The volumetric deficiency of the PR equation is obvious when compared with the translated ones; it gives an average absolute deviation of 6.5% while the other ones have equivalent performance with an average deviation of 0.7%.

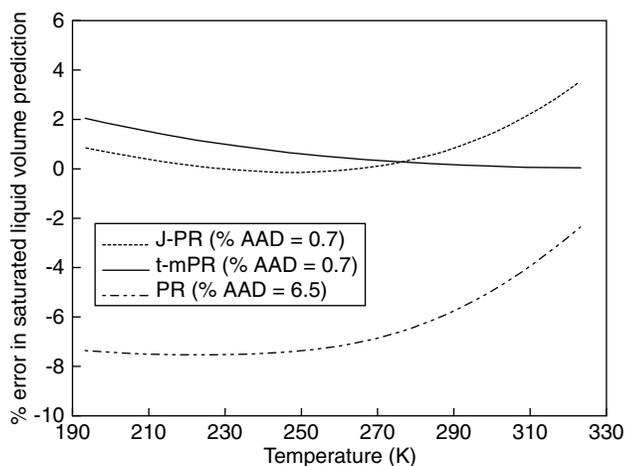


Figure 2

Prediction of the saturated liquid volume of pure H₂S.

The difference between the temperature-dependent and temperature-independent types of the translation factor *t* is demonstrated through the t-mPR and the J-PR EoS for a reduced temperature, $T_r > 0.8$. As expected, a higher deviation is observed for the J-PR. Although this statement has no influence on the following applications, since our volumetric data are not in this temperature range, it must be taken into account for general practical applications.

2 INTERACTION PARAMETERS OF H₂S/HYDROCARBON BINARY SYSTEMS

There are literature references to several attempts for the prediction of interaction parameters of H₂S/hydrocarbon mixtures:

- Moysan *et al.* (1986) presented the first generalized expression for k_{ij} as a function of the acentric factor. They propose a linear function for paraffins and naphthenes and a second-order polynomial for aromatics. Since their database is limited to paraffins up to a carbon number (*CN*) of ten and four aromatic binary systems, the extrapolation capability of their correlation is questionable;
- Valderrama *et al.* (1987) presented another generalized expression for the k_{ij} of H₂S/*n*-alkanes as a function of the acentric factor (second-order polynomial) and the reduced temperature of the hydrocarbon component. Their correlation is applicable to systems with hydrocarbons with $CN > 5$, while for the lighter ones regressed values are suggested. Their limited database (up to *nC*₉) does not justify the complexity of the correlation and does not provide any extrapolation capability;
- Nishiumi *et al.* (1988), using the same as the above limited database, presented a correlation in terms of the ratio of critical molar volumes;
- Carroll and Mather (1995) presented a more comprehensive study for the k_{ij} of H₂S/*n*-alkanes using an extended database up to *nC*₂₀ plus *i*-butane, *i*-pentane and neopentane. They propose two simple correlations: one in terms of the carbon number of the paraffin and the other as a quadratic function of the normal boiling point of the paraffin.

Table 2 includes all the experimental VLE data available in the literature for H₂S/hydrocarbon binary systems. It is notable that all the data for hydrocarbons with a carbon number greater than ten ($CN > 10$) are very recent (after 1992), indicating the recent interest in systems containing H₂S. The system with the heaviest hydrocarbon is that of *nC*₂₀.

The optimum value of the interaction parameter for each binary pair was derived from the correlation of all the system VLE data by minimizing the percent average absolute deviation (% AAD) in bubble-point pressure using the t-mPR EoS. These values are presented in Table 2 along with the resulting % AAD in pressure and are plotted *versus* the acentric factor (ω) of the hydrocarbon in Figure 3. A decrease of the k_{ij} value is observed as the size of the hydrocarbon increases.

Finally, preliminary calculations showed an insignificant dependence of the k_{ij} value on temperature. In addition, the examination of the dependence on pressure was meaningless because of the very low-pressure range of the available VLE data.

TABLE 2

Correlation and prediction results of VLE for binary systems included in the database

System of H ₂ S With <i>n</i> -alkanes	Reference	<i>T</i> (K) Range	<i>P</i> (MPa) Range	Correlation		Prediction	
				<i>k_{ij}^{opt}</i>	% AAD in <i>P</i>	<i>k_{ij}</i> Eq. (4)	% AAD in <i>P</i>
C ₁	Kohn and Kurata, 1958 Reamer <i>et al.</i> , 1951 Robinson and Bailey, 1957 Robinson <i>et al.</i> , 1959	188.7-344.3	1.38-11.03	0.0931	3.4	0.1013	4.2
C ₂	Knapp <i>et al.</i> , 1982	199.9-283.2	0.065-3.09	0.0821	1.6	0.0881	1.7
C ₃	Knapp <i>et al.</i> , 1982	218.7-344.3	0.138-2.76	0.0868	2.9	0.0801	3.1
<i>n</i> C ₄	Leu and Robinson, 1989	366.4-418.1	1.35-8.07	0.0802 (0.0824)*	2.4 (2.1)	0.0731	2.7 (2.5)
<i>n</i> C ₅	Knapp <i>et al.</i> , 1982	277.6-444.3	0.14-8.96	0.0639	3.5	0.0653	4.1
<i>n</i> C ₆	Laugier and Richon, 1995	322.9-422.7	0.43-7.55	0.0592	2.1	0.0581	3.5
<i>n</i> C ₇	Ng <i>et al.</i> , 1980	310.9-477.6	0.16-9.55	0.0676	4.4	0.0505	5.6
<i>n</i> C ₉	Eakijn and de Vaney, 1974	310.9-477.6	0.14-2.77	0.0420	2.3	0.0365	2.7
<i>n</i> C ₁₀	Knapp <i>et al.</i> , 1982	277.6-444.3	0.13-12.41	0.0361 (0.0339)	4.0 (4.1)	0.0295	5.3 (4.1)
<i>n</i> C ₁₂	Feng and Mather, 1993a	313.3-434.3	0.57-5.68	0.0028	3.8	0.0171	5.3
<i>n</i> C ₁₅	Laugier and Richon, 1995	422.6	1.13-11.21	-0.0139	8.1	-0.0014	7.8
<i>n</i> C ₁₆	Feng and Mather, 1993b	323.4-423.4	0.53-7.41	-0.0116	4.7	-0.0075	4.8
<i>n</i> C ₂₀	Feng and Mather, 1992	322.9-423.4	0.40-7.67	-0.0364 (-0.04)	5.7 (5.6)	-0.0306	5.9 (5.8)
<i>n</i> C ₂₆	**	250-450	0.052-13.39	-0.0620	3.8	-0.0644	4.2
<i>n</i> C ₃₂	**	250-450	0.047-12.29	-0.0990	5.8	-0.0999	5.8
<i>n</i> C ₄₀	**	250-450	0.042-10.97	-0.1449	6.1	-0.1494	6.6
Isomers	Reference	<i>T</i> (K) Range	<i>P</i> (MPa) Range	<i>k_{ij}^{opt}</i>	% AAD in <i>P</i>	<i>k_{ij}</i> Eq. (4)	% AAD in <i>P</i>
<i>i</i> C ₄	Leu and Robinson, 1989	344.2-398.1	1.11-8.91	0.0485 (0.0471)	1.7 (1.8)	0.0764	5.2 (6.0)
<i>i</i> C ₅	Leu and Robinson, 1992	323.1-413.1	0.21-8.38	0.0726	4.5	0.0688	4.7
Neopentane	Leu and Robinson, 1992	323.1-413.1	0.36-7.45	0.0721	4.8	0.0735	4.8
Non-alkanes	Reference	<i>T</i> (K) Range	<i>P</i> (MPa) Range	<i>k_{ij}^{opt}</i>	% AAD in <i>P</i>	Suggested <i>k_{ij}</i>	% AAD in <i>P</i>
Benzene	Laugier and Richon, 1995	323.1-422.6	0.46-9.80	0.0058	1.2	0.0	1.3
Toluene	Ng <i>et al.</i> , 1980	310.9-477.6	0.20-11.58	0.0054	3.6	0.0	3.6
<i>m</i> -xylene	Huang and Robinson, 1984	310.9-477.6	0.15-13.12	0.0007	3.5	0.0	3.5
Propylbenzene	Richon <i>et al.</i> , 1992	313.2-473.5	0.395-6.01	0.0302 (0.031)	4.5 (4.7)	0.03	4.5 (4.7)
Mesitylene	Huang and Robinson, 1984	310.9-477.6	0.17-13.75	0.0101	2.8	0.01	2.8
Cyclohexane	Laugier and Richon, 1995	323.0-422.6	0.40-9.50	0.0736	3.7	0.074	3.7
Ethylcyclohexane	Huang and Robinson, 1985	310.9-477.6	0.17-12.50	0.0568	4.1	0.057	4.1
Propylcyclohexane	Huang and Robinson, 1985	310.9-477.6	0.18-13.06	0.0281	3.8	0.028	3.8
CO ₂	Knapp <i>et al.</i> , 1982	266.5-349.8	1.38-8.27	0.0968	1.1	0.097	1.1
N ₂	Knapp <i>et al.</i> , 1982	227.7-300.0	1.73-20.68	0.1648	4.0	0.165	4.0

* Numbers in parenthesis indicate the values for the PR EoS.

** Data predicted with the LCVM model.

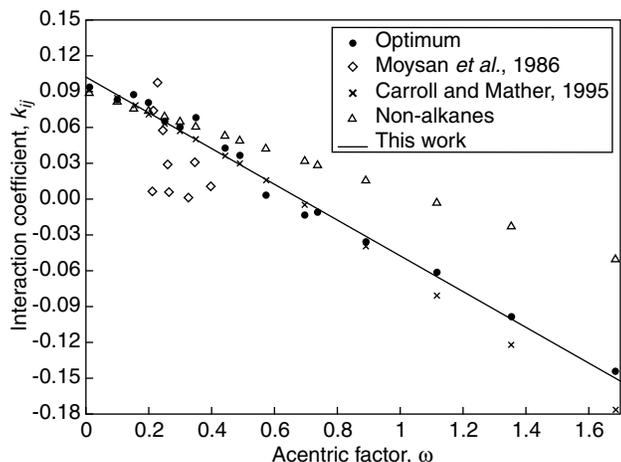


Figure 3

Correlated and predicted interaction parameters (k_{ij}) for the H_2S /hydrocarbon binary systems.

To extend the table of interaction parameters to n -alkanes with $CN > 20$, VLE data for H_2S/nC_{26} , nC_{32} and nC_{40} have been “generated” through the predictive equation of state/excess Gibbs energy (EoS/ G^E) model, LCVm (Boukouvalas *et al.*, 1994). The LCVm model uses the t-mPR EoS coupled with the original UNIFAC G^E model and introduces a new mixing rule, a linear combination of the Vidal and Michelsen ones, for parameter a in the attractive term of the EoS. The original UNIFAC interaction parameter table used with LCVm has been enhanced to include gas/gas, gas/ CH_2 , gas/ACH and gas/ACCH₂ parameters for the gases CO_2 , CH_2 , C_2H_6 , N_2 and H_2S . The use of the LCVm model for this purpose is justified by its successful performance in the VLE prediction for asymmetric systems (Apostolou *et al.*, 1995; Spiliotis *et al.*, 1994a, 1994b; Voutsas *et al.*, 1996; Yakoumis *et al.*, 1996).

The k_{ij} values obtained for these larger n -alkanes are included in Table 2 and are shown graphically in Figure 3. Note that they follow the trend established by the k_{ij} values for $CN < 20$; they are also close to those predicted by the Carroll and Mather correlation (1995) shown in Figure 3. T_c , P_c and ω values for the n -alkanes up to $CN = 20$ were obtained from Magoulas and Tassios (1990); for alkanes with $CN > 20$ values predicted from the same source were used. T_c , P_c and ω values for the rest of the hydrocarbons were obtained from Daubert and Danner (1985, 1989).

A least-squares regression of the optimum k_{ij} values for H_2S/n -alkanes yields the following generalized expression for k_{ij} as a function of the hydrocarbon acentric factor:

$$k_{ij} = 0.1029 - 0.1498\omega \quad (4)$$

The same correlation can be used for the isomers included in the database. For the remaining systems, no trend can be

established, as shown in Figure 3, and the suggested values given in Table 2 should be used.

Prediction results for the bubble-point pressure of the systems used in developing the above equation are given in Table 2. They are very good and fairly close to those found using the optimum values of k_{ij} . The typical results shown in Table 2 with the PR EoS indicate that the proposed correlation and the recommended k_{ij} values can be used with the PR EoS as well.

The results presented in Figure 3 suggest that the proposed correlation and that of Carroll and Mather (1995) have fairly similar performances. Using the LCVm model to generate VLE data for highly asymmetric H_2S/n -alkane systems and to evaluate the change of interaction parameters as the acentric factor increases enhances the extrapolation reliability of the proposed correlation over the one of Carroll and Mather (1995).

The correlation of Nishiumi *et al.* (1988) is not included because experimental V_c values for large n -alkanes are not available. The correlation of Valderrama *et al.* (1987) must be considered unreliable for $CN > 10$.

3 PREDICTION OF PHASE EQUILIBRIA AND VOLUMETRIC BEHAVIOR OF MULTICOMPONENT MIXTURES

3.1 Ternary Mixture of $H_2S/nC_6/nC_{15}$ (Laugier and Richon, 1995)

Bubble-point pressures at temperature $T = 424.5$ K for several liquid compositions with H_2S ranging from 10 up to 64 mol% and the corresponding equilibrium vapor phase compositions were available.

Prediction results with the t-mPR are illustrated in Figure 4. The % AAD in bubble-point pressure is 3.6% with a maximum absolute deviation of 5.6% observed in the first point. The prediction of the vapor phase compositions is also very satisfactory.

Laugier and Richon (1995) presented correlation results using the Redlich-Kwong-Soave and PR EoS with different mixing and combining rules. In the case of combining rules k_{ij} or k_{ij} plus l_{ij} appear in the a or a and b parameter of the EoS respectively, the interaction parameters have been fitted to binary VLE experimental data. Their results show that the correlation of bubble-point pressure is slightly better represented when k_{ij} plus l_{ij} adjustable interaction parameters are used with the PR EoS (3.8% in bubble point and 2% in H_2S vapor phase composition).

The prediction results of this study (3.6% in bubble-point pressure and 1.35% in H_2S vapor phase composition) using the t-mPR EoS and k_{ij} values for H_2S/nC_6 and H_2S/nC_{15} derived from the generalized expression (Eq. (4)) are equivalent to the correlated ones presented by Laugier and Richon (1995).

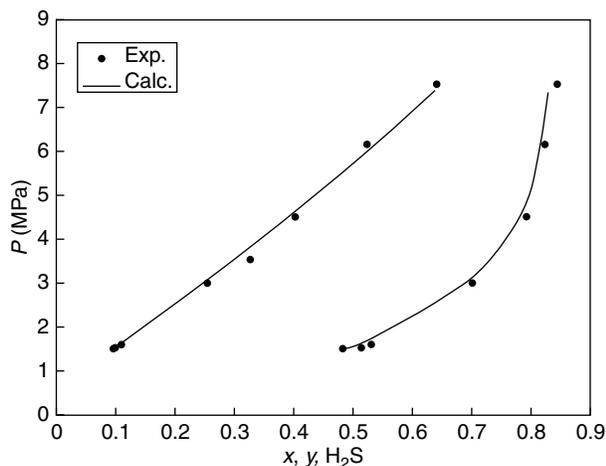


Figure 4

Prediction of the phase envelope for the ternary system $\text{H}_2\text{S}/n\text{C}_6/n\text{C}_{15}$ (Laugier and Richon, 1995), with the t-mPR EoS.

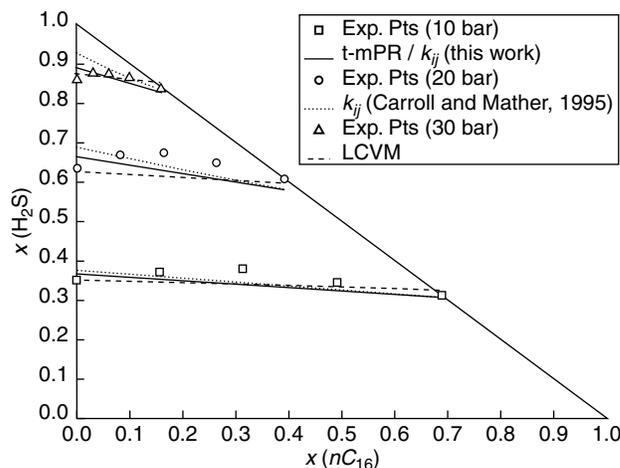


Figure 5

Prediction results for the ternary system $\text{H}_2\text{S}/n\text{C}_{16}/n\text{C}_{20}$ (Feng *et al.*, 1995), with the t-mPR EoS and the LCVM model.

This observation supports the good predictive performance of the proposed correlation for k_{ij} . In this case the results may also be affected by the use of the t-mPR EoS which provides better vapor pressure predictions due to the modification in the expression of m of the parameter a of the EoS.

3.2 Ternary Mixture of $\text{H}_2\text{S}/n\text{C}_{16}/n\text{C}_{20}$ (Feng *et al.*, 1995)

Feng *et al.* (1995) presented experimental data for the solubility of H_2S in mixtures with $n\text{C}_{16}$ and $n\text{C}_{20}$ at 323.2 K and pressures 1, 2 and 3 MPa. As shown in Figure 5 the prediction of these data using the t-mPR EoS with binary interaction coefficients derived from the proposed correlation gives an overall absolute percent error in pressure of 6%, similar to the one obtained by using the Carroll and Mather correlation (1995). The LCVM model provides somewhat better results (5%).

3.3 "Prinos" Reservoir Oil

The "Prinos" case was of special interest since the H_2S content in this reservoir oil was about 42% (mole). Conventional PVT (pressure, volume, temperature) laboratory study was available (North Aegean Petroleum Corporation, 1991) including Constant Composition Expansion (CCE) and Differential Liberation Experiments (DLE) at reservoir temperature (245°F) and at pressures starting from the initial reservoir pressure (5735 psig) up to atmospheric pressure. The bubble-point pressure determined

on the sample selected for the complete PVT study was 1175 psig at 245°F.

The following volumetric parameters have been considered:

- oil formation volume factor (Bo), defined as the volume (in barrels) occupied in the reservoir, at the prevailing pressure and temperature, by one stock tank barrel (standard conditions) of oil plus its dissolved gas;
- solution gas/oil ratio (Rs), defined as the number of standard cubic feet of gas dissolved in one stock tank barrel of oil when both are taken to the prevailing reservoir conditions.

In addition, reservoir oil densities and gas phase compositions are also available. The compositional analysis of the reservoir oil up to C_{7+} and the properties—molecular weight (MW) and specific gravity (SG)—of the heavy fraction C_{7+} are presented in Table 3.

Because of the substantial number of uncertainties involved in natural fluids modeling, the prediction of the PVT behavior of the reservoir oil was based on the following considerations:

- interaction parameters for all non-hydrocarbon/hydrocarbon pairs plus those of methane/hydrocarbons have been calculated through the correlations developed in this laboratory (Avlonitis *et al.*, 1994; Kordas *et al.*, 1994, 1995). For the k_{ij} of $\text{H}_2\text{S}/\text{hydrocarbons}$ the proposed correlation, Equation (4), was used;
- the heavy fraction was treated as:
 - *one pseudocomponent*. This is a reasonable assumption since Prinos oil is not a very volatile one. The critical temperature and the critical pressure of the C_{7+}

pseudocomponent have been estimated from the correlation of Twu (1984) and the acentric factor from that of Kesler and Lee (1976). They are given in Table 3;

- *three pseudocomponents*. Splitting of the C_{7+} in three fractions was made by the method of Whitson (1980) and the properties of the resulting pseudocomponents have been estimated as above (Table 3). Although no significant improvement is expected through this heavy end treatment due to the low oil volatility, splitting of the C_{7+} was considered useful in testing the performance of the proposed k_{ij} correlation when applied to higher molecular weight hydrocarbons as Table 3 indicates for the three pseudocomponents.

It is well known that the treatment of PVT data of reservoir fluids should follow a deeper investigation of the heavy end characterization and of the methods for estimating the thermophysical properties of the heavy fractions. Additionally, tuning of the EoS parameters is an acceptable procedure to match experimental data and should be applied with conscious to avoid unphysical predictions. Such a thorough analysis of Prinos oil reservoir fluid was considered out of the scope of this study. Therefore, no tuning was applied and straight prediction of all the experimental data was made. The main objective was to test the predictive capability of the EoS models enhanced by the incorporation of the specific parameters for pure H_2S and for H_2S /hydrocarbon systems developed in this work.

Both t-mPR and J-PR EoS have been used. In the case of the J-PR the shift parameter for the volume correction of H_2S developed in this study has been used.

Prediction results are satisfactory as shown in Figures 6 to 8. There is a very slight overall improvement when C_{7+} is treated as three pseudocomponents. This observation is in agreement with that of Coats and Smart (1986) who studied the effect of heavy end splitting to phase equilibria and volumetric predictions for several reservoir oils with different volatilities. For one of the oil mixtures included in their study, fairly close to the Prinos one in terms of volatility, they concluded that splitting the C_{7+} resulted in insignificant improvement in the predicted values. Their prediction results for B_o and R_s are equivalent to those obtained here. This is an interesting point, which indicates that although we have an oil mixture where methane is essentially substituted by H_2S , the obtained results are of the same quality as those for a typical oil with the same volatility.

Both EoS perform very well. The prediction of the volumetric parameters, B_o and R_s , is very satisfactory considering that no adjustment of any parameter has been performed and that the calculations cover a wide pressure range (6000 psig up to atmospheric pressure). Figures 6 and 7 show that the maximum absolute average deviation in B_o and R_s prediction is 8 and 11% respectively. The same is valid for the prediction of the oil density in the same pressure range, where the percent absolute deviation does not exceed the value of ten.

There is a small overall advantage of the J-PR EoS with a % AAD of 0.1% in B_o prediction and 6.7% in R_s when the heavy end is treated as three subfractions. It should be mentioned that the volumetric prediction performance of the J-PR EoS is improved by a factor of two when the shift parameter for H_2S is incorporated. Calculations using the

TABLE 3
Composition (mol%) of Prinos reservoir oil

Compound	Composition (mol%)	C_{7+} fractions	Composition (mol%)	MW	SG	T_c (K)	P_c (bar)	ω
N_2	0.06	F1	14.11	128.8	0.809	633.2	27.20	0.3603
CO_2	3.24	F2	14.02	304.3	0.909	855.9	13.61	0.8572
H_2S	41.57	F3	3.78	677.5	1.013	1077.6	8.35	1.3136
CH_4	5.55	C_{7+}	31.91	271	0.913	837.6	15.58	0.7722
C_2	2.41							
C_3	4.39							
iC_4	1.18							
nC_4	2.78							
iC_5	1.87							
nC_5	1.70							
nC_6	3.34							
C_{7+}	31.91							

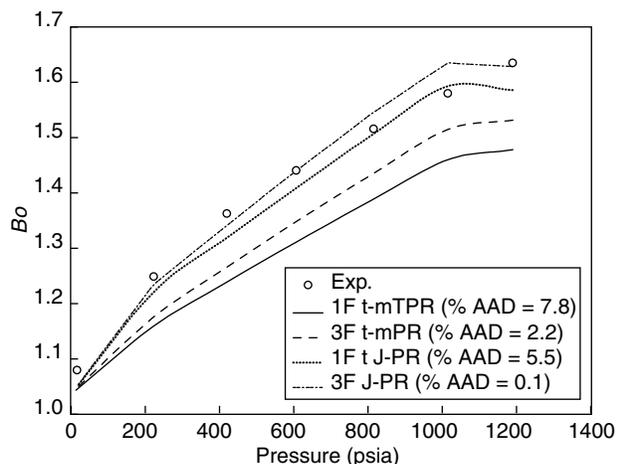


Figure 6

Prediction of the oil formation volume factor (B_o) for Prinos oil.

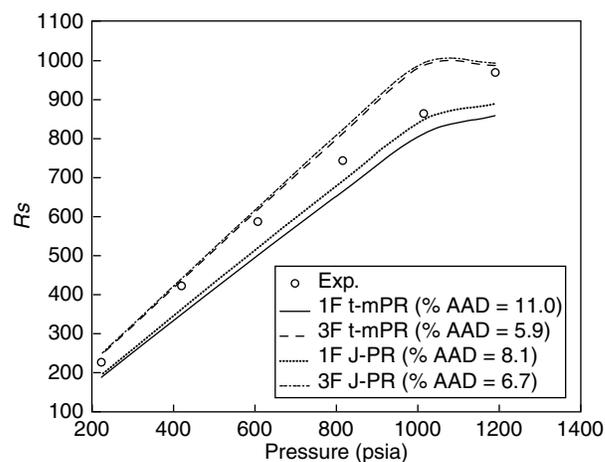


Figure 7

Prediction of the solution gas/oil ratio (R_s) for Prinos oil.

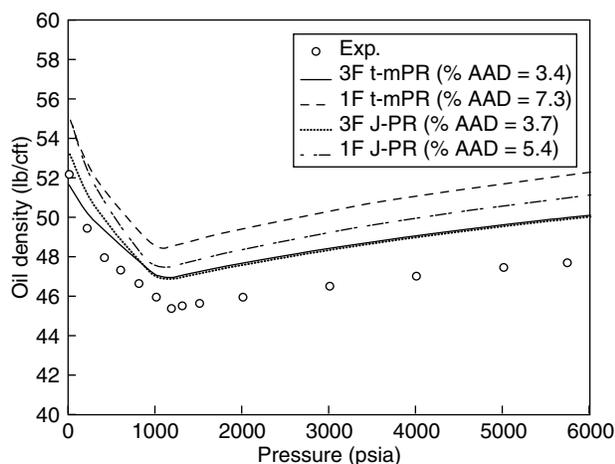


Figure 8

Prediction of the Prinos oil density.

J-PR EoS with no shift parameter for H_2S give a % AAD of 6.2% in oil density prediction, while in the opposite case the % AAD in oil density prediction is 3.7%, as Figure 8 indicates.

However, these prediction results can be further improved if other schemes for the estimation of the critical characteristics of the heavy fractions are tested.

These results suggest that the proposed correlation for the k_{ij} of H_2S /hydrocarbon systems appears to be very satisfactory for a molecular weight range significantly greater than that of the binary VLE database; and for oil whose heavy end is highly aromatic as indicated by its MW and SG values.

CONCLUSIONS

Very satisfactory results were obtained with the t-mPR and J-PR EoS for predicting the vapor pressures and saturated liquid volumes of hydrogen sulfide. The J-PR approach provides results equivalent to the t-mPR results for the saturated liquid volumes when the H_2S shift parameter for the volume correction, developed in this study, is incorporated.

The proposed generalized correlation for the interaction parameters of H_2S/n -alkanes and their isomers gives very good results, fairly close to those obtained by fitting T-P-x VLE data. The correlation of Carroll and Mather (1995) is also recommended for it gives similar results to that developed here. The use of the LCVM model proved very helpful in overcoming the lack of binary VLE for higher hydrocarbon systems. The “generated” VLE data for H_2S /large n -alkanes enhance the extrapolation capability of the proposed correlation to highly asymmetric systems.

Application to multicomponent synthetic mixtures and to natural fluids gives satisfactory results both for phase equilibria and for volumetric predictions using the t-mPR or the J-PR EoS. Furthermore, a comparison of the obtained results with those for conventional (no H_2S) oils suggests that the methodology presented in this study should be applicable to any reservoir oil with high concentration of hydrogen sulfide.

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APPENDIX

The t-mPR

The t-mPR EoS has the following form:

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

where the expressions for the calculation of its parameter values are:

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

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

$$t = t_0 + (t_c - t_0) \exp(\beta|1 - T_r|) \quad (4)$$

$$t_0 = \frac{RT_c}{P_c} (-0.014471 + 0.067498\omega - 0.084852\omega^2 + 0.067298\omega^3 - 0.017366\omega^4) \quad (5)$$

$$\beta = -10.2447 - 28.6312\omega \quad (6)$$

$$t_c = \frac{RT_c}{P_c} (0.3074 - Z_c) \quad (7)$$

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

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (8)$$

where:

$$Z = \frac{PV}{RT} \quad ; \quad A = \frac{aP}{R^2T^2} \quad ; \quad B = \frac{bP}{RT} \quad (9)$$

For the calculation of the critical compressibility factor Z_c the following expression has been assumed (Czerwinski *et al.*, 1988):

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

For the calculation of 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:

$$a_m = x_1^2 a_1 + x_2^2 a_2 + 2x_1 x_2 a_{12} \quad (10)$$

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

$$a_{12} = \sqrt{a_1 \cdot a_2} (1 - k_{12}) \quad (11)$$

where k_{12} is the binary interaction coefficient;

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

$$b_m = x_1 b_1 + x_2 b_2 \quad (12)$$

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

$$t_m = x_1 t_1 + x_2 t_2 \quad (13)$$

The Volume Translation of Jhaveri-PR

Jhaveri and Yougren (1984), based on the PR EoS, suggested a dimensionless correcting factor s that is dependent on the component of interest. This factor is determined as $S = t/b$, where b is the covolume parameter of the EoS and t is the correction of the volume that is given by the EoS ($V = V^{\text{EoS}} - t$). The s values up to nC_6 are obtained by matching the experimental molar volumes at $T_r = 0.7$ of the pure compound and they are presented in Table 1.

TABLE 1

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 ₃ 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 larger hydrocarbons, the following expression is used:

$$s = 1 - \frac{d}{MW^e} \quad (14)$$

where MW is the molecular weight. Values for d , e are given in Table 2.

TABLE 2

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