

A New Cubic Equation of State for Predicting Phase Behavior of Hydrocarbons

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Résumé — Une nouvelle équation d'état cubique pour prédire le comportement de phase d'hydrocarbures — Nous présentons une nouvelle équation d'état cubique à deux paramètres. Les paramètres de la nouvelle équation d'état sont considérés dépendant de la température. Pour calculer les propriétés thermodynamiques d'un hydrocarbure pur, cette équation d'état nécessite de connaître la température critique, la pression critique et le facteur acentrique des hydrocarbures. L'équation d'état proposée est utilisée pour effectuer des calculs PVT et d'équilibre vapeur-liquide de différents hydrocarbures purs et de mélanges de fluides. Les résultats sont comparés à ceux obtenus par deux équations d'état cubiques utilisées classiquement. Les comparaisons indiquent que la nouvelle équation d'état permet d'améliorer la précision des résultats.

Abstract — A New Cubic Equation of State for Predicting Phase Behavior of Hydrocarbons — In this work, a two parameter cubic equation of state is presented. The parameters of the new cubic equation of state are considered temperature dependent. For calculating the thermodynamic properties of a pure hydrocarbon, this equation of state requires the critical temperature, the critical pressure and the acentric factor of hydrocarbon. The proposed equation of state is applied for PVT and VLE calculations of different pure hydrocarbons and fluid mixtures. The results are compared with those obtained by two commonly used cubic equation of state. The comparisons indicate that the new equation of state yields better results.

NOTATION

a, b	parameters in the new EOS
a_c, b_c	parameters at critical point
H	enthalpy
k_{ij}	binary interaction
m	parameter of Equation (3)
m_1, m_2 and m_3	parameters of Equation (11)
n	parameter of Equation (12)
np	number of data point
OF	objective function
P	pressure
P_c	critical pressure
P_{exp}	experimental pressure
P_{cal}	calculated pressure
PR	Peng-Robinson EOS
R	ideal gas constant
RK	Redlich-Kwong EOS
S	entropy
SRK	Soave-Redlich-Kwong EOS
T	temperature
T_c	critical temperature
T_r	reduced temperature
v	volume
v_c	critical volume
v_{tp}	volume at triple point
y_1	mole fraction of component (1)
Z	compressibility factor
Z_{rep}	compressibility factor of repulsive
Z_{attr}	compressibility factor of attraction
Z_c	critical compressibility.

Greek Letters

α, β	reduced temperature function of the new EOS
ϵ, γ, δ	parameters of Equation (3)
ρ_{exp}^l	experimental liquid density
ρ_{cal}^l	calculated liquid density
η	packing fraction
η_{max}	maximum packing fraction (MPF)
φ	fugacity coefficient
Ω_p, Ω_d	weighting parameters.

INTRODUCTION

Equations of state have been used to predict phase equilibria in refinery, petroleum reservoir and other chemical industries. Also properties of compounds such as vapor pressure, density of vapor and liquid, thermal properties and solubility of substances in supercritical fluids are calculated based on

equations of state (Johnston *et al.*, 1982; Hartono *et al.*, 1999; Madras *et al.*, 2003). Cubic equations of state are currently the equations of state considered most applicable for such calculations. Cubic equations of state can be classified into two categories:

- The cubic equations with two parameters for repulsive and attractive terms such as Van der Waals (Vdw) (1873), Redlich-Kwong (1949), Soave-Redlich-Kwong (1972) and Peng-Robinson (1976), etc.
- The cubic equations with three or more parameters such as Patel-Teja (1982) and Patel-Teja-Valderrama (1990), etc.

Although increasing the number of parameters makes a cubic equation of state more accurate for calculating pure component properties, the extensions of the equation of state to mixtures becomes more difficult, *i.e.* more mixing rules are required. The PR and SRK equations of state are the best two-parameter cubic equation of state among the others. Many attempts have been made to improve the prediction ability of these two cubic equations of state. Often, in these modified equations of state attractive parameters generally are considered a function of the reduced temperature and the acentric factor and repulsive parameter is keep constant. Of course, there are many equations of state where the repulsive parameter is considered a function of the temperature. For example, Riazi and Mansoori (1993) and Nasrifar and Moshfeghian (2004), etc. The poor volumetric behavior of Vdw equations of state may be removed by considering the importance of the role of repulsive forces in the behavior of fluids. Recently, Mohsen-Nia *et al.* (2003) introduced a new method to determine a suitable repulsive term for cubic equations of state. In this work, based on this method, a new two-parameter cubic equation of state is presented. Both parameters are considered temperature dependent. Using this equation of state, the vapor pressure, the liquid density, the vapor volume, the enthalpy and entropy of vaporization for pure hydrocarbons are calculated. Then the proposed equation is extended to mixtures. These results are compared with those obtained from the equations of state frequently used for thermodynamic and fluid phase equilibrium. The comparisons show that the new cubic equation of state has better results than other two equations of state.

1 PRESENTATION OF THE NEW EQUATION OF STATE

The compressibility factor, Z , based on perturbation theory is written as (Malanowski and Anderko, 1992):

$$Z = Z_{rep} + Z_{attr} \quad (1)$$

where Z_{rep} is the hard-sphere term for repulsive term (unperturbed term) and Z_{attr} is the compressibility factor for attractive term (perturbed term).

We propose a hard-core equation of state based on packing fraction η , as below:

$$Z_{rep} = \frac{1 + \delta\eta}{1 - \epsilon\eta}; \quad \eta = \frac{b}{4v} \quad (2)$$

Therefore, a new cubic equation of state is defined based on SRK and RK equations of state attractive term as:

$$Z = \frac{v + \delta b}{v - \epsilon b} - \frac{a}{RT^{m+1}(v + \epsilon\gamma b)} \quad (3)$$

By choosing, $m=0, \gamma=\epsilon=1$ the attraction term of the new cubic equation of state can be reduced to the attractive term of SRK equation of state:

$$Z = \frac{v + b}{v - b} - \frac{a}{RT(v + b)} \quad \eta \leq 0.6 \quad (4)$$

By applying the critical point constrains the parameters a and b are calculated as:

$$a_c = 0.47448 \frac{R^2 T_c^2}{P_c} \quad (5)$$

$$b_c = 0.06824 \frac{RT_c}{P_c} \quad (6)$$

$$Z_c = 0.333 \quad (7)$$

In order to test the validity of the new cubic equation of state the maximum packing fractions (MPF) for different hydrocarbons can be determined by considering the triple point and critical density of hydrocarbon according to this equation of state. Minimum volume (v_{min}) is the smallest molar volume of hydrocarbons which approximately define the molar volume at the triple point. The maximum packing fraction is calculated at minimum volume for hydrocarbon as (Mohsen-Nia *et al.*, 1995):

$$\eta_{max} = 0.103 \left(\frac{v_c}{v_{tp}} \right) \quad (8)$$

Where in the above equation v_c and v_{tp} are molar volumes at critical point and triple point, respectively. The maximum packing fractions (MPF) of various hydrocarbons are reported in Table 1.

The results of this table show that the maximum packing fractions are in the allowable range of $0 \leq \eta \leq 0.6$ where the repulsive part of Equation (3) accurately represents the Scott hard-sphere equation of state. For predicting vapor pressure, liquid density and vapor volume of hydrocarbons, it is entirely sufficient to introduce temperature dependent attractive and repulsive parameters.

TABLE 1

The maximum packing fraction (MPF) of various hydrocarbons calculated from the new cubic equation of state

η_{max}	Hydrocarbon
0.3323	CH ₄
0.3940	C ₂ H ₆
0.4254	n-C ₄ H ₁₀
0.4771	n-C ₈ H ₁₈
0.3743	C ₂ H ₄
0.3812	CH ₃ Cl
0.5136	n-C ₁₀ H ₂₂
0.4520	C ₃ H ₆ O
0.4090	CHC ₁₃

It is convenient to express the parameters a and b as a product of its value at the critical point and dimensionless functions of temperature and acentric factor:

$$a = a_c \alpha(T_r, \omega) \quad (9)$$

$$b = b_c \beta(T_r, \omega) \quad (10)$$

Several empirical and theoretical extensions of the attractive and repulsive terms have been proposed. In this work, we propose three parameter forms of the α function and a linear temperature function for the β function in the following form:

$$a = a_c [1 + m_1(1 - T_r) + m_2(1 - T_r)^2 + m_3(1 - T_r)^3]^2 \quad (11)$$

$$b = b_c [1 + n(1 - T_r)] \quad (12)$$

The presented function form for repulsive and attractive term, expressed by Equations (11) and (12) satisfies the basic theoretical conditions for these functions at the critical point:

$$[\alpha(T_r, \omega)] = [\beta(T_r, \omega)] \rightarrow 1 \quad \text{at} \quad T_r \rightarrow 1 \quad (13)$$

The parameters of m_1 to m_3 and n are determined by using the following objective function:

$$OF = \sum_{i=1}^{np} \left\{ \Omega_p \left| \frac{P_{cal} - P_{exp}}{P_{exp}} \right|_i + \Omega_d \left| \frac{\rho_{cal}^l - \rho_{exp}^l}{\rho_{exp}^l} \right|_i \right\} \quad (14)$$

Where in Equation (14) $\Omega_p = 0.8$ and $\Omega_d = 0.2$. The general form of the parameters in Equations (11) and (12) are presented below:

$$m_1 = 0.2513 + 0.4178\omega - 0.0207\omega^2 \quad (15)$$

$$m_2 = -0.1382 - 0.5923\omega - 1.0493\omega^2 \quad (16)$$

$$m_3 = 0.1931 + 1.3955\omega + 0.1961\omega^2 \quad (17)$$

$$n = 0.2155 - 0.9069\omega - 0.206\omega^2 \quad (18)$$

2 RESULTS

The proposed cubic equation of state is applied to calculate phase behavior of various pure hydrocarbons and mixtures of fluids. The vapor pressure and saturated liquid density are the most important properties of pure fluids. However, once an equation of state is developed, it is usually applied to calculate many properties. The thermodynamic relations for the new equation of state are presented in Table 2.

The vapor pressure, saturated liquid density and vapor volume of 20 pure hydrocarbons from the new cubic equation of state are compared with experimental data as well as with the predictions given by the SRK and PR equations of state. Among the 20 pure hydrocarbons, the new cubic equation of state predicts the vapor pressure of 12 compounds better than both the PR and SRK equation of state.

The average of absolute deviations (AAD%) of the predicted vapor pressure using the new cubic equation of state is 1.110% where as it is 1.219% for the PR equation of state and 1.333% for the SRK equation of state. It was also found that the new cubic equation of state predicts the saturated vapor pressure of the pure hydrocarbons much better than the PR and the SRK equation of state. The average of absolute deviations of the predicted saturated liquid densities by use of the new cubic equation of state, the PR equation of state and the SRK equation of state were found to be 6.116, 5.067 and 11.775%, respectively. Also, Table 3 shows that the predictions of the vapor volume by the PR and the SRK equation of state are better than the new cubic equation of state but the average absolute deviation of the new equation of state is acceptable. The average of absolute deviations of the predicted vapor volumes are 3.389, 1.825 and 1.627%, respectively. Table 4 shows the enthalpy and the entropy of vaporization calculated from the three equations of state. It was found that the average of absolute deviations of the predicted enthalpies of vaporization of the 20 hydrocarbons using the new equation of state, the PR and the SRK equations of state are 2.559, 2.077 and 2.619%, respectively. The average of absolute deviations of the predicted entropies of vaporization of the 15 hydrocarbons using the new equation of state, the PR and the SRK equations of state are 2.714, 2.323 and 3.008%, respectively.

These results obtained from the new cubic equation of state are better than those obtained from the PR and SRK equation of state. Figure 1 shows the experimental and the prediction results of saturated vapor pressure of many hydrocarbons.

Figure 2 shows the prediction and the experimental data of liquid and vapor densities of different hydrocarbons.

In Figure 3, the experimental and predicted pressure-enthalpy of many hydrocarbons is presented. Figure 4 shows the entropy of vaporization of some hydrocarbons using the new cubic equation of state. These figures (1-4)

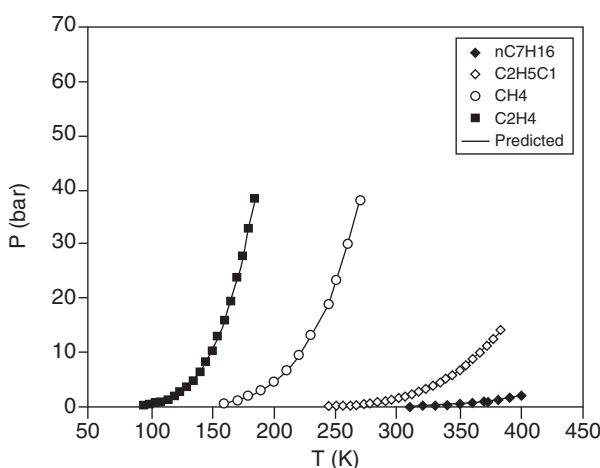


Figure 1

The vapor pressure of different hydrocarbons vs. temperature. (experimental data from R.H. Perry and D.W. Green, 1988).

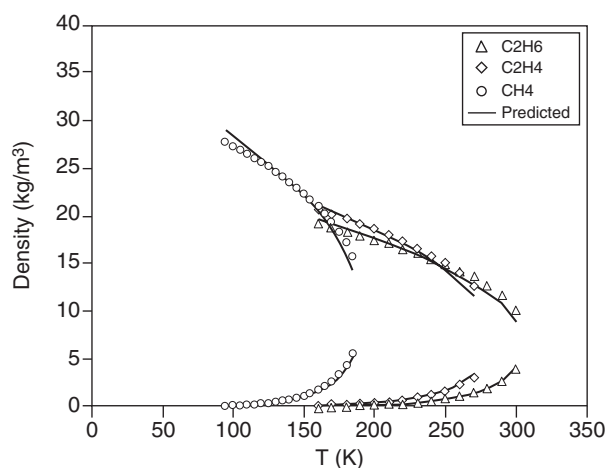


Figure 2

Experimental and predicted liquid and vapor densities of three hydrocarbons as a function of reduced temperature (experimental data from R.H. Perry and D.W. Green, 1988).

show that there is good agreement between the experimental data and the results of the new equation of state.

Figure 5 illustrates the pressure – density diagram of CH_4 . There is acceptable agreement between the predictions and the experimental values for both the saturated liquid and the saturated vapor.

The proposed equation of state is applied for mixture VLE calculations. For this work, mixing rules are needed. The

TABLE 2
Thermodynamic relations for calculating thermodynamic properties using Equation (4)

The EOS in terms of A, B and Z	$Z^3 - Z^2 + (A - B^2 - 2B)Z - (AB + B^2) = 0$ $A = \frac{aP}{R^2T^2}, \quad B = \frac{bP}{RT} \quad \text{and} \quad Z = \frac{Pv}{RT}$
Fugacity coefficient of Component <i>i</i> in mixture	$\ln(\phi_i Z) = 2 \left[\frac{\partial(nb_m)/\partial n_i}{v - b_m} - \ln\left(1 - \frac{b_m}{v}\right) \right] - \frac{a_m/(b_m RT)}{v + b_m} \frac{\partial(nb_m)}{\partial n_i}$ $+ \frac{a_m}{b_m RT} \left\{ \frac{1}{a_m} \left[\frac{1}{n} \frac{\partial(n^2 a_m)}{\partial n_i} \right] - \frac{1}{b_m} \frac{\partial(nb_m)}{\partial n_i} \right\} \ln\left(\frac{v}{v + b_m}\right)$
Enthalpy departure	$H - H^* = RT(Z - 1) + \frac{1}{b} \left(T \frac{da}{dT} - a - \frac{aT}{b} \frac{db}{dT} \right) \ln\left(1 + \frac{B}{Z}\right)$ $- 2PT \frac{(db/dT)}{Z - B} + \frac{aP}{Rb} \frac{(db/dT)}{Z + B}$
Entropy departure	$S - S^* = 2R \ln\left(1 - \frac{B}{Z}\right) + \frac{1}{b} \left(\frac{da}{dT} - \frac{a}{b} \frac{db}{dT} \right) \ln\left(1 + \frac{B}{Z}\right)$ $- 2P \frac{(db/dT)}{Z - B} + \frac{aP}{Rb} \frac{(db/dT)}{Z + B}$

TABLE 3
Prediction of vapor pressure, saturated liquid density and the vapor volume of pure fluids from various equations of state

Hydrocarbon	np	T _r range	Percent of average absolute deviation (%AAD)									Ref.
			Vapor Pressure			Saturated liquid density			Vapor volume			
			New	PR	SRK	New	PR	SRK	New	PR	SRK	
CH ₄	19	0.50-0.97	0.741	0.584	1.820	4.095	8.886	4.472	1.792	0.930	2.335	*
C ₂ H ₆	15	0.52-0.98	0.408	0.757	1.216	5.210	6.570	7.775	1.751	1.173	1.075	*
C ₃ H ₈	17	0.51-0.95	0.637	1.401	0.758	4.426	5.049	8.164	1.535	1.571	0.318	*
<i>n</i> -C ₄ H ₁₀	20	0.54-0.99	0.499	0.814	1.037	6.088	4.875	10.479	2.243	1.138	0.717	*
<i>i</i> -C ₄ H ₁₀	17	0.54-0.98	0.962	1.569	1.658	5.697	5.216	9.518	2.132	2.179	1.479	*
<i>n</i> -C ₅ H ₁₂	22	0.64-0.97	0.606	0.348	1.061	5.858	3.379	12.236	2.782	1.103	0.713	**
<i>i</i> -C ₅ H ₁₂	28	0.53-0.97	1.219	0.244	1.348	6.260	4.747	10.420	2.459	1.219	1.449	**
<i>n</i> -C ₆ H ₁₄	31	0.53-0.97	1.368	1.021	1.770	6.331	2.894	12.737	3.793	1.635	1.597	**
<i>n</i> -C ₇ H ₁₆	11	0.57-0.74	0.598	1.676	0.663	2.995	0.698	12.140	0.665	1.773	0.516	*
<i>n</i> -C ₈ H ₁₈	12	0.60-0.98	0.426	1.590	1.797	7.839	5.916	16.758	5.273	1.961	2.248	*
<i>n</i> -C ₉ H ₂₀	14	0.50-0.94	3.757	2.389	2.231	7.198	4.953	15.904	12.495	6.778	6.638	*
<i>n</i> -C ₁₀ H ₂₂	14	0.55-0.94	2.377	2.362	1.819	7.197	7.428	18.132	6.464	1.928	2.179	*
C ₂ H ₄	12	0.57-0.96	0.501	0.658	0.808	4.396	6.197	7.215	1.444	1.189	0.575	*
C ₃ H ₆	19	0.52-0.98	0.677	1.487	0.900	4.921	6.612	7.128	1.982	1.482	0.387	*
C ₇ H ₁₄	28	0.55-0.97	0.735	0.788	0.822	5.786	3.802	11.179	3.054	1.229	0.975	**
C ₂ H ₂	12	0.65-0.97	0.884	1.496	2.275	6.513	4.192	11.429	3.824	1.248	1.372	*
C ₆ H ₆	25	0.55-0.98	0.626	0.908	0.681	5.270	3.166	11.216	2.554	1.167	0.717	*
C ₆ H ₅ CH ₃	20	0.51-0.98	1.751	1.339	1.148	5.570	2.447	13.273	2.953	2.557	1.874	*
C ₃ H ₆ O	20	0.59-0.94	2.501	2.288	1.631	13.428	12.236	22.475	4.470	2.488	2.207	*
CH ₃ Cl	36	0.51-0.96	0.943	0.661	1.233	7.243	2.093	12.867	4.134	1.768	3.188	**

* Perry, R.H. and Green, D.W. (1988) Perry's Chemical Engineers' Handbook, 6th Edition, McGraw Hill, Tokyo, Japan.

** Smith, B.D. and Srivastava, R. (1986) *Thermodynamic Data for Pure Compounds*, Elsevier.

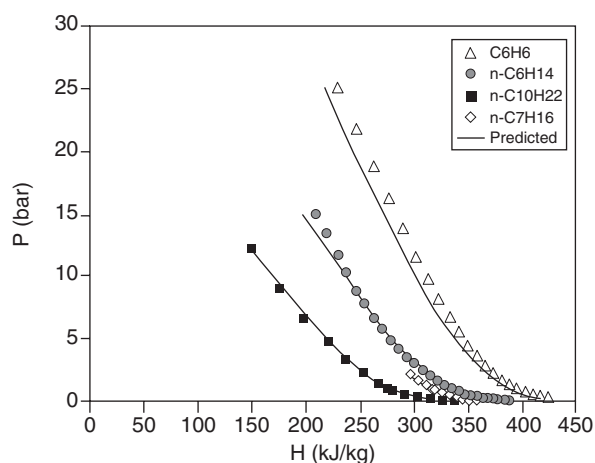


Figure 3

Pressure-enthalpy phase behavior for many hydrocarbons (experimental data from R.H. Perry, D.W. Green, 1988; B.D. Smith, R. Srivastava).

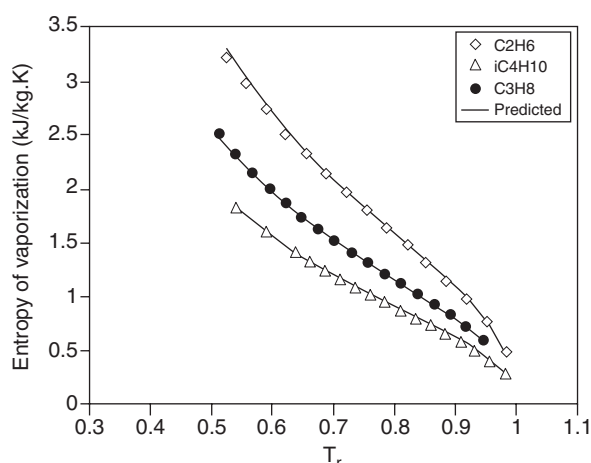


Figure 4

Experimental and predicted entropy of different fluids as a function of reduced temperature (experimental data from R.H. Perry, D.W. Green, 1988).

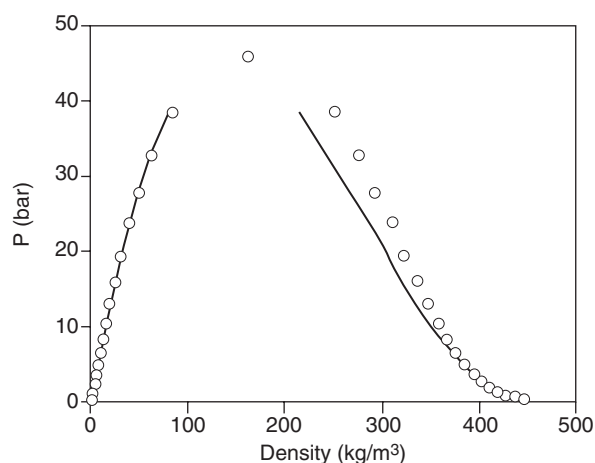


Figure 5

Experimental and predicted pressure-density for CH₄ (experimental data from Vargaftik, N.B., 1975).

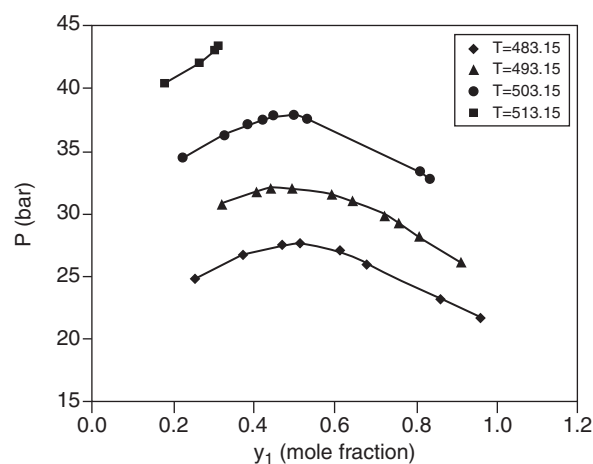


Figure 6

Pressure-equilibrium phase composition for *n*-hexane+1-propanol (experimental data from Oh *et al.*, 2004).

vdW mixing rules for two parameter equations of state usually are used:

$$a = \sum_i^n \sum_j^n x_i x_j (a_{ii} a_{jj})^{0.5} (1 - k_{ij}) \quad (19)$$

$$b = \sum_i^n x_i b_i \quad (20)$$

where k_{ij} is the binary interaction parameter.

The new cubic equation of state is used for the vapor-liquid equilibrium (VLE) calculations of 10 different binary fluid mixtures for which experimental data are available. Table 5 compares results of the VLE calculations using the present equation of state, the PR equation of state and the SRK equation of state with assumption $k_{ij}=0$ for all these equations. According to this table the new cubic equation of state is overall superior of the other equations for the mixtures. In Figure 6 the phase behavior of *n*-hexane+1-propanol binary systems are plotted. As seen in these figure,

TABLE 4
Prediction of the enthalpy and the entropy of pure fluids from various equations of state

Hydrocarbon	np	T _r range	Percent of average absolute deviation (%AAD)						Ref.
			Enthalpy of vaporization			Entropy of vaporization			
			New	PR	SRK	New	PR	SRK	
CH ₄	19	0.50-0.97	1.261	1.418	2.486	2.101	2.394	3.373	*
C ₂ H ₆	15	0.52-0.98	1.543	1.794	2.619	1.538	1.804	2.624	*
C ₃ H ₈	17	0.51-0.95	0.806	1.308	1.048	0.808	1.304	1.050	*
<i>n</i> -C ₄ H ₁₀	20	0.54-0.99	1.980	2.083	2.767	1.912	2.015	2.700	*
<i>i</i> -C ₄ H ₁₀	17	0.54-0.98	1.555	1.343	1.216	1.530	1.354	1.237	*
<i>n</i> -C ₅ H ₁₂	22	0.64-0.97	1.672	1.428	2.200	—	—	—	**
<i>i</i> -C ₅ H ₁₂	28	0.53-0.97	1.709	1.768	2.547	—	—	—	*
<i>n</i> -C ₆ H ₁₄	31	0.53-0.97	2.983	2.368	2.968	—	—	—	**
<i>n</i> -C ₇ H ₁₆	11	0.57-0.74	1.593	0.591	1.194	1.602	0.576	1.203	*
<i>n</i> -C ₈ H ₁₈	12	0.60-0.98	4.425	3.269	4.167	4.487	3.294	4.197	*
<i>n</i> -C ₉ H ₂₀	14	0.50-0.94	6.191	4.956	5.282	6.381	7.442	7.817	*
<i>n</i> -C ₁₀ H ₂₂	14	0.55-0.94	4.753	1.527	2.306	4.653	1.444	2.213	*
C ₂ H ₄	12	0.57-0.96	0.739	1.240	1.662	1.182	2.360	2.785	*
C ₃ H ₆	19	0.52-0.98	1.272	1.691	1.704	1.281	1.699	1.717	*
C ₇ H ₁₄	28	0.55-0.97	2.151	1.450	1.813	—	—	—	**
C ₂ H ₂	12	0.65-0.97	3.613	3.804	4.431	3.563	1.337	4.463	*
C ₆ H ₆	25	0.55-0.98	1.456	1.317	1.403	2.368	2.354	2.235	*
C ₆ H ₅ CH ₃	20	0.51-0.98	2.550	2.936	3.268	2.542	2.958	3.240	*
C ₃ H ₈ O	20	0.59-0.94	5.848	3.839	4.697	4.766	2.524	4.273	*
CH ₃ Cl	36	0.51-0.96	3.086	1.420	2.604	—	—	—	**

* R.H. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, 6th Edition, McGraw Hill, Tokyo, Japan, (1988).

** B.D. Smith, R. Srivastava, Thermodynamic data for pure compounds, Elsevier (1986).

TABLE 5
Relative error in the calculated pressure and vapor phase composition for various binary mixtures

Systems	np	Percent of average absolute deviation (%AAD)						Ref.
		Bubble Pressure			Vapor mole fraction			
		New	PR	SRK	New	PR	SRK	
1-Butene + 1-Hexene	6	4.934	1.644	0.895	5.049	1.382	1.621	I
CO ₂ + iso-butanol	31	17.630	36.600	35.191	0.728	0.667	0.692	II
CO ₂ + iso-pentanol	51	5.636	33.182	31.720	1.203	1.183	1.197	II
CO ₂ + CHC ₁₃	30	5.901	16.384	15.096	7.836	25.738	25.900	III
CO ₂ + toluene	45	16.578	36.002	35.422	2.087	1.949	2.034	III
C ₂ H ₆ + CO ₂	14	19.122	22.922	22.777	2.538	5.226	5.017	IV
CO ₂ + <i>n</i> -C ₄ H ₁₀	38	9.843	17.655	17.674	7.640	17.978	18.411	IV
C ₆ H ₆ + C ₆ H ₅ Cl	7	6.346	3.759	3.343	1.178	2.706	1.659	IV
Methanol + 2-butanone	10	4.910	6.785	6.964	-	-	-	IV
N ₂ + CH ₄	24	8.950	9.506	9.248	0.728	1.318	1.231	IV
Average	256	9.985	18.443	17.833	3.220	6.460	6.418	

I Laugier and Richon, 1996; II da Silva and Barbosa, 2002; III Scurto *et al.*, 2001; IV Winnick, 1997.

there is good agreement between the calculated and experimental values, in these systems.

CONCLUSIONS

A cubic equation of state based on hard-core model has been developed to predict phase behavior of pure hydrocarbons and mixtures. This equation of state predicts accurately the vapor pressure and liquid density of pure hydrocarbons. Using the new cubic equation of state, VLE have been calculated.

The prediction ability of this cubic equation of state for predicting thermal properties is comparable to the PR and SRK equation of state.

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