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Modified Cubic Equation of State for Prediction VLE Phase Behavior of Fluids: Pure and Mixture

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Modified Cubic Equation of State for Prediction VLE Phase Behavior of Fluids: Pure and Mixture

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Abstract: In this paper, a modified form of DPTG (Dashtizadeh-Pazuki-Taghikhani-Ghotbi) cubic equation of state is proposed. To this end parameters of the original DPTG equation (a, b) are also corrected. In order to calculate the saturated vapor pressure, the liquid density, and the vapor volume of 25 pure fluids modified DPTG equation of state is applied and the final results are compared with the SRK and PR equations of state. Finally, the above-mentioned DPTG EOS is used for calculation of the second virial coefficient, enthalpy and entropy of vaporization, surface tension of pure substances, and the density of normal hydrocarbons and Z.

On the other hand, the modified DPTG equation of state is applied to calculate bubble pressure, binary systems mole fraction of the vapor phase, and the density of normal hydrocarbons mixture. The results show that the modified DPTG equation of state could be used for calculation of pure and mixtures of fluids phase behavior with good accuracy.

Keywords: Equation of state, PVT property, phase behavior, fluid

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INTRODUCTION

The equation of state is a crucial factor in the calculation of thermodynamic properties, modeling, and simulation of chemical processes. Solubility of solids in supercritical fluids, precipitation of asphaltene in crude oil, properties of fluids in pipe line, and phase behavior of polymer solutions could be calculated by means of equations of state. Considering parameters *a* and *b* for intermolecular forces and van der Waals molecular volume (1) the first two-parameter cubic equation of state for prediction of phase behavior of substances could be presented. Redlich-Kwang (2), Soave (3), Peng and Robinson (4) have proposed new equations based on vdW EOS. Afterwards, Stryjek and Vera (5), Fotouh and Shukla (6), Zabaloy and Brignole (7), Souahi et al. (8), Feyzi et al. (9) and Gasem et al. (10) have presented new cubic equations of state by further modification on RK, SRK, and PR equations. Recently, many cubic equations of state are presented based on molecular thermodynamic (11–14).

In this work, the *a* and *b* parameter in DPTG (Dashtizadeh-Pazuki-Taghikhani-Ghotbi) EOS are modified in terms of reduced temperature and acentric factor. The pressure-volume-temperature (PVT) properties such as saturation pressure, liquid density, and vapor volume are calculated by modified DPTG EOS. In addition, pure fluids enthalpy and entropy of vaporization, the normal hydrocarbons density, the compressibility factor, second virial coefficient and surface tension of pure substances are estimated by the modified DPTG equation of state.

At the end, the modified DPTG equation of state is used for the calculation of bubble pressure point and vapor phase mole fraction and mixtures of normal hydrocarbons density.

MODIFIED DPTG EQUATION OF STATE

According to the perturbation theory, the compressibility factor, Z, could be written as (13):

$$Z = Z^{ref} + Z^{pert} \tag{1}$$

where subscripts ‘ref’ and ‘pert’ refer to reference and perturbation.

Dashtizadeh et al. proposed a new cubic equation of state based on the perturbation theory for prediction of phase behavior of fluids recently (13):

$$Z = \frac{1 + b_1\eta}{1 - b_2\eta} - \frac{4\theta\eta}{T^{\xi+1}(1 + 4c_1\eta)(1 + 4c_2\eta)} \tag{2}$$

$$\theta = \frac{a}{bRT} \tag{3}$$

$$\eta = \frac{b}{4v} \tag{4}$$

The parameters of the above equation for DPTG equation of state are: $b_1 = 8$, $b_2 = 4$, $\xi = 0$, $c_1 = 0$ and $c_2 = 1$.

Therefore, Eq. (1) would be simplified to:

$$Z = \frac{v + 2b}{v - b} - \frac{a}{RT(v + b)} \tag{5}$$

The above equation in molar volume would be written as:

$$v^3 - \frac{RT}{P}v^2 + \left(\frac{a}{P} - b^2 - \frac{3bRT}{P}\right)v - \left(\frac{ab}{P} + \frac{2b^2RT}{P}\right) = 0 \tag{6}$$

Thermodynamic properties such as saturation vapor pressure vapor and liquid phase densities are obtained by Eq. (6.)

In the present study, parameters a and b in DPTG-EOS have been modified as follows:

$$a = \alpha(T_r, \omega)\left(0.51301\frac{R^2T_c^2}{P_c}\right) \tag{7}$$

$$b = \beta(T_r, \omega)\left(0.058743\frac{RT_c}{P_c}\right) \tag{8}$$

where:

$$\alpha(T_r = 1, \omega) = \beta(T_r = 1, \omega) = 1 \tag{9}$$

The parameters α and β are considered as follow:

$$\alpha^{1/2} = [1 + m_1(1 - T_r^{0.5}) + m_2(1 - T_r^{0.5})^2 + m_3(1 - T_r^{0.5})^3] \tag{10}$$

$$\beta^{1.2} = [1 + n(1 - T_r)] \tag{11}$$

Parameter n and m$_i$ are obtained by minimizing the following objective function (13):

$$\Delta = \sum_i^{np}\left(w_p\frac{|P_{cal,i} - P_{\exp,i}|}{P_{\exp,i}} + w_d\frac{|\rho^1_{cal,i} - \rho^1_{\exp,i}|}{\rho^1_{\exp,i}}\right) \tag{12}$$

where $w_p = 0.8$, $w_d = 0.2$ and np is number of experimental data points.

Parameters m_1, m_2, m_3 and n are plotted in Fig. 1. Using a curve fitting program, the relation between the parameters and the acentric factor is

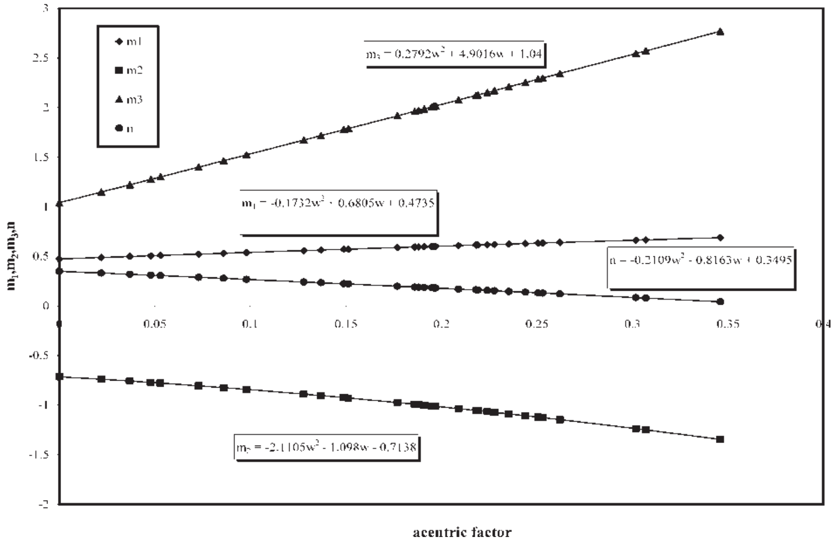

Figure 1. Dependence parameters of new equation of state the reduced acentric factor.

obtained as:

$$m_1 = 0.4690 + 0.7096\omega - 0.2660\omega^2 \tag{13}$$

$$m_2 = -0.6548 - 1.2625\omega - 1.9727\omega^2 \tag{14}$$

$$m_3 = 0.9553 + 5.0064\omega + 0.4159\omega^2 \tag{15}$$

$$n = 0.1723 - 0.3858\omega - 0.1683\omega^2 \tag{16}$$

RESULTS AND DISCUSSION

The modified DPTG equation of state is applied in order to calculate the thermodynamic properties of fluids. In Table 1, the vapor pressure, liquid density, and the vapor volume of 25 pure substances (555 experimental data points) for M-DPTG, are compared with those given by the DPTG and PR equations of state. The average of absolute deviations (AAD %) for predicted vapor pressure using the M-DPTG, PR, and SRK equations of state would be 0.924, 1.325, and 1.440%, respectively. The average of absolute deviations for the predicted saturated liquid density using the M-DPTG, PR, and SRK equation of state would be 5.58, 6.07, and 9.921%, respectively. Also, the average of absolute deviations of the predicted vapor volumes would be 1.50, 1.91, and 1.533 for M-DPTG, PR and SRK equations of state. Table 2 shows predicted normal hydrocarbons

Table 1. Average absolute deviation of vapor pressure, saturated liquid density and the vapor volume of pure compounds from PR, SRK, and New equations of state

			Percent of average absolute deviation (%AAD)									
			Vapor pressure			Saturated liquid density			Vapor volume			
Compound	n	T_r range	NEW	PR	SRK	NEW	PR	SRK	NEW	PR	SRK	Reference
CH_4	19	0.50–0.97	0.88	0.584	1.820	4.32	8.886	4.472	1.26	0.930	2.335	[a]
C_2H_6	15	0.52–0.98	0.478	0.757	1.216	5.40	6.570	7.775	1.31	1.173	1.075	[a]
C_3H_8	17	0.51–0.95	0.691	1.401	0.758	4.55	5.049	8.164	0.69	1.571	0.318	[a]
n-C_4H_{10}	20	0.54–0.99	0.49	0.814	1.037	6.21	4.875	10.479	1.85	1.138	0.717	[a]
i-C_4H_{10}	17	0.54–0.98	0.85	1.569	1.658	5.87	5.216	9.518	1.58	2.179	1.479	[a]
n-C_5H_{12}	22	0.64–0.97	0.52	0.348	1.061	5.91	3.379	12.236	1.86	1.103	0.713	[b]
i-C_5H_{12}	28	0.53–0.97	2.97	0.244	1.348	5.00	4.747	10.420	0.81	1.219	1.449	[b]
n-C_7H_{16}	11	0.57–0.74	0.48	1.676	0.663	2.72	0.698	12.140	0.71	1.773	0.516	[a]
n-C_8H_{18}	12	0.60–0.98	0.46	1.590	1.797	7.91	5.916	16.758	5.05	1.961	2.248	[a]
n-$C_{10}H_{22}$	14	0.55–0.94	1.73	2.362	1.819	6.80	7.428	18.132	0.12	1.928	2.179	[a]
C_2H_4	12	0.57–0.96	0.51	0.658	0.808	4.55	6.197	7.215	0.95	1.189	0.575	[a]
C_3H_6	19	0.52–0.98	0.70	1.487	0.900	5.04	6.612	7.128	1.65	1.482	0.387	[a]
C_2H_2	12	0.65–0.97	0.93	1.496	2.275	6.81	4.192	11.429	4.94	1.248	1.372	[a]
C_6H_6	25	0.55–0.98	0.65	0.908	0.681	5.36	3.166	11.216	1.83	1.167	0.717	[a]
C_3H_6O	20	0.59–0.94	2.56	2.288	1.631	13.55	12.236	22.475	1.80	2.488	2.207	[a]
CH_3Cl	36	0.51–0.96	1.1	0.661	1.233	7.28	2.093	12.867	2.76	1.768	3.188	[b]
$CHCl_3$	14	0.52–0.99	0.62	3.949	4.290	3.033	6.671	8.114	1.73	4.433	4.665	[a]
$C_2Cl_2F_4$	29	0.67–0.96	0.7	0.462	1.045	4.47	4.322	9.019	0.71	0.987	1.227	[b]

(*continued*)

Table 1. Continued

			Percent of average absolute deviation (%AAD)									
			Vapor pressure			Saturated liquid density			Vapor volume			
Compound	n	T_r range	NEW	PR	SRK	NEW	PR	SRK	NEW	PR	SRK	Reference
CF_4	10	0.57–0.97	2.07	1.466	1.794	5.58	6.284	7.585	2.76	2.331	2.843	[a]
CCl_4	27	0.50–0.97	0.49	1.542	0.946	6.64	4.243	10.494	0.58	2.262	0.923	[a]
N_2	13	0.51–0.95	0.51	0.689	1.191	4.11	9.777	3.461	0.45	1.364	1.486	[a]
O_2	17	0.48–0.97	0.28	1.593	1.544	4.17	10.598	3.369	0.72	2.196	1.663	[a]
Ne	9	0.59–0.95	0.14	1.045	1.546	3.84	13.317	4.193	0.99	6.778	1.119	[a]
SO_2	20	0.53–0.98	1.68	2.444	2.144	5.2	2.329	12.948	0.54	2.574	1.900	[a]
Xe	12	0.59–0.97	0.61	1.095	0.813	5.34	7.204	6.441	0.56	2.527	1.025	[a]
Total			0.924	1.325	1.440	5.58	6.07	9.921	1.500	1.991	1.533	

[a] Perry and Green (15).

[b] Smith and Srivastava (16).

Table 2. Prediction of liquid density pure heavy hydrocarbons with new EOS and PREOS (C_5-C_{20}). The experimental data are obtained from Ref. (17)

				AAD%	
Compound	np	ΔP[bar]	ΔT[K]	New	PR
n-C_5H_{12}	19	20–200	393.15	1.994	3.505
n-C_5H_{12}	8	200	293.15–393.15	2.943	4.858
n-C_6H_{14}	17	40–300	483.15	7.510	2.739
n-C_6H_{14}	9	300	343.15–483.15	7.831	4.065
n-C_7H_{16}	9	100–500	573.15	8.475	90.099
n-C_7H_{16}	7	5000	303.15–573.15	10.298	143.288
n-C_8H_{18}	18	30–200	553.15	7.718	4.00
n-C_8H_{18}	8	200	553.15	2.817	0.379
n-C_9H_{20}	10	50–5000	573.15	6.885	78.148
n-C_9H_{20}	6	5000	303.15–573.15	9.559	140.63
n-$C_{10}H_{22}$	19	20.27–202.65	393.15	6.978	5.383
n-$C_{10}H_{22}$	8	202.65	313.15–393.15	9.446	6.419
n-$C_{11}H_{24}$	10	505000	573.15	5.215	76.158
n-$C_{11}H_{24}$	7	5000	303.15–573.15	8.949	138.092
n-$C_{13}H_{28}$	10	50–5000	573.15	4.809	75.753
n-$C_{13}H_{28}$	7	5000	303.15–573.15	9.285	136.11
n-$C_{17}H_{36}$	10	50–5000	573.15	6.630	75.802
n-$C_{17}H_{36}$	6	5000	323.15–573.15	11.533	133.159
n-$C_{20}H_{42}$	10	50–5000	573.15	7.423	76.577
n-$C_{20}H_{42}$	5	5000	373.15–573.15	11.668	130.849
Average	203			7.398	66.3007

$$\mathrm{AAD}\,\% = \frac{1}{np}\sum\left|\frac{\exp - cal}{\exp}\right| \times 100.$$

density from M-DPTG and PR equations of state. The average of absolute deviations for M-DPTG and PR equations of state would be 7.39 and 60.30%, respectively.

Saturation vapor pressure and vapor volume of fluids are shown in Fig. 2 and 3. The aforementioned figures show that there is a good agreement between the experimental data and the obtained results by the modified DPTG equation of state. Different predicted vapor pressure for 25 pure fluids is shown in Fig. 4 and the overall error is between 0–5%. The experimental and predicted enthalpy and entropy of vaporization for some pure substances are also shown in Figs. 5 and 6.

Figure 7 illustrates the predicted and experimental compressibility factor of C_2H_6 versus temperatures and pressures. The reduced temperature changes between 0.92–1.31 and the reduced pressure between 0.02–2.05. It is shown that there is a good agreement between the theoretical and

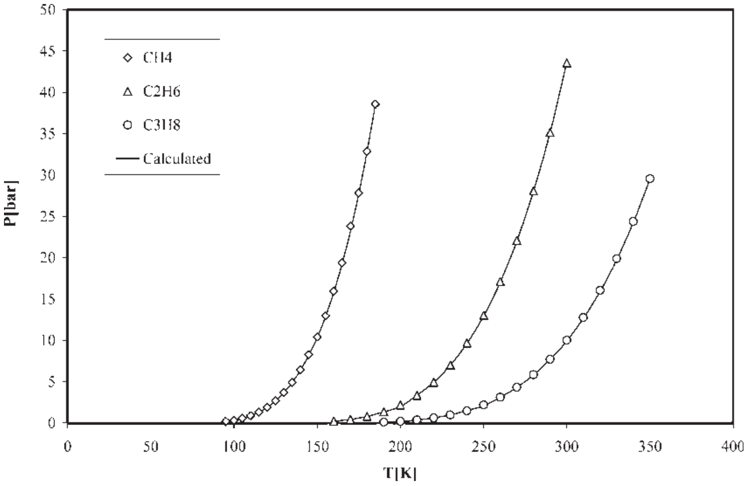

Figure 2. Experimental and predicted vapor pressure of different fluids as a function of temperature.

experimental data at subcritical and supercritical conditions. The second virial coefficient is calculated by using the M-DPTG equation of state by applying the following equation:

$$B(T) = 3b - \frac{a}{RT} \tag{17}$$

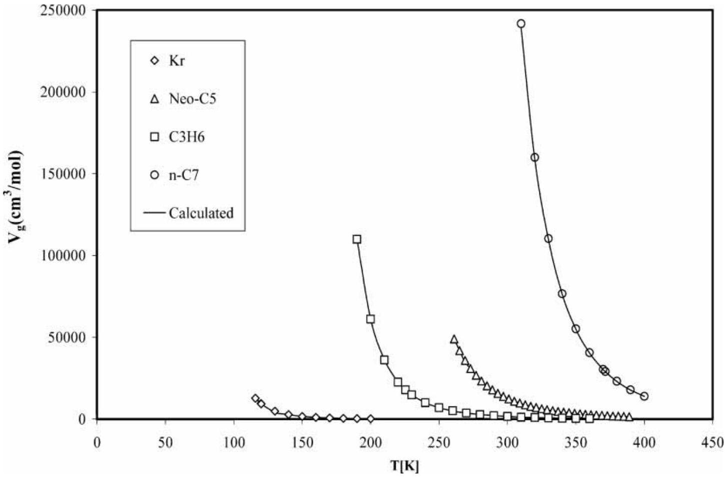

Figure 3. Experimental and predicted vapor volume of different fluids as a function of reduced temperature.

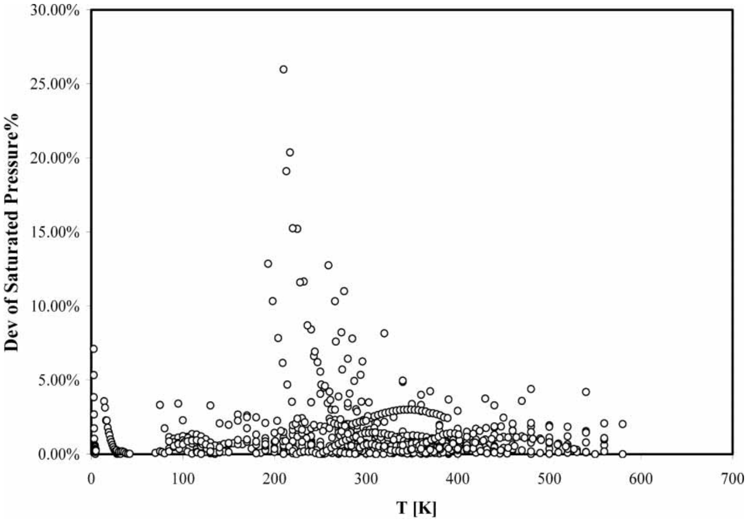

Figure 4. Percent of deviations for predicting the vapor pressure of 25 compounds using the new equation of state.

The experimental values of the second virial coefficient for N_2 and the obtained results by the M-DPTG, PR, and SRK equations of state is shown in Fig. 8.

Also, the surface tension of normal hydrocarbons (C_1–C_{10}) is calculated by the M-DPTG equation. The empirical relation between surface tension and

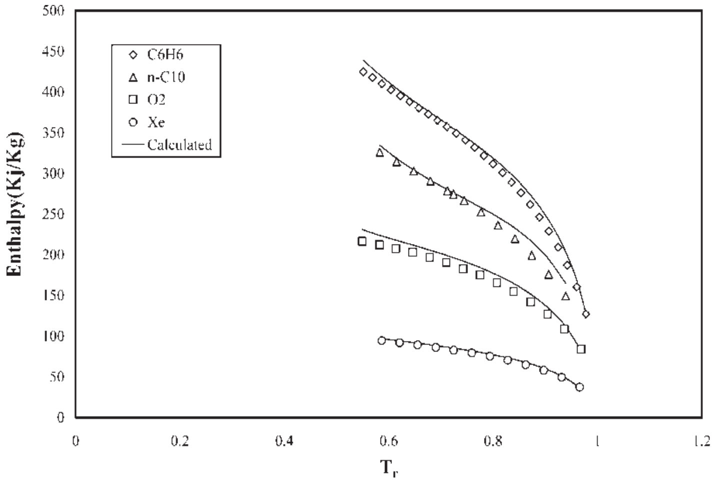

Figure 5. Experimental and predicted enthalpy of different fluids as a function of reduced temperature.

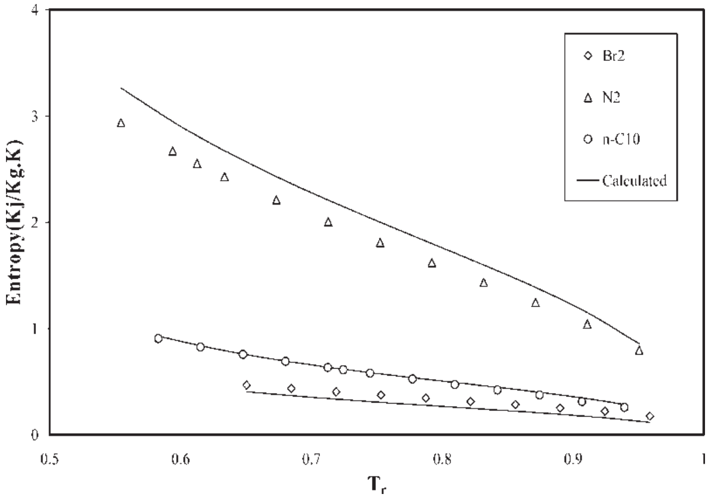

Figure 6. Experimental and predicted entropy of different fluids as a function of reduced temperature.

difference densities of liquid and vapor would be written (19):

$$\sigma = [P_{ch}(\rho_l - \rho_v)]^4 \tag{18}$$

where P_{ch} is Parachor constant which would be different for each component.

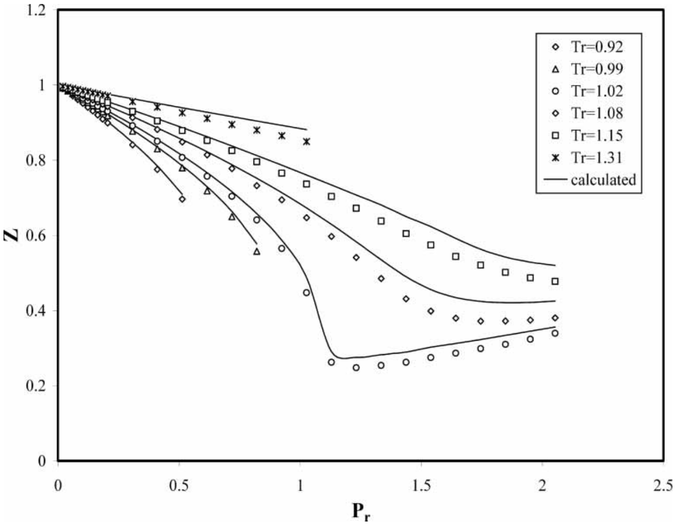

Figure 7. Experimental and calculated compressibility factor of C_2H_6 as a function of reduced temperature (experimental data from Ref. (17)).

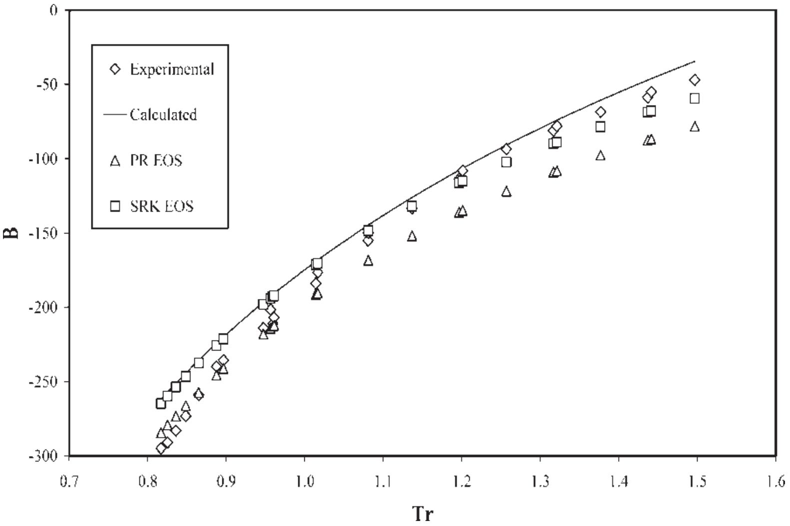

Figure 8. Second virial coefficient of N_2 as a function of reduced temperature (experimental data from Ref. (18)).

Hugill and van der Welsenes proposed the following correlation for the prediction of the Parachor constant (20):

$$P_{ch} = 40.1684(0.151 - 0.464\omega)T_c^{13/12}/P_c^{5/6} \tag{19}$$

Table 3. Parachor constant and average absolute deviation of the new EOS and Hugill Model for normal hydrocarbons

	np	P_{ch}(Model)	AAD%[a]	AAD%[b]
CH_4	6	72.12	0.41	20.81
C_2H_6	6	114.5	2.32	27.96
C_3H_8	6	154.8	11.77	39.50
C_4H_{10}	9	182.9	5.01	25.33
C_5H_{12}	3	223.3	1.50	20.33
C_6H_{14}	6	257.5	3.32	24.60
C_7H_{16}	9	295.3	4.75	26.66
C_8H_{18}	7	319.4	2.74	47.80
C_9H_{20}	9	351.0	4.51	50.20
$C_{10}H_{22}$	9	388.6	5.05	45.87
	70		4.13	32.91

[a] NEW EOS.
[b] Hugill model.

In this work, the Parachor constant is obtained by minimization of the following objective function:

$$\Omega = \sum_i \left| \frac{\gamma_{\exp} - \gamma_{cal}}{\gamma_{\exp}} \right|_i \tag{20}$$

The experimental data of surface tension were reported by Jasper (21). Parachor constant and the absolute of average deviations for M-DPTG are presented in Table 3.

The results show that M-DPTG equation of state can accurately predict surface tension of pure fluids.

Finally, the M-DPTG equation of state is applied to calculate phase behavior of mixtures fluids. For mixtures the van der Waals mixing rules could be applied to estimate *a* and *b*:

$$a = \sum \sum x_i x_j a_{ij} \tag{21}$$

$$b = \sum x_i b_i \tag{22}$$

$$a_{ij} = (a_{ii} a_{jj})^{1/2}(1 - k_{ij}) \tag{23}$$

Table 4. Average absolute deviation the calculated bubble point pressure for many binary mixtures

			T range		(%AAD) P			
No.	Mixture	np	Min	Max	NEW	PR	SRK	Ref.
1	CO_2–Ethanol	56	291.15	313.14	10.717	25.852	22.27	(22)
2	CO_2–i-butanol	31	288.2	313.2	14.420	36.600	35.19	(23)
3	CO_2–i-pentanol	51	288.2	313.2	5.111	33.182	31.72	(23)
4	CH_4–n-C_4H_{10}	24	166.48	381.4	6.972	5.445	3.985	(24)
5	CO_2–n-C_4H_{10}	36	310.93	410.93	7.704	17.954	17.97	(24)
6	CO_2–C_2H_6	7	252.95	252.95	23.840	26.691	26.96	(24)
7	N_2–CH_4	24	88.71	155.37	8.165	9.506	9.248	(24)
8	Methanol–H_2O	18	373.15	473.15	6.670	7.744	7.574	(24)
9	Propanol–H_2O	12	417.76	395.71	24.140	20.229	17.57	(24)
10	Methanol–Buthanol	10	402.35	392.35	3.480	6.785	6.964	(24)
11	Ethanol–H_2O	9	404.35	397.85	39.150	38.072	35.85	(24)
12	Methyl acetate–Methanol	13	370.15	377.55	1.270	4.928	5.136	(24)
13	Ethanol–$CHCl_3$	29	308.15	308.15	11.484	12.264	16.29	(24)
14	C_6H_6–Acetonitrile	6	318.15	318.15	19.660	16.894	19.86	(24)
15	Acetonirile–H_2O	4	349.95	352.55	30.296	17.107	14.09	(24)
16	CO_2–$CHCl_3$	29	303.15	333.15	4.173	16.856	15.53	(25)
17	CO_2–Toluene	43	308.16	328.2	9.040	036.904	36.31	(26)
	Average	402			13.311	19.590	18.971	

where k_{ij} is the interaction parameter and is zero for all binary systems (13). In order to calculate phase behavior of binary mixtures, fugacity coefficient of ith component i is necessary so that it could be obtained by using M-DPTG equation of state as follow:

$$\ln \phi_i = 3\left[\frac{\partial(nb_m)/\partial n_i}{v-b_m} - \ln\left(1-\frac{b_m}{v})\right)\right] - \frac{a_m/(b_mRT)}{v+b_m}\frac{\partial(nb_m)}{\partial n_i} + \frac{a_m}{b_mRT}\left\{\frac{1}{a_m}\left[\frac{1}{n}\frac{\partial(n^2a_m)}{\partial n_i}\right] - \frac{1}{b_m}\frac{\partial(nb_m)}{\partial n_i}\right\}\ln\left(\frac{v}{v+b_m}\right) - \ln Z \qquad (24)$$

The modified DPTG equation of state is applied for VLE calculation of 17 binary mixtures. The results of the bubble point pressures and vapor mole fractions using the NEW, PR, and SRK equations of state are reported in Tables 4 and 5. The average of absolute deviations of bubble pressure are

Table 5. Average absolute deviation the calculated mole fraction of vapor phase for many binary mixtures

			T range		(%AAD) y_i			
No.	Mixture	np	Min	Max	NEW	PR	SRK	Ref.
1	CO_2–Ethanol		291	313.1	0.595	0.516	0.566	(22)
2	CO_2–i-butanol	56	288	313.2	0.718	0.667	0.692	(23)
3	CO_2–i-pentanol	31	288	313.2	1.189	1.183	1.197	(23)
4	CH_4–n-C_4H_{10}	51	166	381.4	0.023	0.010	0.015	(24)
5	CO_2–n-C_4H_{10}	24	311	411	6.750	18.220	18.65	(24)
6	CO_2–C_2H_6	36	253	253	8.940	23.320	23.47	(24)
7	N_2–CH_4	7	88.7	155.4	2.830	5.434	4.462	(24)
8	Methanol–H_2O	24	373	473.2	1.560	1.890	1.640	(24)
9	Propanol–H_2O	18	418	395.7	14.936	15.415	14.48	(24)
10	Methanol–Buthanol	12	402	392.4	2.260	3.606	3.727	(24)
11	Ethanol–H_2O	10	404	397.9	9.092	8.032	7.782	(24)
12	Methyl acetate–Methanol	9	370	377.6	3.260	5.226	5.017	(24)
13	Ethanol–$CHCl_3$	13	308	308.2	21.580	30.980	29.76	(24)
14	C_6H_6–Acetonitrile	29	318	318.2	11.770	19.541	19.50	(24)
15	Acetonirile–H_2O	6	350	352.6	23.864	18.434	16.99	(24)
16	CO_2–$CHCl_3$	4	303	333.2	2.044	1.949	2.034	(25)
17	CO_2–Toluene	29	308	328.2	1.006	0.506	0.491	(26)
	Average	402			6.612	9.113	8.851	

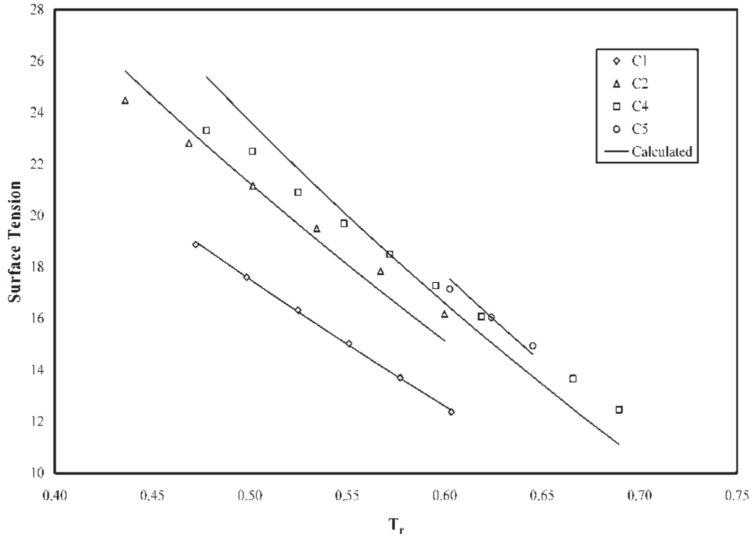

Figure 9. Experimental and predicted surface tension of four normal hydrocarbons as a function of reduced temperature (experimental data from Ref. (21)).

13.311, 14.445, and 18.971% and for vapor mole fraction are 6.162, 6.931, and 8.851% for the NEW, PR, and SRK equations of state (Fig. 9). The bubble point pressures of $CO_2-C_3H_3Cl$ system are plotted in Fig. 10. Also, the calculated results for binary mixtures of hydrocarbons (Tables 6).

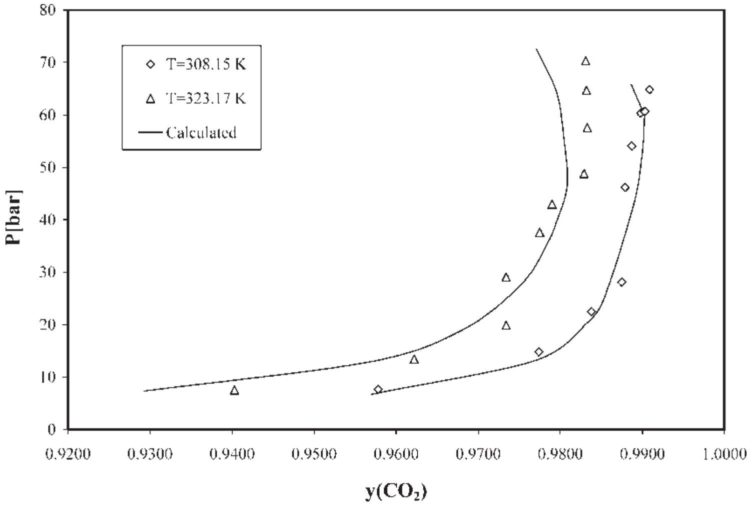

Figure 10. Pressure-equilibrium phase composition for CO_2-C_2H_3Cl (experimental data from Ref. (26)).

Table 6. The average absolute deviation of the calculated density of mixtures of hydrocarbons using NEW EOS, PR, and SRK equations of state

			ΔP	AAD%			
Mixture	T[K]	np	(atm)	NEW	SRK	PR	Ref.
$C_1 + nC_{10}$	423.15	7	10–100	14.699	15.983	7.532	(27)
	373.15	10	10–100	1.912	17.616	8.776	(27)
	348.15	10	10–100	5.526	17.852	9.969	(27)
	323.15	10	10–100	6.774	18.965	10.804	(27)
	298.15	10	10–100	8.334	19.607	11.216	(27)
	273.15	10	10–100	11.432	24.797	15.783	(27)
	248.15	10	10–100	12.197	21.449	12.442	(27)
$C_1 + nC_6$	423.15	10	10–100	15.191	15.760	9.030	(28)
	373.15	10	10–100	4.935	12.347	4.574	(28)
	348.15	10	10–100	2.847	12.545	4.395	(28)
	323.15	10	10–100	1.771	11.831	3.621	(28)
	298.15	10	10–100	2.029	11.574	3.046	(28)
	273.15	10	10–100	3.548	11.422	2.736	(28)
	248.15	10	10–100	4.314	11.773	2.954	(28)
	223.15	8	10–80	5.891	11.912	2.352	(28)
$C_1 + nC_9$	423.15	10	10–100	2.689	16.504	9.171	(29)
	373.15	10	10–100	3.621	15.858	7.964	(29)
	348.15	22	10–313	4.725	15.310	8.883	(29)
	323.15	23	10–318	6.421	15.480	9.097	(29)
	298.15	23	10–319	7.848	15.752	9.445	(29)
	273.15	23	10–318	9.148	16.177	9.843	(29)
	248.15	10	10–100	10.359	19.058	10.075	(29)
	223.15	10	10–100	11.395	19.205	10.072	(29)
Average		276		6.852	16.034	7.990	

The M-DPTG equation of state predicts densities of mixtures more accurately than SRK and PR equations of state.

CONCLUSION

The DPTG cubic equation of state is modified to calculate phase behavior of pure fluids and mixtures. The vapor pressure, liquid density, and vapor volume of pure fluids, the enthalpy and entropy of vaporization, second virial coefficient, normal hydrocarbons density, and the surface tension of pure fluids are calculated by the modified equation of state. Also, M-DPTG is applied for prediction of bubble pressure and mole fraction of vapor phase for binary mixtures and mixtures of hydrocarbons density. The results show that the modified DPTG equation of state can accurately predict phase behavior of fluids.

REFERENCES

1. Van der Waals, J.H. (1873) On the Continuity of the Gases and Liquid State. Doctoral Dissertation, Leiden University, Leiden, The Netherlands.
2. Redlich, O. and Kwong, J.N.S. (1949) On the thermodynamics of solutions, V: An equation of state. Fugacities of gaseous solutions. *Chem. Rev.*, 44: 233.
3. Soave, G. (1972) Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.*, 72: 1197.
4. Peng, D.Y. and Robinson, D.B. (1976) A new two-constant equation of state. *Ind. Eng. Chem. Fundam.*, 15: 59.
5. Stryjek, R. and Vera, J.H. (1986) PRSV: An improved Peng-Robinson equation of state for pure compounds and mixtures. *Can. J. Chem. Eng.*, 64: 323.
6. Fotouh, K. and Shukla, K. (1997) An improved Peng-Robinson equation of state with a new temperature dependent attractive term. *Chem. Eng. Comm.*, 159: 209.
7. Zabaloy, M.S. and Brignole, E.A. (1997) On volume translation in equations of state. *Fluid Phase Equilib.*, 140: 87.
8. Souahi, F. et al. (1998) Development of a new form for the alpha function of the Redlich-Kwong cubic equation of state. *Fluid Phase Equilib.*, 153: 73.
9. Feyzi, F. et al. (1998) Improving cubic equations of state for heavy reservoir fluids and critical region. *Chem. Eng. Comm.*, 167: 147.
10. Gasem, K.A.M. et al. (2001) A modified temperature dependence for the Peng-Robinson equation of state. *Fluid Phase Equilib.*, 181: 113.
11. Mohsen-Nia, M., Modarres, H., and Mansoori, G.A. (1995) A cubic equation of state based on a simplified hard-core model. *Chem. Eng. Comm.*, 131: 15.
12. Mohsen-Nia, M., Modarres, H., and Mansoori, G.A. (2003) A cubic hard-core equation of state. *Fluid Phase Equil.*, 206: 27.
13. Dashtizadeh, A. et al. (2006) A new two-parameter cubic equation of state for predicting phase behavior of pure compounds and mixtures. *Fluid Phase Equilib.*, 242: 19.
14. Dashtizadeh, A., Pazuki, G.R., and Edalat, M. (2005) Simple cubic EOS predicts properties of pure hydrocarbons, mixtures. *Oil and Gas J.*, 103: 46.
15. Perry, R.H. and Green, D.W. (1988) *Perry's Chemical Engineers' Handbook*, 6th Edn.; McGraw Hill: Tokyo.
16. Smith, B.D. and Srivastava, R. *Thermodynamic Data for Pure Compounds*; Elsevier: 1986.
17. Vargaftik, N.B., Vinogradov, Y.K., and Yargin, V.S. (1996) *Handbook of Physical Properties of Liquids and Gases (Pure Substances and Mixtures)*, 3rd Edn.; Begell House, Inc.: New York.
18. Dymond, J.H. and Smith, E.B. (1980) *The Virial Coefficient of Pure Gases and Mixtures: A Critical Compilation*; Oxford University Press: Oxford, U.K.
19. Escobedo, J.A. and Mansoori, G.A. (1996) Surface tension prediction for pure fluids. *AIChE J.*, 42: 1425.
20. Hugill, J.A. and Van Welsenes, A.J. (1986) Surface tension: A simple correlation for natural gas + condensate systems. *Fluid Phase Equilib.*, 29: 383.
21. Jasper, J.J. (1972) The surface tension of pure liquids compounds. *J. Phys. Chem. Ref. Data.*, 1: 841.
22. Day, C.-Y., Chang, C.J., and Chen, C.-Y. (1999) Phase equilibrium of ethanol + CO_2 and acetone + CO_2 at elevated pressure. *J. Chem. Eng. Data*, 44: 365.
23. da Silva, M.V. and Barbosa, D. (2002) High pressure vapor-liquid equilibrium data for the systems carbon dioxide/2-methyl-1-propanol and carbon dioxide/3-nethyl-1-butanol at 288.2,303.2 and 313.2 K. *Fluid Phase Equilib.*, 198: 229.

24. Winnick, J. (1997) *Chemical Engineering Thermodynamics*; John Wiley: New York.
25. Scurto, A.M. et al. (2001) Experimental measurement and modeling of the vapor-liquid equilibrium of carbon dioxide + chloroform. *Fluid Phase Equilib.*, 190: 135.
26. Fink, S.D. and Hershey, H.C. (1990) Modeling the vapor-liquid equilibria of 1,1,1-trichloroethane + carbon dioxide and toluene + carbon dioxide at 308, 323 and 353 K. *Ind. Eng. Chem. Res.*, 29: 295.
27. Beaudoin, J.N. and Kohn, J.P. (1967) Multiphase and volumetric equilibria of methane-n-decane binary system at temperatures between -36° and 150° C. *J. Chem. Eng. Data*, 12: 189.
28. Shima, J. and Kohn, J.P. (1962) Multiphase and volumetric equilibria of methane-n-hexane binary system at temperatures between -1.10° and 150° C. *J. Chem. Eng. Data*, 7: 3.
29. Shipman, L.M. and Kohn, J.P. (1966) Heterogeneous phase and volumetric equilibrium in the methane-n-nonane system. *J. Chem. Eng. Data*, 11: 176.