



A new three-parameter cubic equation of state for calculation physical properties and vapor–liquid equilibria

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ABSTRACT

A new three-parameter cubic equation of state is presented by combination of a modified attractive term and van der Waals repulsive expression. Also a new alpha function for the attractive parameter of the new EOS is proposed. The new coefficients of alpha function and the other parameters of the attractive term are adjusted using the data of the saturated vapor pressure and liquid density of almost 60 pure compounds including heavy hydrocarbons. The new EOS is adopted for prediction of the various thermophysical properties of pure compounds such as saturated and supercritical volume, enthalpy of vaporization, compressibility factor, heat capacity and sound velocity. Following successful application of the new EOS for the pure components, using vdW one-fluid mixing rules, the new EOSs are applied to prediction of the bubble pressure and vapor mole fraction of the several binary and ternary mixtures. The accuracy of the new EOS for phase equilibrium calculation is demonstrated by comparison of the results of the present EOSs with the PT, PR, GPR and SRK cubic EOSs.

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1. Introduction

Equation of state (EOS) is a powerful tool in accurate representation of thermodynamic properties of a wide variety of pure fluids in a wide range of temperature and pressure. It can also be applied for calculation of thermodynamic properties of the mixtures using proper mixing rule. Based on the intermolecular interactions, the developed EOSs have been classified into two categories as was indicated by Wei and Sadus [1]. The first group of EOS is based on the van der Waals type of cubic equation of state and the other group is developed by molecular-based approach. Based on molecular principles, construction of equations of state has been started by thermodynamic perturbation theory that leads to several theories such as SAFT [2] and PHCT [3]. In the recent years the molecular-based approaches have been extended properly to improve the theoretical backbone of EOS using statistical thermodynamics. These molecular-based equations of state have been presented for modeling of the vapor–liquid equilibria of some complex systems such as polymer solutions and associated mixtures [1]; however for hydrocarbon and polar simple molecules the cubic EOS has still superiority so that the improvements in molecular theories are introduced some complexities. Thus, due to relative simplicity of cubic Equation of State, CEOS, it is popular in calculation of physical properties applicable in chemical and physical processes to design of chemical, petrochemical and envi-

ronmental industries. Since van der Waals cubic equation of state, many modifications have been developed to improve accuracy of cubic equations of state for precise calculation of physical properties of pure compounds and mixtures. These modifications may be categorized in two approaches so that the first method is based either on construction of a new equation of state by developing a new attractive or repulsive expression or a new combination of the available attractive and repulsive terms [4–15]. Attempt in the second approach is focused to improve the temperature dependence of the attractive parameter through a new alpha function [16–21].

Following Redlich–Kwong EOS [4], that introduced the co-volume parameter, b , and a simple temperature function in attractive part of vdW CEOS, several modifications on both repulsive and attractive expressions of CEOS have been proposed. These various versions have been extensively reviewed by the others [1,22,23]. The several expressions have been developed for the hard sphere term of CEOS, such as those were proposed by Scott [24], Kim et al. [25] and Mohsen-Nia et al. [12]. Although these modifications of the repulsive term are in better agreement with the simulation data of hard sphere, however the common expression, which is widely used for repulsive term of a cubic EOS, is the vdW repulsive term. The empirical modification of the attractive part of CEOS has been done not only by changing its form, but also in some cases by introducing one or even more extra parameters [10]. On the other hand, the progresses in developing of the new alpha function were mainly started by the soave modification on RK EOS [5], in which an expression in terms of acentric factor was introduced as a temperature dependence polynomial. The various alpha functions with their advantages and disadvan-

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tages were reviewed by the others [21,26,27]. The Soave-type alpha functions, such as Mathias and Copeman [18], have some limitations as passing through minima with increasing temperature. A correct form of the alpha function behaves such that to decrease monotonically with increasing temperature. Several investigators tried to introduce a switching function [16], or components specific parameter [19]; however these types of alpha functions are less desirable than a generalized alpha function. Recently the alpha functions have been improved to correlation of the vapor pressure of the heavy hydrocarbons and polar components so that no need for switch function and correcting of the limiting value at high reduced temperatures [21].

The present work is a combination of the both aforementioned approaches, so in this study, first a modified attractive term is proposed with keeping the vdW repulsive term, and second a new alpha function is proposed, so that a new three-parameter cubic equation of state is introduced. The new alpha function has the characteristics of a correct behavior of an alpha function that has been explained above. In this work, the new CEOS is validated by correlation and prediction of physical properties of the pure components such as saturated vapor pressure, liquid density, vapor volume, enthalpy of vaporization, heat capacity, sound velocity and supercritical properties. Furthermore, using one-fluid vdW mixing rules, the new CEOS is applied for calculation of the bubble pressure and vapor mole fraction of several binary and ternary mixtures. In addition, the phase envelope calculation of a typical synthetic natural gas (SNG) is carried out using the new CEOS.

2. The new cubic equation of state

The three-parameter Patel–Teja EOS was presented as [8]:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+c(v-b)} \quad (1)$$

Alternatively, we may propose another new form of three parameters CEOS as:

$$P = \frac{RT}{v-b} - \frac{a(T)}{(v+nb)(v+mc)} \quad (2)$$

where $a(T)$ is a function of critical temperature, critical pressure and acentric factor. The parameter b is a function of critical temperature and critical pressure. The parameter c as a third parameter was introduced by Patel and Teja [8]. As a matter of fact, Eqs. (1) and (2) are the modification of the PR EOS [3] so that the parameter b in the second parenthesis of the denominator of the attractive term is replaced by third parameter “ c ”. The constants n and m in Eq. (2) have the unique values for a given CEOS, for example, if one takes $n=1-\sqrt{2}$ and $m=1+\sqrt{2}$, PR [3]; $n=0$ and $m=1$, SRK [2]; $n=-0.5$ and $m=3$, TST [10]; $n=1-\sqrt{3}$ and $m=1+\sqrt{3}$ NM [9] cubic equations of state are introduced.

The three parameters, a , b and c are calculated by the critical properties of the pure components through rearrangement of Eq. (2) as

$$v^3 + \left[mc + (n-1)b - \frac{RT}{P} \right] v^2 + \left[nmcb - \left(b + \frac{RT}{P} \right) (nb + mc) + \frac{a(T)}{P} \right] v - \left[nmcb \left(b + \frac{RT}{P} \right) + \frac{a(T)b}{P} \right] = 0 \quad (3)$$

Solving Eq. (2) at the critical point and setting the first and second derivatives of Eq. (2) equal to zero at the critical point, and assigning the following relations for the three parameters of EOS as

$$a(T) = \Omega_a \frac{R^2 T_c^2}{P_c} \alpha(T) \quad (4)$$

$$b = \Omega_b \frac{RT_c}{P_c} \quad (5)$$

$$c = \Omega_c \frac{RT_c}{P_c} \quad (6)$$

$$\bar{Z}_c = \frac{P_c v_c}{RT_c} \quad (7)$$

The following three equations are obtained with $\alpha(T_c)=1$:

$$m\Omega_c = 1 - 3\bar{Z}_c + (1-n)\Omega_b \quad (8)$$

$$\Omega_b^3 + (2-n^2+n-3\bar{Z}_c)\Omega_b^2 + (3\bar{Z}_c^2 + (1+n)(1-3\bar{Z}_c))\Omega_b - \bar{Z}_c^3 = 0 \quad (9)$$

$$\Omega_a = 3\bar{Z}_c^2 - nm\Omega_b\Omega_c + (n\Omega_b + m\Omega_c)(\Omega_b + 1) \quad (10)$$

where R , T_c and P_c stand for gas constant, critical temperature and critical pressure. Ω_b is the smallest positive root of Eq. (9) and the parameter c is calculated by combination of Eqs. (6) and (8) as

$$c = \frac{1}{m} \left[\frac{RT_c}{P_c} (1 - 3\bar{Z}_c + (1-n)\Omega_b) \right] \quad (11)$$

It can be concluded that the parameter c is always proportional to inverse of m . Since the product “ mc ” is appeared together not as two separated constants in all the thermodynamic properties that are derived by the new CEOS, so the value of m will be canceled out by substitution of Eq. (11) for parameter c . Thus, the value of parameter m is arbitrary and consequently the new CEOS will be independent of m . Hence, to represent a close form of the new CEOS, the value of m is chosen as same value as n .

It is common to suppose an empirical critical compressibility factor rather experimental critical compressibility factor, so \bar{Z}_c is expressed as a function of the acentric factor:

$$\bar{Z}_c = k_1 + k_2\omega + k_3\omega^2 \quad (12)$$

where ω denotes acentric factor and the coefficients, k_i , are the adjustable parameters. As mentioned, a variety of the alpha functions were suggested [20,26,27]. In this work, a new alpha function is proposed as

$$\alpha = \exp[(k_4 + k_5 T_r)(1 - (k_6 + k_7\omega + k_8\omega^2)^{\ln T_r})] \quad (13)$$

where $T_r = T/T_c$ is defined as the reduced temperature. Eq. (13) may be deduced as a modification of the alpha function which was proposed by Gasem et al. [21] as

$$\alpha = \exp[(k_4 + k_5 T_r)(1 - T_r^{(k_6 + k_7\omega + k_8\omega^2)})] \quad (14)$$

To apply the new CEOS to real fluids, one needs to determine the unknown constants k_i , n and m in Eqs. (2)–(14). We explain that for optimization of the VLE data either the vapor pressure [21] or the simultaneous data of vapor pressure and saturated liquid density [1,2,12,13,25] of pure components have been used. For calculation the parameters of molecular-based EOS such as SAFT, PHCT and CPA EOSs [1,2], the vapor pressure and liquid density of the pure component were fitted simultaneously. Also, the parameters of the cubic equation of state such as Mohsen-Nia et al. [12], Dashtizadeh et al. [13] and Kim et al. [25] were obtained by the same objective function which used in this work but with the different weighting factors for vapor pressure and liquid density. One should mention that Dashtizadeh et al. [13] reported the weights of vapor pressure and liquid density in their objective function as 0.8 and 0.2, respectively. So to obtain the remaining constants, i.e. k_1 to k_8 and n , calculation of the vapor–liquid equilibria for 58 pure components are performed using the following objective function:

$$\sigma = \sum_{i=1}^{np} \left(0.7 \left| \frac{P_i^{cal} - P_i^{exp}}{P_i^{exp}} \right| + 0.3 \left| \frac{\rho_i^{cal} - \rho_i^{exp}}{\rho_i^{exp}} \right| \right) \quad (15)$$

where P and ρ are the vapor pressure and saturated liquid density of pure component, respectively, and n_p is the number of data points. The superscripts “*exp*” and “*cal*” stand for experiment and calculated, respectively. For more investigation, optimization of the parameters is performed with different weighting of vapor pressure and liquid density in the objective function; however the optimum weights are used as shown in Eq. (15). So to obtain the best results, the following values are obtained for the new alpha function as

$$n = m = -0.5 \quad (16)$$

$$(\bar{Z}_c)_1 = 0.3181 - 0.0375\omega - 0.0300\omega^2 \quad (17)$$

$$(\alpha)_1 = \exp[(4.5298 + 2.8698T_r)(1 - (1.0529 + 0.2065\omega - 0.0487\omega^2)\ln T_r)] \quad (18)$$

For comparison, the alpha function proposed by Gasem et al. [21] is adopted as another alternative alpha function in the new CEOS. So repeating the above optimization, the similar results are obtained as

$$n = m = -0.5 \quad (19)$$

$$(\bar{Z}_c)_2 = 0.3175 - 0.0364\omega - 0.0245\omega^2 \quad (20)$$

$$(\alpha)_2 = \exp[(3.058 + 1.5479T_r)(1 - T_r^{(0.0821+0.3042\omega-0.0730\omega^2)})] \quad (21)$$

Therefore, in this work two new cubic equations of states as the HKM1, i.e. Eqs. (2), (16)–(18) and HKM2, Eqs. (2), (19)–(21), with the two alpha functions 1 and 2 are presented.

3. Results and discussion

To demonstrate the accuracy of the new EOSs, calculation of some thermodynamic properties of the pure components and mixtures are carried out. Table 1 presents the pure fluids, which are used to correlate the physical properties, with the critical properties, acentric factor, number of data points (n_p), and ranges of the reduced temperature for each component. Table 2 shows the percent absolute average deviation, AAD%, to correlate the vapor pressure and liquid density of pure hydrocarbons containing heavy alkanes up to C₂₄, using the original PR, Gasem et al. modification of PR, GPR [21], SRK, Patel–Teja (PT) and new three-parameter equations of state with two new alpha functions 1 and 2, i.e., HKM1 and HKM2 EOSs. In regard to this table, using the new EOSs and the new alpha functions, correlation of the vapor pressure results better agreement with experiment than the other equations of state. Using the new HKM1 EOS, Eqs. (2), (16)–(18), the value of the AAD% for the saturated vapor pressure is 1.42, while this value for PR, GPR, SRK, PT and the HKM2 EOS, Eqs. (2), (19)–(21), are 6.01%, 1.84%, 2.02%, 4.97% and 1.47%, respectively. However, the results of the liquid density show that the HKM1 EOS, with using the new alpha function, presents more accurate results than the PR, GPR, SRK and PT equations of state and is close to the results of the liquid density using the HKM2 EOS. Table 3 shows the AAD% in predicting of the vapor molar volume and enthalpy of vaporization for near 50 pure components using various and the new EOSs. As Table 3 shows the improvement in calculation of the vapor molar volume by the new three-parameter HKM1 EOS is obvious in comparison to the PR, GPR, SRK, PT and HKM2 CEOS. Similarly as Table 3 indicates, the calculation of the enthalpy of vaporization of the pure components shows that the HKM1 EOS can predict the enthalpy of vaporization with higher accuracy than the PR, GPR, SRK, PT and HKM2 CEOS. One should be noted that assigning the different values for the parameter “*m*” has no effect on the results of the calculations of the physical properties using the HKM1 EOS as explained by Eq. (14).

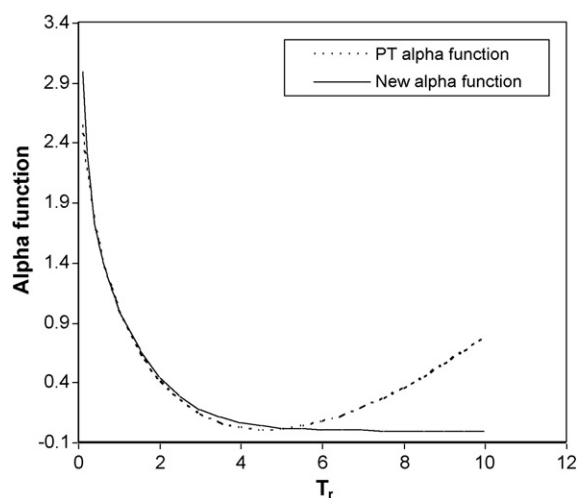


Fig. 1. Variation of the new and PT alpha function for a typical fluid respect to reduced temperature.

Fig. 1 shows a typical fluid that presents the limit of the new alpha function which approaches asymptotically at high temperatures. This demonstrates the theoretical limiting behavior of a precise alpha function as mentioned by the others [20]. However, the alpha function of the original PT EOS, which is a soave-type alpha function, doesn't obey this correct feature.

As shown in Table 4, the predictability of the new EOS is also examined by calculation of the supercritical molar volume. Although the PT EOS presents the highest accuracy in comparison to the other EOSs, however, the predictions of the both new EOSs demonstrate the close results to the PT EOS. On the other hand, one can see the results of the SRK, PR and GPR EOSs indicating less accuracy in prediction of vapor molar volume of the selected pure compounds in the supercritical region. In the next step, the validity and predictability of the new CEOSs with the new alpha function are examined for calculation of the heat capacity, sound velocity and compressibility factor for several pure compounds. Using HKM1 EOS, Fig. 2 shows the calculated heat capacity (C_p) versus temperature for methane at different pressures. This figure demonstrates that the good agreement between the experimental values of methane heat capacity (C_p) and the predicted values by

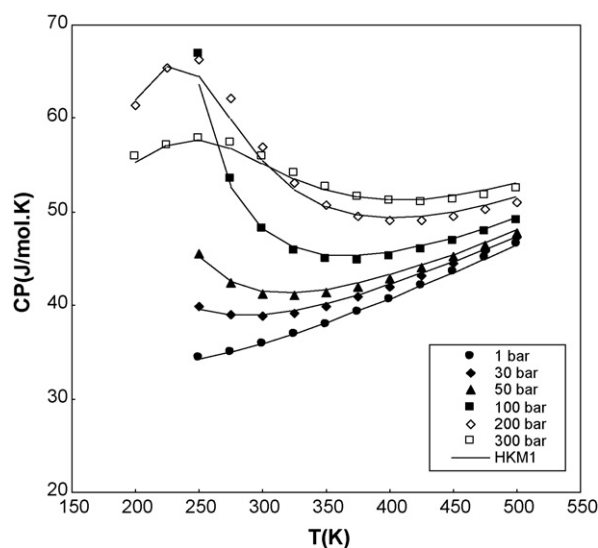


Fig. 2. The experimental values [29] and calculated heat capacity of methane at various pressures.

Table 1

The pure compounds, the number of experimental data points, the range of reduced temperature used in this work.

Component	T_c (K)	P_c (bar)	ω	n_p	T_r range	Ref.
C ₁	190.56	45.99	0.0113	19	0.50–0.97	[28]
C ₂	305.33	48.71	0.1004	15	0.52–0.98	[28]
C ₃	369.82	42.47	0.1542	17	0.51–0.95	[28]
<i>n</i> -C ₄	425.16	37.96	0.2004	20	0.54–0.99	[28]
<i>i</i> -C ₄	408.1	36.48	0.181	17	0.54–0.98	[28]
<i>n</i> -C ₅	469.7	33.7	0.251	57	0.40–1.00	[29]
<i>n</i> -C ₆	507.82	30.34	0.304	30	0.41–0.98	[29]
<i>n</i> -C ₇	540.1	27.35	0.346	11	0.57–0.74	[28]
<i>n</i> -C ₈	568.8	24.97	0.396	12	0.60–0.98	[28]
<i>n</i> -C ₉	594.55	22.81	0.446	30	0.50–0.99	[29]
<i>n</i> -C ₁₀	618.59	21.3	0.4885	14	0.55–0.94	[28]
<i>n</i> -C ₁₂	658.66	18.32	0.5746	28	0.57–0.98	[29]
<i>n</i> -C ₁₄	692.17	15.92	0.6572	10	0.5–0.76	[30]
<i>n</i> -C ₁₄	692.17	15.92	0.6572	11	0.6–0.76	[31]
<i>n</i> -C ₁₄	692.17	15.92	0.6572	16	0.54–0.85	[32]
<i>n</i> -C ₁₆	720.67	13.94	0.7368	10	0.52–0.78	[30]
<i>n</i> -C ₁₆	720.67	13.94	0.7368	26	0.49–0.77	[33]
<i>n</i> -C ₁₆	720.67	13.94	0.7368	20	0.54–0.8	[32]
<i>n</i> -C ₁₆	720.67	13.94	0.7368	16	0.64–0.78	[34]
<i>n</i> -C ₁₈	745.25	12.29	0.8137	17	0.55–0.79	[32]
<i>n</i> -C ₁₈	745.25	12.29	0.8137	23	0.5–0.76	[33]
<i>n</i> -C ₂₀	766.66	10.91	0.8883	21	0.51–0.75	[33]
<i>n</i> -C ₂₀	766.66	10.91	0.8883	21	0.47–0.61	[35]
<i>n</i> -C ₂₀	766.66	10.91	0.8883	29	0.5–0.81	[36]
<i>n</i> -C ₂₀	766.66	10.91	0.8883	32	0.56–0.76	[32]
<i>n</i> -C ₂₂	785.48	9.73	0.9608	16	0.45–0.59	[35]
<i>n</i> -C ₂₂	785.48	9.73	0.9608	12	0.58–0.73	[33]
<i>n</i> -C ₂₄	802.12	8.71	1.0313	12	0.46–0.58	[35]
<i>n</i> -C ₂₄	802.12	8.71	1.0313	13	0.56–0.73	[33]
C ₂ H ₄	282.3	50.403	0.086	12	0.57–0.96	[28]
C ₂ H ₂	308.7	62.47	0.188	12	0.65–0.97	[28]
C ₃ H ₆	365.6	46.65	0.137	19	0.52–0.98	[28]
C ₆ H ₆	562.2	48.979	0.209	25	0.55–0.98	[28]
C ₆ H ₅ CH ₃	591.8	41.04	0.262	20	0.51–0.98	[28]
Ar	150.9	48.98	0	13	0.56–0.96	[28]
CHCl ₃	536.6	54.72	0.228	14	0.52–0.99	[28]
CF ₄	227.5	37.45	0.174	10	0.57–0.97	[28]
CCL ₄	556.4	45.6	0.191	27	0.50–0.97	[28]
CO ₂	304.2	73.83	0.224	14	0.72–0.99	[28]
Cl ₂	417.15	77.1	0.073	19	0.53–0.97	[28]
CO	132.91	34.96	0.048	8	0.72–0.98	[28]
Ne	44.4	26.53	−0.038	9	0.59–0.95	[28]
Xe	289.7	58.21	0	12	0.59–0.97	[28]
Kr	209.39	54.96	0	11	0.55–0.96	[28]
N ₂	126.25	33.96	0.037	13	0.51–0.95	[28]
SO ₂	430.75	78.81	0.244	20	0.53–0.98	[28]
F ₂	144.3	52.15	0.053	15	0.49–0.97	[28]
H ₂	32.98	12.93	−0.22	19	0.42–0.96	[28]
O ₂	154.77	50.87	0.02	17	0.48–0.97	[28]
SF ₆	318.7	37.79	0.221	19	0.70–0.97	[28]
CH ₃ Cl	416	69	0.154	35	0.49–0.99	[28]
[−(CF ₂) ₄ −]	388.5	27.83	0.352	19	0.51–0.98	[28]
CH ₃ CHF ₂	386.41	45.17	0.274	21	0.49–0.98	[28]
CH ₃ CF ₃	346.75	38.32	0.253	18	0.52–0.98	[28]
CH ₃ CClF ₂	410	41.5	0.239	21	0.49–0.98	[28]
CH ₂ FCF ₃	374.18	40.56	0.352	22	0.62–0.98	[28]
CHF ₂ CF ₃	339.4	35.95	0.293	18	0.51–0.97	[28]
CHClFCF ₃	395.65	36.34	0.281	17	0.59–0.99	[28]
CHCl ₂ CF ₃	456.83	36.68	0.285	17	0.55–0.97	[28]
C ₂ Cl ₃ F ₃	487.5	34.11	0.252	25	0.49–0.98	[28]
CH ₂ F ₂	351.4	57.927	0.27	15	0.60–0.97	[28]
CHF ₃	299.1	48.36	0.268	13	0.60–0.97	[28]
CHCl ₂ F	440	43.26	0.232	19	0.57–0.98	[28]
CClF ₃	302	38.7	0.167	17	0.43–0.99	[28]
CCL ₂ F ₂	385	41.31	0.178	21	0.47–0.99	[28]
CCL ₃ F	471.2	44.09	0.187	17	0.51–0.98	[28]
Br ₂	584.2	103.4	0.128	14	0.51–0.96	[28]
H ₂ O	647.3	221.2	0.343	40	0.49–0.96	[28]
H ₂ S	373.1	90	0.096	33	0.5–0.93	[29]

the new EOS. Fig. 3 shows the deviation plot which is implied to show the accuracy of the calculated values of heat capacity (C_p) of carbon dioxide and ethane at 350–600 K and 1–100 bar. This figure demonstrates that the good prediction of the C_p using HKM1

CEOS. Also using HKM1 EOS, the sound velocities of the different components at 100 bar are illustrated in Fig. 4. As one can observe a proper agreement with experimental data is obtained. Since carbon dioxide is an important component that has wide applications in

Table 2

The percent of absolute average deviation in correlation of the vapor pressure and liquid density using various CEOSs for the pure compounds. The experimental data are the same as those given in Table 1.

Component	AAD%											
	Vapor pressure						Liquid density					
	PR	GPR	SRK	PT	HKM1	HKM2	PR	GPR	SRK	PT	HKM1	HKM2
C ₁	0.64	0.98	1.83	1.12	0.54	1.01	8.91	9.00	4.42	3.74	2.37	2.51
C ₂	0.35	0.37	1.43	0.59	0.57	0.63	6.61	6.61	7.72	3.86	2.64	2.70
C ₃	0.83	0.48	1.10	0.59	0.75	0.50	5.21	5.19	7.96	2.69	1.70	1.75
<i>n</i> -C ₄	0.52	0.66	1.24	0.45	0.54	0.39	4.92	4.91	10.43	3.80	2.88	2.93
<i>i</i> -C ₄	1.08	0.96	0.72	0.94	1.01	0.86	5.14	5.11	9.60	3.72	2.81	2.86
<i>n</i> -C ₅	2.15	1.27	1.76	1.57	0.34	0.33	3.61	3.63	11.71	3.06	2.72	2.75
<i>n</i> -C ₆	1.59	0.66	3.00	1.52	1.93	1.84	2.70	2.71	12.76	2.69	2.47	2.48
<i>n</i> -C ₇	1.65	2.34	0.65	0.71	0.91	1.35	0.69	0.73	12.14	0.56	0.80	0.46
<i>n</i> -C ₈	1.57	2.02	1.78	0.95	1.07	1.38	5.91	5.98	16.75	3.50	3.44	3.34
<i>n</i> -C ₉	1.26	0.76	1.87	1.40	0.69	0.62	6.86	6.90	17.52	3.11	3.48	3.16
<i>n</i> -C ₁₀	1.75	1.32	2.11	1.66	0.95	0.92	5.93	5.95	16.81	2.15	3.88	3.25
<i>n</i> -C ₁₂	12.03	3.29	1.98	9.79	0.42	0.38	8.02	7.94	18.3	1.90	5.48	3.84
<i>n</i> -C ₁₄	2.21	4.50	6.43	3.05	4.88	5.13	–	–	–	–	–	–
<i>n</i> -C ₁₄	3.20	0.30	1.06	1.42	0.16	0.15	–	–	–	–	–	–
<i>n</i> -C ₁₄	4.15	0.79	1.72	2.05	0.42	0.40	–	–	–	–	–	–
<i>n</i> -C ₁₆	8.52	3.49	2.87	6.03	3.03	3.06	–	–	–	–	–	–
<i>n</i> -C ₁₆	12.28	3.35	1.47	8.64	3.09	2.79	–	–	–	–	–	–
<i>n</i> -C ₁₆	6.71	0.46	1.73	2.66	0.26	0.37	–	–	–	–	–	–
<i>n</i> -C ₁₆	4.73	0.27	0.85	1.04	0.28	0.08	–	–	–	–	–	–
<i>n</i> -C ₁₈	9.45	0.82	1.91	3.70	0.55	0.80	–	–	–	–	–	–
<i>n</i> -C ₁₈	9.90	3.99	4.89	6.42	3.59	4.00	–	–	–	–	–	–
<i>n</i> -C ₂₀	20.82	3.79	4.43	14.18	4.62	4.33	–	–	–	–	–	–
<i>n</i> -C ₂₀	34.73	4.23	3.42	29.14	2.13	2.33	–	–	–	–	–	–
<i>n</i> -C ₂₀	17.56	1.33	1.37	11.22	0.62	0.46	–	–	–	–	–	–
<i>n</i> -C ₂₀	13.66	0.43	1.21	6.76	0.49	0.34	–	–	–	–	–	–
<i>n</i> -C ₂₂	52.67	5.47	4.34	49.4	3.62	3.36	–	–	–	–	–	–
<i>n</i> -C ₂₂	18.66	0.45	0.79	11.35	0.26	0.32	–	–	–	–	–	–
<i>n</i> -C ₂₄	79.8	13.2	8.94	78.86	4.95	6.98	–	–	–	–	–	–
<i>n</i> -C ₂₄	26.49	0.81	1.96	19.33	0.43	0.62	–	–	–	–	–	–
C ₂ H ₄	0.64	0.55	0.80	1.24	0.41	0.29	6.21	6.20	7.21	3.27	2.12	2.14
C ₂ H ₂	1.48	1.69	2.26	1.73	1.39	1.50	4.19	4.19	11.42	4.10	3.28	3.26
C ₃ H ₆	1.46	1.55	0.88	1.76	0.89	0.96	6.62	6.60	7.12	3.43	2.38	2.50
C ₆ H ₆	0.90	1.13	0.67	0.80	0.75	0.66	3.17	3.16	11.21	2.80	2.75	2.71
C ₆ H ₅ CH ₃	1.32	1.63	1.15	0.94	0.60	0.70	2.45	2.48	13.27	3.42	3.69	3.77
Ar	0.31	1.08	1.64	0.83	0.75	1.14	10.34	10.44	3.62	3.54	2.84	3.12
CHCl ₃	3.96	3.55	4.29	4.03	4.50	4.24	6.67	6.63	8.10	5.01	4.39	4.40
CF ₄	1.38	1.76	1.38	1.63	1.14	1.18	6.14	6.10	7.79	3.71	2.92	3.01
CCL ₄	1.53	1.76	0.93	1.53	1.02	1.04	4.25	4.25	10.49	3.13	2.75	2.67
CO ₂	0.71	0.18	0.39	0.51	0.95	0.61	3.16	3.12	10.88	2.55	2.04	2.06
Cl ₂	1.41	1.10	0.82	1.93	0.87	0.72	4.09	4.10	9.50	5.41	4.85	4.56
CO	0.16	0.13	0.64	0.96	0.29	0.23	7.23	7.24	6.76	4.57	3.63	3.69
Ne	1.02	0.94	1.53	1.72	0.58	0.86	13.33	13.53	4.19	4.33	4.32	4.63
Xe	1.07	0.30	0.80	1.77	0.40	0.15	7.21	7.29	6.44	4.77	3.08	2.80
Kr	0.58	0.72	1.46	0.91	0.27	0.78	9.25	9.35	3.82	3.38	2.09	2.27
N ₂	0.67	0.21	1.19	1.03	0.39	0.46	9.79	9.84	3.46	3.63	2.67	2.91
SO ₂	2.39	2.87	2.08	2.23	1.92	2.13	2.33	2.37	12.98	3.58	3.62	3.67
F ₂	0.43	0.77	1.90	0.72	0.64	0.99	9.49	9.53	3.88	3.94	2.91	3.13
H ₂	4.62	5.79	6.28	6.15	4.50	5.18	19.99	20.82	9.26	6.56	7.03	7.50
O ₂	1.57	0.41	1.54	1.71	0.63	0.39	10.61	10.69	3.37	3.75	2.84	3.11
SF ₆	0.96	0.69	0.85	0.87	1.11	0.87	5.89	5.82	8.09	4.37	4.05	4.06
CH ₃ Cl	2.62	2.66	1.87	2.74	1.83	1.93	4.79	4.78	10.5	3.83	4.15	3.98
[-(CF ₂) ₄ -]	1.45	1.48	1.13	1.27	1.27	1.26	5.62	5.60	8.24	6.71	6.97	6.65
CH ₃ CHF ₂	0.42	0.88	2.08	0.61	0.84	0.84	8.60	8.67	19.10	9.54	9.60	9.71
CH ₃ CF ₃	1.39	1.90	1.49	1.15	0.77	1.09	5.56	5.63	16.44	7.17	7.26	7.32
CH ₃ CClF ₂	3.98	4.43	5.72	4.32	4.41	4.55	3.34	3.31	9.33	2.12	1.39	1.40
CH ₂ FCF ₃	3.86	3.26	3.66	4.57	4.18	3.84	4.03	4.13	15.18	3.02	2.75	2.72
CHF ₂ CF ₃	1.07	1.55	2.07	1.11	1.43	1.47	2.93	2.94	12.04	2.77	2.27	2.25
CHClFCF ₃	0.83	1.50	1.17	0.58	0.49	0.85	4.35	4.34	12.06	4.11	3.58	3.55
CHCl ₂ CF ₃	0.62	0.28	0.99	0.87	0.89	0.57	3.39	3.38	11.58	3.08	2.66	2.60
C ₂ Cl ₃ F ₃	1.46	1.49	0.73	1.18	0.89	0.81	4.95	4.93	9.63	4.01	3.30	3.29
CH ₂ F ₂	1.09	1.77	1.99	0.96	0.88	1.17	17.4	17.49	26.99	18.38	18.30	18.39
CHF ₃	1.07	0.74	1.70	1.28	1.29	1.05	5.72	5.81	16.66	6.88	6.78	6.88
CHCl ₂ F	1.71	1.70	0.68	1.49	1.63	1.55	17.08	17.15	26.69	19.07	19.06	19.08
CClF ₃	2.77	2.59	1.37	2.72	1.77	1.82	6.23	6.21	8.59	3.87	2.81	2.87
CCL ₂ F ₂	1.76	1.68	0.95	1.69	0.98	0.92	5.53	5.51	8.71	3.38	2.51	2.55
CCL ₃ F	1.03	1.26	0.81	0.99	0.67	0.56	10.58	10.53	12.06	7.80	6.94	7.03
Br ₂	1.11	1.11	1.80	0.80	1.77	1.69	16.28	16.24	5.07	10.17	9.87	10.09
H ₂ O	3.33	3.94	5.91	3.96	4.41	4.43	18.44	18.48	27.79	17.49	17.21	17.49
H ₂ S	2.12	1.83	1.17	2.50	1.35	1.30	7.24	7.23	5.22	2.09	1.12	1.28
Overall	5.99	1.85	2.02	5.02	1.43	1.48	7.09	7.13	10.98	4.87	4.49	4.48

Table 3
The percent of absolute average deviation in predicting of vapor molar volume and enthalpy of vaporization using various CEOSs for the pure compounds. The experimental data are those given in Table 1.

Component	AAD%											
	Vapor volume						Enthalpy of vaporization					
	PR	GPR	SRK	PT	HKM1	HKM2	PR	GPR	SRK	PT	HKM1	HKM2
C ₁	1.00	1.56	2.29	1.11	0.99	1.48	1.44	1.88	2.51	2.09	1.47	1.79
C ₂	0.96	1.08	1.5	0.5	1.05	1.15	1.74	1.9	2.75	2	1.68	1.9
C ₃	1.28	0.92	1.27	0.86	1.2	1.02	1.01	0.76	1.4	0.93	0.75	0.69
<i>n</i> -C ₄	1.06	0.89	1.2	0.79	1.2	1.04	2.07	2.15	2.94	2.18	2.02	2.17
<i>i</i> -C ₄	1.19	1.45	0.64	1.00	0.95	0.91	1.22	1.01	1.34	1.16	1.05	0.97
<i>n</i> -C ₅	2.23	1.17	2.01	1.74	0.7	0.65	2.19	1.6	2.31	2.12	1.57	1.7
<i>n</i> -C ₆	2.04	1.02	3.93	2.10	2.48	2.35	1.61	1.25	2.1	1.63	1.46	1.54
<i>n</i> -C ₇	1.76	2.38	0.5	1.07	1.12	1.45	0.59	0.25	1.2	0.5	0.16	0.1
<i>n</i> -C ₈	1.97	1.81	2.27	2.4	2.02	1.92	3.26	3.26	4.16	3.46	3.33	3.31
<i>n</i> -C ₉	1.64	0.89	2.57	2.12	1.18	1.06	1.74	1.48	2.17	1.87	1.39	1.43
<i>n</i> -C ₁₀	1.73	1.53	2.88	2.9	2.08	1.98	1.89	1.85	2.76	2.41	1.91	1.89
<i>n</i> -C ₁₂	9.11	3.1	2.28	8.2	0.82	0.77	2.56	1.34	1.61	2.78	0.54	0.6
C ₂ H ₄	1.17	1.08	0.57	1.11	0.79	0.73	1.23	1.07	1.66	1.21	1.03	0.99
C ₂ H ₆	1.24	0.91	1.4	0.89	1.37	1.17	3.8	3.78	4.43	3.92	3.73	3.78
C ₃ H ₆	1.45	1.56	0.4	1.3	0.98	0.89	1.68	1.41	1.7	1.54	1.42	1.33
C ₆ H ₆	1.15	1.14	0.73	0.85	1.03	0.9	1.31	1.29	1.4	1.27	1.1	1.1
C ₆ H ₅ CH ₃	2.54	2.6	1.87	2.23	2	1.92	2.93	2.66	3.27	2.88	2.56	2.56
Ar	1.57	2.39	2.26	1.21	1.74	2.18	1.27	1.76	2.56	1.94	1.32	1.66
CHCl ₃	4.46	4.46	4.69	4.5	4.93	4.82	4.32	4.71	4.67	4.28	4.35	4.61
CF ₄	1.67	1.6	0.89	1.32	1.52	1.41	–	–	–	–	–	–
CCl ₄	2.24	2.25	0.92	1.92	1.74	1.76	2.07	1.8	1.91	1.99	1.76	1.71
CO ₂	1.45	0.91	1.38	1.3	1.63	1.32	1.16	1.01	1.74	1.28	1.11	1.05
Cl ₂	3.03	2.75	1.35	2.88	2.05	2.05	3.18	2.88	1.98	2.95	2.82	2.74
CO	6.5	6.49	5.03	5.74	5.61	5.75	1.89	1.76	1.88	1.95	1.56	1.6
Ne	1.51	1.6	1.11	1.05	0.71	1.12	1.34	2.06	2.82	2.09	1.54	1.94
Xe	2.5	1.65	1.02	2.04	1.2	1.05	2.48	2	2.51	2.36	2	1.88
Kr	1.9	2.15	2.18	1.35	1.28	1.81	1.87	1.81	2.49	2.02	1.5	1.69
N ₂	1.34	1.18	1.48	1.02	0.85	1.13	1.69	2.04	2.71	2.16	1.64	1.95
SO ₂	2.57	2.66	1.9	2.41	2.29	2.27	1.12	0.73	1.16	1.11	0.93	0.74
F ₂	1.28	1.79	2.15	0.93	1.35	1.76	1.84	1.31	1.98	1.56	1.36	1.23
H ₂	5.84	10.16	9.17	7.26	5.78	8.14	5.68	7.5	8.12	7.8	6.01	6.95
O ₂	2.17	1.41	1.65	1.51	0.98	1.12	2.12	2.04	2.65	2.19	1.68	1.92
SF ₆	1.49	1.48	0.58	1.28	1.51	1.43	2.43	2.43	2.43	2.42	2.38	2.38
CH ₃ Cl	4.98	5.07	3.06	4.77	4.1	4.24	2.45	2.19	2.85	2.42	2.17	2.15
[–(CF ₂) ₄ –]	1.77	1.79	1.33	1.71	1.76	1.75	2.15	1.87	1.8	2.09	1.72	1.72
CH ₃ CHF ₂	1.68	1.1	3.43	2.08	2.3	1.95	–	–	–	–	–	–
CH ₃ CF ₃	1.56	1.18	2.13	1.53	1.37	1.05	1.89	1.73	2.76	1.99	1.91	1.91
CH ₃ CClF ₂	5.59	5.3	7.69	6	6.55	6.25	4.5	4.63	5.67	4.73	4.92	4.85
CH ₂ FCF ₃	5.82	5.03	6.56	6.6	5.94	5.53	3.8	3.68	4.67	4.09	3.88	3.79
CHF ₂ CF ₃	1.47	2.19	1.99	1.48	1.85	2.01	2.15	2.44	1.93	1.98	2.15	2.3
CHClFCF ₃	1.36	1.08	1.81	1.45	1.38	1.16	6.01	5.95	6.89	6.13	6	6.03
CHCl ₂ CF ₃	1.81	1.3	2.09	2.07	2.14	1.86	1.29	1.26	2.25	1.41	1.35	1.37
C ₂ Cl ₃ F ₃	2.25	2	1.07	1.94	1.79	1.68	2.35	2.09	2.43	2.29	1.97	1.94
CH ₂ F ₂	6.71	5.91	7.69	7.08	7.07	6.62	6.5	6.32	7.39	6.73	6.67	6.52
CHF ₃	2.53	1.86	2.77	2.75	2.84	2.47	3.2	3.16	4.16	3.4	3.3	3.28
CHCl ₂ F	3.95	4.63	3.03	3.76	3.56	3.95	6.68	6.9	5.95	6.52	6.52	6.66
CClF ₃	3.12	3.05	1.15	2.68	2.25	2.2	3.59	3.27	3.27	3.46	3.16	3.11
CCL ₂ F ₂	2.76	2.62	1.54	2.31	2.05	1.96	2.42	2.12	2.46	2.33	2.02	2.01
CCL ₃ F	1.24	1.58	0.82	1.01	0.87	0.79	1.47	1.27	1.4	1.34	1.15	1.1
Br ₂	6.57	7.06	7.24	6.78	6.53	6.84	7.28	7.61	7.45	7.39	7.32	7.48
H ₂ O	4.57	4.6	7.43	5.71	5.94	5.63	–	–	–	–	–	–
H ₂ S	1.99	1.75	0.28	1.96	1.21	1.07	–	–	–	–	–	–
Overall	2.63	2.48	2.49	2.55	2.28	2.30	2.59	2.53	3.01	2.72	2.40	2.46

Table 4
The percent of absolute average deviation in predicting of supercritical molar volumes using various CEOSs for a number of pure compounds.

Component	<i>n_p</i>	Ref.	AAD%					
			Supercritical molar volume					
			PR	GPR	SRK	PT	HKM1	HKM2
C ₁	91	[28]	2.26	2.08	1.87	1.20	1.11	1.03
C ₂	78	[28]	2.29	2.27	3.04	1.67	1.79	1.71
<i>n</i> -C ₄	56	[28]	2.27	2.28	3.65	1.93	1.86	1.85
CO ₂	131	[28]	1.49	1.41	1.88	0.85	2.11	1.91
Overall	356		2.08	2.01	2.61	1.41	1.72	1.62

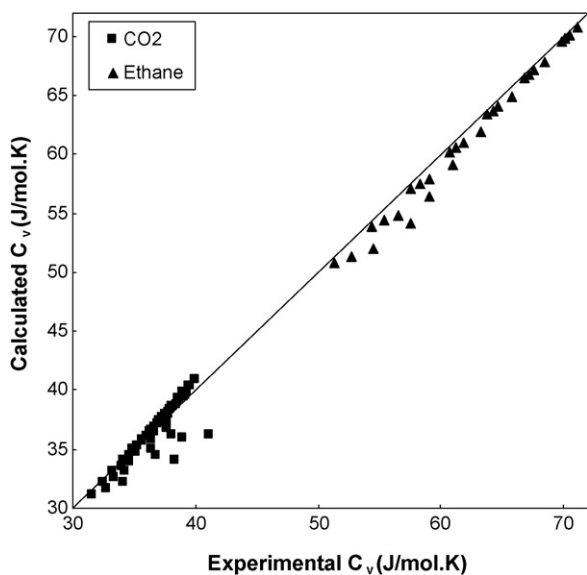


Fig. 3. The deviation plot of heat capacity at constant volume (C_v) for carbon dioxide and ethane. The experimental data are taken from [29].

oil, gas, chemical and supercritical processes, so the compressibility factor of CO_2 is predicted by HKM1 CEOS and compared with the experiment that is illustrated in Fig. 5. Good agreement between the experiment and the calculated value indicates the acceptable accuracy of HKM1 EOS in representing of compressibility factor of CO_2 at the reduced temperature and the reduced pressure of 0.8–1.5 and 0–3, respectively. It is noticed that using the new CEOS, the thermodynamic relationships of the fugacity coefficient, enthalpy of vaporization, heat capacity and sound velocity for pure fluid are derived and given in Appendix A.

To extend the new CEOSs to mixture using vdW 1-fluid mixing rules, several binary systems containing nonpolar and polar components have been selected in a wide range of temperature and pressure and shown in Table 5. Also Table 5 presents prediction ($k_{ij} = 0$) of the bubble points for 36 binary systems using the PR, SRK, PT and the new HKM1 and HKM2 EOSs with the new alpha function and the alpha function proposed by Gasem et al. [21]. As one can see the HKM1 and HKM2 EOSs have the lowest overall AAD% among the other EOSs. Although this table shows that the AADs of predicting of the vapor mole fraction of binaries are almost the same as those obtained using the five EOSs, however the best results have

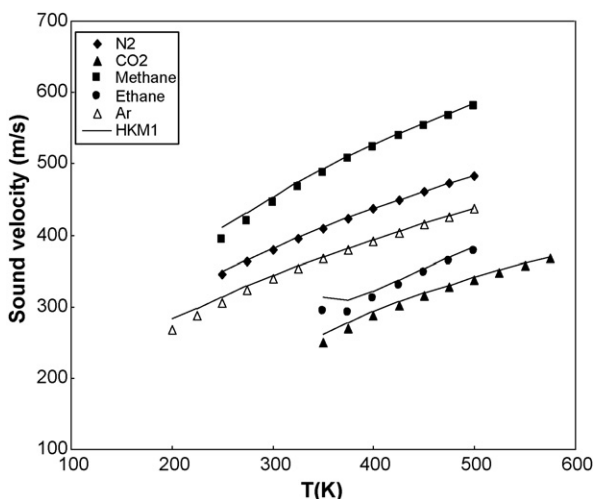


Fig. 4. The predicted and experimental values [29] of sound velocity of different pure components versus temperature at 100 bar.

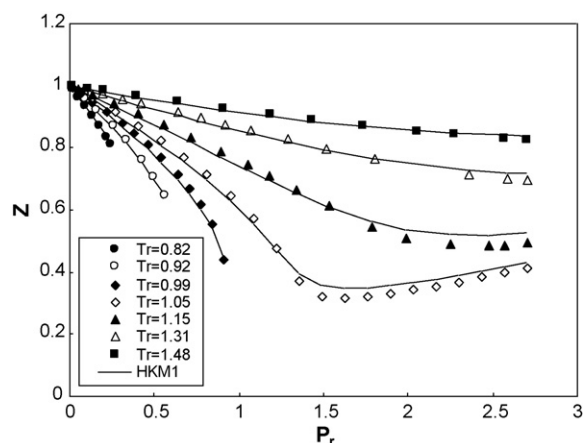


Fig. 5. The compressibility factor of carbon dioxide in different reduced temperatures and pressures using HKM1 EOS, the data were taken from Ref. [29].

been obtained by the new HKM1 EOS. In addition, correlation of the bubble pressure of the binary systems containing ethylene glycol (EG) are carried out using the binary interaction parameters and presented in Table 6. Comparison of the results of the binary EG systems shows that the PT EOS is in better agreement with experiment and the results of the SRK and the new EOSs (HKM1 and HKM2) are closer to those results obtained by the PT EOS, however, the PR EOS shows the highest deviation. Finally, the bubble pressures of the several ternary systems have been predicted by the five EOSs. Table 7 shows the prediction results that are obtained by the SRK, PR, PT and the new HKM1 and HKM2 EOSs so that the AAD% of 8.58, 10.25, 6.6, 4.44 and 5.07 are obtained, respectively. It can be seen that the results of HKM1 EOS is significantly better than PR EOS. Finally, one may pay attention if you have more parameters for a more accurate pure component; you have a better chance at having a more accurate mixture prediction. One should note that the number of the parameters of PR, SRK, GPR, PT EOSs are 3, 3, 5, 6, respectively, and for the new EOS is 8 as shown above.

In the final step to investigate the predictability of the new EOS, calculation of the phase diagram of a synthetic natural gas (SNG) mixture is carried out. The composition of the studied SNG mixture including C_1 , C_2 , C_3 , $i\text{-C}_4$, $i\text{-C}_5$, $n\text{-C}_6$, $n\text{-C}_7$, $n\text{-C}_8$, N_2 , CO_2 is 0.98943, 0.00082, 0.00065, 0.0005, 0.00017, 0.00032, 0.000027, 0.000033, 0.00618, 0.00187, respectively [80]. Fig. 6 shows the experimental and the predicted phase diagram of this SNG mixture. As one can see

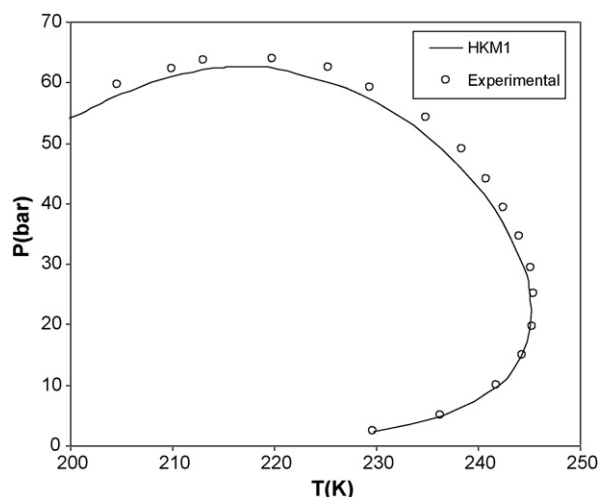


Fig. 6. The predicted phase diagram of a typical SNG mixture obtained by HKM1 EOS and the comparison with experimental data [80].

Table 5

The percent of absolute average deviation in predicting of the total pressure and the vapor phase mole fraction using various CEOSs for several binary systems.

Binary system	n_p	P (bar)	Ref.	AAD%									
				Bubble pressure					Mol fraction				
				SRK	PR	PT	HKM1	HKM2	SRK	PR	PT	HKM1	HKM2
C ₁ –C ₂	114	1.78–51	[37,38]	1.47	1.36	2.36	1.31	1.31	0.64	0.29	0.63	0.35	0.36
C ₁ –C ₃	74	1.38–131.34	[39]	3.08	4.68	1.81	4.13	4.14	–	–	–	–	–
C ₁ – <i>n</i> -C ₄	62	1.38–110.11	[40]	5.07	7.52	4.01	5.86	5.97	–	–	–	–	–
C ₁ –iC ₅	21	34–151	[41]	6.55	6.96	3.06	3.19	4.01	2.34	2.51	2.15	2.23	2.35
C ₁ – <i>n</i> -C ₉	63	10–323	[42]	11.89	13.14	21.02	5.28	6.06	0.37	0.36	0.85	0.28	0.29
C ₁ – <i>n</i> -C ₁₀	16	30–151.4	[43]	12.56	12.23	2.47	4.96	6.51	1.94	2.03	0.99	1.25	1.45
C ₂ –C ₃	151	0.3–19.7	[44]	2.25	1.53	2.22	1.40	1.53	2.42	2.78	2.51	2.72	2.73
C ₂ – <i>n</i> -C ₄	62	0.30–55.50	[45,46]	3.41	3.64	3.01	3.36	3.44	–	–	–	–	–
C ₂ – <i>n</i> -C ₆	27	6.9–75.8	[47–49]	9.76	9.49	10.00	9.37	9.45	3.03	3.04	3.13	3.08	3.11
C ₂ – <i>n</i> -C ₇	32	31.4–85.2	[50]	3.08	2.97	3.54	2.69	2.78	0.38	0.61	0.82	0.75	0.76
C ₂ – <i>n</i> -C ₁₀	100	6.9–117	[51,52]	4.49	4.07	9.88	3.50	3.21	0.79	0.96	0.93	0.94	0.97
C ₃ – <i>n</i> -C ₄	58	15.51–42.92	[53]	0.61	0.52	0.48	0.55	0.51	–	–	–	–	–
C ₃ – <i>n</i> -C ₅	52	6.89–44.81	[53]	1.84	2.02	1.63	1.95	1.94	–	–	–	–	–
C ₃ – <i>n</i> -C ₈	38	22.2–45.3	[54]	2.74	2.38	2.72	1.90	2.02	–	–	–	–	–
C ₃ – <i>n</i> -C ₁₀	50	1.7–68.95	[55]	2.79	2.71	8.61	3.31	3.11	0.26	0.24	0.96	0.48	0.43
C ₃ – <i>n</i> -C ₁₂	25	4.53–76.82	[51]	10.57	10.42	2.89	5.18	6.04	–	–	–	–	–
C ₃ – <i>n</i> -C ₁₆	44	2.05–14.46	[56]	11.37	10.74	21.70	8.43	6.01	–	–	–	–	–
<i>n</i> -C ₄ – <i>n</i> -C ₈	64	6.89–43.09	[57]	1.88	1.77	1.44	1.43	1.54	–	–	–	–	–
<i>n</i> -C ₄ – <i>n</i> -C ₁₄	134	1.2–44	[58]	11.07	11.40	4.50	7.23	7.48	29.63	29.74	28.74	29.37	29.37
<i>n</i> -C ₈ – <i>n</i> -C ₁₀	27	0.2	[59]	1.23	2.23	1.18	1.33	1.39	–	–	–	–	–
<i>n</i> -C ₈ – <i>n</i> -C ₁₂	26	0.2	[59]	1.61	1.60	1.55	0.64	0.60	–	–	–	–	–
<i>n</i> -C ₁₀ – <i>n</i> -C ₁₂	27	0.2	[59]	1.48	1.64	1.46	0.56	0.52	1.53	2.29	1.75	1.68	1.63
CO ₂ –C ₃	29	2.9–35.7	[60]	36.09	36.24	36.21	36.49	36.35	16.24	15.78	16.18	15.84	15.99
CO ₂ – <i>n</i> -C ₄	126	1.2–82.2	[61]	19.25	19.02	19.21	19.04	19.05	6.25	6.02	6.18	5.96	6.07
CO ₂ – <i>n</i> -C ₆	39	7.8–116	[62]	24.95	24.22	23.25	23.57	23.82	2.26	2.15	2.01	2.07	2.13
CO ₂ – <i>n</i> -C ₇	64	1.9–133.2	[63]	21.56	20.71	18.85	19.67	19.96	2.50	2.46	2.29	2.38	2.42
CO ₂ –Benzene	47	1.05–133	[64]	24.14	24.82	24.85	24.92	25.07	7.34	7.46	7.44	7.46	7.47
CO ₂ –Toluene	31	2.6–131.7	[65]	30.42	30.54	29.84	30.13	30.53	1.85	1.85	1.76	1.78	1.83
N ₂ –CO ₂	34	16.96–130	[38,66]	3.45	2.71	5.48	5.86	4.55	–	–	–	–	–
N ₂ –C ₁	56	3.53–48.95	[67]	3.45	3.83	3.54	3.81	3.93	–	–	–	–	–
N ₂ –C ₂	62	8.63–95.04	[68,69]	15.21	18.09	15.47	16.40	16.71	–	–	–	–	–
N ₂ – <i>n</i> -C ₄	14	1.58–285.16	[70,71]	13.68	15.18	11.19	9.93	11.61	–	–	–	–	–
N ₂ – <i>n</i> -C ₅	42	16.7–354.7	[72]	11.49	11.73	8.12	8.07	8.49	–	–	–	–	–
Toluene– <i>n</i> -C ₁₀	34	0.09–1.3	[73]	4.67	5.96	6.23	5.67	5.69	1.80	1.66	3.17	2.30	2.30
Toluene– <i>m</i> xylene	39	0.3–1.3	[73]	2.36	1.18	1.68	1.74	1.39	2.42	2.64	2.45	2.53	2.52
<i>m</i> Xylene– <i>n</i> -C ₁₀	33	0.09–0.61	[73]	2.23	3.01	2.75	2.50	2.49	6.01	5.87	6.53	6.14	6.17
Overall	1917			8.99	9.23	8.84	7.93	8.03	4.50	4.54	4.57	4.48	4.52

Table 6

The percent of absolute average deviation in correlating of the total pressure using various CEOSs for binary of Ethylene glycol systems, the data were taken from Ref. [74].

Binary system	n_p	T (K)	P (bar)	AAD% of vapor pressure					Binary interaction parameters				
				SRK	PR	PT	HKM1	HKM2	SRK	PR	PT	HKM1	HKM2
C ₁ –EG	11	323.15	23.7–395	2.9	4.4	2.7	3.3	3.6	0.1322	0.1566	0.0176	0.1203	0.1244
C ₁ –EG	10	373.15	2–396.2	1.7	1.8	2.0	1.6	1.5	0.2045	0.2214	0.0809	0.1811	0.1873
C ₁ –EG	10	398.15	3.3–396	3.9	5.0	3.3	3.6	3.9	0.2165	0.2308	0.0888	0.1874	0.1945
CO ₂ –EG	11	323.15	8.9–380	5.9	7.8	6.5	7.6	7.7	0.1150	0.1233	0.1004	0.1118	0.1125
CO ₂ –EG	10	373.15	9.5–382	8.6	9.9	8.7	9.6	9.8	0.1344	0.1389	0.1177	0.1288	0.1293
CO ₂ –EG	9	398.15	9.6–384	10.0	10.8	10.0	10.6	10.8	0.1503	0.1546	0.1279	0.1429	0.1449
N ₂ –EG	13	323.15	14.7–396	10.5	10.9	10.3	10.3	10.5	0.1263	0.1771	–0.0035	0.1018	0.1156
N ₂ –EG	10	373.15	15.7–395	14.0	14.4	13.5	13.4	13.6	0.2318	0.2685	0.0766	0.1799	0.1973
N ₂ –EG	10	398.15	18.3–390	14.1	14.2	13.9	13.9	13.9	0.2179	0.2549	0.0512	0.1538	0.1753
Overall	94			8.0	8.8	7.9	8.2	8.4					

Table 7

The percent of absolute average deviation in prediction of the total pressure using various CEOSs for several ternary systems.

Ternary system	n_p	P (bar)	Ref.	AAD% of bubble pressure				
				SRK	PR	PT	HKM1	HKM2
N ₂ –CO ₂ –C ₁	40	45.60–96.26	[75]	5.42	5.95	4.73	4.11	4.55
N ₂ – <i>n</i> -C ₄ – <i>n</i> -C ₁₀	17	275.8	[70]	12.79	16.96	3.8	5.82	7.45
C ₁ –C ₃ – <i>n</i> -C ₁₀	66	27.58–275.79	[76]	10.51	12.72	9.83	4.74	5.14
C ₁ – <i>n</i> -C ₄ – <i>n</i> -C ₁₀	4	275.8	[70]	7.67	10.84	6.09	1.6	2.3
C ₁ – <i>n</i> -C ₄ – <i>n</i> -C ₁₀	64	228.90–128.50	[77]	3.41	2.74	2.53	3.99	3.32
C ₁ – <i>i</i> -C ₅ – <i>n</i> -C ₅	23	34.96–156.37	[41]	6.65	6.85	3.44	2.89	3.88
C ₁ – <i>n</i> -C ₆ – <i>n</i> -C ₁₀	24	9.00–188.47	[78]	11.45	14.04	20.65	7.88	7.89
C ₁ – <i>n</i> -C ₆ – <i>n</i> -C ₁₄	6	17.14–275.80	[79]	10.8	11.86	1.75	4.51	6.03
Overall	244			8.58	10.25	6.6	4.44	5.07

the new three-parameter HKM1 EOS with the new alpha function was accomplished to good representation of the phase envelope. Finally, one may conclude that the new HKM CEOS not only gives satisfactory results for calculation of the thermodynamic properties of the pure fluids, nevertheless, it also can be used to compute the vapor–liquid equilibria of the mixtures with acceptable accuracy.

4. Conclusion

A new three-parameter cubic equation of state was presented in conjunction with introducing a new alpha function that covers some of the recently studied features of the alpha functions. The overall ADD% of 1.43 and 4.49 were obtained to correlation of the vapor pressure and liquid density of 58 pure compounds, respectively. The new HKM EOSs with the new alpha function was used successfully for improvement of the correlation of the physical properties of the heavy hydrocarbons. Also using the new HKM1 EOS allows one to perform the successful predictions of vapor molar volume, enthalpy of vaporization, heat capacity and sound velocity of the pure components. Moreover, the supercritical molar volume of some specified components were predicted correctly by the new EOS. In next step, the new EOS was applied for prediction of bubble points of a number of binary and ternary mixtures so that the better results were obtained for total pressure and vapor mole fraction in comparison with the SRK, PR, and PT EOSs. Finally, it was shown that the new HKM1 EOS has the good capability for construction of the phase envelop of a typical SNG mixture.

List of symbols

a	attraction parameter ($\text{Pa m}^6 \text{mol}^{-2}$)
b	co-volume parameter ($\text{m}^3 \text{mol}^{-1}$)
c	semi-co-volume parameter ($\text{m}^3 \text{mol}^{-1}$)
C_p	molar heat capacity at constant pressure ($\text{J mol}^{-1} \text{K}^{-1}$)
C_v	molar heat capacity at constant volume ($\text{J mol}^{-1} \text{K}^{-1}$)
H	molar enthalpy (J mol^{-1})
k_i	coefficients in Eqs. (11)–(13)
m	constants in Eq. (2)
M_w	molecular weight
N	parameter in Eq. (2)
n_p	number of data point
P	pressure (bar)
R	universal gas constant ($8.314 \text{J mol}^{-1} \text{K}^{-1}$)
T	absolute temperature (K)
v	molar volume ($\text{m}^3 \text{mol}^{-1}$)
v_s	sound velocity (m s^{-1})
y	vapor phase mole fraction
Z	compressibility factor

Greek letters

α	alpha function
ϕ	fugacity coefficient of a pure compound
ϕ_i	fugacity coefficient of component i in a mixture
γ	heat capacity ratio (C_p/C_v)
ρ	mass density (kg m^{-3})
ω	Pitzer acentric factor
Ω	constants in Eqs. (4)–(10)
\bar{z}_c	empirical critical compressibility factor

Subscripts

c	critical
i, j	dummy index
r	reduced

Superscripts

cal	calculated
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exp	experimental
l	liquid
v	vapor
0	ideal gas state property

Appendix A.

1. Fugacity coefficient of pure fluid and component i in a mixture:

$$\ln \phi = -\ln \left(Z - \frac{Pb}{RT} \right) + Z - 1 + \frac{a/RT}{mc - nb} \ln \left(\frac{v + nb}{v + mc} \right) \quad (\text{A.1})$$

$$\begin{aligned} \ln \phi_i = & -\ln \left(\frac{v - b}{v} \right) + \frac{b_i}{b} \left(\frac{b}{v - b} \right) \\ & + \frac{2 \sum_j x_j a_i - a(mc_i - nb_i)}{RT(mc - nb)^2} \ln \left(\frac{v + nb}{v + mc} \right) \\ & + \frac{a}{RT(mc - nb)} \left(\frac{(nb_i - mc_i)v + nm(cb_i - bc_i)}{(v + nb)(v + mc)} \right) - \ln Z \end{aligned} \quad (\text{A.2})$$

2. Enthalpy of vaporization for a pure fluid:

$$\begin{aligned} \Delta H^v = & T \int_{v^l}^{v^v} \left(\frac{\partial P}{\partial T} \right)_v dv \\ = & T \left[R \ln \left(\frac{v^v - b}{v^l - b} \right) - \left(\frac{\partial a}{\partial T} \right) \frac{1}{mc - nb} \ln \left(\frac{v^v + nb}{v^l + nb} \frac{v^l + mc}{v^v + mc} \right) \right] \end{aligned} \quad (\text{A.3})$$

where

$$\begin{aligned} \left(\frac{\partial a}{\partial T} \right) = & \frac{a}{T \ln(k_6 + k_7\omega + k_8\omega^2)} \\ & \times \left[\frac{k_5}{T_c} (1 - (k_6 + k_7\omega + k_8\omega^2)^{\ln T_r}) \right. \\ & \left. - (k_4 + k_5 T_r)(k_6 + k_7\omega + k_8\omega^2)^{\ln T_r} \right] \end{aligned} \quad (\text{A.4})$$

3. Heat capacity at constant pressure (C_p) and constant volume (C_v) for a pure component:

$$C_v = C_{v0} + TP_3 \quad (\text{A.5})$$

$$C_p = C_{p0} + TP_3 - \frac{TP_1^2}{P_2} - R \quad (\text{A.6})$$

$$P_1 = \frac{R}{v - b} - \frac{(\partial a / \partial T)}{(v + nb)(v + mc)} \quad (\text{A.7})$$

$$P_2 = -\frac{RT}{(v - b)^2} + \frac{a(2v + nb + mc)}{[(v + nb)(v + mc)]^2} \quad (\text{A.8})$$

$$P_3 = \frac{(\partial^2 a / \partial T^2)}{mc - nb} \ln \left(\frac{v + mc}{v + nb} \right) \quad (\text{A.9})$$

$$\left(\frac{\partial^2 a}{\partial T^2} \right) = a \left[\left(\frac{\partial a}{\partial T} \right)^2 - dS \right] \quad (\text{A.10})$$

$$\begin{aligned} dS = & \frac{\ln(k_6 + k_7\omega + k_8\omega^2)}{T} \\ & \times \left[\frac{2k_5}{T_c} (k_6 + k_7\omega + k_8\omega^2)^{\ln T_r} + (k_4 + k_5 T_r)(k_6 + k_7\omega + k_8\omega^2)^{\ln T_r} \right. \\ & \left. \times \frac{1 - \ln(k_6 + k_7\omega + k_8\omega^2)}{T} \right] \end{aligned} \quad (\text{A.11})$$

4. Sound velocity

$$\gamma = \frac{C_p}{C_v} \quad (\text{A.12})$$

$$v_s = \sqrt{\frac{-1000\gamma v^2}{M_w P_2}} \quad (\text{A.13})$$

where M_w is molecular weight.

References

- [1] Y.S. Wei, R.J. Sadus, *AIChE J.* 46 (2000) 169–196.
- [2] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, *Ind. Eng. Chem. Res.* 29 (1990) 1709–1814.
- [3] M.D. Donohue, J.M. Prausnitz, *AIChE J.* 24 (1978) 849–859.
- [4] O. Redlich, J.N.S. Kwong, *Chem. Res.* 44 (1949) 233–244.
- [5] G. Soave, *Chem. Eng. Sci.* 27 (1972) 1197–1203.
- [6] D.Y. Peng, D.B. Robinson, *Ind. Eng. Chem. Fundam.* 15 (1976) 59–64.
- [7] G. Schmidt, H. Wenzel, *Chem. Eng. Sci.* 35 (1980) 1503–1512.
- [8] N.C. Patel, A.S. Teja, *Chem. Eng. Sci.* 37 (1982) 463–473.
- [9] M.A. Trebble, P.R. Bishnoi, *Fluid Phase Equilib.* 29 (1986) 465–474.
- [10] M.A. Trebble, P.R. Bishnoi, *Fluid Phase Equilib.* 35 (1987) 1–18.
- [11] C.H. Twu, W.D. Sim, V. Tassone, *Fluid Phase Equilib.* 194–197 (2002) 385–399.
- [12] M. Mohsen-Nia, H. Modarress, G.A. Mansoori, *Fluid Phase Equilib.* 206 (2003) 27–39.
- [13] A. Dashtizadeh, G.R. Pazuki, V. Taghikhani, C. Ghotbi, *Fluid Phase Equilib.* 242 (2006) 19–28.
- [14] F. Esmailzadeh, M. Roshanfekr, *Fluid Phase Equilib.* 239 (2006) 83–90.
- [15] A.H. Farrokhi-Niae, H. Modarress, M. Mohsen-Nia, *J. Chem. Therm.* 40 (2008) 84–95.
- [16] P.M. Boston, P.M. Mathias, *Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Process Industries*, West Berlin, March, 1980, pp. 823–849.
- [17] G. Heyen, *Proceedings of the 2nd World Congress of Chemical Engineering*, Montreal, Canada, 1981, pp. 41–46.
- [18] P.M. Mathias, T.W. Copeman, *Fluid Phase Equilib.* 13 (1983) 91–108.
- [19] C.H. Twu, D. Bluck, J.R. Cunningham, J.E. Coon, *Fluid Phase Equilib.* 69 (1991) 33–50.
- [20] C.H. Twu, J.E. Coon, J.R. Cunningham, *Fluid Phase Equilib.* 105 (1995) 61–69.
- [21] K.A.M. Gasem, W.Z. Gao, R.L. Pan Jr., Robinson, *Fluid Phase Equilib.* 181 (2001) 113–125.
- [22] J.J. Martin, *Ind. Eng. Chem. Fundam.* 18 (1979) 81–97.
- [23] J.O. Valderrama, *Ind. Eng. Chem. Res.* 42 (2003) 1603–1618.
- [24] R.L. Scott, in: H. Eyring, D. Henderson, W. Jost (Eds.), *Physical Chemistry, An Advanced Treatise*, vol. 8A: Liquid State, Academic Press, New York, 1971.
- [25] H. Kim, H.M. Lin, K.C. Chao, *Ind. Eng. Chem. Fundam.* 25 (1976) 75–83.
- [26] B.E. Poling, J.M. Prausnitz, J.P. O'Connell, *The Properties of Gases and Liquids*, fifth ed., McGraw-Hill, 2000.
- [27] E. Neaua, O. Hernandez-Garduzaa, J. Escandella, C. Nicolas, I. Raspo, *Fluid Phase Equilib.* 276 (2009) 87–93.
- [28] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, sixth ed., McGraw-Hill, Tokyo, Japan, 1988.
- [29] NIST, National institute of standard and technology, Standard Reference Database Number 69, June 2005. Available at <http://webbook.nist.gov/chemistry/fluid/>.
- [30] D.R. Stull, *Ind. Eng. Chem.* 39 (1947) 517–540.
- [31] D.L. Camin, F.D. Rossini, *J. Phys. Chem.* 59 (1955) 1173–1179.
- [32] D. Morgan, R. Kobayashi, DOE/PC/80534.T1, 1989, DEC, 31, Rice.
- [33] H.S. Myers, M.R. Fenske, *Ind. Eng. Chem.* 47 (1955) 1652–1658.
- [34] D.L. Camin, A.F. Forziati, F.D. Rossini, *J. Phys. Chem.* 58 (1954) 440–442.
- [35] K. Sasse, J. Jose, J.-C. Merlin, *Fluid Phase Equilib.* 42 (1988) 287–304.
- [36] R.D. Chirico, N. An, W.V. Steele, M.M. Strube, C. Tsonopoulos, *J. Chem. Eng. Data* 34 (1989) 149–156.
- [37] I. Wichterle, R. Kobayashi, *J. Chem. Eng. Data* 17 (1972) 9–12.
- [38] M.K. Gupta, G.C. Gardner, M.J. Hegarty, A.J. Kidnay, *J. Chem. Eng. Data* 25 (1980) 313–318.
- [39] I. Wichterle, R. Kobayashi, *J. Chem. Eng. Data* 17 (1972) 4–9.
- [40] L.C. Kahre, *J. Chem. Eng. Data* 19 (1974) 67–71.
- [41] B. Williams, N.W. Prodany, *J. Chem. Eng. Data* 16 (1971) 1–6.
- [42] M.S. Lee, P.K. James, *J. Chem. Eng. Data* 11 (2) (1966) 176–180.
- [43] H.-M. Lin, H.M. Sebastian, J.J. Simnick, K.-C. Chao, *J. Chem. Eng. Data* 24 (2) (1979) 146–149.
- [44] C.J. Blanc, J.C.B. Setler, *J. Chem. Eng. Data* 33 (1988) 111–115.
- [45] V. Lhotak, I. Wichterle, *Fluid Phase Equilib.* 6 (1981) 229–235.
- [46] V.S. Mehra, G. Thodos, *J. Chem. Eng. Data* 10 (1965) 307–309.
- [47] E.J. Zais, I.H. Silberberg, *J. Chem. Eng. Data* 15 (1970) 253–256.
- [48] K.A. Gasem, A.M. Raff, N.A. Darwish, R.L. Robinson, *J. Chem. Eng. Data* 34 (1989) 397–398.
- [49] K. Ohgaki, F. Sano, T. Katayama, *J. Chem. Eng. Data* 21 (1976) 55–58.
- [50] V.S. Mehra, G. Thodos, *J. Chem. Eng. Data* 10 (3) (1965) 211–214.
- [51] H. Gardeler, K. Fischer, J. Gmehling, *Ind. Eng. Chem. Res.* 41 (2002) 1051–1056.
- [52] N.A. Darwish, J. Fathikalajahi, K.A. Gasem, R.L. Robinson, *J. Chem. Eng. Data* 38 (1993) 44–48.
- [53] W.B. Kay, *J. Chem. Eng. Data* 15 (1970) 46–52.
- [54] J.L. Guillevis, D. Richon, H. Renon, *Ind. Eng. Chem. Fundam.* 22 (1983) 495–499.
- [55] H.H. Reamer, B.H. Sage, *J. Chem. Eng. Data* 11 (1) (1966) 17–24.
- [56] B.B. Breman, A.A.C.M. Beenackers, E.W.J. Rietjens, R.J.H. Stege, *J. Chem. Eng. Data* 39 (1994) 647–666.
- [57] W.B. Kay, J. Genco, D.A. Fichtner, *J. Chem. Eng. Data* 19 (1974) 275–280.
- [58] V.V. de Leeuw, Th.W. de Loos, H.A. Kooijman, J. de Swaan Arons, *Fluid Phase Equilib.* 73 (1992) 285–321.
- [59] A. Dejoz, V. Gonzalez-Alfaro, P.J. Miguel, M.I. Vazquez, *J. Chem. Eng. Data* 41 (1996) 93–96.
- [60] J.C. Acosta, E. Hevia, S. Leipziger, *J. Chem. Eng. Data* 29 (3) (1984) 304–309.
- [61] M.E. Pozo de Fernandez, J.A. Zollweg, W.B. Streett Maria, E. Pozo de Fernandez, J.A. Zollweg, W.B. Streett, *J. Chem. Eng. Data* 34 (3) (1989) 324–328.
- [62] Y.-H. Li, K.H. Dillard, R.L. Robinson Jr., *J. Chem. Eng. Data* 26 (1) (1981) 53–55.
- [63] H. Kalra, H. Kubota, D.B. Robinson, H.-J. Ng, *J. Chem. Eng. Data* 23 (4) (1978) 317–321.
- [64] M.K. Gupta, Y. Hsiao Li, B.J. Hulsey, R.L. Robinson Jr., *J. Chem. Eng. Data* 27 (1) (1982) 55–57.
- [65] W.O. Morris, M.D. Donohue, *J. Chem. Eng. Data* 30 (3) (1985) 259–263.
- [66] F.A. Somait, A.J. Kidnay, *J. Chem. Eng. Data* 23 (1978) 301–305.
- [67] R. Stryjek, P.S. Chappelaar, R. Kobayashi, *J. Chem. Eng. Data* 19 (1974) 334–339.
- [68] B. Yucelen, A.J. Kidnay, *J. Chem. Eng. Data* 44 (1999) 926–931.
- [69] G. Raabe, J. Köhler, *Fluid Phase Equilib.* 222–223 (2004) 3–9.
- [70] F.M. Llave, I.H. Chung, *J. Chem. Eng. Data* 33 (1988) 123–128.
- [71] S.K. Shlbatat, S.I. Sandler, *J. Chem. Eng. Data* 34 (1989) 291–298.
- [72] G. Silva-Oliver, G. Eliosa-Jiménez, F. García-Sánchez, J.R. Avendaño-Gómez, *Fluid Phase Equilib.* 250 (2006) 37–48.
- [73] B. Willman, A.S. Teja, *J. Chem. Eng. Data* 30 (1) (1985) 116–119.
- [74] D.-Q. Zheng, W.-D. Ma, R. Wei, T.-M. Guo, *Fluid Phase Equilib.* 155 (February (2)) (1999) 277–286.
- [75] S.S. Estrera, K.D. Luks, *J. Chem. Eng. Data* 33 (1988) 350–354.
- [76] H.C. Wiese, H.H. Reamer, B.H. Sage, *J. Chem. Eng. Data* 15 (1970) 75–82.
- [77] L.E. Urlic, L.J. Florusse, E.J.M. Straver, S. Degrange, C.J. Peters, *Trans. Porous Media* 52 (2003) 141–157.
- [78] V. Uribe-Vargas, A. Trejo, *Fluid Phase Equilib.* 238 (2005) 95–105.
- [79] K. Chylinski, M.J. Cebola, A. Meredith, G. Saville, W.A. Wakehama, *J. Chem. Thermodynamics* 34 (2002) 1703–1728.
- [80] S. Avila, S.T. Blanco, I. Velasco, E. Rauzy, S. Otn, *Ind. Eng. Chem. Res.* 41 (2002) 3714–3721.