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RESEARCH ARTICLE

Using a New Proposed Influence Parameter of Gradient Theory for CH_4/n-alkane Binary Systems: What Advances Can Be Achieved?

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Abstract
The main aim of this modeling investigation is to improve the performance of the gradient theory for binary systems of methane and n-alkane. To achieve this aim, the gradient theory (GT) is combined with the volume-translated Peng-Robinson equation of state (VTPR EOS) for accurate description of phase equilibrium and surface tensions of methane/hydrocarbon systems. To improve the phase equilibrium calculations, the binary interaction parameters of VTPR EOS for methane/hydrocarbon systems have been determined based on the mole fraction of methane in liquid phase. A new correlation of the influence parameter based on the densities of bulk phases has been suggested. To make the present model predictive, the binary interaction parameters of the mixture influence parameter have been set equal to zero. The results of the model show that the predictions of the present model agree well with experimental surface tensions, especially for very low values of surface tensions (near-critical interfaces).

Keywords
Methane, Hydrocarbons, Surface tension, Gradient theory

1 Introduction

The accurate determination of the physical properties for (oil+gas) systems plays a dominant role in the petroleum industry. Among these physical properties, surface tension is a significant property in the exploration, production and processing of petroleum fluids. It is also an important property for crude oil recovery by using miscible gas injection technique in which very low surface tensions exist. On the other hand, it is known that methane is major component in reservoir fluids so that the surface tensions of methane/hydrocarbon binary systems must be accurately known [1, 2].

Since the experimental measurement of the surface tension and properties is quite difficult, developing a suitable and a reliable model for predictions of surface tension and properties has been an intriguing subject of modeling investigations. According to the previous investigations, the preferential adsorption in the vapor-liquid interface depends on the size and interactions of the molecules; therefore, the models combining density (or volume) with the surface tension are more successful than the models utilizing only surface tension. The gradient theory of fluid interfaces [3-5] is one of the prediction models combining density (or volume) with the surface tension. The gradient theory has two inputs containing the Helmholtz free energy density and the influence parameter for the homogeneous and the inhomogeneous fluids, respectively. The Helmholtz free energy density is calculated based on the thermodynamic model selected. On the other hand, the influence parameter is a molecular theoretical parameter and it is difficult for researchers to use it in practice so that the semi-empirical expression is usually applied for this input of the model.

In recent years, three groups of empirical expressions have been used to determine the influence parameter of the gradient theory: (1) constant influence parameter [6-8]; (2) temperature dependent influence parameter [9, 10]; (3) the influence parameter based on the densities of the vapor and liquid phases [11-16]. The first group makes the theory easer. On the other hand, it was concluded that the second group lead to a significant improvement, but it has some limitations, for example, the temperature dependent influence parameter used by Zuo and

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Stenby [9, 17, 18] is not possible to be applied under supercritical conditions so that the reduced temperature should be set to a single value. In recent years, the third group of influence parameter of the gradient theory [11-16] has been successfully applied to refrigerant mixtures and water/gas systems. The third group of influence parameter has shown the potential to overcome the limitations of the first and second groups.

Since the knowledge of surface tension is necessary for methane/hydrocarbon binary systems to be used in the petroleum industry, this investigation has been dedicated to modeling the surface tension of methane/hydrocarbon binary systems. The gradient theory (GT) in combination with the volume-translated Peng-Robinson equation of state (VTPR EOS) [19] has been applied to describe the surface tension and density profiles of the interface for CH_4/n-alkane binary systems. Furthermore, a new correlation based on the densities of the vapor and liquid phases have been proposed. The performance of new suggested influence parameter has been also compared with the previous proposed influence parameter in [11-16]. Furthermore, the performance of suggested influence parameter has been discussed.

2 Model description

2.1 Gradient theory of fluid interface

The details of gradient theory exist in [2, 10, 20], therefore; the important equations of gradient theory has been presented here. Miqueu et al. [2, 10] formulated the gradient theory of fluid interfaces for the mixtures as follows:

$$\sigma = \int_{\rho_{ref}^V}^{\rho_{ref}^L} \sqrt{2\left(\Omega(\rho) - \Omega_B\right)\sum_i \sum_j \kappa_{ij} \frac{d\rho_i}{d\rho_{ref}} \frac{d\rho_j}{d\rho_{ref}}} d\rho_{ref} \tag{1}$$

In Eq. (1), $\Omega_B = -P$; P shows the pressure at equilibrium condition; ρ is the local mole density through the interfacial phase; σ denotes the surface tension. ρ^L and ρ^V are mole densities relating to the liquid and vapor phases, respectively. Subscript ref relates to the reference component. $d\rho_i/d\rho_{ref}$ is mole density profile of component i and κ_{ij} is the influence parameter. The grand thermodynamic potential, $\Omega(\rho)$, is computed by using the following equation:

$$\Omega(\rho) = f_0(\rho) - \sum_i \rho_i \mu_{is} \tag{2}$$

in which $f_0(\rho)$ is the Helmholtz free energy density of the homogeneous fluid. μ_{is} denotes the chemical potential of component i relating to the bulk phases.

The density profile that is perpendicular to the interface can be computed by using Eq. (3):

$$z = z_0 + \int_{\rho_{ref}^0}^{\rho_{ref}^{(z)}} \sqrt{\frac{\sum_i \sum_j \kappa_{ij} \frac{d\rho_i}{d\rho_{ref}} \frac{d\rho_j}{d\rho_{ref}}}{2\left(\Omega(\rho) - \Omega_B\right)}} d\rho_{ref} \tag{3}$$

2.2 The free energy density and VTPR EOS

The Helmholtz free energy density of a homogeneous fluid can be computed by utilizing the following equation [20]:

$$f_0(\rho) = \sum_i \rho_i \mu_i(\rho) - P(\rho) \tag{4}$$

In this modeling investigation, the volume-translated Peng–Robinson (VTPR) equation of state [19] has been employed both for computing the thermodynamic properties of the vapor and liquid phases and the Helmholtz free energy density of the homogeneous fluid. The VTPR EOS is defined as:

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

in which a denotes the energy parameter and b is the volume parameter. The parameters of the PR EOS can be expressed as a function of critical properties. The critical properties of pure fluids [21] are shown in Table 1.

$$a = 0.45724 \frac{(RT_c)^2}{P_c} \alpha(T) \tag{6}$$

$$b = 0.0778 \frac{RT_c}{P_c} \tag{7}$$

in which P is the pressure, T is the temperature, v is the molar volume and R is the universal gas constant. The subscripts c and r show the critical and reduced properties, respectively. The other parameters of PR EOS can be illustrated as follows:

$$\alpha(T) = \left(1 + m\left(1 - T_r^{0.5}\right)\right)^2 \tag{8}$$

$$m = \begin{cases} 0.37464 + 1.54226\omega - 0.26992\omega^2 \\ \omega \le 0.49 \\ 0.379642 + 1.485030\omega - 0.164423\omega^2 + 0.016666\omega^3 \\ \omega > 0.49 \end{cases} \tag{9}$$

in which ω represents the acentric factor.

Table 1 Critical properties of fluids

Fluid	T_c (K)	P_c (bar)	V_c (cm^3/gmol)	ω
methane	190.6	46	99.2	0.0115
propane	369.8	42.5	203	0.153
n-butane	425.2	38	255	0.199
n-pentane	469.7	33.7	313	0.251
n-hexane	507.5	30.1	370	0.299
n-heptane	540.3	27.4	432	0.349
n-decane	617.7	21.1	600	0.489

The temperature-dependent volume translation parameter, c, is determined as follows:

$$c = c_c f\left(T_r\right) \tag{10}$$

$$c_c = \left(0.3074 - Z_c\right)\frac{RT_c}{P_c} \tag{11}$$

$$f(T_r) = \begin{cases} \beta + \left(1+\beta\right)\exp\left(\chi\left(1-T_r\right)\right) & T_r \leq 1 \\ \beta + \left(1+\beta\right)\exp\left(0.5\chi\right) & T_r > 1 \end{cases} \tag{12}$$

$$\beta = -2.8431\exp\left(-64.2184\left(0.3074 - Z_c\right)\right) + 0.1735 \tag{13}$$

$$\chi = -99.2558 + 301.6201 Z_c \tag{14}$$

In Eqs.(10)-(14), Z_c is the critical compressibility factor.

In this work, the classical van der Waals mixing rule is applied to the vapor-liquid phase equilibrium:

$$a = \sum_i \sum_j a_{ij} x_i x_j \tag{15}$$

$$a_{ij} = \sqrt{a_i a_j}\left(1 - k_{ij}\right) \tag{16}$$

$$b = \sum_i b_i x_i \tag{17}$$

in which x_i denotes the mole fraction of component in phases.

The phase equilibrium calculations has been performed based on the applied flash calculations in [13, 14].

2.3 The proposed influence parameter

As it is mentioned in the introduction section, the influence parameter is the second required input of the gradient theory. In previous investigations [11-16], the following form of influence parameter was used as a function of liquid and vapor densities.

$$\kappa = \left|\frac{\rho^L - \rho^V}{A\rho^V + B\rho^L}\right| \tag{18}$$

In this work, this form of influence parameter has been proposed for gradient theory.

$$\kappa = A v_c^{3.2}\left|\rho^L - \rho^V\right|^{3.2} + B \tag{19}$$

in which v_c is the critical molar volume.

In order to apply gradient theory (GT) to mixtures, the influence parameter for each component in the mixture (κ_i) must be described in terms of the mole density of each component i in the liquid and vapor phases. Also, it is assumed that the binary interaction coefficient of the influence parameter (l_{ij}) is zero.

$$\kappa_i = \left|\frac{\rho_L x_i - \rho_V y_i}{A\rho_V y_i + B\rho_L x_i}\right| \tag{20}$$

$$\kappa_i = A_i v_{ci}^{3.2}\left|\rho_L x_i - \rho_V y_i\right|^{3.2} + B_i \tag{21}$$

In Eqs. (20) and (21), x and y are the mole fractions of component i in the liquid and vapor phases, respectively.

2.4 The gradients of molar density

The gradients of molar densities for each component through the interfacial phase has been calculated by solving an algebraic equation on the basis of using the geometric combing rule for the influence parameters ($l_{ij} = 0$). Equation (22) has been derived according to the minimization of Helmholtz free energy [2, 10, 20]:

$$\frac{d\rho_1}{d\rho_2} = \frac{\sqrt{c_2}\left(\frac{\partial\mu_1}{\partial\rho_2}\right)_{T,P,\rho_1} - \sqrt{c_1}\left(\frac{\partial\mu_2}{\partial\rho_2}\right)_{T,P,\rho_1}}{\sqrt{c_1}\left(\frac{\partial\mu_2}{\partial\rho_1}\right)_{T,P,\rho_2} - \sqrt{c_2}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,P,\rho_2}} \tag{22}$$

3 Results and discussion

3.1 Pure fluids

Prior to modeling the surface tension and interfacial properties of methane/hydrocarbon systems, the influence parameters for each pure hydrocarbon containing methane (C_1), propane (C_3) n-butane (nC_4), n-hexane (nC_6), n-heptane (nC_7) and n-decane (nC_{10}) should be determined. The surface tensions of pure fluids have been taken from [22]. The coefficients of influence parameter of the gradient theory have been presented in Table 2. The average absolute deviation of surface tension in liquid phase has been defined as follows:

$$AAD_\sigma\% = \frac{1}{N_P}\sum_{i=1}^{N_P}\left|\frac{\sigma_i^{\exp} - \sigma_i^{calc}}{\sigma_i^{\exp}}\right| \times 100 \tag{23}$$

Table 2 The coefficients of influence parameter of pure components

Fluid	Eq. (18)		$AAD_\sigma\%$	Eq. (19)		$AAD_\sigma\%$
	$A\times10^{-20}$	$B\times10^{-20}$		$A\times10^{20}$	$B\times10^{20}$	
methane	−1.0601	0.6387	2.54	0.0279	1.1275	1.76
propane	−0.1985	0.0961	2.01	−0.1147	13.13	1.78
n-butane	−0.1476	0.0584	2.85	−0.1041	20.081	1.22
n-pentane	−0.0813	0.0360	1.95	−0.3151	36.14	1.87
n-hexane	−0.0654	0.0243	2.08	−0.1494	45.86	2.06
n-heptane	−0.0013	0.0173	3.22	−0.2041	64.30	2.32
n-decane	−0.0145	0.0081	3.49	−0.3657	135.82	2.85

3.2 Binary systems

As it is mentioned in the introduction section, the gradient theory has been used for computing the surface tension of (C_1/hydrocarbon) binary systems. To achieve this aim, first, the phase equilibrium of the applied binary systems has to be determined. Based on the mole fraction of methane in liquid phase, the temperature dependent binary interaction coefficient is determined. The average absolute deviation of mole fraction in liquid phase has been defined as follows:

$$AAD\% = \frac{1}{N_P}\sum_{i=1}^{N_P}\left|\frac{x_i^{\exp} - x_i^{calc}}{x_i^{\exp}}\right| \times 100 \tag{24}$$

Then, the surface tension of (C_1/hydrocarbon) binary systems can be computed by using the gradient theory of fluid interfaces. In this section, first, the C_1/C_3 binary system has been considered. The experimental phase equilibrium data are taken from [23]. The temperature and pressure of experimental data range from 227 K to 344 K and 21 bar to 85 bar, respectively. The experimental surface tensions are taken from [24]. The following temperature dependent binary interaction coefficient has been determined for C_1/C_3 binary system.

$$k_{ij} = 1.393 \times 10^{-5} T^2 - 0.0079T + 1.1267 \tag{25}$$

The AAD% of 2.76 for phase equilibrium shows a good description of phase equilibrium for C_1/C_3 binary system by using VTPR EOS. The experimental and calculated surface tensions are presented in Table 3 and Fig. 1. The results of model prove that the results of gradient theory in combination with applied influence parameters (Eqs. (20) and (21)) are in a quite good agreement with experimental surface tensions for C_1/C_3 binary system. Furthermore, one can see that the gradient theory in combination with the influence parameter obtained from Eq. (21) allows a very good description of surface tension for near critical condition so that a new correlation of the influence parameter can be appropriate for describing near-critical interfaces. The density profiles of C_1 and C_3 through the interface have been shown in Fig. 2. Figure 2 indicates that the density profile of C_1 is not a monotonic function of z so that C_3 should be considered as reference fluid to produce these surface tensions. Also, the density profile of C_1 has a peak which shows that C_1 adsorbs at the interface.

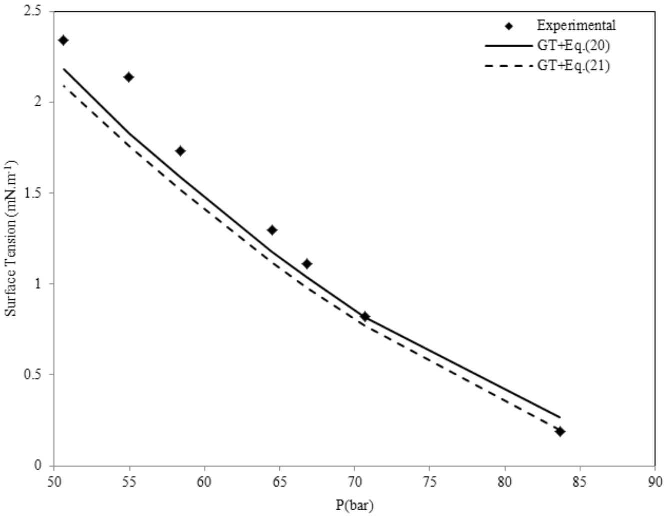

Fig. 1 The experimental [23] and calculated surface tension vs. pressure for C_1/C_3 binary system at $T = 303.15$ K

Table 3 The experimental and calculated surface tensions of C_1/C_3 binary system

T (K)	P (bar)	σ (mN.m^{-1})		
		Exp	GT+Eq.(20)	GT+Eq.(21)
258.15	74.42	1.23	1.37	1.31
258.15	70.54	1.51	1.76	1.66
258.15	60.34	2.88	2.91	2.52
258.15	40.81	5.56	5.11	5.09
258.15	21.36	8.64	7.74	8
283.15	82.31	0.5	0.58	0.53
283.15	75.44	0.98	0.99	0.93
283.15	62.31	2.04	2.05	1.88
283.15	52.58	2.97	2.87	2.91
303.15	83.67	0.19	0.27	0.197
303.15	70.68	0.82	0.82	0.77
303.15	66.80	1.11	1.04	0.98
303.15	64.48	1.3	1.18	1.12
303.15	58.36	1.73	1.59	1.52
303.15	54.96	2.14	1.83	1.76
303.15	50.61	2.34	2.18	2.09
318.15	66.80	0.64	0.69	0.62
318.15	60.74	0.97	0.98	0.92
318.15	59.31	1.06	1.06	1
318.15	55.85	1.3	1.24	1.2
318.15	49.86	1.68	1.6	1.57
318.15	49.52	1.7	1.62	1.59
318.15	47.07	1.87	1.78	1.75
318.15	42.38	2.23	2.09	2.08
318.15	42.10	2.3	2.11	2.11
318.15	35.23	2.79	2.6	2.63
338.15	63.60	0.22	0.26	0.213
338.15	56.46	0.54	0.58	0.46
338.15	48.84	0.87	0.89	0.8
338.15	41.83	1.28	1.24	1.16
338.15	32.65	1.87	1.75	1.71
338.15	29.59	2.05	1.94	1.91
338.15	23.12	2.57	2.35	2.35
Overall AAD$_\sigma$%			7.7	7.6

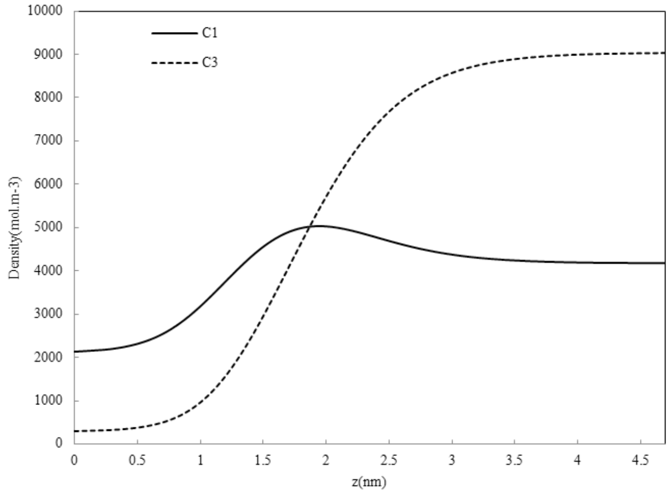

Fig. 2 The density profiles of C_1 and C_3 through the interface at $T = 258.15$ K and $P = 40.81$ bar

The second system considered here is C_1/nC_4 binary system. Although the gradient was applied by Nilssen [25] to this system, this calculation repeated in this investigation to recognize the advantages of new influence parameter. The experimental phase equilibrium data and surface tensions are from [26] and [27], respectively. To illustrate the effects of temperature and pressure, the experimental phase equilibrium calculations are done at temperatures ranging (294-344) K and pressures ranging (82-130) bar. The calculations concerning C_1/nC_4 binary system are similar to the ones performed for C_1/C_3 binary system. Based on the equilibrium compositions of C_1 in liquid phase, the following temperature dependent binary interaction coefficient has been regressed for C_1/nC_4 binary system (AAD% = 3.54).

$$k_{ij} = 1.017\times10^{-5}T^2 - 0.006307T + 0.9937 \tag{26}$$

Table 4 compares the results of the present model with the experimental data and the model used by Nilssen [25]. Also, nC_4 has been considered as a reference fluid for calculation of surface tension. One can see that the coupling of gradient theory (GT) and Eq. (21) as an influence parameter has the best performance, especially for very low surface tensions (near-critical interfaces). In comparison with work of Nilssen [25], the present model is more accurate for description of near critical interfaces so the present model shows an advance for description of near critical interfaces.

Subsequently, the present model has been done for two other binary systems containing C_1/nC_5 and C_1/nC_6 at 310.93 K and 298.15 K, respectively. The range of pressures considered here is (10-168) bar. Similar to previous systems, binary interaction coefficient has been determined for these two binary mixtures. The experimental phase equilibrium data have been taken from [28, 29]. The optimum values of binary interaction coefficient are −0.0261 and 0.0307 for C_1/nC_5 and C_1/nC_6, respectively. The AADs% of phase equilibrium are 3.31 and 0.77 for C_1/nC_5 and C_1/nC_6 systems, respectively.

The experimental [30, 31] and calculated surface tensions of these two binary systems have been compared in Figs. 3 and 4. nC_5 and nC_6 are considered as reference fluids. For C_1/nC_5 binary system, the AAD$_\sigma$% of surface tension is 13.85 when gradient theory is used in combination with Eq. (20). This value is 5.82 when gradient theory is used in combination with Eq. (21); therefore, the new proposed influence is more accurate than the one in Eq. (20) suggested in previous investigations [11-16]. For C_1/nC_6 binary system, the performance of these two influence parameters is approximately the same. The AAD$_\sigma$% are 6.15 and 6.12 by using Eq. (20) and Eq. (21) in combination with gradient theory, respectively.

Table 4 The experimental and calculated surface tension of C_1/nC_4 binary system

T (K)	P (bar)	σ (mN.m^{-1})			
		Exp	GT+Eq. (20)	GT+Eq. (21)	Ref. [25]
310.93	106.97	0.93	1.06	0.96	1.02
310.93	103.42	1.15	1.2	1.14	1.19
310.93	99.97	1.39	1.37	1.32	1.38
310.93	96.52	1.64	1.54	1.5	1.57
310.93	93.08	1.91	1.73	1.7	1.78
310.93	89.63	2.18	1.92	1.91	1.99
327.59	99.97	0.93	1.06	0.96	1.02
327.59	96.52	1.16	1.21	1.12	1.19
327.59	93.08	1.37	1.37	1.28	1.36
327.59	89.63	1.58	1.53	1.46	1.55
335.93	96.52	0.912	1.05	0.92	0.96
335.93	93.08	1.12	1.19	1.08	1.12
335.93	89.63	1.32	1.34	1.24	1.29
344.26	93.08	0.869	0.994	0.844	0.88
344.26	89.63	1.03	1.13	0.98	1.03
Overall AAD$_\sigma$%			7.70	5.34	6.58

The present model has been extended to two additional binary systems including C_1/nC_7 and C_1/nC_{10}. To our knowledge, the gradient theory was used by Miqueu et al. [2] to these systems. The gradient theory has been reapplied to recognize the advances when new proposed influence parameters are used. Similar to previous systems, the binary interaction coefficient are determined. The ranges of temperature and pressure are presented in Table 5. The binary interaction coefficient of C_1/nC_7 is obtained as follows:

$$k_{ij} = 8.701\times10^{-6}T^2 - 0.005947T + 1.0101 \tag{27}$$

For C_1/nC_{10}, the binary interaction parameter is expresses as follows:

$$k_{ij} = 3.961\times10^{-6}T^2 - 0.002962T + 0.5623 \tag{28}$$

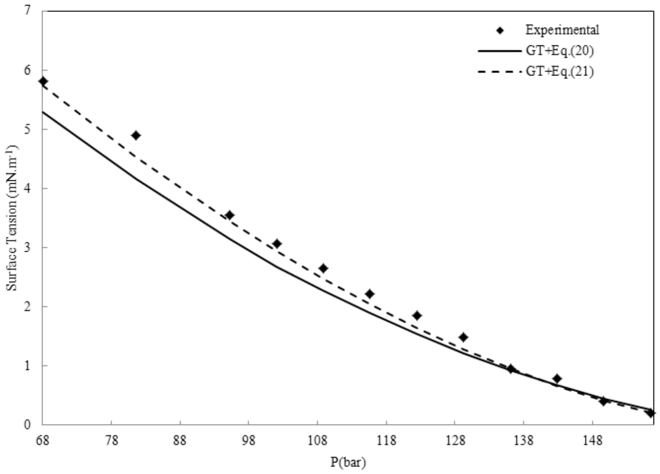

Fig. 3 The experimental [30] and calculated surface tension vs. pressure for C_1/nC_5 binary system at $T = 310.93$ K

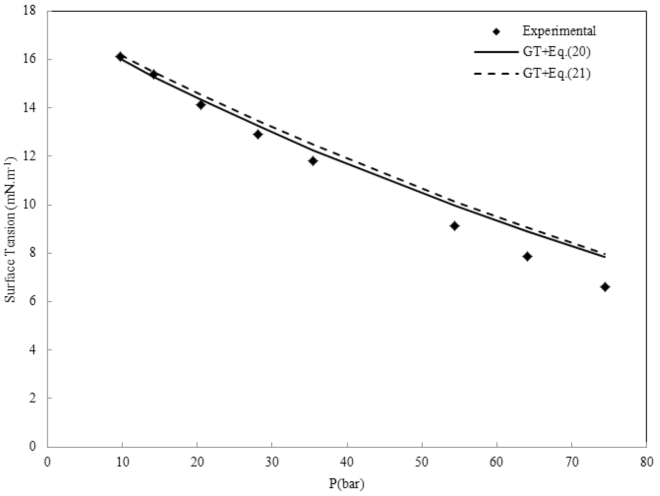

Fig. 4 The experimental [31] and calculated surface tension vs. pressure for C_1/nC_6 binary system at $T = 298.15$ K

Table 5 The range of thermodynamics conditions and AAD% of phase equilibrium calculations for C_1/nC_7 and C_1/nC_{10} binary systems

System	*T* range (K)	*P* range (bar)	AAD	Ref.
C_1/nC_7	310-344	55-241	4.06	[32]
C_1/nC_{10}	310-423	55-310	5.05	[33]

Table 6 shows the range of thermodynamic conditions in which the surface tension modeling has been performed. The references of experimental surface tension are also reported in Table 6. As it is shown in Table 6, the performance of Eq. (20) is better than Eq. (21) for C_1/nC_7 binary system and the performance of these two equations are approximately the same for C_1/nC_{10} binary system. Miqueu et al. [2] applied gradient theory for these two systems only at 310.93 K. In this study, by using the proposed influence parameter and suggested influence parameter in previous investigations [11-16], gradient theory is applicable for wider ranges of temperature, so an advance can be seen in comparison with the work of Miqueu et al. [2]. Figures 5 and 6 compare the experimental and calculated surface tensions for C_1/nC_7 and C_1/nC_{10} binary system.

Table 6 The range of thermodynamics conditions and AAD_σ% of surface tension calculations for C_1/nC_7 and C_1/nC_{10} binary systems

System	*T* range (K)	*P* range (bar)	AAD_σ%		Ref.
			Eq. (20)	Eq. (21)	
C_1/nC_7	310.93-394.26	54.42-224.28	6.89	8.66	[30]
C_1/nC_{10}	310.93-410.93	54.42-306.12	6.07	6.37	[30]

One can see that the present model is accurate for modeling the surface tension of both systems, especially for near critical interface. For C_1/nC_7 binary system, the density profiles of C_1 and nC_7 has been shown in Fig. 7. Similar to C_1/C_3 binary system, C_1 adsorbs at the interface.

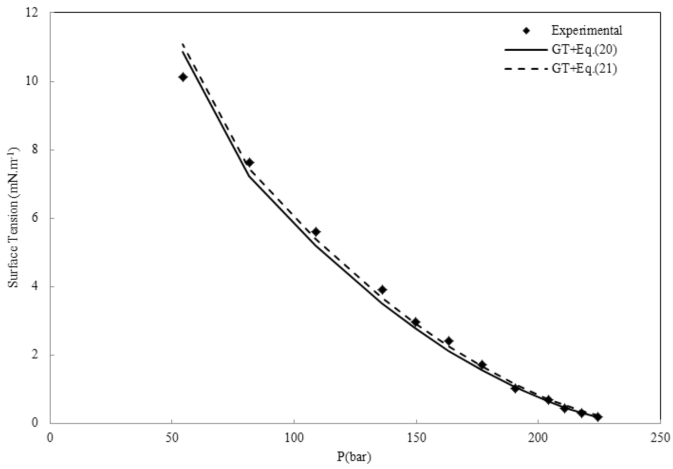

Fig. 5 The experimental [30] and calculated surface tension vs. pressure for C_1/nC_7 binary system at $T = 338.7$ K

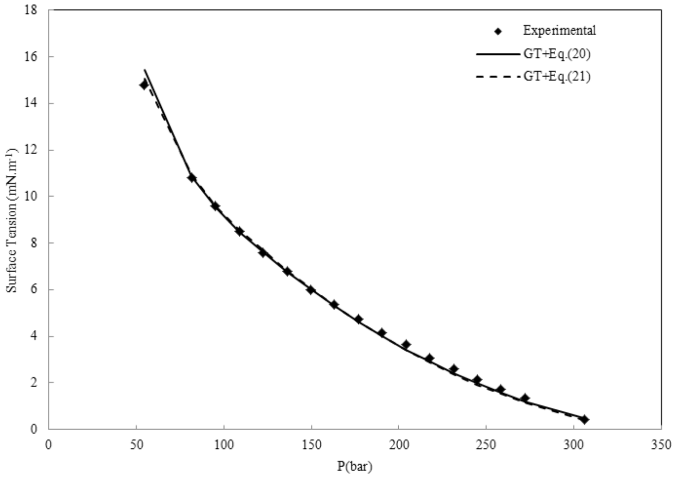

Fig. 6 The experimental [30] and calculated surface tension vs. pressure for C_1/nC_{10} binary system at $T = 366.48$K

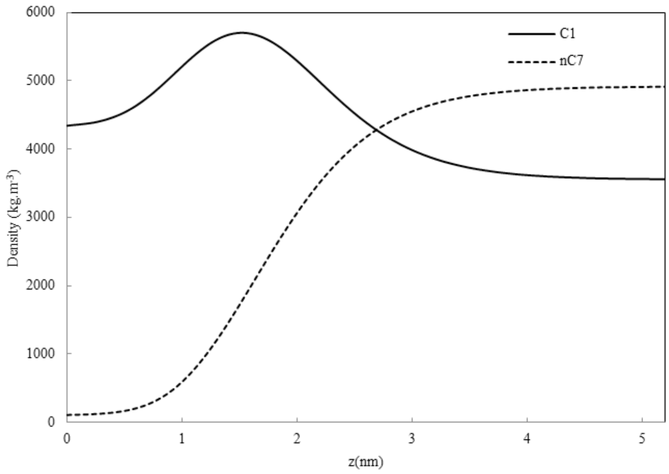

Fig. 7 The density profiles of C_1 and nC_7 through the interface at $T = 338.87$ K and $P = 108.84$ bar

4 Conclusions

In this work, the gradient theory of fluid interface in combination with the volume-translated Peng-Robinson equation of state (VTPR EOS) has been used to model the surface tension of methane/n-alkane binary systems. Also, a new correlation of the influence parameter is suggested for the gradient theory. The results of this modeling prove that the present model performs well methane/n-alkane binary systems and it successfully describes near critical interfaces.

Nomenclature

A	fitting coefficient of the influence parameter
a	energy parameter for PR equation of state
AAD	average absolute deviation (%)
b	volumetric parameter for PR equation of state
B	fitting coefficient of the influence parameter
c	temperature-dependent volume translation
calc	calculated result
exp	experimental
f_0	Helmholtz free energy density
L	liquid
N_p	the number of experimental points
P	pressure
R	universal gas constant
ref	reference
T	Temperature
V	vapor
VTPR	volume translated Peng-Robinson
x	mole fraction in liquid phase
y	mole fraction in vapor phase
z	position in the interface
Z_c	critical compressibility factor

Greek letters

κ	influence parameter
μ	chemical potential
ρ	mole density
σ	surface tension
v	molar volume of phases
ω	acentric factor
Ω	The grand thermodynamic potential

Subscripts

c	critical property
i,j	components *i* and *j*
ref	reference fluid

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