Factors influencing the surface tension of binary hydrocarbon mixtures

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HIGHLIGHTS

- Quantitative analysis of key factors influencing surface tension modeling.
- Liquid density is more important at low pressures.
- Gradient theory can effectively predict mixture surface tensions.

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ABSTRACT

The surface tension plays a major role in interfacial transport and reaction processes in many combustion processes. Since the surface tension is related to differences between the vapor and liquid phases, the saturated vapor pressure, vapor composition and liquid density are three of the key factors influencing the surface tension. However, there are few quantitative analyses of the effects of these factors on the surface tension. This study uses gradient theory combined with cubic equation of state (EOS) and van der Waals mixing rule to make a quantitative study of the influence of the saturated vapor pressure, vapor composition and liquid density on surface tension calculation. The effects of the saturated vapor pressure and vapor composition are analyzed by comparing the results of setting the binary interaction parameter k_{ij} in the van der Waals mixing rule to zero and the correlated value. The effect of the liquid density is investigated by comparing the results of using Peng–Robinson (PR) EOS and Volume Translation Peng–Robinson (VTPR) EOS. The results show that, for the binary hydrocarbon mixtures investigated, the liquid density has much more influence on surface tension compared with the saturated vapor pressure and vapor composition. And the gradient theory combined with VTPR EOS and the van der Waals mixing rule can accurately predict the surface tension with an average error of ±1% for the binary hydrocarbon mixtures.

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1. Introduction

The surface tension is one of the most important thermophysical properties that directly influences interfacial transport and reaction processes. The surface tension is important in many applications in oil exploitation, gas fuel liquefaction, liquid fuel atomization and many other areas in the fuel and energy power industries [1,2]. Taking fuel atomization for example, the fuel's surface tension directly influences the droplet formation with a high surface tension making drop formation difficult and a low surface tension facilitating drop formation [1]. Investigation of the surface tension of binary hydrocarbon mixtures is crucial to research on

real fuels composed of many complex hydrocarbons and other organic compounds [3,4]. Experimental methods are needed to measure the surface tension of these complex fluids. However, the expensive and harsh temperature, pressure and composition conditions complicate experiments. Surface tension prediction for a wide range of conditions requires theoretical methods. Since the surface tension cannot be deduced from other thermophysical properties using thermodynamic relationships, many theoretical methods have been developed to predict the surface tension [5–8]. As the surface tension arises from the differences between the vapor and liquid phases; therefore, the saturated vapor pressure, vapor/liquid composition and density all have the greatest influence on the surface tension. All theoretical methods take these key factors into account. Further investigations of the influences of these factors on the surface tension are of great importance. However, there are few good quantitative analyses of the influences of these factors. This paper describes a theoretical method combining gradient theory with a

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Nomenclature

a	attractive parameter in the EOS ($J\,m^3/mol^2$)
b	covolume in the EOS (m^3/mol)
c	volume translation parameter (m^3/mol)
f	Helmholtz free energy density (J/m^3)
F	Helmholtz free energy (J)
k	binary interaction parameter in the EOS
n	number density (mol/m^3)
N	number of components
OF	object function
p	pressure (MPa)
r	unit volume (m^3)
R	universal gas constant ($J\,mol^{-1}\,K^{-1}$)
T	temperature (K)
v	molar volume (m^3/mol)
V	volume (m^3)
x	mole fraction in liquid phase
y	mole fraction in vapor phase
z	position across the interface (m)

Greek symbols

$\bar{\delta}$	average deviation
κ	influence parameter ($J\,m^5/mol^2$)
μ	chemical potential (J/mol)
ρ	density (kg/m^3)
σ	surface tension (mN/m)

Subscripts

0	homogeneous state
a	absolute
cal	calculated value
exp	experimental value
i	component i
j	component j
L	liquid phase
r	relative
s	saturation
V	vapor phase

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cubic equation of state (EOS) and van der Waals mixing rule that is used in a quantitative investigation of the influences of saturated vapor pressure, vapor composition and liquid density on the surface tension for binary hydrocarbon mixtures.

Gradient theory uses inhomogeneous statistical mechanics to model the surface tension based on the interface's microstructure in a more physical realistic manner. Gradient theory is becoming one of the most important methods for modeling surface tension because of its wide range of applicability, good accuracy and strong theoretical fundamentals. The gradient theory can be a predictive method for mixtures based on the pure fluids' surface tension data. The gradient theory not only can precisely calculate the surface tension but also can describe the density profile across the vapor–liquid interface. By combining with EOSs, the gradient theory becomes more suitable for application. Many EOSs have been combined with the gradient theory for surface tension calculations for mixtures. Carey et al. [9,10] combined gradient theory with Peng–Robinson (PR) EOS to calculate the surface tension of hydrocarbon/hydrocarbon (HC/HC) and alcohol/alcohol mixtures. Sahimi et al. [11] used the PR EOS and gradient theory to calculate the surface tension of CO_2/HC mixtures. Cornelisse et al. [12,13] combined the PR and APACT EOSs with gradient theory to calculate the surface tension of CO_2/HC and H_2O/ethanol systems. Zuo and Stenby [14] used the PR, SRK and PT EOSs with gradient theory to predict the surface tension of HC/HC and CO_2/HC mixtures. Miqueu et al. [15–17] used the PR and Volume Translation Peng–Robinson (VTPR) EOSs and gradient theory to calculate the surface tension of HC/HC and CO_2/HC mixtures. Mejía et al. [18,19] used the PR EOS with gradient theory to calculate the surface tension of HC/alcohol, alcohol/water and HC/HC mixtures. Fu et al. [20,21] combined the PC-SAFT EOS with gradient theory to calculate the surface tension of HC/HC and CO_2/HC mixtures. The gradient theory has been successfully applied to a wide variety of fluids including hydrocarbons mixtures and polar compounds mixtures, and has also been applied to near critical interfaces and other liquid–liquid interfaces [15].

In mixtures' surface tension calculation, mixing rules are important, which directly influence the calculation accuracy of saturated vapor pressure, vapor/liquid composition and density which are all key factors for surface tension. For mixtures containing polar or supercritical components (e.g., alcohol or CO_2), more complicated mixing rule, like UNIQUAC and other G^E-EOS mixing rules, should

be used. However, for non-polar mixtures (e.g., hydrocarbon or hydrofluorocarbon mixtures), the van der Waals mixing rule is suitable. In the previous work, Lin et al. [22] proposed expressions for the influence factor and volume translation parameter using the VTPR EOS combined with gradient theory to calculate the surface tension for 80 pure fluids with an uncertainty of 0.19 mN/m. They then used the van der Waals mixing rule to extend gradient theory to mixtures. Based on the Lin's work, the van der Waals mixing rule was introduced into the gradient theory combing with EOS to investigate the key factors influencing the surface tension of binary hydrocarbon mixtures. The effects of the saturated vapor pressure and vapor composition are analyzed by setting the binary interaction parameter k_{ij} in the van der Waals mixing rule to zero and the correlated value. The effect of the liquid density is analyzed by comparing results for the PR and the VTPR EOS.

2. Theory

2.1. Gradient theory

Gradient theory has been described in many papers [9–22]. Hence, only the key principle used in this work will be introduced here. More details on gradient theory were provided in the previous work [22]. In gradient theory, the Helmholtz free energy density of a mixture is expanded as a Taylor series and truncated at the second order spatial derivatives of the density to one homogenous and one inhomogeneous term as:

$$F = \int \left[f_0(n) + \sum_{i,j} \frac{1}{2} \kappa_{ij} \nabla n_i \nabla n_j \right] d\boldsymbol{r} \tag{1}$$

where F is the Helmholtz free energy, $f_0(n)$ is the Helmholtz free energy density of a homogeneous fluid, κ_{ij} is the influence parameter between components i and j, n is the number density, and $\boldsymbol{r}$ is the unit volume.

Using the least energy principle and assuming that the influence parameter is a weak function of the number density, the interfacial density profile at a planar interface can be expressed as:

$$\sum_j \kappa_{ij} \frac{d^2 n_j}{dz^2} = \mu_i(n_1, n_2, \cdots, n_i) - \mu_{is} \tag{2}$$