



Prediction of minimum miscibility pressure in oil reservoirs using a modified SAFT equation of state

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HIGHLIGHTS

- ▶ A SAFT EOS is modified to better predict some thermodynamic properties of petroleum fluids.
- ▶ A robust method is developed to predict the MMP.
- ▶ Vaporizing miscibility mechanism presented as forward multiple contact model is applied.
- ▶ It is shown that the methodology applied herein is reliable and accurate.

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ABSTRACT

In a miscible gas flooding to heavy oil reservoirs, multiple-contact miscibility between injected gas and reservoir oil can be achieved at pressure greater than a minimum value that is referred to Minimum Miscibility Pressure (MMP). This research includes two parts: first, modification of simplified SAFT (*m*SAFT) equation of state is derived to describe vapor-liquid equilibrium calculations and second, prediction of MMP according to forward multiple contact model is done. With respect to objective function, adjustable parameters of SSAFT and *m*SAFT were obtained for 21 pure compounds. Comparison of AAD% of the results of *m*SAFT, SSAFT and PR EOSs in predicting vapor pressure, liquid density and enthalpy shows that *m*SAFT is the most accurate of all. Also, accuracy of these three EOSs for various mixtures has been verified, and the results confirm the reliability of *m*SAFT EOS. At last, AAD% of MMP prediction by mentioned EOSs (*m*SAFT is 2.20%, SSAFT is 3.25% and PR is 4.13%) proves that Statistical EOSs are more reliable than cubic EOS in modeling MMP.

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1. Introduction

In recent years, much attention has been paid to enhanced oil recovery, which includes many techniques, e.g., water injection, gas injection, water alternating gas injection, thermal methods, foam and polymer gel injection, chemical methods and microbial methods [1]. Miscible gas injection is one of the most efficient methods. An effective parameter in miscible gas injection process is Minimum Miscibility Pressure (MMP), the pressure at which the local displacement efficiency approaches 100% [2]. In fact, the pressure at which interfacial tension of two phases becomes zero and there is no difference between oil and injected gas densities.

Consequently, compressibility factor and specific volume of two phases will be the same at miscible condition [3]. It is well documented that the development of miscibility in a CO₂/oil displacement is the result of extraction of some hydrocarbons from the oil by dense CO₂ [4]. Orr and Jensen stated that there is considerable evidence that the extraction of hydrocarbon from crude oil is strongly influenced by the density of CO₂. Improvement of extraction with the increase in CO₂ density, that accompanies increasing pressure, accounts for the development of miscibility. The presence of impurities can affect the pressure required to achieve miscible displacement [5]. There are two common idealizations of the way in which a two-phase gas and liquid system achieves miscibility through multiple contact. In the vaporizing mechanism, fresh (original) liquid phase is contacted with a vapor phase whose composition is altered by repeated equilibration with the liquid [6]. In the condensing mechanism, the composition of the liquid phase is altered by equilibration with fresh vapor phase.

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Nomenclature

a	molar Helmholtz energy per mole of molecules	ΔP	pressure difference
d	temperature-dependent segment diameter, Å	AAD	average absolute deviation
H	enthalpy of vaporization	AD	average deviation
k	Boltzmann's constant $\approx 1.381 \times 10^{-23}$ J/K	EOS	equation of state
m	effective number of segments within the molecules (segment number)	MMP	minimum miscibility pressure
M	number of association sites on molecules	MW	molecular weight
n	carbon number/ mole number	O.F.	objective function
np	number of points	PR	Peng-Robinson
N	number of data	SSAFT	simplified statistical associated fluid theory
N_{Av}	Avogadro's number $\approx 6.02 \times 10^{23}$ molecules/mole	Z_m	maximum coordination number
K	K-value	z	mole fraction
P	pressure, Pa		
R	gas constant	<i>Subscripts</i>	
T	temperature, K	C	critical
u/k	temperature-dependent dispersion energy of interaction between segments, K	i	component i
V	total volume	j	component j
V^*	closed – packed molar volume of a segment	r	reduced property
X^A	monomer mole fraction (mole fraction of molecules not bonded at site A)	s	segment
Z	compressibility factor	<i>Superscripts</i>	
η	pure-component reduced density, the same for segments and molecules	assoc.	associating, or due to association
ρ	density (kg/m^3)	disp.	dispersion
x	mole fraction of components in oil/fluid phase	hs	hard sphere
y	mole fraction of components in injected gas	ideal	ideal gas
f	fugacity	l	liquid
ω	acentric factor	res.	residual
ϕ	fugacity coefficient	seg.	segment
		v	vapor

The generally accepted definition of MMP is that pressure, at a fixed temperature, above which miscibility occurs for a given feed (i.e., liquid of oil) and pressurizing gas solely through the multiple contact equilibrium process. The computation of this pressure bound is dependent on the mechanism invoked; the MMP is assumed to be under the two bounds [7]. Applying Wang and Orr [8] method of MMP calculation needs reliable equation of state (EOS) to describe phase behavior of crude oil and injected gas. Recently, Nasrifar and Moshfeghian applied an improved EOS to describe phase behavior of oil and gas in MMP calculations [9]; in addition, Esmailzadeh and Roshanfekr presented a new cubic equation of state and consequently, computed MMP by this new cubic EOS [10]. Fazlali et al. [11] presented an algorithm for rapid calculation of MMP using a cubic equation of state. Chapman et al. extended Wertheim's theory to develop the statistical associating fluid theory (SAFT) equation of state for associating fluid [12]. Huang and Radosz [13] assumed the segment–segment interaction to be described by the square-well potential to improve the SAFT equation of state for real compounds. This equation of state has been applied to both pure non-associating and associating components. Huang and Radosz [13], then, extended the SAFT equation to mixtures containing associating compounds. In the SAFT equation of state of Huang and Radosz [13], the residual Helmholtz energy for a pure component has four contributions: the hard sphere, dispersion, chain, and association terms. The hard sphere, chain, and association terms were derived from statistical thermodynamics. For the dispersion term, Huang and Radosz [13] used a double power series in temperature and density which had been fit to argon physical property data. Fu and Sandler [14] simplified the SAFT equation of state by using the single attraction terms of Lee et al. [15] for the square-well fluid to replace the multi-term double ser-

ies dispersion term, while keeping the original hard sphere, Chain, and association terms [14].

In this study, we first modify SSAFT (called modified simplified SAFT or *m*SSAFT) equation of state and obtain adjustable parameters for both SSAFT and *m*SSAFT. Subsequently, average absolute deviation (AAD%) of vapor pressure, liquid density and enthalpy of some pure hydrocarbons and also density of some mixture fluids have been calculated and compared with Peng-Robinson (PR) EOS [16] results. Then, MMP calculation is done by the latter three EOSs according to forward multiple contact model based on vaporizing miscibility. Finally, comparisons of average deviation of MMP calculation by three EOSs are verified.

2. SSAFT and *m*SSAFT equations of state

In the SSAFT equation of state, the residual Helmholtz energy per molecule for a pure component has hard sphere, dispersion, chain, and association contributions and is written as follows:

$$a^{res} = a^{hs} + a^{disp} + a^{chain} + a^{assoc} \quad (1)$$

The single hard sphere contribution a^{hs} to the Helmholtz free energy is calculated using the expression of Carnahan and Starling [17]:

$$\frac{a^{hs}}{RT} = m \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (2)$$

The Helmholtz free energy for the dispersion term derived by Lee et al. [15] for the square-well fluid is:

$$\frac{a^{disp}}{RT} = mZ_m \ln \left(\frac{V_s}{V_s + V^*Y} \right) \quad (3)$$

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