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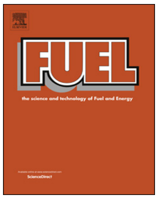

Full Length Article

Experimental measurements and theoretical modeling of high-pressure mass densities and interfacial tensions of carbon dioxide + n-heptane + toluene and its carbon dioxide binary systems

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ABSTRACT

Experimental determination and theoretical predictions of the isothermal (344.15 K) mass densities and interfacial tensions for the system carbon dioxide (CO_2) with heptol (n-heptane + toluene) mixtures varying liquid volume fraction compositions of toluene (0, 25, 50, 75, 100% v/v) and over the pressure range 0.1–8 MPa are reported. Measurements are carried out on a high-pressure device that includes a vibrating tube densimeter and a pendant drop tensiometer. Theoretical modeling of mass densities phase equilibria and interfacial properties (i.e., interfacial tension and interfacial concentration profiles) are performed by employing the Square Gradient Theory using an extension of the Statistical Associating Fluid Theory equation of state that accounts for ring fluids. The experimental bulk phase equilibrium densities and interfacial tensions obtained are in very good agreement with the theoretical predictions. Although there are no previous experimental data of these mixtures at the conditions explored herein, the results follow the same trends observed from experimental data at other conditions. The combination of experimental and modeling approaches provides a route to simultaneously predict phase equilibrium and interfacial properties within acceptable statistical deviations.

For the systems and conditions studied here, we observe that the phase equilibrium of the mixtures display zeotropic vapor-liquid equilibria with positive deviations from ideal behavior. The mass bulk densities behave ordinarily whereas the interfacial tensions decrease as the pressure or liquid mole fraction of CO_2 increases and/or the ratio toluene/heptane decreases. The interfacial concentration along the interfacial region exhibits a remarkable high excess adsorption of CO_2, which increases with pressure and it is larger in n-heptane than in toluene. Toluene does not exhibit any special adsorption activity whereas n-heptane displays surface activity only at low pressure in a very narrow range for the case of CO_2 + (25% n-heptane + 75% toluene) mixture.

1. Introduction

Enhanced Oil Recovery (EOR) refers to the procedures and processes put in place to raise the efficiency of oil recovery from existing hydrocarbon reservoirs fields. In a traditional EOR, a pressurized miscible gas fluid (*e.g.*, CO_2) is injected into the reservoir to aid in the displacement of the remaining crude oil in the well. This miscible displacement process maintains reservoir pressure and improves the oil displacement playing on the decrease in the interfacial tension (IFT) between oil and water. In this tertiary stage, approximately, from 30% to 60% of the original oil may be extracted. In order to control and to obtain an efficient recovery in EOR, it is necessary to know the IFT of mixtures composed of the miscible gas fluid, water, paraffinic hydrocarbons (from methane to triacontane or larger) and aromatic hydrocarbons (e.g., benzene, pyridine, toluene, etc.). IFT data allows establishing the minimum miscibility pressure, below which the gas flood becomes immiscible and EOR becomes inefficient (see Refs. [1–4] and references therein). In addition, the magnitude of IFT controls the wetting behavior between fluid–fluid and fluid–solid phases (*i.e.*, distribution of gas, oil, and water in the reservoir) [5–7]. The knowledge of IFT between CO_2, hydrocarbons (paraffinic and aromatic), and water are not only needed for the understanding, improvement and optimization of oil recovery by EOR processes, but also to control other physicochemical problems associated to oil extraction such as asphaltene precipitation. In fact, the dramatic change of the slope of IFT – pressure provides a route to find the onset pressure at which asphaltene precipitation occurs [4,8]. In addition to miscibility issues, EOR in hydrocarbon reservoirs takes place at extreme thermodynamic

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Nomenclature

a_1	first-order perturbation terms of hard sphere
a_2	second-order perturbation terms of hard sphere
a_3	third-order perturbation terms of hard sphere
a	Helmholtz energy density
A	Helmholtz energy
c_i	influence parameter
C	constant for the Mie potential
d_e	equatorial diameter of the drop
d_i	hard-sphere diameter of fluid *i*
d_n	internal diameter of the needle
d_s	horizontal diameter of the drop
f	Laplace Capillary function
g	local gravitational constant
$g_{ii}^{Mie}(\sigma)$	radial distribution function of the Mie potential
k_B	Boltzmann's constant
k_{ij}	interaction parameter for the EoS mixing rule
m_{si}	molecular chain length (spherical segments) of component i
n_c	number of components
N	number of molecules
N_{av}	Avogadro's constant
P	absolute pressure
r_{ij}	center-center distance
T	absolute temperature
u_c	combined standard uncertainty
v	volume fraction for toluene in liquid state
V	volume
V_d	volume of the drop
x, y	mole fractions for liquid and vapor phases, respectively
Wo	dimensionless Worthing number

Greek

α	van der Waals' constant
β	$1/(k_B T)$
χ	parameter in SAFT EoS
$\delta\Delta\rho$	standard uncertainty in density
δp	standard uncertainty in pressure
ε	potential well depth
ϕ^{Mie}	Mie potential
γ	interfacial tension
η_i	packing fraction of fluid *i*
Λ	thermal de Broglie's wavelength
λ_a	attraction parameter of the intermolecular potential
λ_r	repulsion parameter of the intermolecular potential
μ	chemical potential
ρ	molar density
$\hat{\rho}$	mass density
σ	effective segment diameter
$\sigma(\gamma)$	standard deviation of γ
Ω	grand thermodynamic potential

Superscripts

CHARI	chain and ring contribution in SAFT-EoS
hs	Carnahan and Starling hard sphere
MONO	monomer contribution in SAFT-EoS
IG	ideal gas contribution in SAFT-EoS
V	vapor bulk phase
L	liquid bulk phase
0	equilibrium state

Subscripts

exp	experimental
i,j,k	components
L	liquid bulk phase
V	vapor bulk phase

conditions ($T > 310$ K and $P > 8$ MPa) [9–11], where CO_2 + hydrocarbon mixtures exhibit complex multiphase equilibria (see for instances Refs. [12–14]) affecting the interfacial properties.

Because of the extreme *T* and *P* conditions and the complex behavior of phase equilibria, recent works on interfacial properties of CO_2 + hydrocarbon mixtures involved in EOR extraction have been carried out by using complementary techniques, where experimental determinations, theoretical approaches and molecular simulations are the most common approaches. From an experimental point of view, IFT of these mixtures has been measured by using pendant drop tensiometry (see for instance Refs. [15–17] and references therein). On the other hand, theoretical descriptions of these mixtures have been made by employing Density Functional Theory (see for example Refs. [18,19]) and more commonly the Square Gradient Theory (SGT) (see for instances Refs. [16,17,20–28]). Furthermore, molecular simulations based either on Molecular Dynamics or Monte Carlo schemes have also been employed [16,29,30]. As it was previously showed (see for instances Refs. [16,17,29]), a complete description of bulk phase and interfacial properties, including IFT, are obtained when experimental determinations are combined with theoretical models and/or molecular simulations. This interrelated combination provides a route to extrapolate the experimental data to extreme conditions, exploring unmeasurable quantities such as interfacial concentration along the interfacial region, surface activity, etc. or to validate theories and the force fields used in molecular simulations.

As part of our ongoing research work, which is devoted to the description of interfacial properties for CO_2 + n-alkanes mixtures [16,17,20–22,29], this work is focused on the experimental determination and theoretical modeling of bulk phase equilibrium densities and interfacial tensions of the CO_2 + {n-heptane (n-C_7H_{16}) + toluene (C_7H_8)} (or CO_2 + *heptol*) mixtures with different liquid volume fraction compositions of toluene (0, 25, 50, 75, 100 %*v*/*v*) at 344.15 K (160 °F) and over the pressure range 0.1–8 MPa. These temperature and pressure conditions have been selected as a reference for temperature and pressures observed in oil reservoirs. Measurements are carried out on a high-pressure device that includes a vibrating tube densimeter and a pendant drop tensiometer. Theoretical modeling of mass densities phase equilibria and interfacial properties, including interfacial tension and interfacial concentration profiles, are calculated by employing the van der Waals Square Gradient Theory (SGT) using a new extension of the Statistical Associating Fluid Theory (SAFT VR Mie) [31] equation of state (EoS) that includes an extra term that accounts not only for monomer-like fluid (CO_2), chain-like fluid (n-C_7H_{16}) but also for ring-like fluids (C_7H_8) [32].

1.1. Reported values

Recently, Al Ghafri et al. [33] reported experimental data and theoretical modeling for the phase equilibria for the CO_2 + n-C_7H_{16} + C_7H_8 ternary system. The experimental conditions cover the temperature range from 298 K to 423 K at pressures up to 16 MPa, whereas the theoretical modeling was carried out by using the Statistical Associating Fluid Theory (SAFT) based on Mie potentials where the involved molecular parameters were obtained from the group-