



# Thermodynamic phase behaviour and miscibility of confined fluids in nanopores

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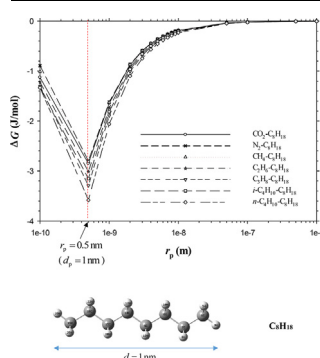
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## HIGHLIGHTS

- A semi-analytical equation of state for confined fluids in nanopores are developed.
- Two modified correlations are proposed to predict the shifts of critical properties.
- Nanoscale thermodynamic free energy and solubility parameter derived and calculated.
- The bottom limit of the liquid–gas miscibility in nanopores is determined.
- Nanoscale phase behaviour/miscibility change mainly due to critical property shifts.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this paper, thermodynamic phase behaviour and miscibility of confined pure and mixing fluids in nanopores are studied. First, a semi-analytical equation of state (EOS) is developed, based on which two correlations are modified to predict the shifts of critical temperature and pressure. Second, the thermodynamic free energy of mixing and solubility parameter are derived, quantitatively calculated, and applied to study the conditions and characteristics of the fluid miscibility in nanopores. Third, an improved EOS model with the modified correlations is proposed and used to calculate the phase properties and miscibility-associated quantities of three mixing fluids. The critical temperature and pressure of confined fluids are always decreased by reducing the pore radius. The negative pressure state is validated for a confined liquid, whose upper temperature limit is quantitatively determined and found to be lowered with the reduction of pore radius. The liquid–gas miscibility is beneficial from the pore radius reduction and the intermediate hydrocarbons (e.g., C<sub>2</sub>, C<sub>3</sub>, *i*- and *n*-C<sub>4</sub>) perform more miscible with the liquid C<sub>3</sub> in comparison with the lean gas (e.g., N<sub>2</sub> and CH<sub>4</sub>). Moreover, the molecular diameter of single liquid molecule is determined to be the bottom limit, the pore radius above which is concluded as a necessary condition for the liquid–gas miscibility. The calculated phase behaviour and minimum miscibility pressures (MMPs) of the three mixing fluids agree well with the literature results, which reveals that the shifts of critical properties dominate the phase behaviour and miscibility changes of confined fluids from bulk phase to nanopores.

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**Nomenclature***Notations*

$a$	equation of state constant
$A$	contact surface area
$b$	equation of state constant
$c$	coefficients
$d_p$	pore diameter
$E$	cohesive energy
$F$	Helmholtz free energy
$G$	Gibbs free energy
$H$	enthalpy
$k$	Boltzmann constant
$L$	length
$N$	total molecules
$P$	system pressure
$P_c$	critical pressure in bulk phase
$P_{cap}$	capillary pressure
$P_{cp}$	critical pressure in nanopores
$P_i$	parachor of $i$ th component
$P_L$	pressure of the liquid phase
$P_V$	pressure of the vapour phase
$R$	universal gas constant

$r_p$	pore radius
$S$	entropy
$T$	system temperature
$T_c$	critical temperature in bulk phase
$T_{cp}$	critical temperature in nanopores
$T_r$	reduced temperature
$U$	internal energy
$U_0$	internal energy of the ideal gas
$V$	system volume
$V_r$	reduced volume
$x_i$	mole percentage of $i$ th component in the liquid phase
$y_i$	mole percentage of $i$ th component in the vapour phase

*Greek Symbols*

$\gamma$	interfacial tension
$\varepsilon$	Lennard-Jones energy parameter
$\sigma$	Lennard-Jones size parameter
$\rho_L$	density of the liquid phase
$\rho_V$	density of the vapour phase
$\delta$	Hildebrand solubility parameter
$\theta$	contact angle of the vapour-liquid interface with respect to the pore surface

**1. Introduction**

In recent years, confined fluids in porous media attract more attentions due to its wide and practical applications, for example, inorganic ions pass through the cell membranes [1], industrial separation process [2] and heterogeneous catalysis [3], and oil/gas production from shale reservoir [4]. The confinement effect becomes much strengthened when the pore radius reduces to the nanometric scale, which is comparable to the molecular size and causes dramatic changes of fluid phase properties even in qualitative views [5]. In a confined fluid, for instance, the slight energy dissipations caused by frictions can induce a series of significant static or dynamic changes (e.g., shear stress, compressibility, or viscosity), which may not even be detected in bulk phase [6]. In general, the phase behaviour of the confined fluids in nanopores are studied mainly from the theoretical perspective while few laboratory experiments are available for confined fluids in nanopores because of the extremely high requirements of precision, enlargement in observation/imaging system, and associated cost [7]. The theoretical methods, which include equation of state (EOS) [8,9], Kelvin equation [10,11], density functional theory [12,13], and molecular simulation [14,15], are extensively used to study the phase behaviour of the confined fluids in nanopores. However, the last three theoretical methods are always time-consuming due to their intensive mathematical and computational frameworks, plus some underlying physical mechanisms cannot be clearly revealed. Hence, the cubic EOS is always regarded as an available and appropriate approach to calculate the phase properties of the confined fluids in nanopores.

Nowadays, unconventional oil reservoirs draw remarkable attentions because of their tremendous amount of original oil in place (OOIP) and continuously increasing demands from the human society [16]. The shale oil/gas in the extremely tight formation, as a typical example of confined fluids in nanopores, undergo substantial phase behaviour changes due to the shifts of the critical properties [17,18]. For example, the bubble point pressure of a Bakken oil-CO<sub>2</sub> system is found to be significantly decreased while the upper dew-point pressure increases and lower dew-point pressure decreases with an increasing confinement effect [9]. The minimum miscibility pressure (MMP), which is defined as the lowest operating pressure at which the oil and gas phases become miscible in any portions at an oil reservoir

temperature [19], is significantly decreased with the reduction of the pore radius [20]. More specifically, two respective reductions of 1.8 MPa and 4.1 MPa in MMPs for two different live light oil-pure CO<sub>2</sub> systems are obtained when the pore radius is decreased from 1000 nm to 4 nm at a constant temperature [8]. The above-mentioned fluid phase behaviour/MMP studies in nanopores are all based on two existing correlations for predicting the shifts of critical temperature and pressure under a strong confinement effect [21]. Although the correlations have been proven to be accurate to certain extent, a further modification is still necessary for complex mixing fluids like shale oil, gas etc. In addition, the systematic studies of the fluid miscibility in nanopores have never been found even though there are some pioneer laboratory and/or theoretical methods to determine the MMPs.

In this study, first, a semi-analytical EOS is developed to calculate the thermodynamic phase behaviour of confined pure and mixing fluids in nanopores, on a basis of which two correlations are modified to predict the shifts of critical properties under the confinement effect. Second, the conditions and characteristics of the fluid miscibility in nanopores are specifically studied by means of the thermodynamic derivations and quantitative calculations of the free energy of mixing and solubility parameter. Finally, an improved EOS model with the modified correlations is proposed and applied to calculate the phase properties and miscibility-associated quantities of three mixing fluids, which are compared with and validated by the literature results.

**2. Material**

In this study, pure CO<sub>2</sub>, N<sub>2</sub>, and a series of alkanes from C<sub>1</sub>-C<sub>10</sub> are used, whose critical properties (i.e., temperature, pressure, and volume), van der Waals (vdW-EOS) constants, and Lennard-Jones potential parameters are summarized [22–24] and listed in Table 1. In addition, as three hydrocarbon mixture systems, a ternary mixture of 4.53 mol.% *n*-C<sub>4</sub>H<sub>10</sub> + 15.47 mol.% *i*-C<sub>4</sub>H<sub>10</sub> + 80.00 mol.% C<sub>8</sub>H<sub>18</sub> [25] and two live light crude oil (i.e., oil P and B) [8,9] are applied to study the phase behaviour and miscibility of the mixture fluids. The compositional analyses of the ternary HC mixture and two live oil systems as well as the detailed experimental set-up and procedures for preparing the oil samples were specifically introduced in the literature [25–27].

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