Fluid Phase Equilibria 405 (2015) 157–166

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Equation-of-state modeling of associating-fluids phase equilibria in nanopores

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ARTICLE INFO

Article history:
Received 8 May 2015
Received in revised form 22 July 2015
Accepted 23 July 2015
Available online 26 July 2015

Keywords:
Porous mediums
Confined fluids
Capillary condensation
Associating fluids
Nanopores

ABSTRACT

Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT) is coupled with Young–Laplace equation to investigate and represent phase equilibria for associating fluids in nanopores. Despite of stronger fluid–fluid and fluid–wall interactions, the equation of state was found to perform as well as it did for non-associating fluids in the preceding work (Tan and Piri [1]). When the information obtained for pure substances is applied to mixtures in the same porous mediums, the phase equilibrium is accurately predicted, except for strongly-associating mixtures in polar mediums, for which it requires further studies. The promising results presented in this work complement those for non-associating fluids in the preceding study [1] to develop an effective model toward engineering applications in real settings of confined fluids such as chemical systems encountered in unconventional reservoirs (e.g., shale oil and shale gas).

1. Introduction

The effects of confinement in porous mediums on the phase equilibria of entrapped fluids have been successfully represented using the PC-SAFT equation of state (EOS) coupled with the Laplace equation for some simple gases and *n*-alkanes [1]. The approach takes advantage of the robust statistical associating fluid theory in calculating accurate condensed-phase densities and the simple formulation of the Laplace equation in describing the effects of the fluid interfacial curvature on the pressure of the confined system.

There have been efforts to couple the Laplace equation with other simpler EOS, e.g., that of cubic EOS family, to describe confined fluids, but without validation with actual systems [2]. There are also approaches that apply Kelvin's equation to deal with the effects of the confinement [3,4]. Kelvin's equation is obtained when the Laplace equation is used to describe the condensation of simple confined systems where the gas phase is considered ideal and the condensed phase is assumed incompressible, the conditions of which are not valid for fluids confined in nanosize pores. Some other more rigorous approaches apply additional energy term to an EOS that explicitly accounts for the interaction between fluid molecules and the pore walls, such as that by Travalloni et al. [5–7]. Unfortunately, this approach has not been validated for applications at capillary condensation, thus the phase equilibria of real confined systems.

It is found that the macroscopic formulation of the Laplace equation may still be used for nanoscale pores with some modifications [1]. In principle, with an additional parameter derived from experimental data, the calculated pure-substance properties at capillary condensation (such as critical temperature, critical pore radius, surface tension, condensed-phase equilibrium pressure, and saturated densities) are found to be consistent with experimental data, theoretical models, and molecular simulations. The EOS is also proven to work well with binary mixtures in nanopores, which validates the approach for nanoscale applications [1].

Nevertheless, all substances used in the first part of this work series [1] are non-associating in nature, while associating molecules such as water are frequently present in porous mediums not only in shale oil or shale gas, but also in biological structures, top soils, and other industrial applications. Molecular associations, such as that in water, originate from hydrogen-bonding and/or dipolar type of interactions.

An important issue that exists with associating molecules is their strong interactions with the pore walls while they also strongly associate with one another. For water, these fluid–wall interactions are qualitatively expressed using the so-called philicity or its opposite phobicity. If the pore wall "likes" water, the attractive interaction is hydrophilic, otherwise the interaction is not as strong and it is said to be hydrophobic. However, the boundary of these high and low philicities is not clearly defined.

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http://dx.doi.org/10.1016/j.fluid.2015.07.044
0378-3812/

Nomenclature

List of symbols

$\tilde{A}$	dimensionless Helmholtz energy
a_{ij}	binary parameter for the surface tension of mixtures Eq. (5)
b_{jk}	coefficients in Eq. (3) for λ parameter
c_{ij}	binary parameter for the surface tension of mixtures Eq. (5)
k_B	Boltzmann constant ($J\,K^{-1}$ molecule^{-1})
k_{ij}	binary interaction parameter
m	segment number parameter
P	pressure (bar = 10^{-1} MPa)
$\wp$	parachor (dn$^{\frac{1}{4}}$cm$^{\frac{11}{4}}$/mol)
R	gas constant ($J\,K^{-1}\,mol^{-1}$)
r_p	pore radius (nm)
T	temperature (K)
$\mathbf{x} = \{x_i\}$	mole fractions in adsorbed phases
$\mathbf{y} = \{y_i\}$	mole fractions in the bulk vapor phase

Greek letters

ε_i	LJ energy depth; segment energy parameter of component i (k_B K)
ε_{ik}^{DA}	association energy parameter between site D in a molecule of component i and site A in a molecule of component k (k_B K)
γ	surface tension (dn/cm = mN/m)
κ_{ik}^{DA}	association volume parameter between site D in a molecule of component i and site A in a molecule of component k
λ	parameter
ρ	molar density (mol/cm^3)
σ_i	segment diameter parameter of component i (Å)

Subscripts/superscripts

A	proton-acceptor type of association site
assoc	association
C	critical
cap	capillary
chain	chain
D	proton-donor type of association site
disp	dispersion
hs	hard sphere
i, j	of component i, j
ij	between component i and j
L	of the condensed phase (liquid)
p	pore
res	residual
sat	saturated
V	of the vapor phase (in the bulk)

Abbreviation

EOS	equation of state
PC-SAFT	Perturbed-Chain Statistical Associating Fluid Theory
VLE	vapor–liquid equilibria

For example, MCM-41 silica is considered hydrophilic, and thus can imbibe water spontaneously under ambient pressure [8], but at the same time it is classified as hydrophobic material as it adsorbs more organics than water [9]. Some researchers even consider that water does not wet the MCM-41 inner surface [10], while the others render MCM-41 hydrophilic due to the silanol groups covering the silica surfaces that were revealed by infrared spectroscopy [11]. For discussions on the definition and ambiguity of hydrophobicity of nanoporous materials, the readers are referred to a comprehensive review paper [9]. However, as it happens with any types of fluids in pores, the exact nature of the interactions between the solid walls and the fluid molecules is unknown.

To understand the different behavior between non-associating fluids and their associating counterparts, Fig. 1 shows the experimental capillary-condensation pressure of some associating fluids (water [12,13], ethanol [14,15], and acetone [15]) compared to that of non-associating fluids (N_2 [16], CO_2 [17] and argon [17]). Pressures and temperatures are scaled using bulk properties, i.e., the saturated pressure P_0 and the critical temperature T_C. While the data of water, ethanol, and acetone in porous plates [13,15] were directly measured, the other data were derived from adsorption isotherms where the condensation pressures were estimated when the isotherms undergo abrupt change [1]. This estimation procedure may introduce some uncertainties but they are insufficient to cause ambiguity in interpreting Fig. 1 because MCM-41 and SBA-15 have pores with uniform size and simple geometrical shape, which in turn give a narrow range of condensation pressure on the adsorption isotherms [1].

As shown in Fig. 1, associating fluids condense at relative pressures higher than those of the non-associating fluids in MCM-41 with small pore sizes. In this case, one may deduce that water molecules associate the strongest; in other words, the fluid–wall interaction for water is weakest among the others.

On the other hand, at much larger pore sizes, the associating fluids apparently condense at relative pressures much lower than the non-associating nitrogen does, which means that the fluid–wall interaction for associating fluid molecules is stronger. This behavior is evident from associating fluids in stainless steel and carbon plates, which have pore radii of 6.75 μm and 15 μm, respectively. Despite the much larger sizes, their capillary-condensation pressures are of the same order of magnitudes as that of nitrogen in SBA-15 with a radius of 18 nm. In this case, the fluid–wall interaction for water is apparently strongest, followed in order by ethanol, acetone, and nitrogen. At this point, it can be

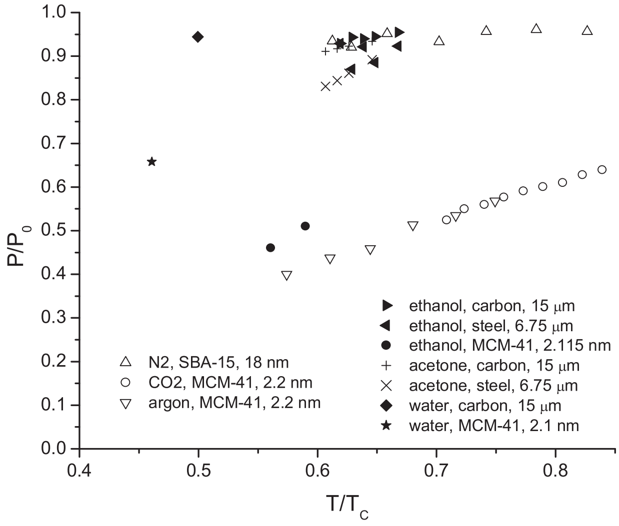

Fig. 1. Capillary condensation of associating molecules compared to that of non-associating molecules. Experimental data: water in MCM-41 [12]; water in carbon plate [13]; ethanol in MCM-41 [14]; ethanol and acetone in steel and carbon plates [15]; N_2 [16]; CO_2 and argon 17]. The numbers next to the porous mediums are the pore radii.