



Measurements of hydrocarbon bubble points in synthesized mesoporous siliceous monoliths

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HIGHLIGHTS

- Crack-free silica monoliths having only nano-sized pores were synthesized.
- DSC thermograms of decane saturated in the monoliths showed two peaks.
- TGA profiles of decane saturated in the monoliths showed early evaporation.
- Bubble points of hydrocarbon mixtures in the monoliths were lower than in the bulk.

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ABSTRACT

Silica based crack-free monoliths having the same pore size range as the oil and gas producing north-american shales were synthesized using a new synthesis procedure. Crack-free monoliths were synthesized by controlling the evaporation rate. Evaporation rate of 0.4 g/cm² was found optimal for making monoliths in cylindrical enclosures of different sizes for experimentation. The focus of this work was to understand the effects of nano-sized porous media on the saturation pressures of a hydrocarbon mixture of methane and decane. The physicochemical properties of the synthesized monoliths were measured using X-ray diffraction (XRD), nitrogen adsorption/desorption isotherm (BET), pore size distribution curve, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of decane in saturated monoliths revealed different boiling points in comparison to pure decane. The experimentally measured saturation pressures at two different temperatures of the bulk hydrocarbon mixture (decane-methane) matched well with the simulated results. The bubble point pressures of a hydrocarbon mixture in the nano-sized monolith were lower (about 18%) than those in the bulk.

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1. Introduction

Shale reservoirs are the focus of new oil and gas exploration and development. This growth is aided by technological breakthroughs in horizontal drilling and hydraulic fracturing (Pitakbunkate et al., 2014). These shale reservoirs have lower permeability and porosity, with pore size distributions ranging between 1 and 20 nanometers (nm). Unlike conventional reservoirs, they can be the source rocks that contain hydrocarbons (Pitakbunkate et al., 2014; Firincioglu et al., 2013). During production, fluids are depressurized, isothermally in reservoirs. This fluid expansion followed by bubble point transition with gas evolution takes place inside the nanometer sized pores. Fluid confinement in these pores

may affect important thermodynamic fluid characteristics. The phase behavior of reservoir fluids is essential in reserve evaluation, well performance prediction, reservoir management, and enhanced oil recovery.

It is well known that shales have a complex mineralogy characterized by the presence of clays and organic matter in various amounts (Kuila and Prasad, 2013). Loucks et al. showed that siliceous mudstone samples from the Mississippian Barnett Shale of the Fort Worth basin in Texas, (based on scanning electron microscopy images) consisted of pore sizes of about 5 nm (Loucks et al., 2009). Fluid phase behavior in confined materials has been a subject of many studies. It has been observed that fluids' phase envelope shifts, and hence the critical properties change under confinement (Pitakbunkate et al., 2014, 2016; Didar and Akkutlu, 2013). Many of the researchers who studied this fluid behavior under confinement performed their research theoretically

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(Firincioglu et al., 2013; Pitakbunkate et al., 2016; Didar and Akkutlu, 2013; Xiong et al., 2015; Nojabaei et al., 2013; Teklu et al., 2014; Travalloni et al., 2010). For example, using Monte Carlo simulation, Didar and Akkutlu demonstrated the effect on a temperature-density phase diagram as a decrease in critical temperature after a certain minimum pore size had been reached (Didar and Akkutlu, 2013). Also, using Grand Canonical Monte Carlo simulations, Pitakbunkate et al. described the reason for the change in interaction as being due to the different orientation and distribution of molecules (Pitakbunkate et al., 2016). Recently, Dong et al. reported the simulation result of fluid behaviors from both capillary pressure and adsorption effects (Dong et al., 2016). Different previous studies show that thermodynamic properties of fluids under confinement deviate from their bulk value; however, there are few experimental studies so far (Sigmund et al., 1973; Tsukahara et al., 2012; Buzinov and Peshkin, 1976; Luo et al., 2016a).

In one of the few existing experimental studies, Sigmund et al. reported the effect of porous media on the phase behavior of hydrocarbon binaries (methane-butane and methane-pentane) (Sigmund et al., 1973). They designed a PVT cell that was packed with glass or steel spheres as porous media. From their study of the effect of curvature on dewpoint pressures, they found that any differences in behavior between packed and unpacked PVT cells were within the limits of experimental error. They hypothesized that the effect of curvature on equilibrium pressure will not be of practical significance until the particle size approaches the clay-size range (less than 1 μm radius). Luo et al. presented the experimental results on the bubble points of octane and decane confined in controlled-pore glasses with pore sizes of 4.3 and 38.1 nm using differential scanning calorimetry thermograms (Luo et al., 2016a). They found the bubble point was dramatically affected by pore diameter: the bubble point shift of confined hydrocarbon was negligible at 38.1 nm, and the bubble point shift was as great as $\pm 15\text{ K}$ at 4.3 nm. Recently, additional DSC data of boiling points of hydrocarbons in different mesoporous materials were published (Luo et al., 2016b; 2016c). Direct measurement of bubble points of hydrocarbon mixtures in mesoporous materials were reported earlier by this group (Cho et al., 2017). These results show that the bubble points may be lower in nano-sized porous media. There has been no published research focusing on the relationship between exclusively nano-sized pores and saturation pressure. To accomplish these measurements, materials with only nano sized pores must first be synthesized.

Therefore, silica based mesoporous materials having the same pore size range as shales were chosen to understand the phase behavior of hydrocarbons in shales. Ordered mesoporous materials have attracted much attention as adsorbents, catalysts, and catalyst supports because of their high surface area and large pore volume with narrow pore size distribution (Topka et al., 2011; Hsu et al., 2007). One of the most investigated materials among ordered mesoporous materials is SBA-15 which has highly ordered hexagonal mesoporous silica structures. However, packing SBA-15 into a tube for saturation pressure measurements creates macroporosity between particles. It is desirable to eliminate this macro-porosity to get an understanding of the effect of nano-sized pores on saturation pressures. To figure out the effect of only the nano-sized pores on the thermodynamic properties, silica based mesoporous monoliths were synthesized using the same reactants used in the synthesis of SBA-15. These monoliths can be synthesized into desired shapes by putting them into customized containers. These monoliths only have intragranular pores, not intergranular pores, so that the effect of the nano-sized pores on the saturation pressure was separated. The mesoporous monoliths can be promising substrates for macromolecular

separations because of their lack of external surface area (Liu et al., 2009; Kendall et al., 2014).

It has been challenging to synthesize crack-free monoliths. Cracks form in the process of creating monoliths making them unsuitable for use as media for saturation pressure measurements. A couple of techniques have been proposed for the creation of crack-free monoliths, only with partial success. For example, in the super critical CO_2 drying, which is one of the methods, the diffusion of CO_2 inside the gel is difficult to control. The processing period is also too long, which limits the practical application of monolithic mesostructured silica (Van Bommel and De Haan, 1995; Garcia-Gonzalez et al., 2012; Rogacki and Wawrzyniak, 1995). Yang et al. reported a fast way for preparing crack-free mesostructured silica monoliths using liquid paraffin (Yang et al., 2003). When poured onto the silica gel to conduct thermal treatment, the liquid paraffin seeps into the interface between the monoliths and the container when the monoliths shrink, thus avoiding exposing the gel to the atmosphere. However, it is difficult to remove the liquid paraffin completely after the monoliths have been synthesized.

In this work, the crack-free monoliths were synthesized by controlling the evaporation rate and the monoliths were used to find the effect of a confined system on saturation pressure. The effect of different container types on synthesizing monoliths was also studied. The synthesized crack-free monoliths were characterized using X-ray diffraction (XRD), nitrogen adsorption/desorption isotherm (BET), pore size distribution curve, transmission electron microscopy (TEM), and scanning electron microscopy (SEM). Finally, using the synthesized monoliths, the phase behavior change in a confined system was studied. For single component phase behavior experiments, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used. The synthesized monoliths saturated with decane were used to obtain DSC and TGA profiles. From these results, the temperature of the phase change in a confined system was shown. Also, the experimentally measured saturation pressure of the hydrocarbon mixture (decane-methane) in the nano-sized porous media was obtained from a pressure-volume graph. To be a standard for the saturation pressure of a bulk system, the phase diagram of the binary mixture of decane and methane (90:10 mol ratio) was modeled using a commercial reservoir simulator from CMG (Computer Modelling Group). By comparing the saturation pressure results of the monoliths to the bulk, the phase behavior change in confined systems was observed.

2. Materials and methods

2.1. Synthesis of the silica based monoliths

A procedure to synthesize SBA-15 was altered to create the silica based monoliths (Zhao et al., 1998). The chemicals required to synthesize these monoliths are 2 M hydrochloric acid (HCl), deionized water (DI water), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic P123), and tetraethyl orthosilicate (TEOS). The first step in this process is to create a mixture of 120 mL of 2 M HCl and 30 mL of deionized water (DI water). Then, approximately 4 g of Pluronic P123 were dissolved in the HCl water solution. When the solution was fully dissolved, 9.1 mL of TEOS were added and allowed to mix for about 15 mins. This solution was then poured into a container or mold. Paraffin film was placed on top of the containers and some holes were created in the paraffin film using a needle. The solution was then placed into an oven at $50\text{ }^\circ\text{C}$. The monolith solution was left in the oven for varying times depending on the size of the containers. The smaller the container, the less time the monolith required to form

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