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Experimental investigation of confinement effect on phase behavior of hexane, heptane and octane using lab-on-a-chip technology

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A R T I C L E I N F O

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A B S T R A C T

The study of phase behavior of hydrocarbons inside shale rock has garnered significant attention in contemporary literature. The present work focused on experimental techniques for addressing this challenge. To this end, lab-on-a-chip technology was integrated with high-resolution imaging techniques (inverse confocal microscopy equipment) for investigating the phase behavior of hydrocarbons inside nanoscale capillaries (nanochannels). Experiments were performed to measure the bubble point temperature of pure Hexane, Heptane, and Octane inside nanochannels to study the confinement effect. The novel method of employing a nanofluidic chip enabled the visualization of fluid behavior inside nano-scale channels. The method was found to be highly promising for experimental investigation of the phase behavior in nano-scale pores, which has always been one of the biggest research challenges. The experimental results revealed that for nanochannel depth of 50 nm, the confinement effect in the form of wall–molecule interactions is almost negligible. Additionally, the Peng–Robinson equation of state (PR-EOS) with and without capillary pressure was used for modeling the hydrocarbon phase behavior. Experimental validation of numerical predictions obtained from these thermo-physical models describing the effect of phase behavior for confined fluids were performed in this study.

1. Introduction

Concerns about mitigating the world's energy demands are definitely not new. The ever-increasing global population and subsequent mounting energy demands for limited conventional resources has resulted in a more acute situation. New technical advances (e.g., horizontal drilling, hydraulic fracturing, and state-of-the-art reservoir characterization methods) have enabled the development of “unconventional resources”, especially organic-rich shale, as economically viable alternatives. Despite the promising potential of these unconventional resources, their consideration as energy sources has presented a number of new challenges related specifically to shale rock media. The phase behavior and pressure-volume-temperature (PVT) properties of fluids confined in tiny pores of unconventional oil reservoirs have always been important research topics. Unlike conventional petroleum reservoirs, shale matrix consists of small-sized pores categorized as micropores, with pore diameters below 2 nm, mesopores with pore diameters ranged between 2 and 50 nm, and macropores defined as the pores with diameter larger than 50 nm. On an average basis, more than 70% of the pores range below 50 nm in shale rock media [1,2]. In such small sizes, wall–fluid interactions play dominant roles in defining the fluid's behavior [3]. Owing to its predominant effect on the estimation of reserves, the accuracy of simulated PVT properties of unconventional reservoir fluids has always been a challenge in the petroleum industry.

Micro/Nanofluidic devices are used in various fields such as biomedical science, electrical engineering, fluid mechanics, and pharmaceutical science for both fundamental and applied research [4–8]. Such devices also provide methods to directly visualize fluid phase behavior. The resolution of this imaging process can be as low as the size of a single protein molecule [9]. Such nanochannel devices are fabricated by standard semiconductor manufacturing processes [10]. Recent studies have shown that nanofluidic devices can be used to directly visualize fluid flow and fluid phase behavior in 100-nm channels [11,12].

Several models and simulations have been targeted at predicting the properties of confined fluids; three from among such

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methods have garnered the most attention from researchers: (1) equation of state–based models [13–19], (2) density functional theory [20,21], and (3) molecular simulation [22-24]. Derouane [15] used the van der Waals equation of state to describe the physical state of molecules adsorbed in microporous media, when the sites are fully saturated or near saturation conditions. They introduced a new term for molecule-wall interactions and calculated the PVT properties with the new model. The results is consistent with molecular dynamic simulation results, yet lacking experimental verification. Kotdawala et al. [21] proposed a model based on density functional theory using approximation of a narrow slit pore. They focus on both polar and nonpolar mixtures and conclude that the effect of fluid-wall interactions are extensively higher than fluid-fluid effect. Pitakbunkate et al. [24] performed molecular dynamic simulation in order to find phase diagrams for confined fluids. They used Grand Canonical Monte Carlo simulation (GCMC) in which chemical potential, temperature and pressure are kept

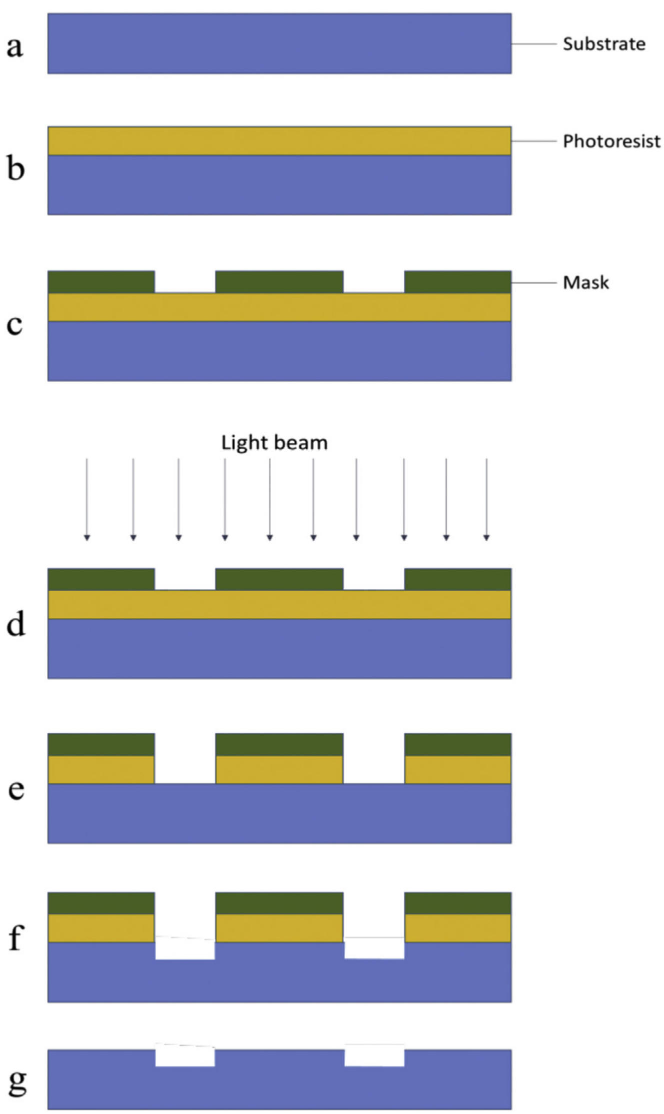

Fig. 1. Photolithography process: a, b) a layer of photoresist is spin-coated on the substrate; c) the photomask is mounted and aligned on top of the photoresist; d, e) the pattern of the mask is replicated on the photoresist by illuminating the system; f) the pattern is developed and etched on the substrate (using dry etching or wet etching techniques); and g) the photoresist is removed (stripped). This process can be repeated, along with surface deposition of multiple layers of materials, for obtaining additional surface features until the desired pattern is obtained.

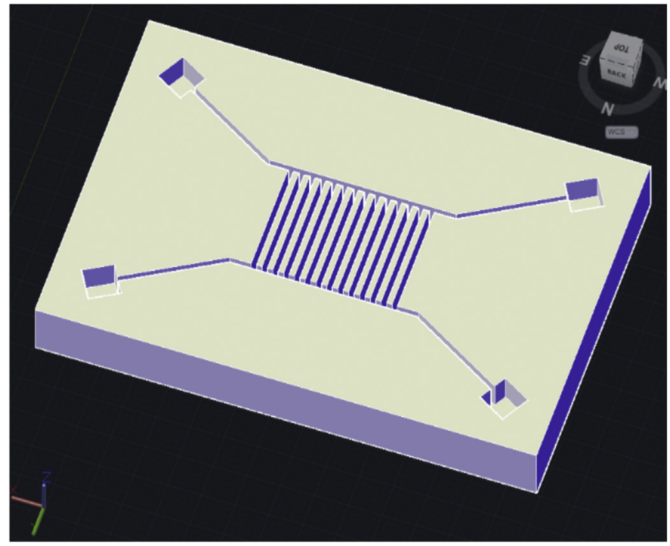

Fig. 2. Schematic of nanofluidic chip used in this work (with enlarged sizes).

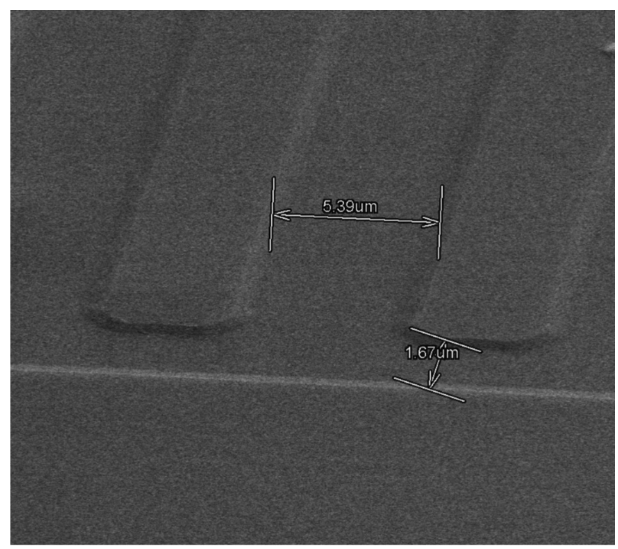

Fig. 3. SEM image of fabricated nanofluidic chip for calibration.

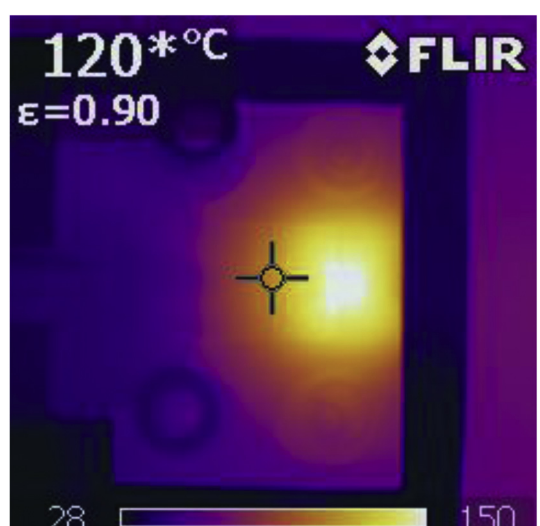

Fig. 4. Image recorded by an IR camera is shown here. The measurements from the IR camera were validated using measurements from the surface mounted thermocouples for performing temperature calibration.