Bubble nucleation and dissolution in multicomponent fluids near a phase boundary using a rapid heat pulse

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ABSTRACT

We report a novel means of nucleating a second phase using a miniature thermal nucleation source that operates with fluid mixtures at elevated temperature and pressure. This rapid nucleation source locally creates a short-lived (millisecond) but large (up to 10^7 K/m) thermal gradient that we exploit to overcome the nucleation barrier in single and multicomponent fluids, eliminating the need for traditional mechanical agitation. We find good agreement between the phase envelope measured with this method and that measured using a conventional apparatus with mechanical agitation acting as a nucleation source for several binary alkane mixtures. Consistent with expectations, we find that thermal nucleation cannot trigger production of a second phase for temperatures and pressures higher than that of the critical point for single-component fluids, However, we find a range of temperatures and pressures completely outside the phase envelope for multi-component mixtures where thermal nucleation temporarily and anomalously appears to produce a second phase, contrary to expectations based on equilibrium thermodynamics. The relationship between the magnitude of undersaturation and the rate of bubble dissolution is studied in single and multi-component fluids. Direct observations of the morphology that is created during nucleation reveal a sharp interface between coalescing droplets, consistent with the second phase possessing an interfacial tension with respect to the continuous phase.

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1. Introduction

Many industries rely upon an accurate knowledge of the phase behavior of fluids [1–5]. Accurate measurement of the saturation pressure of multi-component fluids is challenging in part due to the nucleation barrier that must be overcome to form a second phase. Without vigorous agitation a fluid can remain in a meta-stable single-phase state (supersaturated) at pressures well below the thermodynamic bubble point. This nucleation barrier can be overcome by aggressive mechanical or acoustical mixing in laboratory-based measurements with a measurement that can take hours, but the space required for such equipment is similar in size to that of an automobile. As well, the large fluid volume required by this equipment creates a significant risk due to the stored energy of pressurized samples. Furthermore, the oven needed to heat such samples is sufficiently large that temperature stabilization can require many hours itself. By miniaturizing the sensors and reducing the measured volume of fluid we can

dramatically reduce the time to thermally stabilize a sample while minimizing the risk due to stored energy. However, the challenge of mixing in a microfluidic cell where fluid flow is typically laminar (low Reynolds number) makes standard mechanical mixing methods less suitable for microfluidic sensors or those with small internal volumes. In response, we have developed a non-mechanical thermal nucleation method that uses a millijoule heat pulse delivered by a thin wire to temporarily overcome the nucleation barrier, the science of which is the focus of this manuscript [6,7].

There is a rich literature on nucleation and boiling resulting from fast heat pulses emanating from thin wires immersed in single-component fluids such as water, but little is known about similar phenomena in multi-component fluids [8–11]. Rapid heating is used in a variety of microfluidic applications, such as for bubble-based pumps or for ink-jet printer heads [12]. In these cases, the heat pulse sufficiently superheats the fluid such that nucleation becomes kinetically favorable and occurs on short time-scales. However, there has been little work performed on thermal pulses applied to *single-component systems* that are above their critical pressure, where thermal pulses would not supersaturate the fluid and the formation of a separate phase would not be

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Nomenclature

ρ	density (g/cc)	R_{PR}	resistance, in Ohms, of precision resistor
η	viscosity (cP)	V_{PR}	voltage across precision resistor
T	temperature (°C)	I	current in amperes
ΔT	temperature increase of wire (°C)	r	wire radius
P	pressure (psi)	L	wire length
P_b	bubblepoint pressure	t	time t in seconds
V	volume (units of milliliter (mL) or microliter (μL) used in this manuscript)	ρ_w	density of wire in mass per volume
		ρ_r	resistivity of wire
R	bubble radius (typically in microns)	$\dot{R}$	bubble interface velocity
m	mass of wire (typically in kilograms)	GOR	Gas Oil Ratio (scf/bbl, or standard cubic feet of gas/barrel of oil)
C_p	specific heat		
E	energy dissipated by wire with each pulse		
R_{wire}	resistance, in Ohms, of heater wire		

thermodynamically favorable (pseudo-boiling) [13–15]. Furthermore, we are unaware of any work studying wire-based thermal pulses near or above the phase boundary in *multi-component fluids*, outside of our group, one of the subjects of this manuscript.

Our primary motivation in studying nucleation originates from our interest in developing a ruggedized instrument that measures saturation pressure in multi-component fluids without a mixer. Results herein indicate that the behavior of thermally nucleated phases can be used to determine whether a fluidic system is in the single or two phase region of its phase diagram. In order to determine the limits of this technique it was necessary to perform extensive benchmarking and to develop a rudimentary understanding of the nucleation mechanism. In single-component fluids we find, as expected, that local heating is only capable of producing a distinct second phase at pressures and temperatures below the boiling line. In multi-component fluids, however, we find thermal nucleation of a second phase occurs at pressures and temperatures where only single phase fluids should be thermodynamically stable, an unexpected result which we refer to as *anomalous nucleation,* where the term anomalous is used because of the unknown mechanism by which the phase is thermally nucleated. This nucleation occurs at higher pressures than the cricondenbar, far outside of the metastable region between the spinodal and the binodal. Results suggest that anomalous nucleation is a consequence of the Soret effect (thermodiffusion) which creates a temporary compositional inhomogeneity in response to the thermal gradient.

2. Experimental method

2.1. Choice of single component fluids and multicomponent mixtures

Fluids were identified where the maximum pressure of two phase coexistence was accessible to our experimental system, which is operable between 0 °C and 150 °C and at pressures up to 15,000 psi. For single component fluids this pressure limit is found at the critical point, which is well-characterized and documented for a variety of different components; ethane and carbon dioxide were chosen based on their critical points and natural occurrence in hydrocarbon reservoirs. Unlike single component fluids, where the critical point properties are generally available from the literature, formulation of multicomponent mixtures with the desired phase behavior generally requires laboratory experimentation and iteration. For simplicity and to roughly approximate the behavior of crude oils, binary mixtures of methane were generated with a variety of liquid *n*-alkanes where the composition was tailored to match the following experimental needs. In some cases, we chose compositions where the maximum pressure of two phase

coexistence (termed the *cricondenbar*), was accessible by our experimental apparatus. This was feasible since the cricondenbar depends largely on the composition of both of the fluids in the mixture and their relative concentrations. For certain studies, similar considerations were made concerning the *critical point* of the mixture. Toward that end, equation of state modeling can be used to guide the formulation of mixing ratios of the two or more components such that the cricondenbar is accessible to our apparatus and the critical point temperature is above the cricondenbar temperature. We used two separate equation of state modeling programs, GERG-2008 [16] and REFPROP, the latter being provided by the National Institute of Standards and Technology (Gaithersburg, MD). These equations of state programs are limited in their functionality by the difficulty in appropriate mixing rules, so these calculations were taken as merely an approximate indication of the true phase behavior. However, these programs provided a useful guide in choosing fluids and their relative fractions in prepared mixtures. As we will describe in Section 2.3, the reference phase behavior of most fluids was measured using a conventional apparatus for the purpose of comparison with the phase behavior measured by thermal nucleation. Finally, studies with alkane mixtures were complemented with fluids consisting of "dead" crude oils (flashed so as to remove dissolved gas) subsequently recombined with gas mixtures to simulate live crude oil samples.

2.2. Sample preparation

Single-component fluids were obtained in gaseous form with manufacturer-stated purities of 99.5%. No further purification of single-component fluids was performed. These were pressurized to liquid form in a Single-phase Sample Bottle (SSB) provided by Schlumberger Oilphase-Aberdeen laboratories of Aberdeen, United Kingdom [17,18]. The SSB consists of a high-pressure cylinder separated by a short piston. One side of the cylinder contains the fluid sample while the other side of the cylinder contains a hydraulic fluid that can be pressure-controlled using a high pressure syringe pump. The total cylinder volume, shared between the hydraulic and sample sides, is 600 mL.

Binary mixtures were prepared directly in SSB bottles. First, the SSB bottle was filled with a predetermined mass of liquid while open to the atmosphere. The bottle was then closed, leaving some amount of air in the bottle along with the liquid, but the initial sample volume was minimized to reduce the amount of contamination. The sample side of the SSB was then filled with high pressure methane gas, allowing the sample side to displace all fluid from the hydraulic side, filling the entire 600 mL of the SSB with sample fluid. This two phase system was then pressurized to at