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Evaluation of rate of cyclopentane hydrate formation in an oscillatory baffled column using laser induced fluorescence and energy balance

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ABSTRACT

We report a novel method using laser induced fluorescence (LIF) for observing cyclopentane hydrate formation in an oscillatory baffled column (OBC). In LIF, a dye fluoresces in a hydrate system when induced by a laser; this highlights the areas in which hydrates are present, allowing the hydrate formation regimes to be identified and rates evaluated. Using temperature measurements of the system, the rates of hydrate formation are also determined by a thermal method. The work shows that there is a high correlation between the LIF and the thermal techniques in obtaining kinetic information on cyclopentane hydrate. The results indicate that there are possibly three mechanisms governing hydrate growth. With the absence of mixing, a film formation is observed. At high mixing intensities uniform droplet dispersion is resulted, where fluid mechanics is the controlling parameter. At low mixing conditions a combination of the two mechanisms co-exists, interfacial mechanics is thought to be the dominant factor. The trends in the rates of hydrate formation are different in each of these regimes.

1. Introduction

When pressurised, cooled and mixed with a range of (guest) molecules, from hydrocarbon gases (methane, ethane and propane) to water soluble and insoluble solvents (tetrahydrofuran and cyclopentane) as well as some non-hydrocarbon gases (carbon dioxide and hydrogen), water will form crystalline compounds known as clathrate hydrates. Through hydrogen bonding the water (host) molecules arrange into a framework containing large cavities that can be occupied by the guest molecules. These structures are similar to crystal framework formed by freezing pure water to ice, however, due to non-bonded interactions between the encaged guest molecules and the water cavities, these clathrate hydrates are thermodynamically stable at conditions typically unsuitable for ice [1], e.g. at atmospheric pressure ice melts at 273.2 K, whereas cyclopentane hydrates at 280.9 K [1]. Depending on the nature and size of the guest molecules, hydrates will form one of three structures: sI, small pentagonal dodecahedron and large tetrakaidecahedron cages [2]; sII, small pentagonal dodecahedron and large hexakaidecahedron cages [3] or sH, small pentagonal dodecahedron, medium irregular dodecahedron and large icosahedron cages [4].

In seeking to discover more about the equilibrium and kinetics of hydrates, numerous techniques have been employed ranging from rheometry [5], differential scanning calorimetry [6,7], scanning electron microscopy [8] and neutron spectroscopy [9], to molecular scale measurements through scattering of X-rays [10] as well as Raman spectroscopy [11,12]. At macroscopic level, particle video microscopy [13] and infrared imaging [14] have also been utilised to obtain information relating to fluid mechanical conditions under which hydrates are formed. However, to date no work has been published regarding the use of laser induced fluorescence (LIF).

LIF is a spectroscopy technique employed in studies of flow visualisation and measurement. Areas of applications can be found from combustion of gases and liquids [15,16], human and cell biology [17,18] to reaction kinetics and energy transitions [19–21]. LIF relies on the absorption, excitation and emission (fluorescence) of energy from certain molecules, generally a special dye. When illuminated with laser light of a certain wavelength (high energy photons), e.g. 510 nm, the molecules are promoted to a higher energy state (excitation). However, these higher energy states are unstable and quickly decay back to the lower one. During this decay photons of a lower energy than the ones applied are emitted at a higher wavelength, e.g. 590 nm. This can be utilised by recording the light emission using a digital camera coupled with a filter to only accommodate light of the higher wavelength. In this way, an image recording of such a light emission due to fluorescence can be obtained; in turn this is closely related to the physical or chemical changes of the focused element occurring in a system.

Although numerous models exist for the nucleation and growth of clathrate hydrates the majority of models are based on mass transfer being the limiting factor [1]. Therefore, a reactor that

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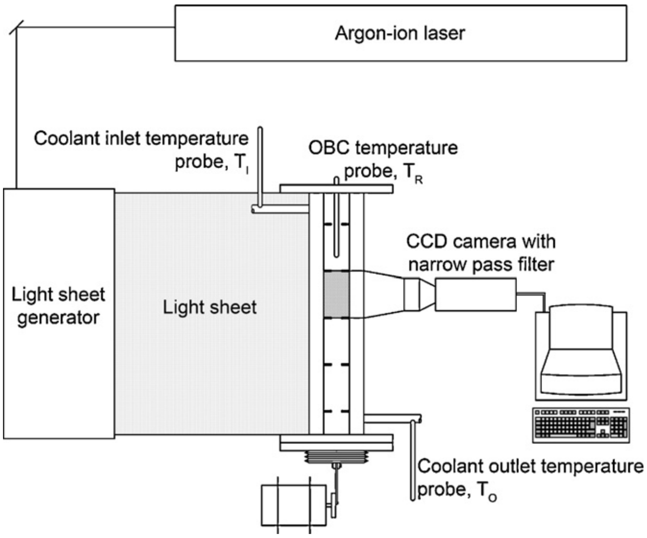

Fig. 1. Experimental setup (hatched area represents one baffled cell).

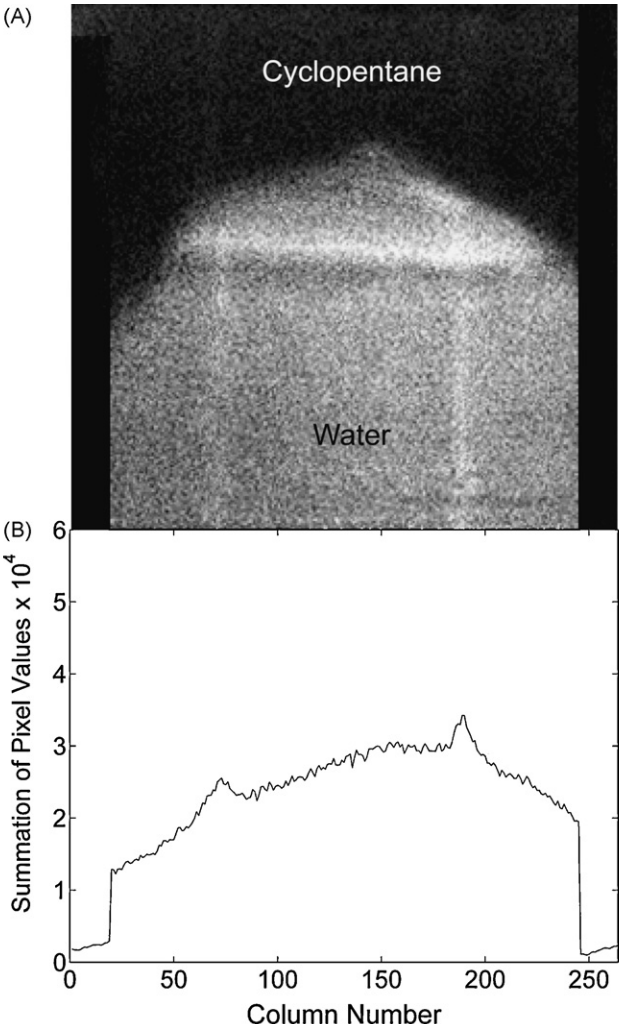

Fig. 2. (A) LIF image before hydrate formation and (B) the area plot for one image frame.

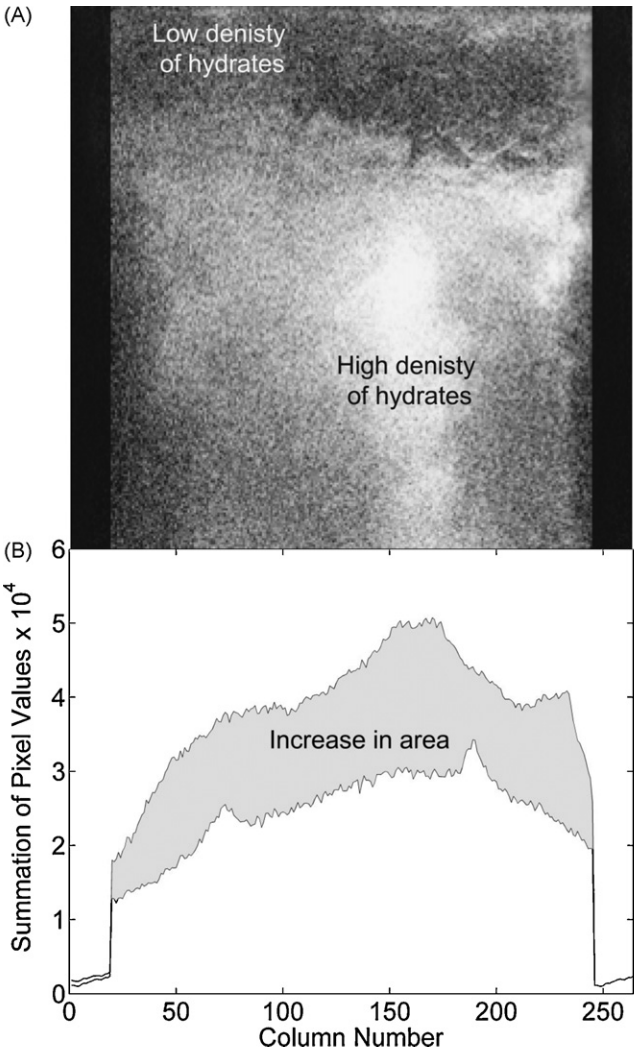

Fig. 3. (A) LIF image after hydrate formation and (B) a plot showing area difference.

enhances mass transfer rates would be desired, to this extent an oscillatory baffled column (OBC) was employed.

The mixing in OBC is achieved by eddies that are created when oscillatory motion of fluids pass through stationary orifice plates. Previous studies show that the mixing is uniform [22–25] and mass

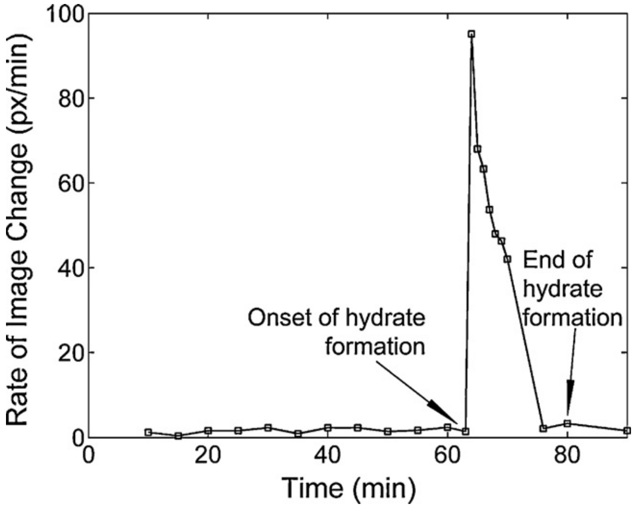

Fig. 4. Rate of image change as a function of time (Re$_o$ = 767, St = 0.637).