In situ Raman spectroscopic investigation of flux-controlled crystal growth under high pressure: A case study of carbon dioxide hydrate growth in aqueous solution

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ABSTRACT

We developed a high-pressure in-situ non-invasive technique to measure the solute concentration distribution in the solution around a growing crystal, in order to study the effect of increasing flux to the crystal surface on the growth process. Growth rates of carbon dioxide hydrate in pure water in a capillary high-pressure optical cell were determined at 20 and 40 MPa and 275.15, 278.15, 280.15, and 283.15 K. During the growth of the hydrate, CO_2 was supplied through diffusion in the aqueous phase from the liquid CO_2–aqueous solution interface, and the dissolved CO_2 concentrations along the diffusion path were monitored by Raman spectroscopy. We demonstrated that the hydrate growth rates could change a lot under constant driving force, such as under the same degrees of super-saturation, super-cooling or over-pressurization of the system, and that the growth rates depend on the mass transfer flux to the surface of the hydrate crystal; with the increasing flux to the crystal surface, the rate-dominant process changes from "diffusion controlled" to "interfacial reaction controlled" after the diffusion flux reaches a critical (maximum) value. The interfacial reaction coefficient k_r is estimated to be 1.31×10^{-6} m/s at 20 MPa and 280.15 K, and the molar volume and hydration number of CO_2 hydrate vary from 21.7 to 22.0 cm^3/mol and 7.09 to 7.67, respectively. These observations and measurements could be useful for the design of crystal growth.

1. Introduction

Natural gas components like methane, ethane, propane, carbon dioxide, nitrogen and hydrogen sulfide are known to form hydrates at high pressure and low temperature. The growth kinetics of crystal from solution under high pressure is of great interests in industrial and geological processes (e.g., geological CO_2 sequestration as a means to mitigate the global warming [1] and production of CH_4 from CH_4 hydrates with the injection of CO_2 [2]). However, only limited accurate data exist for the hydrate crystal growth rate [3]. The growth rate and the morphology of the crystal are controlled by the surface reaction as well as transport of mass and heat, usually depend both on the diffusion rate and the reaction rate. To better understand the phenomena of crystal growth in solution under high pressure and improve the processes designed

for the crystal growth under high pressure, it is necessary to develop high-pressure in-situ non-invasive techniques to measure the solute concentration distribution in the solution around a growing crystal and determine the ratio of surface flux to mass transport flux, because the rate-dominant process depends on the ratio of surface flux to mass transport flux. Furthermore, an accurate value for the reaction rate constant of hydrate formation is required for the design of proper reactor for a large-scale hydrate production [4].

Kinetic studies of hydrate growth are often carried out in a controlled environment using a semi-batch stirred tank reactor, where liquid water and hydrate former gas are in contact at suitable temperature and pressure to form gas hydrate. On the basis of experimental and theoretical analyses, models were established to describe the formation kinetics. For example, a fugacity model, proposed in the pioneering work of Englezos et al. [5], can be used to determine the reaction rate constant of hydrate formation. Skovborg and Rasmussen [6] limited hydrate growth to a mass-transfer problem and considered the transport of gas molecules

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Nomenclature

List of symbols

m_i	molality of component i in liquid phase in mol/kg H_2O
H_r	peak height ratio
D_i	diffusion coefficient of component i in water in m^2/s
T	absolute temperature in Kelvin
P	pressure in MPa
J	diffusion flux
ρ_i	density of component i
x_i	mole fraction of component i in liquid phase
V_φ	apparent molar volume of dissolved CO_2
V_i	volume of component i in cm^3
$V_{m,\,i}$	molar volume of component i in cm^3/mol
$L_{sol,\,t}$	length of aqueous solution at time t in m
$L_{H,\,t}$	length of hydrate at time t in m
t	time in s
A	cross-section area in m^2
C	constant of integration

y	hydration number
n_i	moles of component i
M_H	molecular weight of hydrate in g/mol
K'	overall transfer coefficient in m/s
K	reaction rate constant in mol/(m^2 MPa s)
k_d	mass transfer coefficient
k_r	reaction coefficient
Π_H	flux controlled coefficient
A_H	crystal surface area in m^2
c	bulk fluid concentration in mol/kg H_2O
c_{eq}	concentration at equilibrium in the presence of hydrate
f_i	fugacity
Φ_i^L	fugacity coefficient
c_{tot}	constant total molar concentration

Subscripts

sol	solution
H	hydrate

from the gas phase to the liquid water phase as the rate-determining step in the overall hydrate formation process. Hashemi et al. [7] modified the gas hydrate growth model of Englezos et al. [5] based on a concentration driving force, where the equilibrium concentration at the hydrate surface was determined at the surface pressure and temperature. In most of these studies, heat and mass transfer resistances were designed to be negligible by using high agitation rates in semi-batch stirred tank reactors, even though the growth or dissolution of crystal may be controlled either by mass or heat transfer or by interface reaction [8]. On the other hand, the role of hydrate intrinsic kinetics has been more recently suggested to play a smaller role in hydrate growth in real systems than heat and mass transfer effects [1]. In addition, although attempts have been made to use particle size measurement techniques in recent studies, for example, Herri et al. [9] used turbidimetry measurements to characterize kinetic inhibitors during the crystallization of methane hydrate, and Clarke and Bishnoi [10] used a focused beam reflectance method probe to measure the particle size distribution to obtain the intrinsic rate constant, accurate measurement of the amount of hydrate crystal is still a challenge for studying gas hydrate kinetics.

In the present study, a new reactor has been used for hydrate growth, in which the size of crystal, the transfer of CO_2 and the consumption of CO_2 and water can be accurately determined. CO_2 hydrates are formed in a capillary high-pressure optical cell, a section of which can be fully filled by the crystal. The length of the sections for hydrate crystal and solution were measured as a function of time. An in situ measurement technique based on Raman spectroscopy was established to directly measure the CO_2 concentration distribution in the solution around a growing hydrate crystal, in order to determine the mass transfer rate and analyze the rate-determining process. Growth rates of carbon dioxide hydrate in water were determined at 20 and 40 MPa and 275.15, 278.15, 280.15, and 283.15 K. The conversion of the rate-determining step from mass transfer to interfacial reaction was observed.

2. Experimental section

2.1. Experimental apparatus and procedures for growing single crystal

A capillary high-pressure optical cell (HPOC, [11,12]) in combination with a Linkam CAP500 heating–cooling stage was used for the Raman spectroscopic study of mass transport flux in the aqueous solution during the hydrate growth at high pressure and low temperature (Fig. 1). The HPOC was constructed from a round cross-sectional flexible fused silica capillary tube with 375 μm OD, 50 μm ID and about 25 cm in length. One end of the tube was sealed with a hydrogen flame and the other end of the tube was epoxied inside a stainless steel high-pressure capillary tubing (1.59 mm OD, 0.5 mm ID and 4 cm long), which was connected to a pressure line by a sleeve-gland assembly and a high-pressure valve (HIP 15-15AF1). The cell was inserted into the sample chamber of the heating–cooling stage, its closed end was located near the center of the window of the heating–cooling stage, where the temperature could be maintained with accuracy of ±0.2 K from 273 to 373 K [13].

A section of ultrapure water (about 1.85 cm long) with resistivity of 18.24 MΩ·cm was loaded to the closed end of the capillary cell after the water was boiled for several minutes to expel possible dissolved air. Carbon dioxide (99.99%, Air Products) was loaded into the pressure line and the cell, after they were evacuated, and then pressurized by using a pressure generator. One day was allowed to let the carbon dioxide diffuse into pure water. The pressure was read from a Setra 206 digital pressure transducer with a Datum 2000 manometer (9999 psi full scale; accurate to ±0.14%). Hydrates were nucleated in the solution near the closed end of the optical tube by placing about 5 mm section of the cell in the heating–cooling stage and adjusting the temperature to 238 K for a few minutes. The whole cell was then warmed to a target temperature to let a single crystal grow under a concentration gradient at a fixed temperature–pressure condition. After the crystal fully occupied a section of the HPOC (Fig. 2), we started to record the images of the sample continuously and perform Raman spectroscopic measurements.

2.2. In situ monitoring of the concentration distribution of dissolved carbon dioxide

Quantitative Raman spectroscopy was used to measure the solute concentration distribution in the solution around the growing crystal. Raman spectra of dissolved carbon dioxide in solution were acquired by a JY/Horiba LabRam HR Raman system, using a 532.06 nm (Frequency doubled ND: YAG) laser excitation whose output laser power is 45 mW, a 50× long-work-distance Olympus objective with 0.5 numerical aperture, and a 300-groove/mm grating. The aperture of the confocal hole is 200 μm. Raman peak