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A unified approach for description of gas hydrate formation kinetics in the presence of kinetic promoters in gas hydrate converters

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ABSTRACT

The kinetic promoters have found wide applications in enhancing the rate of energy conversion and storage via gas hydrate formation processes. Effects of different kinetic promoters such as anionic surfactants sodium dodecyl sulfate (SDS), dodecylbenzene sulfonic acid (DBSA), and sodium dodecyl benzene sulfonate (SDBS); cationic surfactants, Cetyl trimethyl ammonium bromide (CTAB), dodecyl trimethyl ammonium bromide (DTAB) and non-ionic surfactants, alkylpolyglucoside (APG), dodecyl polysaccharide glycoside (DPG), TritonX-100 (TX100) on methane (CH_4), ethane (C_2H_6) and propane (C_3H_8) gas hydrate formation processes are investigated in this work. A macroscopic kinetic model based on the time variations of reaction chemical potential is also presented for global description of gas hydrate formation processes. Experimental gas hydrate formation data are employed to validate the proposed kinetic model. Effects of promoter's concentrations and agitation intensities on the gas consumption profiles are also investigated. A universal correlation and a unified kinetic map have been proposed for macroscopic description of gas hydrate formation kinetics in the presence or absence of kinetic promoters. According to the presented unified kinetic map, a unique region of gas hydrate formation is identified for the first time. For negligible amounts of kinetic promoters, the presented region disappears and approaches to a unique path at high agitation intensities. The presented unified approach is very useful for global understanding of gas hydrate formations processes in the absence or presence of kinetic promoters.

1. Introduction

Gas hydrates are ice-like crystalline compounds which may form when water and light gases such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), Nitrogen (N_2), carbon dioxide (CO_2) and Hydrogen sulfide (H_2S) are present at low temperatures and high pressures [1,2]. Unlike freezing phenomena in NGL plants [3], existence of free water is essential for gas hydrate formation. Gas hydrates can be considered as future energy source and their environmental and economic perspectives with respect to their prospects as storage and transport alternative to the liquefied natural gas (LNG) technology makes them become more and more significant [4].

The main challenge to use gas hydrates in industrial processes is their slow formation rates [5]. Studies have shown surfactants, in particular sodium dodecyl sulfate (SDS), have a pronounced effect on hydrate formation [6,7]. There is now much interest in understanding and characterizing the mechanism by which surfactants promote hydrate growth [8,9]. This information could help to guide the synthesis or selection of surfactants with properties better suited to promote hydrate growth.

The rate of gas hydrate formation in the presence of kinetic promoters is governed by different process variables such as supersaturation, rate of mass and heat transfer, agitation intensity, gas composition, promoter structure and concentration [10–12]. Regardless of so many influencing parameters, the hydrate formation kinetics is usually followed by recording the gradual pressure decline in the crystallizer. Therefore the microscopic description of the effects of so many parameters on the gas hydrate formation especially in the presence of kinetic promoters is rather difficult. Due the complexity and stochastic nature of such a process, it would be useful to develop a macroscopic model to avoid the microscopic complications of the gas hydrate formation process description.

The chemical affinity approach has been used for macroscopic description of chemical reactions in isothermal–isochoric systems [13]. Considering the gas hydrate formation process as a chemical reaction between water and a gas hydrate former, a similar approach has also been employed for description of gas hydrate formation in such systems [14–17]. However in those studies no attempt has been made to correlate the material balance of the species with the chemical activities. Also, it has been assumed that

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Nomenclature

A_i	the chemical affinity (reaction chemical potential) at state i, kJ/mol
A_{Si}	pseudo chemical affinity at state i defined in Eq. (12)
$-A_s/RT$	model kinetic parameter in Eq. (11)
AAD	average absolute deviation defined in Eq. (14)
c	promoter concentration, ppmw
N	impeller speed, RPM
ND	number of data points in Eq. (14)
n_{Hi}	moles of produced hydrate up to time ti
n_{ci}	moles of gas consumed up to time ti
n_{cf}	total moles of consumed gas
n_o	initial moles of gas in the vessel
n_i	moles of gas at time t_i
P	system pressure, MPa
R	universal gas constant, 0.008314 kJ/mol K
T	system temperature, K
t	time, s
V	gas volume, m^3
Y	variable in Eq. (14)
Z	compressibility factor

Subscripts

o	initial condition
eq	equilibrium condition
i	state i
j	data index in Eq. (14)
calc.	calculated
exp.	experimental

Greek letters

μ_j	chemical potential of component j, kJ/mol
μ_j^o	chemical potential of component j at reference condition, kJ/mol
a_j	activity of component j, kmol/m^3
α	a positive proportionality constant in Eq. (6)
υ_j	stoichiometric coefficient of component j
λ_1, λ_2	proportionality constants in Eqs (3) and (4)

the rate of affinity change is inversely proportional to growth time without any scientific justification. Unfortunately, a chemical affinity correlation in terms of system pressure has also been assumed without any clear evidence. In addition, effects of influencing parameters such as agitation intensity and species concentrations on the gas hydrate formation processes have not been integrated in a general framework. In order to resolve above shortcomings, a general kinetic model according to a sound theoretical basis has been developed in this work and a unified framework for description of gas hydrate formation processes in the absence or presence of kinetic promoters is proposed. Trend of change of reaction chemical potential of the system for description of the gas hydrate formation process has been theoretically determined and a correlation is presented for studying the gas hydrate formation kinetics during growth period in the absence or presence of kinetic promoters. Effects of different kinetic promoters on methane, ethane and propane gas hydrate formation processes are investigated in this work. Different sets of experiments have been performed for examining the proposed model validity.

2. Experimental procedures

Different gas hydrate formers such as CH_4, C_2H_6, and C_3H_8 with the purity of about 99.5% and anionic, cationic and non-ionic surfactants with the purity of at least 97% are provided as displayed in Table 1.

The experiments are carried out in a 300 cm^3 stirred jacketed batch reactor equipped with a data acquisition system as shown in Fig. 1. The cell pressure is measured by a pressure transmitter with the accuracy of about ±0.08 bar and the temperature is measured with accuracy of ±0.1 K. The signals of pressures and temperatures are acquired by a data acquisition system driven by a personal computer. The temperature of reactor is controlled by the flow of ethylene glycol solution through the jacket.

After washing and rinsing the reactor with de-ionized water, the vessel is evacuated and then a proper amount of aqueous solution with a definite surfactant concentration is charged to the vessel. The reactor is pressurized to about 0.2 MPa below the equilibrium pressure for the hydrate formation at the specified experimental temperature. The constant temperature bath is turned on and the reactor is allowed to reach the constant experimental temperature. When the thermal equilibrium is maintained, the reactor is pressurized to the desired experimental pressure by supplying gas from the cylinder. The mixer is started and data collection begins until the hydrate sample in the reactor reaches equilibrium condition. The experiments have also been carried out without using promoters. Effect of agitation intensity on the gas hydrate formation process has been studied at different impeller speeds in the range of 400–900 RPM (revolution per minute) by using different gas hydrate formers with and without using kinetic promoters. The ranges of operating conditions for different runs are given in Table 1.

3. Modeling of the process

In this work, a macroscopic kinetic model based on the time variations of reaction chemical potential is presented for global description of gas hydrate formation processes. Considering gas hydrate formation process as a homogeneous chemical reaction between gas and water proceeding in an isochoric system at a fixed temperature, the chemical affinity [13] change of the system in terms of species chemical potentials can be written as:

$$dA_i = -d\sum_j (\upsilon_j \mu_j)_i = -d\sum_j \left(\upsilon_j \mu_j^o + RT \ln a_j^{\upsilon_j}\right)_i = -RTd\sum_j \ln\left(a_j^{\upsilon_j}\right)_i \quad (1)$$

where A_i is the chemical affinity (reaction chemical potential) at state i such that at equilibrium state $A_i = 0$ and in any state prior to equilibrium $A_i > 0$. μ_j and μ_j^o are chemical potential of component j at the system and reference conditions respectively. a_j is the activity and υ_j is the stoichiometric coefficient of component j respectively.

Eq. (1) can be written at the time instant of $t = t_i$ in the following form:

$$dA_i = -RT\sum_j \upsilon_j \left(\frac{da_j}{a_j}\right)_i \quad (2)$$

Since gas hydrate formation reactions are customarily carried out under conditions of sufficient dilution, the total fractional change in activities of all species can be written in terms of molar change of produced hydrate as follows: