



Formation and agglomeration of gas hydrates in gas – organic liquid – water systems in a stirred reactor: Role of resins/asphaltenes/surfactants

Andrey S. Stoporev^{a,b,c}, Anton P. Semenov^{c,*}, Vladimir I. Medvedev^c, Rais I. Mendgaziev^c, Vladimir A. Istomin^{d,e}, Daria V. Sergeeva^e, Andrey Yu. Manakov^{a,b}, Vladimir A. Vinokurov^c

^a Nikolaev Institute of Inorganic Chemistry SB RAS, Ac. Lavrentiev Ave. 3, Novosibirsk, 630090, Russian Federation

^b Novosibirsk State University, Pirogova Str. 2, Novosibirsk, 630090, Russian Federation

^c Gubkin University, Department of Physical and Colloid Chemistry, Leninsky Prosp. 65, Building 1, Moscow, 119991, Russian Federation

^d Gazprom VNIIGAZ LLC, Moscow Region, Razvilka Village, 115583, Russian Federation

^e Skolkovo Institute of Science and Technology (Skoltech), Nobelya Str. 3, Moscow, 121205, Russian Federation

ARTICLE INFO

Keywords:

Gas hydrate
Crude oil
Surfactants
Resins
Asphaltenes
Nucleation

ABSTRACT

In the present work, the nucleation and growth of methane hydrate and C₁–C₃ mixed hydrate in the systems with organic liquids (*n*-decane, toluene, crude oils) have been studied. The experiments were carried out in an autoclave at a stirring rate in a range of 100–600 rpm and at a constant cooling rate of 8.4 °C/h under isochoric conditions. In the case of *n*-decane, the experiments were conducted both with the addition of 0.5 wt % of non-ionic surfactants (Span 80 or Surfynol 420) and without them; in the case of toluene the experiments were performed with addition of natural resins and asphaltenes. It was shown that Surfynol 420 had the lowest anti-agglomeration activity with respect to hydrate particles in comparison with Span 80 and oils used. Gas hydrate nucleation occurred at a lower degree of supercooling in the case of oils with a higher content of resins and asphaltenes. The change of resistance to flow in the obtained disperse systems had a reverse trend. Based on the obtained data it can be concluded that the unambiguous effect of the stirring rate on the hydrate nucleation in systems with different composition is not observed. At the same time, an increase in the stirring rate leads to an increase in the amount of gas hydrate formed in a system.

1. Introduction

Gas hydrates are crystalline non-stoichiometric inclusion compounds in which hydrogen-bonded water molecules form a host framework, while the guest molecules (C₁–C₃ hydrocarbons, hydrogen sulfide, nitrogen, carbon dioxide, etc.) occupy cavities in this framework (Sloan, 2007). The problem of gas hydrate formation in wells, gathering and processing systems is relevant for the oil and gas industry. The agglomeration of hydrate particles and their adhesion to the pipeline walls leads to the formation of hydrate plugs (Wang et al., 2018). This encourages researchers to look for more effective ways to manage gas hydrate formation and deposition (Sloan, 2007; Wang et al., 2018; Sloan et al., 2010; Kelland, 2006; Perrin et al., 2013; Lederhos et al., 1996; Istomin et al., 1996; Istomin and Kwon, 2004; Venancio et al., 2018; Kim et al., 2018).

In technological processes of hydrocarbons recovery, hydrate formation takes place in the presence of a liquid phases (oils, gas condensates) (Ning et al., 2010; Greaves et al., 2008; Delgado-Linares et al.,

2013; Turner et al., 2009; Sjöblom et al., 2010). In particular, the formation and agglomeration of hydrates in hydrocarbon drilling fluids at 4 °C and 20 MPa has been studied in the work (Ning et al., 2010). It was shown that the hydrate formation in the hydrocarbon fluids used in deep-sea drilling occurs with a smaller induction period and a higher rate than in aqueous drilling muds. This is due to the formation of a water-in-oil emulsion in such systems with a high concentration of hydrate-forming gas close to the water – oil interface. To prevent hydrate formation in this case, greater amounts of monoethylene glycol (MEG) as thermodynamic inhibitor are required. This inhibitor also acts as an anti-agglomerant, preventing the hydrate particles sticking (Venancio et al., 2018; Kim et al., 2018; Ning et al., 2010). Greaves et al. investigated formation and decomposition of methane hydrate in water-in-oil emulsions with high water cut (> 60 vol %) (Greaves et al., 2008). It was discovered that the formation and subsequent dissociation of the hydrate destabilized the water-in-oil emulsions. The hydrate formation in such an emulsion led to rapid agglomeration of hydrate particles. Hydrate formation in reverse type emulsions based on mineral

* Corresponding author.

E-mail addresses: semenov.a@gubkin.ru, semyonovanton@mail.ru (A.P. Semenov).

<https://doi.org/10.1016/j.petrol.2019.02.002>

Received 14 August 2018; Received in revised form 10 December 2018; Accepted 1 February 2019

Available online 07 February 2019

0920-4105/ © 2019 Elsevier B.V. All rights reserved.