SURFACTANT EFFECTS ON HYDRATE FORMATION FROM A METHANE + ETHANE + PROPANE MIXTURE

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ABSTRACT
This paper describes an experimental study about the effects of surfactant additives on the formation of clathrate hydrates from a model natural gas, i.e., a mixture of methane, ethane, and propane in a 90 : 7 : 3 molar ratio. The specific process of interest in this study is the hydrate formation in a semibatch-type reactor containing a quiescent aqueous phase and a well-mixed gas phase to which the above methane + ethane + propane mixture is continuously supplied to compensate for the loss of the gas due to hydrate formation and thereby maintain a constant pressure inside the reactor. We performed continual gas-chromatographic measurements of the gas phase inside the reactor during each hydrate-forming operation to know how the gas-phase composition chronologically changes as the result of the fractionation accompanying the hydrate formation. These measurements showed an anomalous pattern of change in the gas-phase composition such that the methane fraction first increased and subsequently decreased, while the fractions of ethane and propane inversely change. The mechanism of this finding is discussed in this paper.

Keywords: clathrate hydrates, gas hydrates, surfactant, gas storage, hydrate technology

NOMENCLATURE
\( n_g \) moles of the feed gas supplied to the test chamber after the onset of hydrate formation
\( n_{g0} \) moles of the feed gas with which the test chamber was initially charged
\( p \) pressure inside the test chamber
\( t \) time lapse after the onset of hydrate formation
\( T \) temperature inside the test chamber
\( V_g \) volume (NTP) of the feed gas supplied to the test chamber after the onset of hydrate formation
\( x_1 \) mole fraction of methane in the gas phase
\( x_2 \) mole fraction of ethane in the gas phase
\( x_3 \) mole fraction of propane in the gas phase
\( \omega \) rotation rate of the stirrer for mixing the gas phase

INTRODUCTION
It is widely recognized that the hydrate formation from a hydrate-forming gas and liquid water is significantly promoted by adding a trace amount of an appropriate surfactant to water. It is of particular interest that such surfactant addition leads to a quite high rate of hydrate formation even in the absence of any mechanical means for mixing the gas and the liquid (see, for example, [1–8]). As already pointed out in some previous studies [1, 3, 4, 8], such a high rate of hydrate formation inside a reactor containing an aqueous surfactant solution is presumably caused by the formation and growth of porous hydrate layers over the reactor wall and by the successive sucking of the solution into the layers, which should extend the effective gas-to-solution contact.