Experimental measurements and modelling of carbon dioxide hydrate phase equilibrium with and without ethanol

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ABSTRACT

In this study, three-phase equilibrium conditions of liquid water-hydrate-vapour (L_W-H-V) were experimentally determined for carbon dioxide hydrates with and without ethanol, a thermodynamic hydrate inhibitor, at temperatures ranging from 275.65 to 281.65 K and pressures up to 3.5 MPa. A thermodynamic model for predicting hydrate dissociation conditions was developed. The model was based on the van der Waals−Platteeuw statistical model for the solid hydrate phase, and on the Cubic Plus Association (CPA) equation of state for the vapour and liquid phases. The Kihara potential parameters for the hydrate model were estimated using experimental and literature (L_W-H-V) equilibrium data. The agreement between the experimental and the predicted dissociation pressure was in general acceptable, with an average absolute deviation of about 2.10%.

1. Introduction

Gas hydrates are non-stoichiometric compounds in which hydrogen-bonded water molecules are arranged in an ice-like framework, forming polyhedral cavities occupied by guest molecules (*e.g.*, methane, ethane, propane, carbon dioxide, *etc.*) [1].

Oil and gas production lines usually contain light hydrocarbons, non-combustibles (i.e., carbon dioxide, nitrogen), and produced/formation water. The combination of low temperatures, high pressures, light components and water suggests that oil and gas pipelines can operate within the hydrate stable region. Hydrate formation is the most concerning issue in the flow assurance of oil and gas flowlines. Indeed, hydrates can severely affect production operations by either impairing or causing those operations to completely halt due to their accumulation and eventual blockage of flowlines. Moreover, hydrate plug remediation is not only costly, but develops into potentially hazardous conditions [2].

Several methods are available to prevent or suppress hydrate occurrence in situations where they are likely to form. In some cases, controlling the system temperature and pressure is an adequate strategy to avoid hydrates. Water removal or dehydration of the fluids can be very effective. However, in some cases the implementation of any of those methods may not be cost-effective. In those situations, the injection of thermodynamic hydrate inhibitors (THIs), such as alcohols and glycols, is typically an option, as these chemicals tie-up water and displace the hydrate formation conditions to lower temperatures and higher pressures. These inhibitors are soluble in the aqueous phase and they inhibit hydrates by competing for water molecules, impeding the formation of hydrogen bonds between water molecules and thus preventing the formation of the hydrate structure. In the 1990s, kinetic hydrate inhibitors (KHIs) were introduced, as a mean of THIs replacement. This technology requires kinetic inhibition by preventing crystal growth for a period exceeding the free-water residence time in a pipeline [1].

Exploration and development of the Brazilian pre-salt fields represent a multifaceted deep-water scenario. Reservoirs in this domain are complex layers of heterogeneous carbonates, thus making the accurate reservoir characterization a very challenging task. Those wells are proving to be extremely difficult to drill. In particular, hydrate-related flow assurance issues are especially challenging due to the fluid properties and reservoir conditions. In addition, the pre-salt fields have been found to contain significant amounts of carbon dioxide (CO_2) [3]. This scenario emphasizes the

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Nomenclature

A	SRK attractive energy parameter [Pa m^6 mol^{-2}]
a_w	activity of water [-]
AD	absolute deviation [%]
AAD	average absolute deviation [%]
B	SRK co-volume parameter [m^3 mol^{-1}]
c_i	CPA pure component parameter [-]
C_{pm}	molar specific heat [J mol^{-1} K^{-1}]
f_i	fugacity of species i [Pa]
g	radial distribution function [-]
k	Boltzmann constant [$\approx$ 1.38065E-23] [J K^{-1}]
k_{ij}	binary interaction parameter [-]
H_m	molar enthalpy [J mol^{-1}]
M	molecular mass [kg kmol^{-1}]
P	pressure [Pa]
R	Universal constant of the gases [$\approx$ 8.31451] [kJ kmol^{-1} K^{-1}]
T	temperature [K]
T_c	critical temperature [K]
V_m	molar volume [m^3 kmol^{-1}]
v_k	number of cages of type k per water molecule [-]
w	mole fraction in the hydrate phase [-]
$w_{ik}(r)$	spherically symmetric cell potential [J]
w_{EtOH}	ethanol mass fraction [$g_{EtOH} \, g_{H2O}^{-1}$]
x	mole fraction in the liquid phase [-]
y	mole fraction in the vapour phase [-]
Y	occupancy factor [-]

z	number of water molecules in cage [-]
Z	compressibility factor [-]
Greek	
$\Delta^{A_i B_j}$	association strength [Pa m^3 mol^{-1}]
Δ	polynomial defined in Eq. (20) [-]
ε	depth of intermolecular potential well [J]
$\varepsilon^{A_i B_j}$	association energy [Pa m^3 mol^{-1}]
$\beta^{A_i B_j}$	association volume [-]
μ	chemical potential [J mol^{-1}]
ρ	molar density [kg kmol^{-1}]
σ	molecular size parameter [Å]
Subscripts and superscripts	
A	association site A
B	association site B
cal	calculated
CSM	referring to CSMGem
exp	experimental
H	hydrate phase
i,j,l	component
L	liquid water phase
m	cavity type m
MF	referring to Multiflash
w	water
0	property at ice point
$1,2$	component
β	empty hydrate phase

importance of studying the phase equilibrium aspects inherent to carbon dioxide hydrates and their formation.

Since their discovery by Sir Humphrey Davy in 1810 [1], hydrates and their behaviour have been under continuous investigation and to this date numerous experimental and modelling studies have been published. Shahnazar and Hasan [4] observed that whenever investigating some common hydrate applications or areas of studies, the issue that should be first considered is the temperature and pressure condition in which gas hydrates form. Therefore, a significant number of publications are devoted to the experimental investigation of the thermodynamic conditions in which hydrates occur. In parallel to experimental studies, many of those studies focused on the prediction of the formation conditions by means of correlations and models. There is a large amount of studies on hydrate formation conditions, both experimental and theoretical. Due to the diversity of those publications, only a selected number of publications in this field based on their scientific impact, number of citations, number of data points and absolute errors are mentioned in the modelling section.

Notwithstanding the relatively abundant number of publications on pure CO_2 hydrate phase equilibrium and physical properties [5–30], there is a lack of studies dealing specifically with CO_2 hydrate phase equilibrium in the presence of ethanol ($C_2 H_5 OH$) as thermodynamic inhibitor. Mohammadi et al. [29] reported experimental gas hydrate dissociation data for carbon dioxide with 0.05 and 0.1 mass fraction ethanol aqueous solution systems in the 271.3–280.1 K temperature range and pressures up to 4.54 MPa. These experimental data have been measured using an isochoric method and were compared with the predictions of a general correlation. Maekawa [31] presented experimental equilibrium conditions for carbon dioxide hydrates in the presence of ethanol aqueous solutions for temperatures ranging from 264.1 to 283.1 K and pressures up to 3.45 MPa, also using an isochoric method.

This article presents an experimental and modelling study for three-phase equilibrium conditions of liquid water-hydrate-vapour (L_W-H-V) for carbon dioxide hydrates with and without ethanol. Experiments in an equilibrium cell by the static-synthetic method and isothermal procedure for temperatures ranging from 275.65 to 281.65 K and pressures up to 3.5 MPa were performed. Additionally, a model for the three-phase equilibrium has been numerically implemented and compared to the measured experimental and literature data. The applied model uses the Cubic Plus Association (CPA) [32] equation of state for the fluid phases and the van der Waals and Platteeuw solid solution model [33] for the hydrate phase.

2. Methods and materials

2.1. Experimental apparatus and procedure

Phase equilibrium of liquid water, carbon dioxide hydrate and carbon dioxide vapour is measured in the experimental apparatus shown in Fig. 1, consisting of a static-synthetic apparatus, according to the classification of Dohrn et al. [34]. The equilibrium cell (1), illustrated in details in Fig. 2, is made of stainless steel (AISI 316). It can operate at a maximum working pressure of 25 MPa in a temperature range from 233 up to 473 K. The cell sits at a horizontal position and it has a 17.2-mm ID and 176 mm of length, providing a maximum volume of 25 cm^3. The cell is equipped with two sapphire windows (2 and 3) for visual inspection of the fluids. The rear part is sealed with a back plug (4). The front part has two additional ports (5): one for temperature measurement with a Pt-100 RTD, and another for fluid charging and absolute pressure measurement. The temperature of the system is set by a thermostatic bath (6) that circulates water through a cooling jacket where the equilibrium cell (1) is inserted. The equilibrium cell is lighted by a LED lamp through