



Measuring and modelling of the combined thermodynamic promoting effect of tetrahydrofuran and cyclopentane on carbon dioxide hydrates

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ABSTRACT

This work documents both experimental data, and by thermodynamic modelling, the synergistic effect occurring in promoted carbon dioxide hydrate systems at the simultaneous presence of tetrahydrofuran and cyclopentane.

Cyclopentane has previously been considered a reference among gas hydrate promoters due to its significant pressure reducing effect in hydrate forming systems such as those related to carbon dioxide capture.

The present work shows that hydrate dissociation pressures may be lowered by up to 22% compared to those of the cyclopentane promoted carbon dioxide hydrate system by addition of tetrahydrofuran to the aqueous phase. It is shown experimentally that addition of approximately 5 mol% tetrahydrofuran to the aqueous phase of the cyclopentane promoted system, reduces hydrate formation pressures by approximately 20% compared to those of the cyclopentane promoted system at similar temperatures.

A thermodynamic model, based on the van der Waals–Platteeuw model and the cubic-plus-association equation of state is applied to model the mixed promoter system. The model accurately predicts the data measured in this work. Furthermore, the model explains the synergistic effect by the fact that tetrahydrofuran displaces cyclopentane from the large cavities of the sII hydrate structure. The most pronounced synergistic effect (largest pressure reduction) is predicted at scenarios, where approximately half of the cyclopentane in the hydrate phase has been substituted with tetrahydrofuran.

The model predicts the maximum pressure reduction compared to the cyclopentane promoted system to be approximately 22%. This happens at tetrahydrofuran concentrations of approximately 2.8–3.1 mol% in the aqueous phase, depending on the system temperature.

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1. Introduction

There is growing consensus that our climate is changing due to anthropogenic emissions of greenhouse gases. Carbon dioxide coming from anthropogenic sources is suspected a main contributor to the observed climate change [1]. Within the last two centuries, the amount of carbon dioxide present in the atmosphere has increased from 280 ppm to a level of about 390 ppm in 2010 [2,3]. Much

focus is currently on developing existing or new technologies for removal or limitation of carbon dioxide emissions from central locations such as e.g. electrical power stations. Carbon Capture and Sequestration (CCS) has been pointed out by IEA as an important technological challenge for the future [4]. Separation of carbon dioxide from gas streams has been done on industrial level the last 70 years or more [5]. Specialised chemical solvents (often amines such as MEA, MDEA, DEA or carbonates) have been developed in the petroleum industry to remove carbon dioxide from natural gases. Other applications of carbon dioxide removal are found in the food-processing or energy production industry, where similar solvents are used to remove or recover carbon dioxide [5]. Despite these technologies being considered relatively mature, they are energy

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List of abbreviations and symbols

Abbreviations

AAD	average absolute deviation
BIP	binary interaction parameter
CPA	cubic-plus-association
HLVE	hydrate liquid vapour equilibrium
HLLVE	hydrate liquid liquid vapour equilibrium
LLE	liquid liquid equilibrium
THF	tetrahydrofuran
TBAB	tetra-n-butyl ammonium bromide
TBACl	tetra-n-butyl ammonium bromide
TBAF	tetra-n-butyl ammonium fluoride
VLE	vapour liquid equilibrium
VLLLE	vapour liquid liquid equilibrium

Symbols normal characters

H	hydrate phase
L	liquid phase
k_{ij}	CPA binary interaction parameter [dimensionless]
P	pressure [MPa]
T	temperature [Kelvin]
V	vapour phase
x	liquid phase mole fraction [dimensionless]
y	vapour phase mole fraction [dimensionless]

Subscripts

i	Component i
j	Component j
w	Water liquid phase
a	Organic liquid phase

demanding and not yet ready for application in large scale post-combustion carbon dioxide capture [4].

Recently, a gas (clathrate) hydrate based separation process has been proposed, exploiting physical adsorption of gases into solid, crystalline formations of water, so-called gas clathrate hydrates. Gas separation from gas mixtures was successfully demonstrated using gas hydrate technology [6–17].

Gas clathrate hydrates, more commonly known as gas hydrates, are solid compounds of sufficiently small molecules and water. These solid compounds form when the constituents come into contact at conditions of low temperature and/or high pressure [18–20]. Gas hydrates are often referred to as non-stoichiometric solid inclusion bodies, where water (host) forms a lattice by hydrogen bonding [21,22]. The lattice formation generates a number of empty cavities, in which small gas molecules (guests) may be enclathrated.

Focus in the field of gas hydrate research is now also on finding ways to promote their formation at moderate temperatures and pressures (hydrate promotion). Sun et al. [23] and Eslamimanesh et al. [24] have reviewed recent advances in gas hydrate research including applications of so-called promoted gas hydrate formation in processes for methane/natural gas storage, fuel gas (hydrogen) storage, and gas separation (e.g. carbon dioxide capture).

A thermodynamic gas hydrate promoter is a component that participates actively in the hydrate formation process and stabilises the hydrate structure at high temperature and/or low pressure. This is of interest in most separation processes, since the feed gases are often delivered to the separation facility at pressures much below hydrate forming conditions. Thermodynamic promotion of gas hydrates is a consequence of active formation of mixed promoter/gas hydrates at moderate conditions of temperature and pressure. The hydrates formed may therefore contain significant amounts of the added promoter. Both experimental and theoretical

studies presented in the open literature have pointed out cyclopentane and tetrahydrofuran as two of the most efficient pressure reducing additives in classical hydrate forming systems, where the gas phase component of interest readily stabilises the small cavities of the hydrate structure. Other components with promoting effects are acetone, propane (gas phase additive at ambient conditions) or a range of quaternary ammonium salts (tetra-n-butyl ammonium halides such as e.g. TBAB, TBACl and TBAF) which form semi-clathrate hydrates.

For the specific case of carbon dioxide separation from flue- or fuel gases, Eslamimanesh et al. [24] point out tetrahydrofuran (THF) and TBAB as two of the most extensively studied promoters. THF, however, is stated to have the disadvantage of being volatile, unlike TBAB, which due to its nature as an electrolyte is expected to stay in the aqueous liquid phase. Tetrahydrofuran is a five-sided cyclic ether, which is fully miscible with water at ambient conditions. Hydrate formation conditions depend strongly on the amount of tetrahydrofuran present in the aqueous phase. It has been shown, like for most other water-soluble sII hydrate formers, that the largest pressure reduction is obtained for systems containing 5–6 mol% promoter in the aqueous phase [25,26]. A stoichiometric sII hydrate phase, completely filled with promoter in the large cavities, contains 5.56 mol% promoter.

Cyclopentane (five-sided cyclo-alkane) shows little solubility (ppm order of magnitude) in water under typical conditions of hydrate formation and thus forms an additional organic liquid phase when used in excess amounts. Hydrate forming conditions are often independent or depend only little on the amount of cyclopentane present in the system. From a kinetic point of view, the two hydrate promoters (tetrahydrofuran and cyclopentane) also act differently. Since tetrahydrofuran may be evenly distributed in the aqueous phase at the stoichiometric hydrate concentration, nucleation in THF promoted systems often occurs quickly. Cyclopentane, due to its limited solubility, is available in lower amounts in the aqueous phase. Hence, the occurrence of clathrate like aggregates formed in the aqueous phase, combining to form the hydrate nuclei, becomes less probable from a statistical point of view. Thus, induction times are often high for cyclopentane promoted hydrate systems, and nucleation occurs at the liquid-liquid interface. Once the cyclopentane hydrate starts to form, crystal growth however occurs at high rates.

More details on tetrahydrofuran- and cyclopentane promoted carbon dioxide hydrates may be found elsewhere [27]. In a recent communication [27], it was suggested that the simultaneous presence of tetrahydrofuran and cyclopentane in CO₂ hydrate forming systems provides an enhanced thermodynamic promotion of the gas hydrate phase. A synergistic effect was reported, at which the combination of the two thermodynamic gas hydrate promoters provided lower hydrate dissociation pressures than any of the two individual promoters.

The present communication revisits the quaternary system of water, carbon dioxide, tetrahydrofuran and cyclopentane. Experimental hydrate dissociation pressures are measured for promoted carbon dioxide hydrates formed at the presence of the individual promoters (tetrahydrofuran or cyclopentane) and at the presence of a mixture of the two (tetrahydrofuran and cyclopentane). Finally, the measured thermodynamic data are compared to predictions by a thermodynamic model, developed specifically for these systems [28].

2. Experimental

2.1. Experimental Set-up

Fig. 1 illustrates a schematic of the equilibrium cell utilised in the present work. It consists of a jacketed crystalliser with an internal

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