Separation of CO$_2$ and CH$_4$ from biogas by formation of clathrate hydrates: importance of the driving force

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ABSTRACT

This paper relates to the upgrading of model biogas mixtures, typically 60/40 CH$_4$/CO$_2$, by clathrate (gas) hydrates, which have recently been considered as a safe alternative to high-

pressure or liquefied gas storage, and as an economic, chemical-free process for the separation of gas mixtures. Several factors affecting the driving force to hydrate formation are considered, such as the presence of chemical promoters and the degree of over-pressurization. Promoters used were several anionic and zwitterionic surfactants which demonstrated to affect the hydrate-forming ability of water. Some lignin derivatives were also tested as hydrate promoters. Promoted hydrates were also compared to hydrate-based separation starting from non-promoted water. Separation experiments were conducted under pressures of 4 MPa and 2.5 MPa at 274 K, either under pressure-dropping or constant pressure conditions. Results show that the separation ability of clathrate hydrates, as determined by the separation factor S, is highest when no promoter is added to the water phase; the well known promoter sodium dodecyl sulfate (SDS) shows a value of S which is approximately half the value in pure water, while higher separations were obtained with some lignin derivatives and a non-surface-active naphthalene sulfonate derivative. We also show that the contribution of CO_2 solubility in water to S is a main player in the overall process. Finally, the separation ability of hydrates seems to be inversely proportional to the amount of gas mixture enclathrated, i.e. the occupancy.

KEYWORDS: Biogas separation; Clathrate hydrates; Promoters; Surfactants; Lignins; Driving force; Selectivity of separation.

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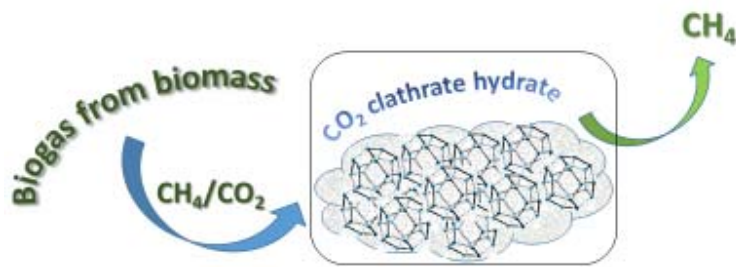
SYNOPSIS

Parameters affecting CH_4/CO_2 clathrate hydrates are identified and discussed with the aim of optimizing a cheap, chemical-free process for biogas upgrading.

INTRODUCTION

Biogas represents a promising renewable resource, and the enhancement of its production and use is currently under active investigation.[1] Biomethane in particular is being increasingly developed as a substitute for fossil natural gas, and is obtained by biogas upgrading in order to remove CO_2 as the main contaminant. Established technologies for the separation and purification of gas mixtures, such as chemical (e.g., amine scrubbing), physical (e.g., pressure swing adsorption), and solid adsorption (e.g., clay binders) processes, may be also applied to biomethane production, but they all have drawbacks.[2,3] Recent work has focused on the possibility of using clathrate hydrate formation for providing such a separation.[4]

Clathrate hydrates (also called gas hydrates) are ice-like inclusion compounds that form under particular conditions of temperature and pressure. In hydrates, water molecules enclose small guests such as methane, carbon dioxide, tetrahydrofuran, etc., into a hydrogen-bonded, crystal

network of Eulerian polyhedra.[5] Hydrates are mainly studied because their formation causes plugs in oil and gas pipelines, representing a major problem in the gas and oil industry. To prevent this, several kinds of chemical additives are used: thermodynamic inhibitors such as methanol and glycols,[5,6] low dosage hydrate inhibitors (LDHIs),[7-9] and biological inhibitors.[10] Also, hydrates are being exploited for their potential in the field of gas storage and transportation for natural gas[11-16] and hydrogen.[16-18] In particular, hydrates are safer and their formation occurs under milder conditions of temperature and/or pressure with respect to, e.g., canisters or liquefied gas, and this also entails a minimization of energy requirements.[18]

Crystal structures for hydrates were determined by crystallographic methods, as structure I (sI), structure II (sII) and structure H (sH). Of relevance in the present paper is structure sI, because both CH_4 and CO_2 are enclathrated into this structure. The crystal unit of sI is composed by 8 cages: 2 pentagonal dodecahedra (5^{12}) plus 6 composite polyhedra having 12 pentagonal and 2 hexagonal faces ($5^{12}6^2$). The 5^{12} cages are smaller than the $5^{12}6^2$. A comprehensive review of crystallographic methods and hydrate structures is reported in the reference book by Sloan and Koh.[5]

Formation ranges of gas hydrates are described by their phase diagrams, and clathrate hydrate-based processes for separating CO_2 from H_2 (e.g., in a pre-combustion mixture), or CO_2 from N_2 (as in a post-combustion gas) have been devised due to the very different phase equilibria between those gases. Conversely, methane and carbon dioxide hydrates present phase diagrams which are quite similar in terms of equilibrium pressures and temperatures, which makes a separation process based on hydrate formation harder.[19] In this regard, it has recently been suggested that an increase of the "driving force" to hydrate formation, i.e., the degree of over-pressurization and/or sub-cooling of the reaction system, leads almost invariably to a decrease in

the CH_4/CO_2 separation ability.[20-22] However, some authors dispute that the selectivity problem is more complex, partly based on the observed shifting of CO_2 vs. CH_4 capture with time.[19,23-26]

The latter findings point to another fundamental problem that should be kept in mind, i.e. CH_4 and CO_2 have very different solubilities in water. This suggests that the hydrate-based separation of feed gas mixtures with different methane and carbon dioxide compositions is actually controlled, at least to an extent, by their partition into the liquid phase, based on the respective solubilities.[27] Therefore, several studies have focused onto this aspect of gas hydrates, by analysing the driving force to hydrate formation in terms of the fugacity of the hydrate-former gas.[28,29] Those studies revealed, *inter alia*, that the solubility of CO_2 in water shows little variability during the hydrate formation process, and is time-independent.

An interesting study in this regard was the experimental determination of the mole fraction of CH_4 and CO_2 in water when the system is kept under hydrate-liquid-vapor (H-Lw-V) equilibrium, showing that the solubility of methane increases with increasing pressure and decreasing temperatures, and the solubility of CO_2 increases with decreasing pressures and increasing temperatures. The observed trend is opposite to the solubility for CH_4 and CO_2 as simple gas hydrate formers under H–Lw equilibrium.[31] Overall, different findings seem to suggest that a *decrease* of the hydrate formation *driving force* (in the form of any of its various components) may be conducive to a higher separation performance, at least within the condensed phase.

Another recognized problem has a kinetic origin, because hydrates of CO_2 and, particularly, methane tend to form slowly and apparently in a *stochastic, non predictable way*. This problem has been addressed by several authors by using promoters, such as thermodynamic co-formers (tetrahydrofuran and other cyclic ethers, propylene oxide, cyclopentane, etc.) and their mixtures

with kinetic promoters,[16] semi-clathrate formers (tetra-alkyl ammonium salts, e.g., tetrabutylammonium bromide),[32,33] and anionic surfactants.[11,34-36] The former two families of promoters act by decreasing the hydrate equilibrium pressures, but have their main drawbacks in the amounts needed (several mol%), which raises an environmental concern when considering that a separation technology based on hydrates is targeted to very large volume applications, such as landfill biogas plants. Furthermore, the relatively high amounts of thermodynamic or semiclathrate former promoters decrease the occupancy of the gas components to be separated, thus dramatically reducing the overall yield of the process. In any case, even with added promoters of the former two families above, i.e., coformers and semiclathrate formers, the key problem remains the low separation efficiency, which in turn entails a low energy efficiency.[20,37] Also, mixtures of thermodynamic cofermers, e.g. tetrahydrofuran and cyclopentane, and kinetic promoters, e.g. sodium dodecylbenzene sulfonate and sodium dodecyl sulfate (SDS), have shown that a higher gas uptake leads to a lower separation selectivity.[16]

A kinetic selectivity for CO_2 versus CH_4 is described in some works, but this selectivity seems to be dependent on technological issues such as the experimental conditions and reactor design.[38,39]

While the practical aspects of the thermodynamic and kinetic promotion of gas hydrates are well described in the cited literature, the supramolecular mechanisms underlying the action of promoters are still poorly understood. Notable kinetic promoters are surfactants, which areamphiphilic molecules. In water solution, they aggregate by forming supramolecular structures such as spherical and rod-like micelles and multilayers, among others. A surfactant solution in water contains free molecules, whose maximum concentration is given by the critical micelle concentration (cmc), and above this specific value micelles are formed.[11,40] Relevant to

the present subject is the role exerted by surfactant on the promotion of hydrate formation and, particularly, the role of surfactant micellization on observed effects. We have demonstrated that at least for some important surfactants, e.g., SDS, the promotion effect is exerted by nonmicellized surfactant molecules, i.e., at concentrations well below their cmc's.[11] This hypothesis is however still debated,[40] and further studies have suggested that the observed promotion may be due to an interfacial growth driven by capillary forces.[33] This finding lends support to an action of promoters (but also nhibitors) which is based on their gas−liquid interfacial behavior, rather than the formation of supramolecular aggregates such as micelles.

The present study was carried out as an attempt to collect the main parameters affecting the formation of CO_2 and CH_4 hydrates, i.e., difference of gas solubilities in water, amount and quality of the "driving force" enacted, structure and properties of promoters, final occupancy of produced hydrates, and so on, under the same framework and to compare the results with the aim of obtaining a more efficient CO2/CH4 separation with a hydrate-based process. As will be seen, a general finding resulting from this work is that the optimization of biogas upgrading from hydrate formation will possibly be achieved through the minimization of the forces enhancing hydrate formation.

EXPERIMENTAL SECTION

Apparatus

The experimental reactor is shown schematically in Fig. 1, and has been designed and assembled by RDPower srl (Terni, Italy). This apparatus permits the preparation of gas mixtures
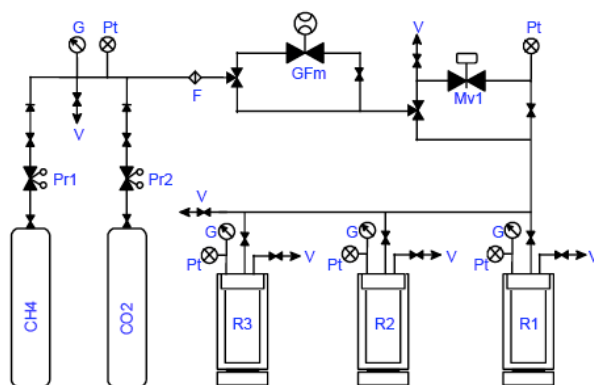

Figure 1 Scheme of the multiple-reactor apparatus. CH4/CO2: gas cylinders; Pr1/Pr2: pressure regulators; V: venting/vacuum/sampling; G: pressure gauges; Pt: pressure transducers; F: filter; GFm: gas flow meter; Mv1: metering valve; R1/R2/R3: reactors.

of any desired composition directly into the reactor. In the present setup, three reactors operate simultaneously in order to increase the experimental throughput. The AISI 316L stainless steel reactors have an internal volume of 230 mL, their operating pressure reaching up to 20 MPa. The reactors are equipped with cooling/heating Peltier units which allow operating temperature ranges from 253 K to 353 K. A chiller with a cooling power of 1000 W is used as heat sink for the Peltier units. The reactors are provided with an internal stirring device, also assembled in house by RDPower, which can operate up to 40 MPa with a torque of 25 Nm. While loading the reactors, the gas flow is regulated by means of a CC Series micro metering valve provided by Tescom. The gas flow is measured by a F131M series thermal mass flow meter provided by Bronkhorst (Bronkhorst High-Tech B.V., The Netherlands) with a measuring range of 50–2000 NmL/min and operating pressure of 40 MPa. Each reactor is provided with a 4-20 mA pressure

transducer purchased by Gems Sensors & Controls (United Kingdom) with a measuring range of 0-40 MPa. Two further pressure transducers are assembled along the gas loading line before and after the metering valve in order to measure the pressure during the mixture preparation process. Each reactor is provided with three resistive temperature detectors (RTD) PT100 class 1/3 DIN purchased by OMEGA Engineering, Inc. (USA). We assembled a custom-built process controller for pressure, temperature, and gas flow using an Arduino microcontroller (arduino.cc). This controller reads the temperatures of each reactor and drives the Peltier power supply in order to apply cooling or heating power when required. Temperature set point is maintained by using a PID algorithm embedded into the Arduino controller. A sketch of the apparatus is reported in Figure 1.

In order to determine the gas mixture composition before and after hydrate formation and dissociation, an IR detector was assembled by using the Premier series of IR gas sensors by Dynament (UK) for CO_2 and CH_4. Sensors have a measuring range of $0-100\%$ and an accuracy better than 2% of the full scale. A dedicated algorithm for Peltier control was developed in order to supply the reactor with a quantifiable cooling or heating power. Such an algorithm was conceived in order to minimize thermal oscillations during hydrate formation and dissociation. Our apparatus for gas quantification was previously standardized by using gaseous mixtures with known ratios of CO_2 and CH_4 that were also analyzed by a common GC apparatus equipped by a stainless-steel packed column (Carboxen 60/80 mesh, 4.6 m length, 3.15 mm E.D. and 2.1 mm I.D.) and a TCD detector (473 K). The GC was set as follows: He was the carrier gas (30 mL/min); after the injection of the gaseous mixture (0.5 mL), the oven was kept under isothermal conditions (323 K) for 6 min. Then, the temperature was raised up to 453 K at a rate of 288 K/min (held for 1 min).

Materials

CH$_4$ and CO$_2$ were provided by RIVOIRA S.p.A. CH$_4$ was 2.5 grade (99.5% methane) and CO$_2$ was a SS grade (99.8% carbon dioxide). CH$_4$/CO$_2$ mixtures (60/40) were prepared by measuring the respective amounts with a mass flow meter (Dynament, see above). SDS, >95.0% and N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate, >97.0% (**T5**) were provided by Sigma-Aldrich (Italy). The **C**, **AM**, **S**, **CRO**, **SRO** lignins were a gift from Burgo Group S.p.A. (Tolmezzo, Italy) and **KrLig** was purchased from Sigma-Aldrich. For quantitative elemental analysis of lignins see Supporting Information. Water was from a MilliQ water purification system (Millipore Merck).

The following list reports the molecules tested in this study as promoters, with their abbreviations. Some of those molecules are novel compounds, whose synthesis and characterization is reported in the Supporting Information:

SDS: sodium dodecyl sulfate;

T1: sodium 2-[4-(octyloxy)phenyl]ethyl sulfate;

T2: sodium 3-[4-(octyloxy)phenoxy]propane-1-sulfonate;

T3: 2-hydroxyethanammonium-4- (dodecyloxy)benzene sulfonate;

T4: sodium 3-(naphthalen-2-yloxy)propane-1-sulfonate;

T5: N-Dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate;

C (CaLig): Calcium lignosulphonates;

AM (AmLig): Ammonium lignosulphonate;

S (NaLig): Sodium lignosulphonate;

CRO (CaRO): Calcium low-sugar lignosulphonate;

SRO (NaRO): Sodium low-sugar lignosulphonate;

KrLig: Kraft lignin alkali, Low sulfonate content.

Procedure

The experiments were performed in a batch mode under either constant pressure or pressure dropping modes. Gas mixtures were 60/40 CH_4/CO_2, and were prepared into a steel cylinder by flowing each pure gas through the F131M flow meter for quantitation. The mixture was then analyzed by gas chromatography. Hydrate-forming solutions were prepared by using 80 cm^3 of MilliQ water in the absence or presence of promoter. Prior to filling into the reactor (230 cm^3), the latter was cleaned with deionized water and dried. To ensure the absence of air, the reactor was connected to a line vacuum pump for 20 minutes with stirring at 200 rpm. The amount of gas mixture (60/40 CH_4/CO_2) charged into the reactor was measured with the F131M flow meter. Filling of the reactor was operated under a constant temperature of 293 K. The starting point of the hydrate formation experiment was taken at the beginning of cooling (with a final setpoint at 274 K). Temperature and pressure data were collected by a data acquisition unit (Arduino, *supra*) and logged into the computer every 1 s. Hydrate formation was assessed from a decrease of gauge pressure (under pressure dropping conditions) or a flow reading from the mass flow meter (under constant pressure conditions). Hydrate formation was considered terminated either when the pressure no longer decreased over at least 2 hours, or when the flow reading was zero for at least 2 hours. Before the analysis, the reactor was quickly supercooled down to ca 253K to avoid hydrate dissociation during the purging. Then, the gas phase into the reactor was analysed by purging through the IR gas sensors for relative and absolute quantitation of CO_2 and CH_4. Each experiment was done in triplicate and the results averaged. The coefficient of variation was calculated at 0.08 or lower.

Based on the gas compositions and amounts measured at the beginning and the end of the experiments, the number of moles of the gas mixture incorporated into the hydrate phase (gas uptake) was calculated by

$$\Delta n_H = n_{g,0} - n_{g,t} = \left(\frac{PV}{zRT}\right)_0 - \left(\frac{PV}{zRT}\right)_t \qquad (1)$$

where $n_{g,0}$ is the number of moles of the gas mixture in the vessel at time 0 (gas load read from the F131M flow meter) and time t (from gas phase at the end of the experiment), z is the compressibility factor calculated using the Peng–Robinson equation of state, T is the absolute temperature, P is the pressure in the rector, V is the volume of the gas phase and R is the gas constant. It was assumed that the volume of gas phase was constant during the experimental process for the reason that the phase transitions were neglected.

The separation factor was calculated according to

$$S = \frac{n_{CO_2}^H \times n_{CH_4}^{gas}}{n_{CO_2}^{gas} \times n_{CH_4}^H} \qquad (2)$$

The recovery of CO_2 was according to

$$R_{CO_2} = \frac{n_{CO_2}^H}{n_{CO_2}^{feed}} \times 100\% \qquad (3)$$

where n_{CO2}^H is the number of moles of CO_2 in the hydrate phase at the end of the experiment and n_{CO2}^{feed} is the number of moles of CO_2 in the feed gas (measured with the F131M flow meter). Similarly, the recovery of CH_4 was as follows:

$$R_{CH_4} = \frac{n_{CH_4}^{gas}}{n_{CH_4}^{feed}} \times 100\% \qquad (4)$$

where n_{CH4}^{gas} is the number of moles of CH_4 in the residual gas phase at the end of the experiment and n_{CH4}^{feed} is the number of moles of CH_4 in the feed gas (as measured with the flow

meter). It should be noted that the use of a flow meter reading allows to duly consider the moles of CO_2 dissolved in water before hydrate formation.

RESULTS AND DISCUSSION

The addition of a thermodynamic or kinetic promoter to hydrate-forming water solutions has invariably been considered as a necessity in the optimization of any processes involving hydrate formation, e.g., in the natural gas storage and transportation through hydrates.[11-16] In the present work, we investigated known and novel promoters in a first attempt to elucidate their effects on the upgrading of biogas mixtures. The promoters investigated in this study were the well-known anionic surfactant SDS, four newly synthesized anionic surfactants, i.e., T1-T4 and a commercial sulfobetaine, T5. Moreover, several lignin species, known for their activity as bio-surfactants, were studied. Lignin-derived polymers can show good performance in lowering the surface tension; in fact, despite lignins from black liquors not having the chemical structures of conventional amphiphilic molecules, they exhibit a certain surface activity. It is hypothesized that lignin adsorbs at the air/water and oil/water interfaces forming a condensed, viscoelastic surface or interfacial film. In the literature, lignin molecules have been categorized as polymeric surfactants when separated from spent black liquors, e.g., lignin sulfonates.

Surface activity and nanoparticle-stabilization properties have been demonstrated in the case of lignins obtained directly from black liquors, with little or no modification, after chemical derivatization and also in combination with other species.[41,42]

Upgrading a biogas mixture means essentially enriching one of the two components, i.e., CH_4 or CO_2, while depleting the other in either of the two phases under investigation, i.e., the gas

phase and the condensed (hydrate) phase. A hydrate-based upgrading process should therefore promote a differential sequestration of one component at the expense of the other.

This statement raises a potential problem in that we know that hydrates of carbon dioxide and methane share the same crystal structure, i.e., structure sI, and, to a first approximation, similar formation kinetics. Under this conceptual framework, the use of surfactant promoters should serve at least two functions, i.e., kinetic promotion and importantly induction of selectivity. By the latter we obviously mean that a good kinetic promoter should also enhance the sequestration of one of the components with respect to the other into the hydrate lattice.

Constant-pressure experiments

Under constant-pressure conditions, the "driving force" of hydrate formation, i.e., pressure, is kept constant throughout the process. This is achieved by operating an electro-pneumatic pressure regulator driven by a pressure signal as sent by an Eurotherm 2604 PID controller. When hydrate formation starts, pressure into the reactor begins to drop and is automatically restored by means of the regulator within a small variation (<1 bar). All results are reported in Table 1.

Table 1: Results of gas uptake and separation experiments carried out on 60/40 CH_4/CO_2 mixtures at 2.5 MPa under constant pressure.

System	C ppm	n gas load[b]	R (CO_2^H)[c]	R (CH_4^g)[d]	S[e]	Kinetics[g]	n gas uptake[f]	Occupancy (%)
H_2O	na	0.313	65.9	72.1	5.0	s	0.135	22.3

	[b]					[g]		
H_2O [a]	na	0.439	47.5	78.8	3.4	m	0.137	22.6
H_2O, SDS	300	0.323	62.2	65.9	3.2	f	0.145	23.8
H_2O, T1	300	0.451	72.6	47.0	2.3	f	0.274	45.3
H_2O, T2	300	0.352	65.4	60.4	2.9	f	0.174	28.7
H_2O, T3	300	0.383	69.9	57.1	3.1	f	0.206	33.9
H_2O, T4	300	0.300	61.8	73.5	4.5	s	0.120	19.7
H_2O, T5	300	0.393	66.0	52.9	2.2	f	0.215	35.5
H_2O, NaLig	1000	0.333	67.2	65.6	3.9	f	0.158	26.1
H_2O, NaLig	2500	0.366	69.8	60.3	3.5	f	0.190	31.3
H_2O, NaRO	1000	0.317	63.5	69.3	3.9	s	0.139	22.9
H_2O, NaRO	2500	0.312	61.2	68.4	3.4	s	0.133	22.0
H_2O, CaLig	2500	0.339	65.9	62.7	3.2	f	0.163	26.9
H_2O, CaRO	2500	0.317	62.3	67.5	3.4	f	0.139	22.9
H_2O, AmLig	2500	0.291	55.6	72.2	3.2	f	0.112	18.4
H_2O, KrLig	2500	0.347	63.8	60.7	2.7	f	0.169	27.8

[a] 4 MPa; [b] Gas charged into reactor. [c] Recovery of CH_4. [d] Recovery of CO_2. [e] Separation factor. [f] Number of moles of the gas mixture incorporated into the hydrate phase. [g] "Fast" (f), "medium" (m), and "slow" (s) refer to a formation which starts in less than 1 h, within 1-2 h, or more than 3 h, respectively.

A blank experiment was performed without any promoters, i.e. with water alone under a constant pressure of 2.5 MPa CH_4/CO_2 (60/40). Hydrate formation was slow, as usually happens with non-promoted hydrates. The gas uptake by the hydrate was 0.135 moles, and the IR analysis of CH_4 and CO_2 in the gaseous and hydrate phases yielded a separation factor, S, of 5. SDS is a well-known promoter, and was tested in our system at its usual hydrate-promoting concentration of 300 ppm, i.e., about one order of magnitude lower than its cmc under the experimental

conditions.[11] Formation rate with SDS was much faster than with water alone, with a gas uptake slightly higher; however, the separation was remarkably lower (S = 3.2). The other surfactants used (except T5) are novel molecules that were synthesized (see Supporting Information) to loosely mimic some of the structural features of known promoters, e.g., SDS and long-chain alkyl benzenesulfonic acids and salts (LABSAs). For example, surfactant T1 carries a sulfate anion bound to a mixed aromatic-aliphatic hydrocarbon chain. T1 was also tested at 300 ppm, which is 3 times lower than its cmc. Hydrate formation with T1 was fast, with the highest gas uptake observed in the present study (0.274 mol). However, its separation factor was among the lowest obtained (ca. 2.3). Surfactant T2 has a sulfonate head group, as in the LABSA salts, and a hydrocarbon tail with a dialkoxybenzene spacer. Hydrate formation rate was also fast, with the highest gas uptake observed in the present study (0.274 mol). However, its separation factor was among the lowest obtained (ca. 2.3). Surfactant T2 has a sulfonate headgroup, as in the LABSA salts, and a hydrocarbon tail with a dialkoxybenzene spacer. Hydrate formation rate was also fast, the gas uptake slightly (20%) higher than that with SDS, and the observed S = 2.9 was lower than those in water and SDS. Specifically, $S_{T2}/S_{SDS} = 0.91$, while $S_{T2}/S_{water} = 0.58$. Surfactant T3 also has a sulfonate polar group and a dodecyloxy benzene moiety as a tail. It also has a peculiar counterion, i.e. a 2-hydroxyethanammonium cation. It gave a fast formation with a good uptake and S = 3.1.

An interesting behavior was found with promoter T4, which is a sulfonate salt with a naphthalenyloxy-ended short alkyl chain. This promoter, which is not properly a surfactant, showed a very low gas uptake (occupancy =19.7%), and a very slow formation rate. However, its separation factor was the highest among all tested promoters (S = 4.5), while being still 10% lower than the separation obtained with nonpromoted water. A compound with a similar anionic

moiety as T4 is the commercial sulfobetaine N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (T5). However, T5 is a zwitterion and lacks the counterion, moreover it has a high surface activity. This sulfobetaine showed a fast formation with a remarkable gas uptake (occupancy = 35.5%), but a low separation ($S = 2.2$).

A second class of surface-active molecules tested in this work comprised lignin derivatives, particularly sulfonated lignins in that they have enhanced surface properties.[43] As opposed to classical surfactants, such as SDS and T1-T5 discussed above, lignins cannot be defined by a standard critical micellar concentration (cmc), such as determined by surface tension or conductimetry. However, some reports recognize the formation of pseudomicelles by lignins and lignin complexes with other biomolecules.[44] For this reason, their addition amounts were not selected by referring to a cmc value, rather they were set at two values of 1000 and 2500 ppm based on a range published in the work by Wang et al. on the promotion of methane hydrates by lignosulfonates.[45] Again referring to Table 1, an overall finding with lignins is that they behave better on average in terms of separation factors, as compared to surfactants T1-T3, T5 and SDS. However, their separation factors never approached that for non-promoted water ($S = 5$). Also, tested lignins are found to be kinetic promoters, except for deglycosilated lignin CRO and SRO, which show a very slow formation of hydrate. Interestingly, the latter is also the best performing lignin in terms of separation ($S = 3.9$ at 1000 ppm).

In the attempt to find a rationale at the basis of the observed behaviors, we may focus onto the driving forces of hydrate formation. A driving force is usually defined as an increase of pressure and/or a decrease of temperature, which tend to enhance hydrate formation. In this study, however, it may be useful to enlarge such a definition to include also factors influencing the process kinetics, e.g., the presence of kinetic promoters. The latter are known to affect the

17

induction time of hydrate formation, also enhancing the mass transfer of gas into the forming hydrate, thus leading to different occupancies within a given experimental time. In turn, this affects the observed occupancy even in the absence of any thermodynamic effects. In this work, the occupancies, i.e., the ratio of the absorbed gas to the theoretical amount (ca. 170 normal volumes of gas per volume of water), were determined and are reported in Table 1. If we focus our attention on the relation of those parameters to the separation factor, then we may observe that any increases of the driving force toward hydrate formation lead to a decrease in the separation power as reflected by S.

Indeed, nonpromoted water, which shows a slow formation rate and a low occupancy (22%), provides the highest observed separation (S = 4.98). If the same nonpromoted system is subjected to a driving force enhancement by increasing the pressure to 4 MPa, then it is observed that hydrate forms faster, and S decreases to 3.36.

A wider modulation of the driving force can be observed when promoters are used. In this case, strong kinetic promoters, i.e. those that make hydrates form in less than 1 hr, almost invariably led to a decrease in S. In contrast, bad promoters, such as T4 and low-sugar lignins SRO and CRO, gave enhanced separations. Those promoters which also increase the occupancy, such as T1, T5, and lignin alkali, and those with low sulfur content (KrLig), are among the worst performers in terms of separation, i.e., lowest S. It therefore seems that a classical kinetic promotion as it is presently understood and reported in the literature is detrimental for the separation of gas mixtures, e.g., biogas upgrading, due mainly to a lack of specificity of the promotion mechanism, i.e., the hydrate formation process is promoted irrespective of the kinds of gas molecules. As a corollary to this, a kinetic promotion, e.g., by surfactants, leads to the enhancement of hydrate formation primarily favoring the entrapment of the less water soluble
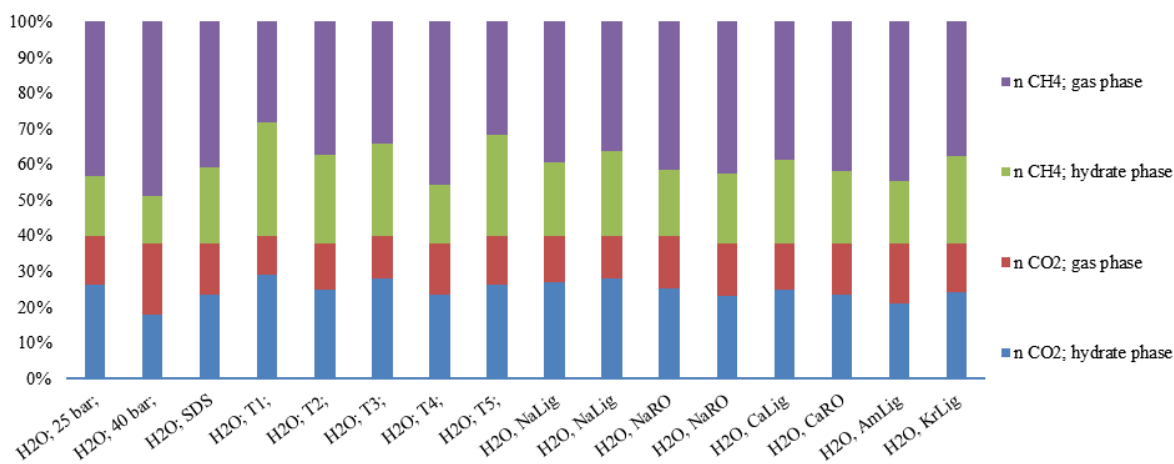
Fig. 2 Normalized CH_4 and CO_2 amounts into hydrate as compared to the residual ones in the headspace gas. Except where noted, the experiments was conducted in constant pressure at 2.5 MPa and 274 K. Absolute data are in the Figure S1.

gas in the mixture, i.e., methane, thus leading to the observed reduction of separation. Figure 2 reports a summary of normalized CH_4 and CO_2 amounts into hydrate as compared to the headspace content. In particular, from Figure 2 it can be inferred that promoters increase the amount of mixed gas hydrate but decrease the selectivity toward CO_2 hydrates. As an example, the first (H_2O) and fourth (T1) columns show a similar capture of CO_2 into hydrate (blue area), but the latter system (T1) shows a much higher capture of CH4 than does the former (green area).

Pressure-dropping experiments

There are several ways for modulating hydrate formation, some of discussed above. Another approach to investigate this aspect is to shift from constant-pressure to pressure-dropping conditions. In the latter, the gas mixture pressure into the reactor is not restored when hydrates

begin to form and decreases down to a constant value corresponding to reaching either (i) a fully saturated hydrate or (ii) the equilibrium curve. Under pressure-dropping conditions, the driving force as represented by a certain overpressurization, e.g., about 2 MPa in the case of the present experiments at 4 MPa and 274 K, is steadily decreased during the process of gas uptake by hydrate-forming water, i.e., during hydrate formation.

In this way, the hydrate is increasingly inhibited during the experiment due to the system approaching the equilibrium curve.

Let us now consider two experiments carried out under pressure-dropping conditions (Table 2), where nonpromoted water was subjected to hydrate formation from our CH_4/CO_2 mixture (60/40) starting at 4.0 and 2.5 MPa, respectively.

Table 2: Pressure dropping experiments without promoters

System	n gas load[a]	Final pressure	$R (CO_2{}^H)$[b]	$R (CH_4{}^g)$[c]	S[d]	Kinetic	n gas uptake[e]	Occupancy (%)
H_2O, 4.0 MPa	0.269	2.00 MPa	65.3	62.6	3.1	slow	0.131	21.6
H_2O, 2.5 MPa	0.211	2.00 MPa	55.1	85.2	7.1	slow	0.065	10.8

[a]n moles of gas charged into reactor. [b]Recovery of CO_2. [c]Recovery of CH_4. [d]Separation factor. [e]Number of moles (n) of the gas mixture incorporated into the hydrate phase.

It is observed that the less driven system, i.e., the one under a lower pressure (2.5 MPa), performs much better than that at 4.0 MPa, reaching a separation factor higher than 7, which is the best result obtained in this work. Again, a decrease in the hydrate driving force leads to an increase in the separation factor, S, as also observed with the promoters discussed above.

Figure 3 clearly shows this general behavior where the driving force is embodied by the gas uptake. Similar considerations can be also made when dealing with kinetic promotion, overpressurization, and so on.
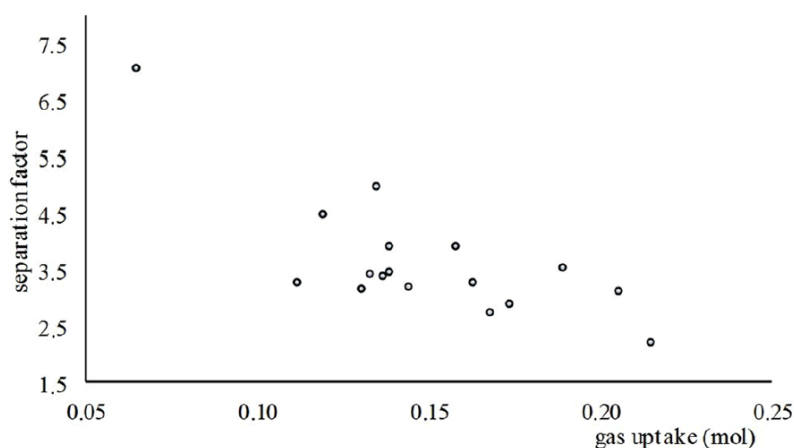

Fig. 3: Separation factor as a function of gas uptake; data points from Tables 1 and 2.

A further insight in the CH_4/CO_2 separation process can be gained when comparing the final amounts of the two molecules in the hydrate and gas phases at the end of the experiment.

Figure 4a shows the normalized CH_4 and CO_2 amounts into hydrate and gas phases, as limited to the best performing systems, i.e., nonpromoted water. From Figure 4a, it is interesting to note that the contribution of dissolved CO_2, i.e., CO_2 dissolved in liquid water before any hydrates

form, is substantial. Furthermore, any increases of CO_2 capture due to hydrate formation are paralleled by a similar increase of methane entrapment (as hydrate). It might therefore be
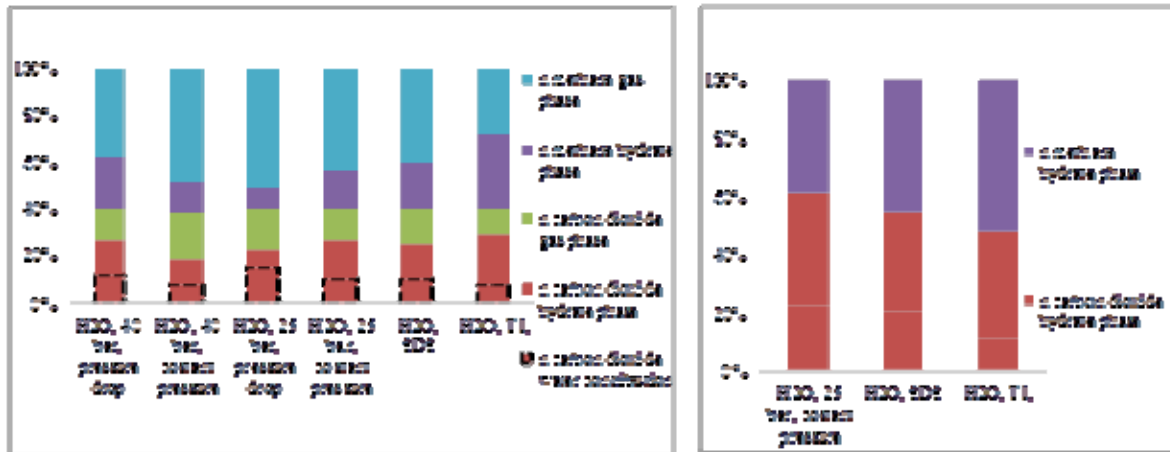
surmised that any events leading to an enhancement of hydrate formation, such as the addition of a kinetic promoter, an increase of pressure, and so on, also entail a loss of specificity due to an almost equivalent capture of the two gases into the hydrate. This is particularly apparent when using kinetic promoters such as SDS and T1 which are known to enhance methane hydrate formation. In fact, if we compare the relative uptake of CH_4 and CO_2 from a promoted water solution to that without promoter, then we observe that the increase in gas capture within the hydrate is biased toward methane as opposed to the approximately similar increase observed with nonpromoted water (Figure 4b).

Fig. 4: a) Methane and carbon dioxide into hydrate and gas phases after the separation process as carried out both under constant pressure and pressure-dropping conditions. Dotted boxes represent the contribution of CO_2 dissolved in liquid water. b) Methane and carbon dioxide into hydrate phases after the separation process as carried out under constant pressure conditions. Absolute data are in the Figure S2.

Conclusions

Gas hydrates have the peculiar ability of concentrating huge amounts of gases under relatively mild conditions and low energetic cost. However, when dealing with the separation of gas mixtures, e.g., a model biogas mixture of CH_4 and CO_2 as studied in the present work, hydrate formation tends to occur with a very low selectivity, increasingly so when the formation is enhanced by kinetic promoters, over pressurization, stirring, and other means for increasing the process driving force. Borrowing a concept (now obsolete) from physical organic chemistry, we may be facing a process governed by a kind of reactivity−selectivity principle. We have studied several surface active molecules, some of which are novel structures, with the aim to optimize the hydrate-based separation process, only to find that the more we promoted the process the lower the separation ability turned out to be. The best performing molecules were a synthetic sulfonate with a naphthalen-2-yloxy structure, which was a bad hydrate promoter, and a low-sugar lignin, which also showed a slow hydrate formation.

To overcome those problems, we propose the investigation on different approaches based on (i) the use of nonpromoting, selectivity-improving molecules or (ii) novel gas feeding devices. The basic idea is to develop a hydrate-based upgrading process which uses tailored, specific molecules, which will be effective in the parts per million range that will promote the entrapment of one of the two gases while inhibiting hydrate formation by the other. Also, an ideal process will be tuned to be the least driven toward hydrate formation, i.e., as close as possible to the equilibrium curve, in order to further increase the selectivity of separation. The result would be a process clearly more sustainable than established amine-based methodologies.

ASSOCIATED CONTENT

Supporting Information

Analytical methods, processes for the syntheses of novel promoters T1, T2, T3, T4, quantitative elemental analysis of lignins plus relevant references.

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