

NOVEL NANOTECHNOLOGY FOR EFFICIENT PRODUCTION OF BINARY CLATHRATE HYDRATES OF HYDROGEN AND OTHER COMPOUNDS

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ABSTRACT

The efficient production of hydrogen hydrates is a major goal in the attempt to exploit those materials as an alternative means for storing hydrogen. Up to now, a few processes have been reported in the literature which yield less than 1 wt% of hydrogen stored into clathrate hydrate or semi-clathrate forms. One main obstacle to the entrapment of sensible amounts of hydrogen (i.e., up to 4 wt%) into a clathrate matrix appears to be of a kinetic origin, in that the mass transfer of hydrogen gas into clathrate structures is drastically limited by the (relatively) macroscopic scale of the gas-liquid or gas-ice interfaces involved.

In this communication, we present a novel process for an enhanced production of binary hydrates of hydrogen and other hydrate-forming gases, which is characterized by the use of nanotechnology for reducing the size of hydrate particles down to a few nanometers. This drastic reduction of particle size, down to three orders of magnitude smaller than that obtainable by macroscopic methods, allows to reduce the kinetic hindrance to hydrate formation. This process has a huge potential for increasing the amount of hydrogen stored, as it has provided ca. 1 wt% of hydrogen, with THF as a co-former. The present process also allows to use several non-water soluble coformers; first reports of hydrogen/cyclopentane and hydrogen/tetrahydrothiophene hydrates are presented.

Keywords: hydrogen hydrates, nanotechnology, kinetic upgrade, stabilization, novel co-formers, surfactants, QSAR

NOMENCLATURE

CC5: cyclopentane

DIOXO: dioxolane

DHF: dihydrofuran

MIF: molecular interaction field

QSAR: Quantitative Structure Activity
Relationship

QSPR: Quantitative Structure Property
Relationship

THF: tetrahydrofuran

THP: tetrahydropyran

THS: tetrahydrothiophene

W₀: molar ratio of water to surfactant

INTRODUCTION

Hydrogen storage is one of the most important and challenging problems that researchers both in the industry and the academy are facing toward the development of a hydrogen-based economy. To date, the main methods employed to store

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hydrogen are: 1) under high pressure as a gas, 2) in liquid form, 3) adsorbing hydrogen in the form of a hydride in hydride-forming metals, and 4) other inorganic and organic compounds. Those methods all have severe drawbacks. Storing hydrogen as a gas requires heavy-duty containers, and the pressures required to obtain an economically viable mass ratio are inherently hazardous, no matter how technologically advanced the container is [1]. Also, composite materials for high-pressure containers are currently being developed, but their cost is high [2]. Storing hydrogen as a liquid also poses safety problems; further, a large fraction of the stored energy is lost when considering converting hydrogen gas to the liquid phase, and keeping it as a liquid at extreme temperatures (22K). On the other hand, inorganic and organic supports (metals, intermetallic compounds, carbon nanotubes, etc.) can adsorb reversibly variable amounts of hydrogen at ambient temperature and pressure; however, desorption therefrom requires a high energy input and usually takes place at elevated temperatures [3].

Since 1999, it has been known that hydrogen forms clathrate hydrates under very high pressure/low temperature [4]. In 2002, Mao et al. found that hydrogen hydrate crystallizes in structures labeled as structure-II (sII) clathrates [5]. The structure of the hydrogen clathrate was resolved by neutron diffraction as a function of pressure and temperature. The hydrogen occupancy in the clathrate was found to change proportionally to changes in pressure and/or temperature, while leaving the host structure virtually intact.

Use of a co-former (e.g., THF) drastically reduces the equilibrium pressure of hydrogen hydrates [6], thus potentially opening the way to a clathrate hydrate-based technology for hydrogen storage. However, THF turns out to be particularly suitable as a co-former, mainly due to its complete miscibility with water, and only limited insights can be gained from studies with less water-soluble molecules due to inherent experimental difficulties [7].

Strobel, Sloan et al. [8] recognized the need of decreasing the size of ice particles to increase the surface-to-volume ratio in order to maximize hydrogen uptake. Another method for hydrogen storage is described in a patent by Peters and Sloan [9], wherein the clathrate is formed starting from a composition of water and a co-former (promoter) in the presence of pressurized hydrogen, the co-

former having the role of reducing the pressure and/or increasing the temperature needed to form a clathrate hydrate of hydrogen. Loskhin and Zhao [10] also described a method for hydrogen clathrate hydrate synthesis, in which ice and hydrogen gas are firstly supplied to a container at a first temperature and pressure, and then the container is pressurized with hydrogen gas to a second, higher pressure, where hydrogen clathrate hydrates are formed in the process.

In the above documents, besides the difficulties of enclosing hydrogen into clathrate cages, which is inherent in the small size of H₂ molecules, also the problem of an efficient mass transfer between the gaseous and the liquid and/or hydrate phases is acknowledged and discussed, and macroscopic approaches to its improvement have been proposed (e.g., crushing ice down to a few tens of microns).

On the other hand, Irvin et al. [11] recognized that reverse micelles can be used to increase the surface area for gas-water contact. The authors also state that the presence of specific double-tailed surfactants serve to form reverse micelles to encapsulate water, which can then be converted to hydrates leading to a very uniform deposition technique. However, the authors do not recognize the role of the bulk organic solvent in the solubilization of poorly water-miscible molecules, e.g. a water-insoluble co-former in hydrogen hydrates, or even the hydrate former of interest, such as hydrogen or methane. Furthermore, no mention is made about the use of the process for storing hydrogen, and the role of the molecular structures of the surfactants and the structural features of reverse micelles is completely neglected. Methods are also known for the extraction of organic molecules from W/O microemulsions under hydrate forming conditions [12].

Lee et al. [13] discussed the the feasibility of obtaining high-content binary hydrates of THF and hydrogen, but their process takes weeks to complete. On the other hand, a similar hydrogen storage ratio, but with a much faster uptake, is achieved when adsorbing the water phase onto silica.

In the present paper, we present the results of a comprehensive study aimed at achieving a novel, efficient method for preparing hydrogen hydrates, which is based on the formation of amphiphile-aided nanoemulsions. According to this method, a binary hydrogen hydrate has been obtained, which

contains up to ca. 1 wt% H₂. Also, two novel cofomers have been successfully tested, i.e., cyclopentane and tetrahydrothiophene.

In more detail, this study can be divided into two branches, which are described as follows:

1. A NANOTECHNOLOGY (BOTTOM-UP) APPROACH TO THE MASS-TRANSFER UPGRADE

The "ice-crushing" method of Sloan et al. makes a lot of sense, because increasing the surface-to-volume ratio of ice particles enhances dramatically the surface area exposed to gas molecules to be absorbed and clathrated. However, this is a classical "top-down" approach, and the smallest sizes achieved (tens of microns) are still in the realm of the macroscopic world.

Following a "nanotechnologic" approach, we tried to devise a process which could be able to form hydrate nanoparticles from "bottom-up", starting with water-in-oil nanoemulsions, i.e., water pools or droplets a few nanometers across (i.e., *three orders of magnitude smaller* than the smallest crushed ice particles) which are stabilized by a monolayer of amphiphile molecules into a bulk organic solvent. The system thus obtained (a *nanoemulsion*) is macroscopically homogeneous, and the water droplets can then be induced to form hydrate nanoparticles when the system is put under the appropriate P and T conditions. The extremely small sizes of those nano-droplets allow for an enhanced gas flux to be captured under hydrate form, with a resulting hydrogen hydrate formed within tens of minutes at a nominal 1 wt% H₂.

A "nanoemulsion" method is also advantageous in that:

- i) the presence of an organic solvent allows for a much broader choice of *co-formers*: the presence of a bulk, dispersing phase formed by e.g. an organic solvent allows to employ also water-insoluble co-formers, and the bulk organic phase serves as a reservoir of the co-former which is kept ready for hydrate formation when the latter begins. On the other hand, the bulk dispersing phase acts also as a "partition buffer" to limit the concentration of very water-soluble molecules (e.g., THF) into the water droplets, thus ideally enhancing the concentration of the hydrate former (e.g., H₂) in water.
- ii) the reaction system can be kept under homogeneous conditions avoiding clogging of the reactor, due to agglomeration of hydrate fine particles. Indeed, hydrate nanocrystals which form

from the water pools precipitate to the bottom of the reactor in form of a slurry which is free-flowing and does not tend to clog, e.g., a discharge pipeline.

iii) the present process can be made continuous by simply adding water and co-former; addition of fresh water/co-former mixture substantially replenishes the shrinking, surfactant-coated water pools, leading to a continuous production of hydrogen hydrate.

iv) the presence of a bulk organic phase enhances the concentration of hydrate former in the liquid phase.

Materials and Methods

The structural and functional characteristics of a nanoemulsion are extremely variable, and strongly dependent on the amphiphilic molecules used to stabilize their interfaces. A limited number of nanoemulsion-forming molecules are known in the art, most of which refer to particular classes of anionics (AOT and derivatives) or non ionics (Shell's NEODOLs) amphiphiles. However, given the strong dependence of nanoemulsions from their stabilizing molecules, remarkable improvements can be made for any particular applications if proper, custom-made amphiphiles can be designed and synthesized for a particular application.

Therefore, we started our studies on hydrate-forming nanoemulsions from the known emulsion stabilizers (AOT from Sigma-Aldrich, NEODOLs kindly donated by Shell, etc.), by using iso-octane (Sigma-Aldrich, anhydrous 99.8%) as a bulk organic phase.

In a typical nanoemulsion preparation to be subjected to hydrogen hydrate formation, 200 ml of iso-octane as a dispersing medium are used, and a proper amount of AOT is dissolved in the solvent, so to obtain a concentration of 0.1M AOT in iso-octane. Then water is added in such an amount to keep the system in the stability region of the nanoemulsion and avoiding phase separation. Finally, a co-former (e.g., THF) is added in an amount depending of its partition equilibrium between water and the organic solvent, and also depending on the target amount of co-former in the final hydrate structure.

As relates to the present example of THF-H₂ hydrate formation by a water-AOT-iso-octane nanoemulsion, it is possible to synthesize THF-H₂ hydrates in a simpler way as compared to the known approaches. In particular, due to the

existence of the partition equilibrium of co-former between water and organic solvent, the kinetics of pure co-former hydrate formation, that is in competition with the binary co-former-H₂ hydrate, is suppressed in a predictable way through the total amount of THF added to the system. The use of a hydrocarbon (e.g., iso-octane) as a dispersing medium enhances the hydrogen mass transfer to the hydrate, because of a much higher solubility of hydrogen in iso-octane as compared to bulk water, thus upgrading hydrate formation and reducing the induction time.

The presence of a surfactant that gives water nanodroplets dispersed into hydrocarbon (reverse micelles), maximizes the surface contact between water and hydrogen gas, and provides for the formation of the first hydrate crystals which are orders of magnitude smaller than those with the existing processes. Figure 1 shows an exemplary H₂ hydrate formation process.

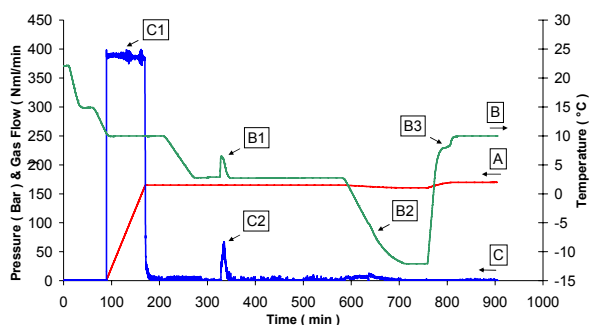


Figure 1 - P/T/Gas Flow profiles vs. time.

In Figure 1 the temperature, pressure and gas flow profiles for nanoemulsion-aided hydrogen hydrate formation are shown. Curve B is related to temperature values, and shows a first phase of cooling to bring the system down to the chosen formation temperature, where, after a certain induction time a peak of temperature (B1) related to the heat of formation is apparent. After all parameters were stabilized at the target set-points, a sub-cooling phase (B2) starts to bring the system down to a temperature below the water freezing point, -12°C in this specific case. After further stabilization of parameters, a warming ramp starts in order to dissociate the synthesized hydrate, for detecting the dissociation temperature indicated in B3. Curve A shows the system pressure profile, where a first loading ramp is carried out up to a selected experimental pressure, and then the reactor is kept under constant pressure mode by

the experimental device, which is as described in WO/2007/122647 [14]. Curve C shows the gas flow profile, with the first constant flow step (C1) corresponding to the pressure loading phase and an absorption peak related to the hydrogen trapping in the hydrate phase (C2).

The presence of reversed micelles enables to control non-converted water; in fact, hydrate obtained in this way is not swelled with non-converted water because the latter remains trapped in the reverse micelles and is available for further conversion into hydrate, as shown in Figure 2 (B2).

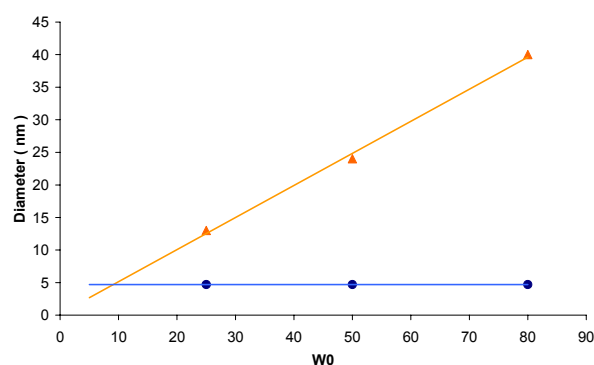


Figure 2 - Diameters of nanoemulsions by DLS

Figure 2 shows the results of *Dynamic Light Scattering* measurements carried out on three samples of water-in-oil AOT nanoemulsions prepared as described above, to obtain information about the sizes of the nano-aggregates. The three samples differ in the amount of water and THF added; specifically, water was added in order to obtain a value of W_0 (molar ratio of water to surfactant) of 25, 50, and 80 and, for each sample, a corresponding amount of THF was added such as to keep a stoichiometric molar ratio of THF hydrate (THF/H₂O 1/17). Light scattering measurements were made by using ca. 1 mL of sample in 6 mm diameter Pyrex glass culture tubes, fitted into the center of a toluene-filled fluorimeter cuvette to provide refractive index matching against stray light reflections. The cuvette was housed in a aluminum cell block, whose temperature was regulated by a Peltier element. The light source was a Coherent Innova 70-3 argon-ion laser operating at 4880 Å. Light scattered at 90° was collected from approximately one coherence area and imaged onto a photomultiplier tube. A 64-channel Nicomp Model 370 computing autocorrelator (PSS Nicomp, Santa Barbara, CA) was used to calculate and display the

diffusion coefficient, D , and associated derived parameters from cumulants analysis fits to the intensity autocorrelation function. The hydrodynamic radii, R_h , can be estimated by applying the Stokes-Einstein relationship:

$$D = kT/6\pi\eta R_h \quad (1)$$

where η is the viscosity of the solution, which can be approximated to that of the dispersion phase (i.e., iso-octane). The recorded data, as reported in Figure 2, were 13, 24 and 40 nm, as the diameter of the micelles, respectively for the samples at W_0 of 25, 50, 80.

Then the samples were subjected to hydrate formation by simple cooling at a temperature lower than the hydrate equilibrium temperature. After hydrate formation, an aliquot of the remaining liquid phase was taken for each of the samples, which were again measured by Dynamic Light Scattering. Recorded data for all the three post-formation samples show a *constant size of the aggregates*, around a value of ca. 4.7 nm. As for these systems a well known linear relationship between W_0 and micelle size ($D = \text{diameter}$) exists, we can write it down as:

$$D = A \times W_0 \quad (2)$$

Once this behavior is known, it is possible to determine (a) the value of parameter A , which is the slope of the D - W_0 line, in this case being of ca. 0.5, and (b) the W_0 value for the residual aggregates left after THF hydrate formation, which, as shown in Figure 2, is of ca. 9 (intersection of the two linear fitting curves).

In this way, by means of a simple Light Scattering investigation, it is possible to demonstrate that at least part of unconverted water remains trapped into reversed micelles while the formed hydrate is separated as a solid or slurry phase, which is easily separable and recoverable from the liquid system.

As mentioned at the beginning of this section, it is possible to enhance the hydrate-forming potential of nanoemulsions by using more suitable amphiphiles. These molecules were designed and synthesized in an organic synthesis effort which led us to the achievement of several novel molecules, some of which proved extremely promising for application to hydrogen hydrates.

These novel molecules can be classified according to: i) head group (non ionic, anionic, cationic, zwitterionic), and ii) number and type of lipophilic chains (single chain, twin-chain, gemini, etc.). Several of those molecules were synthesized and tested for hydrogen hydrate formation, according to the general nanoemulsion method as described above, and some of those systems allowed us to reach an estimated 1 wt% of hydrogen with formation temperatures of 1-8°C and pressures of 50-150 bar. A complete disclosure of the novel molecules synthesized, and the results obtained therefrom, are beyond the scope of this paper, and are fully reported in EP07010346 [15].

An additional comment on the role of organic bulk solvent should also be added at this point. In hydrate-forming nanoemulsions, the organic solvent may also have a dual function as both the dispersing medium *and* the clathrate *co-former*. This could help when the supply of co-former from the organic dispersing medium would not take place at a sufficient rate in cases where the co-former would have such a partition coefficient as to be essentially in the organic phase.

2. CO-FORMER STRUCTURE-PROPERTIES RELATIONSHIPS

A co-former in binary hydrates is a hydrate-former by itself, but its role is generally to stabilize the (larger) hydrate cages, thus allowing hydrogen to remain entrapped into the smaller cages (even if a stabilizing role of hydrogen itself has also been recently proposed) [16]. As mentioned and widely known, the presence of a co-former such as, e.g., THF, allows to obtain hydrogen hydrates at much milder P and T conditions than without THF.

However, THF is not the only co-former which is capable of stabilizing binary hydrates, and other molecules were already described for that role, such as tetrahydropyran (THP), dioxane, dioxolane (DIOXO), dihydrofuran (DHF), furan, etc. [7]. These molecules have shown variable stabilizing properties, although THF seems to show the best performances.

The supramolecular mechanisms through which an organic molecule can induce stabilization of clathrate cages are not clear. A recent hypothesis is that the presence of heavier molecules into the larger cages induces a distortion in the smaller ones, such a distortion inducing a change in the energy quantum levels of the hydrogen contained into the cage [17].

Starting from the finding that different molecules show different stabilization effects, it should be possible to find a relationship(s) between a chemical moiety and/or structure of co-former and the stabilization effect. Thus, a knowledge of that relationship could not only offer a better understanding of the stabilization phenomena, but it should be also possible to *predict* novel molecules featuring a higher stabilization.

A suitable tool in this respect is given by *Chemimetry*. Chemimetric approaches are *Quantitative Structure Activity Relationships* (QSARs) or more in general *Quantitative Structure Property Relationships* (QSPRs). QSAR and QSPR are commonly used in drug design in order to relate the structure of certain drugs to their pharmacological activity.

Carrying out a QSAR or QSPR analysis is not a trivial matter: generally a chemical moiety or portion of a molecule affects, in different ways, more than one property. On the other hand, a certain property may result affected by different moieties. Therefore, properties and structure are related by non-linear and multi-parametric relationships. Multivariate mathematical approaches are thus required to carry out a QSPR analysis, and there exist several, dedicated software packages. Generally, a QSPR analysis requires a first collection of property datasets, usually obtained by using specific strategies in order to minimize the number of experiments, and getting homogeneous data. Then, through molecular modeling, molecular descriptors are obtained, which are mathematical elements that describe the molecule at the finest feasible level in terms of structure, interaction energies, chemical moieties etc. Finally, by the use of further mathematical tools, non significant descriptors are ruled out and those that show correlation with properties are retained, thus obtaining a mathematical relationship among properties and structural descriptors of the molecule. Once that relation is obtained, it is possible to predict the properties for new molecules, or even design a suitable novel molecule in order to obtain certain properties.

1. Comparative data collection

First, several data available in the literature [7] were repeated according to our experimental apparatus [14] and by using the process described herein. Particularly, known co-former molecules tested were: tetrahydrofuran (THF, freshly

distilled in order to remove the stabilizer, BHT), tetrahydropyran (THP; >99% GC), 2,5-dihydrofuran (DHF, 97%), and 1,3-dioxolane (DIOXO, >99%). Further, cyclopentane (CC5, >99%), tetrahydrothiophene (THS, >99% GC) (all from Sigma-Aldrich) were successively tested as co-formers previously unknown to give binary hydrates with hydrogen, and pinacolone (98% GC) as a probable sH-former with methane.

Figure 3 shows results of P/T data obtained for THF/H₂ hydrate according to the process described herein as compared to those reported in the literature [7].

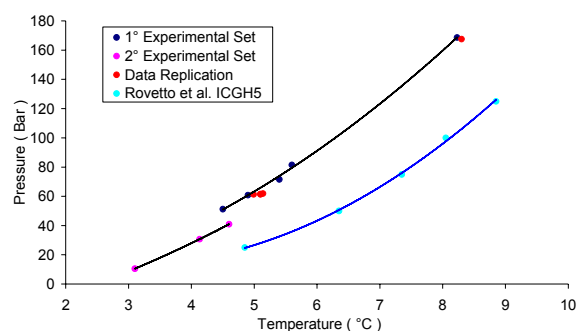


Figure 3 - Comparison among our data (higher lines) and literature data (lower line) from two different experimental sets. Good accordance with experimental data replicas (red dots).

In the above comparison, it is evident how the obtained data represent a classical equilibrium P/T profile. The observed shift at higher pressures due to the different water/THF ratios. Furthermore, it should be kept in mind that the two data sets were collected by following two completely different experimental procedures and set-up, and that the nanoemulsion process allows for a broader choice of co-formers, and a higher tuning ability of the same.

Also several data replicas were obtained, reported in the graph as red dots, that show a very good reproducibility of the experimental procedure. The same agreement was generally obtained for the other known co-formers.

2. VolSurf calculations

Molecular structure descriptors of co-formers tested in the above section (1) were obtained by using VolSurf [18], which is an automated procedure to convert 3D molecular interaction fields (MIFs) into physico-chemically relevant molecular descriptors. The basic concept of

VolSurf is to extract the information present in 3D molecular field maps into few quantitative numerical descriptors which are easy to understand and analyze. Basically, VolSurf analyzes a 3D-MIF in terms of volumes and surface of isopotential interaction returning these analysis with numbers that quantify hydrophilic interaction, hydrophobic interaction, etc. By means of VolSurf, it is possible to generate up to 120 molecular descriptors that represent all the possible molecular interactions between a molecular target and other molecules (*probes*). Once such descriptors are obtained, it is possible to proceed with the further steps of correlating such values to the target property data, measured for a certain molecule, by using a multivariate mathematical analysis.

The descriptors matrix was then elaborated with PLS (*partial least squares*) strategy to select only those descriptors showing a correlation with the pressure and temperature arrays.

Significant descriptors that were found to be correlated to relevant hydrate parameters were generated by the so-called *Dry* and *Water* probes.

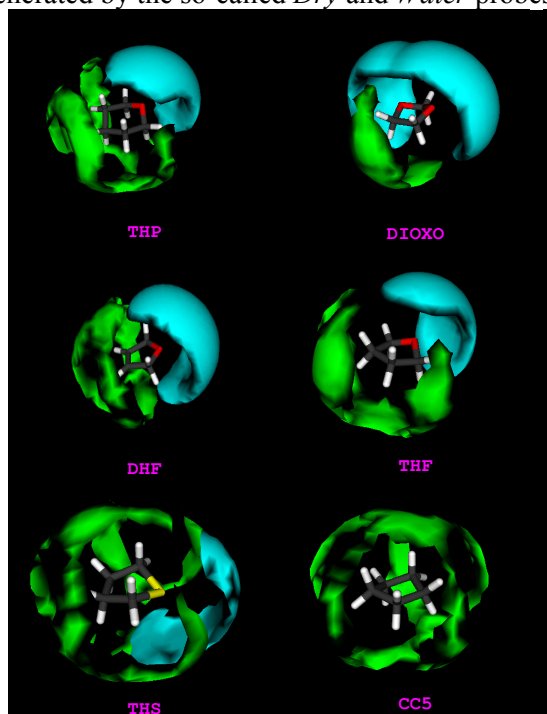


Figure 4 - Volumes of interaction at a specific energy for the *Water* (cyan) and *Dry* (green) probes, obtained from VolSurf analysis of relative MIFs

The *Dry* probe generates a descriptor which is related to the "hydrophobicity" of the target

molecule. The *Water* probe generates a descriptor which is related to the "hydrophilicity" of the target moieties, where the best correlation was found around a (low) interaction energy level of -0.5 Kcal/mol.

This latter descriptor, at this particular interaction level, is also an estimation of molecular volume and polarizability. Figure 4 reports a graphical representation of molecular interaction volumes of tested co-formers with *Dry* and *Water* probes.

The obtained results (Figures 5 and 6) suggest, for example, that neither H-bonds nor water-lone pair interactions, which are the strongest interactions in water, seem to be involved in hydrate stabilization effects by co-formers; conversely, the descriptors of hydrophilicity (*Water*) and hydrophobicity (*Dry*) show a correlation with the equilibrium temperatures of literature data taken under 100 bar of H₂ pressure [7]. In particular, an increase of *Water* is related to a decrease of equilibrium temperature (Fig. 5), while an increase of *Dry* is related to an increase of equilibrium temperature (Fig. 6) [19].

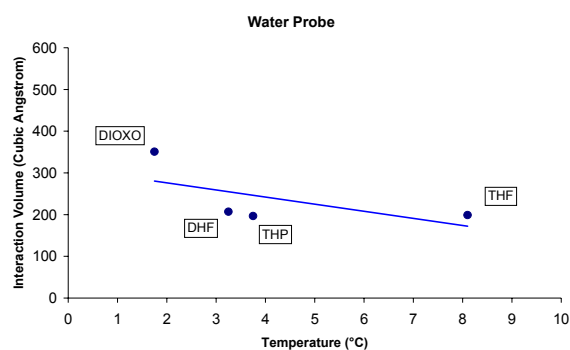


Figure 5 - Correlation between dissociation temperatures at 100 bar H₂ and the hydrophilicity descriptor (*Water*).

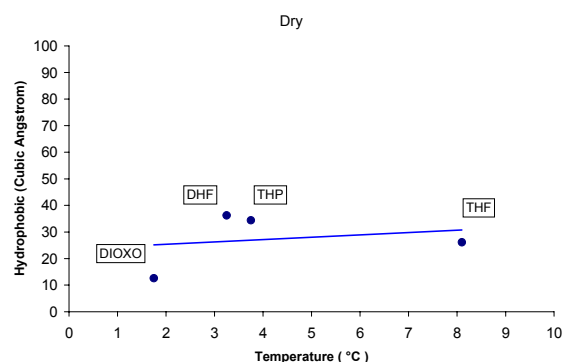


Figure 6 - Correlation between dissociation temperatures at 100 bar H₂ and the hydrophobicity descriptor (*Dry*).

Without going into further detail, which is described elsewhere [20], the above correlations suggest that novel co-formers should be sought among more hydrophobic and/or less polarizable molecules. With this hint, further calculations and experiments were carried out as described in the following section.

3. Prediction and further experiments

Two novel co-former molecules, i.e. cyclopentane (CC5) and tetrahydrothiophene (THS) were chosen as representative species featuring an increase in hydrophobicity and polarizability, respectively, in order to have a predicted better and worse co-former as compared to THF (Figure 7). These molecules are "novel" with the meaning that THS was previously unknown to form any kind of clathrate hydrates, whereas CC5 is a known hydrate former except with hydrogen.

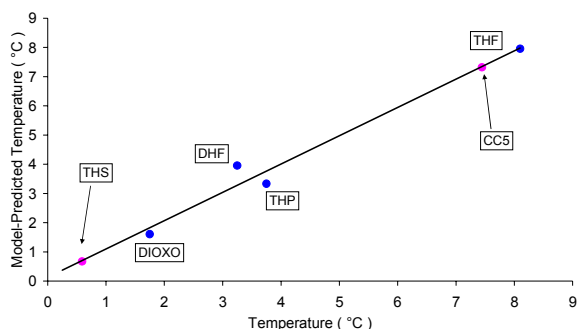


Figure 7 - Predicted dissociation temperatures for THS and CC5 (pink dots) according to the QSAR model generated from literature data [7].

According to the model reported in Figure 7, T values predicted for THS and CC5 were 0.67°C and 7.44°C, respectively.

By following the nanoemulsion process described above, we formed binary clathrates of CC5 and THS, plus all the other co-formers considered, with hydrogen, in order to obtain a homogeneous data set, measuring their equilibrium T at 100 bar [20]. Experimental dissociation temperature for CC5 is 7.22°C, which is in remarkable agreement with the predicted value. On the other hand, experimental T for THS is 4.58°C, which is almost four degrees higher than predicted.

Another experimental deviation from prediction was found for CC5 under different tuning conditions, for which a highest dissociation temperature of 8.9-9.4°C was unexpectedly recorded. This temperature is higher than the highest known dissociation temperature of THF/H₂

binary hydrates under the same pressure (8.1°C/100 bar) [7].

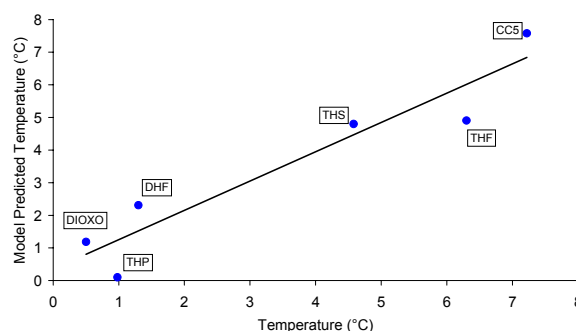


Figure 8 - VolSurf modeling for the experimental data.

Also the model built on our data set shows the same correlation of the Dry and Water descriptors with the equilibrium temperatures, when compared with literature data (cf. Fig. 7).

Incidentally, it should be added that an attempt to form binary hydrates of CC5 or THS and H₂ failed when using a usual experimental setup formed by a biphasic system of co-former/water kept under H₂ pressure and vigorous stirring.

CONCLUSIONS

Assuming that hydrogen can be stored under clathrate hydrate form at a concentration close to its theoretical capacity, it is important to develop processes which are able to overcome the huge kinetic problems of hydrogen hydrate formation, without adding further weight to the system and, possibly, while keeping a process which is simple and amenable to scale-up.

The basic idea that we followed in the development of the process presented in the present paper, is typical of the nanosciences, where "going nano" usually results in the discovery of novel properties and materials. A peculiar feature of hydrate-forming systems, however, is that they are basically composed by water, which is hardly caused to form "nanoparticles" in solid form. A method of grinding water ice goes into the right direction, but it is a "top-down" approach, and ground ice crystals are in the tens of microns as a lower size limit.

Water "nanodroplets", instead of nanoparticles, seemed a more suitable candidate to be able to force water into the realm of nanodimensions. However, water nanodroplets exist in that they are

suspended into a water-immiscible medium (e.g., organic solvent) and this is something of an impossible feat to achieve. Unless you *decrease the surface tension* at the water/solvent interface. This can be done by using *surface active agents*, which stabilize that interface by reducing the interfacial tension sufficiently for the system to be thermodynamically stable. Water droplet sizes typically range from a few nanometers to tens of nm, evolving from nearly spheres to bicontinuous systems when the amount of added water is increased.

However, the effectiveness of surfactants to stabilize nanoemulsions is widely variable, and very few amphiphiles are known which are effective at that purpose (notably, AOTs and NEODOLs). Therefore, our first effort was that of designing and synthesizing novel molecules which could be tested as effective nanoemulsion stabilizers. This nanoemulsion process for making binary hydrogen hydrates proved very effective, as it gave rise to about 1 wt% of H₂ entrapped with some combinations of surfactant/co-formers, as calculated by integrating high-precision gas flux data. Also, the kinetic of the process was quite favorable, being the gas absorption complete within a time span in the range of tens of minutes.

We believe that a major cause of the above performance is the huge increase of surface-to-volume ratio of water available to interact with hydrogen dissolved into the bulk organic phase, as compared to, e.g., a bulk aqueous phase or even 50-micron ice granules in contact with a given gas atmosphere. Furthermore, the enhanced solubility of hydrogen into hydrocarbons, e.g. iso-octane, as compared to that in water, may be playing a role in causing more H₂ to contact the aqueous *pseudo-phase*. Finally, the bulk medium may act as a "buffer" for controlling the water solubility of certain water-miscible co-formers, or enhancing the co-former/water contact for water-immiscible molecules.

The role of the co-former in the stabilization of large cages in H₂ hydrates is crucial, therefore a deeper comprehension of the molecular/supramolecular mechanisms underlying its effects should be obtained. A QSAR approach such as implemented into *VolSurf* allows to deal with a high number of physico-chemical parameters, and correlate them to structural descriptors based on complex MIFs, without undue calculation time and effort. By applying this approach to literature data, it was possible to predict equilibrium temperatures

for new co-formers. The temperature predicted for CC5 was 7.44°C, which is very close to the experimentally determined value (7.22°C). Equilibrium temperature prediction for tetrahydrothiophene was not successful (0.67°C predicted vs. 4.58°C experimental); however, in this case it is worth noting that, while CC5 is a known SII structure former [21], THS was not previously tested as a hydrate former. Thus in this case a structural characterization would be mandatory in order to clarify if THS really forms a SII structure, because the QSAR model was built thereon.

Another deviation from prediction was found for the equilibrium T of CC5 when its "tuning" effect was modulated. This was possible due to the employment of the nanoemulsion process, which allowed to finely change the ratios of bulk solvent/co-former/water. This deviation from the predicted T also testifies of the importance of the tuning effect of the co-former in stabilizing H₂ hydrates. The following figures show the remarkable role of co-former tuning both with a water-miscible molecule (THF) and a completely water-immiscible co-former (THS).

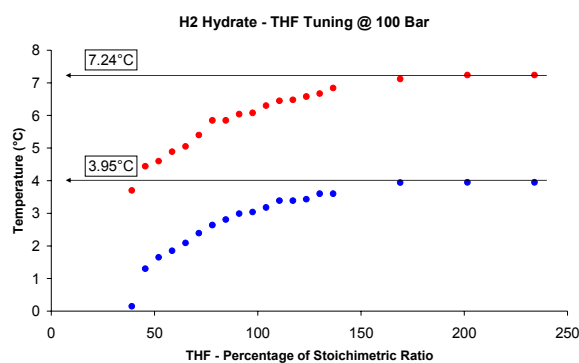


Figure 9 - Equilibrium temperatures for various THF amounts

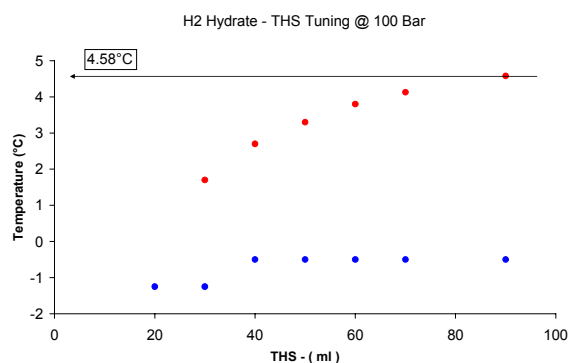


Figure 10 - Equilibrium temperatures for various THS amounts

Finally, it should be stressed that a QSAR approach based on a few experimental points as used in the present work is quite unstable in terms of prediction ability, with the meaning that predicted values may oscillate remarkably. However, it still preserves a good qualitative predictivity, as clearly demonstrated.

Hydrogen storage technologies in compressed or liquefied form are still without competitors among the "novel" technologies based on metal hydrides, carbon nanotubes, covalent hydrogenated compounds (ammonia), etc. Moreover, enthusiasm with the latter ones is fading as the inherent difficulties and energetic costs thereof are clarified [22]. Although an industrially feasible hydrogen storage technology based on clathrate hydrates seems out of reach at present, nevertheless their comprehension is still at an early stage. Will a fuel cell ever be supplied with hydrogen from a clathrate ice? We are confident in a future positive answer [23].

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