Experimental report

15/09/2023

Proposal: 5-22-818 **Council:** 4/2023

Title: Structural study of the incorporation kinetics of CO2 and N2 in semi-clathrates hydrates by neutron diffraction

Research area: Engineering

This proposal is a new proposal

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Samples: TBAB+D2O+CO2+N2

Instrument	Requested days	Allocated days	From	To
D1B	3	1	29/08/2023	30/08/2023

Abstract:

Hydrate Based Separation Process (HBSP) is a promising alternative solution to reduce anthropogenic carbon dioxide (CO2) emissions from numerous industrial activities(1). The interest is to study Carbon Capture and Storage (CCS) by HBSP from CO2-based semi-clathrate hydrates of TBAB (Tetra-Butyl-Ammonium Bromide). In our previous work, we reported the guest-induced modifications of the semi-clathrate structures of TBAB upon CO2 or N2 incorporation(2) or temperature annealing(3). Under gas pressure, type B is preferentially formed. In order to reveal the conditions of the structural transition upon guest encapsulation kinetic(5), and the reversibility of the process, in-situ diffraction data are necessary. This will allow the tuning of functional properties (melting temperature, gas capacity and selectivity) and optimize hydrate-based CO2 capture.

Proposal 5-22-818 (30.08.2023), Scientific report – Bertrand CHAZALLON (main proposer)

Purpose of the proposal:

Among capture technologies aimed at reducing anthropogenic greenhouse gas emissions (e.g. CO2), the existing and widely spread amine technology has a high environmental impact and is not economically viable [YAL-2020]. Other solutions must be found quickly to overcome this problem. The hydrate-based separation process (HBSP) is investigated intensively [CHE-2022] as it could be an efficient and sustainable alternative that can be applied to trap CO_2 from flue gases. Water aided by promoters such as ammonium salts forms under soft conditions (low pressure, mild temperature) semi-clathrates that can separate gases and capture CO_2 with a fast kinetic. The aim of the project is to investigate the structure of tetra-n-butyl ammonium bromide (TBAB**) semi-clathrate hydrates (hereafter** *"**sch**"*) using the D1B powder diffractometer at ILL in order to reveal how the incorporation of guest molecules like CO_2 (or N_2) impact the initial ***sch-s***tructure and how the kinetic of the transformation takes place. This work was carried out as part of the PhD program of R. Haidar.

Work carried out, main results and discussions:

Strategy: Because the allocated beam time was reduced to 24h (instead of 72 h demanded in the original proposal), mainly 2 samples were studied. 1) A ***sch*** of TBAB-D_2O formed from an aqueous solution at 40 wt% TBAB, and 2) A ***sch*** of (CO2) + 40wt.%TBAB-D2O (10°C, 20bar). Two distinct strategies were adopted as follows. Protocol (A): the ***sch*** (without guests) were first formed (quenching followed by annealing (2K/min)) and stabilized at 283 K and atmospheric pressure. Subsequently, a contact of the solution was made with a gas reservoir (CO_2 gas) at ~20 bar to initiate CO_2 enclathration; Protocol (B): the aqueous solution (D_2O-TBAB) and the gas reservoir initially in contact at 298 K were cooled down to ~261 K to form the solid ***sch*** and subsequently annealed at 283 K.

Sample preparation and experiments: The aqueous solution of 40wt%-TBAB-D_2O was carefully prepared at the Chemistry-Lab at ILL in a glove box. The sample was inserted into a dedicated capillary (~4 mm diameter, ~6.5 cm length) provided by ILL (we thank Claude Payre and his colleagues for their assistance). The capillary was inserted into the high-pressure cell (model similar to the 08PG10AL12) provided by ILL. The ensemble was further screwed at the bottom of the stick (model similar to 190ILHP49) under a continuous flow of CO_2 gas to prevent air contamination. The stick was then inserted into the cryostat pre-regulated at 243 K on the D1B diffractometer (λ = 2.526 Å).

In Protocol (A), the sample, placed at residual atmospheric pressure (mainly CO2 gas) and at a temperature of 243 K, crystallizes immediately. The main diffraction peaks are observed at 2θ = 6.07, 8.57, 12.37, 12.97, 13.67, 16.77, 17.87, 19.47 etc (Fig.1) and were found to be characteristic of **a *sch*** of tetragonal structure. It should be remembered that this phase is expected to be vacant from any CO_2 molecules (i.e., with vacant dodecahedral cages). No structural change was observed up to 283 K (Fig.1). A Lebail refinement was applied to the pattern collected at 283 K (Fig.3). The most consistent refinement (Rw = 1.94%) was obtained with the lattice of a = 23.662 (4) Å, c = 12.680 (3) Å, (S.G. P4/m m m), which could correspond to that found by Rodionova's group (1) [ROD-2013], [STO-2021]. Other crystalline phases (e.g. trigonal R_3c) as in [ZHO-2019a,b] are not found in our treatment. Fig.4 shows the time dependent evolution of the pattern of the tetragonal ***sch*** after CO_2 injection. A Lebail refinement (Rw = 5.5%) (Fig.5) of the pattern obtained after 124 min exposure is attempted and gives: a = 23.673(6) Å, c = 12.683(5) Å, which suggests no specific structural modifications of the ***sch***. Note that a less goodness was obtained, due to the lower statistic of the pattern during the kinetic run. In contrast to earlier results [ZHO-2019b], the structure remains stable within the next 2h of data accumulations. In a next attempt, we adopt protocol (B): the sample was dissociated and subsequently cooled down to 258 K (Fig.6). The ***sch*** with tetragonal structure is observed already at ~263 K. The peaks continue to grow as the temperature reaches 258 K. The sample was heated up to 283 K (fast heating of ~5K/min) and the time dependent evolution of the pattern was followed.

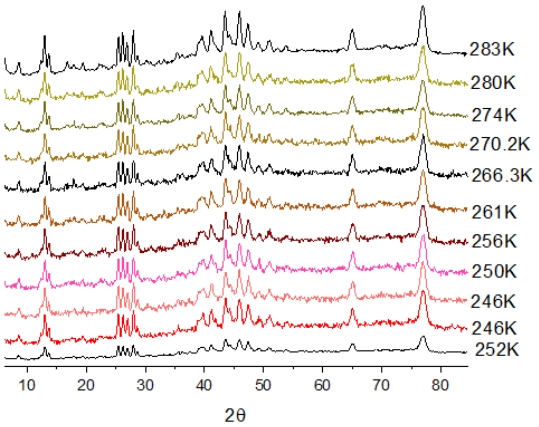

Fig.1 Sample 40wt%TBAB-D_2O (without CO_2 gas) as a function of temperature from 252K to 283K (Annealing protocol)

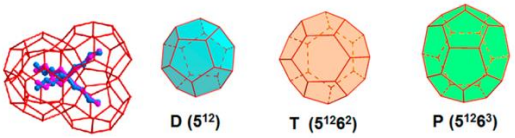

Fig.2 TBAB-semi-clathrate, with TBAB molecules occupying 4 large cages made-up with water molecules

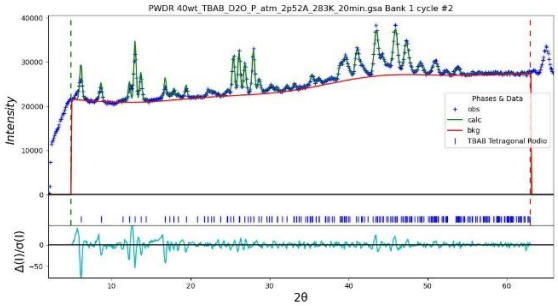

Fig. 3 Lebail Refinment of 40wt%TBAB-D_2O sample at 283 K

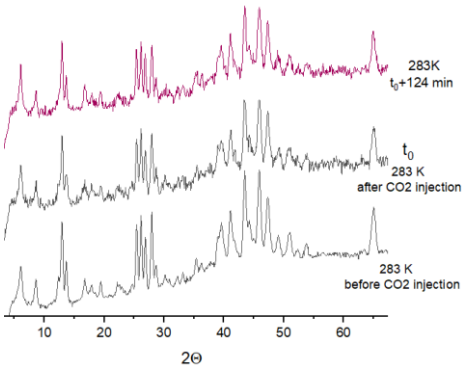

Fig.4 Protocol (A), Diffraction patterns followed (124 min) after CO2 injection at 20 bar, 283 K

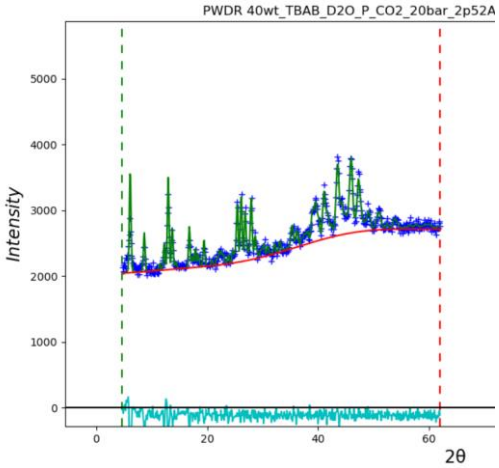

Fig.5 Lebail refinement of 40wtTAB-D2O+20bar CO2 gas (see text for details)

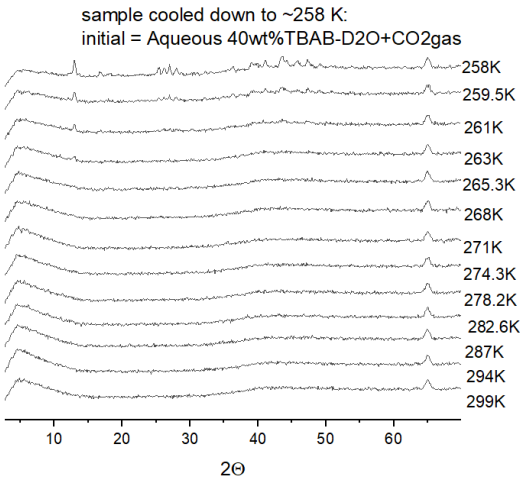

Fig.6 Cooling of aqueous solution of 40wt%TBAB + 20 bar CO2 gas.

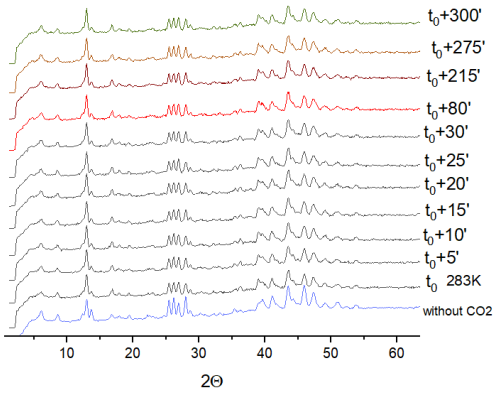

Fig.7 Diffraction pattern of ***sch***- 40wt%TBAB-D2O (blue) compared with time dependent sch-CO2(20bar) + 40wt TBAB-D2O

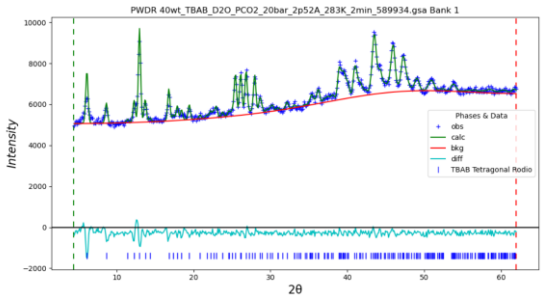

Fig. 8 Lebail Refinment of ***sch***-CO2(20bar)+40wtTBAB-D2O (see text for details)

Small but noticeable changes were observed when comparing the blue (***sch***-without gas) and the green (***sch***-with CO2 enclathrated). Main differences occurs in relative peak intensities, between 2θ = 25° and 30° and at around 13°. A Lebail refinement (Rw = 2.418%) applied to the pattern collected at t_0+300min confirms the occurrence of the tetragonal phase, with lattice a = 23.659(5)Å and c = 12.695(3)Å (S.G. P4/m m m). Of note, the unit cell volume slightly increases from 7099 Å^3 (***sch***-without CO_2) to 7108Å^3 (with CO_2 gas enclathrated). This indicates that CO_2 molecules haves been incorporated in the vacant cavities (dodecahedral cages). It should be noted that no change of structure from tetragonal to orthorhombic triggered by the presence of CO_2 is reported even after 300 min. This markedly differs from previous X-ray diffraction/Raman investigation from [ZHO-2019b] who reported a structure change within the first 90 min. using protocol (A). In both of our protocols, the structure remained unchanged within the time frame of the experiment (~124 to 300 min). In the next step, we had planned to increase the temperature up to 289K to follow possible structure change on approaching dissociation (as already observed by Raman, [ROD-2020]. Unfortunately, a problem occurred during the last run of the experiment (last 9h), whereby the "Nomad server" crashed and we were unable to restart the server during the night on D1B. The sample decomposed at 289K within the next 9h.

Future proposal:

The progress made at ILL -within this short time of experiment -on the structural behavior of TBAB-***sch*** when subjected to CO_2 gas pressure is considerable. Our results address a gap in the literature concerning the structural study with CO_2-filled-***sch***. The diffraction results confirm a tetragonal structure for 40 wtTBAB that remains stable up to ~288 K (as can be explained by the isotopic effect of D_2O instead of H_2O), with a lattice of symmetry P4/mmm. Two protocols were tested for the CO_2 capture and none of them reported the change of structure from tetragonal to (orthorhombic + trigonal) in less than 90 min, as was explained by [ZHO-2019b]. In contrast, the time dependent evolution of the diffraction pattern reveals that the tetragonal structure remains stable at least within the first 300 min. With the success of this experiment at ILL, we consider in a next proposal the same protocols with a complete follow of the kinetic close to dissociation and we will investigate the effect of pressure on the CO2-induced structural change. The objective will be to carry further studies in this matter (specifically on the 40 wt%-TBAB-*sch* and also on the 5wt%-TBAB-*sch*). The dilute TBAB-sample was recently shown to provide higher CO_2 capture in comparison to the 40wt%TBAB.

References: [CHE-2022] Z. Cheng et al., Renew.Sustain. Energy Rev. 2022 154, 111806; [ROD-2020] C. T. Rodriguez, Chem. Eng. J. 2020, 382, 122867 ; [ROD-2013] T. Rodionova et al., J. Phys Chem. B 2013 117 10677-10685; [STO-2021] A. Stoporev et al., Mendeleev Comm., 2021, 31 17-19; [YAL-2020] S. Yalcin et al., Greenhouse Gas Sci Technol. 2020, 10(4) 664; [ZHO 2019a] X. Zhou et al., Energy and Fuels 2018, 32, 9683-9691; [ZHO 2019a] X. Zhou and D. Liang, Chem. Eng. J. 378 (2019) 122128.