



Clathrate Chemistry Hot Paper

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Managing Hydrogen Bonding in Clathrate Hydrates by Crystal Engineering

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Introduction

- 1. Crystal engineering is the management of host–guest hydrogen bonding and a key process for stable encapsulation of alcohol guests into hydrate cages.
- 2. The role of methanol as a possible hydrate guest has been controversial, the hydrate community considered methanol as a hydrate inhibitor as methanol–water hydrogen bonding disrupts the lattice and a stable clathrate cannot be made.
- 3. Here, in this work doping of ammonium fluoride into a clathrate hydrate host framework greatly reduces the destabilizing effect of methanol and elevates it from a hydrate inhibitor to helper guest status.
- NH₄F acts as a lattice stabilizer by providing sites for strong hydrogen bonding of the normally disruptive methanol hydroxy group.
- 5. NH₄F and methanol can be considered key materials for crystal engineering of clathrate hydrates, as the modified lattices allow preparation of hydrates of non-traditional water-soluble guests such as alcohols and diols.

Background

In this work, they have synthesized methanol in H_2O/NH_4F clathrates of sI, sII, and sH str.



Ripmeester, J. A., Tse, J. S, Ratcliffe, C. I., and Powell, B. M. (1987): "A New Clathrate Hydrate Structure", Nature, 325, 135 von Stackelberg, M. and Müller, H. R. (1954): "Feste Gashydrate", Z. für Elektrochemie, 58³, 25

Experimental method

- An aqueous solution of ammonium fluoride (27 mol%) was prepared and the stoichiometric amount of methanol and/or 1,2-propanediol was slowly added into the solution. The ammonium fluoride was always first dissolved in pure water to avoid forming a precipitate of solid ammonium fluoride.
- 2. The well-mixed solutions were rapidly quenched by dripping into liquid nitrogen, followed by grinding into fine powders for PXRD and NMR measurements.
- 3. For the immiscible systems, the 27 mol% ammonium fluoride solution was first quenched in liquid nitrogen and ground to a fine powder.
- 4. This powder was then immersed into excess liquid mixtures of methanol with either TBME, iso-amyl alcohol, 2-methyl THF, or ethanol, which had been precooled to dry ice temperature, and the mixtures were kept in a dry ice bath for 3 days. Then, each sample was put under vacuum for 6 hours at dry ice temperature in order to remove residual liquid.

Different clathrate hydrates

Host molecules	Guest molecules	Structure
H ₂ O/NH ₄ F	Methanol/Methanol	sl
H ₂ O/NH ₄ F	Methanol/1,2-propanediol	sll
H ₂ O/NH ₄ F	Methanol/TBME	sH
H ₂ O/NH ₄ F	Methanol/Ethanol	sl
H ₂ O/NH ₄ F	Methanol/Isoamyl alcohol	sll
H ₂ O/NH ₄ F	Methanol/2-Me THF	sll



(a) The PXRD pattern of the methanol clathrate hydrate with ammonium fluoride at 183 K and the Rietveld refinement results. Tick marks indicate the Bragg positions for the ammonium fluoride–water Str. I clathrate (top) and the ammonium fluoride–water solid solution (bottom).

(b) The methanol molecules (brown: $-CH_3$ and red: -OH) in the 5¹²6² (right) and the 5¹² cage (left) of Str. I.

So far, there has not been any direct evidence of clathrate hydrate formation with methanol as the sole guest.



Figure 2. a) The PXRD pattern of the binary 1,2-propanediol + methanol clathrate hydrate with ammonium fluoride at 190 K and the Rietveld refinement results. Tick marks indicate the Bragg positions for the cubic sII hydrate (top) and the hexagonal H_2O/NH_4F solid solution (bottom).

b) The 1,2-propanediol in the 5¹²6⁴ (right) and the methanol molecule in the 5¹² cage (left) of the sII clathrate (carbon: brown; hydroxyl group: red)



PXRD pattern of 1,2-propanediol/ H_2O/NH_4F mixture at 170 K. There exists *P63/mmc* solid solution phase (*a* = 4.4548(50) Å and *c* = 7.2509(77) Å) with unknown impurities. There is no clathrate phase.

Without methanol 1,2-propanediol did not form any clathrate phases even in the presence of $\rm NH_4F$ $_8$



Figure 3. a) The PXRD pattern of the binary methyl MTBE + methanol H_2O/NH_4F clathrate at 188 K and the Rietveld refinement results. Tick marks indicate the Bragg positions for the sH hydrate (top), the H2O/NH4F solid solution (middle), and the NH4F solid (bottom).

b) The MTBE in the $5^{12}6^8$ cage (left), the methanol in the $4^35^66^3$ cage (top right), and the methanol in the 5^{12} cage (bottom right) of sH (carbon: brown; hydroxyl group: red)

MTBE=Methyl tert-butyl ether

The sH H₂O clathrate hydrate has a good thermodynamic stability in combination with a high storage capacity ⁹



Fig 4. a) PXRD pattern of the binary sI ethanol + methanol H_2O/NH_4F clathrate (a=11.8824(8) , Pm3⁻n) at 160 K with impurity (H_2O/NH_4F solid solution, a=4.4603(3) and c=7.2574(6) , P63/mmc),



Fig 4. b) PXRD pattern of the binary sII isoamyl alcohol + methanol H_2O/NH_4F clathrate (a=17.2129(11), Fd3⁻ m) at 170 K with impurities (H_2O/NH_4F solid solution, a=4.4621(3) and c=7.2579(6) , P63/mmc; sI methanol H_2O/NH_4F clathrate, a=11.8102(15) Pm3⁻ n; NH4 F solid, a=4.4432(3) and c=7.1777(8), P63/mmc)



Fig 4. c) PXRD pattern of the binary sII 2-MeTHF + methanol H_2O/NH_4F clathrate (a=17.1513(11) , Fd3⁻m) at 150 K with impurities (H2O/NH4F solid solution, a=4.4585(3) and c=7.2500(5) , P63/mmc; sI methanol H_2O/NH_4F clathrate, a=11.8059(7), Pm3⁻n; NH4F solid, a=4.4373(3) and c=7.1510(6), P63/mmc)



The broadness is possibly due to the disorder introduced by the NH4F, giving rise to a distribution of slightly different cage environments.

Figure 5. CP ¹³C NMR spectra of the three structural types of methanol H_2O/NH_4F clathrates at 183 K.

Summary

- 1. In summary, they have synthesized methanol in H_2O/NH_4F clathrates of sI, sII, and sH and demonstrated that methanol can be a guest if the lattice framework contains a kind of stabilizer like NH_4F for the hydroxyl group.
- 2. Methanol has been an important material in the study of clathrate hydrates for a long time, but treated as a thermodynamic inhibitor or a kinetic promoter only.
- 3. The stability of the modified methanol clathrate can be attributed to the strong methanol CH₃OH····F⁻ or CH₃OH····NH₄⁺ hydrogen bonding which leaves the water– water hydrogen bonding network intact, whereas, in pure water-methanol clathrate where the methanol–water hydrogen bonding disrupts the lattice and a stable clathrate cannot be made.