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Some New Halogen-containing Hydrate-formers for Structure I and II Clathrate Hydrates[1]

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The clathrate hydrate-forming capabilities of 15 hydrofluorocarbon (HFC), fluorocarbon (FC), hydrochlorofluorocarbon (HCFC) and chlorofluorocarbon (CFC) guests are reported. These molecules form stable clathrate hydrates at T > 0°C and have been characterized in detail by X-ray powder diffraction and the measurement of the decomposition temperature, T_{decomp}. The clathrate hydrate structure type depends on the size of the guest molecule and is consistent with the known trend: guest $r_{VDW} = 4.1–5.9$ Å gives structure I, guest $d_{VDW} < 4.1$ Å or = 5.6–6.9 Å gives structure II. In addition, the phase diagram of the 1,1-dichloro-1-fluoroethane (R-141b) clathrate hydrate system is reported with a quadruple point of $T = 8.4$°C and $P = 415$ mbar. A number of guests give hydrates with relatively high decomposition temperatures ($T \sim 10$°C) at low vapour pressures ($P < 1$ bar) that may be suitable for industrial applications.

INTRODUCTION

The study of clathrate hydrates, host-guest materials consisting of hydrogen-bonded frameworks of water molecules surrounding guest molecules, dates back to Davy's report of chlorine clathrate hydrate in 1811.[2] The pioneering work of von Stackelberg and Müller,[3,4] Claussen,[5] Pauling and Marsh[6] in the late 1940's and early 1950's led to the characterization of the two basic clathrate hydrate crystal structures, Structure I (cubic, *Pm3n*, $a = 12$ Å) and Structure II (cubic, *Fd3m*, $a = 17.2$ Å), by means of X-ray powder diffraction. Ripmeester and coworkers have used X-ray powder diffraction and NMR spectroscopy,[7] as well as recently, single crystal X-ray diffraction,[8] to discover and characterize a third clathrate hydrate structure type, Structure H (hexagonal, *P6/mmm*, $a = 12.2$, $c = 10.1$ Å). Lists of confirmed clathrate hydrate formers and hydrate properties have been compiled.[9,10]

Guest molecules interact with the cages of the surrounding network of hydrogen-bonded water

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molecules by weak van der Waals' interactions, and stabilize the ice lattice in such a manner that many clathrate hydrates persist as solids at temperatures greater than the melting point of ice. This stability of clathrate hydrates lends itself to the study of fundamental phenomena such as hydrophobic hydration, and since hydrates form in a variety of industrial and natural environments the attempts to control hydrate formation and to determine their role in nature provides continuing challenges in chemical and petroleum engineering as well as earth and environmental sciences. For example, in the energy industry, conditions under which oil and gas are produced, transported, and processed are often suitable for the formation of troublesome solid hydrate deposits which must be controlled.[11] On the other hand, large deposits of naturally-occurring clathrate hydrates, primarily with methane and other hydrocarbons as guests, are anticipated to be a future energy source.[12] Such methane clathrate hydrates may also play a role in stabilizing or altering the global climate.[13] Favourable properties of clathrate hydrates also provide opportunities for technological innovations in areas such as the desalination of sea water, thermal energy storage, chemical separations, storage and transportation of natural gas and of dangerous chemicals.[14]

Guests containing fluorine and/or chlorine are of particular interest as clathrate hydrate- formers as many are of appropriate size to fit into the clathrate cages. They have higher boiling points than their hydrocarbon counterparts thus are more convenient for hydrate synthesis, and the resulting clathrate hydrates are stable at relatively high temperatures and low pressures;[9,10] together, these features render this class of clathrate hydrate-guest compounds attractive for some of the applications described above. Applications to desalination and cool energy storage have been described or reviewed for a number of hydrate formers.[15,16] In the past decade, the attractiveness of CFCs such as R-11 has been mitigated by their high atmospheric ozone-depletion potential, and as a result, interest has shifted to CFC, HFC, HCFC and FC molecules which share a number of the attractive physical properties but are not strong atmospheric ozone-depleters.

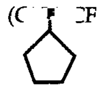
This paper reports the clathrate hydrate-forming abilities of a number of CFCs, HFCs, HCFC's and FCs. For those species that form clathrate hydrates, X-ray powder diffraction and decomposition studies were performed in order to characterize the new clathrate hydrates. In addition, a clathrate hydrate phase diagram of the R-11 replacement, 1,1-dichloro-1-fluoroethane (R-141b), was constructed.

RESULTS AND DISCUSSION

The X-ray powder diffraction data and decomposition temperatures for fifteen new clathrate hydrates are collected in Table I; also included are the boiling points and estimated van der Waals diameters d_{VDW} for the HFC and HCFC molecules. Other than the fact that smaller guests form structure I clathrate hydrates and the larger guests form structure II, there is no apparent correlation between the properties of the hydrate formers and the structure and the behavior of the resulting clathrate hydrates. Neither the boiling point of the hydrate former, the size of a clathrate hydrate guest as estimated by d_{VDW}, nor the number or type of halogen atoms on the guest are related to the size of the unit cell or the T_{decomp} of the clathrate hydrates that they form.

A sample X-ray powder diffraction pattern of 1,3-difluoropropane clathrate hydrate, a structure II hydrate, is presented in Figure 1. The data were collected at 90K using Co K_{α} radiation and show 17 indexed clathrate hydrate peaks as well as the presence of ice I_h. Typically, between 15 and 20 peaks of the new clathrate hydrates are unambiguously indexed.

TABLE I New clathrate hydrates based on fluorinated and chlorofluorinated hydrocarbon guests

Hydrate Former	*Boiling Point/°C*[a]	d_{VDW}/Å[b]	*Hydrate Structure*	*Lattice Constant/Å*[c]	T_{decomp}/°C[d]
$CHCl_2F$	8.9	5.8	II	17.145(1)	9.9
CH_3CCl_2F	32	6.5	II	17.234 (3)	8.4
CH_3CF_3	–4.6	5.7	II	17.111(2)	*e*
CH_2FCHF_2	5.0	6.1	II	17.103(4)	7.7
$CHClFCF_3$	–12	6.9	II	17.208(2)	4.9
CHF_2CF_3	–48.5	6.1	II	1 7.105(2)	11.8
CF_3CF_3	–78.1	6.1	II	17.174(3)	e
CH_2=CHF	–72	5.8	I		
	11.914(2)	2.0			
CH_2=CF_2	–83	5.8	I	11.937(2)	2.5
cis-CHF=CHF	–28	5.8	I	11.906(3)	12.3
CH_3CHFCH_3	–10	6.3	II	17.129(6)	11.4
$CH_2FCH_2CH_2F$	41.6	6.9	II	17.143(2)	7.1
$CF_3CF_2CH_3$	e	6.9	II	17.187(9)	3.8
(C [illegible] F	11.2	6.3	II	17.194(6)	8.7
	51–52	6.2	II	17.253(5)	10.5

[a]taken from the literature
[b]maximum van der Waals diameter
[c]Structure I: cubic, *Pm3n*; Structure II: cubic, *Fd3m*
[d]decomposition temperature of clathrate hydrate in a sealed tube under vapour pressure of guest, ± 0.2°C
[e]not characterized

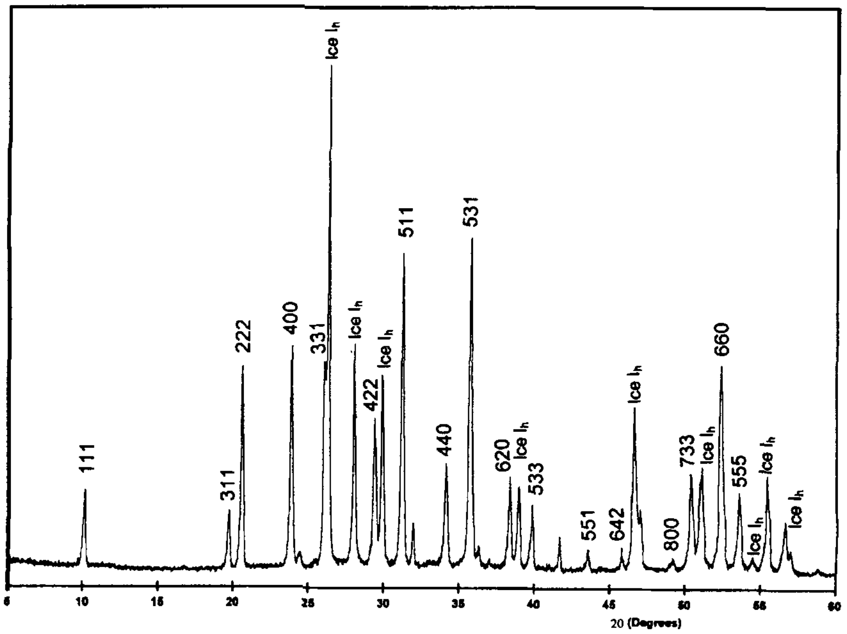


FIGURE 1 X-ray powder diffraction pattern of 1,3-difluoropropane clathrate hydrate, a structure II clathrate hydrate, collected at 90 K using Co K_α (λ = 1.788965 Å) radiation.

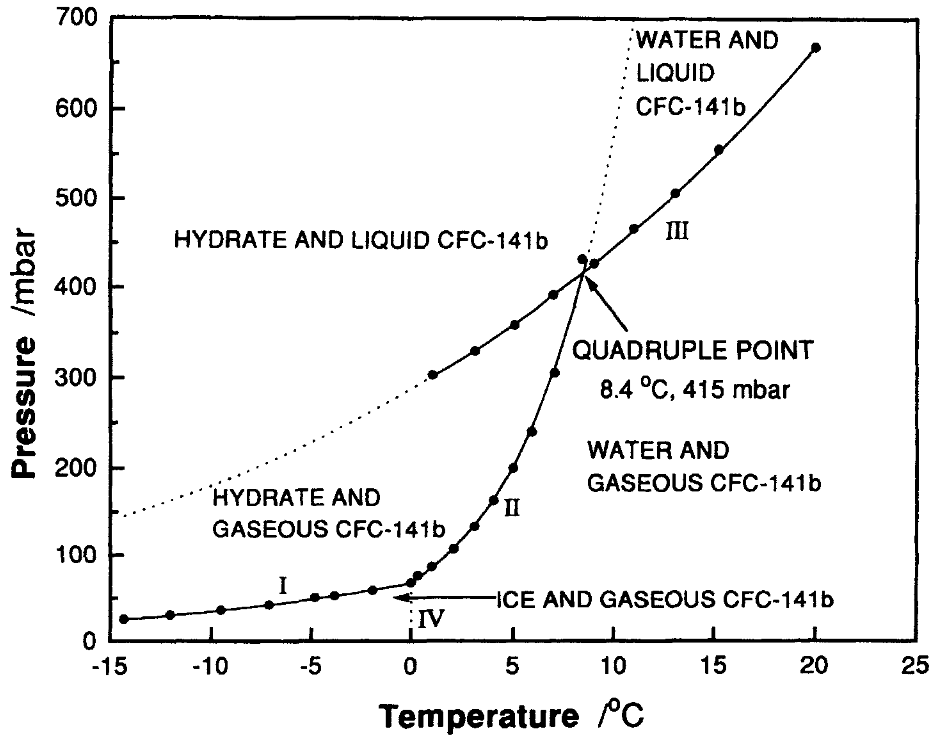


FIGURE 2 Phase diagram of 1,1-dichloro-1-fluoroethane (R-141b) clathrate hydrate.

A number of CFC, HFC and FC molecules fail to form clathrate hydrates stable above 0°C: $CHCl_2CF_3$ (d_{VDW} = 6.9 Å), CClF = CF_2 (d_{VDW} = 7.0 Å), CHCl = CF_2 (d_{VDW} = 7.0 Å), CHCl = CHF (d_{VDW} = 7.0 Å), CHF_2CHFCF_3 (d_{VDW} = 6.9 Å), and $CF_3CF_2CF_3$ (d_{VDW} = 6.9 Å). These six molecules are relatively large, having d_{VDW} near 7.0 Å, and appear to be unable to form simple clathrate hydrates although they should form stable hydrates in the presence of small help molecules such as H_2S that occupy the small cages of the ice lattice and provide added stability to the clathrate hydrate.[17]

The hydrate stability region of one clathrate hydrate system was studied in greater detail. The phase diagram of the R-141b and water system is presented in Figure 2. Curve I was constructed from pressure readings of only the R-141b clathrate hydrate and represents the equilibrium:

$$\text{R-141b} \bullet x\,H_2O\,(s) \leftrightarrow \text{R-141b}(g) + x\,H_2O\,(s)\ \Delta H_s$$

Curve II was constructed from pressure measurements of a stirred slurry of water and clathrate hydrate and represents the equilibrium:

$$\text{R-141b} \bullet x\,H_2O\,(s) \leftrightarrow \text{R-141b}(g) + x\,H_2O\,(l)\ \Delta H_l$$

Curve III was constructed from vapour pressure measurements of pure R-141b at various temperatures. Lastly, curve IV simply represents the water-ice equilibrium. The phase diagram is essentially a detailed account of what happens when the simple decomposition temperature of a clathrate hydrate is measured. In such measurements, the pressure within the sample cell is due to only the vapour pressure of the system's various components. Similarly, the pressures measured for the phase diagram arise from the vapour pressure of the clathrate hydrate and water system. Therefore, the observed decomposition temperature of a clathrate hydrate corresponds to the quadruple point, the temperature and pressure at which clathrate hydrate, water, liquid and gaseous hydrate guest are at equilibrium. As indicated in Figure 2, the quadruple point of the R-141b clathrate hydrate system is at 8.4°C and 415 mbar.

The heats of reaction for the decomposition of the clathrate hydrate, ΔH_s and ΔH_l, are calculated to be 136.6 ± 0.7 kJ mol^{-1} and 40.6 ± 0.3 kJ mol^{-1} respectively from the slopes of the plot of ln P vs. $1/T$ according to the Clausius-Clapeyron equation:

$$\Delta \mathrm{H} = \frac{\mathrm{d} \ln \mathrm{P}}{\mathrm{d} 1/\mathrm{T}} \mathrm{R}$$

Von Stackelberg[4] estimates the hydration number of a clathrate hydrate, x, by dividing the heat of fusion of ice, ΔH_f, where ΔH_f is simply the difference of ΔH_s and ΔH_l, by the molar heat of fusion of ice, 6.008 kJ mol^{-1}. For the R-141b clathrate hydrate, the hydration number, $x = 16.0$, is consistent with a structure II hydrate with an expected hydration number of 17.0.

MATERIALS AND METHODS

Preparation of Halogen-containing Guests

Most of the guests in this investigation were obtained from commercial sources and were used without further purification. *t*-Butyl fluoride and fluorocyclopentane were synthesized from the corresponding alcohols utilizing HF/melamine as the fluorinating agent.[18]

Preparation of t-butyl Fluoride

Over a period of ten minutes, *t*-butyl alcohol (14.9 g, 0.2 mol) in cyclohexane (110 mL) was added to a polypropylene flask containing 86% HF/melamine (65 mL) cooled to 0°C in an ethylene glycol bath. After 2 h, the reaction vessel was removed from the cold bath and was left at room temperature for 12 h. The aqueous layer was separated from the organic layer with a polypropylene separatory funnel. The organic layer was washed with cold water and *t*-butyl fluoride (b.p. 12°C, 4 mL, 30% yield) was distilled into a dry ice/acetone cold trap.

Preparation of Fluorocyclopentane

Cyclopentanol (8.89 g, 0.11 mol) was added dropwise to a polypropylene flask containing NaF (0.52 g, 36 mmol) dissolved in 86% HF/melamine (70 mL) and cooled in a dry ice/acetone bath. The reaction mixture was stirred moderately as it was warmed to room temperature. After 72 h of stirring at room temperature, the organic phase was separated, washed with water and 5% sodium bicarbonate solution, mixed with a few drops of bromine followed by a small amount of zinc dust and water to remove excess bromine, filtered, distilled under reduced pressure, and dried over sodium sulfate. The product (0.2330 g, 3% yield) was characterized by ^{13}C NMR: δ96.9 (d, $^1J_{C\text{-}F} = 172$ Hz), 33.6 (d, $^2J_{C\text{-}F} = 22$ Hz), 23.3 ppm.

Preparation of Clathrate Hydrates[19]

CFC, HFC and FC guests were condensed via vacuum line into a cold glass finger containing a known amount of degassed and frozen water. The approximate molar ratios of water to clathrate hydrate guest used to prepare structure I hydrates (~ 7:1) and structure II hydrates (17:1) were based on the guest's maximum van der Waals' diameter (d_{VDW}) as estimated from standard parameters and geometric relationships. Guests with $4.1 < d_{\mathrm{VDW}} < 5.9$ Å usually form structure I hydrates and structure II hydrates are known to form with guests having $5.6 < d_{\mathrm{VDW}} < 6.9$ Å.[10] The Pyrex tube containing the water-guest mixture was flame-sealed under vacuum and the contents agitated with a vortex mixer while periodically dipping the tube in liquid nitrogen briefly to induce hydrate formation. The presence of clathrate hydrate was confirmed by the persistence of the solid material when the sample tube was submerged in a cold bath slightly above 0°C. The samples were conditioned for at least one week in an ice bath or freezer.

X-ray Powder Diffraction

Clathrate hydrate samples were ground into a fine powder at liquid nitrogen temperature and loaded onto a cold flat plate sample holder of a Rigaku Geigerflex D/max-B powder diffractometer. Diffraction patterns of Cu K_α ($\lambda = 1.540562$ Å) or Co K_α ($\lambda = 1.788965$ Å) radiation were collected at temperatures ranging from 80 to 100 K. Diffraction patterns, typically consisting of between 15 and 20 resolved peaks, were analyzed using the TREOR[20] trial and error fitting program to give an indication of the structure of the clathrate hydrate sample. The peaks were indexed and lattice constants refined by a least-squares fitting program. The errors associated with the lattice constants reported in Table I are the errors of the least-squares fits. A realistic estimate of the error associated with the lattice constants is ± 0.01 Å due to the degree of uncertainty in the peak positions from which the lattice constants are calculated.

Decomposition Temperature, T_{decomp}

Sealed tubes containing clathrate hydrate samples were immersed in an ice bath which was allowed to warm slowly to ambient temperature. The temperature at which the solid clathrate hydrate completely disappeared was recorded as the decomposition temperature.

Phase Diagram

In order to construct the phase diagram of 1,1-dichloro-1-fluoroethane (R-141b) and water, a series of pressure and temperature readings were acquired. A slurry of water and R-141b clathrate hydrate was placed in a 50 cm^3 glass vessel (equipped with magnetic stirring, a thermocouple and a pressure gauge) which was immersed in an alcohol bath (T ± 0.1°C). For various temperatures, pressure measurements were taken once the system reached equilibrium. In addition to the slurry of water and clathrate hydrate, pressure and temperature readings were taken of pure R-141b in a similar fashion.

SUMMARY

This work reports the structural and physical characterization of new clathrate hydrates formed with CFC, HCFC, HFC and FC guest molecules. In keeping with the known trend, the smaller guests form structure I hydrates and larger guests form structure II hydrates; some guests with r_{VDW} near 7.0 Å appear to be too large to form stable clathrate hydrates. There is no clear correlation between the properties of the hydrate former and the resulting clathrate hydrate in terms of lattice constants and decomposition temperatures. The phase diagram of the clathrate hydrate formed by R-141b, a replacement for R-11, is relevant for applications involving R-11 clathrate hydrate for cool energy storage.

The work reported herein is preliminary investigation of a few of the various fluorinated and chlorofluorinated derivatives of methane, ethane, propane, ethylene, propylene, cyclopropane, cyclobutane, and cyclopentane that may be potential clathrate hydrate formers. We anticipate that the many additional guests possible by partially fluorinating hydrocarbons will yield a rich and diverse clathrate hydrate chemistry. The observation of simple clathrate hydrates melting at temperatures near 10°C at relatively low pressures indicates that these may be especially useful for industrial applications.

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