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Some New Clathrate Hydrates†

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Seventeen new clathrate hydrates of hydrogen and/or fluorine containing molecules have been identified, mostly from the characteristic nuclear magnetic resonance line shapes observed when the hydrates are prepared from D_2O.

A considerable number of new clathrate hydrates have been identified since the most recent list of 69 hydrates was published in 1973.[1] The new clathrate hydrates known to the authors at the time of writing are given in the table. These are simple, i.e., two-component, hydrates whose stability with respect to liquid water (or ice) and the gaseous hydrate-forming component M is considered to have been established. The majority of these new hydrates have been identified in this laboratory and are reported here for the first time.

The previously-unreported hydrates were prepared, as indicated in the table, by one of the following methods.

A) A mixture of liquid M and liquid H_2O (or D_2O) was out-gassed, sealed in a glass tube, and alternately shaken vigorously and cooled until most of the liquid had solidified. The sample was stored for some weeks at $-13°$ or $5°$, depending on the decomposition temperature of the hydrate.

B) Liquid M was condensed on finely-powdered ice in the absence of air and the sealed sample conditioned at $-13°$ for several weeks.

C) Out-gassed liquid D_2O was subjected to a pressure of about 3 atm of gaseous M and frequently cycled between about $-30°$ and $5°$. The pressure was adjusted periodically during the growth of deuteriohydrate to compensate for the gas consumed.

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TABLE I

Hydrate former M	Boiling point of M (°C)	Method of hydrate formation[a]	Hydrate decomposition temp. (°C)	Hydrate structure	Properties studied
sulfuryl fluoride, SO_2F_2	−55	C		I	CW, T_1
perchloryl fluoride, ClO_3F	−47	C		I	T_1, T_2
selenium hexafluoride, SeF_6	−35	B		II	CW, T_1
tetrachloromethane, CCl_4	77		0.67[15]	II	P-T diagram[15]
trifluoroiodomethane, CF_3I	−22	A	6.2 (1 atm)*	II	CW, T_1, diel.
1,1,1-trifluoroethane, CH_3CF_3	−47	B		II	CW
hexafluoroethane, CF_3CF_3	−79	B		II	CW
2,2-difluoropropane, $CH_3CF_2CH_3$	−1	A		II	CW
2-chloropropane, $CH_3CHClCH_3$	37	A	4.3	II	CW

cyclobutane, C_4H_8	13	A	>14	II	CW
methyl cyclopropane, C_4H_8	5	A	5	II	CW
ethanethiol, C_2H_5SH	36	A	3.4	II	CW
dimethyl sulphide, CH_3SCH_3	36	A	2.6	II	CW
ethylene sulphide C_2H_4S	55	B	12.2	II	CW
				I	CW
propylene sulphide, C_3H_6S	74	A	2.6	II	CW
trimethylene sulphide, C_3H_6S	94	A	11.7	II	CW
tetramethylene sulphide, C_4H_8S	121	A	3.8	II	CW
dimethyl ether, CH_3OCH_3	−25		−20.7[24] −28.6[24]	II tetragonal	P-T diagram, CW diel.[24, 25]
1,4-dioxane, $C_4H_8O_2$	101		−12.3[18], −13.5[22]	II	T-comp. diagram[18, 22], CW, T_1, diel.[11]
1,3-dioxane, $C_4H_8O_2$	105		−3.5[18], −2.3[21]	II	T-comp. diagram[18, 21] CW, T_1, diel.[23]
isoxazole, C_3H_3NO	95		−2.0[19]	II	T-comp. diagram[19], CW, diel.[10]
isothiazole, C_3H_3NS	115		−2.0[20]	II	T-comp. diagram[20]

[a] See text.

The formation of clathrate hydrates is so general that, if M is less than about 6.9 Å in longest van der Waals dimension, any M-containing solid formed in the presence of water which melts appreciably above the melting point of M itself is probably a clathrate hydrate. (M, however, must not react with water, ionize, or, like alcohols and amines, form strong hydrogen bonds with water.) The best confirmation of clathrate formation is provided by observation of a powder X-ray diffraction pattern characteristic of the structure I or structure II lattice. The X-ray diffraction method was first used by von Stackelberg[2] to show that a large number of already known gas hydrates had one or the other of these two cubic clathrate structures and has since been frequently used to identify new hydrates. Although not always easy to determine accurately,[1,3,4] the composition—$M \cdot 6H_2O$ to $M \cdot 8H_2O$ for structure I and close to $M \cdot 17H_2O$ for structure II—may also provide a good indication of the presence and structure of a clathrate hydrate.

Recent dielectric and NMR studies[1,5–13] have established another feature characteristic of clathrate hydrates: a reorientation rate of the encaged or guest molecule which is exceptionally fast for a molecule of this size in the solid state. Thus dipolar guest species exhibit dielectric loss curves with peaks at sub-MHz frequencies which seem always to occur below 60 K, the details depending on the size and shape of the guest molecule and of the cage occupied. Proton (or ^{19}F) CW magnetic resonance spectra of the encaged species, most conveniently studied in D_2O hydrates, undergo narrowing, with disappearance of their very low temperature structure, in the same low temperature range. Species enclathrated in D_2O normally give rise to structureless lines some 1 to 3 G wide at ~77 K and 0.7 to 2 G wide above ~150 K which may be readily distinguished from the broader, frequently structured, lines characteristic of solid M. *The presence of such a line at temperatures well above the melting point of M is an almost certain indication of the presence of a clathrate hydrate.* The spin-lattice relaxation time (T_1) associated with reorientation of the guest molecule characteristically passes through a minimum at a relatively low temperature (below ~70 K for a Larmor frequency of the order of 10 MHz).

An additional diagnostic feature common to the relaxation behavior of all clathrate hydrates is the presence of very broad distributions of guest-molecular reorientation rates. The dielectric loss curves are much broader, NMR line narrowing occurs over a much broader temperature range, and T_1 minima are much shallower than are normally found in solids. These distributions originate mainly with the frozen-in disorder of the orientations of the H_2O or D_2O molecules.[1,14]

Of these criteria, we have used especially the presence of characteristic NMR CW spectra in D_2O to establish the clathrate nature of the previously-unreported hydrates given in the table.

Except for the hydrates formed by the more water soluble species (the last five in the table), the new hydrates decompose above 0°C at the temperature and pressure of Q_2, the quadruple point of coexistence of hydrate, water-rich liquid, M-rich liquid, and gas.[1] Approximate values of these temperatures, as determined by simple melting point measurements, are listed in the table for hydrates for which the decomposition pressures do not exceed one atmosphere. With the exception of CCl_4 hydrate, for which vapor pressures have been measured by Lameris,[15] the pressure-temperature phase diagrams of these $M—H_2O$ systems remain to be determined.*

An interesting new group of relatively stable hydrates is provided by ethanethiol, dimethyl sulphide, and the four cyclic sulphides. Hydrates of unusual stability are already known to be formed by hydrogen sulphide and methanethiol. The hydrates formed by dimethyl sulphide and the cyclic sulphides have comparable or higher decomposition temperatures than the hydrates formed by the corresponding ethers. Ethanethiol was reported[16] to form a high hydrate 100 years ago. From the decomposition temperature of 12 to 14° reported, however, and the method of preparation, it is likely that this was a double hydrate with H_2S. The only more recent report of ethanethiol hydrate appears to be the remark of Stupin *et al.*[17] that it forms when an $EtSH–H_2O$ mixture is shaken at 2°.

Rosso and Carbonnel have reported the hydrates of the dioxanes,[18] isoxazole,[19] and isothiazole[20] to decompose at peritectic temperatures corresponding to hydrate → ice + liquid, although Morcom and Smith[21] found 1,3-dioxane hydrate to melt congruently. All of these thermal analysis measurements, as well as those of Nakayama and Tahara,[22] were performed with samples prepared in the presence of air, which is known[1] to have a small stabilizing effect on clathrate hydrates. These four hydrates have been identified as structure II from their X-ray diffraction patterns.[10,11,20,23]

Dimethyl ether (DME) forms two hydrates, one identified as structure II by von Stackelberg and Müller.[2] The noncubic hydrate stable at lower temperatures has not been definitely identified, but its composition[24] and unique NMR and dielectric behavior[25] suggest that it is isostructural with the tetragonal bromine hydrate.[26] This clathrate structure contains 14- and 15-hedral cages large enough to contain DME molecules. For complete occupancy of these cages, the composition is $DME \cdot 8.6H_2O$.

Most of the remaining hydrates are formed by molecules considerably too large to occupy structure I cages and the presence of structure II is confirmed by characteristic features of the NMR behavior. Of these, the most useful has proved to be the width of the guest proton (or ^{19}F) line observed in the D_2O

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* Decomposition pressures of CF_3I hydrate and deuteriohydrate have now been reported (D. Y. Stupin and V. N. Tevikov, *Zh. Prikl. Khim.*, **49**, 2337 (1976)).

hydrate at temperatures above about 200 K. For structure II the second moment of the line width at these temperatures is close to the small value (0.1 to 0.2 G^2) calculated[1] for isotropic rotation of molecules in the nearly spherical 16-hedral cages, whereas for structure I, not only is the moment calculated for isotropic rotation considerably larger (0.25 to 0.5 G^2) but the experimental moment often exceeds the isotropic value because of the persistence of some anisotropy of reorientation in the ellipsoidal 14-hedra.[13] The hydrates formed by SO_2F_2 and ClO_3F are found to be structure I on this basis, and also from T_1 measurements which show the guest molecule reorientation rates to be appreciably slower than for larger molecules like SF_6 and SeF_6 in structure II. Ethylene sulphide, a molecule of intermediate size, forms two hydrates, which are assigned to structures I and II from the high-temperature second moments. Cyclopropane[27] and trimethylene oxide[28] have been previously found to form hydrates of both these structures.

Not listed among the new hydrates in Table I are the unstable clathrate hydrates recently found[29] to be formed by ethanal and propanal. Except at very low temperatures these structure II aldehyde hydrates are found to slowly decompose, presumably because of the slow (but acid-catalyzed) conversion of aldehyde RCHO to *gem*-diol $RCH(OH)_2$. It is likely that the isobutanal hydrate, said[30] to be a structure II hydrate with a hydration number of 34, is also unstable, since the equilibrium constant for diol formation is only slightly smaller for isobutanal than for the lower aldehydes.[31]

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