Journal of Thermal Analysis and Calorimetry, 83 (2006) 3, 525–531

HYDROPHOBIC HYDRATION
Ecological aspects

J. Lipkowski[*]

Institute of Physical Chemistry, Laboratory of Physico-Chemistry of Supramolecular Complexes
Kasprzaka 44/52, 01 224 Warszawa, Poland

The problem of interaction between organic and water moieties (neutral or ionized water molecular species) is of particular interest in chemistry in view of its implications to physico-chemical behavior of chemical and biological systems. Hydration patterns which result from interaction between hydrophilic and hydrophobic species are non trivial in chemistry. The key issue is that water molecules are able to aggregate in extremely large variety of structural modes. Tetrahedral geometry of intermolecular bonding around water molecule is analogous in geometrical terms to that of intramolecular geometry of carbon atom, known as a source of infinite number of organic structures.

In general, space filling with hydrogen bonded water molecules is rather low. It may be illustrated in the following way: volume of neonium atoms is comparable to that of water molecules whilst having atomic mass just 10% higher than molecular mass of water. Thus, liquid neonium and liquid water would have similar densities if molecular packing is of comparable efficiency. The real values are much different, however. Liquid neonium at its boiling temperature has density of 1.20 g cm^{-3}, thus displaying significantly denser packing that that of water molecules. It certainly means that solid or liquid water has a 'porous' structure and may lead to molecular inclusion of foreign (guest) species in the intermolecular space of water framework. This property is not that simple, however, since inclusion of foreign (guest) species is, as a rule, associated with rearrangement of the host framework structure [1]. Anyway, inefficient packing of the mono-component host solid phases may be considered as a prerequisite for its pronounced clathration ability.

Keywords: *hydrophobic hydration, methane hydrate, supramolecular architecture*

Basic physico-chemical characteristics

Inclusion of hydrophobic species in porous structure of water is closely associated with the idea of clathrate inclusion compounds. Although clathrate formation was first observed early in the last century [2], the physico-chemical nature of clathrate compounds was not understood until the middle of the last century [3]. The concept of guest molecules 'closed or protected by cross bars of trellis' was originally proposed by Powell [4] to explain the high kinetic stability of SO_2 inclusion with crystalline β-quinol (the latter serving as the respective host structure). The presence of guest species in clathrate cavities is not simply of a fortuitous nature. Thermodynamic theory has made clear that guest-host intermolecular interactions are of primary importance, and the guest species may (as often happens) influence the host in such a way that the 'imprisonement' becomes more effective or is even made possible.

During the past five decades the chemical definition of clathrate has been extended to cover inclusion-type interactions in the solid-state, and in liquid (or solution) phases. The latter issue seems to be one of the most important recent developments in the field because of its relevance to biological and geological systems.

In recent years the term 'lattice inclusion' has been widely used [5] to describe, in a rather general manner, the situation whereby a foreign (guest) species is accommodated in a crystalline lattice of the host component. In such a way the distinction between pure 'clathration' or 'complexation' becomes less important, while special emphasis is put on the steric fit between the two components, i.e. the crystalline host and the guest species. The latter may be monomolecular or oligomeric, electrically neutral or ionic. If the crystal is a molecular solid, the term 'lattice inclusion' is equivalent to description of the compound as interstitial. And, in turn, it follows that we consider interstitial solid solutions of the guest in the host lattice (provided there is no significant chemical bonding forces between the components, otherwise we should speak of interstitial complexes).

A common characteristic is that the host itself cannot form close packed crystal structures, and packing efficiency is attained by using a second (i.e. guest) component. As a rule, an 'empty' clathrate (i.e. a 'clathrate without any guest') is thermodynamically unstable and may only be prepared as a metastable, and in rather rare cases.

It is commonly assumed that no specific chemical bonds exist between the host and guest in clathrate compounds. There is even a system of nomenclature of

---

[*] klatrat@ichf.edu.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

inclusion-type compounds [6] in which the term clathrate is meant as the opposite of complex. In other words, clathration refers to physical incorporation rather than chemical bonding, for which the term complex is more appropriate.

One motivation behind the exploration of new areas of inclusion chemistry is aimed at engineering molecular recognition (separation science, selective bonding at an active receptor site, selective transport, molecular devices, etc.) and even at engineering crystalline phases. Some authors have attained spectacular successes in designing and engineering host systems suitable for efficient separation of mixtures which are otherwise separable only with difficulty, like enantiomeric mixtures, and to control chemical reactions in the solid-state [7]. Studies of inclusion properties are also of practical importance for the pharmaceutical industry. Many pharmaceuticals show pronounced ability to co-crystallize with solvent(s). The resulting polymorph structure of the compound, in addition to the presence of a foreign component, may have a strong influence on the dissolution rate, bioavailability and/or stability of the drug. Among recent examples crystal structures of loperamine hydrochloride tetrahydrate [8] and 5-methoxysulphadiazine [9] serve as illustrations of the above mentioned phenomena.

Clathrate hydrates

Supramolecular architecture of water as host

Water molecule is commonly known to form, in condensed phases, four hydrogen bonds, donating two and acting as the acceptor of the other two. The resulting tetrahedral geometry of the intermolecular bonding may be realized in the dodecahedral arrangement of water molecules in which oxygen atoms occupy vertices while hydrogen bonds lie along edges of this regular figure. Indeed, almost a perfectly regular dodecahedron (Fig. 1) may be found in clathrate hydrates [10], and has also been found as a building block of composite cavities [11]. It is interesting to note that such a geometric figure formed by water molecules has been identified in molecular beam experiments [12]. Accordingly, it may be taken as a proof that water molecules have inherent tendency to form dodecahedral cavity structure. An even more striking observation coming from the cited above experimental work is that the cavity contains an extra water molecule (or H_3O^+ ion) enclathrated inside the $(H_2O)_{20}$ cavity. Such a model has been suggested by Pauling in his theory of the structure of water. (An extra molecule inside the cavity might, presumably, be the reason for water's increasing density upon melting of ice and, bonded in a hydrophobic manner, contribute to the dynamic properties of liquid water, although this has never been confirmed by any solid-state structure of water or its clathrates.) The structures of $(H_2O)_{20}$, $H^+(H_2O)_{20}$ and $H^+(H_2O)_{21}$ were also analyzed theoretically [13] and their stabilization energies calculated. Water molecules can be replaced by methanol up to $(H_2O)_{13}(CH_3OH)_8$ with the formation of clathrate-like structures of mixed water-methanol $(H_2O)_n(CH_3OH)_mH^+$ clusters [14]. Packing of dodecahedra leads to the formation of additional cages, since five-fold symmetry of the dodecahedra does not allow efficient space-filling in a crystalline form. Put in other words, packing of dodecahedra produces crystal structures which contain some additional cavities, usually larger than the dodecahedral ones. The simplest solution, known in the literature as hydrate type I, contains a combination of dodecahedra and tetrakaidecahedra in the proportion 3:1. Internal cavity radii of the cavities are approx. 3.9 Å (small cavity=dodecahedron) and 4.3 Å (large cavity), respectively. Common description of cavity structure of hydrates is 5^{12} for dodecahedra and $5^{12}\cdot 6^2$ for tetrakaidecahedra what means the former is built of 12 pentagons and the latter of 12 penta- and 2 hexagons. This kind of notation is commonly used, thus, e.g. $5^{12}\cdot 6^8$ represents icosahedron observed in hydrates type H, thus far the largest (radius=4.06 Å) single cavity found in clathrate hydrates [15]. Clathrate hydrates type II are built of the 5^{12} and $5^{12}\cdot 6^4$ cavities in proportion 2:1, the internal radius of the hexaidecahedron is equal 4.7 Å.

When considering the ability of hydrophobic molecules to form hydrates of the structures mentioned above, it is common to use, as the first approximation, geometric fit of molecular sizes to the cavities. Small molecules, like nitrogen N_2, may enter both small and large cavities but their contribution to stabilize the cavities is not high, however. On the other hand, methane or hydrogen disulphide fit very well to the dodecahedral cavities, thus being efficient hydrate 'formers'.

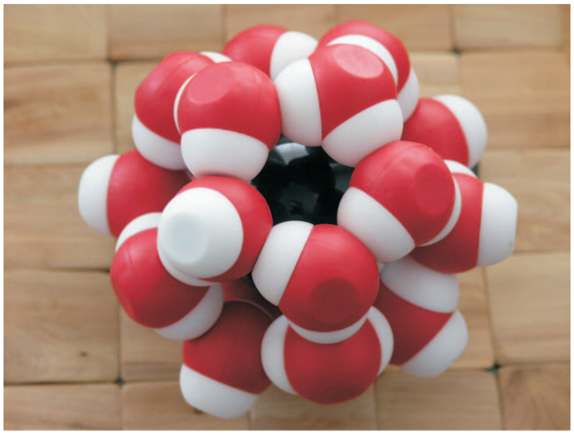


Fig. 1 Space filling model of dodecahedron 5^{12} formed by water molecules and containing a foreign guest species topologically bonded within the cavity

Although hydrate types I, II and H are commonly listed as the basic ones for hydrophobic hydration, the complete structural information may still be far from completeness. Although this problem will not be discussed here, it seems important to mention that basic structural chemistry of gas hydrates is still an open field for interesting discoveries.

Very important and interesting is the formation of large polyhedra, typically combined of four basic units (Fig. 2), which take on open structures in which the tetrahedral, intermolecular bonds of water molecules, are preserved only partially. This leads to a variety of possible three-dimensional structures.

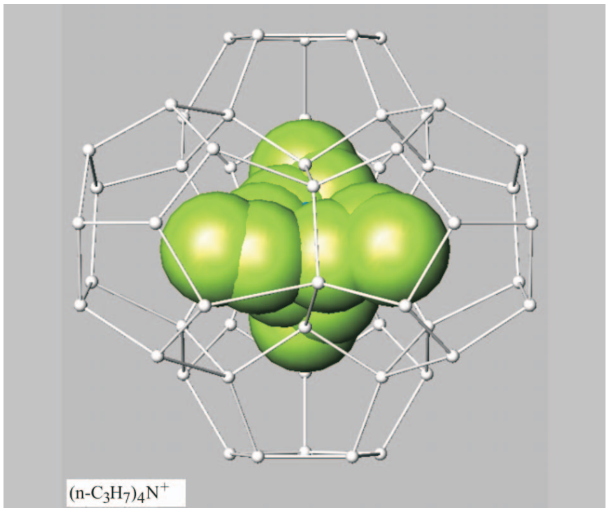


Fig. 2 A combined cavity (often called Jeffrey-type after original works by Jeffrey *et al*.) built of four dodecahedra 5^{12} and containing a guest tetra(*n*-propyl)ammonium cation (reproduced from: K. A. Udachin and J. Lipkowski, Supramol. Chem., 8 (1997) 181)

Guest-host interactions

In recent years much new information concerning clathrate hydrates has been provided both from experimental and theoretical studies. In the latter a major breakthrough may be consideration of the host-guest coupling in the normal mode analysis for the accommodation of large (relative to the cavity size) guests [16] when cage distortion occurs (like CF_4 guest molecules in the small cavities of clathrate hydrates). The classic theory of van der Waals and Platteeuw is based on an ideal solid-solution model and thus ignores the guest-host vibrational coupling and host lattice distortions. These contributions cannot, in real structures, be neglected. By taking them into account [17] the stability of Xe and CF_4 clathrate hydrates could be calculated. Encaging non-spherical propane molecules required taking into account the anharmonicity of vibrational free energy associated with the non-spherical nature of the guest. The calculated thermodynamic properties are, reportedly, better approximation to the experimental data [18] than those previously available. By examining the temperature dependence of the dissociation pressure of Xe and Ar clathrate hydrates it has been concluded that the predicted pressures agree well with experiments at higher temperature range [19].

It has also been demonstrated, with the use of advanced NMR studies, that the distribution of guest species (Xe) between small and large cages is more complex than that predicted from simple theory of clathrate solutions [20], or by simple rules of classical size-structure dependence. As shown by spectroscopic methods, carbon dioxide [21], oxygen [22], nitrogen and carbon monoxide [23] can form hydrates of type II from vapour-deposited amorphous solid water. X-ray studies give similar results with respect to the natural air-hydrate in Greenland Dye-3 deep ice core [24]. It seems likely, however, that some of the structure II hydrates undergo the II–I phase transitions at high-pressure conditions [25]. There are many subtle structural features of clathrate hydrates, and related structures like e.g. semiclathrates, which are a subject of interest in advanced studies which employ solid-state NMR [27]. In addition to guest order-disorder phenomena, rather common in clathrate compounds, hydrates show proton disordering around host water oxygen atoms. These systems are dynamic at room temperature, freeze down to rather complex static patterns at lower temperatures [26]. It has been found by neutron diffraction study of the structure II clathrate hydrate of xenon/carbon tetrachloride (3.5:8:136) that the D_2O molecules are disordered at 13 and 100 K in 6 H-bonded orientations [27]. It has recently been demonstrated that polar guest molecules may alter the rearrangement process in a defect-bearing solid clathrate hydrate network [28]. It was found that the rearrangement dynamics in a clathrate hydrate encaging polar guests follows a different mechanism from that proposed for Bjerrum for crystalline ices.

Hydrophobic hydration

Methane hydrate

The apparently most important clathrate hydrate at present is methane hydrate since its potential as an energy source is becoming widely recognized, as well as hazards associated with conceivable gas eruption on clathrate decomposition [29]. However, it is not unlikely that clathrate hydration plays a more substantial role, at least for the biosphere, in formation and stabilization of biological supramolecular systems. For example, it has been shown that the behavior of protein-containing reversed micelles may be significantly modified when the species are subjected to clathrate hydrate formation conditions [30]. It was shown that clathrate hydrates of methane can form in protein-containing reversed micellar systems; their effect is to reduce the water content in the micelles. This observation has possible important implications since it has been known that, e.g., enzyme activity is dependent on water content.

Semiclathrate structures

A series of novel semi-clathrate structures of water have recently been found. In semiclathrates the water intermolecular structure contains some deviations from a four-connected, three-dimensional polyhedral network.

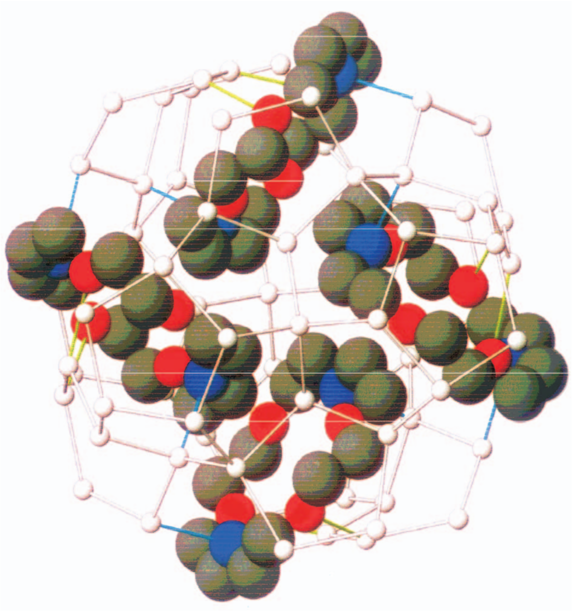


Fig. 3 Polyhydrate of 1,10-diaza-18-crown-6, reproduced from K. A. Udachin and J. Lipkowski, Mendeleev Commun., 3 (1995) 237

A series of recently reported structures of this type is based upon cavity architectures in which the network formed by host water molecules is more or less distorted from the regular shape. This is the case of 1,10-diaza-18-crown-6 hydrate (Fig. 3). Rather characteristic for these systems is that more than one hydrate is formed under slightly different experimental conditions. The next example shown (Fig. 4) represents a somewhat more open structure in which guest cations (methylammonium) are arranged, together with 18-crown-6 receptor molecules, parallel channels to the water framework which assumes an open channel structure presumably able to transport simple ions or small molecules through the crystal along the *z* axis. The tetra-*n*-propylammonium fluoride complexed with 18-crown-6 and hydrated [31] shows a layered structure (Fig. 5) in which the three-dimensional intermolecular bonding between water molecules is preserved only partially, i.e. within the layer formed by H_2O molecules.

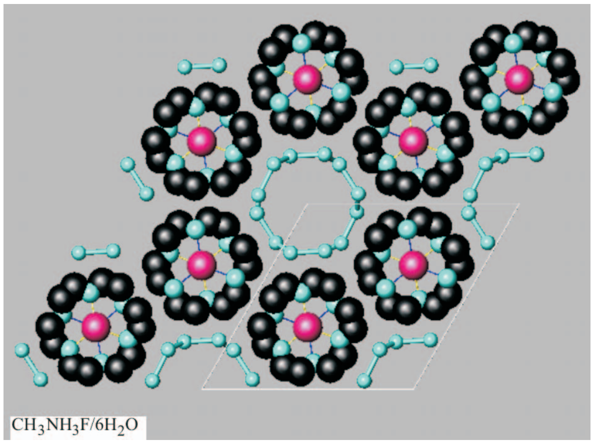


Fig. 4 View along the *z* axis of the structure of hydrated 18-crown-6 complexed with methylammonium fluoride (fluoride anions not shown, probably are disordered within the water channels shown as light blue part of the drawing), reproduced from K. A. Udachin and J. Lipkowski, Zh. Strukt. Khim., 43 (2002) 757

When going from the cage structures to the layered one, fewer and fewer intermolecular water–water hydrogen bonds are seen and, at last, one can hardly identify any ‘host’ or ‘guest’ component in the structure. By inspection of the structures, and of the corresponding phase diagrams of these systems, it may be concluded that the type of structure of the host-guest associates is strongly dependent upon the composition of the solution phase from which the solid crystallizes. If, for example, a layered structure is obtained for which less host material is necessary when compared to the cage type, then at higher guest concentrations in solution the crystallization of layered compounds is observed.

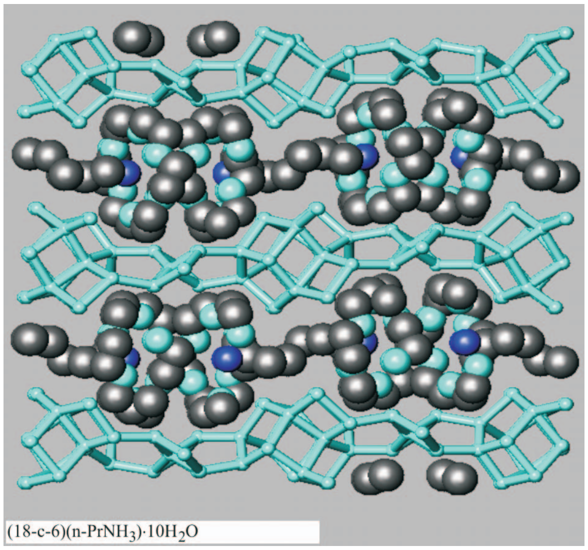


Fig. 5 Decahydrate of the 18-crown-6 complexed with *n*-propylammonium fluoride (fluoride anions incorporated in the water hydrogen bonded framework). Reproduced from K. A. Udachin and J. Lipkowski, Mendeleev Commun., 5 (1996) 195

Hydrophobic and hydrophilic hydration may thus co-exist and cooperate. Bonding via hydrophobic hydration is an important contribution, in terms of attractive interactions, to overall stability of intermolecular compounds.

When the internal crown ether receptor site is blocked by complexation of another species, (e.g. by an amino acid or peptide moiety), then water-crown hydrogen bonding is no longer feasible. Regardless, high hydration of the complexes is possible as has been shown recently [32]. In extreme cases water may play the role of just bridging those molecules able to form hydrogen bonds, as is the case of the 1:1:6 ternary complex of 18-crown-6, hydroquinone and water [33].

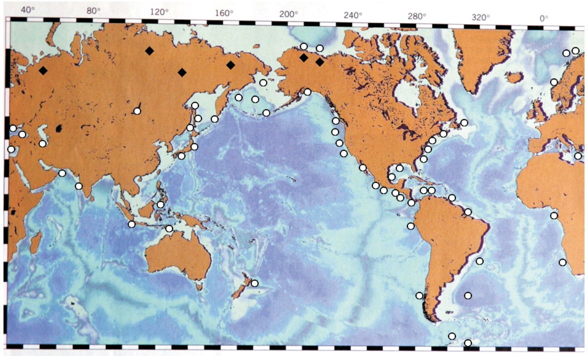
The examples shown above are intended as simple model illustrations of structural situations which may play, and presumably do, important role in biochemical systems. It seems appropriate to say, at this instant, that there are many more examples of X-ray structures of hydrophobically hydrated organic structures, some of them being reviewed recently [34]. The structures which are most stable at given conditions and environment are the ones which represent the function of the system. Water is a predominant component in biosphere and its interactions with any other components are of major importance. What is taken as granted is that water is a hydrophilic molecule. It is, of course, true statement. However, this truth is incomplete. Water may, as shown on selected examples above, behave as a combination of hydrophilic and hydrophobic molecule. If hydrophilic functions (hydrogen bonds) are saturated by forming sufficient bonding to the surrounding hydrophilic species (other water molecules, e.g.), what remains is hydrophobic interactions geometrically situated in between the tetrahedrally arranged hydrogen bonds. These interactions are not negligible, in many cases these are the structure determining factor. The phenomenon is of great importance in biochemistry. There are many protein structures in which hydrophobic hydration, i.e. hydration without hydrogen bonds between water and the second component, plays decisive role and it may well be referred to smaller blocks of protein structures. Many details still await complete discovery but the role of 'hydrophobic water' in chemists' understanding of structure and function of biological systems is growing.

Natural gas hydrates on earth

Chemists have known about the importance of gas hydrates since 1930s when gas hydrate formation was found to be the reason of pipeline blockage even at temperatures above 0°C. In permafrost regions drilling through icy ground has caused serious accidents due to sudden effluences of methane and water.

Engineers working on natural gas production and transportation are very well aware now on the risks associated with formation (blocking pipelines) and destabilization (risks for drilling platforms) of gas hydrates. Transportation is secured with the use of regular injections of methane or other chemical agents which prevent formation of hydrate deposits in the pipelines. The global cost associated with that is estimated as 10^9 US$ annually.

Knowledge about methane deposits on the see bottom on earth came originally from seismic studies. The estimated amounts varied enormously from one source to another, but in all studies the results was that this amount is high. Development of drilling technologies contributed very significantly by verifying the results obtained by seismic techniques. Below, I quote some illustrations taken from German Spektrum der Wissenschaft journal reporting on the results of probing the sea deposits for the content of methane hydrate.



Weltweit wurden Gashydrate in den Schelf- und Kontinentalhangbereichen der Meere (gelbe Punkte) sowie in Permafrostgebieten (rote Karos) an Land nachgewiesen.

Fig. 6 Natural gas hydrate deposits on earth: a – in permafrost regions (black squares) and b – underwater deposits (white circles)

On the map (Fig. 6) locations of methane deposits confirmed by direct evidence are denoted, whilst on the following diagram (Fig. 7) relative amounts of the, so-called, organic carbon are shown. It is important to note the predominant contribution of methane present in the form of hydrate, and to compare the total amount to the, say, amount of oxygen in the atmosphere. There is approximately $8\cdot10^{17}$ m^3 of O_2 in the atmosphere and $2\cdot10^{16}$ m^3 of CH_4 deposited on earth.

The importance of natural gas hydrates is threefold: resource, climate change and hazards. The first is not discussed here. There are no, to the authors' knowledge, technologies to efficiently produce methane from natural hydrates in marine sediments, this question will surely be resolved in the future – taking into account enormously high resources of this sort and the importance of the problem. There may well be much more progress made in the field than it appears

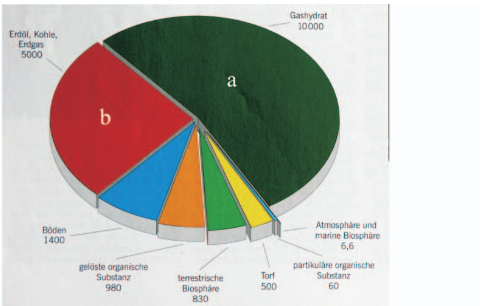


Fig. 7 Relative amounts of organic carbon on earth: a – gas hydrate, b – oil, coal and gas in 'conventional' sources

to be, technological data being scarcely published in this important field of national economies. What is known, for instance, is that Japan, the nation missing its energy independence, has started a huge project aimed at gathering hydrates form the Sea of Japan. Large scale projects were realized even before. It seems, based on the joint project of ARCO and Exxon [35] on the North Slope of Alaska, that the problem is rather complex; the significance of geothermal gradients, gas chemistries, pore fluid salinities, pore pressures and rock grain sizes having been clearly pointed out. Gas recovery from permafrost deposits seems technologically feasible, a variety of techniques are tried and tested as thermal stimulation method, inhibitor injection and depressurization. A case study of gas recovery at Messoyakha has been reported in the Sloan's monograph book cited above.

Climate change

Climate change is a very serious problem, the possible influence of methane from hydrate sources being quite often underestimated. Hydrates are soft chemical materials in the sense of their stability. They simply melt when temperature rises above their critical temperature and evolve the guest component – methane. Warming of climate may easily lead to destabilization of large amounts of continental hydrates thus producing a positive feedback to global warming. On the other hand, it is believed that global warming may stabilize oceanic gas hydrates due to melting of glacial ice sheet and thus increasing the sea level (higher pressure stabilizing gas hydrate).

It has to be stated at this point that there is still large uncertainty with respect to the possible importance of methane derived from hydrates upon climate change. This issue requires much more studies since the hypotheses presented in the literature are often contradictory. It should be noted that methane is 10–20 times stronger as the greenhouse gas as compared to CO_2. Its present contribution to greenhouse effect on earth is estimated to be as much as about 14% but hydrates are not usually mentioned as a major source of methane in the atmosphere; agriculture and other biological sources seeming more significant in that respect. Anyway, reservoirs of hydrate methane must be kept in mind as a possible climate impact on earth.

Experimental evidence for natural gas hydrate instability during Quaternary Interstadials has been provided with the use of carbon isotope studies [36]. Polar ice cores document large oscillations in atmospheric methane associated with climate cycles. There is also difference shown in oxygenation (aerogenation) of deep water, depending on the stability of the methane hydrate deposits at a given geological era. This phenomenon, clearly associated with transformations of methane and its hydrate, may have significantly influenced biological life in the sea.

Gas hydrates as geohazard

Another issue which comes to the knowledge of researchers nowadays is geohazards associated with natural gas hydrates. Sloan, in his monograph book cited above, reports on significant movement of earth in deep-water ocean environments caused by hydrates. An ancient slide of sediment (5600 km^3–290 km long and 450 km thick traveled a distance of more than 800 km) off Norway, triggered an earthquake loading and gas hydrate decomposition. Experimental evidence on hydrate dissociation over a short period of time in the Gulf of Mexico has been reported as well. Concerns have been expressed about the effect of hydrates on foundation of platforms and pipelines. A hydrate mound is typically 30 m high by 300–500 m across, and so could produce large volumes and instability.

Environmental aspects of hydrates are not limited to methane clathrates only. The other important gaseous component, of much importance to the environment, is CO_2, a hydrate forming agent. In the past there was much effort done aimed at technology of waste CO_2 removal by pumping it deep into the sea where, hopefully, it would be trapped in the form of stable hydrate. Although there are several patents in that field the idea does not seem extremely promising. There are two major reasons: far more complex phase diagram of the CO_2/H_2O system as compared to methane/water, and solubility of CO_2 hydrate which may be eluted and thus destabilized.

Air molecules, N_2 and O_2, are possible guests in hydrate structures. Being smaller molecules than that of CH_4 or CO_2, nitrogen and oxygen contribute less to hydrate's stability. Under elevated pressures, however, air is important clathrate forming agent as observed in Antarctica ice. The common picture is that air is present in ice deposits in the form of bubbles, but at deep levels (more than 900 m) bubbles disappear what is a visible evidence of hydrate formation.

Conclusions

Hydrophobic hydration is the concept derived in the 1950s from thermodynamic studies from which it became clear that, in addition to hydrogen bonding, water has the ability to bind, without hydrophilic interactions, molecular species which are considered hydrophobic. The outcome, e.g. in the form of stable compounds of water and hydrocarbons, is impressive. This binding is based upon structure effects, namely on aggregation of water molecules around a 'structure-directing agent' (as named by silica chemists) or 'template' (commonly used by organic synthetic chemists) or, simply, guest component. This is a typical collective phenomenon, not easily corresponding to the classical tools of molecular chemistry which prefers to rationalize interactions in terms of bonds between specified atoms. Hydrate solids are often non-stoichiometric, phenomenon which is certainly unknown in molecular chemistry while rather common in solid-state sciences.

Hydrophobic hydration is a common phenomenon and is important from different viewpoints: (a) directly as a source of special type of material which may be of practical importance, and (b) indirectly as a means of facilitating synthesis of organic and/or inorganic substances either in nature (as illustrated above on the example of porous silica materials) or in the laboratory.

Ecological aspects of hydrophobic hydration are manifold. Climate change due to stabilization/destabilization of huge deposits of natural gas in the form of 'soft' hydrate material seem the most important on large time scale whilst geohazards and resource of energy are important also on the short time scale. Common occurrence of hydrophobic hydrates on earth is a firm basis for further research of these complex systems, so important for biological life on our planet.

References

1 J. Lipkowski, in G. A. Webb (Ed.), Annu. Rep. Prog. Chem., 92C (1996) 307.
2 Sir H. Davy, Philos. Trans. R. Soc., London, 101 (1811) 30.
3 J. H. van der Waals and J. C. Platteeuw, Adv. Chem. Phys., 2 (1959) 1.
4 H. M. Powell, J. Chem. Soc., (1948) 612.
5 I. Goldberg, in Topics in Current Chemistry, 149, Springer-Verlag, Berlin Heidelberg 1988, pp. 1–44.
6 E. Weber and H.-P. Josel, J. Inclusion Phenom., 1 (1983) 79.
7 F. Toda, Adv. Supramol. Chem., 2 (1992) 141.
8 M. R. Caira, J. J. Gerber and A. P. Lötter, Supramol. Chem., 5 (1995) 225.
9 M. R. Caira and R. Mohamed, Supramol. Chem., 2 (1993) 201.
10 G. A. Jeffrey and R. K. McMullan, Progr. Inorg. Chem., 8 (1967) 43.
11 G. A. Jeffrey, in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Eds) Inclusion Compounds, Academic Press, London 1984, Vol. 1, Ch. 5, pp. 135–190 and references therein.
12 X. Zhang and A. W. Castleman Jr., J. Chem. Phys., 101 (1994) 1157.
13 A. Khan, Chem. Phys. Lett., 217 (1994) 443.
14 Z. Shi, S. Wei, J. V. Ford and A. W. Castleman Jr., Chem. Phys. Lett., 200 (1992) 142.
15 K. Udachin, G. E. Enright, C. I. Ratcliffe and J. A. Ripmeester, – 2nd Intern. Conf. Natural Gas Hydrates, Toulouse 1996, 2–6 June.
16 P. Englezos, Ind. Eng. Chem. Res., 32 (1993) 1251.
17 H. Tanaka, Chem. Phys. Lett., 202 (1993) 345.
18 H. Tanaka, Chem. Phys. Lett., 220 (1994) 371.
19 H. Tanaka and K. Nakanishi, Mol. Simul., 12 (1994) 317.
20 J. A. Ripmeester and C. I. Ratcliffe, 1991, in J. L. Atwood, J. E. D. Davies and D. D. MacNicol (Eds) Inclusion Compounds, Vol. 5, Oxford University Press, pp. 37–89 and references therein.
21 F. Fleyfel and J. P. Devlin, J. Phys. Chem., 95 (1991) 3811.
22 A. Hallbrucker, J. Chem Soc. Faraday Trans., 90 (1994) 293.
23 A. Hallbrucker and E. Mayer, J. Chem. Soc. Faraday Trans., 86 (1990) 3785.
24 T. Hondoh, H. Anzai, A. Goto, S. Mae, A. Higashi and C. C. Langway Jr., J. Inclusion Phenom. Mol. Recognit. Chem., 8 (1990) 17.
25 M. G. E. van Hinsberg, M. I. M. Scheerboom and J. A. Schouten, J. Chem. Phys., 99 (1993) 752.
26 C. I. Ratcliffe, S. K. Garg and D. W. Davidson, J. Inclusion Phenom. Mol. Recognit. Chem., 8 (1990) 159.
27 R. K. McMullan and A. Kvick, Acta Cryst., B46 (1990) 390.
28 K. Koga and H. Tanaka, J. Chem. Phys., 104 (1996) 263.
29 K. V. Kvenvolden, in Ann. N.-Y. Academy, (International Conference on Natural Gas Hydrates) Eds E. D. Sloan, J. Happel and M. A. Hnatow, 715 (1994) 232.
30 H. Nguyen, V. T. John and W. F. Reed, J. Phys. Chem., 95 (1991) 1467.
31 J. Lipkowski, R. Luboradzki, K. Udachin and Yu. A. Dyadin, J. Inclusion Phenom. Mol. Recogn. Chem., 13 (1992) 295.
32 J. Lipkowski, O. V. Kulikov and W. Zielenkiewicz, Supramol. Chem., 1 (1992) 73.
33 B. Belamri, C. Bavoux and A. Thozet, J. Inclusion Phenom. Mol. Recogn. Chem., 8 (1990) 383.
34 J. Lipkowski and M. Asztemborska, in Molecular and Structural Archeology: Cosmetic and Therapeutic Chemicals, Eds G. Tsoucaris and J. Lipkowski, Kluwer Academic Publishers, II. Mathematics, Physics and Chemistry, 117 (2002) 241.
35 E. Dendy Sloan Jr., Clathrate Hydrates of Natural Gases, 2nd Ed., Marcel Dekker, Inc., New York–Basel–Hong Kong, Chapter 7.
36 J. P. Kennett, K. G. Cannariato, I. L. Hendy and R. J. Behl, Science, 288, 7 April 2000.

DOI: 10.1007/s10973-005-7391-3