On the topology of layered motifs (H$_2$O)$_\infty$

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On the basis of Infantes–Motherwell classification of water clusters in organic hydrates combined with the theory of planigons, feasible topologies of water layers were derived. A value of the protic excess for water motifs was introduced. Its dependence on the nature of an organic molecule, and its impact on the topology of a water layer, were analyzed.

1. Introduction

Infantes and Motherwell[1] introduced a convenient symbolism intended for finite and infinite water clusters that were realized in organic hydrates: discrete chains (D), continuous chains (C), rings (R), tapes (T) and layers (L). On the basis of data retrieved from the CSD[2] they analyzed the abundance of respective graphs over pure water motifs[1] and motifs extended by hydrogen bond donors and acceptors of an organic molecule.[3] Afterwards, a search for the conditions of formation of a hydrate was performed and the distribution of water molecules by types of coordination was presented.[4]

Amongst various water clusters layered water motifs L$m_1(n_1)m_2(n_2)\ldots m_k(n_k)$, composed of m_1-, m_2-, …, m_k-membered rings, which share nodes (oxygen atoms) with $n_1, n_2, \ldots, n_k$ adjacent cycles[1] present a particular interest in our opinion. Firstly, some of these layers can be unalterably transported into a 3D framework, *e.g.* layer L5(7), which occurs in hexahydrates of pinacol (CSD refcode PINOLH) and piperazine (PIPERH), can also be visualized in the structure of water ice XII.[5] Secondly, water networks can not only be formed on a relatively flat surface, but also on other 2D surfaces. Platonic and Archemedean solids that are in fact cells of hydrate clathrates, are formed on spherical surfaces. For instance, layer L5(7) is made up of dodecahedron patches. On a cylindrical surface tubes are formed, *e.g.* the structure of 18-crown-6·CH$_3$NH$_3$F·6H$_2$O (LUQJEM[6]) which contains water nanotubes of the topology L6(6), identical with those of carbon (single-wall graphene nanotubes). The most important challenge is to derive feasible motifs on arbitrary 2D manifolds.

The current communication represents a deductive derivation (topological analysis) of feasible water layers L$m_1(n_1)m_2(n_2)\ldots m_k(n_k)$ according to the stoichiometry of a hydrate.

2. Regular partitions of a flat surface

There are merely 11 regular partitions of a flat surface into equal polygons (planigons), called Laves nets.[7] Yet only four of them (Fig. 1) account for water layers, since the others have nodes with a degree more than 4, while H$_2$O, strictly speaking, is capable of

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forming no more than 4 hydrogen bonds within a cluster (H$_2$O)$_m$. Two nets correspond to symbol L5(7), one to symbol L6(6) and one to L4(8). Any other symbol L$m(n)$ does not fit a (H$_2$O)$_\infty$ layer.

Symbols L$m_1(n_1)m_2(n_2)\ldots m_k(n_k)$ with $k > 1$ behave in a different way. Apparently, as any of respective motifs is periodic, it can be mapped as a certain regular net with equal cells divided into k polygons. In particular, the most widespread in organic hydrates layer L4(6)5(7)6(8) can be transposed into its topologic equivalent, shown in Fig. 2(a), with a hexagonal fundamental region. Taking into consideration that in this layer one 4-membered ring is accompanied by one 6-membered and two 5-membered rings, a symbol reproducing the stoichiometry would be L4(6)5(7)5(7)6(8). Naturally, there are other topologically non-equivalent nets L4(6)5(7)5(7)6(8) (Fig. 2(b)), as well as truly L4(6)5(7)6(8) (Fig. 2(c)), though none of them have been found in a crystal structure of a hydrate so far.

For the regular nets composed of equal t-sided polygons the following equation from a well-known Euler formula (eqn (1)) was derived:[7]

$$F - F \cdot \frac{t}{2} + F \cdot \left(\frac{1}{\alpha_1} + \frac{1}{\alpha_2} + \ldots + \frac{1}{\alpha_t} \right) = \beta(F) \qquad (1)$$

where F is the number of t-sided polygons within a certain simply connected domain, $t/2$ is the number of ribs per one polygon, α_i is the degree of node i ($i = 1, \ldots, t$), and $\beta(F) \ll F$. This equation follows from the fact that the ratio of a number of polygons adjacent to a simply connected domain to the number of its interior polygons (F)
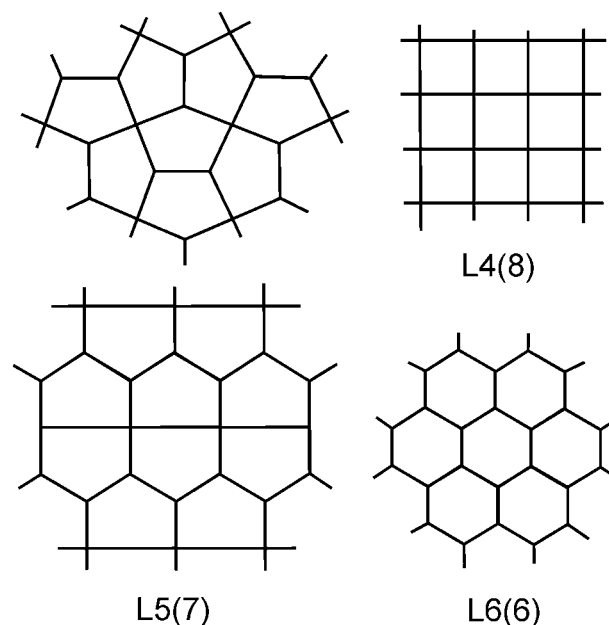

L4(8)

L5(7)

L6(6)

Fig. 1 Laves nets applicable for description of layered motifs (H$_2$O)$_\infty$.
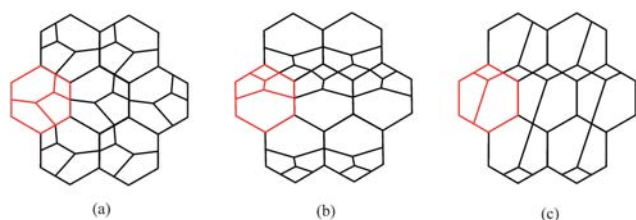
Fig. 2 Instances of topologically non-equivalent layers L4(6)5(7)5(7)6(8) (a, b) and L4(6)5(7)6(8) (c). Laves planigons are marked in red.

decreases with increase of F. There are $E = F \cdot t/2$ edges, $V = F \cdot (1/\alpha_1 + 1/\alpha_2 + \ldots + 1/\alpha_t)$ vertices, and F faces per a domain, with $(V - E + F)$ being as many times smaller than F as needed.

We have modified this formula (eqn (2)) for nets $(H_2O)_\infty$ containing merely tri- and tetra-coordinated nodes. Taking into consideration that each polygon $m_i(n_i)$ consists of $(n_i - m_i)$ tetra- and $(2m_i - n_i)$ tri-coordinated nodes, we obtain:

$$F \cdot k - F \cdot \frac{\sum_{i=1}^{k} m_i}{2} + F \cdot \left(\frac{\sum_{i=1}^{k} n_i - \sum_{i=1}^{k} m_i}{4} + \frac{2\sum_{i=1}^{k} m_i - \sum_{i=1}^{k} n_i}{3} \right) = \beta(F) \quad (2)$$

Designating $\sum_{i=1}^{k} m_i \equiv M$, $\sum_{i=1}^{k} n_i \equiv N$ we obtain, that in the limit $F \to \infty$

$$M + N = 12k \quad (3)$$

at that $M \leq N$. If $k = 1$, four nets formally satisfy eqn (3): L6(6), L5(7), L4(8) and L3(9), the latter not existing, since a triangle has 6 adjacent polygons at most.

It is not difficult to show that the layer L4(6)5(7)6(8) also satisfies eqn (3), if $k = 3$.

3. Protic excess

The *protic excess* of water motif $(H_2O)_m$ is the average number of hydrogen atoms per molecule H_2O, which do not belong to the ribs of the O_m graph, designated as p. Evidently, $0 \leq p \leq 2$; $p > 1$ for discrete chains (D), $p = 1$ for continuous chains (C), for tapes generally $1/2 < p < 1$. Since a tri-coordinated atom O possesses, on average, 1/2 an excess of protons, and a tetra-coordinated atom O has no excess protons, each layer L containing merely tri- and tetra-coordinated nodes has $p \leq 1/2$.

Let the stoichiometry of a hydrate be $Y \cdot nH_2O$, where Y is the organic component. Then $p \cdot n \cdot Z'$ is the number of excess protons, and $(2 - p) \cdot n \cdot Z'$ is the number of binding protons, per asymmetric unit. If O atoms do not occupy specific positions (site symmetry higher than 1) and are not disordered, then $p \cdot n \cdot Z'$ and $(2 - p) \cdot n \cdot Z'$ are both integers or non-integers. Excess protons can not occupy specific positions, otherwise the adjacent O would occupy the same position (generally a rotational axis), therefore when $p \cdot n \cdot Z'$ is a non-integer, some excess protons are disordered. On the contrary, binding protons can not be disordered, otherwise adjacent atoms O would be also disordered. Consequently, when $(2 - p) \cdot n \cdot Z'$ is a non-integer, some binding protons occupy specific positions. In Fig. 3 water dimers D2 are shown, in which the only binding proton is located in
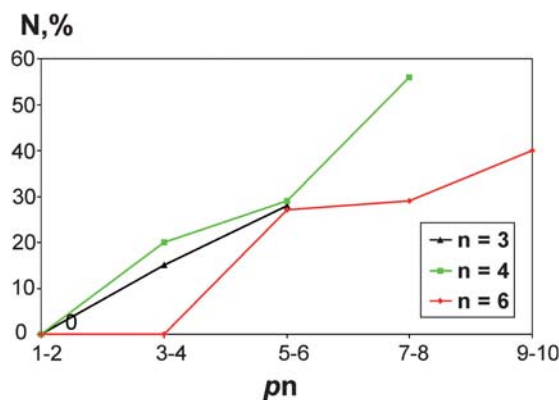

Fig. 3 Distribution of 158 trihydrates, 90 tetrahydrates, and 33 hexahydrates (only organic; with 3D-coordinates determined; number of residues = 2; $Z' = 1$) retrieved from the CSD.[2] The construction of motifs $(H_2O)_m$ was performed using the Mercury program[8] for bonds $H_2O \cdots OH_2$ not longer than 3.04 Å (in accordance with van der Waals radii proposed by Bondi[9]).Dimers D2 with protons ordered (a) and disordered by means of an inversion centre (b).

the common position (Fig. 3(a)) and in the inversion centre (Fig. 3(b)). The latter case implies excess protons being disordered.

For structures with no disorder $p \cdot n \cdot Z'$ is mostly integer. When $Z' = 1$, $p \cdot n$ becomes an integer. In many cases this value equals the number of H-acceptors of an organic molecule H-bound with the motif $(H_2O)_m$. As it was shown previously,[4] just about 15% of hydrate water molecules do not saturate donor H-bonds. Our results show unequal distribution over dimensionalities of $(H_2O)_m$ motif (Fig. 4). Low values of $p \cdot n$, in general, accounting for layers and for the majority of tapes, entail practically complete saturation of excess protons, whereas higher values of $p \cdot n$ entail less saturation.

If water motif is a layer containing merely tri- and tetra-coordinated atoms O, then:

$$x \cdot n = 2j, j \in N \quad (4)$$

where $x = 2p$ denotes fraction of tri-coordinated nodes. One may utilize eqn (4) in order to derive the most popular layers $(H_2O)_\infty$ in hydrates of different n. In monohydrates ($n = 1$) water layers can not occur, because $x < 1$. In dihydrates there can be merely a layer, in which every node is tri-coordinated, *i.e.* L6(6). In trihydrates, there can be a layer with $x = 2/3$, in tetrahydrates a layer with $x = 1/4$ and L6(6), *etc.*

Let us express the protic excess of a layer *via* topologic characteristics M and N. For that we should count the number of binding protons per a simply connected domain of cycles $m_i(n_i)$, $i = 1, \ldots, k$, by dividing the number of its ribs by the number of its nodes (eqn (5)):
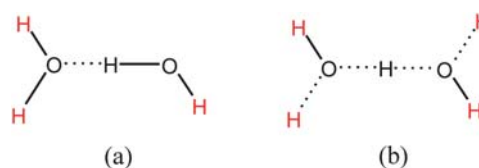

Fig. 4 Dimers D2 with protons ordered (a) and disordered by means of an inversion centre (b).

$$2 - p = \frac{M/2}{(N-M)/4 + (2M-N)/3} \quad (5)$$

It follows that:

$$\frac{M}{N} = \frac{2-p}{4-5p} \quad (6)$$

and, taking into account eqn (3),

$$p = 1 - \frac{2k}{M-2k} \quad (7)$$

Dividing the arisen ratio by k, and designating $M/k = \bar{m}_i$ (the mean size of cycles m_i), we obtain:

$$p = 1 - \frac{2}{\bar{m}_i - 2} \quad (8)$$

Eqn (7) and eqn (8) may be utilized to predict water layers in hydrates $Y \cdot nH_2O$ with different n. For instance, in trihydrates, as it was shown above, $p = 1/3$, therefore $M = 5k$. Layers L5(7), L4(6)6(8) and L4(6)5(7)6(8) satisfy this criterion, and, taking into account that H_2O tends to form 4-, 5- and 6-membered rings, the mentioned layers are likely to be merely plausible, when $k \leq 3$. By means of the reverse speculation one may find that the mentioned layers are to be realized in hydrates with n divisible by 3.

For layers $Lm_1(n_1)m_2(n_2)\dots m_k(n_k)$ containing not only tri- and tetra-coordinated nodes, but bi-coordinated nodes, too, it is not complicated to prove the validity of the following equations:

$$M + N - Y = 12k \quad (3')$$

$$\frac{M}{N-Y} = \frac{2-p}{4-5p} \quad (6')$$

where $Y = \sum\limits_{i=1}^{k} y_i$

and y_i is the number of bi-coordinated nodes in cycle $m_i(n_i)$. However, the form of eqn (7) should not be revised.

4. Conclusion

It was shown that integer-valued number of protons not belonging to a graph O_∞ (excess protons), per asymmetric unit, facilitates the prediction of plausible symbols $Lm_1(n_1)m_2(n_2)\dots m_k(n_k)$. For layered hydrates $Y \cdot nH_2O$ this value, as a rule, equals the number of H-acceptors of Y bound with water molecules. Thus, the topology of water layer is implicitly defined by the nature of organic compound. The values

$$\sum\limits_{i=1}^{k} m_i, \quad \left(\sum\limits_{i=1}^{k} n_i - \sum\limits_{i=1}^{k} y_i \right)$$

where y_i is the number of bi-coordinated nodes in cycle $m_i(n_i)$, and k, are interrelated. Hence, the protic excess corresponds to the mean size of cycles $\bar{m}_i$.

Acknowledgements

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