

L'eau, patrimoine commun de l'humanité parce que droit fondamental

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Le lien indissociable entre vie et eau (l'eau est avec l'air l'élément naturel indispensable - et insubstituable à la vie) constitue le point de départ de l'argumentation en faveur de l'eau en tant que bien commun/patrimoine de l'humanité.

L'accès à l'eau en tant que droit individuel et collectif, humain et social, en constitue le deuxième élément. Ainsi, ni un Etat, ni un groupe de personnes, ni une communauté locale ne peuvent s'arroger le droit de propriété sur l'eau ce qui pourrait, en quelque sorte, soumettre le droit d'accès à des conditions restrictives du point de vue politique, civil, culturel, social. En revanche, toute personne et toute communauté humaine - locale, régionale, nationale, mondiale - ont le droit d'accès à l'eau là où elle se trouve en solidarité avec les autres personnes et communautés et avec les générations futures.

Le principe d'utilisation solidaire et durable de l'eau à l'échelle globale - dans l'intérêt de toutes communautés humaines locales - est

à la base du troisième élément. Ainsi, il n'y a pas de société mondiale sans reconnaissance de la nécessité du « vivre ensemble » (et donc, sans la volonté de le faire) en partageant des biens et des services communs de base indispensables à la vie individuelle et collective. L'eau doit être reconnue comme le premier bien commun mondial du vivre ensemble à l'ère des sociétés qui ont pris conscience de la mondialité de la condition humaine.

Enfin, la reconnaissance croissante au cours notamment des années '90, des problèmes mondiaux, des opportunités et des solutions mondiales font apparaître l'urgence de la nécessité de la reconnaissance de l'humanité en tant que sujet juridique et politique. L'eau révèle l'inévitabilité de la définition et de la mise en oeuvre d'une nouvelle « ingénierie politique » (juridique et sociale) mondiale concernant l'humanité et son existence.

Origin of life:

The role of water in the transition from non-living to living matter

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Introduction

Liquid water is a component of all living cells and its role is so important and fundamental that it is difficult to imagine any form of life without liquid water. Water not only contributes to the structure of living matter but also to its reactivity and therefore to the functioning of living cells. Due to the relationship between life and water, the search for water in the Solar System, and even outside the Solar System, is of importance. The discovery of water, or at least traces of it, on other bodies of our Solar System sometimes leads to the audacious conclusion that if water is (or was) present, life could also be (or have been) present. This kind of extrapolation is dangerous and is the result of a pernicious shift: the expression "no life without water" has become "if water, then life".

Until now liquid water has only been found on Earth. It is highly unlikely that liquid water exists on the surface of any other body of our Solar System but if it is present elsewhere in the Solar System, it could

perhaps be present in the Martian underground or below the icy crust of a Jupiter satellite like Europa. Water vapor and solid water (ice) are of course abundant in the Solar System. Water vapor is present in the atmosphere of many planets and comets are described as "dirty snowballs". Comets eject water molecules when they are heated by the Sun and become active and this is when they acquire their coma and tails. The ejection rate of water by the Hale-Bopp comet, when it was near its perihelia, was around 300 tons per second (1). Water is also present in the form of crystallization water in the mineral matrix of a class of meteorites called carbonaceous chondrites which, in some cases, have a water content higher than 20% by weight (2).

Liquid water being of major importance for all living species on Earth, any scenario concerning the origin of life must take into consideration the processes by which liquid water was able to accumulate on the surface of the young Earth. It must also take into account the role of water in the transition steps from non-living to living matter. In this review article we will not examine the role of water as reactant in reactions involving covalent bond breaking or forming, we will only consider the role of water in non covalent chemical steps involved in

the complexity increase which characterizes the molecular evolution from non-living matter to the first living unicellular organism.

The origin of liquid water on earth

The origin of water on Earth remains a subject of debate between specialists and the successive chapters of a very recent book (1, 3-5) is clear-cut proof of this state of affairs. The water content in the mineral matrix of meteorites coming from the external part of the asteroid belt (and therefore from the region closer to Jupiter) is much higher than the water content of meteorites coming from the inner part of the belt (and therefore from the region closer to Mars). On the basis of this observation, it has been suggested that the young Earth, which was closer to the Sun than Mars, was essentially formed by the accretion of planetesimals with a low, to very low, water content (4). According to this scenario, water on Earth is the result of post-accretion processes involving the impact of asteroids, meteorites, micrometeorites and comets coming from the external parts of the Solar System. The young Earth, just after accretion, is described as a "hot and dry" body, heavily bombarded by impactors of various sizes. One of these impactors was large enough to strip matter off the external shell of the Earth, which led to the formation of the Moon (around 60 to 100 My after the Earth's accretion) (4). After this dramatic event, the bombardment by massive bodies was slowly replaced by a very important flux of micrometeorites characterized by a high content of volatiles like dinitrogen, carbon dioxide and water. This Early Micrometeorite Accretion model, called EMMA by Maurette and his coworkers (5,6), seems to explain sufficiently well the formation of the atmospheres of the terrestrial planets and also to explain the formation of the Earth's hydrosphere. In particular, the H/D isotopic ratio of the ocean water is well explained by the EMMA model. Nevertheless, and as pointed out by Maurette himself in a very recent review article (6), the EMMA model alone cannot explain the total amount of water found on Earth, which is too large by a factor of 3 with respect to what can be predicted on the basis of the model. This could be proof that carbonaceous chondrites also contributed to the Earth's water content (7,8). However, the energy associated with the impact of large objects, is sufficient to atomize most of the molecules constituting the impactor. This suggests that the post-accretion delivery of water and other small molecules was only done by small or moderated sized objects.

Another scenario, called the endogenous scenario, is sometimes also evoked to explain the origin of liquid water on the Earth's surface. It is associated with the degassing of the Earth's crust and mantle. Even if this scenario is currently considered to be less plausible than the exogenous scenario, this does not exclude the possibility that a certain percentage of the water present on the surface of the young Earth was the result of the violent volcanism which was certainly taking place during the first hundreds of millions years of the young Earth's life (4). This endogenous scenario implies that the young Earth had already a non negligible water content and therefore that planetesimals coming from the external part of the Solar System must have contributed to the first phase of the accretion.

Initially, water on the Earth was present as crystallization water in rocks or as water vapor in the atmosphere. Indeed, the temperature and pressure conditions were incompatible with the existence of liquid water. Just after accretion the Earth was a hot body, its quasi-spherical shape and the differentiation between nucleus, mantle and crust are proof that the temperature was such that the constitutive matter of the Earth was partially melted. However, the cooling by radiative processes was certainly very efficient and, after a few tens of millions years the

solid crust was formed. It is then that the impact leading to the formation of the Moon but also to a young Earth without any atmosphere occurred. During the following period of time, various post-accretion phenomena took place and an atmosphere slowly surrounded the lithosphere. The radiative heat transfer between the hot planet and outer-space was such that it can be estimated that the surface temperature of the young Earth would have quickly reached values too low for liquid water to be able to accumulate. Furthermore, the young Sun in its T-Tauri phase was most probably a "pale Sun" with a less intense electromagnetic spectrum than today at least in the UV-visible region of the spectrum (the amount of X-rays was probably much higher than today (9)). The light intensity in the UV-visible range was probably 25% lower than the present value. The only way to explain how liquid water managed to accumulate, and to solve what is often called the "faint solar paradox", is to imagine the presence of an intense green-house effect, much more efficient than the green house effect known today (10,11). Authors agree that an atmospheric pressure of few bars of carbon dioxide is probably a good hypothesis to solve the paradox and to explain how, 4.2 Gy ago, liquid water was present on the Earth's surface (4,10). Of course, it is impossible to know with certainty when the first terrestrial hydrosphere started to accumulate, but the presence of sedimentary rocks 4 Gy old and the existence of zircons, which seem to be 4.2 Gy old, are sufficient evidence to suggest that the first oceans were indeed present 4.2 Gy ago. This date gives the upper limit for what is frequently considered as the first steps of the process leading from non living matter to living matter. Of course, it could be argued that earlier steps, including the nucleosynthesis of carbon itself, are already part of this process. The search for "the origin" is vain and we have decided arbitrarily to consider, as starting point, the presence of liquid water on the Earth's surface. We consider that 4.2 Gy corresponds to the beginning of the chemical evolution of carbon containing molecules (or prebiotic evolution) which lead to the emergence of very organized living matter. From failures to a final success, this evolution took a few hundreds of millions of years. Indeed, indirect proof of fossil living matter has been detected, in western Greenland, in sedimentary rocks which are 3.85 Gy old (12).

The role of water in prebiotic evolution

Research devoted to the processes by which matter evolved from "non living" to "living" must take into account the role of water. It seems impossible to imagine any primitive form of life in absence of liquid water but, on the other hand, the possibility of certain forms of life without DNA and even without proteins is conceivable; the "RNA world" could be an example (13,14). In a way, water appears more important than DNA or proteins for prebiotic evolution!

Membranes and Water

A living cell is a system which is physically distinct from its environment : a semi-permeable frontier acts as a barrier between the "inside" and the "outside". In living cells as we know them today, this frontier is a layer (in fact a double layer) made of amphiphilic molecules. Phosphoesters of fatty acids (N-acyl phospholipids) are probably the best known examples of membrane components. We will not consider here the other membrane components such as cholesterol or triterpenes, proteins and glycoproteins which obviously also play important functions in the cell machinery.

For authors like Ourisson, Nakatani and Luisi, (15-20) the spontaneous formation of membranes is one of the primordial steps in prebiotic evolution, not only because it creates a difference between the

"in" and "out" environments but also because membranes represent an apolar medium in which certain condensation reactions can occur, while they are impossible in water because they involve the elimination of a water molecule. Spherical membranes are furthermore characterized by directional properties; the internal shell of a double layer is characterized by a negative curvature while the external shell is characterized by a positive curvature. The polar heads covering the surface with a negative curvature are in contact with internal water and are lower in number than the polar heads covering the surface with a positive curvature which are in contact with the external water molecules.

The spontaneous formation of vesicles or liposomes is a well known and reproducible phenomenon even if, *a priori*, it could appear to be counterintuitive. Indeed, if we compare an ensemble of phospholipid molecules dispersed in water to the well structured spherical double layer, it is evident that the vesicle is the more ordered system. The spontaneous formation of the vesicle must necessarily be accompanied by a decrease in the free energy of the system. If we focus on the entropy component of the free energy, two sub-systems must be considered: the lipid molecules and the water molecules. The auto-association of the lipid molecules is accompanied by an entropy decrease but this decrease is overcompensated by an entropy increase of the second sub-system. The origin of the increase of the water entropy will be discussed in the following section. Since the two sub-systems are coupled, the spontaneous evolution of the overall system, from isolated phospholipidic molecules dissolved in water to vesicles suspended in water, is associated with an overall increase in entropy; the entropy increase of water can be described as the driving force (21). To summarize in a dramatic way we could say: "without water, no vesicle formation", "without water, a primordial and fundamental step in prebiotic evolution would never have occurred". This implies that without liquid water, life based on cells separated from the external world by membranes would never have appeared on Earth.

Proteins and Water

Liquid water appears to be of fundamental importance in membrane formation but water also plays a determining role in the folding of proteins, another important aspect of living matter. Even if the possibility of certain forms of life without proteins seems conceivable, proteins were probably selected very early on by the first living cells as efficient catalysts, more efficient than ribozymes.

When describing the structure of proteins, a distinction is generally made between primary, secondary and tertiary structures (without considering the quaternary structure of polymolecular complexes). The terms "primary", "secondary" and "tertiary" give the misleading impression of a hierarchical classification. Of course, it can always be argued that it is the sequence of the amino-acids residues which determines the conformation of the molecular backbone, which itself determines the side-chain conformation. Nevertheless, it is important to remember that if the substitution of an amino-acid residue by another does not modify the molecular conformation at the level of the active site, the protein generally maintains its activity. In some way, it is the "same protein" even if its primary structure is different. It is the conformation of the protein, and especially the conformation of the active site (and also the of ancillary sites in the case of proteins requiring the presence co-factors in order to be active) that are important and, as we said, the classical three-level way of describing protein structures is therefore sometimes misleading.

A protein reaches its native conformation through a very complex process called folding. Starting from the so-called "denatured state" which has no particular conformation, folding towards the native con-

formation is spontaneous and must therefore be associated with a free energy decrease. This free energy decrease has been estimated to around 40 to 60 kJ/mole (22). This value is large enough to explain why proteins adopt their so-called native conformation. This value is however small with respect, for example, to the free energy associated with the cleavage of a covalent bond and it is therefore not so surprising that certain proteins can adopt different conformations. The so-called conformational diseases, like the Creutzfeld-Jacob disease, seem to be associated with a conformational switch between a "good" conformation and a "bad" conformation (23).

All studies devoted to the protein folding problem emphasize the role of water even if it would be an oversimplification to consider that the increase of water entropy associated to the process is the unique driving force of the folding. There are many enthalpic and entropic contributions which are different in the denatured and in the native protein and it is a subtle balance between these terms which leads to the lower free energy of the native conformation (22). The water entropy increase associated with protein folding is however always positive and large, at least at room temperature. Furthermore, all proteinic enzymes have water molecules trapped inside their folded conformation. These water molecules participate in H-bonds which contribute to the stabilization of the native conformation of the protein (22). The trapped water molecules are, strictly speaking, part of the protein structure: a dehydrated protein loses its function because it is a "different molecule", even if the primary structure is unchanged. It is interesting to emphasize this last point because it is related to the remark made previously about the absence of any hierarchy between primary, secondary and tertiary structure. Generally, when a protein is dehydrated or when a protein is immersed in a solvent other than water, it loses its properties. To describe water as a solvent and the protein as the solute does not mean that the solute is "more important" than the solvent. It is however obvious that we generally make this implicit assumption. Sometimes, it is useful to explicit it!

Ions and Water

It is essentially impossible to imagine any living system which does not require the presence of ionic species and ionic gradients between the intra-cell and the extra-cell media. Even without discussing the role of ions in living cells, it is obvious that their role is highly dependant on the presence of water. Water is a unique molecule in ionic chemistry, not only because its dielectric constant is high, but also because water molecules interact efficiently with many anions via H-bonds and with many cations via coordination between the lone pairs on the oxygen atom and empty orbitals of the cations. In particular, water has a special affinity for protons and all biochemical textbooks describe in details the role of the hydroxonium ion in the cell machinery (24). Water has been a necessary component of the chemical systems which have been involved in the passage from non-living to living matter. In this case also, water is not "just" a solvent but is an essential component of the systems. In a hydroxonium ion, it would be absurd to consider that the proton is more important than the water molecule and the same comment can be made for all solvated ions.

It appears thus that the role of liquid water is determinant for membrane formation, for protein folding and for ionic chemistry. It would be easy to find other examples of the determinant role of liquid water in vital processes, from molecular recognition to supramolecular chemistry and polynucleotide structure (25).

Hydrophobicity-hydrophilicity : water as a "judge"

When we describe the properties of the molecules found in a living cell, it is helpful to classify these molecules in three groups : hydrophilic, hydrophobic and amphiphilic. It is interesting to observe that this type of classification is based only on the behavior of the molecules towards liquid water. There is no better proof that water plays a prominent role in life!

Water acts as a "judge" in the sense that it determines which category each molecule fits into. Any molecule or ion, whether hydrophilic or hydrophobic, placed in liquid water interacts with the water molecules and, very importantly, modifies the water network. Liquid water is unique because it is a highly structured medium which can be described as a fluctuating lattice of water molecules linked to each other by H-bonds. The introduction of another molecule in this fluctuating lattice perturbs the lattice and it is this perturbation which is at the origin of hydrophobicity. It is important to insist on the fact that since the lattice fluctuates, and is therefore time dependent, this perturbation must be described in terms of space and time. Of course, hydrophobic molecules are able to interact with each other and with water molecules through the attractive London forces and the short-range repulsive forces but they are not able to make H-bonds nor able to participate in strong electrostatic interactions. On the other hand, hydrophilic molecules are generally able to give rise to H-bonding with the water molecules (acting as H-donor or H-acceptor) or, at least, to be involved in strong electrostatic interactions with the water molecules.

Even if the old Frank-Evans model is an oversimplification of what really happens to the water structure in the vicinity of a hydrophobic solute (26), it has some value. It gives a simple image of the very complex processes associated with the introduction of an hydrophobic molecule in liquid water and its major advantage is that it leads to a very simple explanation for the large and negative entropy contribution observed when a hydrophobic molecule is transferred from the gas phase (or from an apolar medium like the pure liquid) to water. The "iceberg model" or "hydrate model" of Frank-Evans suggests that the water lattice is rigidified in the vicinity of the hydrophobic solute. Neither direct experimental evidence nor theoretical results have ever fully substantiated this model even if, as we will see in the next paragraph, the results of some recent computer do not contradict it (27). In any case, a model always corresponds to a simplified and partial description of the real world and its quality is measured by its ability to depict, necessarily in an imperfect way, this real world.

The "hydrate model" helps us to remember the direction of the entropy variation when a hydrophobic solute is placed in water and also why the solubility of hydrophobic solutes in water is low. It also helps us to "understand" why two (or more) hydrophobic molecules when put in water are "pushed together" by the so-called hydrophobic forces to form complexes or aggregates. Indeed, the total surface that the bimolecular, or polymolecular, complex offers to the water molecules is lower than the sum of the surfaces offered by the separated partners. Therefore, the loss of entropy associated to the hydration of the complex is lower than the loss of entropy associated to the hydration of the individual partners. Consequently, the complex formation is linked to an entropy increase of the water sub-system. It is the same phenomenon that we took into account previously to explain the role of water in vesicle formation and protein folding. This positive entropy contribution plays an important role in molecular recognition phenomena in water (25), in the attraction between macroscopic hydrophobic objects immersed in water (28) but also in the reactivity of hydrophobic solutes in water (27).

To come back to the role of water in prebiotic evolution, it is certain that liquid water, through hydrophobic forces, has played an important role in the increase and efficiency of intermolecular interactions involving hydrophobic and amphiphilic molecules. It has therefore contributed to the spontaneous development of this extreme case of supramolecular chemistry which characterizes the chemistry of life.

Hydrophobicity: an elusive concept

As mentioned above, the "hydrate model" has never been convincingly substantiated neither experimentally nor theoretically. Even if a discussion on the origins of hydrophobicity is not the aim of this review article, it seems useful to insist on the results of few recent studies. Hydrophobicity is actually a particular aspect of a more general phenomenon called solvophobicity which was, for many years, a research field in our laboratory (29,30).

The dissolution of a gaseous solute in a solvent can be formally described as a two steps process. The first step corresponds to the formation of cavities able to accommodate the solute molecules in the solvent while the second step corresponds to the interaction of the solute, placed into the cavity, with the solvent molecules. The second step is exergonic while the first step is endergonic. Indeed, the formation of cavities requires breaking the cohesion of the solvent. In the large majority of solvents, polar and apolar, the positive free energy contribution associated to the cavity formation is mainly of enthalpic origin but in water, the negative entropy contribution always seems to be largely dominant. Clearly, the particularity of water as a solvent is directly related to its structure. Due to the small size of the water molecule, the interstitial cavities are smaller in water than in the large majority of other solvents. The creation of a cavity in liquid water is necessarily associated to a strong perturbation of the water network. Apparently, this can be done without breaking a large number of H-bonds but it requires a reorganization of the network in the so-called hydration shell (31-34). The space extension of this shell remains a subject of research via computer experiments (33). Theoretical work based on information theory (35) looks very promising because it offers an explanation for the origin of hydrophobicity but also for the origin of the hydrophobic forces and their temperature and pressure dependence. Interestingly, the model used in these studies describes the solute molecule as a hard sphere unable to make attractive interactions neither with the water molecules nor with other solute molecules. It is possible to calculate the probability associated with the spontaneous formation of a cavity which can accommodate a solute molecule of a particular size. Hydrophobicity therefore appears to be due essentially to solvent properties, the solute playing a role only through its size. Such a simple model seems nevertheless able to depict many characteristics of hydrophobicity and to explain for example why protein unfolding (denaturation) can be obtained by a temperature increase but also by a pressure increase.

As pointed out by Hummer et al in 1998 (36), the number of papers devoted to hydrophobicity (with this word in the title or in the list of key words) and published between 1974 and 1998 is close to 30,000. It increases monthly but it is doubtful that a definitive description of hydrophobicity and hydrophobic forces will be reached soon. Many models will continue to coexist and depending on the problem under study, researchers will prefer a two-state thermodynamic approach (37,38), an approach based on molecular dynamics and computer experiments (33) or a theoretical approach (35). Their conclusions will always converge regarding the peculiar nature of liquid water, at least at normal temperatures (liquid water behaves much more as a "com-

mon" solvent at high temperatures). Their conclusions will also converge on the fact that even if the old "hydrate model" corresponds to an oversimplification, it has some validity. This is the attitude we have adopted in this paper.

Conclusions

In this short review article, we have emphasized the role of water in various chemical processes which are so important in all living cells that it is highly probable that they were already present in LUCA, our Last Unique Common Ancestor. It is important to examine why water plays such a peculiar and universal role in the living world and to see if it is conceivable that this extraordinary triatomic molecule was able to play these roles at the level of prebiotic systems, well before a genetic code appeared. It is very important to insist on a unique characteristic of a living cell: it is a naturally coded system. All living species, from Bacteria to roses, from Archea to Man follow the laws of physics and chemistry of open systems exchanging matter and energy with their surroundings. It is not always sufficiently emphasized that these systems are coded to behave as they behave. Any research, or thinking, devoted to prebiotic evolution (or physico-chemical evolution) must consider how "not yet coded" and even "not yet open" systems can evolve. It must consider why, in such systems, in near-equilibrium conditions, structural and functional complexity was able to appear spontaneously through a "simple" free energy decrease. Clearly, liquid water was a prominent actor in this near-equilibrium evolution: the entropy decrease associated with the complexity increase being overcompensated by the entropy increase of water. The strong coupling between the two sub-systems is obviously a prerequisite: it happens and it is at the origin of the so-called hydrophobic forces.

Water molecules and also liquid water have unique physico-chemical characteristics which give water a very special status in matter evolution. It is not excessive to say that water has allowed the jump from non-living to living matter and no other molecule, abundant on the primitive Earth, abundant in the Solar System was able to play this role. It is even highly probable that any other form of life in the Universe, if it exists, is based on liquid water.

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