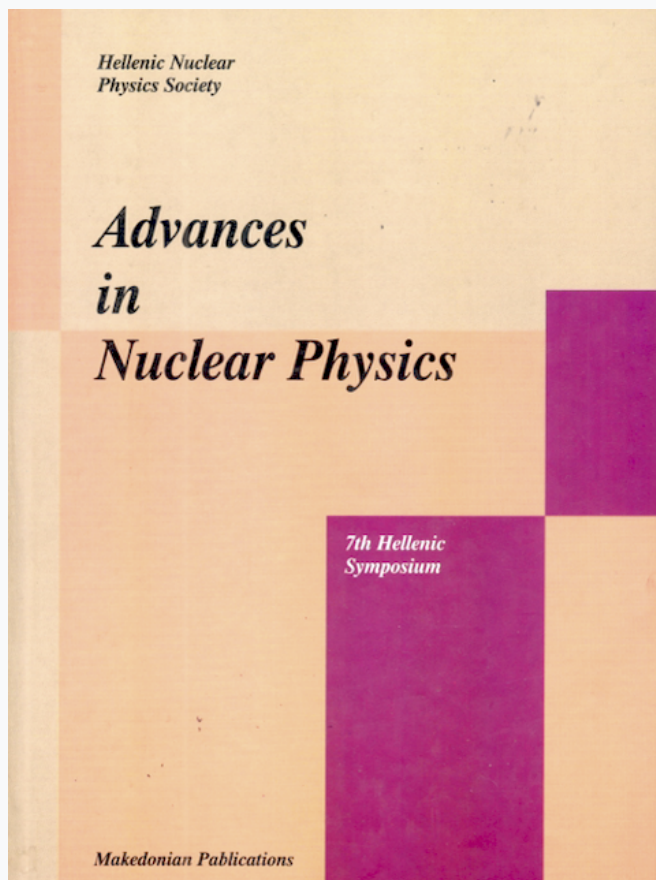


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Molecular Water Clusters in Water Environment. Third Phase of Water

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1 Introduction

Cluster study today constitutes a hot topic in Physics and Chemistry. Atomic clusters is already a flourished branch and molecular clusters received the maximum of recognition by rewarding the discovery of the third phase of carbon in the form of fowlerines. The present study goes also along the lines of molecular clusters and supports the existence of a third phase for water. Specifically, it supports, theoretically and experimentally, that besides the usual water phase of H₂O molecules and their solid phase in the form of ice these molecules may appear in a third phase in the form of molecular clusters. That is, H₂O molecules may be arranged in space forming certain structures which can survive in water environment, which means that the H₂O molecules forming these structures are not interchangeable with the H₂O molecules of the surrounding liquid phase. This behavior is similar to that of the ice interacting by hydrogen bonds, called basic clathrate. in water environment where H₂O molecules of the liquid phase (environment) are not interchanged with H₂O molecules of the solid phase (ice). The present work consists of a theoretical model and several experimental verifications of the model predictions together with some introductory necessary information related to the hydrogen bonding and the formation of clathrate hydrates which in the model present the third phase of the H₂O molecules.

2 Essential Information on Hydrogen Bond and Clathrates

Clathrate is the term for an inclusion compound made here strictly from molecules of the solvent arranged in such a way that a space is left in the interior[1]. For the special case where the solvent is water, the particular terminology clathrate- hydrate is used.

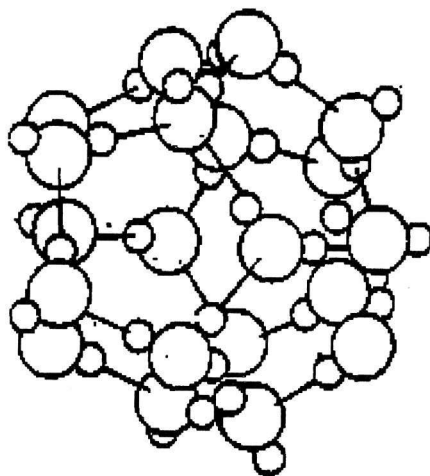


Figure 1. Pentagonal dodecahedron made of 20 water molecules

The basic building block in forming a clathrate hydrate is the pentagonal dodecahedron (Fig. 1) composed of 20 water molecules [2], i.e. $20\text{H}_2\text{O}$. Specifically, there are 20 oxygen atoms at the vertices of this polyhedron and 30 (out of 40) hydrogen atoms may be considered along its edges. The remaining 10 hydrogen atoms (directed outwards of the polyhedron) may be used for hydrogen bonding to oxygen atoms of adjacent water molecules thus acting as donors and 10 of the oxygen atoms (those whose both hydrogen atoms are considered along the edges of the polyhedron) can thus act as acceptors for hydrogen bonds with hydrogen atoms of surrounding water molecules [3] (Fig. 2).

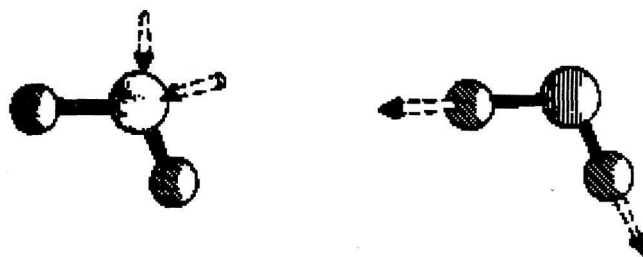


Figure 2. (a) Hydrogen bonds donated; (b) hydrogen bonds accepted.

The internal angle of the pentagon is 108° , which is very close to the ideal hydrogen bond geometry for a water molecule [4] where the angle H-O-H is 104.6° (Fig. 3). This condition makes the pentagonal dodecahedron a tightly hydrogen-bonded entity and thus such a configuration could be seen as a very stable one. Another stable clathrate-hydrate could be thought of as composed by several pentagonal dodecahedra sharing one or more faces [2] or something else where again the dodecahedron plays a dominant role.

Although colloid stability is somewhat peripheral to the main subject pursued in the present work, we emphasize here the fact that structured water has been proposed to exist surrounding micro-sized colloidal particles. Similarly, we propose that structured water is formed around a hydrophobic solute in a water environment (solvent).

3 The Clathrate Model

In the present brief presentation of the clathrate model, the tetraisoanylammonium fluoride in water is taken as an example, because the stereochemical structure of its molecule and all details (form and size) of its corresponding clathrate-hydrate are precisely known [1,4].

In Fig. 4a, b, c, all three stages in the preparation of a advanced dilution, according to the clathrate model, are demonstrated and are separated from each other by heavy horizontal lines. As stage one the molecule of the tetraisoanylammonium fluoride is shown at the center of Fig. 4a depicted by bold circles, while the water molecules of the corresponding clathrate hydrate are depicted by larger open circles.

It is apparent that the overall form of the clathrate shape resembles that of the molecule of the initial hydrophobic substance. Even more important is the remark that the three volumes comprising the clathrate are pentagonal dodecahedra which by two have a common face. This remark holds true for many clathrate-hydrates.

In Fig. 4b the second stage in the preparation of a advanced dilution, according to the clathrate model, is demonstrated. During this stage the separation of the molecule of the initial substance from its clathrate hydrate, when a forceful mechanical impulse, e.g. via supersonic waves, is applied to the dilution, takes place (Fig. 4b2-b1). This separation is obtained due to the different inertial kinematic behavior between the (relatively large density) molecule of the initial substance and that of the (relatively small density, because of the much larger size) clathrate hydrate and also due to the repulsive forces between the water molecules and the hydrophobic molecule of the initial substance. The inertia

of the clathrate-hydrate is additionally increased due to its connections, via hydrogen bonds, with water molecules of the water layers immediately after the clathrate-hydrate.

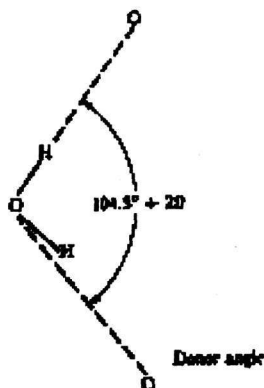


Figure 3 Ideal hydrogen bond geometry for water molecules ($104^{\circ}.6$) and its association to the donor angle $\alpha=108^{\circ}$ in a pentagonal arrangement of oxygen atoms, where $\Omega=1/2(\alpha-104^{\circ}.6)$.

The molecule of the initial substance at its new, relocated position (Fig. 4b2) interacts with water molecules and forms a new clathrate hydrate identical to the initial one (Fig. 4b2). At the same time, the left-over empty clathrate (Fig. 4b1) acquires a more compact structure than before (due to the absence of the hydrophobic repulsive forces between initial substance and water molecules of the clathrate). Simultaneously, the water molecules of the water layer immediately after the clathrate are affected by the symmetry of the shrunken clathrate (now called core clathrate) and form another clathrate (called mantle clathrate) imitating the shape of the previous clathrate vertex by vertex (Fig. 4b1). The mantle clathrate is apparently looser than the core clathrate due to the apparently larger distances between its oxygen atoms located at the mantle-clathrate corners forming hydrogen bonds with hydrogen atoms located along its edges. The size of these distances is further increased due to the repulsive forces between hydrogen atoms of the two clathrates, especially between pairs of hydrogen atoms along pairs of parallel edges of the core and mantle clathrates.

In Fig. 4c the third stage in the preparation of a advanced dilution is presented, where the separation of the core clathrate from the mantle clathrate is obtained, when a forceful mechanical impulse is applied on the dilution (Fig. 4c2 and c1). This is possible due to the different inertial kinematic behavior between the compact core clathrate (behaving like a solid) and the loose mantle clathrate (behaving like a liquid with an increased viscosity), whose inertia is additionally increased due to its connections, via hydrogen bonds, with water molecules of the water layers immediately after the mantle clathrate.

The core clathrate at its new, relocated position (Fig. 4c2) interacts with water molecules, and forms a new mantle clathrate identical to the initial mantle clathrate (Fig. c2). The left-over empty clathrate (Fig. 4c1) acquires a more compact structure than before, since, due to the absence of the core clathrate, shorter distances between oxygen atoms at the vertices of the mantle clathrate are permitted. Simultaneously the water molecules of the water layer immediately after the clathrate are affected by the symmetry of the shrunken clathrate (now becoming core clathrate) and form another (mantle) clathrate imitating the shape of the previous clathrate vertex by vertex (Fig. 4c1). This new mantle clathrate is identical to the mantle clathrates of Fig. 4b1-c2.

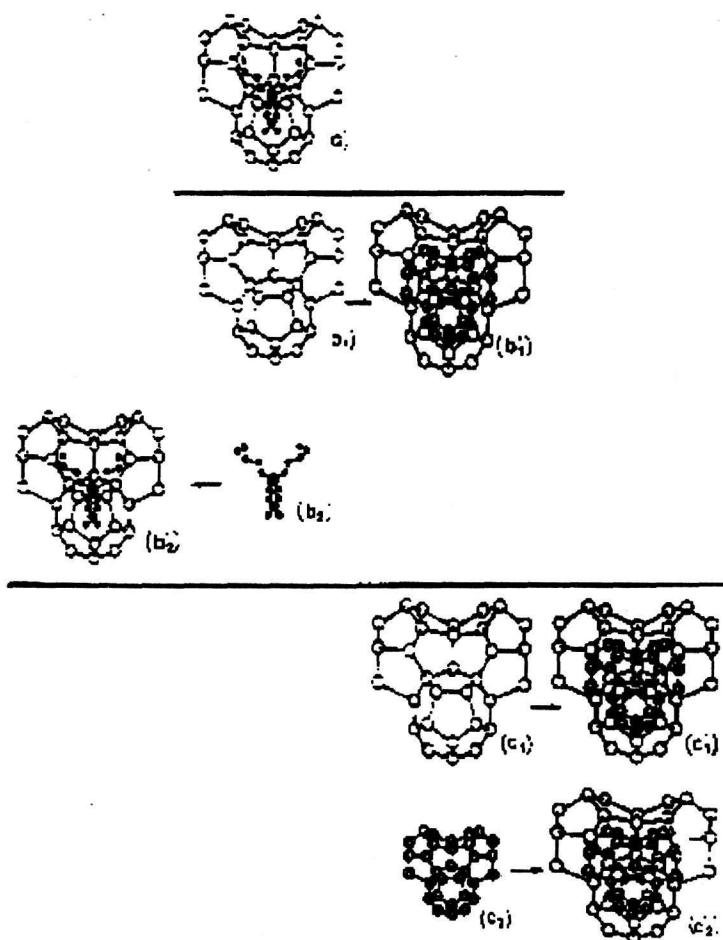


Figure 4 The three stages in preparing an advanced dilution, where the tetraisoanyl-ammonium fluoride is employed as a hypothetical initial substance for which the molecular stereochemical structure and the corresponding clathrate hydrate structure are precisely known; (a) Clathrate (host) formation round a

molecule of the initial substance (guest) after its dilution in water. That is, stereochemical molecular structure of the initial substance at the center and clathrate (cage) round it made of water molecules; b_1 and b_2 clathrate and molecule of the initial substance, respectively, coming from (a) after their separation due to a forceful mechanical impulse applied on the solution. b'_1 and b'_2 evolution of b_1 and b_2 , respectively, shortly after having applied the mechanical impulse. Specifically, the initial molecule in b_2 interacts with surrounding water molecules and, as a result another clathrate hydrate is formed leading to b'_2 which is identical to (a). At the same time, b_1 shrinks (due to absence of hydrophobic forces with the molecule of the initial substance) and interacts with surrounding water molecules leading to the formation of another (mantle) clathrate round the previous (core) clathrate as shown in b'_1 . c_1 and c_2 mantle and core clathrate, respectively, coming from b'_1 after their separation due to a forceful mechanical impulse applied on the solution. c'_1 and c'_2 evolution of c_1 and c_2 , respectively, shortly after having applied the mechanical impulse. Specifically, the core clathrate in c_2 interacts with surrounding water molecules and, as a result, a new mantle clathrate is formed leading to c'_2 , which is identical to b'_1 . At the same time, c_1 shrinks (due to absence of repulsive forces between hydrogen atoms along parallel edges of the mantle and the core clathrates in b'_1) and interacts with surrounding water molecules leading to the formation of another new (mantle) clathrate as shown in c'_1 which is identical to c'_2 and b'_1 .

An essential feature of the model is the assumed stability of clathrates involved (full or empty) which is going to be tested experimentally.

4 Experimental Support

By following the procedure described in the previous paper section, we can reach to any advanced dilution we may wish, where the solution could be thought of as effectively composed of only empty clathrates and of molecules of the solvent. In this respect, since the clathrates are also made of molecules of the solvent, advanced dilutions could be thought of as comprised of two phases of the solvent, i.e., the one of the free molecules of the solvent and the other of the bound molecules of the solvent in the form of clathrates. Thus, experimental techniques distinguishing free from bound molecules of the solvent (e.g., dielectric measurements [5-7] (DRS)) or techniques detecting change of phase occurring, for example, during heating of the solution (e.g., differential scanning calorimetric (DSC) measurements [8]) are appropriate for testing the predictions of the clathrate model. Both techniques have been applied and others are planned. The results are really in favor of the clathrate model as will become apparent shortly.

4.1 Dielectric Measurements

Dielectric methods are very powerful in hydration studies. They make use of the different dielectric relaxation time of hydration water molecules compared to that of free water molecules due to disturbance of their microdynamics by the solute molecules.

It has been pointed out in a previous paper [5] that one may avoid problems in the analysis of the measurements by using the depolarization thermocurrent (DTC) method. In the DTC method the measurements have to be carried out in frozen solutions at subzero temperatures. For interpretation, the results of these measurements have to be compared with those of DTC measurements in pure ice.

The DTC method is as follows [6,7]. The sample is polarized by an applied electric field E_p at a temperature T_p . This polarization is subsequently frozen in by cooling the sample to a temperature T_o sufficiently low to prevent depolarization by thermal energy. The field is then switched off and the sample is warmed at a constant rate b , while the depolarization current is detected by an electrometer. In the case of a single relaxation process obeying the Arrhenius equation, the depolarization current density $J(T)$ is given by Eq. 1

$$J(T) = (P_o/\tau_o) \exp(-W/k_B T) \times \exp(1/b\tau_o \int_{T_o}^T \exp(-W/k_B T') dT'), \quad (1)$$

where τ is the relaxation time, W the activation energy of the relaxation, τ_o the preexponential factor, T the absolute temperature, k_B Boltzmann's constant, and P_o the initial polarization. The analysis of the shape of this curve makes it possible to obtain the activation energy W , the pre-exponential factor τ_o , and the contribution $\Delta\epsilon$ of the peak to the static permittivity [6,7].

The DTC apparatus (of the National Technical University of Athens) used in the present study consisted of a cryostat, in which the sample temperature could be varied from 77 to 400 °K, at heating rates between 0.8 and 15.0 °K min^{-1} . The measuring capacitor was made of brass. The sample temperature was measured by a copper-constantan thermocouple attached to the upper (grounded) electrode. The current was measured with a Keithley 610C electrometer and recorded, simultaneously with the temperature of the sample, with a YEW 3083 XY recorder. The temperature was controlled by a Barber-Colman 520 controller.

We repeatedly performed dielectric measurements on several samples rather shortly after their preparation. The samples were chamomile extract prepared by exclusive use of de-ionized, double distilled water at room temperature (i.e., no alcohol was used at any stage of their preparation). The dilutions employed were 10^0 , 10^{-2} , 10^{-12} , 10^{-24} , and 10^{-60} .

The results of dielectric measurements were positive for all samples in the sense that a substantial percentage of bound water molecules was detected in all cases as shown in Figs 5 and 6, and discussed below.

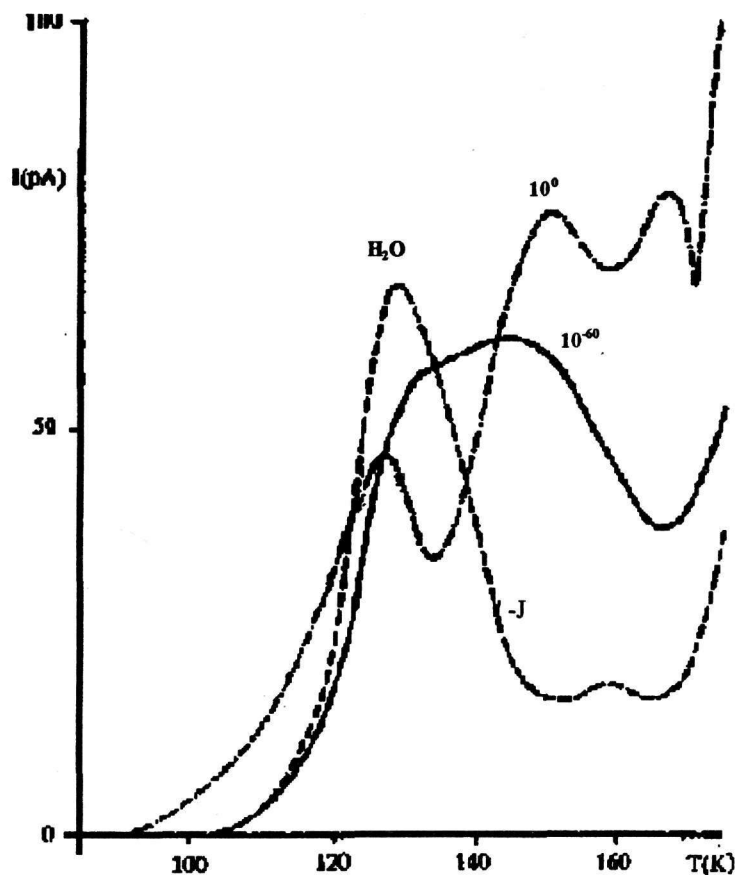


Figure 5: Dielectric measurements plots for chamomile-extract water solutions of 10^0 and 10^{-60} together with the reference plot for water.

Figure 5 presents three curves labelled H_2O , 10^0 and 10^{-60} . The H_2O curve stands for DTC measurements of pure water and its characteristic peak at about $130^\circ K$ is used as a reference for the other two curves and, in general, for any other curve derived from such measurements as, e.g., for those shown in Fig. 6.

The 10^0 curve in Fig. 5 stands for DTC measurements of the initial substance (here chamomile extract). It is noticeable that its peak at about $130^\circ C$ presenting unbound water (since its temperature about coincides with that of

the reference peak for unbound, pure water in curve labeled H_2O) is shorter (it corresponds to less pA) than the second peak (at about $150^\circ K$ presenting bound water (since it does not appear at all in the reference curve H_2O for unbound water). This difference in the height of the two peaks means that a greater percentage of water molecules are bound than unbound in the extract of the initial substance.

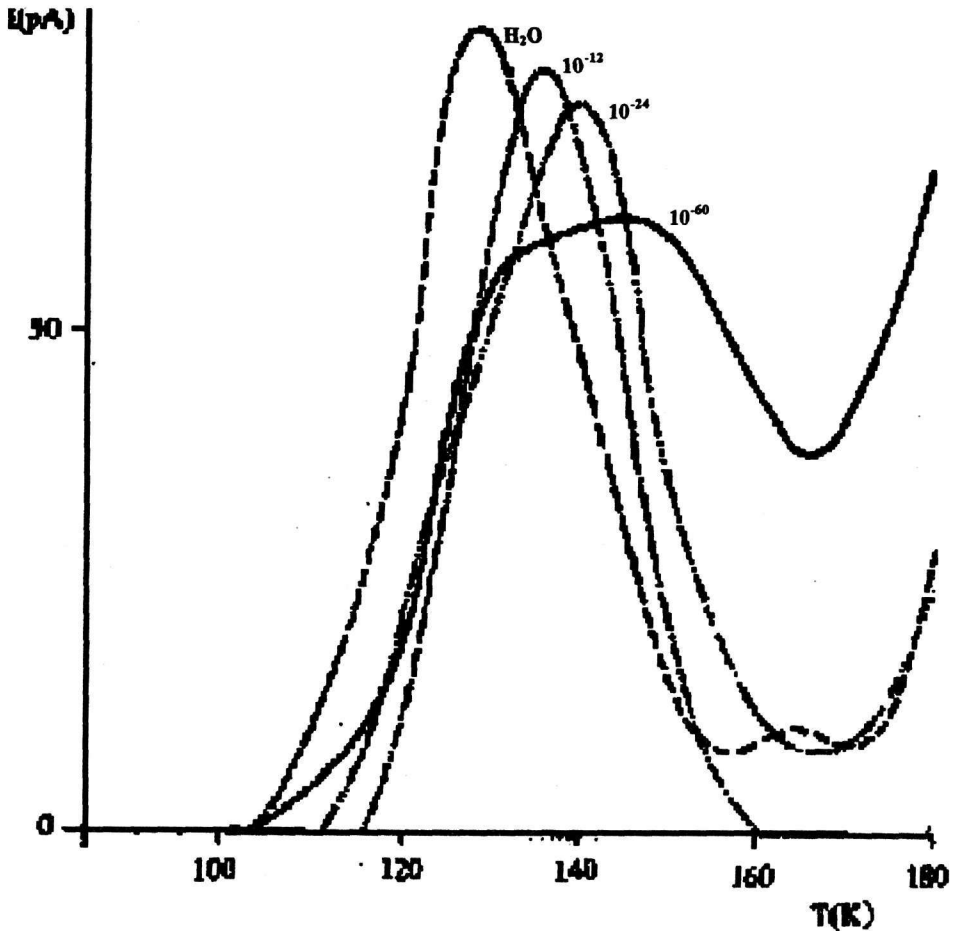


Figure 6: Dielectric measurements plots for chamomile-extract water solutions of 10^0 , 10^{-24} and 10^{-60} . Going from lower to higher dilutions, a shift of the plot to higher temperature is noticeable.

This, of course, is not surprising since in our dense chamomile extract many water molecules, e.g., in the form of clathrate hydrates are bound (i.e., they have restricted motion with respect to molecules far apart from "impurity" - chamomile origin - molecules).

The 10^{-60} curve stands for similar measurements of the homonymous dilution. Again, like in 10^0 curve, two peaks appear at about 130°K and 150°K . The first stands for unbound water and the second for bound water in slightly more advanced percentage. Additional peaks at different temperatures in all three parts of Fig. 5 are not meaningful for the present discussion. The basic meaning of Fig. 5 is that a large percentage of bound to free water molecules exist in the dense 100 solution, where they are many "impurity" molecules coming from chamomile, but also in the 10^{-60} solution where effectively there is not even one "impurity" molecule. This important conclusion is consistent with the predictions of the clathrate model, where the "impurity" molecule and the core clathrate can form new clathrates during the application of mechanical impulses in the solution.

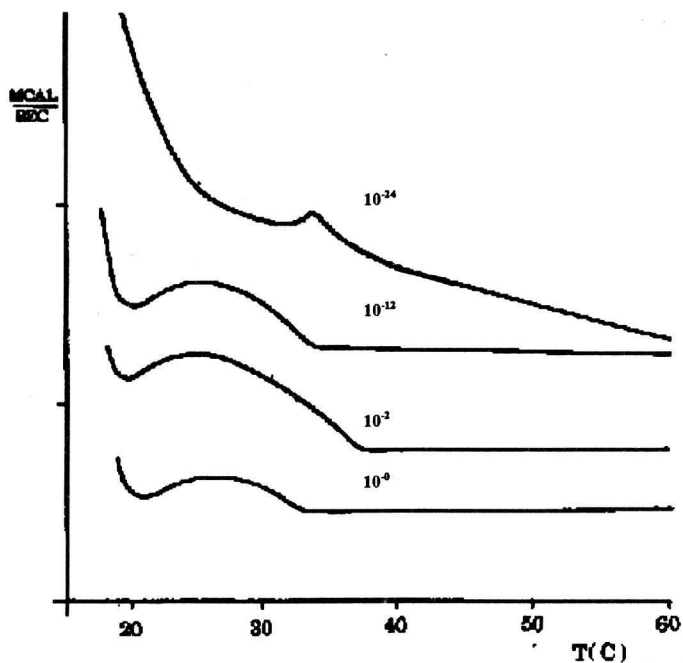


Figure 7: Differential Scanning Calorimetric plots for chamomile-extract water solutions of 10^0 , 10^{-2} , 10^{-12} , and 10^{-60} potencies.

Figure 6 presents also three curves labeled 10^{-12} , 10^{-24} , and 10^{-60} . Two main remarks could be drawn from this figure. The one is that the peak of bound water, relatively to the peak of free (unbound) water, is more pronounced for the lower dilutions in such a way that the free water peak hardly can be seen in the curve 10^{-12} . This could be thought of as related to the presence of molecules coming from chamomile which becomes more and more as we go to lower and lower dilutions. The presence of such molecules in lower dilutions seems that makes the creation of new water formation, during the application of forceful mechanical impulses, on each solution more and more efficient than

the absence of such molecules in more advanced dilutions. Of course, more and more water formations (e.g., in the form of clathrates) means more and more bound water molecules. The reason for observing bound water molecules in the dilutions 10^{-24} and 10^{-60} apparently has no relationship to molecules coming from the chamomile extract which, for these dilutions, are practically zero. The appearance of bound water in these dilutions, however, is explained by the clathrate model.

The second remark is that the peak of bound water shifts more and more to the right (i.e., to higher and higher temperature) as we go to more and more advanced dilutions. This could be attributed to the formation of stronger and stronger structure of water formations, made of bound water molecules for example in the form of clathrates, as we go to more and more advanced solutions. Such possibility is permissible in the framework of the clathrate model.

By assuming hydrophobic forces between water and molecules coming from chamomile, water molecules are bound among themselves via hydrogen bonds and form a filled clathrate around each chamomile molecule (like that presented by Fig. 4a-b2), which is energetically weaker than an empty clathrate formed by water molecules alone (like that presented by Fig. 4c2). This is reasonable, since the absence of hydrophobic forces in the case of an empty clathrate makes the corresponding structure more compact and thus stronger.

However, another possible reason for an increased stability of water formations in advanced dilutions is the presence of a huge number of clathrates in these solutions. Indeed, when the number of clathrates is substantial with respect to the number of free water molecules, extra hydrogen bonds may occur among the clathrates themselves. Such extra bonds increase the average stability of water formations. Indeed, such a prediction, according to the clathrate model, is consistent with the results of our dielectric measurements on advanced dilutions of chamomile extract.

Hence, all experimental findings coming from our dielectric measurements are consistent with the predictions of the clathrate model.

4.2 Differential Scanning Calorimetric Measurements

The differential scanning calorimetry (DSC) measures the amount of energy which is absorbed or released from a sample during its heating or cooling, or when the sample is maintained at a constant temperature [8]. Thus, any change of phase of a material can be studied in the temperature range from 77 °K to 900 °K. In the case of solutions, the heat of each dilution, its dependence from the temperature, the thermal capacity of solutions and their mixing entropy

can be calculated. The apparatus (of the Kapodistrian University of Athens) used in our experiments was a DSC-4 model of Perkin Elmer.

We have repeatedly performed differential scanning calorimetric measurements on the same samples with those used in dielectric measurements. That is, we used again chamomile extract of 10^0 , 10^{-2} , 10^{-12} , 10^{-24} , and 10^{-60} dilutions. The results of our DSC measurements were positive for all samples in the sense that a change of phase was observed in all cases (Fig. 7). This change of phase, according to the clathrate model, implies the destruction of the clathrate structures at about a certain temperature. It is noticeable that this temperature shows a small shift to more advanced values as we proceed from low to advanced dilutions. This shift reminds one of the similar shift observed in the dielectric measurements discussed above and, according to the clathrate model, has the same explanation.

By using the DSC technique the following two additional series of experiments were performed. The one was a repetition of the previous experiments on the same sequential dilutions of chamomile extract but without applying any mechanical impulse on any dilution. For all dilutions no detectable effect was observed. Thus, mechanical impulses are absolutely necessary for the appearance of a measurable physicochemical effect. Of course, up to 10^{-24} dilutions some molecules (and their clathrates) coming from the chamomile extract are present, but there are not enough of them for a sizeable (detectable) effect by the DSC technique. The mechanical impulses, according to the clathrate model, multiply the number of clathrates and make their effect detectable.

The other additional series of experiments was a repetition of the same experiments but using de-ionized, double distilled water as initial substance in the place of chamomile extract and applying again a number of mechanical impulses on each dilution. For all dilutions again no effect was observed. Thus, the presence of an initial substance for the preparation of a advanced dilution is essential, a fact which is also consistent with the predictions of the clathrate model, according to which the first (full) clathrates are formed round the molecules of the initial substance (see Fig. 1a-b2), which specifies the kind of clathrates. Without these starting clathrates no further clathrates can be formed.

Another series of DSC experiments was performed by employing methanol ($\text{CH}_3\text{-OH}$) as initial substance in the place of chamomile extract. All other parameters were kept the same as for the experiments described above. Again the results were positive with respect to the predictions of the clathrate model. That is, again a change of phase is observed at a certain temperature, where according to the model a destruction of the clathrate structures occurs (Fig. 8). However, it is not clear here if an upward shift of this characteristic temperature occurs by going from lower to more advanced dilutions, as it has

clearly been noticed in the chamomile DSC experiments.

What is important in this series of experiments is the difference, with respect to the chamomile experiments, in the characteristic temperature where we observe the change of phase. That is, while this temperature is about 24°C for the chamomile extract, it is about 52°C for the methanol. This difference in temperature constitutes a further justification of the clathrate model. Indeed, for a different initial substance, a different clathrate is expected which, in general, requires a different amount of heat in order to be destroyed. Since all masses involved in the experiment are kept constant (i.e., the same masses for the chamomile extract and for the methanol experiments), the different amount of heat necessary for the destruction of the different clathrates involved corresponds to different temperature.

In Fig. 8 we observe two instead of one peak for the 10^{-24} dilution. While many other explanations could exist, the following is a plausible one. That is, that the initial water formation (clathrate) is transformed during the procedure of preparation or of heating into two simpler (and thus probably thermally weaker) clathrate structures. Each of these two structures is sensitive at its own temperature.

Hence, all differential scanning calorimetric findings are consistent with the predictions of the clathrate model and also with the previous findings of dielectric measurements.

5 Conclusions

In the framework of the clathrate model for an understanding of water advanced dilutions, the formation of clathrate hydrates around the molecules of the initial substance in water is essential. In general, a specific clathrate hydrate is formed around each molecule of a given initial substance, which is different for each different substance. Substances which do not form such a structured water around them, according to the model, cannot form advanced dilutions as well. Also, in obtaining such dilutions the application of forceful mechanical impulses, e.g. via supersonic waves, on the dilution is absolutely necessary. Thus, both formation of clathrate-hydrates and mechanical impulses above a certain threshold of strength, characteristic of the specific substance, are required. Hence, in the clathrate model, an advanced dilution in water possesses a structure that of the relevant clathrate-hydrate.

All experiments performed so far either by applying Dielectric Measurements or Differential Scanning Calorimetric Measurements are in favor of the predictions of the Clathrate Model. It is the structure which makes the advanced

dilutions meaningful. That is, while these dilutions of a substance have identical chemical composition with that of the relevant solvent (here water), they have physically detectable properties, in addition to the properties of the solvent, revealable by following standard scientific methodology. This structure is due to the presence of clathrate-hydrates which are formed by permanent H_2O molecules and which thus constitute a sort of a third phase of water.

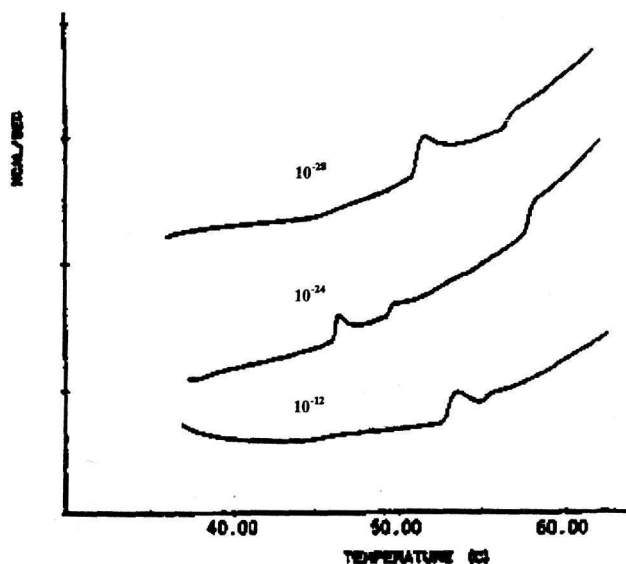


Figure 8: Differential Scanning Calorimetric plots for methanol ($\text{CH}_3\text{-OH}$) water solutions of 10^{-12} , 10^{-24} , and 10^{-28} dilutions.

However, despite the experimental successes described here, due to the very delicate character of the matter under investigation, we emphasize that many more series of experiments using different initial substances should be performed by employing the present and other experimental techniques before a final conclusion is drawn.

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