

## Fundamental considerations about liquid water

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**Abstract** - After consideration of the observable differentiations in liquid water and of the anomalies observed in supercooled water and in superheated water, an attempt is presented to rationalize all of the results. The contributions of the different "kinds" of water molecules, namely (i) those at the interface, (ii) those around the dissolved gas molecules, (iii) those around hydrophilic solutes and (iv) the so-called "normal" water molecules, are evaluated with regard to the existential requirements of the liquid, both in thermodynamic equilibrium and in metastable states. The concept of "supermolecular system organization" is applied to liquid water, and suggestions are made about the role of water in the supermolecular system organizations in non-aqueous solvents.

### INTRODUCTION

Most of the efforts in solution chemistry are based on the molecular concept and in the first place made in order to describe solvent effects on structure and properties of the dissolved species. Effects of the latter on structure and properties of the whole of the solution are usually neglected. For example, elementary electrostatic considerations are based on the "sphere in continuum model", and the changes of the medium are not considered by the concept of the donor number and of the acceptor number (ref. 1).

Attempts to describe structure and properties of a pure liquid are usually made by starting from those of its molecules, as may be illustrated by the following statement (ref. 2): "In order to interpret the properties of liquid water, we must understand the water molecule". This approach allows a limited knowledge for local structural changes without providing a real understanding of the continuous relationships. A fundamental difficulty is the fact that all structural data about liquid water refer to the so-called "diffusionally averaged structure", corresponding to averaged relaxation times of  $10^{-11}$  s. Thus, the actual differentiation of the molecules in the liquid remains disguised in the statistical data.

### EVIDENCE FOR DIFFERENTIATIONS IN LIQUID WATER

#### Limitations of the molecular approach

The molecular concept is indispensable for solving quantitative questions in chemistry but molecules have *molecular properties*, such as dipole moment, ionization potential, bond length, bond angle, whereas material systems have *sensually perceptible properties*, such as vapor pressure, strength, viscosity, density etc.

The bridge between molecular properties and material properties is provided by quantum mechanics. It describes in principle the whole universe as *one* charge density pattern, fluctuating in space and time. Chemists consider

the causes and the effects of the redistributions within certain areas of the charge density pattern. Rules have been formulated in terms familiar to the chemist on the basis of the extension of the donor-acceptor concept (ref. 1). It considers all molecules and all clusters as part of the whole of the extremely flexible and adaptable structural network (ref. 1).

Accordingly, *liquid water* may be considered as a huge "super-molecule", which is highly differentiated in itself. Any change at one point, for example by dissolution of a solute, leads to a certain rearrangement within the whole unit, and this means that each change has certain consequences for every part of the system, and not only in the immediate environment of the interaction. This is expressed by the *bond length variation rules* (ref. 1), according to which the dissolution of a hydrophilic solute leads to a contraction of the water structure in its environment (hydration shell) and at the interface.

In order to learn more about the differentiations of solutions, we shall first of all review the experimental evidence about the differences in properties of water molecules within liquid water and, in a second step, try to rationalize all of the facts with respect to the requirements for the existence of liquid water.

#### Molecules at and near the phase boundary of liquid water

The molecules at and near the phase boundary are in high states of tension (surface energy), under great strain (surface tension, bond contraction) (ref. 3,4), dynamically very active (vapor pressure, high amplitudes and high frequencies of their vibrations) and *not* in thermal equilibrium. The latter point may be illustrated by referring to the following experimental results: Water in 14 nm diameter silica pores is approximately 3% less dense than in the bulk water (ref. 5) and the heat capacity of liquid water in 24 nm diameter silica pores is considerably greater than that of bulk water (ref. 6) (Fig. 1). The surface tension of water condensed in a micropore of radius 20 nm is much lower than that of bulk water. Particularly interesting is the fact that water in extremely thin layers exhibits very low phase transition temperatures. Fig. 2 shows that a "bilayer" of water molecules appears to remain liquid down to  $-38^{\circ}\text{C}$  (ref. 7), i.e. it behaves like supercooled water (see later).

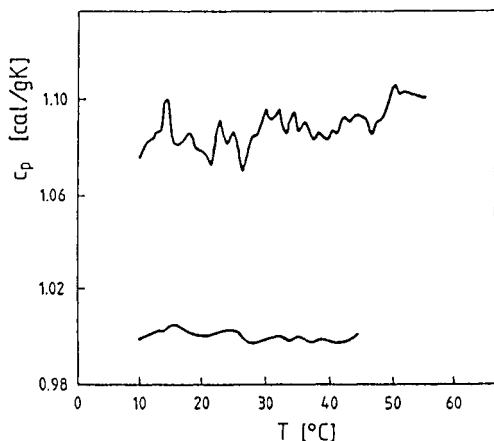


Fig. 1. Heat capacity of bulk water (lower curve) and water in 24 nm silica pores (upper curve) as a function of temperature (ref. 6).

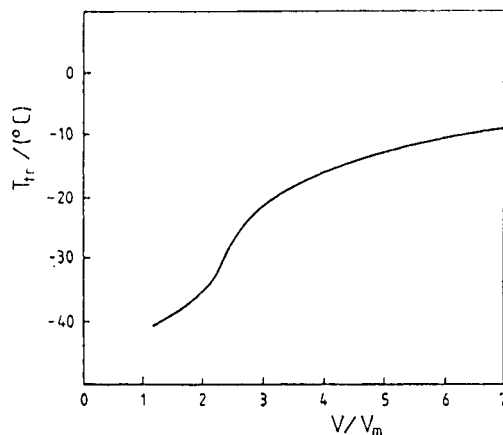


Fig. 2. Phase transition temperature  $T_{tr}$ , plotted against  $V/V_m$ . ( $V_m$  represents a monolayer capacity and  $V$  the adsorbed amount) (ref. 7).

The well-pronounced dynamic features at the interface allow both defensive and active missions towards the environment. They allow the liquid to respond specifically to all changes, while the main characteristics of the liquid are preserved, and this requires that the interface must be in continuous relationships with all other parts of the liquid (ref. 8).

### Water molecules around dissolved gas molecules

Whereas it is clear that a liquid could not exist without boundary areas, it is less obvious that the same applies to the presence of dissolved gas molecules. Although it is known that gases are usually dissolved more readily as the temperature is lowered, it is hardly anticipated that the liquid is to disappear when the gas concentration falls below a certain amount. For example, small water droplets in benzyl benzoate may be obtained at a temperature as high as 279°C, but they explode within a few seconds. They are stabilized, however, under pressure, as in this way the gas content is increased. Even from liquid alloys and molten salts the last traces of dissolved gases cannot be completely removed. These findings suggest that the *presence of dissolved gases is an essential requirement for the existence of a liquid* (ref. 9).

The oxygen and the nitrogen molecules dissolved in liquid water are found in holes which are much greater than required for their accommodation (ref. 10) and which provide freedom for their rotations. The  $c_p$ -values of the dissolved gases are even greater than in the gas phase (ref. 11). Some of the holes may be free from gas molecules. All of them are confined to "inner surfaces" at which the water molecules are more tightly bonded to each other than in the bulk (ref. 12), but the water structure as a whole appears to be loosened by the presence of such holes. The mutual interactions between the rotations or vibrations by the gas molecules and the oscillating water-network is seen from the fact that after dissolution of hydrophobic solutes the vibration spectrum of the solution resembles that of the original liquid at a lower temperature. The amplitudes of the vibration of the gas molecules are in continuous contact with the flexible and yet somewhat resistant "walls" of the voids, which may be considered as providing some kinds of boundary conditions for the motions of the gas molecules. By their oscillations the oscillating pattern of the liquid (solution) is influenced, which - at the same time - exerts an influence on the oscillations of the gas molecules. In this way a kind of "harmony" must be established between the oscillating pattern of the liquid and that of the dissolved gas molecules.

### Water molecules around hydrophilic solutes

Hydration structures have been studied in much detail, but little emphasis is usually paid to the fact that even pure liquid water is bound to contain a certain amount of hydrophilic solutes. Even after careful purification of liquid water, hydrated hydrogen ions and hydrated hydroxide ions are always present due to the self-ionization equilibrium. It may therefore be concluded that the *presence of hydrophilic solutes is a requirement for the existence of liquid water*.

Around a hydrophilic solute the water molecules are more tightly packed, the  $c_p$ -values of the solution smaller in the presence of such solutes, and the vibrational spectrum resembles that of "pure" water at a higher temperature. Structural informations from the solute are spread over the hydration shell, in which the static structural aspects are better developed than in the pure liquid. Since there is no borderline for the hydration shell, the information from the solutes reaches in principle every part of the liquid. Although this is not obvious from the structural data, observable changes are found at the interface: the concentration of the water structure within the immediate surrounding of the solute is reflected in (less pronounced) contractions of the water structure at the interface (ref. 8).

Such changes occur also at the inner surfaces of the holes, so that structural information from the hydrophilic solutes must be present at the inner boundary conditions for the oscillations of the dissolved gas molecules, which therefore contain structural informations from the hydrophilic solutes.

TABLE 1. Changes in solution properties by addition of hydrophilic and hydrophobic solutes (ref. 9)

Property	Hydrophilic Solute	Hydrophobic Solute
Surface tension	increased	decreased
Vapour pressure	decreased	increased
Density	increased	decreased
Specific heat	decreased	increased
Water structure	more dense	less dense
Particle movement	one-dimensional	rotation
Vibration spectra, correspond to those of pure water at	higher temperature	lower temperature
Actions on the static aspects of "water structure"	increasing	decreasing
Actions on the dynamic aspects of "water structure"	decreasing	increasing

Thus *hydrophilic and hydrophobic solutes have complementary functions not only for structure and properties of the whole liquid, but rather for its very existence*: the hydrophilic solutes provide more of the static aspects and the hydrophobic solutes more of the dynamic aspects of the information. We may say, that the solution structure is "shaped" by the specific interactions with the hydrophilic solutes present, and that all of their characteristic informations are provided both in the inner and in the outer surface areas. The oscillating properties of the dissolved gas molecules are readily adapted towards the given structural conditions; they are acting as a kind of "dynamically maintained points of inner rest" or "synchronization nodes" within the oscillating network of the liquid (ref. 13). The complementary effects of hydrophilic and hydrophobic solutes on the properties of the solution can be seen from table 1.

#### All other water molecules

The vast majority of water molecules appears less influenced by the external environment than the interface molecules and less influenced by the internal environment than the molecules around solutes. They are considered as "normal" or "bulk" molecules. Because of their overwhelming number, the statistical results of the liquid are mainly determined by their properties. This means that the differentiations within the liquid, even those which have been discussed so far, cannot be found in the statistical results of spectroscopic, structural, thermodynamic or kinetic investigations. In order to learn more about the different "kinds" of water molecules, we drew attention to the properties of liquid water at temperatures down to  $-44^{\circ}\text{C}$  ("supercooled water") and up to  $279^{\circ}\text{C}$  ("superheated water"). In these "metastable" states a number of *anomalies* has been found, which may be briefly summarized in the following section.

#### "Anomalies" in supercooled water

Supercooled water is obtained in capillary tubes (ref. 14,15), in emulsions (ref. 13,14) and in the cloud chamber (ref. 16,17). The liquid range is extended to lower temperatures, the smaller the diameter of the capillary tube (ref. 18) and the smaller the droplets in emulsions (ref. 9,14) or in the cloud chamber (ref. 17). The liquid range is greater, the higher the purity of water (ref. 19) and the greater the hydrophobicity of the immediate environment (ref. 20). The lowest temperature that has ever been reported for supercooled water is  $-44^{\circ}\text{C}$  in the cloud chamber, with droplet diameters below  $1\ \mu\text{m}$  (ref. 16,17).

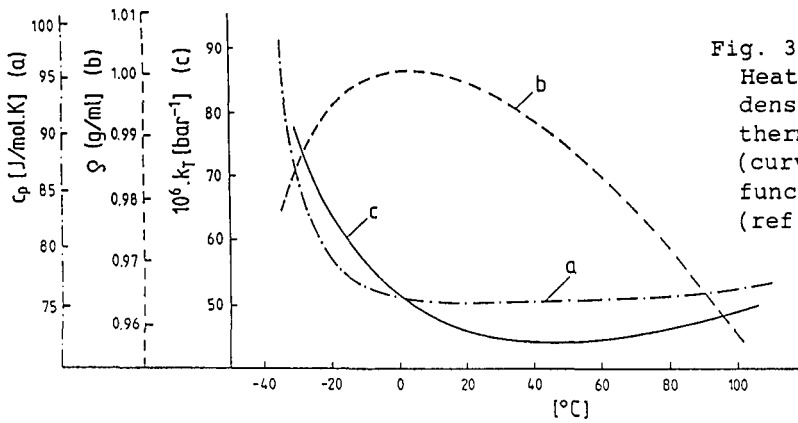


Fig. 3.

Heat capacity (curve a), density (curve b) and isothermal compressibility (curve c) of water as a function of the temperature (ref. 13).

The molar heat capacity of liquid water - which shows a minimum value at  $+37,5^{\circ}\text{C}$  - is dramatically increased as the temperature is lowered. At  $-35^{\circ}\text{C}$  it is found to be by 35% higher than at  $+100^{\circ}\text{C}$  (ref. 14) (Fig. 3, curve a). The density is decreased in supercooled water as the temperature is increased. At  $-34^{\circ}\text{C}$  the density has the same value as at  $+70^{\circ}\text{C}$  (ref. 21, curve b). The isothermal compressibility is greater the lower the temperature and at  $-26^{\circ}\text{C}$  found to be by 45% higher than at  $+100^{\circ}\text{C}$  (ref. 22) (Fig. 3, curve c). The concentration of dissolved gases is drastically increased as the temperature is lowered (ref. 23) (Fig. 4). The increase in gas concentration at lower temperature is paralleled by increasing  $c_p$ -values, decrease in density and by increase in isothermal compressibility.

The free energy of supercooled water is higher than that of ice and the free energy differences between them become greater the lower the temperature. The differences of the free energies between ice and water in emulsions  $\Delta G_{em}$  and in capillaries  $\Delta G_{cap}$  are greatest between  $-20^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$ . At a given temperature the entropy difference of water in emulsions and in ice  $\Delta S_{em}$  is greater than that of water in capillaries and ice  $\Delta S_{cap}$ ; the differences  $\Delta S_{em} - \Delta S_{cap}$  are greatest in the temperature range between  $-20^{\circ}\text{C}$  and  $-30^{\circ}\text{C}$  (ref. 13).

#### "Anomalies" in superheated water

Highly purified water may be superheated in capillaries up to  $240^{\circ}\text{C}$  (ref. 24) or in small drops in a hydrophobic liquid, such as benzyl benzoate up to  $279^{\circ}\text{C}$  (ref. 25). Under these limiting conditions the droplets explode within a few seconds (ref. 26). The liquid range is extended to higher temperatures as the system is subjected to an external pressure, and this may be regarded as due to the presence of dissolved gases; as the temperature is increased, the gas content is lowered, but as the pressure is increased, the gas content is increased.

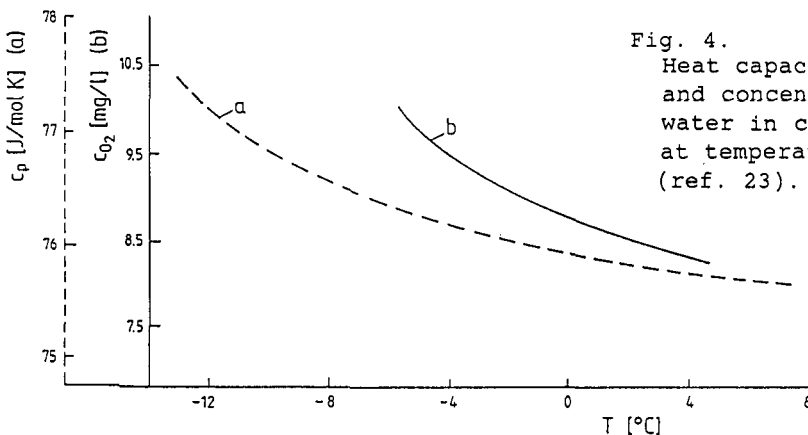


Fig. 4.

Heat capacity of water (curve a) and concentration of oxygen in water in capillaries (curve b) at temperatures below  $0^{\circ}\text{C}$  (ref. 23).

## RATIONALIZATION OF THE FACTS

### The question of "supermolecular" system organizations

Both supercooled and superheated water are *in metastable states*. In order to obtain and to preserve supercooled water, some kind of mechanism must be in operation that forces all of the water molecules to have more developed dynamic properties than in ice. In order to obtain and to preserve superheated water, some kind of "mechanism" must operate by which the dynamic properties of the water molecules are lower than in the gas phase.

Because each system acts as one unity, Bohm (ref. 27) has suggested to start the investigation from the whole and not from the parts and to look for the "implicate order". Because the implicate order, i.e. the continuous relationships between the parts within the whole is not directly observable, we suggest to start again from the observable parts, but to pay full attention to all changes due to changes in boundary conditions.

The continuous relationships between the parts within the whole have been expressed (for living systems) by Weiss (ref. 28) as follows: "We have to conclude, therefore, that a patterned structure of the dynamics of the system as a whole coordinates the activities of the constituents. Since any movement or other change of any part of the system deforms the structure of the whole complex, the fact that the system as a whole tends to retain its integral configuration implies that every change of any part affects the interactions among the rest of the population in such a way as to yield a net countervailing resultant; and this for every single part. Couched in anthropomorphic language, this would signify that *at all times every part "knows" the stations and activities of every other part and "responds" to any excursions and disturbances of the collective equilibrium, as if it also "knew" just precisely how best to maintain the integrity of the whole system in concert with the other constituents.*"

These activities of the parts require that they have different properties and different "abilities". A part that has additional properties or abilities is superior to a part devoid of such properties or abilities. This means that superordinations and subordinations must be present, as they are characteristic for a so-called "hierarchic order" or "system organization" (ref. 13). Because in a liquid the molecules serve the supermolecular system, we may refer to the organization of a liquid as "*supermolecular system organization*".

At this point it may be emphasized that the term "*hierarchy*" is frequently met with scepticism, simply because of the obvious faults of such hierarchies, which have been artificially established by man, and which are executed by man. Such faults are, however, not due to hierarchy itself, but rather consequences of faultily designed and not properly executed orders by man. For this reason, we shall not follow immediately synergetics (ref. 29), because in this approach relationships are artificially constructed from the properties of the parts.

In order to illustrate this point, we may consider a computer, which is a system constructed and operated by man. It serves a certain purpose (determined by man), and this is fulfilled by means of a program, the so-called *software*, which is also determined by man. Neither purpose nor software can be directly observed, but knowledge about them may be obtained from those who constructed the system or who have been instructed by them. The conductance of the program requires certain static boundary conditions, the so-called *hardware*, and this may be investigated more directly. In a simplified way, the main hierarchical features are illustrated in Fig. 5.

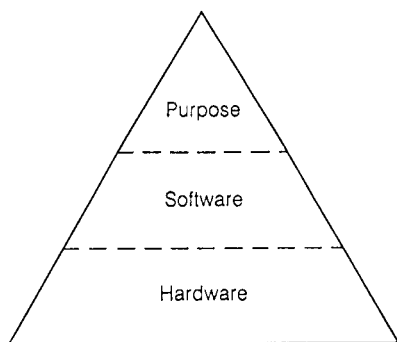


Fig. 5. Illustration of the main elements of the system organization of a computer (in fact the hierarchic levels indicated in this illustration show further differentiations).

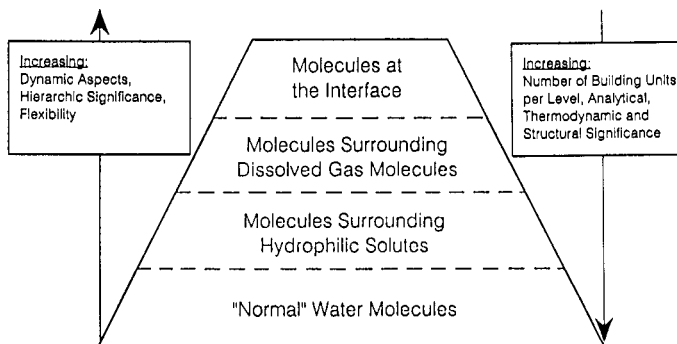


Fig. 6. Illustration of the system organization of liquid water (ref. 13).

Just as a computer cannot be understood from the consideration of its hardware alone, a natural object cannot be fully understood from the consideration of its structural, thermodynamic and kinetic properties, because, like in a computer, in each natural system an operating device, a kind of software, of dynamically ordered relations must be in operation.

As these relations cannot be directly observed, one feels reminded of the following words of Robert Louis Stevenson (ref. 30):

"Who has seen the wind?  
Neither you nor I.  
But when the trees bow down their heads  
The wind is passing by...."

In order to overcome the fundamental difficulty of the *unobservability and immeasurability of the system organization*, we suggested to introduce (artificially) discontinuities by means of abstractions (ref. 3). Such "*hierarchic levels*" do not exist as entities themselves, but rather as parts of the whole within the whole, and hence they cannot be really separated from each other. They are chosen as tools in the course of the investigation and chosen in such ways as to express certain differences in dominance between different "groups" of molecules.

#### System organization of liquid water

We have suggested (ref. 3,9,13) to consider each of the four groups of water molecules as one of the hierarchic levels. Their arrangement according to their specific significance for the whole of the liquid is illustrated by means of a truncated pyramid shown in Fig. 6.

In rationalizing all of the facts discussed so far, the molecules at the interface have been appropriated a prime position (ref. 3,9,13). They provide the first line of defense of the system, they show greatest resistance and greatest adaptabilities towards changes, and they appear to provide a kind of primitive "memory" to previous conditions. Because the interface "belongs" to two phases, and because the interface is dynamically maintained by the continuous interactions between the two phases, it is bound to be in a state of tension. The highly developed dynamic actions of the molecules at the interface have decisive effects on all of the other molecules, which appear to be under a certain "control" by them. For these reasons the interface molecules are considered as serving the highest hierarchic level of liquid water (that is observable).

Immediately subordinated to this level appears that of the dissolved gas molecules and the water molecules surrounding them. A kind of "synchronization" must be established between the oscillating pattern of the liquid solution structure and the motions of the gas molecules, which appear to act as a kind of "relais", by which certain weak actions are amplified and certain strong actions distributed over the whole system. In these ways the regions around the gas molecules help to regulate and to control the structural and dynamic features of all other molecules.

The molecules around hydrophilic solutes are dynamically less active, but responsible for the static structural aspects of the liquid. They appear subordinated to the regions around the gas molecules, but superordinated to the so-called "normal" water molecules. The latter are under the influence of the forces of all of the higher levels. Because this level provides the more static boundary conditions for the higher levels, it has a certain "guiding" influence on them. This means that the lowest level is under control of the higher levels, but it is neither "exploited" nor "enslaved" by them. Instead it appears to be "respected" and used by the higher levels according to their specific roles. Most of the properties of liquid water can be accounted for by consideration of the lowest level, because it contains the statistical and hence quantitative informations, but it is not independent, as it is under the influence of the higher levels, which appear to "sweep" like a network over it.

#### **System organization in supercooled water**

Based on these considerations we are in a position to gain a new understanding for the conditions which are necessary in order to obtain supercooled water. The enormous increase in the number of interface molecules provides for an increase in differentiation in the highest level and for an appropriate gain in energy within the extended framework of interface molecules. At the same time the increase in concentration of dissolved gases provides an increase in differentiation in the level that is immediately subordinated to the highest hierarchic level. Because of the dominating actions of the forces in the highest levels on the molecules of the subordinated levels, the dynamic features of all of the molecules of the liquid are improved to that extent that the system is prevented from solidification (ref. 13).

The dynamical informations from the highest levels are adequately passed on to the lower levels, as long as no interference is taking place. In the presence of other hydrophilic solutes, however, interactions are taking place, which hinder the normal solvent molecules from taking over the complete information from the highest levels. For this reason water should be as free as possible from hydrophilic solutes, i.e. the differentiation in the lower levels should be as small as possible.

In other words: *The system organization is improved as the informations from the higher levels can reach the lowest level as undisturbed as possible, i.e. as the higher levels become more differentiated and the differentiations at the lower levels remain as small as possible (ref. 13).*

#### **System organization in superheated water**

The preservation of the liquid state at high temperatures requires a decrease in the dynamic properties of all molecules. The highest level is again drastically differentiated, but its subordinate level is lowered in differentiation, because of the decrease in concentration of gases. In this way the molecules in the lowest level fulfil the conditions for the liquid state rather than those for the gaseous state. Because of the preserving actions of the level of the dissolved gases, a certain minimum differentiation is, however, required in this level. All informations from the higher levels can reach the lowest level as unperturbed as possible, if the concentration of hydrophilic solutes is as low as possible.



Whereas for the existence of supercooled water, both of the higher hierarchic levels are considerably improved in differentiation, the existence of superheated water requires a high differentiation only in the highest hierarchic level and low differentiation in all subordinated levels.

### System organization in non-aqueous solutions

The term "non-aqueous solutions" is frequently interpreted as "water-free solutions". However, the last traces of water have never been removed from a non-aqueous solvent. For this reason the term "non-aqueous solution" refers actually to a solution that is different from water and that contains at least trace amounts of water. Even after careful dehydration the water content can frequently be determined by Karl Fischer titration. Although, in some cases, the water content is below the sensitivity of this method, water is always present in the ppm region. It may therefore be of interest, in what ways these small amounts of water are integrated in the organization of the system under consideration. In addition, the presence of dissolved gas molecules in non-aqueous solvents is just as unavoidable as in liquid water (ref. 11).

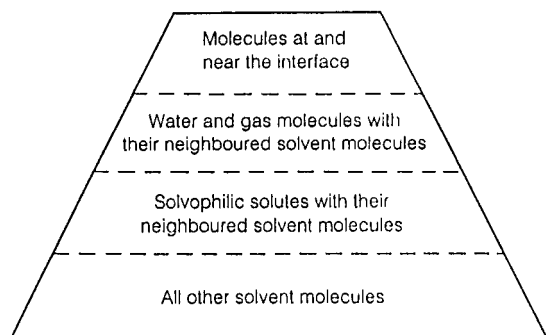


Fig. 7. Illustration of the system organization of a hydrophobic solvent, such as benzene.

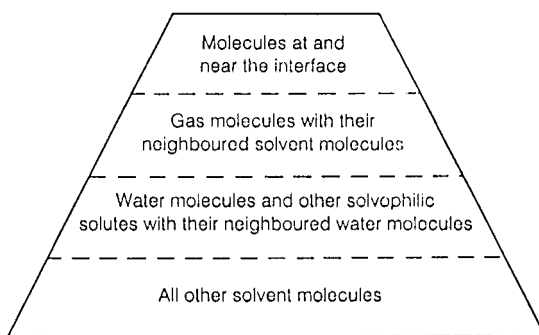


Fig. 8. Illustration of the system organization of a hydrophilic solvent, such as ethanol.

The role of the molecules in the highest hierarchic levels of water, i.e. that of the interface molecules and that of the surrounding dissolved gas molecules may be analogous to that in aqueous solutions. With regard to the role of the dissolved water molecules, more experimental evidence is required. In its absence it may be suggested that their contributions to the system organization may depend on the nature of the specific solvent-water interactions. In a hydrophobic solvent, such as benzene, the water molecules may be expected to act on the level of the dissolved gas molecules and hence on that immediately subordinated to the interface molecules. On the other hand, in a hydrophilic solvent, such as ethanol, one would expect a contraction of the solvent molecules due to strong donor-acceptor interactions (with formation of a solvation shell) and hence an improvement of the static structural aspects of the solution. In this case, the water molecules and the solvent molecules surrounding them may be considered as acting on a level that is subordinated to that of the dissolved gas molecules and their surrounding water molecules.

Such expected differences in the hierarchic significance of water in hydrophobic and in hydrophilic solvents may be formulated as follows: The smaller the solubility of water, because of weak water-solvent interactions, the greater is the stabilizing effect of water and hence the greater its significance for the existence of the liquid under consideration.

### CONCLUDING REMARKS

Each observable system appears to be subject to a system organization (ref. 31). The organization of a given system is improved, as the equilibrium system is moved into a state of metastability, and hence this approach may contribute to an understanding of metastable systems.

The author is well aware of the difficulties involved in following this approach, because it is based on a substantial change in philosophical attitude, the discussion of which is, however, outside the scope of this lecture (ref. 32,33) and possibly not of interest to many scientists.

### Acknowledgement

The development of this approach would have been impossible without the initiative by Dr. Gerhard RESCH. Sincere thanks are due to Dr. Edwin SCHEIBER for his help in developing this view and for the precise measurements of the gas concentration in supercooled water in capillaries and to Christiana KUTTENBERG for her valuable help in literature studies.

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