

Water in Heterogeneous Matter

Interfacial Water—from Non-organic to Organic Systems

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Abstract— Water is the universal solvent of nature. Does this imply, however, that its interaction with its environment is also universal in its character? We present evidence that the broadening of the dielectric spectra of water presents universal features of dipolar interactions with different types of matrixes. The state of water adsorbed in heterogeneous materials is determined by various hydration centers of the inhomogeneous material (the matrix) and it is significantly different from the bulk. In both cases, the dielectric spectrum of water is symmetrical and can be described by the Cole–Cole (CC) function. The phenomenological model that describes a physical mechanism of the dipole–matrix interaction in complex systems underlying the CC behavior has been applied to water adsorbed in porous glasses, clays and hydrated proteins.

Keywords — water, ice, dielectric properties, Cole – Cole Function, heterogeneous materials

I. INTRODUCTION

Water is of fundamental importance for all life and plays a critical role in many biological and chemical systems. Any organism can behave and function only if its macromolecules are hydrated, while the properties of minerals and chemical compounds can be sensitively determined by their water content. Even water itself is highly complex system (CS), because it possesses strongly polar hydrogen bonds that are responsible for a striking set of anomalous physical and chemical properties [1, 2]. Just how these same molecular properties translate into water's ability to solvate and interact with macromolecules is a hotly debated topic; Even more so how, in turn, macromolecular interfaces and interactions affect water's structure and properties?

In general, associating systems, like liquids, polymers, and glasses, form dynamic short-lived mesoscopic structures, e.g., clusters. These combine in macroscopic networks that exhibit cooperative effects. Clusters that involve water molecules are formed due to hydrogen bonds. This hydrogen bond network, its fluctuations and the dynamics of its rearrangement, determine the properties of soft matter materials containing water. The hierarchy and scaling of molecular motion in such H-bonded systems, as biomolecules in an aqueous environment, are even more complex [3, 4]. The properties of the H-bonded networks in associated systems, including

formation of an infinite (spanning) network, are directly related to three problems: i) influence of spanning and non-spanning H-bonded networks on the properties of aqueous solutions; ii) relation between percolation transition and thermodynamic phase transition and iii) crucial role of a spanning network of hydration water in biological activity [5].

For frequencies up to 40 GHz the complex permittivity spectra of bulk water can be described by the Debye function [6, 7]

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon_l + \frac{\Delta\varepsilon}{1 + i\omega\tau_D} \quad (1)$$

where ε' is the real component and ε'' the imaginary component of the complex dielectric permittivity, τ_D is the relaxation time, $t^2 = -1$, $\omega = 2\pi\nu$, ν is the frequency and $\Delta\varepsilon = \varepsilon_l - \varepsilon_h$ is the dielectric strength, with ε_l and ε_h denoting the extrapolated low-frequency and high-frequency permittivity limits, respectively. The Debye character of the dispersion corresponds to a single exponential dipole autocorrelation function of the polarization process. However, the single relaxation time τ_D of the Debye process is not related to the simple rotational diffusion of one water molecule in a viscous media [8], even though accounting for it can predict with reasonable accuracy the hydrodynamic radius of the water molecule. However, the simple cumulative effect of many water molecules independently undergoing continuous rotational diffusion (CRD) cannot account for water's strong dielectric response [8, 9]. A preferable model [8, 10, 11] depicts the dielectric response as a consequence of an apparent dipole moment of the water cluster. It is the cumulative reaction of these apparent moments, rather than the reorientation of uncoordinated water molecules, that leads to the large dielectric response of bulk water and the validity of (1) [6, 7, 10].

Whenever water interacts with another dipolar or charged entity, a symmetrical broadening of its dielectric loss peak of main dispersion of the solvent occurs [12-14]. In different complex systems, water can be considered as the dipole subsystem, while the other components may be defined as a matrix. The morphology, dynamics, and the dielectric properties of matrixes (porous materials, ionic and no-ionic

aqueous solutions) are essentially different from the properties of water [4].

The broadening of water dispersion in different complex systems can be described by the phenomenological Cole-Cole (CC) function [15]:

$$\varepsilon^*(\omega) = \varepsilon_h + \frac{\Delta\epsilon}{1 + (i\omega\tau)^\alpha}, \quad (2)$$

where parameter α is an empirical exponent describing the broadening of the loss peak. Below we will discuss dielectric spectrum broadening of water at the interface in non-organic and organic heterogynous materials.

II. WATER IN POROUS MATERIALS

A. Water in porous glasses and clays

The above approach was used for water absorbed on the inner pore surface of the porous silica glasses [12]. The complex dielectric behavior of such systems can be described in terms of four relaxation processes [16]. Here, we will consider only the first CC process, observed at temperatures from -100 °C to +10 °C. It was assigned to the dielectric response of ice-like water cluster structures. The activation energies of this process are dependent on the water content, the microstructure of the pore surface and the amount of the silica gel inside the pores. We will briefly review the application of a 3D trajectory approach to porous silica glasses labeled in [16] as A, B, C, D, I, II, III.

TABLE 1. THE PARAMETERS OF POROUS SILICA GLASS SAMPLES *A*, *B*, *C*, *D*, *I*, *II*, *III* [16]. HERE *d* IS THE AVERAGE PORE DIAMETER, *h* IS THE HUMIDITY AND ΔE IS THE ENERGY OF ACTIVATION FOR THE FIRST DIELECTRIC PROCESS.

Sample	<i>d</i> (nm)	<i>h</i> (%)	ΔE (kJ/mol)
<i>A</i>	50-70	1.2	50
<i>B</i>	50-70	1.4	42
<i>C</i>	280-400	3.2	67
<i>D</i>	300	1.6	19
<i>I</i>	20	3.6	64
<i>II</i>	88	0.63	36
<i>III</i>	70-100	3.39	61

A 3D approach considers the parameters of equation (2) as a description of a quasi-thermodynamic state of the active component of the material giving rise to the dielectric process. As the temperature is varied these same parameters trace out a trajectory that describes the evolution of the response. The state is described by $\ln(\tau)$, by α and by the Froehlich *B* function [14], that depends on ΔE . An extremum in this trajectory indicates changes in the underlying state of the relaxing dipole. The 3D trajectories for the water rich sample **I** and the water poor sample **II** are shown in Fig. 1. In contrast to glasses **C** and **D** [12], the glasses **I** and **II** are essentially different not only by their fabrication [16], but also by their porous size, water content and activation energy ΔE (see Table

1). In the case of the water rich sample **I**, a pronounced extremum is observed in two projections: XY ($\ln B / \ln \tau$) and XZ ($\ln B / \alpha$). This extremum corresponds to a specific temperature and reflects the transition of the dipole system orientation. For the water poor sample **II**, this transition is observed at a much higher temperature (see Fig. 1b). In general, for a temperature driven dielectric relaxation the non-monotonic dependence of *B* versus *T* was qualitatively interpreted by Froehlich [14]. An increase in *B* with *T* reflects a tendency of the dipole moments to anti-parallel orientation, while a decrease of *B* with *T* reflects an increasing tendency towards parallel orientation.

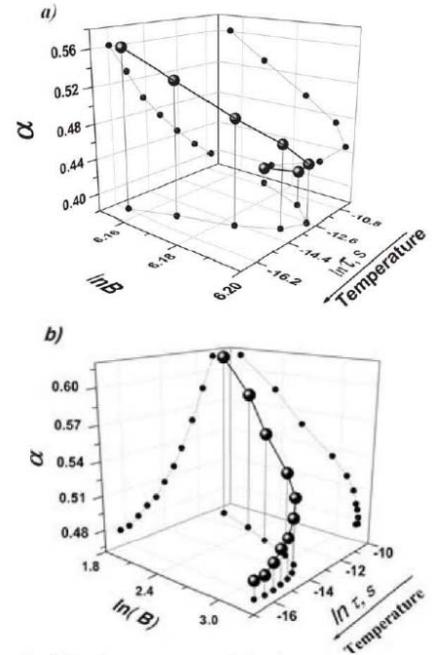


Fig. 1, Trajectories in 3D phase space of the low temperature CC relaxation processes for water confined in the porous silica glasses: (a) -sample I and (b) - sample II.

The results and the discussion of this transition for all the glasses are given in details in [13]. In particular they highlight a noted difference in the nature of the relaxation depending on whether it is a water rich or water poor sample [14].

The similar dielectric response can be observed from water absorbed on the inner pore surface of two types of natural layered aluminosilicates with exchangeable cations, montmorillonite (K^+ , Co^{2+} and Ni^{2+}) and kaolinite (K^+ and Ba^{2+}) [17]. As in the porous borosilicate glasses, the complex dielectric behavior of clay materials could be described in terms of four relaxation processes. However, due to the exchangeable cations at low temperatures (-121°C to -75°C) the spectra of montmorillonites consist of two relaxation processes marked I.1 and I.2 correspondingly (See Figure 2). Both these processes are characterized by a CC relaxation and exhibit a strong temperature dependence. In contrast, in the kaolinite samples when measured with the same protocol, the low temperature process I is not observed.

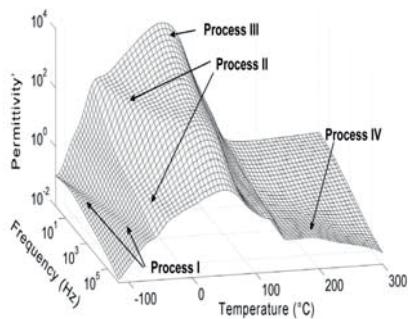


Fig. 2, 3D plots of the frequency and temperature dependences of the dielectric losses for montmorillonite Ni. (Reproduced with permission from [17] Copyright 2014, Geoscience).

This process can be associated with the relaxations of interlayer water molecules, which are absent in kaolinites [17]. In montmorillonites the water molecules responsible for the low temperature relaxations are located near the inner hydrophilic centers of interlayer channels (siloxane bonds and trapped cations) and around the interlayer cations [17]. This is reflected by the formation of two types of structure in the low temperature region. The slower relaxation process I.1 almost coincides with the low temperature relaxation behavior of water adsorbed in porous silica glasses [16] (See Figure 3). The activation energy values of this process for montmorillonite samples are in the same range as that reported earlier for the porous glass materials [16].

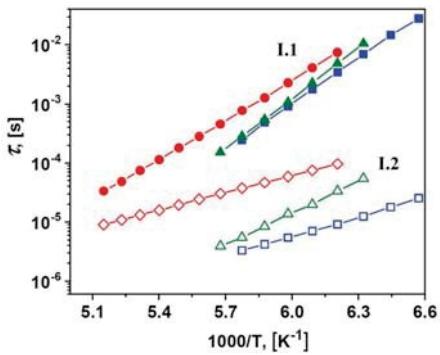


Fig. 3, The temperature dependences of the relaxation times of the low temperature processes for the montmorillonites (-♦- K -○- ; -■- Co -□- ; -▲- Ni -Δ-). Filled symbols correspond to the I.1 process; open symbols are related to the I.2 process. (Reproduced with permission from [17] Copyright 2014, Geoscience).

Therefore, it was assumed that the I.1 relaxation process corresponds to ice-like water structures formed on the interior surface of interlayer channels. The second, faster relaxation process I.2 reflects the water structures near the hydrated cations located in the interlayer channels. Thus, it means that the nature of the hydration center plays an important role in the dynamics of adsorbed water in inorganic materials. Note, that the type I.2 process was not observed in the glass materials [17]. There is only one type of hydration center in these materials. In both processes (I.1 and I.2) the activation energy depends on the type of interlayer cations present in the structure of the clay mineral and on the water content. The

detailed dielectric investigation of the hydrated clusters formation and their structures as a function of the exchangeable cations and water content in the montmorillonites is an open question for continued research.

B. Water in Hydrated Proteins

For the dielectric spectra to be directly sensitive to the hydration shell, the system must be quenched or placed in a regime of tight confinement. In this case, water can be considered as a dipole sub-system, while other components may be defined as a matrix [14]. The morphology, dynamics and the dielectric properties of the matrixes will have an influence on the nature of the relaxation of hydrated water, due to the dynamic interaction between it and the hydration centers (for instance, hydrophilic groups on the protein's surface) of the matrix. It is worth noting, that with inorganic structures such as clays, carbon nanotubes and so on, water does not significantly influence the structure of the underlying matrix. However, the same cannot be stated for protein powders. In this case, the structure of the protein particles is strongly altered by the presence of water. In turn, the modified structure leads to a modified water dynamic. The study of this mutual interaction of water and protein matrix is one of the important questions of protein dynamics.

A step in this direction has already been taken, with a recent study of hydrated Lysozyme powders [18, 19]. One result of this paper was the identification of a low temperature process related to hydration water that showed a strong dependence on the hydration level of the powder (see Fig. 4a) [18, 20]. The temperature behavior of its characteristic relaxation time is shown in Figure 4b as an Arrhenius plot.

There exists a marked change in behavior – a crossover – around 180 K -190 K [18, 19]. This crossover is strongly dependent on the humidity level of the powder and disappears for low humidity. A similar crossover was revealed in other globular hydrated proteins [21]. Currently it is agreed that the physical nature of these observations is related to a broad glass transition in a particular temperature range [19, 22, 23]. However, its origin is not yet clear and remains a subject of active discussion [23]. It is worth noting that a similar crossover was observed also in hydrated inorganic materials (such as silica, clay, etc.) [21]. In these materials, it was linked to water confined to pores or cavities. Such pores are frequently found in protein powders as well, for instance Lysozyme. Polar groups located on the surface inside the cavity of Lysozymes act as hydration centers for water adsorption [19, 24, 25] (see Fig. 5).

In these materials, it was linked to water confined to pores or cavities. At a high hydration level, the pores/cavity are filled with water to the extent that there is enough water to create ice particles. However, the conditions of strong confinement lead to a suppression of water crystallization, in accordance with the Gibbs-Thompson law [26, 27]. Recently we have proposed a scenario, where the origin of this dynamic crossover was assigned to the phase transition of the confined water only [19].

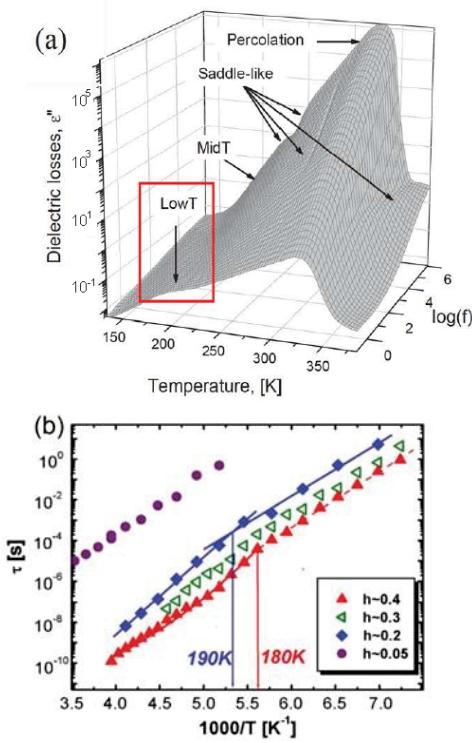


Fig. 4, a) Dielectric losses of hydrated lysozyme powder ($h = 0.28$) vs temperature and frequency. The red rectangle denotes the process (Low T) related to hydration water; b) Arrhenius behavior of relaxation time of the main process in hydrated lysozyme at different hydration levels. Arrows indicate inflection points.

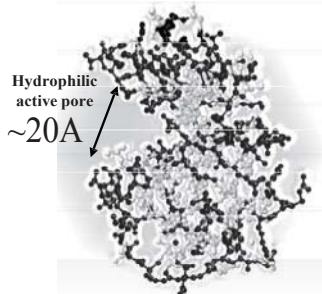


Fig. 5, 3D structure of lysozyme with active center inside the pore. The pore is the preferred location for water molecules.

In summary, water at an interface will lead to dielectric relaxation having a universal character. While the microscopic explanation is dependent on the solute and its condition, the Cole-Cole macroscopic relaxation behavior is independent. The application of a 3D trajectory approach was shown to be effective in unlocking the microscopic mysteries of this macroscopic dielectric behavior.

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