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LETTER TO THE EDITOR

The connectivity of water in hydrophilic confinements of different dimensionality

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Abstract. Recently it was observed that the viscosity of water is dramatically enhanced in various hydrophilic confinements such as lipid bilayers and micelles of microemulsions. Now computer simulations of the hydrogen bond connectivity based on a percolation model demonstrate that this effect exists up to characteristic dimensions of some 10 nm. This theoretical result is in fact in agreement with the experimental data and predicts similar influences on water confined in ultranarrow capillaries.

In this letter we present experimental and theoretical data of the properties of water near hydrophilic surfaces, i.e. between lipid bilayers and in microemulsions. It is both amusing and fascinating that the anomalously high viscosity claimed for the speculative polywater in ultranarrow capillaries [1] has been rediscovered for water near hydrophilic surfaces in lipid bilayer systems as well as in micelles of surfactants in microemulsions [2-5]. Now computer simulations have confirmed the experimental findings for the first time and simulations have also been performed for water in ultranarrow capillaries, a system not readily verified by experiment. One- and three-dimensional confinements of water can easily be designed with the aid of amphiphilic molecules that form self-organising structures like the sandwich structures of lipid bilayers and microemulsions. However, glass capillaries only 10 nm in diameter cannot be supplied.

Dynamics and structure of membranes are governed by the water in the vicinity of the amphiphilic lipid molecules [2]. It was found that only up to a well defined number are water molecules built in between adjacent lipid bilayers, corresponding to a one-dimensional confinement. This inter- and intrabilayer water, usually called 'bound water', differs greatly from bulk water in its chemical potential and viscosity [2, 3]. The dynamic viscosity of water follows from the dielectric response at microwave frequencies which directly probe the dipole relaxation time of the water molecules. The viscosity η is displayed in figure 1 for water bound (stored) between two adjacent lipid bilayers. The presented values are measured with DMPC[†] model membranes. As a general result, the average viscosity of water increases drastically with decreasing amount of interbilayer water, i.e. the water near the lipid surface is much more viscous than bulk water.

[†] DMPC = di-myristoyl-phosphatidyl-choline.

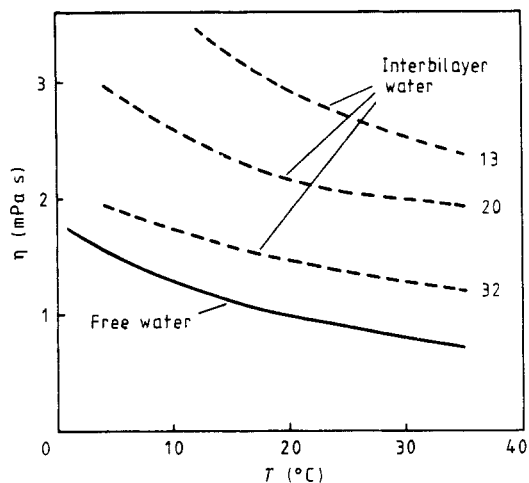


Figure 1. Viscosity η of water bound between DMPC bilayers (parameter is the number of H_2O molecules per DMPC molecule) against temperature T (broken curves) compared to that of bulk water (full curve). The viscosity η of the bound water was determined by measuring the water dipole relaxation time τ (since $\eta \propto \tau$ holds [17]) by microwave spectroscopy [3].

This effect is *a fortiori* expected in confinements of higher dimensionality. Similar results have indeed been discovered for water in a three-dimensional confinement of micelles in microemulsions [4, 5]. There the dielectric response of two different systems has been measured to study the phase transition into and out of a microemulsion state, respectively.

At the clearing point (60°C), a five-component water-oil (w/o) emulsion makes a transition from an opaque gel state into that of micellar water. This is accompanied by a drastic decay of the dielectric response, which is obtained by the water component of the emulsion. Obviously the micellar water narrowly confined in three dimensions by the surfactant is much less mobile and hence more ice-like than in the gel structure below the clearing point [4].

In a w/AOT†/O (water/surfactant/decane) microemulsion, the micellar confinement of the water breaks down upon approaching the cloud point and, in contrast to the gel-microemulsion transition mentioned before, now the water droplets become poly-disperse and eventually enter the bulk water state. Again it was found that micellar confinement of water is responsible for a lengthened dipole relaxation and in consequence an increased viscosity [5].

The studies on the different systems have in fact demonstrated that the viscosity of water near a hydrophilic surface is enhanced like that of toffee or soft ice in agreement with a statement on interfacial water by Davies and Rideal [6]. We interpret this phenomenon by an increased hydrogen bond connectivity which is effective up to some ten molecular distances. This model was recently confirmed by percolation calculations [2, 7, 8] to be introduced in the following.

In the picture of chemical bonding, the ice state is characterised by a maximum of four intact hydrogen bonds for each oxygen atom. According to Pauling [9] only a small fraction (less than 20%) of these bonds break when ice melts. In liquid water

† AOT = sodium dioctyl sulphosuccinate.

therefore most oxygen atoms still have four intact hydrogen bonds to their neighbouring atoms. This fraction decreases very slowly as the temperature is raised, its value being about 0.77 at room temperature in the bulk liquid [10]. Hence water may be looked at as a space-filling network of hydrogen-bonded oxygen atoms. Blumberg *et al* [11] proposed correlated site percolation calculations to describe the properties of liquid water. In their model each water molecule with four intact hydrogen bonds is represented by an occupied site with four occupied neighbours. Examining the properties of the clusters of those four-coordinated sites they could interpret the anomalies of water, e.g. the changes in density depending on temperature [11, 12]. The general aspects of percolation theory are treated elsewhere [13, 14].

Weiss *et al* [7] applied this model to the properties of water near hydrophilic surfaces. The simulations were carried out in the simple cubic lattice and in the diamond lattice structure [8], the latter being quite similar to the ice-lattice structure. The influence of nearest-neighbour interactions was also taken into account and found to be small.

The result of the computer simulation is that the molecules near hydrophilic surfaces tend to clump together, i.e. the cluster size increases. The larger and the more ice-like the clusters, the higher the viscosity is expected to be as was shown more recently [15]. In consequence the water close to such surfaces is more viscous than bulk water.

While there is convincing experimental evidence for the enhanced viscosity of water confined in one and three dimensions, the situation is different for a two-dimensional confinement.

There have been wild speculations on anomalous 'polywater', i.e. water in ultranarrow capillaries. Due to the lack of a proper geometry the experimental results were essentially irreproducible and eventually the phenomena were related to impurities [16]. Initiated by this provoking dispute on capillary water and reverting to our experimental and theoretical data for water near hydrophilic surfaces we performed a computer simulation on what we termed 'macaroni water'. Analogous to the inter-bilayer water the hydrogen bond connectivity of water in hydrophilic capillaries was calculated, assuming a diamond lattice for the bonding structure. The capillaries were simulated in a toroidal geometry with periodic boundary conditions. All molecules forming the cylindrical walls were assumed to represent occupied sites with four intact hydrogen bonds reaching to their neighbours. Results of the cluster size as a function of capillary diameter are presented in figure 2. At the extremely small diameter of 1 nm the number of clusters doubles the bulk water value. The connectivity of the capillary water becomes bulk-like only at diameters exceeding 10 nm. With increasing connectivity we have less molecules available performing with zero to three hydrogen bond neighbours. These molecules are in charge of the dielectric response and the viscosity [15].

That the viscosity of water becomes more and more ice-like in ultranarrow capillaries is indeed an intriguing result. Did Derjaguin and his collaborators observe an increased viscosity in their experiments? Two difficulties are likely to impede such an experimental observation. Firstly, it seems impossible to manufacture capillaries having diameters of 10 nm or less and secondly it is difficult to avoid impurities in such capillaries. These shortcomings are avoided in the present computer simulation.

The property of confined water reported here is observed only within about 10 nm of a hydrophilic surface in agreement with the new computer simulation.

Various experimental data obtained from water near hydrophilic surfaces have shown that 'bound water' is markedly different from bulk water. Bound water is more

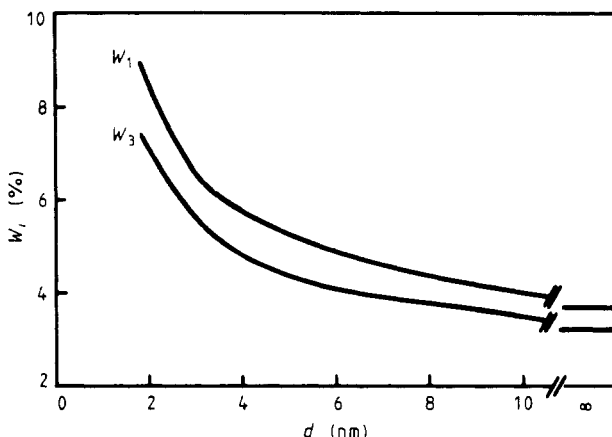


Figure 2. Fraction of water monomers (W_1) and water clusters of sizes 4 to 6 (W_3) relative to the total number of occupied sites as a function of capillary diameter D . The weight functions W_1 and W_3 have been calculated for room temperature where the fraction of intact hydrogen bonds in free water ($d \rightarrow \infty$) is $p = 0.77$.

viscous or more ice-like. This amazing state of water near hydrophilic surfaces is now understood in terms of an increased hydrogen bond connectivity confirmed by percolation calculations. The new results bear consequences of interdisciplinary interest as there are many states of water confinement in physics, chemistry, and particularly in biology.

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References

- [1] Derjaguin B V 1970 *Sci. Am.* **223** 52
- [2] Nimtz G 1986 *Phys. Scr.* **T13** 172
- [3] Enders A and Nimtz G 1984 *Ber. Bunsenges. Phys. Chem.* **88** 512
- [4] Nimtz G, Binggeli B, Börngen L, Marquardt P, Schäfer U and Zorn R 1986 *Europhys. Lett.* **2** 103
- [5] Marquardt P and Nimtz G 1986 *Phys. Rev. Lett.* **57** 1036
- [6] Davies J T and Rideal E K 1961 *Interfacial Phenomena* (New York: Academic)
- [7] Weiss W, Enders A and Nimtz G 1986 *Phys. Rev. A* **33** 2137
- [8] Weiss W 1987 *J. Physique* to be published
- [9] Pauling L 1960 *The Nature of the Chemical Bond* (Ithaca, NY: Cornell University Press) 3rd edn
- [10] Fortuin C M and Kasteleyn P W 1972 *Physica* **57** 536; **58** 393; **59** 545
- [11] Blumberg R, Stanley H E, Geiger A and Mausbach P 1984 *J. Chem. Phys.* **80** 5230
- [12] Stanley H E and Teixeira J 1980 *J. Chem. Phys.* **73** 3404
- [13] Stauffer D 1985 *Introduction to Percolation Theory* (London: Taylor and Francis)
- [14] Binder K and Stauffer D 1984 *Topics in Current Physics* **36** *Applications of the Monte Carlo Methods in Statistical Physics* (Berlin: Springer)
- [15] Nimtz G and Weiss W 1987 *Z. Phys. B* submitted
- [16] Barnes P, Cherry I, Finney J L and Petersen S 1971 *Nature* **230** 31
- [17] Fröhlich H 1949 *Theory of Dielectrics* (Oxford: Oxford University Press)