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The Properties of Water and their Role in Colloidal and Biological Systems

Carel Jan van Oss

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The Properties of Water and their Role in Colloidal and Biological Systems

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PREFACE

Of all liquids on this Earth, liquid water is the most pervasive and its properties are the most influential in all colloidal and, especially, in all biological systems. However, it was only since the late 1980's that it became possible to understand the non-covalent physicochemical properties of water and their influence on everything that is immersed in it, in a truly quantitative manner. The most important property of liquid water, with a major influence on all surfaces, particles, cells and molecules that are immersed in it is its very strong energy of cohesion, which is for 30% due to van der Waals attractions and for 70% a consequence of the hydrogen-bonding driven (i.e., polar) attraction between the water molecules.

This polar attraction between water molecules in liquid water causes the strong *attraction* between all hydrophobic (non-polar) molecules and particles immersed in it, known as "*the hydrophobic effect*." Conversely, the polar attraction between water molecules and hydrophilic (polar) molecules and particles, is the cause of "*hydration pressure*," i.e., the *repulsion* between such hydrophilic molecules and particles when immersed in water.

A few, out of the many examples of the influence of the properties of water on colloidal or biological systems treated in this book are:

Hydration pressure effects in water keep our blood cells from clumping together in our peripheral blood circulation and they also keep our blood serum proteins in stable solution.

In the liquid form, water occurs in clusters of about 4.5 water molecules per cluster, at room temperature. Increases in the water temperature causes a decrease in the cluster size of water, thus increasing the electron-accepticity of water, which in turn causes the aqueous solubility of most hydrophilic solutes to be greater in warm than in cold water.

The aqueous solubility of solute molecules is directly linked to their interfacial tension with water, so that such interfacial tensions, which often are difficult to measure directly, can be derived from the known aqueous solubility of these solute molecules.

Hydrophobic macro-molecules or particles clump together when immersed in water, driven by the "hydrophobic effect," which is caused by the hydrogen-bonding energy of cohesion of the water molecules that surround these hydrophobic entities. On the other hand, *single* hydrophobic atoms or small molecules, immersed in water, become individually surrounded by a sphere of water molecules, thus forming water-cages or "clathrates."

It can be demonstrated that, paradoxically, the water–air interface is the most hydrophobic (= "water-fearing) surface known to Man. For instance, "Rough" solid surfaces, when in contact with water, give the appearance of being hydrophobic because of the air trapped between the solid protrusions that are the cause of the roughness.

Hydration pressure causes the osmotic pressure of hydrophilic, electrostatically neutral, concentrated solutions of polymers (such as dextran or polyethylene glycol) to generate osmotic pressures of up to 300 atmospheres, which is hundreds of times higher than would be predicted when using the classical van 't Hoff equation that normally governs osmotic pressures.

Carel Jan van Oss
2008

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CHAPTER ONE

GENERAL AND HISTORICAL INTRODUCTION

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PREAMBLE

Water is the most polar[1] liquid known to Man. At room temperature (20 °C) its total free energy of cohesion, $\Delta G^{\text{cohesion}} = -145.6\ \text{mJ/m}^2$, consisting of $\Delta G^{\text{van der Waals}} = -43.6\ \text{mJ/m}^2$ and $\Delta G^{\text{Polar}} = -102\ \text{mJ/m}^2$. Thus the van der

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[1] There is of course mercury (Hg), which is also a liquid at room temperature and which has an apolar (van der Waals) free energy of cohesion that is about 9.2 times greater than that of water and a non-van der Waals part of the total free energy of cohesion that is about 5.6 times greater than that of water, but that non-van der Waals part is not really *polar*, as it is more accurately described as a *metallic* bond (see Chaudhury, 1987, and see also van Oss et al., 1988, 1994, p. 157).

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Waals part of the free energy of cohesion of liquid water represents only 30% and the polar part represents 70% of the total. This was already known since Fowkes (1963, 1964, 1965). In addition, with respect to the interaction energies between non-polar molecules (e.g., alkanes), *when these are immersed in water*, the combining rules for apolar interactions in such cases generally causes $\Delta G^{\text{van der Waals}}$ to be rather small, leaving mainly the polar free energy of attraction of -102 mJ/m^2, which thus represents close to 100% of the total free energy of interaction in water among non-polar molecules or particles.

As was only realized much later, these -102 mJ/m^2, representing the polar (in this case the hydrogen-bonding) free energy of cohesion of water, also happen to be the sole driving force for the *hydrophobic effect*. Notwithstanding these new data and probably mainly due to a continuing indecisiveness as to which forces were apolar and which were polar (see Sub-section 2.3, below) no significant advances were made in this matter for about another 20 years after Fowkes (1963, 1964, 1965). Finally, based on important clarifications proposed by Chaudhury (1984) and starting in early 1985, Chaudhury and I began (mainly *via* long-distance telephone) to develop the combining rules which allow the quantitative expression of polar free energies in SI units (van Oss, Chaudhury and Good, 1987, 1988). The ensuing results allowed the polar free energies of interaction to be combined with the van der Waals interaction energies (and the electrical double layer interaction energies where applicable), into a complete system comprising all non-covalent interactions taking place in and with liquid water (see also van Oss, 1994, 2006).

Now, more than another two decades past 1987, this book aims to treat the combined non-covalent non-polar, polar and electrical double layer interactions taking place in and with water, from the viewpoint of all the germane physical and physico-chemical properties of liquid water.

1. SOME EXAMPLES OF POLAR FORCES INTERACTING IN THE MAMMALIAN BLOOD CIRCULATION

Essentially all repulsive as well as attractive non-covalent interactions at a colloidal scale occurring in biological systems take place in water. Some examples of such interactions in water, looking for instance at the mammalian peripheral blood circulation, include:

1. Repulsion:

   The mutual, non-specific repulsion between protein molecules, which keeps them dissolved in blood serum and permits them to avoid precipitation.

   The mutual, non-specific repulsion between leukocytes, platelets, etc., which keeps them in stable suspension in the blood and lymph circulation and thus prevents the formation of thrombi.

   (Thus the principal constituents of blood can safely circulate in their aqueous environment.)

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