Feature Article

Derjaguin's Water II: a surface hydration phenomenon

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Abstract. B.V. Derjaguin's promotion of anomalous water II (polywater) in the early 1970s was an embarrassing point in the career of an illustrious chemist, and quickly repudiated by Derjaguin himself. Water II does not exist as a bulk liquid. And yet a theoretical model of the hydration of ions developed by I. Klugman, consistent with electrolyte properties such as equivalent conductivity, diffusion coefficient, and viscosity, found a density of water molecules in the hydration shell of ions to be 1.4 g/cm^3, close to the density of water II reported by Derjaguin and Churaev. Given Derjaguin and Churaev's use of adsorption in fine capillaries, Klugman postulates that their anomalous experiments can be understood as measuring the hydration layer of adsorbed water rather than bulk water. Derjaguin's last publication in 1994 on violation of Archimedes' Law during adsorption may be intended to hint at this conclusion. Perhaps Derjaguin's involvement with water II can, in the end, be celebrated not as a study of bulk liquid but as a study of adsorption phenomena and hydration.

Keywords. Derjaguin, water II, polywater, water, water anomalies, electrolyte, adsorption, Archimedes' Law.

Allow me to introduce myself: I am Ilya Klugman, born 1924, engineer by profession, now retired. I met B.V. Derjaguin personally at the end of the 1960s, when I presented a talk at his Seminar Series on the theme of my doctoral dissertation concerning the dielectric properties of crude oil emulsions. My presentation was successful and received a positive reaction from B.V. Derjaguin. A series of my papers were published in *Kolloidn. Zh.* [1–7], of which B.V. Derjaguin was the chief editor. Strange then, at that time I knew nothing of Derjaguin's work on the topic of water II, or polywater as it came to be known in the west.

In the 1980s I moved to Israel, where I worked intensively as an engineer for more than 11 years. Entering into retirement, I decided to return back to my own work which had been interrupted by the move. I knew that the theory of electrolytes, leaning on the work of Debye-Hückel, was far from complete. My first efforts building a new approach for electrolyte theory were published in the journal *Elektrokimiya* [8–15]. I developed a hydration model of electrolytes, with only two ion parameters drawn from first and second

hydration shells, that enabled various electrolyte properties to be determined. But once I had finished developing the first variant of this theory, the editorial office of the journal *Elektrokimiya* changed, and my articles started to meet rejection.

Discovering that the volume of water molecules changes on entering into the hydration shell of an ion, I proposed that this must be driven by denser packing, a result of their attraction towards the ion. We know that a water molecule at 25°C occupies a volume of $v=30\text{Å}^3$, while at the same time the intrinsic volume of the water molecule itself equals $v_w=11.25\text{Å}^3$. It follows that a water molecule in water occupies a volume more than three times in excess of its intrinsic volume. In order to characterise the density of the molecule in the hydration shell, I introduced a "density coefficient" K_p equal to the ratio of the intrinsic volume v_w of a water molecule, to the volume v that it occupies in the hydration shell, $K_p = v_w/v$. Calculations indicated that for all monovalent ions investigated, the ratio was a uniform $K_p = 0.535$. This result seemed incorrect to me, since I supposed that as the ion radius falls, the strength of attraction of water molecules towards the ion must increase, in which case the packing coefficient K_p would increase.

At this time I happened to read a popular book by I. Asimov[16] , written during the period when a great amount of attention was being given to "anomalous" water, water with a density of 1.4 g/cm³, boiling point 250°C, freezing point -40°C and a linear coefficient of expansion across the entire temperature range. The packing coefficient I had calculated, $K_p = 0.535$, corresponds to a water density of 1.422 g/cm³, essentially equal to the density of anomalous water. If water transforms into the anomalous modified phase upon forming the hydration shell around an ion, then it follows naturally that the packing coefficient will be constant.

It was necessary to develop my interpretation based the foundation of these works. Let us be clear: the anomalous bulk phase liquid, called water II by Derjaguin[17], does not exist. But when molecules of ordinary water with its well known parameters (let us label it W1) cross into the hydration shell of an ion, a consequence of the interactions between them, they transform into molecules with the properties measured by Derjaguin and Churaev[18,19] (we shall label this water as W2). It follows that, even if water II does not exist as an independent liquid phase, the molecules of this type of water exist in any body of water around ions and other particles where adsorption takes place. Under conditions where W1 water contains only a negligible amount of W2-type molecules, their presence will not be detectable. But when the number of W2 molecules becomes comparable

to the number of W1 molecules, the properties of W2 molecules will start to become evident. The effect can be observed in electrolytes, where not only does the density increase with concentration, but also the boiling point rises and the freezing point falls.

Following these concepts, I applied my electrolyte model using the density 1.4 g/cm³ of anomalous water as measured by Derjaguin and Churaev. The correctness of my proposed electrolyte model was confirmed by the result that, with the help of two parameters: the radius of a hydrated ion, characterising the first hydration shell, and the thickness of the buffering layer (an exclusion zone around the ion) driven by the second hydration shell, it was able to determine to an accuracy of 4% such electrolyte properties as equivalent conductivity λ, diffusion coefficient D, and viscosity η. In order to compute the equivalent conductivity λ, I used the formula of Stokes taking the radius of hydrated ion instead of the intrinsic ion radius, and added an amendment for the decreased viscosity caused by secondary hydration. In the computation of the diffusion coefficient D I took into account that the same ions participate in diffusion as well as in equivalent conductivity and the only difference is that in the diffusion coefficient the ions move in the same direction with the same velocity and in the equivalent conductivity they move in different directions with different velocities. In the computation of viscosity the increase of viscosity caused by hydrated ions is obtained by Einstein's formula and decrease of viscosity caused by the second hydration is defined by the thickness of the buffering layer.

A chief argument of Derjaguin's opponents was the absence of anomalous water in nature (indeed, Derjaguin himself agreed that this was a significant argument). Derjaguin had extracted W2 molecules via a process of adsorption in very fine capillaries. With multistage distillation in specialised equipment it was possible for samples to be extracted with nearly equal quantities of W2 and W1. Because of the difference in molecular densities, 1.4/1.0, and the long separation path, they were able to separate W2 molecules and measure their parameters. For this reason it is possible to assert that Derjaguin did indeed measure properties of the group of W2 molecules. Calculation using my electrolyte model confirmed that the density of water molecules in the hydration shell was equal to 1.4 g/cm³, i.e. W1 water molecules transformed to W2 molecules upon crossing into the hydration shell under the influence of the field of an ion. Additional proof of this fact can be found in the change of other electrolyte properties in the presence of W2 molecules, the elevation of the boiling point and depression of freezing point. Moreover, the proposed

electrolyte model allows the freezing point of an electrolyte solution to be predicted. According to literature data the freezing point of NaCl solution at 2.9%w/w concentration falls to -1.8°C, while the electrolyte model predicts -1.7°C.

In a letter written to the chief editor of Colloid Journal seeking to publish my study, I wrote that after the scandal of water II it is necessary to show courage to return to the theme once again. I suggested that, if my conclusions hold up to peer review, it would be an honour to publish a manuscript rehabilitating the work of Derjaguin and his group, given that the first paper on the topic of water II was published in that journal. However, I received a reply from the chief editor proposing instead that, since Derjaguin had recanted from water II, my manuscript served more as opposition against Derjaguin. I was therefore encouraged upon reading a foreword written by Barry Ninham prefacing a collection of Derjaguin's works[20], in which he showed that in many scientific debates Derjaguin was in the end proven correct, and even in the story of water II there remains an array of unanswered questions. I think that it is possible to demonstrate the significance of the results obtained by Derjaguin's group and remove the label of "the biggest mistake of scientists in the 20th Century" from their work. Could it be I am mistaken?

I then became acquainted with the last paper of Derjaguin in *Kolloidn. Zh.*[21] (in English, published in Colloid and Surfaces A[22]) on the violation of Archimedes' Law during adsorption. Keeping in mind that the Derjaguin group obtained water II by adsorption in capillaries, it is possible to deduce that the chief aim of this paper, although not stated so directly, was to show that during adsorption water molecules with new properties are found, i.e. molecules of water II, and that this process changes water so significantly that even Archimedes' Law is violated. The same process occurs in hydration.

From Derjaguin's article, I understood that a parameter which I had used to define volume, could in the context of the violation of Archimedes' Law be called the coefficient of violation of Archimedes' Law. I wrote a manuscript on how it can be used to define hydration properties and parameters of a model I proposed for 1:1 electrolytes. So as not to antagonise the established scientific community, in the manuscript I did not speak about molecules of water II, but rather introduced the concept described above of the density coefficient K_p of water molecules in the hydration shell, and showed that with K_p=0.526, corresponding to the density of water in the hydration shell, 1.4 g/cm^3, the proposed model allows the calculation of equivalent electrical conductivity of an electrolyte at infinite dilution. I published the manuscript in *Problems in Applied Physics*, published by Saratov University[23]. In two following papers [24,25] I showed that this model also permits to determine the dielectric constant, and to construct a basis for a hydration model of electrolytes.

In this way there are now a few publications, one based on experimental data[21,22] and the other based on theoretical considerations[23-25], which confirm that during adsorption or hydration the properties of a water molecule change significantly. The concept of a surface hydration layer, or surface induced water ordering, is not unknown to the scientific community. It is known in Gouy-Stern theory as the Helmholtz layer and is crucial for understanding the capacitance of surfaces[26]. Devanathan and Tilak estimated[27] the dielectric constant of the surface hydration layer 0.37 nm thick at electrode surfaces to fall from 78 (bulk water) to 7.2.

As for the existence of W2 in nature, although it cannot exist as a bulk liquid, nevertheless it does exist. My conjecture is that plants use capillaries and charged particles in order to transform molecules of W1 into W2 and this can explain why some plants are capable to survive the extreme heat of deserts and extreme winter cold without drying or freezing.

These publications, it seems to me, must ease the process of rehabilitating the work of the Derjaguin group, all the more given that Derjaguin himself continued to study the question of water II, arising during adsorption. When I told my wife (Z. Bykova) about Derjaguin's final paper, she expressively called it the "final will and testament of Derjaguin". I would like to express my admiration for the beautiful experiments of Derjaguin and Churaev. As B. Ninham wrote,[20] "Derjaguin was, and remains controversial, and in the controversies that occasionally best him, usually is right in the end."

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