Colloid Polym Sci 275:162–169 (1997)
© Steinkopff Verlag 1997

ORIGINAL CONTRIBUTION

H. Stobbe
G. Peschel

Experimental determination of the static permittivity of extremely thin liquid layers of water dependent on their thickness

Received: 28 May 1996
Accepted: 30 September 1996

H. Stobbe
Beijing University of Chemical Technology
P.O. Box 278
Peking, P.R. China

Prof. Dr. G. Peschel (✉)
Institüt für Physikalische und Theoretische
Chemie der Universität GH-Essen
Universitätsstraße 5–7
45117 Essen, Germany

Abstract A new method for determining the static permittivity (dielectric constant) of extremely thin liquid interlayers is illustrated.
A special condenser, which can be filled with a test liquid, is constructed. Both condenser plates – one planar, the other spherically curved – are made of vitreous carbon and are supplied with a high-grade politure.
In order to adjust plate separation distances from 10 nm up to about some μm the planar plate can be easily shifted by a piezoelectric translation stage; the plate separation is monitored by an optical system supported by displacement transducers.

The measuring frequency was kept constant at 1 MHz. Water was chosen as the test liquid. At 19.8 °C thin water layers having thickness smaller than 0.3 μm exhibit a decrease of the dielectric constant. The experimental data are consistent with a decay length α^{-1} of the order of 1 nm which in view of the underlying crude model must be regarded as approximative.

Key words Permittivity – dielectric constant – thin water layer – decay length of surface orientation – surface polarization

Introduction

Earlier studies of the dielectric properties of water adsorbed on, for example, silica gels or other porous and nonporous substrates, respectively, had been carried out by many of authors, as reviewed in detail by Young and Crowell [1] in 1962 and later by McIntosh [2] etc. in 1966.

Much less is known, however, about the dielectric constant of water in multimolecular layers near solid walls or confined between two solid surfaces, respectively. Zhilenkov [3] in his tests found that the dielectric constant of the second molecular layer of water near silica gel surfaces appears to be not higher than 8–10. Surprisingly this turned out to be the case up to the 20th molecular layer.

Metzik et al. [4], in their well-known paper, determined the dielectric constant of water films between plane-parallel mica platelets. For film thicknesses smaller than 1.4 μm the dielectric constant obviously dropped down to a value of about 4.5.

An important contribution with strong relevance to the present work is due to McCafferty and Zettlemoyer [5] who determined the dielectric constant of α-Fe_2O_3 stepwise covered with water layers from 5° up to 35 °C at a frequency of 100 Hz. From a coverage of one monolayer (dielectric constant value of about 2) the dielectric constant rose sharply up to a value of 30–40 when a coverage of 3 or 4 monolayers was achieved for temperatures not exceeding 15 °C.

The purpose of the present work is to determine the dielectric constant of thin aqueous layers confined by two conducting plates of high surface quality inserted in a newly developed experimental device.

Theory

The planar/spherical condenser system in vacuo and filled with a homogeneous substrate, respectively

Let us base the following calculations on a physical model which had been developed for evaluating the potential gradient along the surface of an electrical conductor [6]. This enabled us to treat the capacitance problem of a condenser consisting of two plates having the curvature radii R_1 and R_2, respectively, when the local plate separations δ are sufficiently small.

In a first step, we obtained the proper unit area capacitance at any point P for the vacuum case:

$$C_p = \frac{\varepsilon_0}{\delta}\left[1 + \frac{\delta}{2}\left(\frac{1}{R_1} + \frac{1}{R_2}\right)\right]; \tag{1}$$

ε_0 is the vacuum permittivity.

Hence, for the total surface of the condenser plate and for the actual case characterized by $R_1 = R$ and $R_2 = \infty$ we find, when dF is a differential surface element and C' an integration constant.

$$C = \varepsilon_0 \int \frac{dF}{\delta} + \frac{\varepsilon_0}{2R} \int dF + C' . \tag{2}$$

Further approach may be done with reference to experimental conditions as depicted in Fig. 1. Here ρ is the radius of the spherical segment at the height coordinate $h + \xi$ reckoned from the planar plate surface; $\rho_{\max}$ is the radius of the spherical plate at the proper height coordinate $h + \xi_{\max}$.

The condenser system in Fig. 1 may be designed in that way that the relation

$$\rho_{\max} \gg \xi_{\max} \gg h \tag{3}$$

is valid.

From this it follows that the area of the face F_s of the spherical plate is practically identical with that of the face F_p of the planar one. Hence, we have:

$$F_s = F_p = \pi \rho_{\max}^2 . \tag{4}$$

Definite integration of Eq. (2) in the limits $\rho = 0$ and $\rho_{\max}$ then yields:

$$C = \varepsilon_0 \int_{\rho=0}^{\rho_{\max}} \frac{1}{h + \xi} 2\pi \rho d\rho + \frac{\varepsilon_0 \pi \rho_{\max}^2}{2R} . \tag{5}$$

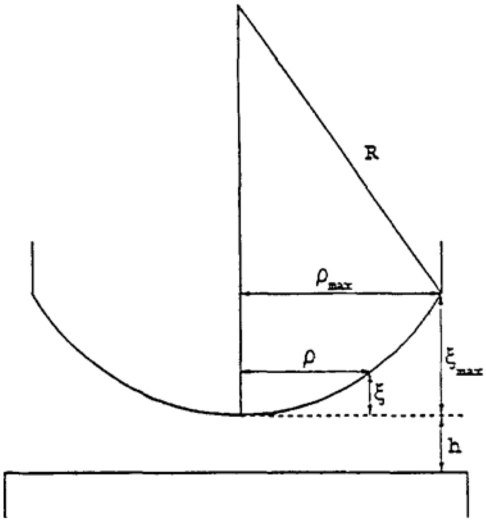

Fig. 1 Schematic illustration of the spherical/planar condenser system

With the approximation $\rho \gg \xi$ (Fig. 1), one can write:

$$\xi = \frac{\rho^2}{2R} \quad \text{and} \quad \rho d\delta = R d\xi .$$

From this it follows by regarding Eq. (5):

$$C = \varepsilon_0 \left[\frac{R}{2} [\ln(h + \xi_{\max}) - \ln h] + \frac{\xi_{\max}}{4}\right] . \tag{6}$$

This method for evaluating C can be replaced by an iteration process which, to be sure, is entirely reliant on the availability of a fast computer since the number of computing operations for a given plate separation is extremely high ($\sim 10^6$).

At first sight this procedure appears to be rather laborious, but the advantage becomes clearly evident in the case of a condenser whose liquid interlayer shows locally varying dielectric properties.

This particular calculation requires subdivision of the macroscopic spherical condenser plate into concentric spherical segments of differential small thickness (Fig. 2). Each spherical segment thus forms a differential annular condenser. Summing up the capacitances of these subcondensers leads to the vacuum capacitance of the spherical/planar condenser system which amounts to

$$C = \sum_{i=0}^{\frac{\xi_{\max}}{d} - 1} \frac{2\pi \varepsilon_0 R d}{h + \frac{d}{2} + id} . \tag{7}$$

When subdividing the spherical plate into an extremely large number of spherical segments a limiting value for the total capacitance can be obtained.

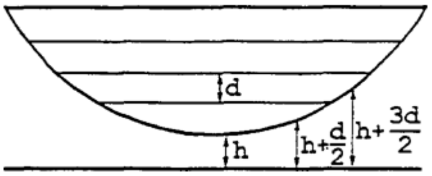

Fig. 2 Subdivision of the spherical condenser plate into annular segments

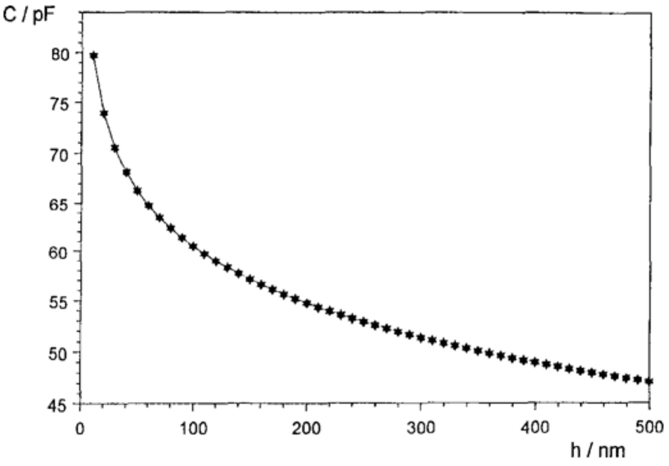

Fig. 3 Comparison of the iteration method with the integral method. -*- iteration method - — - integral method

Applying both methods the vacuum capacitance for a particularly designed condenser was calculated for varying h between 100 nm and 500 nm. The result is presented in Fig. 3 which clearly shows total agreement for both approaches. The essential message of Fig. 3 is that the iteration method can be applied on solving the capacitance problem without any reservation.

The real case of a spherical/planar condenser with a thin liquid interlayer nonhomogeneous in its dielectric properties

With reference to real conditions the next step should be the evaluation of the capacitance of a condenser containing a liquid interlayer whose dielectric properties vary when passing from one plate to the second one. This ought to be the case if solid surfaces by virtue of adsorptive interaction impose some degree of immobilization on the adjacent dipolar molecules, which might result in a drop of the dielectric constant nearby.

A tentative model for the local change of the dielectric constant in the liquid interlayer is shown in Fig. 4. The adsorption layers adjacent to both the solid walls constitute the subcondensor (a) with the thickness and the dielectric constant ε_s.

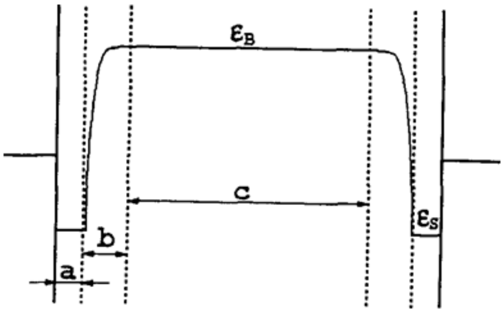

Fig. 4 Model of the five-layer condenser

This procedure, however, has a serious drawback, since it is rather difficult to ascribe to an absorption layer of molecular dimensions a dielectric constant as a macroscopic quantity which is regarded as an approximation to throw a bridge from the microscopic to the macroscopic approach. This step has sometimes been used in literature. The key work of McCafferty and Zettlemoyer [5], for instance, might be quoted as an illustration. The authors determined the dielectric constant of water adsorbed on $\alpha - Fe_2O_3$ as a function of coverage. To the first monolayer they attributed a dielectric constant having a value of about 2, whereas with the following monolayers there was a significant rise of the dielectric constant.

In the light of liquid theory the assumption of the dielectric constant of the first adsorbed layer is rather questionable; it only helps in a more mathematical sense to describe the molecular immobilization in the liquid very close to a solid surface.

A fundamental problem with which we are faced beyond that is that water structure near a solid surface owing to its orienting power appears to be anisotropic, so that the dielectric constant of oriented water is a tensor. Assuming that owing to experimental difficulties the dielectric constant of the interlayer can be determined in one direction only it will be obtained as a scalar quantity and, hence, will not reveal any structural characteristics about vicinal water. Despite this obvious drawback the decay length of the molecular immobilization effect should be attainable by experiment so that the extension of the ordered surface zone might be assessed without obtaining details about vicinal water structure.

The subcondenser (c) with the thickness c refers to the bulk liquid having the dielectric constant $\varepsilon_c = \varepsilon_B$. For the transition region intermediate between the subcondensers (a) and (c) we have in a former paper [7, 8] introduced the dielectric constant

$$\varepsilon_b = \varepsilon_B + \beta\exp(-\alpha x)\,, \tag{8}$$

when x is a coordinate lying in the common central axis of both the condenser plates. x is reckoned from the distance a from the condenser plate surface. α and β are constants which can be evaluated via a fitting process when experimental data are available for the intervening liquid layer.

The combination of the five subcapacitances in Fig. 4 is in series. In order to obtain the total capacitance of a plane-parallel condenser having the plate area F and an intervening liquid for which the relative dielectric constant $\varepsilon_r = \varepsilon_c \cdot \varepsilon$ can be measured let us for the first instance determine the capacitances of the individual subcondensers.

We find for subcondenser (a)

$$C_a = \frac{\varepsilon_s \varepsilon_0 F}{a} \tag{9}$$

and for subcondenser (c)

$$C_c = \frac{\varepsilon_0 \varepsilon_B F}{c} \,. \tag{10}$$

Evaluation of the capacitance of the transition zone (b) is, however, much more difficult, because a detailed mathematical analysis is necessary.

When V is the potential and Q_b the electrical load of subcondenser (b), we can write with regard to Eq. (8) and putting $\beta' = \beta\varepsilon_0$:

$$\frac{dV}{dx} = -\frac{Q_b}{F\varepsilon_b \cdot \varepsilon_0} = -\frac{Q_b}{F(\varepsilon_B \cdot \varepsilon_0 + \beta' \exp(-\alpha x)} \,. \tag{11}$$

Integration of Eq. (11) in the limits $x = 0$ and $x = b$ yields for the first case

$$V_1 = -\frac{Q_b}{F}\left[\frac{1}{\alpha\varepsilon_B \cdot \varepsilon_0} \ln(\varepsilon_B \cdot \varepsilon_0 + \beta')\right] \tag{12}$$

and for the second one

$$V_2 = -\frac{Q_b}{F}\left[\frac{b}{\varepsilon_B \cdot \varepsilon_0} + \frac{1}{\alpha\varepsilon_B \cdot \varepsilon_0} \ln(\varepsilon_B \cdot \varepsilon_0 + \beta' \exp(-\alpha b))\right] \,. \tag{13}$$

Finally, we have

$$C_b = \frac{Q_b}{V_1 - V_2} = \frac{F}{\frac{b}{\varepsilon_B \varepsilon_0} + \frac{1}{\alpha\varepsilon_B \cdot \varepsilon_0} \ln(\varepsilon_B \cdot \varepsilon_0 + \beta' \exp(-\alpha b)] - \frac{1}{\alpha\varepsilon_B \cdot \varepsilon_0} \ln(\varepsilon_B \cdot \varepsilon_0 + \beta')} \tag{14}$$

This expression can be alternatively written:

$$C_b = \frac{\varepsilon_B \cdot \varepsilon_0 \alpha F}{\alpha b + \ln\left[\frac{\varepsilon_B \cdot \varepsilon_0 + \beta' \exp(-\alpha b)}{\varepsilon_B \cdot \varepsilon_0 + \beta'}\right]} \,. \tag{15}$$

Combining the five subcapacitances in series takes the form

$$\frac{1}{C} = \frac{2}{C_a} + \frac{2}{C_b} + \frac{1}{C_c} \,. \tag{16}$$

Substituting Eqs. (9), (10), and (14) in Eq. (16) yields:

$$\frac{1}{C} = \frac{1}{F}\left(\frac{2a}{\varepsilon_s \cdot \varepsilon_0} + \frac{2\left[\alpha b + \ln\left(\frac{\varepsilon_B \cdot \varepsilon_0 + \beta' \exp(-\alpha b)}{\varepsilon_B \cdot \varepsilon_0 + \beta'}\right)\right]}{\varepsilon_B \cdot \varepsilon_0 \alpha} + \frac{c}{\varepsilon_B \cdot \varepsilon_0}\right) \,. \tag{17}$$

On the other hand, it is possible to write

$$C = \frac{F\varepsilon}{2a + 2b + c} \,. \tag{18}$$

Together with Eqs. (17) and (18) we arrive at an expression for the measurable effective dielectric constant ε_r

$$\varepsilon_r = \frac{2a + 2b + c}{\varepsilon_0} \times \left[\frac{2a}{\varepsilon_s} + \frac{2\left(\alpha b + \ln\left(\frac{\varepsilon_B \cdot \varepsilon_0 + \beta' \exp(-\alpha b)}{\varepsilon_B \cdot \varepsilon_0 + \beta'}\right)\right)}{\varepsilon_B \alpha} + \frac{c}{\varepsilon_B}\right]^{-1} \,. \tag{19}$$

Replacing in Eq. (7), which refers to the vacuum case, ε_0 by ε_r from Eq. (19) the total capacitance of the spherical/planar condenser can be calculated for the case that the dielectric constant in the interlayer shows a local change as depicted in Fig. 4.

Construction of a measuring device

With refererence to a former device which we had designed for the same purpose [7, 8] the geometry of the condenser plate system was again chosen to be spherical/planar. This time the adjustment of the plate separation distances was done with piezoelectric translation stage which carried the lower part of the measuring cell and together with this the planar condenser plate. By introducing this mechanism a good deal of disturbing mechanical vibrations originating in the surroundings was suppressed. A detailed picture of the condenser is shown in Fig. 5. The top plate (1) to which the spherically formed condenser plate was attached was rigidly fixed in the apparatus. The planar condenser plate was glued to a gilded support (4) made of titanium.

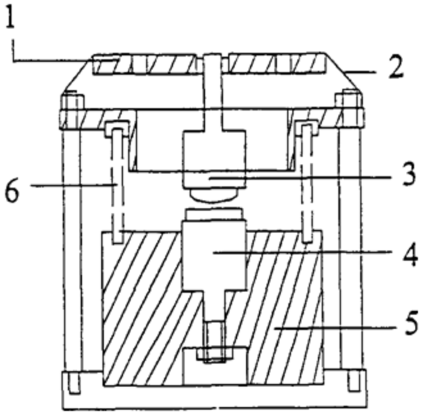

Fig. 5 Schematic illustration of the measuring condenser 1) top plate to which the spherical plate 3 is attached 2) ring-like collar made of rubber, 4) support for the planar plate, 5) Teflon block, 6) quartz glass tube

The whole system was inserted in a cylindrically formed Teflon block (5) which guaranteed perfect electric isolation and could be moved up and down by means of piezoelectric translation stage in order to regulate the plate separation distances as desired. The condenser plate was particularly placed in a tightly sealed quartz glass tube so that the movement of the planar plate together with its support could be easily observed from outside. The top plate (1) was connected with the condenser system via a ringlike collar made of rubber so that the movement of the planar plate was not hindered in any way. The glass tube which was pressed against the Teflon block could be filled with the test medium by a special device. All metallic parts of the condenser were made of stainless steel.

The capacitance of the condenser for different plate distances could be determined by using a low frequency impedance analyzer (HP 4 192A, Hewlett Packard) linked up with a computer. The voltage applied to the condenser plates could be varied down to about 5 mV which was significant for preventing voltage breakdowns in the interlayer; the frequency used was 1 MHz. To suppress the disturbing influence of the lead capacitance, of the lead resistances and the stray field high-grade coaxial cables with double screenage (Hewlett Packard) were employed. Lead effects were compensated by adjusting an electronic zero balance in the measuring instrument.

According to the kind of liquid to be investigated and the interlayer thickness the capacitance ranged from about 50 pF to about 10 nF.

The displacement of the bottom part of the condenser and together with this that of the planar condenser plate could be measured by an optical method (RM 600, Rodenstock) which works with a laser diode emitting infrared radiation at a wavelength of about 800 nm. This optical technique was supported by the operation of a displacement transducer (8AGZ 0.5, Sangamo, Schlmberger). This system had three ranges of measurement, the most accurate cue (3 μm) had a limit of resolution of 2 nm.

A particular difficulty encountered in the construction of the apparatus was the search for suitable material for manufacturing the conductive condenser plates. Indeed, vitreous carbon (Sigradur K from Sigri Elektrographit, GmbH, Meitinghen) proved to be useful substrate. It consists of phenol resins which during a slow process at about 3000 °C turn into pure carbon by pyrolysis. Because of its special molecular skeleton glassy carbon displays on its surface open pores with a diameter of about 1–3 nm.

This is, of course, a limit for applying a high-grade politure. With respect to our experiments it is of great importance that vitreous carbon has a good electrical conductance. The spherically formed circular condenser plate was given a curvature radius of 150 mm.

Experimental procedure

Cleaning of the measuring condenser

In order to remove any polluting surface films the vitreous carbon plates were in the first instance treated with hot chromosulfuric acid, then with tripled distilled water, and finally with ethanol and *n*-pentane which had been carefully purified before use. The plates were then run dry in a flow box. All other separate parts of the measuring cell were cleaned in the same way, only the treatment with chromosulfuric acid was omitted. Before each start of an experiment the condenser was composed very cautiously from its separate parts in the flow box just mentioned.

Determination of the contact point between the condenser plates

Determination of the separation distance between the condenser plates required the definition of a reference point on the common central axis. This point could be experimentally indicated by bringing about a short-circuit between plates associated with the flow of an electric current from 4 μA up to about 90 μA. Considering the mean surface roughness of the plates (1–3 nm) and the accuracy of the optical measuring system (2 nm) the maximum error in fixing the contact point should not exceed 5–6 nm.

Measurement of the no-load capacitance

For calculating the permittivity of the test liquid from the capacitance of the filled condenser precise knowledge of the no-load capacitance was necessary. Figure 6 reflects

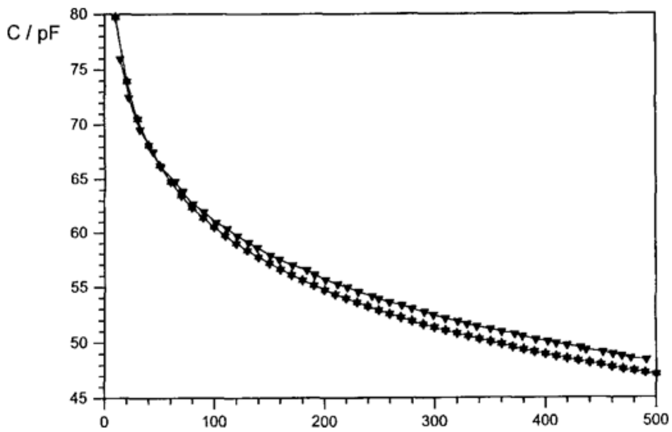

Fig. 6 Comparison of the calculated with the experimentally obtained capacitance * iteration method -- integral method - △ - measured no-load-capacitance

the distance dependence of the no-load capacitance calculated by the iteration and the integral method, as outlined in this paper and as found by experiment. To be sure, the deviations which become larger with increasing plate distances played a minor role only.

Problem of measuring separation distances in the condenser filled with water

When fixing the contact point by leveling the planar plate a specific difficulty arose with great regularity, when comparing tests with dry nitrogen as the interlayer medium with those in the presence of water. In the first case a very small pressure force brought about a typical metallic contact. In the later case, however, closing the circuit required a noticeable squeezing force to overcome an electric resistance which was obviously due to an extremely thin water layer between the plates. But the critical nature of this effect was that it caused an apparent shift of the contact point by which the plate distances appeared too large.

By a particular approach we succeeded in solving this problem fairly well. We made the reasonable assumption that, for example, separation distances $h \geq 500\,\mu$m the magnitude of anomalous apparent dielectric surface effects might be neglected; in principle, under these circumstances, practically the bulk value of the dielectric constant should be found. Starting from this sophisticated model a computer program was developed which, on the basis of the experimental data obtained, finally provided a realistic permittivity plate distance diagram.

The question of dielectric saturation phenomene

The special construction of the condenser with very closely spaced plates suggested that rather strong electric fields might arise in the liquid interlayer leading to dielectric saturation phenomena which are likewise associated with dielectric saturation phenomena. Tests with *n*-butanol as the interlayer medium by applying potential drops with amplitudes of 10 mV, 100 mV, and 1 V in the separation regime 50 nm–0.95 μm provided with the limits of error identical diagrams. Typical for all tests was a noticeable drop of the dielectric constant below a plate separation distance of 20 nm which was obviously due to molecular immobilization effects [9].

Results

In Fig. 7 the effective dielectric constant ε_r of water in a thin layer confined by two vitreous carbon plates at a temperature of 19.8 °C as a function of the plate separation distance is shown.

The simple relation

$$\varepsilon_r = \frac{C(h)}{C_0(h)} \tag{20}$$

is taken as a basis for the experimental determination of ε_r.

$C(h)$ is the load capacitance and $C_0(h)$ the no-load capacitance of the condenser both for a leveled separation distance h. $C_0(h)$ was determined by performing tests with the condenser filled with dry nitrogen.

In Fig. 7 the straight portion of the curve for $h > 0.5\,\mu$m which is obtained by experimental runs parallel to the abscissa. From this portion the bulk value $\varepsilon_B = 81.31$ for water at 19.8 °C can be derived which, in fact, exceeds the literature value [10] by only about 1.5%. This supports the correctness of our experimental method and advocates the applicability of our method.

At first sight the dielectric anomalies which become evident for plate distances $h < 0.3\,\mu$m might be regarded as a direct consequence of orientational immobilization of water near the two hydrophobic surfaces. To substantiate this view results referring to analogous tests with a polar liquid *n*-heptane are presented in Fig. 8. In fact, in this case, as is expected, no dielectric surface anomalies come into play as long as the plate separation is not too small to give rise to artificial effects.

Computer simulations of the dielectric anamolies in thin water layers bounded by two solid surfaces

An interesting study has been the attempt to model the distance dependence of the effective dielectric constant ε_r by fitting the simulated diagram to that which was obtained by experiment. This problem could, according to

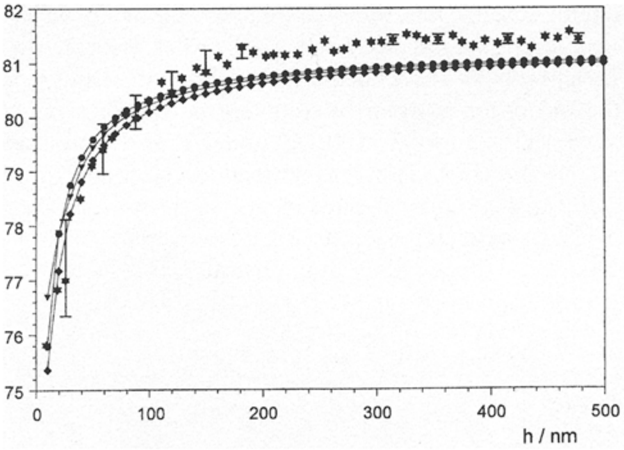

Fig. 7 Dielectric constant of water in an interlayer confined by two glassy carbon plates as dependent on the interlayer thickness at 19.8 °C. Measuring frequency 1 MHz. Inserted are the three calculated simulation curves -●- calculation I -▼- calculation II -◆- calculation III -*- data obtained by experiment

our experience, be treated by the iteration method outlined in the foregoing (Fig. 3). Equation (19) was taken as the basis for calculation. To be sure, h appears as the independent variable but according to

$$h + 2a + 2b + c \tag{21}$$

it becomes evident that we have the freedom to dispose of the layer thicknesses a and b if only the layer thickness c is left as the proper variable parameter.

Figure 7, in addition to the data obtained by experiment, reflects the results of three simulation calculations. In these the adsorbed layer thickness $a = 0.28$ nm [11] is always kept constant, but the space distance b of the transition layer and the dielectric constant ε_s of the adsorbed layer are subjected to variation. ε_s is with reference to literature data [4, 12, 13] varied between 5 and 10, b is altered from 1 nm up to 12 nm.

As stressed in the foregoing we must be aware that, for example, the use of ε_s for the adsorbed monolayer can only be a very crude approximation which prevents deriving details of vicinal water structure from the data obtained.

By fitting the calculated data to those attained by experiment the decay length α^{-1} can be evaluated for each of the three calculated curves. For $h > 0.15\,\mu$m there is a notable deviation from the experimental data, evidently due to the use of the very crude model.

Discussion

The results of the present study obviously add further evidence to the occurrence of structured immobilized water, particularly at hydrophobic surfaces. At any rate the dielectric anomalies seem not to be created by

i) too great roughness of the vitreous carbon surfaces
ii) mechanical instability of the moveable condenser plate system
iii) pollution of the vitreous carbon surfaces and the test water
iv) thermal drift of the displacement indicating instrumentation.

The surface roughness of the condenser plates did not exceed the order of a few nm which is by far much smaller than the closest surface separations adjusted during experiment.

A special vibration-free positioning of the whole device prevented the occurrence of a disturbing noise level in the measuring cell, as can be checked by employing displacement transducers. Taking extreme care of cleaning the condenser system prior to each experiment provided highly reproducible data. Precise thermostating kept the temperature within the measuring cell constant within ± 0.1 °C.

In order to meet with simple conditions we had from the first assumed that the dielectric constant of the liquid exhibited an exponential decay away from the solid surface.

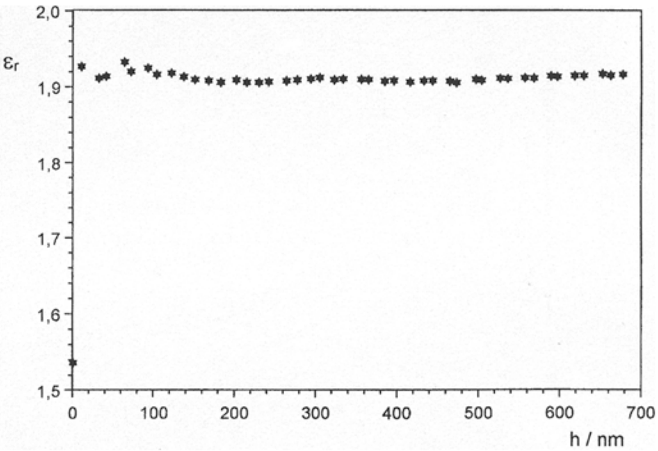

Fig. 8 Dielectric constant of n-heptane in an interlayer confined by two glassy carbon plates at 20 °C. Data obtained by experiment

Table 1 Simulation parameters

Calculation	ε_s	b/nm	α^{-1}/nm
I	5	1.0	0.10
II	9	12.0	1.07
III	6	8.0	0.71

The experimental evidence which we have obtained actually supports this assumption. To be sure, our findings are consistent with the existence of a decay length α^{-1} of about 1 nm, keeping in view that our model is rather crude.

In connection with our experiments it must be emphasized that Israelachvili and Pashley [14] determined the hydration forces between two microscopic curved hydrophobic surfaces in water. Over the distance regime extending from 1 up to 10 nm they detected a decay length of interaction in the order of 1 nm in excellent accord with the postulation by Marcelja et al. [15].

Surveying the body of papers which have appeared with reference to investigation of surface solvation effects by employing the method of disjoining force measurements in thin aqueous interlayers [16, 17] let us stress the point that the present method provides results for individual solvation layers without the occurrence of mutual interpretation of solvation layers which creates highly complex conditions.

Acknowledgement Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

1. Young DM, Crowell AD (1962) Physical Adsorption of Gases Butterworths, London
2. McIntosh R (1966) Dielectric Behaviour of Physically Adsorbed Gases. Marcel Dekker, New York
3. Zhilenkov AP (1963) Abstract of Doctor's Dissertation. Institute of Physical Chemistry of the Academy of Sciences, USSR
4. Metzik JS, Perevertaev VD, Liopo VA, Timoshchenko GT, Kiselev AB (1973) J Colloid Interf Sci 43:662
5. McCafferty E, Zettlemoyer AC (1971) Discuss Farad Soc 52:239
6. Geiger H, Scheel K (1926) Handbuch der Physik Bd 12, Springer-Verlag
7. Peschel G, Schnorrer R (1974) Ber Bunsenges Phys Chem 78:1286
8. Peschel G, Schnorrer R (1974) Ber Bunsenges Phys Chem 78:1294
9. Stobbe H, Peschel G, being prepared
10. Conway BE, Desnoyers JE, Smith AC (1964) Phil Trans Roy Soc London 256:389
11. Weast RC (1977) CRC Handbook of Chemistry and Physics, CRC Press, Cleveland
12. Gupta A, Shamura MM (1992) J Colloid Interf Sci 149:392
13. Luck WAP (1974) Structure of water and aqueous solutions, Verlag Chemie, Weinheim
14. Israelachvili JN, Pashley RM (1982) Nature 300:341
15. Marcelja S, Mitchell DJ, Ninham BW, Sculley MJ (1977) J Chem Soc Faraday
16. Israelachvili JN (1985) Intermolecular and Surface Forces, Academic Press
17. Peschel G, Belouschek P, Müller MM, Müller MR, König R (1982) Colloid Polym Sci 260:444