Thermodynamic Investigations of Thin Liquid Layers Between Solid Surfaces

II. Water Between Entirely Hydroxylated Fused Silica Surfaces

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By a special method the disjoining pressure of water caused by a molecular long range orientation between fully hydroxylated and highly polished fused silica surfaces at different temperatures (0—74 °C) and plate distances ≤ 1000 Å was determined. Four marked maxima were found at about 15°, 32°, 45°, and 61 °C for not too small plate distances. At these temperatures many authors have detected anomalies in the temperature dependence of some physical properties of water. This evidence is discussed in regard to our results which particularly imply thermodynamic quantities derived from the aqueous surface zone.

Many experimental observations have led to unequivocal evidence that the properties of water in the vicinity of solid surfaces differ from those of the bulk liquid[1]. This could be especially demonstrated by DERYAGIN[2] already in 1933 who succeeded in measuring the modulus of rigidity of water layers having a thickness up to 1500 Å and existing between a convex lens and a planar plate both made of glass. Recent determinations of the same property by DERYAGIN and coworkers[3] led again to a boundary thickness of about 1600 Å.

Another sort of experiment was carried out by DERYAGIN and OBUCHOV[4] who pressed flat plates of mica or steel, immersed in water, against each other and detected a disjoining pressure at plate distances of about 10^{-4} cm and smaller. This pressure, keeping the surfaces apart and ranging in the order of $10^4 - 10^5$ dyne/cm^2, was attributed to a molecular long range orientation in the vicinity of solid surfaces and to a corresponding decrease of the chemical potential in the surface zone compared with that of the bulk liquid.

Further experiments by DERYAGIN et al.[5] revealed the existence of a disjoining pressure even in a liquid layer between a gas bubble and a planar mica surface, the equilibrium thickness of a water film being 300 Å at room temperature for a given gas pressure. The film thickened with decreasing and thinned with rising temperature.

That boundary layers of water exhibit liquid-crystalline properties, was pointed out above all by DERYAGIN and GREENE-KELLY[6] who could show that layers of water about 200 Å thick were formed between the silicate layers of swollen montmorillonite. The viscosity of boundary water likewise differs appreciably from that of the bulk[7, 8].

A today well-known problem can be brought into connection with all these phenomena. Some years ago DERYAGIN and FEDYAKIN[9] reported that water in quartz capillaries forms liquid columns with anomalous properties when condensation takes place from the vapor phase. Since the radii ($2 \cdot 10^{-4}$ cm $- 10^{-2}$ cm) of the capillaries used were rather large, so that the influence of the capillary walls could not completely account for the anomalous properties of the liquid columns, DERYAGIN regarded the anomalous water as a new modification. In the last months, however, papers were published which actually present evidence against the existence of anomalous water[10, 11]. Particularly, most of the

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[1] J. C. HENNIKER, Rev. Mod. Phys. **21**, 322 [1949].

[2] B. V. DERYAGIN, Z. Phys. **84**, 657 [1933].

[3] B. V. DERYAGIN, Disc. Faraday Soc. **42**, 109 [1966].

[4] B. V. DERYAGIN and E. OBUCHOV, Acta Physicochim. URSS **5**, 1 [1936].

[5] B. V. DERYAGIN and M. M. KUSAKOV, Acta Physicochim. URSS **10**, 25, 153 [1939]; Izv. Akad. Nauk SSSR, Ser. Khim. **5**, 1119 [1937]. — B. V. DERYAGIN, M. M. KUSAKOV, and L. LEBEDEVA, Dokl. Akad. Nauk SSSR **23**, 671 [1939].

[6] B. V. DERYAGIN and R. GREENE-KELLY, Trans. Faraday Soc. **60**, 449 [1964].

[7] A. KLEMM, Phys. Z. **39**, 783 [1938].

[8] G. PESCHEL and K. H. ADLFINGER, Ber. Bunsenges. Physik. Chem. **74**, 351 [1970]; Naturwiss. **56**, 558 [1969].

[9] B. V. DERYAGIN and N. N. FEDYAKIN, Dokl. Akad. Nauk SSSR **147**, 402 [1962].

[10] D. H. EVERETT, J. M. HAYNES, and P. J. MCELROY, Nature London **226**, 1033 [1970].

[11] M. DE PAZ, A. POZZO, and M. E. VALLAURI, Chem. Phys. Letters **7**, 23 [1970].

"anomalous" water specimens left behind a jelly-like residue on evaporation. This residue turned out to be silicic acid to a notable amount[11], and therefore it cannot be excluded that "anomalous" water is a hydrosol of silicic acid with long range oriented solvation shells. In this way the problem of "anomalous" water is closely related to that presented in this paper.

I. Experimental Determination of the Disjoining Pressure between two Solid Surfaces

If two highly polished fused silica discs are immersed in water and brought into face to face contact, a repulsive force arises when the plate distance is smaller than about 1000 Å. This simple device, however, implies two serious problems. First, the plates cannot be kept exactly parallel throughout the measurement; second, one is faced with appreciable difficulties in defining the plate distance since the surface roughness even of highly polished ($\lambda/20$) surfaces lies in the order of magnitude of the depth of molecular long range orientation. In order to avoid the first of these problems, we used a plate system with one plate planar and the other one spherical (curvature radius $R = 100$ cm)[12]. Besides, dust particles are not as disturbing in this system as in the plane-parallel system[13]. Presuming the dependence of the disjoining pressure on distance to be

$$\Pi(\xi) = C\,e^{-n\xi} \tag{1}$$

where ξ is the distance between two corresponding surface elements facing each other, and C and n are parameters which must be determined experimentally, we succeeded[14] taking account of the surface roughness presented in form of a surface profilogram[15]. Just this point was neglected hitherto by authors investigating boundary layers. As a basis for the evaluation of C and n we obtained the equation:

$$\begin{aligned} {}^{k}K = 2\,\pi\,C\,e^{-nh}\Big[& \frac{e-nfr_f}{n^2\,f^2} + \frac{R}{n}\exp\{-n(r_g{}^2/2\,R + 2\,R_b\} \\ & - \frac{1+n\,f\,r_g}{n^2\,f^2}\exp\{-n\,f(r_g + r_f)\}\Big]\,. \end{aligned} \tag{2}$$

h is the smallest plate distance in the planar/spherical system, ${}^{k}K$ is the contact force with which the plates are pressed against each other, R_b represents the level in the surface profilogram to which the roughness is smoothed by pulling down the humps and filling up the valleys; f, r_f, and r_g are parameters of the interlocking surface asperities[14]. Eq. (2) can also be written:

$${}^{k}K = a^2\,\pi\,\Pi(h) \tag{3}$$

where a is the radius of a virtual circular area. Taking the logarithm of Eq. (3) the relation:

$$\ln {}^{k}K = \ln(a^2\,\pi\,C) - n\,h \tag{4}$$

is obtained. Plotting $\ln {}^{k}K$ vs. h the parameters C and n can be determined. A number of such plots are represented in one of the cited papers[14] giving fairly good straight lines for $h > 0$, i. e. before the plates get into contact.

In our experimental set-up[12] the planar fused silica plate is mounted to the bottom of a container which can take up the water to be investigated. The spherically formed plate facing the planar one is fastened to one end of a balance which can be moved by operating an electromagnet fed by a stabilized power supply. The deflections of the balance which correspond to different plate distances can be measured by an inductive displacement transducer connected with an electronic strain gauge measuring bridge which is followed by an xy-recorder.

The apparatus is placed in a big kettle which can be evacuated in order to suck the water into the container. In this way the formation of disturbing gas bubbles in the region between the plates is entirely excluded. The water used for investigation and thermostated to about ±0.2° in the range 0 – 74 °C was distilled from a weakly alkaline potassium permanganate solution. The electrical conductivity was less than 10^{-6} [Ω^{-1} cm^{-1}].

II. Special Thermodynamic Relations for Liquid Boundary Layers

Presuming the existence of a disjoining pressure in a liquid boundary layer the free energy which is required to approach two surface areas, each having 1 cm^2, from a plate distance h^+ to a distance

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[12] G. Peschel, Z. Physik. Chem. (N.F.) **59**, 27 [1968].

[13] A. T. J. Hayward and J. D. Isdale, Brit. J. Appl. Phys. (J. Phys. D) Ser. 2, **2**, 251 [1969].

[14] K. H. Adlfinger and G. Peschel, Z. Physik. Chem. (N.F.) **70**, 151 [1970]; Z. Angew. Physik **29**, 136 [1970].

[15] K. H. Adlfinger and G. Peschel, Z. Angew. Physik **29**, 265 [1970].

$h < h^+$ is given by:

$$(\varDelta F^{\mathrm{E}})_h = - \int_{h^+}^{h} \Pi(h')\, \mathrm{d}h'. \qquad (5)$$

The index "E" denotes the fact that $(\varDelta F^{\mathrm{E}})h$ and all its subsequent derivatives are excess quantities. Now let us regard a liquid layer of infinitesimal thickness in the central plane between two unit surface areas. The work to remove this layer, i. e. diminishing h by dh, is consequently:

$$\mathrm{d}(\varDelta F^{\mathrm{E}})_h = - \frac{\partial (\varDelta F^{\mathrm{E}})_h}{\partial h}\, \mathrm{d}h\, . \qquad (6)$$

In the real case, the layer thickness under consideration cannot be less than a molecular diameter $\varDelta h$. As long as $\varDelta h \ll h$ is valid, Eq. (6) must thus be written in the form:

$$\varDelta(\varDelta F^{\mathrm{E}})_h = - \frac{\partial (\varDelta F^{\mathrm{E}})_h}{\partial h}\, \varDelta h \qquad (7)$$

where $\varDelta(\varDelta F^{\mathrm{E}})_h$ has the character of a differential excess free energy.

Exact conversion into the molar quantity $\varDelta(\varDelta F^{\mathrm{E}}_{\mathrm{m}})_h$ is only possible if the density of the liquid surface zone and its corresponding distance dependence is known. In default of better data we regard the surface zone as having the density of bulk water, but one must account for the fact that the error made by evaluating molar quantities for the liquid surface zone might be of the order of 20% and more[16].

The temperature derivative of $\varDelta(\varDelta F^{\mathrm{E}}_{\mathrm{m}})_h$ is defined as the differential molar excess entropy $\varDelta(\varDelta S^{\mathrm{E}}_{\mathrm{m}})_h$ of the molecular layer in question. Using the definition

$$\varDelta(\varDelta F^{\mathrm{E}}_{\mathrm{m}})_h = \frac{M}{\varrho} \frac{\varDelta(\varDelta F^{\mathrm{E}})_h}{\varDelta h} = \frac{M}{\varrho}\, C\, e^{-nh} \qquad (8)$$

$\varDelta(\varDelta S^{\mathrm{E}}_{\mathrm{m}})_h$ writes:

$$\varDelta(\varDelta S^{\mathrm{E}}_{\mathrm{m}})_h = \frac{M}{\varrho} \left[\frac{C}{\varrho}\, e^{-nh} \frac{\mathrm{d}\varrho}{\mathrm{d}T} - e^{-nh} \frac{\mathrm{d}C}{\mathrm{d}T} + h\, C\, e^{-nh} \frac{\mathrm{d}n}{\mathrm{d}T} \right]. \qquad (9)$$

The corresponding differential total molar excess energy can be obtained by the relation of HELMHOLTZ:

$$\varDelta(\varDelta U^{\mathrm{E}}_{\mathrm{m}})_h = \varDelta(\varDelta F^{\mathrm{E}}_{\mathrm{m}})_h + T\, \varDelta(\varDelta S^{\mathrm{E}}_{\mathrm{m}})_h\, . \qquad (10)$$

In deriving thermodynamic quantities introduced above one must be sure that Π, when being measured, corresponds to an equilibrium state. This is actually the case for not too large plate distances ($h < 500$ Å), since no hysteresis was found in the data when approaching and separating the plates. Moreover, no alteration of Π was detected at constant temperature over a period of days. For larger plate distances, i. e. very small disjoining forces, it is difficult to attain equilibrium because vibrations of the upper plate arise which are due to the mechanical noise level and which partially destroy the orientation of the more distant water so that the disjoining pressure effect is apparently somewhat too small.

It should be emphasized that all thermodynamic quantities refer to a molecular layer under the influence of *two* solid surfaces. Because of the cooperative character of the orientational effects it is not possible to draw conclusions from these quantities on the properties of molecular layers influenced by only *one* solid surface.

III. Experimental Results

Using Eqs. (1) and (4), the disjoining pressure in water layers between fully hydroxylated fused silica surfaces was determined for the temperature range 0 – 63 °C. At 74 °C and above no effect could be detected. For each temperature chosen, Eq. (4) yielded a straight line for sufficiently small values of h. The results for n, based on three different measurements, are shown in Fig. 1; the mean values of n were obtained by drawing an average curve. The mean values for C can be found by a similar method, but in this case the scattering of the data is greater (cf[14]). The mean values of n and C are given in Table 1.

t [°C]	$n \cdot 10^{-6}$ [cm^{-1}]	$C \cdot 10^{-6}$ [dyne/cm^2]	t [°C]	$n \cdot 10^{-6}$ [cm^{-1}]	$C \cdot 10^{-6}$ [dyne/cm^2]
0	2.6	4.7	35	0.7	1.0
5.5	1.4	7.1	1.0	1.0	1.3
10	0.7	2.4	40	1.4	1.1
12.5	0.6	2.0	42.5	1.0	0.8
15	0.5	1,7	45	0.6	1.0
17.5	0.6	1.3	47.5	0.6	1.1
20	0.9	1.2	50	0.7	1.3
22.5	1.0	1.5	52.5	0.8	1.3
25	0.9	1.1	55	0.9	1.2
27.5	0.7	0.7	57.5	0.8	1.1
30	0.5	0.5	60	0.5	1.0
32.5	0.4	0.8	62.5	0.7	1.0

Table 1. Mean values of the parameters n and C for different temperatures.

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[16] B. V. DERYAGIN, D. S. LYCHNIKOV, K. M. MERZHANOV, YA. J. RABINOVICH, and N. V. CHURAEV, Dokl. Akad. Nauk SSSR **181**, 823 [1968]. — B. V. DERYAGIN, Z. M. ZORIN, and N. V. CHURAEV, Dokl. Akad. Nauk SSSR **182**, 811 [1968].

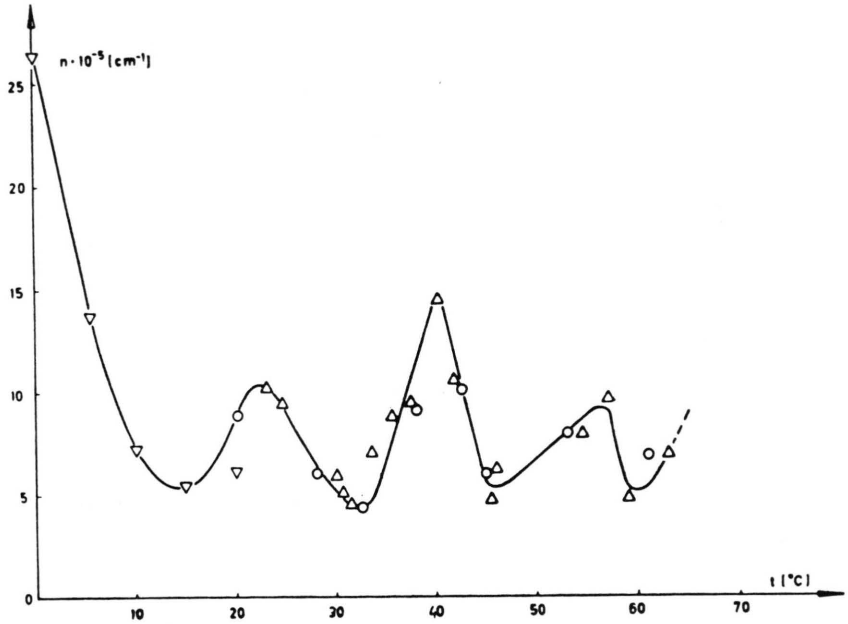

Fig. 1.
Temperature dependence
of the parameter *n*.
Three series of measurements.
(○, △, ▽) are presented.

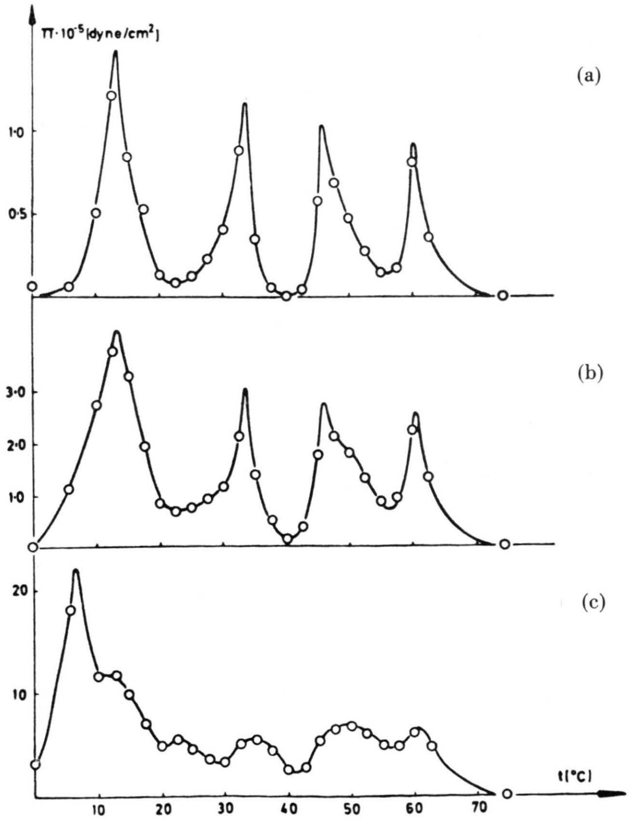

Fig. 2. Temperature dependence of the disjoining pressure for plate distances (a) 500 Å, (b) 300 Å, and (c) 100 Å.

In Fig. 2 the disjoining pressure $\Pi(h)$ calculated by Eq. (1) with $\xi = h$ is plotted against temperature for $h = 100,300$ and 500 Å. In accordance with DERYAGIN and OBUCHOV [4], the order of magnitude of the disjoining pressure lies in the range $10^4 - 10^6$ dyne/cm². First measurements carried out by us in this field lacked sufficient accuracy [17]. A new and striking evidence is the existence of several maxima of the disjoining pressure. For $h = 300$ Å and larger plate distances the maxima are found at about 15°, 32°, 45°, and 61 °C.

Other anomalies of water have been discovered at these temperatures [18]. For plate distances smaller than about 300 Å the maxima are less pronounced and their positions are slightly shifted. For $h = 100$ Å new maxima are evident at about 8°, 12°, 23°, 35°, 50°, and 60 °C.

In Fig. 3 the differential molar free excess energy $\Delta(\Delta F_{\mathrm{m}}^{\mathrm{E}})_h$ derived from Eq. (8) is plotted against the temperature for $h = 500$ Å. Because of the very small temperature dependence of ϱ the values of $\Delta(\Delta F_{\mathrm{m}}^{\mathrm{E}})_h$ are almost proportional to those of $\Pi(h)$. For the whole range of plate distances between 100 and 500 Å and temperatures between 0 and 63 °C the values of $\Delta(\Delta F_{\mathrm{m}}^{\mathrm{E}})_h$ lie between $3 \cdot 10^{-4}$ and 0.77 cal/mole.

The corresponding diagram of the differential molar excess entropy $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h$ calculated by Eq. (9)

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[17] G. PESCHEL and K. H. ADLFINGER, Naturwiss. **54**, 614 [1967].

[18] W. DROST-HANSEN, Ind. Eng. Chem. **57** (4), 18 [1965]; **61** (11), 10 [1969].

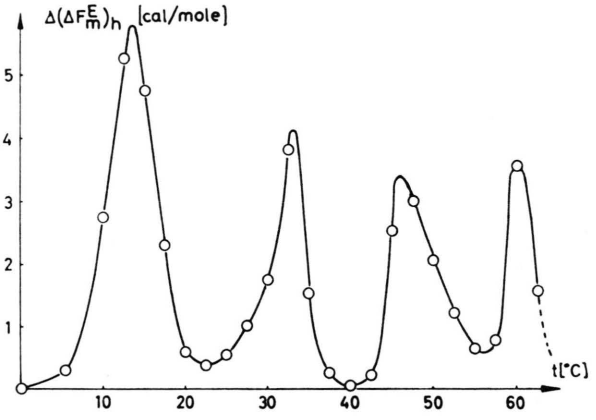


Fig. 3. Temperature dependence of the differential molar free excess energy for a plate distance of 500 Å.

is given by Fig. 4. Since $\Delta(\Delta S^E_m)_h$ is the negative temperature derivative of $\Delta(\Delta F^E_m)_h$ the entropy function must show zero points at the characteristic temperatures mentioned.

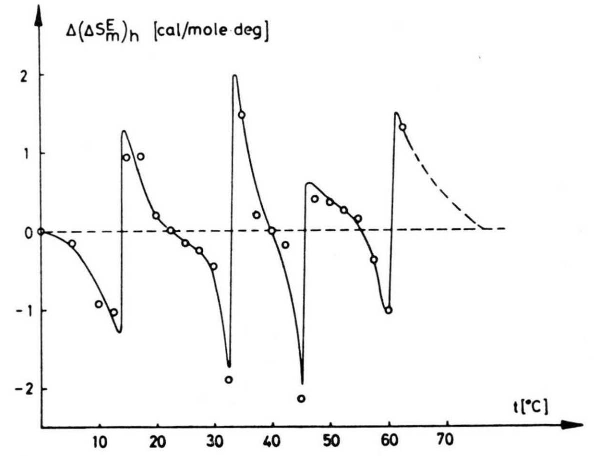


Fig. 4. Temperature dependence of the differential molar excess entropy for a plate distance of 500 Å.

The temperature dependence of the differential molar total excess energy $\Delta(\Delta U^E_m)_h$ is represented by Fig. 5. The great similarity with the diagram in Fig. 4 is due to the fact that the entropy term in Eq. (10) largely outweighs the free energy term. Consequently, it is admissible to assume the disjoining pressure to be created mainly by orientational effects in the liquid surface zone.

Choosing a plate distance of 100 Å, the differential excess energy obtained lies in the range between −33 and +30 cal/mole; for $h = 500$ Å, $\Delta(\Delta U^E_m)_h$ has still values between −4 and +4 cal/mole. These results, which may imply an error of perhaps ±80% nevertheless demonstrate the fact that $\Delta(\Delta U^E_m) \ll RT$.

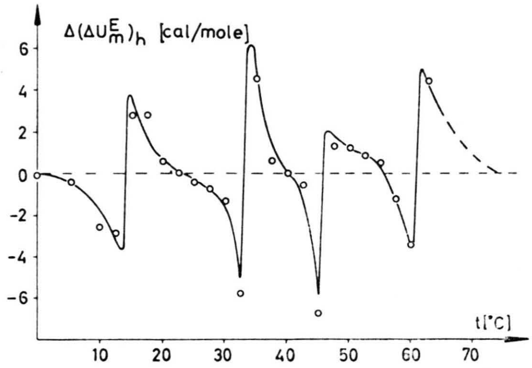


Fig. 5. Temperature dependence of the differential molar total excess energy for a plate distance of 500 Å.

The values of the differential molar excess heat $\Delta(\Delta C^E_{v,m})_h$ maximally change between +2 and −1 cal/mole·K for $h > 100$ Å. Finally, in Fig. 6 the plate distance h^+ at which $\Pi = 10^4$ dyne/cm² is reached, is plotted against temperature. The representation gives an impression of the extension of the long range orientation. These values must not be mixed up with the real values of the surface zone extension because our apparatus lacks sensitivity for very small disjoining pressures.

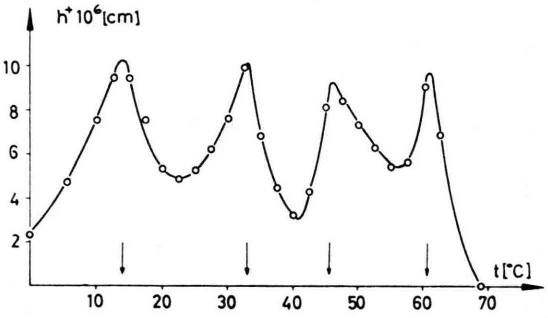
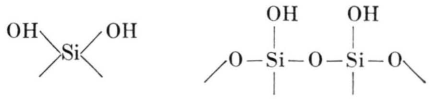


Fig. 6. Temperature dependence of the plate distance h^+ at which $\Pi = 10^4$ dyne/cm² is reached.

IV. Water Adsorbed on Silica Surfaces

The oriented liquid surface zone was bounded by two fused silica surfaces entirely covered by hydroxyl groups. In order to start our investigations under these conditions the fused silica plates were placed in a moist atmosphere for some months[19]. Fully hydroxylated fused silica plates contain about five OH-groups[20] per 100 Å^2. After Kiselev and Muttik[21] the first adsorbed layer of water molecules is bound to the surface hydroxyls by means of one or two hydrogen bonds. The surface hydroxyl groups may exist in two states:



Water adsorbed on silicate surface and hydrogen bonded to the surface hydroxyls is localized and partially immobilized as could be proved by nmr-results[22]. Water molecules of the second layer bound to the first layer will consequently also show some immobilization and a changed packing density compared with that in bulk water. Similar conditions will be found in the following molecular layers, the effect decaying rather slowly with the distance from the surface.

V. Discussion

Generally speaking the results of Deryagin and coworkers could be confirmed, but for the extension of the surface zone between fused silica plates we found smaller values due to the insensitivity of our set-up for larger plate distances. Another method which was developed by us and refers to the determination of the surface zone viscosity of water yields Deryagin's value (1500 Å at about room temperature) when account is taken of the surely not negligible surface roughness of the polished fused silica plates[8]. If the surface zone effect were created by only long range dispersion forces it had to be much smaller and proportional[23] to h^{-3}. In the present case there is certainly involved an additional special solvation effect of the solid surfaces. In trying to describe the distance dependence of the disjoining pressure the exponential form of Eq. (1) proved to work very well[14].

As a matter of fact, numerous dipolar organic liquids investigated by us showed likewise an anomalous behaviour by exerting a disjoining pressure between fused silica plates, but, moreover, only in a small limited temperature range which could be ascribed to a rotational transition of the liquid molecules[24]. Comparing water with other liquids (e. g. halogenobenzenes, pyridine, benzonitrile, nitrobenzene, aniline) it is difficult to understand why water, the molecules of which are smaller and less anisotropic in shape than those of the liquids cited above, should yield the larger extension of the surface zone.

Concerning the molecular rotational motions in bulk water Magat[25], on the basis of spectroscopic evidence, advocates the view that the temperature range around 35 °C is that of a rotational transition about the molecular C_2-axis. On the other hand, the fact that the disjoining pressure of water shows four maxima (for $h > 300$ Å) opposes the assumption that these are only due to rotational transitions.

It is of some interest for the present work that Deryagin[16, 26] developed an own concept for the structure of "anomalous" water which he believes to be composed of small molecular aggregates. If the "anomalous" water is actually long range ordered water vicinal to silicic acid particles, Deryagin's concept has strong relations to our problem. Obviously, the piling up of molecular aggregates which might be loosely connected by hydrogen bridges, should lead to a wider range of orientation than in the case of monomers so that the large effect of water could be explained in this way. A related subject was published by Deryagin and coworkers[27], who found that the anomalous surface zone effects get larger with the size of the molecules participating in the packing effect; the authors used polyvalent ethers in these experiments.

[19] S. P. Zhdanov, Dokl. Akad. Nauk SSSR **123**, 716 [1958]. — B. V. Iljin, V. F. Kiselev, and K. G. Krasilnikov, Vestnik. Moskov. Univ., Ser. Math. Mekh., Astron., Fiz. Khim. **12**, 35 [1957].

[20] H. P. Boehm, Kolloid-Z. Z. Polymere **227**, 17 [1968]. — A. A. Agzamkhodzaev, L. T. Zuravlev, and A. V. Kiselev, Izv. Akad. Nauk SSSR, Ser. Khim. **1968**, 1186.

[21] A. V. Kiselev and G. G. Muttik, Jubilee Conf. Moscow State Univ. **1955** (1).

[22] D. M. Anderson, J. Colloid Interf. Sci. **25**, 174 [1967]. — T. Wu, J. Geophys. Res. **69**, 1083 [1964].

[23] J. Frenkel, Kinetic Theory of Liquids, Dover Publications, Inc., New York 1955.

[24] K. H. Adlfinger and G. Peschel, Disc. Faraday Soc. (in press); paper presented at the Discussion of the Deutsche Bunsenges., Molecular Motion in Liquids, Herrenalb 1970. — R. Schnorrer and G. Peschel, being prepared.

[25] M. Magat, Disc. Faraday Soc. **33**, 114 [1937].

[26] B. V. Deryagin, I. G. Ershova, V. K. Simonova, and N. V. Churaev, Teor. Eksp. Khim. **4**, 527 [1968].

[27] N. N. Zakhavaeva, B. V. Deryagin, A. M. Khomutov, and S. V. Andreev, Research in Surface Forces, ed. B. V. Deryagin, Vol. II, p. 156, Consultants Bureau, New York 1966.

Furthermore, the existence of four maxima of the disjoining pressure were not so dubious if they might be created by different molecular aggregates which Drost-Hansen [18] considers to be possible elements of bulk water structure, stabilized in limited temperature ranges. If postulating the existence of such aggregates which is moreover done by Frank and Quist [28] and in a certain way by Wicke [29] the "uniform structure" models of water are obviously ruled out in favour of the mixture models.

Additional evidence for the existence of the temperature ranges in question was given by determining the surface zone viscosity η_G of water between fused silica plates [8]; η_G displays maxima just at the same temperatures as the disjoining pressure. Calculations of the corresponding activation energies of flow point also to a special mechanism mainly determined by small structural units in the surface zone.

A well-known model for the zone of changed water structure is introduced by Frank and Wen [30] (Fig. 7) for the case of the hydration shell of an ion. In region A the water dipoles are all oriented to the central ionic charge and are highly immobilized so that water in this region is said to be more ordered than in the bulk phase. Water in region B is subject to the orienting forces of the ion and the directional forces of the mainly tetrahedrally structured distant water as well; zone B exhibits a larger disorder than the bulk liquid C.

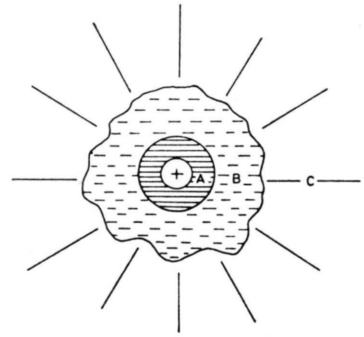


Fig. 7. Model of the hydration shell of an ion after Frank and Wen.

It has been established that – similar to the case of a polar solid surface – the ability of ions to alter the vicinal structure of water depends on the strength of the primary ion-water interaction, on the polarization of water molecules by the primary complexes, and on the degree of structural mismatch between the primary hydration complex and the normal water structure. The 'water-like' solvent structure in numerous electrolyte solutions leads to the presumption that "remnants" of water structure might exist even in the presence of the electrostatic field of an ion. Drost-Hansen [31] emphasizes that the "kinks" found for many physical properties of electrolyte solutions at the characteristic temperatures 15°, 32°, 45°, and 61 °C favour the concept of structural groupings of water existent in such solutions. This presumption is supported by calculations made by Vaslow [32] who suggests that ions – at least smaller ions – may suffer incorporation into the structural groupings so that the ion is surrounded by water molecules linked by hydrogen bonds.

A very accurate work in this respect seems to have been done by Blandamer et al. [33]. They found that the first absorption band maximum of iodide in aqueous solutions is extremely sensitive to temperature. This temperature function can be represented by stepwise linear portions, the kinks lying at 11.1°, 24.8°, 35.3°, 41.1°, 50.2°, 59.8°, 67.8°, 75.8°, and 81.0 °C. Possibly there might be strong relations to the additional characteristic temperatures we found at plate distances below 300 Å.

Disregarding electrolyte solutions the most reliable and direct study of small molecular aggregates of water was certainly made by Pimentel et al. [34]; their ir-spectroscopic investigations yielded results which can only be explained by assuming the formation of tri-, tetra-, and perhaps higher molecular units. The theoretical possibility of a resonance stabilization of cyclic groups of hydrogen bonded water molecules is discussed by Bass [35].

Concerning all the evidence that is particularly notable by thermal anomalies one has to draw the conclusion that the existence of structural groupings in hydration shells cannot be excluded at least. This,

[28] H. S. Frank and A. S. Quist, J. Chem. Phys. **34**, 604 [1961].

[29] E. Wicke, Angew. Chem. **78**, 1 [1966].

[30] H. S. Frank and W.-Y. Wen, Disc. Faraday Soc. **24**, 133 [1957].

[31] W. Drost-Hansen, Adv. Chem. Ser. **67**, 70 [1967].

[32] F. Vaslow, J. Phys. Chem. **67**, 2773 [1963].

[33] M. J. Blandamer, T. A. Claxton, and M. F. Fox, Chem. Phys. Letters **1**, 203 [1967].

[34] M. van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys. **27**, 486 [1957].

[35] G. E. Bass, Proc. Nat. Acad. Sci. US **62**, 345 [1969].

on the other hand, would support the concept of hydration shells to be looked upon as reduced oriented surface zones.

The possibility that the experimentally found disjoining pressure is mainly caused by electrostatic effects of ionic double layers at the solid surfaces might be ruled out because of the extreme purity of the water used. The complicated temperature dependence of the disjoining pressure turned out to be highly reproducible within the limits of error.

The origin of the disjoining pressure was discussed by DERYAGIN[5] already in 1937. For the present case he quoted a diagram shown in Fig. 8. This graph says that a positive disjoining pressure (connected with a repelling force) increases with dropping plate distance, but that it turns over to a negative disjoining pressure due to a relatively strong solid/solid attraction force at sufficiently small plate distances. This effect was thoroughly discussed by FRENKEL[23]. For larger plate distances the solid/liquid interaction leading to extensive solvate layers outweighs the solid/solid interaction that can be derived from long range dispersion forces. Our special experimental design admits only positive disjoining pressures to be open for investigation.

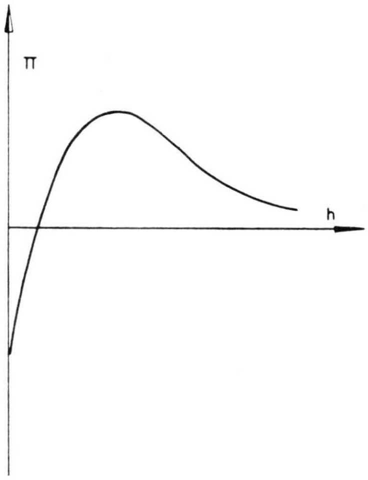


Fig. 8. Distance dependence of the disjoining pressure for the common case.

The order-disorder problem of an aqueous surface zone was treated by DROST-HANSEN[18] in 1969. His considerations are based on the graph shown in Fig. 9. This diagram says that water directly vicinal to the solid surface is always more ordered than bulk water, which is in accordance with the concept that water bound to surface hydroxyl groups is highly immobilized. At larger plate distances a range of higher disorder should be found until the structure of the bulk liquid is reached. The disordered range is due to the mismatch between the structure of the first adsorbed layer and the bulk structure. If this mismatch is appreciably large the zone of disorder might become very extensive. But Drost-Hansen's model seems to be much too simple in respect to the alternating temperature function of $\Delta(\Delta S^{\mathrm{E}}_{\mathrm{m}})_h$ (Fig. 4) and might only reflect special conditions which follow in their main features the model of Frank and Wen for hydration shells of ions (Fig. 7).

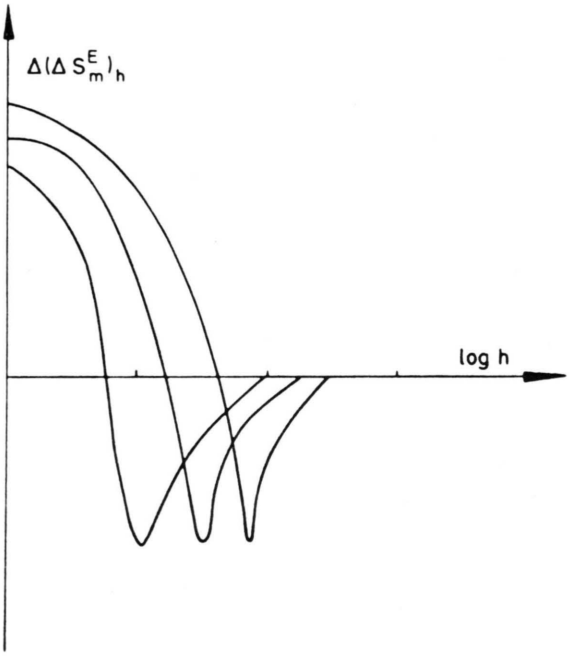


Fig. 9. Differential molar excess entropy $\Delta(\Delta S^E)_h$ vs. log h for water vicinal to highly polar surfaces (three possible curves after Drost-Hansen).

An explanation of our results might be given in the following way. Starting at the melting point one finds a disordered zone until 15 °C are reached. Directly vicinal to the surface a more ordered less extensive zone may exist. Within this temperature range the formation of small groupings of water seems to be favoured in the boundary layer with rising temperature. In the same extent a disjoining pressure arises since the free excess energy of the surface zone increases. At about 15 °C the small groupings probably undergo a "melting" process, and the disjoining pressure falls off until the existence range of another sort of structural grouping is reached which gets destroyed above 32 °C. In this way one can proceed in explaining the other two maxima at higher temperatures.

In comparison with the results obtained for other more simply structured liquids [24] one would regard the maxima to be at least partially due to structural transitions of higher order in the bulk since the present effects refer only to the difference between bulk water and the surface zone. To be sure, DROST-HANSEN [18] cites several papers which describe anomalies in physical properties of bulk water at about the characteristic temperatures, but till now no decision can be made if structural transitions of higher order really occur in the bulk liquid at these temperatures or if the observed anomalies are possibly due to some sort of "melting" processes of small structural entities vicinal to impurities still present in the water. Also the influence of the experimental designs which were used for these investigations and which might create likewise oriented surface zones on their part should by no means be underestimated.

Still another point must be mentioned. The removal of the molecular layer in the central plane between the fused silica surfaces might also be looked upon in a sense as a "melting" process. Phenomenologically, the total entropy of "fusion" for this layer can be written:

$$\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h = \Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h^{\mathrm{v}} + \Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h^{\mathrm{j}} . \qquad (11)$$

$\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h^{\mathrm{v}}$ is due to the volume increase which actually occurs during this "melting' process [16], for the "anomalous" water which could be compared with the oriented surface zone under certain aspects shows a density of about 1.2 – 1.4. $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h^{\mathrm{j}}$ is the change of molecular and/or intermolecular properties. Regarding the higher density in the surface zone $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h^{\mathrm{v}}$ should always be positive. On the other hand, the total entropy of "fusion" $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h$ can assume negative values in certain temperature ranges (Fig. 4). For these ranges the configurational part of the entropy $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h^{\mathrm{j}}$ is surely dominant which e. g. indicates a change of the number and the degree of bending of hydrogen bonds.

The change of the number of hydrogen bonds per molecule in the surface zone might be responsible to a large extent for the altered thermal conductivity of very thin water layers between sheets of mica, as was reported by METSIK and TIMOSCHENKO [36]. At lower temperatures the thermal conductivity of water layers was found to be tens of times larger than the normal bulk value. The effect vanishes at about 60 – 70 °C which is in excellent agreement with our findings.

Conclusional Comments

The present work confirms the view that the surface zone of water adjacent to a higly polar surface, such as fused silica covered with hydroxyl groups, is structurally changed over relatively large distances. Moreover, there is some reason to regard the aqueous surface zone at polar solid surfaces as an enlarged model of the hydration shell of an ion. In the case of "anomalous" water our work supports the view of many authors which believe that "anomalous" water is a hydrosol of silicic acid which on its part induces a long range orientation in the surrounding solvate layer.

DERYAGIN [37] in a recent paper ascribes to the aqueous surface zone a liquid-crystalline-like character and, moreover, the ability to form a new modification strikingly different from the bulk. But it must be emphasized that the values for $\Delta(\Delta S_{\mathrm{m}}^{\mathrm{E}})_h$ and $\Delta(\Delta U_{\mathrm{m}}^{\mathrm{E}})_h$ given in this paper are rather small and exhibit a strong distance dependence. Thus it remains a serious question if the surface zone actually represents a new structural modification.

The importance of thin water layers in biological tissues is evident and adds biophysical aspects to the problem treated above.

We are indebted to Prof. Dr. G. BRIEGLEB and the Deutsche Forschungsgemeinschaft for support of this work.

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[36] M. S. METSIK and G. T. TIMOSCHENKO, Issled. Obl. Poverkh. Sil., Sb. Dokl. III. Konf. **1966**, 456.

[37] B. V. DERYAGIN, Sci. Amer. **223** (5), 52 [1970].