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Recent Thermodynamic Data on Vicinal Water and a Model for Their Interpretation*

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Results of recent measurements on vicinal (i. e. surface modified) water are reported, particularly data for the density, thermal expansion coefficient, and viscosity. The results are discussed and related to previous studies, suggesting that vicinal water extends over large distances, probably in the range of 30 to 100 molecular diameters. It is proposed also that vicinal water is induced not only by proximity to a »solid« interface but may also occur as vicinal hydration of macromolecules larger than a certain minimum size, likely in the range of 1000 to 5000 Daltons. The temperatures (T_k) at which the thermal anomalies in the properties of vicinal water occur have been confirmed by an extensive DSC study. The critical temperatures are found to be independent of the chemical nature of the solid substrate, based on DSC measurements with porous quartz, polystyrene suspensions and diamond powder, thus lending credence to the reality of the »Paradoxical Effect«. Finally, a percolation model of vicinal water, based on the work by Stanley and Teixeira, is discussed. The model leads to a predicted value for the density of vicinal water of 0.97 g/cm^3 in good agreement with the observed value. However the model does not predict the occurence of the thermal anomalies.

I. INTRODUCTION

The primary purpose of this paper is to discuss some novel aspects of vicinal water. However, before elaborating on the more recent studies, a few examples will be discussed of previous evidence for vicinal water, together with an enumeration of other properties also suggesting the existence (and extent) of vicinal water.

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Earlier in this century the notion was quite prevalent that changes in solvent structure likely occurred at interfaces. Unfortunately, the evidence for this contention was often weak and indirect. Furthemore, no direct structure information was available and progress only made slowly in understanding the structure of bulk water — an undertaking which is, at present, still far from complete.At the same time, notable advances were made in the field of colloid and surface chemistry through theories such as the Deryaguin-Landau-Verway-Overbeek (DLVO) treatment of colloidal stability. In fact, few conceptual constructs have achieved such success in this complex field as has the DLVO theory. The success is so firmly established that one must assume the fundamental correctness of the theory — at least to within the limits to which the theory aspires, namely, as a firstorder approximation. One notes, however, that the theory does not allow for any detailed consideration of the structure of bulk water, let alone for possible structural effects induced by proximity to an interface. In the following sections, it is intended to show that details of vicinal water structure must sooner or later be taken into account if a truly correct, comprehensive theory of aqueous colloidal behavior is ever to be achieved.

The concept of vicinal water was originally introduced to explain a large number of anomalous thermal responses observed in aqueous surface and colloidal systems[1]. The anomalies could be explined if it was assumed that the interfacial water was structured differently from bulk and able to undergo some type of phase transitions within certain, specified, relatively narrow temperature ranges (for instance near 14 to 16 °C or 44 to 46 °C.) — in other words, allowing for (several) allotropic forms of water (see particularly Drost-Hansen[2,3]). Frequently the anomalies were sufficiently pronounced quantitatively that it was necessary to assume that the thickness of the vicinal water layer was large compared to the size of an individual water molecule.

Over the past several years, we have attempted to make more specific estimates of the thickness of the vicinal water layers, based on quantitative analysis of some (mostly) thermodynamic data. Some of these results have been discussed recently by one of us[4] and more detailed considerations will be presented here. Our current best estimates of the thickness of the vicinal layer range from several tens of molecular diameters to a few hundred (0.02 μm to 0.05 μm.) In addition, one of us[5] has developed a theoretical model of vicinal water which will be discussed in connection with the available thermodynamic data.

II. EARLIER STUDIES OF VICINAL WATER

A few of the earlier experimental studies will be reviewed in this section as a means of »setting the stage« for the discussion of vicinal water and the examination of some of the more recent results. Most of the examples refer to work done in the 1970's, while one example of thermal anomalies — the surface tension of water (as derived from capillary rise measurements) — provide an instance of study going back more than 130 years.

II A.1. Viscosity and Disjoining Pressure Studies by Peschel and Co-Workers

Professor Peschel and co-workers have developed a highly sensitive electromechanical balance for studying the proporeties of water between closely spaced solid surfaces (mostly quartz, either fully hydroxylated or partly hydroxylated). Peschel has developed a theory which allows for the effects of surface rugosity on the observed parameters, allowing measurements to be carried out over plate separations down to 100 Å[6]. In this experimental set-up, one plate is fixed rigidly to the main body of the apparatus, while the motion and force acting on the movable top plate can be determined with great precision. Both plates are exceedingly highly polished, the bottom plate being planar, while the top plate has a radius of curvature of 1 m. The balance system to which the top plate is attached allows for displacement by an electromagnetic coil. The plate separations are measured by a displacement transducer placed on the balance arm and connected with a strain gauge measuring bridge to a recorder.

II A.2. Viscosity Measurements

Allowing the top plate to settle onto the bottom plate, the dynamics of this motion can be followed with great precision. Peschel has worked out the theory for calculating the (average) viscosity of the intervening fluid layers, being squeezed out (radially) from between the plates. Typical data for the viscosity of the liquid between the plates as a function of plate separation are shown in Figure 1[7]. The different curves correspond to different applied forces and thus, to different effective shear rates. Note that for plate separations of about 0.05 μm (i. e., 500 Å), the apparent average viscosity exceed that of pure water by a factor of about 10 under the smallest applied force studied in this investigation. Such apparent high viscosities for interfacial water have been reported previously by other authors, for instance, as

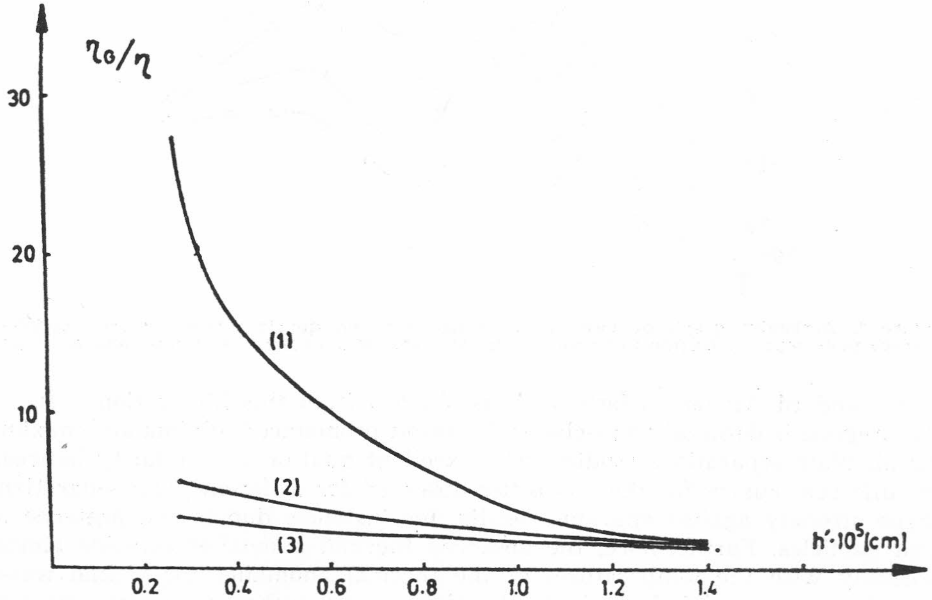

Figure 1. Relative viscosity of water at 20 °C between quartz plates as a function of plate separation. Data for three values of applied force: (1) $F = 253$; (2) $F = 523$ and (3) $F = 657$ dynes. Data by Peschel and Adlfinger.

early as 1935 by Deryaguin[8], who measured the viscosity with a rotating bob viscometer and observed extremely high values for the viscosity of water when the plates were in close proximity. Such measurements have often been discounted on grounds that the data may be spurious, reflecting either (a) the presence of »dust particles« of other mechanical obstructions and/or (b) »swelling« of the quartz layers to produce essentially a gel-like, highly hydrated amorphous silica material. It would appear that the reproducibility and the rough qualitative correspondence between the various values obtained by different investigators would argue against the possibility of spurious disturbances due to discrete, colloidal »dust.« On the other hand, it is more difficult to discount the possibility of the existence of »gel-like« hydration layers. The apparent shear rate dependence of the viscosity would qualitatively also tend to discredit the first hypothesis (namely, that the anomalously high values were obtained as a result of the spurious presence of dust particles). However, once again, notable shear rate dependence might indeed be expected from the presence of gel-like hydration structures.

In subsequent studies, Peschel and Adlfinger[9] have measured the viscosity of the water between the quartz plates as a function of temperature. The results are shown in Figure 2. In this illustration, the viscosity is plotted in a standard Arrhenius fashion. It is obvious from this illustration that the flow regime is definitely non-classical, exhibit pronounced minima and maxima for all plate separations studied. The excellent qualitative similarity between the different curves for the viscosities observed for different plate separations argue strongly against spurious results, for instance, due to the presence of dust particles. Furthermore, the observed thermal anomalies coincide almost precisely with the temperatures of the thermal anomalies for vicinal water have been reported independently by the present author over many years[10]. (The nature and extent of the thermal anomalies are reviewed briefly in the sections below). It appears from all of the available evidence[3,4] that vicinal

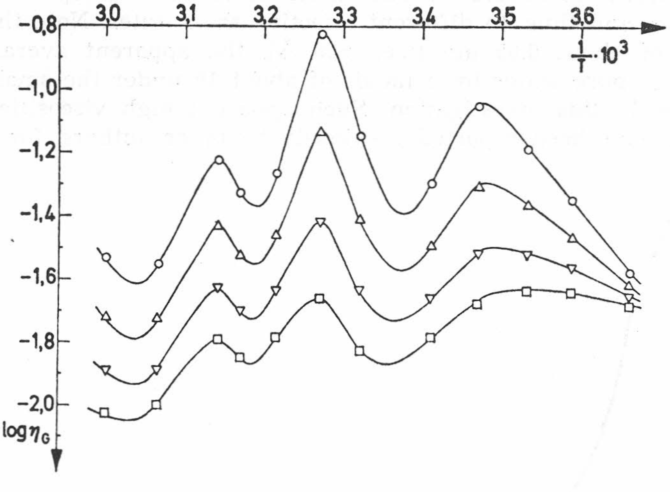

Figure 2. Arrhenius graph of viscosity of water between quartz plates for four different average plate separations (top to bottom: 0.03; 0.05; 0.07; 0.09 μm.) Data by Peschel and Adlfinger.

water undergoes notable thermal anomalies and conversely, it is inferred that the occurence of thermal anomalies in indicative of the presence of vicinal water. While indeed — through some unexplained mechanism — gel-like surface layers of »colloidal silica« might conceivably have remarkable thermal properties, it is unlikely that the temperatures of the anomalies in the properties of such gels should conincide almost precisely with the thermal anomalies obtained in systems distinctly different from the quartz plates used by Peschel and co-workers.

In summary, the viscosity of water between quartz plates suggests the existance of extensive vicinal hydration, differing from the bulk structure, with viscosities notably larger than the viscosity of pure water and with thermal properties exhibiting rather large and relatively abrupt changes.

II A.3. Disjoining Pressure Measurements

In an alternative mode of operation of the apparatus constructed by Peschel and co-workers, the force acting between the plates can be measured with great sensitivity. This allows for the direct experimental determination of the total disjoining pressure between the plates as a function of plate separation, electrolyte concentration and as a function of temperature.

Figure 3 shows some of the results reported by Peschel and Adlfinger[11]. It should be noted in passing that this type of result has been quantatively reproduced on many occasions over a period of close to a decade (Peschel, private communication, 1982).

The disjoining pressure data shown in Figure 3 clearly indicate the existence of abrupt thermal anomalies in the vicinity of 15, 30, 45 and 60 °C — that is, within the experimental error, at the temperatures long advocated by the present author as the temperatures for vicinal water in general. Note also the great similarity in the temperature responses between the measurements made with different plate separations (excepting, to some extent, the measurements at the smallest possible plate separation — 100 Å).

From the observed disjoining pressure data, Peschel and Adlfinger have deduced various thermodynamic properties for vicinal water. Thus, Figure 4 shows the estimated differential molar excess entropies (for pure water, midway between fully hydroxylated, fused silica plates with a separation of 500 Å). We return to the question of the entropy of vicinal water in another example to be discussed in this section.

It is important also to note that the internal free energy between the vicinally structured water and bulk, unaffected water structure appears to be of the order of 10 (to 100) cal/mol (for a plate separation of 100 Å); this compares favorably with the preliminary estimates reported by the present author[3] and the results recently obtained from our DSC studies (see Section IV E).

II. B.1. Ion Selectivity Studies

Wiggins[12] has reported some highly interesting ion selectivity data obtained from a study of the distribution of sodium and potassium between a bulk phase and the vicinal water in the pores of silica gel.

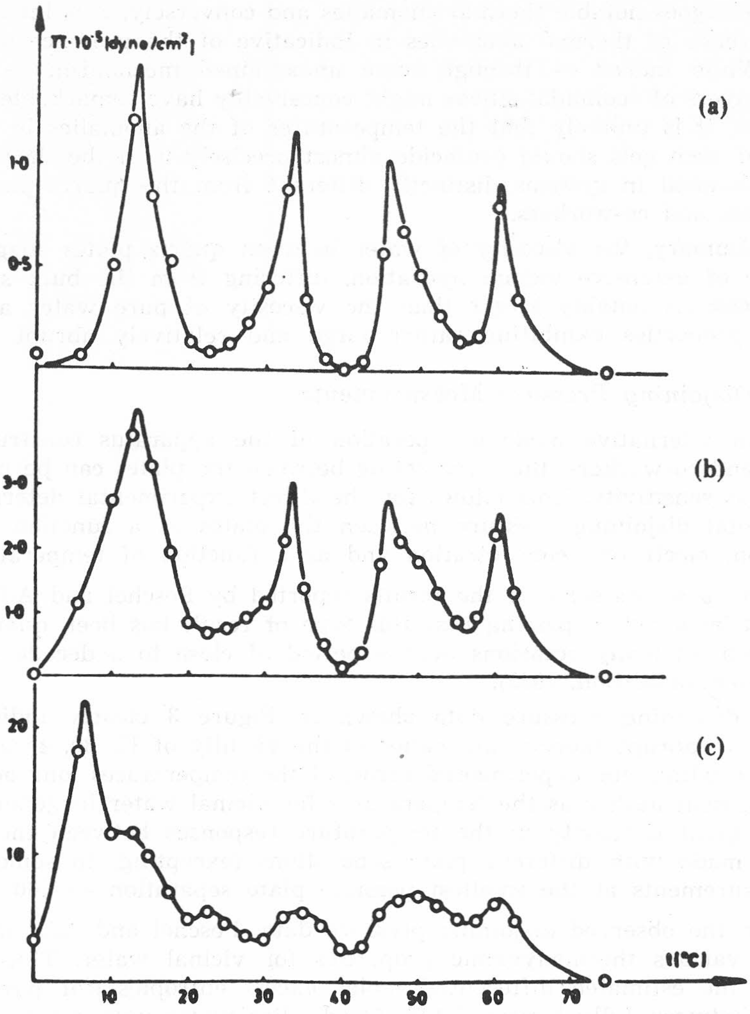

Figure 3. Disjoining pressure of water between quartz plates as function of temperature for three plate separations (top to bottom: 0.05; 0.03 and 0.01 μm). Data by Peschel and Adlfinger.

In these experiments, Wiggins equilibrated equimolar solutions (mixture) of sodium and potassium chloride with a Davison No. 950 silica gel, measuring the apparent partition coefficients for potassium and sodium ions, defined through the expressions:

$$\lambda_K = \frac{[K^+]_i}{[K^+]_o}$$

$$\lambda_{Na} = \frac{[Na^+]_i}{[Na^+]_o}$$

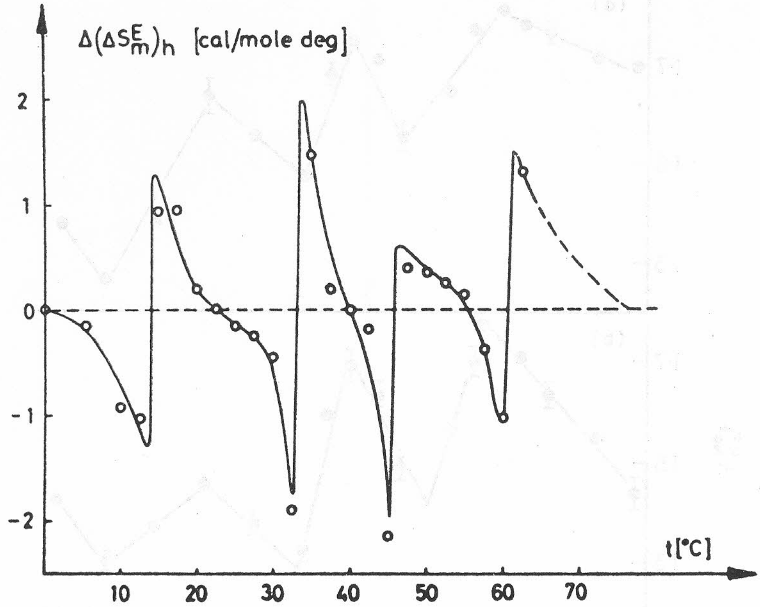

Figure 4. Differential molar excess entropy of water between quartz plates as function of temperature. Plate separation 0.05 μm. Data by Peschel and Adlfinger.

where the subscripts i and o refer, respectively, to the concentration inside the pores and in the bulk (equilibrated) supernatant solution. A selectivity coefficient, K, was defined as the ratio of the apparent partition coefficients for the two ion — i. e., $K = \lambda K/\lambda_{Na}$ (the reason for forming the ratio is to minimize systematic errors due to difficulties in analytical techniques as such errors will tend to cancel out when forming the ratio). Wiggins performed the measurements of the partition coefficients as a function of temperature and her data are shown in Figure 5.

An inspection of Figure 5 immediately shows two primary feature: (A) the values for the selectivity coefficient is always larger than 1, indicating that the concentration of the potassium ions is selectively enhanced in the pores of the silica gel compared to the sodium ions; (B) the selectivity coefficient is strongly temperature dependent, again showing sharp extrema at the temperatures of the vicinal water transition temperatures; namely, maxima near 15, 30, 45 and 60 °C.

Wiggins has carried these studies considerably further, including measurements of the selectivity coefficient for potassium and sodium in a living tissue (rat kidney cortex) and obtained qualitatively similar behavior, at least to the extent that thermal anomalies are again observed in the form of sharp maxima in the selectivity coefficient at 14 and 29 °C. The present author has speculated upon this observation[13] and Wiggins has presented a detailed study of »metabolic control of intracellular water«[14] based on the concept of vicinal water as a controlling factor in ion distribution in cells.

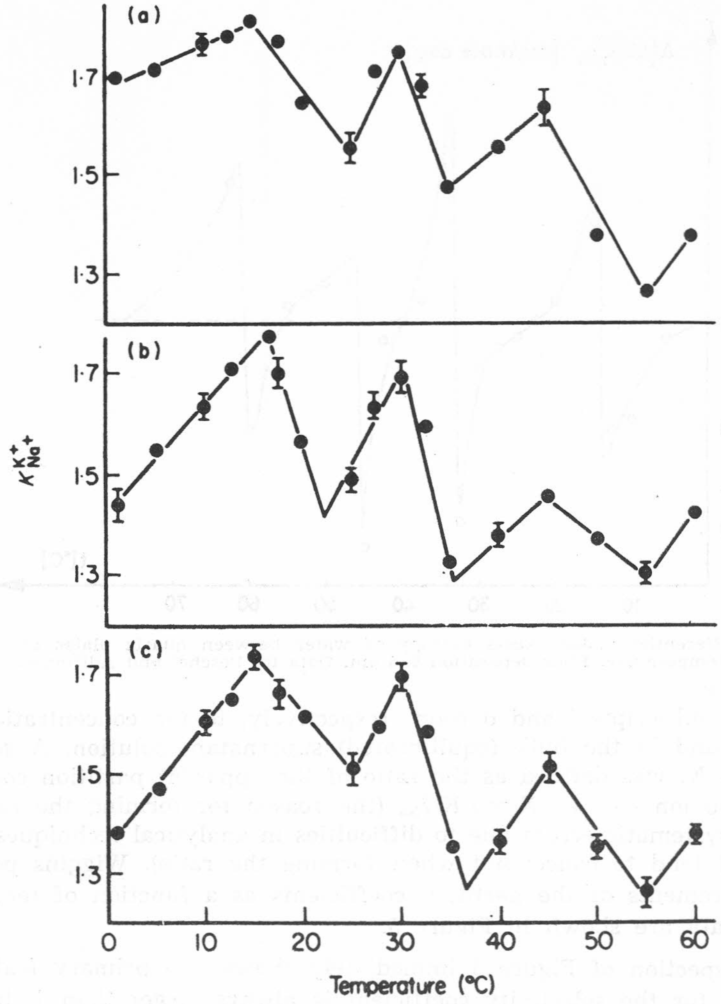

Figure 5. Selectivity coefficient of water in silica gel as function of temperature (top to bottom for $K^+ - Na^+ - SO_4^{--}$; $K^+ - Na^+ - I^-$; $K^+ - Na^+ - Cl^-$). Data by Wiggins.

Because of the obvious importance of this study, it was of considerable interest to corroborate Wiggins' finding. Thus, Hurtado and the present author[15] have repeated the measurements by Wiggins. In our own study, the silica gel employed was a Davison silica gel, No. 62 (pore volume 1.15 cm^3/gram, surface area 340 m^2/gram). The average pore diameter in this case was about 140 Å. The results obtained confirmed the findings by Wiggins, almost quantitatively: the value for the selectivity coefficient is large than 1 and the coefficient shows sharp maxima at 15 and 30 °C (with a slightly less distinct peak at 45 °C). The two sets of data are almost identical.

Note finally that in the study by Wiggins the observed selectivity coefficient was practically independent of the anion present (chloride compared to iodide, compared to sulfate).

II B.2. *Study by Horne and Young*

The »solute exclusion« effect studied by Wiggins and by Hurtado and Drost-Hansen was anticipated by Horne and Young[16].These authors measured the exclusion of cations as a liquid front permeated a column of silica gel. The sequence of exclusion of the ions was in the same order as observed by Wiggins — namely, the lithium ion being the most rejected, while the cesium ion the least rejected; the measurements were made on 0.1 molar aqueous solutions of the alkali chloride metals. From the quantitative estimates, Horne and Young concluded that the distance over which the electrolyte is excluded is roughly 170 Å, »extending out from the boundary for many water molecules, and we conclude therefrom that we are dealing, not with a surface geometric effect, but with a relatively deep perturbation of the water structure.« Horne and Young also correlated the observed ion exclusion with the viscosity B-coefficient. In this connection, see Section IV-F where a somewhat similar quantitative relationship has been observed from our recent viscosity work.

In passing, it should be noted that ion exclusion effects have been reported also by Maatman[17], but, as pointed out by Horne and Young, the effect proposed by Maatman must imply »intimate« contact between the ions and the surface. As discussed elsewhere[3] and summarized in Section IV-E, vicinal water appears to differ energetically only slightly from bulk water and the ion exclusion effects referred to by Horne and Young, by Wiggins, and by Hurtado and Drost-Hansen most probably reflect low energetics changes only. This point is of considerable interest in connection with some theoretical studies by Plesner and Michaeli, to be discussed below.

II B.3. *Study by Plesner and Michaeli*

Plesner and Michaeli[18] have made a theoretical study of adsorption (and subsequent phase separation) in monolayers of ions adsorbed on solid interfaces. The authors have studied the possibility that in the presence of two cations (with a common, monovalent anion), a solid surface may adsorb selectively one or the other of the ions (below a threshold potential). Plesner and Michaeli concluded that even though the larger ion is present in high concentration in the bulk phase, the smaller ion may be preferentially adsorbed. It is indeed possible that such a phenomenon may occur. However, it is unlikely that this effect can account for the results obtained by Wiggins and by Hurtado and Drost-Hansen. Thus, Plesner and Michaeli assumed the existence of a strong bond between the ion and the surface. It would appear from our studies that such a »strong bond« — in other words, a highly energetic bond — is not encountered in vicinal water. Furthermore, there is no simple way in which the theory by Plesner and Michaeli can be extended to account for the remarkable temperature dependence which has been reported for ionic selectivity. Finally, the results by Wiggins and our own results clearly indicate that it is the larger ion which tends to become selectively adsorbed — although one might argue that what is important is not the size of the ion itself, but rather the size of the hydrated ion. In that case, however, the ion is then unlikely to come sufficiently close to the surface for the strong attraction to occur on which Plesner and Michaeli's study is based.

II C. Surface Tension Studies

Figure 6 shows the observed capillary rise heights of water as a function of temperature; the data obtained by Brunner[19]. Although the author did not comment on the apparent, rather sudden inflection near 17 °C, the data clearly suggest an anomaly. To the best of the author's knowledge, this is one of the earliest reported set of data suggesting the occurrence of a thermal anomaly of interfacial water — Brunner's paper having been published in 1847.

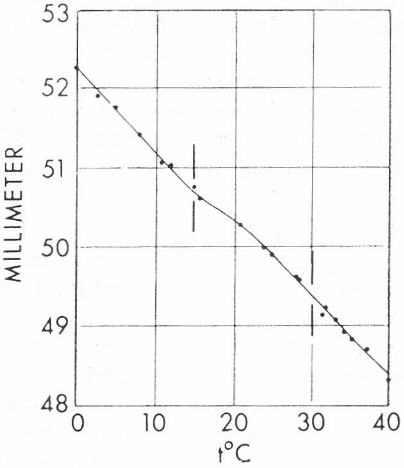

Figure 6. Capillary rise height of water as function of temperature. Capillary diameter 0.585 cm. Data by Brunner (1847).

In the 1930's, Timmermans and Bodson[20] reported surface tension data for both ordinary water and heavy water. For the H_2O data, the capillary rise method, a drop-weight method and bubble pressure measurements were used. It is interesting that all the data fall on a curve showing a distinct inflection point in the vicinity of 11 °C (with an inflection point in the data (obtained by the capillary rise method) for D_2O in the vicinity of 16 °C).

A general overview of surface tension data for water has been presented by the present author[21]. From this paper, we finally consider the entropy of surface formation values, derived from three sets of surface tension measurements. Figure 7 shows the temperature derivative data of the reported surface tensions — in other words, the temperature derivative of the surface free energy, thus, the entropy of surface formation (see loco cit., p. 23 for a discussion of the limitations on this interpretation). In all three sets of data, the surface entropies seem to decrease in the vicinity of 27 °C. This is followed by a notable increase in the vicinity of 30 to 31 °C followed by a precipitous drop near 35 to 37 °C. For all three sets of data, the entropy again increases rapidly to reach a relatively shallow maximum in the vicinity of 42 to 43 °C. In connection with these data, compare the entropy data discussed above, obtained by Peschel and Adlfinger from their measurements on water between quartz surfaces.

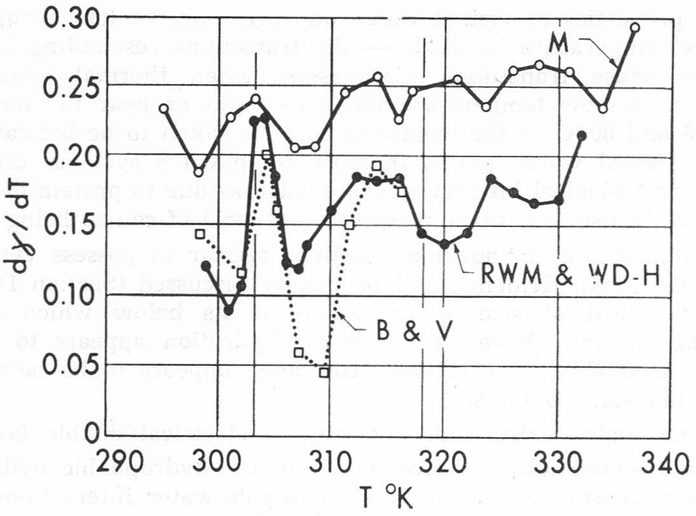

Figure 7. Numerically differentiated surface tension data for water as function of temperature.

III. GENERALIZATIONS ABOUT VICINAL WATER

Before proceeding, it is important to note that thermal anomalies in the properties of aqueous systems are likely manifestations of interfacial structural effects and not due to any changes in bulk properties. For many years, it was considered likely that the thermal anomalies reflected changes in the bulk structure of water. However, all the anomalies reported for what were presumably bulk systems were most likely caused by spurious effects of the (almost invariably) unavoidable surfaces of the confining vessels. Highly reliable data, for instance for ultrasonic velocity, dielectric constant, and other properties which can be measured essentially far from any solid interface, have failed to suggest the occurrence of thermal anomalies. The problem was essentially resolved in a brief paper by one of the present authors entitled »Thermal anomalies in Aqueous Systems — Manifestations of Interfacial Phenomena?« in 1969[22].

On the basis of the currently available experimental information, it is possible to make some generalizations about vicinal water. These are outlined below in summary form.

A) Vicinal water appears to exist adjacent to most (or all) solid interfaces and extending into the aqueous phase for a distance of at least 100 Å (and *possibly* for as much as 500 Å) (in other words, distances ranging from 0.01 μm up to 0.05 μm). This corresponds roughly to 30 to 150 molecular diameters.

B) Within certain limits (discussed in Section IV E), vicinal water appears to occur relativelly independently of the specific details of the chemical nature of the solid surface and relatively independently of the nature and concentration of the solutes (see, however, Peschel and Belouschek). This phenomenon is referred to as the »paradoxical effect«.

C) The properties of vicinal water undergo more or less abrupt changes over narrow temperature intervals — the transitions resembling first and/or higher-order phase transitions. Conversely, when thermal anomalies are observed over narrow temperature intervals — at or near the temperatures of 15, 30, 45 and 60 °C — the anomalies may be taken to be indicative of the presence of vicinal water. (Note: In more complicated systems, especially of biochemical or biological interest, changes, such as due to protein denaturation or lipid phase transitions (in lipid/aqueous systems) of course being excluded).

D) Macromolecules in aqueous solutions appear to possess vicinal water (»vicinal hydration«). Evidence will be briefly discussed (Section IV—I), suggesting that a critical size of the solute exists below which no vicinal hydration occurs and above which vicinal hydration appears to occur frequently (or invariably). The critical size range appears to be between 1,000 and a few thousand Daltons.

E) Vicinal water exists independently of electrical double layers.

F) Vicinal water does not owe its origin to »hydrophobic hydration« (in the traditional sense) nor to ion-water or dipole-water interactions (such as, for instance, involved in the hydration of ionic sites on macromolecules).

G) The effects of vicinal water are superimposed on those effects which are normally discussed in surface and colloid chemistry (i. e., London-van der Walls forces, electrical double layer effect, etc.).

H) By virtue of the paradoxical effect, it is concluded that vicinal water must also exist in all cellular systems — consistent with the observation that many thermal anomalies have been reported in cellular functioning at the temperature ranges where vicinal water in physico-chemically well defined systems exhibit such anomalies.

IV. RECENT STUDIES OF VICINAL WATER

IV. A. Preliminary Remarks

The occurrence of thermal anomalies in aqueous interfacial properties is firmly established and the anomalies are surely indicative of structural changes in vicinal water. However, the structure, extent and energetics of the vicinal water remain to be determined unequivocally. The question of the structure of vicinal water will be briefly discussed in Section V and VI while the energetics is considered in part in Section IV E. As for the geometric extent of vicinal water, it is difficult to separate this question from the unresolved question of its structure. Essentially only two possibilities exist: either vicinal water exists, »fully formed«, over a definite distance from the surface or else vicinal water represents a structural »attribute« which becomes progressively less pronounced as one goes away from the interface. It the latter situation prevails, then vicinal water structure attributes may, for instance, decay exponentially as a function of the distance to the surface. At present, we favor this second possibility on intuitive grounds, but, are unable to offer any substantiation for this. For practical purposes, however, we frequently use a model, purely for »arithemetic convenience«, in which it is assumed that vicinal water exists up to a certain well-defined distance from the surface, beyond which the aqueous phase has the properties of the normal bulk solution.

IV. B. Density of Vicinal Water

The density of vicinal (i. e. interfacially modified) water has been measured directly by pycnometry on a porous quartz/water system by Etzler and Fagundus[23]. The porous material used was a silica gel (Davison Code 62) with nominal pore diameter of 140 Å. This is the same material used in our ion-selectivity studies (See Section II, B) and in our DSC measurements (See Section IV, E.). The reader is referred to the original article for a discussion of possible sources of error in these measurements. The result of this study strongly suggests that the density of vicinal water is distinctly lower than for bulk water, namely in the range of 0.965 to 0.97 g/cm[3 8]. Similar type measurements with liquids which are not expected to form long-range vicinally modified structures (acetone and methanol) yield densities in close agreement with the corresponding bulk values. Relatively few data have been reported in the literature for the density of interfacial water (for a brief review, see 4). The most interesting data appear to be those of van Gils[24] who finds $\varrho_{\mathrm{vw}} > \varrho_{\mathrm{bulk}}$ and those by Low[25] and by Ash and Findeneeg[26] who observed values for $\varrho_{\mathrm{vw}} < \varrho_{\mathrm{bulk}}$.

Based on the available evidence we favor a value for ϱ_{vw} less than the density of bulk water. (For a discussion of the density of water in cellular systems, see Clegg and Drost-Hansen[27].

IV. C. Thermal Expansion Coefficient

The coefficient of thermal expansion $\left(\alpha = \frac{1}{V}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_{\mathrm{p}}\right)$ reflects the assymmetry of the intermolecular potential energy function. Thus, any difference in α between bulk and vicinal water must be explained by structural effects reflecting changes in the intermolecular potential energy function.

We have analyzed[4] the thermal expansion data by Schufle et. al. on water in capillaries and have observed notably larger values of α for the capillary-held water than for bulk water. These data have been used to estimate the thickness (Δr) of the vicinal water layers for different assumed values of α_{vw}. The result is a likely range of Δr between 0.05 and 0.1 μm. More recently, we have started direct measurements of α on aqueous suspension of polystyrene spheres (PSS) to be reported elsewhere).

An automatic high-precision dilatometer has been constructed[28]. In this device the thermal expansion of the test sample is translated into the movement of a mercury column in a capillary; this motion is not observed directly by optical means (such as a measuring microscope or cathetometer) but is sensed instead as a change in capacitance between the mercury column and a (concentric) layer of conducting paint on the outside of the capillary. The capacitance change is either measured directly on a capacitance brindge or used as a variable capacitance in an RC circuit, the frequency of which can be measured precisely. Sensitivities of the order of 0.1 μm displacement of the mercury meniscus can easily be recorded. The experimental system will be described in detail elsewhere[29]. By slight modification this device may also be used for (relatively) low pressure isothermal compressibility and internal energy measurements.

IV. D. Isothermal Volume Changes in Suspensions

Using the automatic, recording dilatometer we have studied the volume properties of PSS suspensions as a function of the state of the suspensions and as a function of temperature[28]. At constant temperature, totally *reversible* changes in total volume of the suspensions were observed over periods of time ranging up to 150 hours. For a 0.945 μm diameter particle PSS suspension, stirred slowly isothermally (by a magnetic stirrer), no volume changes were observed over long time periods (of the order of days). However, upon cessation of stirring, changes in volume occurred reproducibly over periods of time from 30 to 120 hours. The change was always a decrease in volume, and reached a new equilibrium value after about 130 hours. Furthermore, upon renewed agitation (by stirring) the volume increased over a matter of a few hours to the initial volume.

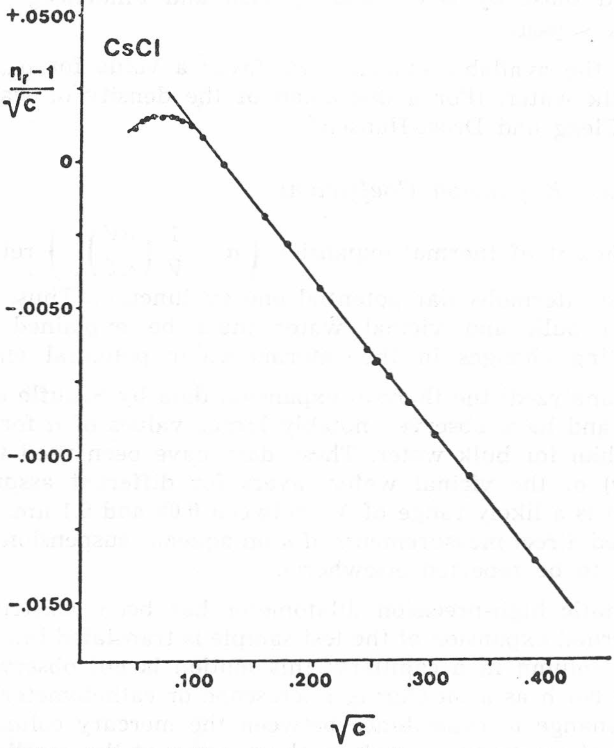

Figure 8. Jones-Dole graph for CsCl in the concentration range 2.11×10^{-3} to 1.51×10^{-1} M.

In all probability, these volume changes reflect the »squeezing out« of vicinal water from the hydration hulls around each particle as the particles slowly settle to form a rather loose sediment. This notion is consistent with later observations by LeGault[30] who did not observe any volume change with polystyrene spheres of 0.176 and 0.091 μm diameters. These supensions do not settle out at any time.

IV. E. DSC Measurements

Extensive measurements[31] have been made of the thermal properties of vicinal water by Differential Scanning Calorimetry (DCS) in the range from about 30 to 80 °C. More than 100 runs have been made, allowing us to make statistical estimates for a number of thermal parameters. The following table summarizes briefly some of the results obtained for various aqueous systems:

AVERAGE TRANSITION TEMPERATURES

Series	Systems	T_3	T_4	T_5
A	Silica Gel	45.9 ± 1.65	60.9 ± 1.95	73.2 ± 1.54
B	Diamond Powder	45.4 ± 1.58	59.8 ± 2.28	74.4 ± 1.36
C	0.176—0.945 PSS	45.2 ± 1.93	58.9 ± 2.75	74.6 ± 2.29
D	0.176 PSS, Bulk	45.9 ± 2.37	57.8 ± 1.79	75.0
E	0.945 PSS, Bulk	44.5	—	75.0

The silica gel used was Davison Code 62, pore diameter 140 Å. The diamond powder was wetted with about 50% water; particle size in the range 5.0 to 6.3 µm. Two diameters of PSS were used, 0.176 and 0.945 µm. In series C, samples of the two types of suspensions were run against each other (double differential measurements).

It is seen that the anomalies near 45° and 60 °C, respectively (transitions T_3 and T_4, see Drost-Hansen[13], are indeed close to or identical with the temperatures orginally proposed (Drost-Hansen, 14). Note also that the temperature of the transitions are independent of the nature of the solid substrate, as previously inferred (the Paradoxical Effect; see Drost-Hansen, 3,34). Finally, note that a transition appear also to occur near 74°—75 °C (T_5). Measurements have been made also of the specific heat of vicinal water, using the water/porous silicagel system. The value for C_p was found to be 1.27 ± 0.08 cal/°C-gram, in excellent agreement with our previous value of 1.25 (Braun and Drost-Hansen, 35). An inspection of all the thermograms reveals what appears to be both first and higherorder, phase transitions. As stressed by Lumry and Rajender[36], the occurence of abrupt changes in the temperature coefficients of thermal properties requires the existence of heat-capacity spikes in thermograms (which, at the time of Lumry and Rajender's review, had not been reported.) We have now observed such heat-capacity spikes at the temperatures of the thermal transitions in more than 80 different DSC scans. The corresponding peak areas correspond to energies of transitions of the order of 1 to 20 cal/mol (of vicinal water).

IV. F. High Precision Viscometry Measurements

Dordick, Korson and Drost-Hansen[37] have recently reported high-precision viscosity data for dilute aqueous solutions of the alkali chlorides. In the region of low concentrations, say below 10^{-3} molar, systematic deviations were observed

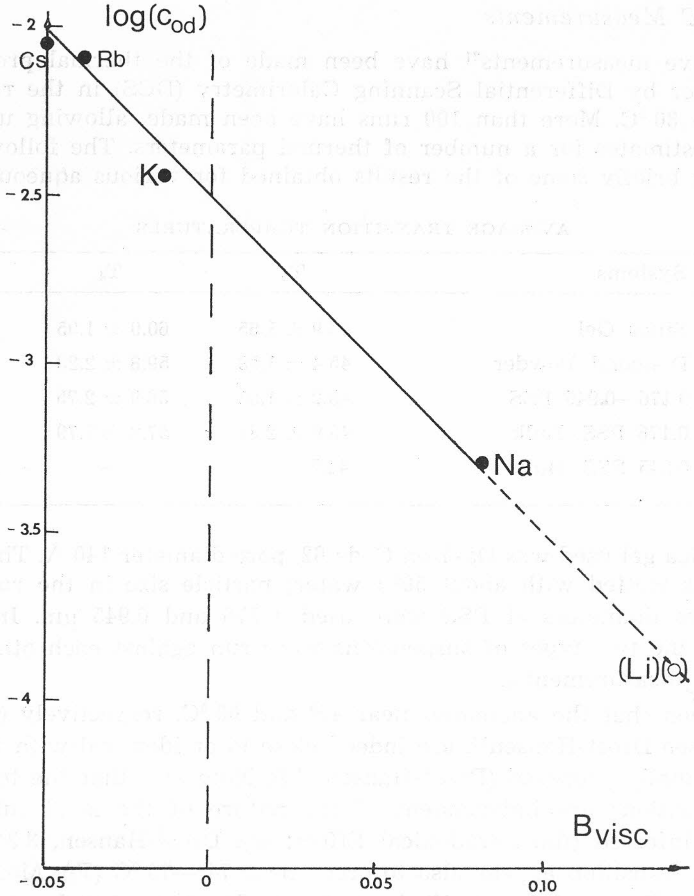

Figure 9. log (concentration of onset of deviation) as function of viscosity *B*-coefficient for Cs, Rb, K, and Na Chloride. Value for LiCl by extrapolation.

from the Jones-Dole equation: ($\eta_{\mathrm{rel}} = \eta_s/\eta_o = 1 + A\sqrt{c} + Bc$). Figure 9 shows such a case, namely the »Jones-Dole function« ($(\eta_r - 1)/\sqrt{c}$) versus $\sqrt{c}$ for CsCl. The onset of deviation from the straight line occurs at about 9.10^{-3} molar. In the paper[37] deviations from a straight line were reported for the Na^+, K^+, Rb^- and Cs^+ chlorides, but no evidence was obtained for such behavior for LiCl. It was proposed that the cause of the deviations was associated with an »experimental artifact,« namely a distinct change in the viscous properties of the solutions at the water/glass (capillary wall) interface. In this connection, recall the unusual (and anomalously high) viscosities of inter-facial water reported by Peschel and co-workers (section II-A).

As implied in the paper by Dordick, et al., a decrease in the effective radius of the diameter by 0.02 μm (2.10^{-6} cm) from 125 to 124.98 μm would give rise to a change in the flow rate of about 0.0064% — a relatively large change compared to the precision of the measurements of about 0.0005%. While it is not claimed that an effectively non-flowing layer of vicinal water extends

TABLE I

Thickness, δ, of the »Rigid Hydration Hull« of Aerosil Particles, as Determined by Strenge from Viscosity Measurements

Dispersion medium	δ/Å
water	22—28
10^{-2} n KCl	31
1 n KCl	32
10^{-2} n KOH	27
10^{-2} n H_2SO_4	30
water 25 °C	36
water 50 °C	36
water 75 °C	33

over such a range, it appears at least reasonable to consider the observed effect due to a change in the effective viscosity over a distance of, say 0.01 μm — in other words, in the same range as many other estimates for the thickness of vicinal water.

The onset of deviations from linearity depends on the size of the cation present. It is interesting to compare this to the claim made by Wiggins[12] that the more an ion appears to be a »structure breaker« the more its concentration is enhanced in the vicinal water. The viscosity B-coefficient is recognized as an expression of the structure breaking tendency of the ion and Figure 10 shows a graph of the (logarithm) of the concentration at which deviation from the linearity begins as a function of the B-coefficient. The trend is rather clear: the more positive B is, the lower the concentration at which non-linearity is observed. It is seen also that for LiCl the »critical« concentration is of the order of 10^{-4} molar; for some of our measurements on NaCl and KCl this concentration range was indeed studied, but our measurements on LiCl were not extended to quite such high dilutions. Thus, it is not surprising that the deviation from linearity was not observed in this case.

In summary then, it appears from the viscosity data on dilute solutions that (A) the flow regime — and thus, probably, the structure of the solvent near an interface (the glass capillary/water interface) — is modified over a distance which appears large compared to molecular diameters and that (B) vicinal water possesses unusual »solvent properties« compared to bulk water, consistent with the findings by Wiggins, by Horne and Young, and by Hurtado and Drost-Hansen.

IV. G. Viscosity of Aqueous Suspensions

We have measured the effects of temperature on the flow of some suspensions (polystyrene latexes, manufactured by Dow Diagnostics).[1] In the present work, 10% suspensions were used; average particle diameter: 0.091 μm.

Assume the viscosities of the suspensions obey an Einstein type equation (see, for instance, 38):

$$\eta_s = \eta_o \cdot (1 + 2.5\,\Phi + \Sigma\, k_m\, \Phi^m)$$

where η_s and η_o are, respectively, viscosities of the suspension and the pure solvent; Φ is the volume fraction of the dispersed solid. The temperature coefficient of the viscosity is:

$$d\,\eta_s/d\,T = (d\,\eta_o/d\,T)\,(1 + 2.5\,\Phi + \Sigma\,K_m\,\Phi^m) + \eta_o\,(d/d\,T)\,(1 + 2.5\,\Phi + \Sigma\,k_m\,\Phi^m)$$

However, in this expression the second term may be neglected as the thermal expansion contribution due to the dispersed solid is very small compared to $d\,\eta_o/d\,T$. Thus, in terms of energies of activation for flow, the value of $\Delta\,E_s^{\ddagger}$ for the suspension should essentially be the same as $\Delta\,E_o^{\ddagger}$ — the energy of activation for the flow of bulk water.

From measurements at 24⁰ and 27 °C, we find $\Delta\,E_s^{\ddagger}$ to be 4.65 kcal/mol compared to $\Delta\,E_s^{\ddagger} = 3.75$ kcal/mol (see Korson, Millero and Drost-Hansen, 39) — in other words, notably different values. The measurements were made on the PSS suspension as received withouth any prior purification; thus, it must be recognized that some detergent is likely present (perhaps as much as 0.1 to 0.5%) as well as some electrolytes, probably mostly K_2SO_4. However, it appears extremely unlikely that this can account for such a large difference in the apparent energies of activation. Instead, it is more likely that the observed difference in $\Delta\,E^{\ddagger}$ is due to vicinal water surrounding each latex particle. If the »local viscosity« of the vicinal water differs from that of the bulk (and most likely it is higher) then an increase in the overall energy of activation may result. Furthermore, the thermal stability of vicinal water differs from that of the bulk; hence, the ratio of vicinal water to bulk water will also change, effectively changing the apparent volume fraction (of the *hydrated* particles) and thus, also contribute to $\Delta\,E^{\ddagger}$ (reflecting the change in the thickness of the vicinal hydration layer). Thus, $d\,\Phi_s/d\,T$ (where Φ_s is the apparent, effective volume fraction of the suspended particles) will change — and, infact, likely far more than due to $d\,\Phi/d\,T$ alone (i. e., related merely to the difference in thermal expansion of the solid polymer and the pure solvent).

Regarding the uncertainty in the results which might be ascribed to the presence of the detergent (which is the major impurity present) it should be noted that pronounced thermal anomalies were also observed in the ultrasonic excess absorption and ultrasonic velocity in the identically same types of suspensions[4]. As the thermal anomalies occurred at the same temperatures at which thermal anomalies have generally been reported for surfactant-free, well defined »pure« systems, it appears unlikely that the surfactant is the causative agent. We draw similar conclusions from dielectric studies (loss tangent measurements at 5 GHz) on a large number of PSS with widely differing particle diameters[41,42].

IV. H. Other Viscosity Studies on Suspensions

Strenge[43] has attempted to measure the thickness of the »immobile« water layers on the surface of silica particles by viscosity measurements on relatively dilute suspensions. Some of the results reported by Strenge are shown in the tables (below), the concentration of suspended material being approximately 2% by weight.

It is noteworthy that (A) the average thickness of the hydration shell is of the order of 25 Å, corresponding to roughly 10 molecular diameters of water. Furthermore, (B) the apparent thickness of the vicinal hydration hylls appears to be unaffected by the presence of electrolytes, even in relatively high concentration. This is in agreement with the »paradoxical effect« discussed elsewhere in the present paper. (C) It appears also that the thickness of the hydration hull is essentially independent of the particle size. (D) Finally, below 75 ^{0}C, temperature does not appear to affect the extent of the vicinal hydration significantly. All of the above observations are in reasonably good agreement with what would have been predicted on the basis of vicinal water structuring as discussed by the present author and his co-workers over the past decade.

It is recognized that the estimates obtained by Strenge for the thicknesses of the hydration hull are small compared to the distances over which we have claimed vicinal water to be manifested. Strenge's results indicate 10 molecular layers of essentially (or, completely) immobile water. It should be kept in mind that these are indeed absolute minimum estimate — namely, assuming that the water is essentially completely immobile. If, instead, it is assumed that the relative viscosity of the vicinal hydration water differs only by a factor of 2—10 (compare the study by Peschel and Adlfinger, discussed in Section II — A), the net distance over which the vicinal water may be manifested is obviously considerably larger, likely by an order of magnitude or more. Note also the independence of the presence of electrolytes — including potassium chloride, strong acids and strong bases — which makes it unlikely that the observed viscosity effects are merely due to swelling of the silica particle surfaces and makes it highly unlikely that the effect is a manifestation of electrical double layers.

IV. I. Molecular Weight Dependence

Macromolecules in aqueous solutions may be »vicinally hydrated« while small solutes (small ions; small non-electrolyte molecules) do not have such hydration (but of course will, in general, have other types of hydration, such as ion-hydration or »hydrophobic hydration«).

If one accepts that macromolecules are vicinally hydrated while small solutes are not, the question which must be answered is then »is there a critical size of molecules above which vicinal hydration occurs?« We do not yet have a definitive answer to this question, but some of the material, presented below, suggests that the answer is in the affirmative, and that the »critical size« corresponds to molecular weights (*MW*) in the range from 800 to a few thousand Daltons.

Stein and Nir[44] have reported on the available data for diffusion of a variety of solutes in water. Figure 10 show a graph of the diffusion constant as a function of log (molecular weight). It is quite apparent that a relatively abrupt change in slope occurs at around MW = 10^3. While Stein and Nir used this information to discuss the possible existence of two different flow mechanisms, it is proposed here that the change is caused by the »onset« of vicinal hydration for molecular weights at about 1,000 Daltons. Above this value, the derivative, $\mathrm{d}\,D/\mathrm{d}\,(MW)$, is notably less than for lower molecular weights; in other words, above *MW* of 1,000, the increase in size does not decrease the diffusion constant as much as would have been expected. Below the »critical value« for the molecular size, we may assume that the diffusing species is essentially »bare« or, at most, surrounded by a small number of relatively tightly bounded water molecules — either way, molecular species not »compatible« with the overall bulk water structure. On the other hand, above the critical size, where the molecules are vicinally hydrated, the »vicinal structures«

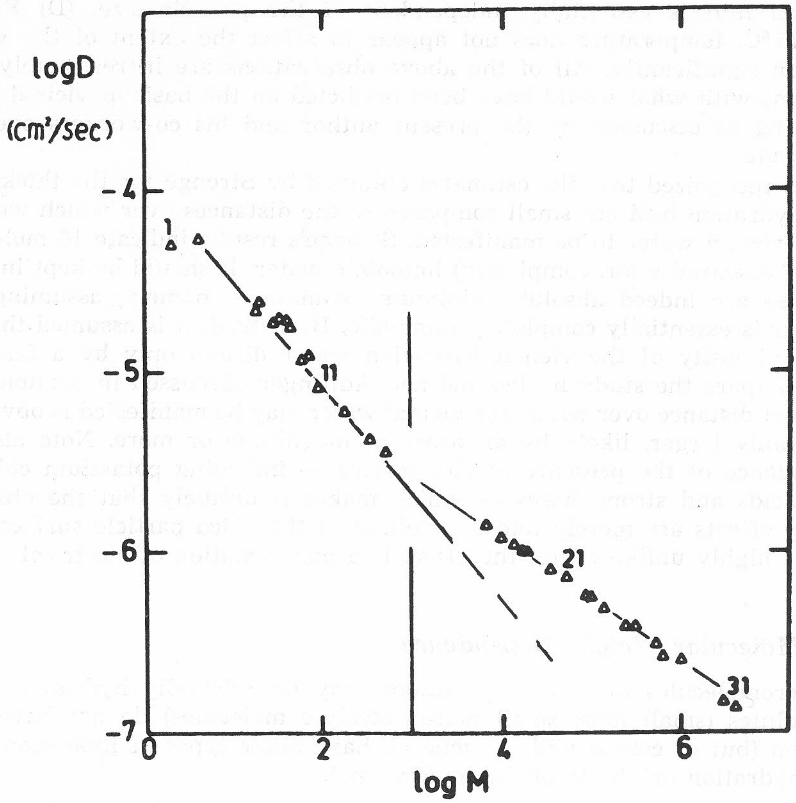

Figure 10. log (diffusion constant) as function of log (molecular weight). The points represent data for solutes ranging from H_2 (# 1) to hemocyanin (# 31). Data by Stein and Nir.

resemble the bulk structure enough to facilitate the relative motion of the diffusing species: far less pronounced, transient, structural rearrangements are necessary as the solute moves through the bulk structure. If, indeed, this explanation is correct, it would be of great interest to determine heats of transport in non-isothermal systems for a variety of solutes covering the entire molecular weight range of interest.

The case discussed above is primarily of inspirational value and unfortunately, only a few examples which may provide a clue to the question of a possibly more or less sudden onset of vicinal hydration can be obtained from the literature. One such case, however, is viscosity data for a series of poly(ethylene oxides) (Polyox) in water[45]. Figure 11 shows the log (intrinsic viscosity) of polyox as a function of log (*MW*). It is seen that at a molecular weight of about 3,000, the slope of the curve changes. Again, it is tempting to propose that the change is due to the onset of vicinal hydration for polyox molecules above this *MW* value. Obviously, one must be concerned with the possibility that the change may be due instead to such mechanisms as onset of coiling or other effects merely related to the change in linear dimensions. It is noted in passing that an unusual *MW*-dependence is also seen in the ultrasonic absorpt-

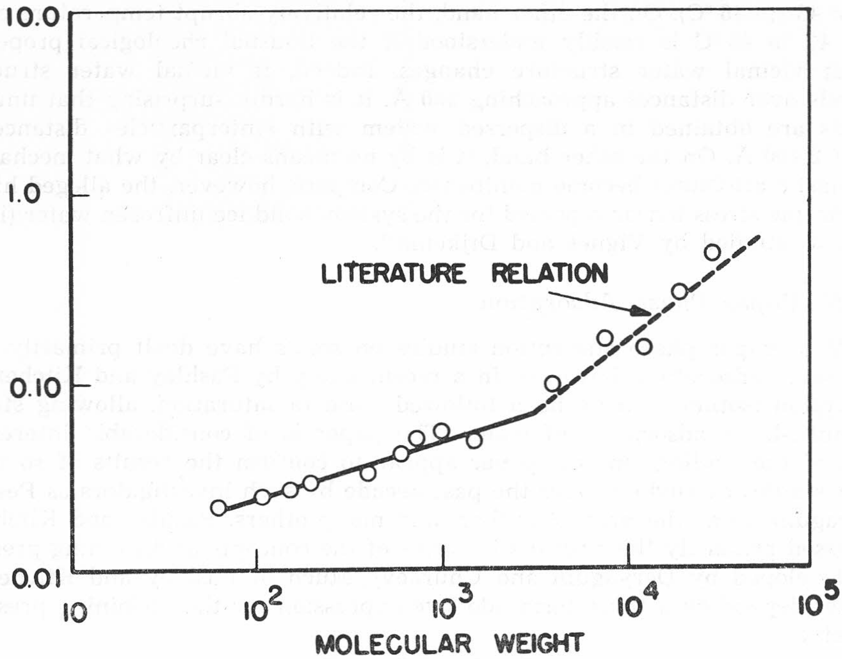

Figure 11. Intrinsic viscosity of polyethylene oxide in water (at 30 °C) as function of molecular weight. Data by Schick, quoted by Bailey and Koleske.

ion by aqueous solutions of polyethylene glycols. At all frequencies studied (6, 10, 30, and 60 MHz), Kessler, et. al.[46] observed increasing absorption up to $MW \simeq$ (800 to), 2,000 Daltons, and then a distinct leveling off.

IV. J. Aqueous Elastic Liquids

In connection with the structural attributes of vicinal water, see also the papers by Ulmius, et al.[47] and Gravsholt[48] who have studied the viscoelastic properties of some surfactant solutions, especially solutions of cetyltrimethylammonium salicylate. While Ulmius, et al. propose that the unusual rheological properties are due to the formation of periodic colloidal structures formed because of repulsive forces between the aggregates, it is proposed here that the effect specifically reflects the rather slow recreation (after mechanical disruption) of the vicinal hydration hylls of the surfactant micelles. It should be noted that Ulmius, et al. discount this mechanism as it is claimed that long-range effects on water structure in amphiphilic systems is unlikely. However, the assumption that the »lipid« does not notably affect the interfacial water structures is most likely incorrect. In this connection, see, for instance, the papers by Marčelja[49], Marčelja and Radić[50], by Parsegian[51], or by Chapman, et al.[52] and the present author[53]. It is difficult to see how the very weak repulsive dispersion forces between micelles alone, separated on the average 2,400 Å (in an 0.19 mM solution), can give rise to notable ordering. It is also difficult to see how the dispersion forces can account for the observed temperature dependence: the critical concentration of solute increasing rapidly above 43 (to 46 °C). On the other hand, the relatively abrupt temperature effect near 43 to 45 °C is readily understood if the unusual rheological properties reflect vicinal water structure changes. Indeed, if vicinal water structure extends over distances approaching 500 Å, it is hardly surprising that unusual results are obtained in a dispersed system with »interparticle« distances of about 2,400 Å. On the other hand, it is by no means clear by what mechanism the elastic attributes become manifested. Compare, however, the alleged highly anisotropic stress tensor reported for the system: solid ice/unfrozen water/(inert) solid, as studied by Vignes and Dijkema[54].

IV. K. Vapor Phase Adsorption

Most vapor phase adsorption studies on solids have dealt primarily with monolayer adsorption; however, in a recent study by Pashley and Kitchener[55], adsorption isotherms have been followed close to saturation, allowing studies on multi-layer adsorption of water. The paper is of considerable interest as most of the findings in this paper appear to confirm the results of so many other studies carried out over the past decade by such investigators as Peschel, Deryaguin, Low, the present author, and many others. Pashley and Kitchener discussed primarily their results in terms of the concepts of disjoining pressure (as developed by Deryaguin and Churaev). Much of Pashley and Kitchener's studies depend on a three term additive expression for the disjoining pressure, namely:

$$\pi = \pi_{\mathrm{vdw}} + \pi_{\mathrm{el.}} + \pi_{\mathrm{str.}}$$

where the first term is a macroscopic, van der Walls pressure, the second is an electrical double layer pressure, and the third is a »structural« component. Unfortunately, the authors, however, have not made use of the available information about the structural component of the disjoining pressure, as, for instance, discussed at length by Peschel and co-workers. Thus, the fact that the disjoining pressure in Peschel and Adlfinger's studies vary in a highly unusual manner with temperature is completely ignored. Recall that the study by Peschel and Adlfinger showed that the structural component is highly temperature sensitive — in other words, a feature which cannot by any stretch of imagination be ascribed to the electrical double layer contribution. Furthermore, as mentioned elsewhere in this paper (and other papers by the present author and his associates), it is obvious that vicinal water is essentially unaffected by electrical double layers. In short, therefore, one must take issue with the conclusion by Pashley and Kitchener that »these very thick films are controlled by long-range double-layer repulsion.« While indeed electrical double layer repulsion must play a prominent role, it appears from the other studies discussed in this paper (and elsewhere) that one cannot ignore the structural contributions to the vicinal water — particularly not for films of about 1,500 Å, as discussed in the paper by Pashley and Kitchener.

It is interesting that, below saturation, the thickness of water layers on clean quartz surfaces appear much thicker than predicted by the DLVO type forces. It seems reasonable to suggest that indeed the contribution is from the structural part of the disjoining pressure — in other words, the vicinal water.

Finally, in passing, it should be observed that Pashley and Kitchener conclude that the thick wetting films observed were probably not due to gel layers formed on the quartz surface. This was based on ellipsometrical measurements suggesting that, at most, a 5Å layer of water existed with low refractive index — and even this observation might be explainable in terms of the intrinsic surface rugosity.

V. STRUCTURAL ASPECTS

At present the structure of bulk water still escapes a detailed, »eindwandfrei« description. Rice[56] has succintly stated the current situation regarding the structure of bulk water:

> *»Despite the effort expended, our factual knowledge is meager and our understanding rudimentary. For, under ordinary conditions the interpretation of the observed properties of water is rendered difficult by the simultaneous presence of positional, orientational and thermal disorder, along with a small but not neglible molecular dissociation. Furthermore, neither the existing studies of the liquids studied, nor the available methodologies of statistical mechanics, have yet provided a compact, useful description of liquids composed of molecules between which there are strong non-central, saturable, forces, such as exist in water.«*

In view of this state of affairs, it is then hardly surprising that our knowledge of vicinal water is meager and even more incomplete. The two major questions to be posed about vicinal water are: (A) what kind of structure (or, probably more precisely, structures) does (do) vicinal water have, and (B) what is the geometric extent of vicinal water?

The experimental evidence presently available makes the existence of vicinal water appear almost inescapable. However, it is indeed unfortunate that our understanding of vicinal water remains so fragmentary and incomplete. Thus, there is a remarkable and serious lack of information about some of the most immediate properties and structural attributes of vicinal water. As indicated, for example, very few measurements are available of the density of water at interfaces, although at least conceptually, this subject should be accessible to fairly simple experimentation. Perhaps even more profound is our lack of an adequate model for the extent of vicinal water: does vicinal water, in a bulk phase adjacent to a semi-infinite solid, extend over a finite distance, with a »reasonably sharp« boundary between the interfacially modified phase and the remainder of the solvent, or is there a gradual decrease in »structuredness« (or, »unstructuredness«) away from the interface? The question of the distance over which the vicinal water occurs (and decays) is crucial to the quantitative calculation of the properties of vicinal water from data on model systems.

V. A. »Water Polymorphs«

It is well known that »solid water« may occur with a large number of different structures, namely, as the high-pressure ice polymorphs and the clathrate hydrates.(Although the clathrate hydrates do contain guest molecules, the role played by the guest molecules is merely to stabilize the intrinsic water structure and the guest molecules only rarely play a functional (structural) role in the clathrate lattice network). At least nine high-pressure polymorphys of ice exist together with amorphous ice (see discussion below) and cubic ice. One of the most striking features of the high-pressure ice polymorphs is the small energy differences between these — often crystallographically extremely different — forms of solid water.

Rice and co-workers (see, for instance, Rice[56]) have proposed the study of amorphous solid water — denoted as H_2O (a. s.) — as a model of bulk water. The advantage is that, if indeed amorphous, solid water is essentially merely extensively supercooled liquid water, the study of water is facilitated as it becomes possible at low temperatures to separate the effects of thermal excitation and positional and orientational disorder.

In connection with the amorphous solid water, Rice points out that at very low temperatures, the specific heats of an amorphous solid may appreciably exceed the value for the corresponding crystalline solid. (Rice gives as examples germanium oxide and amorphous selenium). He also goes on to note that »it seems likely that this will also be true for H_2O (a. s.)« (in other words, for amorphous water). Thus, if vicinal water has attributes of amorphous nature, this might explain the large specific heats discussed elsewhere in this paper, particularly the data obtained by Braun and Drost-Hansen (see Section IV. E.). However, the structure could certainly not entirely correspond to an amorphous solid, partly because of the mobility (viscosity) being essentially of the order of magnitude of bulk water (within a factor of 10 or 100), partly because, were the water completely amorphous, it is unlikely that one could account for the thermal anomalies. The thermal anomalies appear to exhibit the nature of mixed first and higher-order phase transitions, which would seem to require elements of crystallinity. On the other hand (Rice, loco cit., p. 111) (note added in proof to the article by Rice), it is now generally recognized that there may exist several forms of amorphous water. Thus, once again, the possibility does exist that the different structures of vicinal water — representing the different stability domains within consecutive temperatures of thermal anomalies — may reflect transitions from one type of amorphous structure to another. Hence, it may be argued that proximity to an interface may well suffice to achieve a lower (minimum) energy for the water molecule, considering particularly the likelihood that the structures will exhibit cooperative behavior. If indeed this argument is correct, then it should not come as a surprise that thermal transitions occur — in fact, it should almost have been predicted from the knowledge of the high-pressure ice polymorphs. Again, it is by no means implied that the vicinal water structures, stabilized at interfaces, possess attributes of the ice polymorphs. After all, the viscosity of vicinal water, while possibly one or, at most, two orders of magnitude larger than that of bulk water, does not suggest the existence of crystalline lattice rigidity. (Compare in this connection also the Pauling theory of water structure, involving water as its own clathrate hydrate, but allowing for sufficient rearrangements to account for fluidity).

In the section below is discussed the studies by Rice (and co-workers) on various models of water, based on the study of amorphous ice and the high-pressure ice polymorphs. Other authors, for instance, Eyring and Marchi[57], as well as Rice, have suggested that water might be represented in terms of structured elements resembling the high-pressure ice polymorphs. More precisely expressed, Rice notes »We are, therefore, lead to propose that low temperature H_2O (a. s.) has a random network structure of *mixed lattice parentage*, i. e., that the structure is characterized by locally random 000 angle deviations from Ice-Ih or Ic, Ice-II and Ice-III type lattices« (emphasis by present author).

In view of the considerations presented above, it would seem reasonable to propose that between different, consecutive intervals of thermal anomalies, different types of »transient lattice structures« may be stabilized at the interface between water and a solid surface. These transiently stabilized structures may indeed be of high-pressure ice polymorph parentage, but must possess the attributes of fluidity and thus, probably be characterized by some distributions of lifetimes. (see, for instance, Eisenberg and Kauzman, 58, p. 150—154 or the paper by the present author[3]). Thus, it would not be unreasonable to propose that the vicinal water represents merely the transient stabilization of some potential structured entities with lifetimes of the order of one to two orders of magnitude greater than the dielectric relaxation time (in other words, relaxation times of the order of 10^{-9} to 10^{-10} sec). Obviously, if this is so, it should be particularly amenable to dielectric studies.

Rice has also pointed out the »relative ease of alteration of the many water molecule potential energy surfaces. That is, the evidence of the existence of many different crystalline ices, and the nature of their structures, suggests that a modest arrangement of the positions of a group of water molecules can (and does) generate new minima in the potential energy surface, and that these new minima correspond to qualitatively different connectivities of the hydrogen bond network.« This consideration may be as applicable to the vicinal water structures as it is to the low temperature form of water. In other words, the lattice energies of the different high-pressure ice polymorphs are very similar. (in the case of amorphous ice the individual water molecule mobility is indeed extremely low which is obiously not the case for vicinal water).

Returning to an argument similar in nature to the argument by Rice, one may interpret the existence of multiple thermal anomalies for vicinal water as manifestations of energetically closely spaced but structurally distinct entities, existing over narrow temperature ranges. This then, would suggest that notwithstanding the small energy differences, distinct populations may be maintained, differing from the »average bulk structure.« The same argument was made by Rice; we quote (p. 192):

»*... but why should the model we have proposed have a multimodal distribution of environments? Is it not possible (likely?) that a molecular mobility and thermal excitation blur all environmental distinctions and that there is only a unimodal, broad distribution of environments? Perhaps, but our basic argument is that the many molecule potential energy surface is such as to generate a multimodal distribution of environments.*«

Again, Rice points to the existence of several (in fact, many) solid forms of water (in terms of the high-pressure ice polymorphs) which have essentially identical nearest neighbor oxygen separations. Rice stresses that this appears to be a characteristic of the potential surface and, quite important, leading to the suggestion that such distribution may persist in the liquid with the result that the thermally broadened distribution still cannot be adequately described as unimodal. As regards vicinal water, it would seem appropriate then to follow Rice in suggesting (even if intuitively and only qualitatively) the use of different distinct »species« in vicinal water. Once again, vicinal water is neither amorphous ice nor crystalline ice, but, it certainly appears difficult to explain the occurrence of multiple temperature anomalies without invoking different distinct structures.

The existence of thermal anomalies in the properties of vicinal water appears firmly established. It seems also inescapable that the thermal anomalies must reflect structural events. The obvious question then is: do the thermal transitions reflect first-order phase transitions or second-order and/or higher-order phase transitions? Lumry and Rajender addressed themselves to this question:

»Since in systems at constant pressure, the occurrence of a sharp change in the slope of a parameter plotted as a function of temperature can occur only if there is a large entropy change, the kinks have been attributed to the cooperative behavior of a number of water molecules. However, such behavior must reveal itself by heat-capacity spikes which have thus far defied detection.«

The present author and his co-workers have attempted to resolve this problem. (See, particularly, the heat capacity measurements discussed in Section IV. E.).

Finally, it appears that the thermal anomalies are subject to considerable thermal hysteresis. This may not only explain why such data are conspicuously lacking in the literature, but explain also the lack of reproducibility and inconsistencies between different authors, often reported or implied in the literature. As for the possibility that any one of the thermal anomalies may represent the more or less sudden »melting« of some structurally induced different phase, see the discussion by the present author[3] and the comments by Franks and Ives[59].

VI. A MODEL FOR VICINAL WATER

Etzler[5] has recently developed a model (to be referred to as the EST model) for vicinal water based on a percolation theory treatment of bulk water structure, proposed by Stanley and Teixeira[60]. Etzler's treatment resembles that of a two-state mixture model without the need to invoke the existence of long-lived geometrically indentifiable structures (»icebergs«); the model retains the short life-times of hydrogen-bonds; of the order of 10^{-12} seconds. No doubt because of this feature, the model fails to predict the occurrence of thermal anomalies, but the EST model does predict some properties of vicinal water in fair agreement with some of the observed values discussed in the present paper. The model takes as its starting point the observation by Stey[61] that the single-particle enthalpy distribution function for water is bimodal, suggesting that water consists of two »types« or, more accurately, two microstates in phase-space (not implying a preponderance of separate, stable, geometric entities.) These two states are separated by about 2.5 kcal/mol. In the Stanley-Teixeira model of water (at low temperatures) the molecules are assumed to be in one of five hydrogen-bonding configurations, namely 0, 1, 2, 3, or 4-bonded. In the percolation model (considering the bond connectivity) »ice-like« configurations (i. e., 4-bonded species) occur (at 25 °C) the extent 0.14 — in remarkable agreement with Stey's calculations. The EST model for vicinal water assumes a (rather slight) increase in stabilization of the 4-bonded state due to proximity to the solid, — without specifying a mechanism for this stabilization. Based on the previously reported value for the specific heat of water (Braun and Drost-Hansen, 35) of 1.25 cal/°C — gram and now confirmed by the measurements reported here by Cianci and Drost-Hansen, the model predicts a 30% increase in the H-bond probability, corresponding to 0.4 of molecules being 4-H-bonded. The EST model also allows for estimates to be made of the density of vicinal water (assuming the volume properties of the 4-H-bonded species resemble those of ice). Based on the volume fraction discussed above, this leads to a value of 0.97 g/cm^3 for the density of vicinal water, in good agreement with the data presented above (Etzler and Fagundus, 23). Finally, the EST model (with some additional assumptions) leads to an estimate of about 750 cal/mol for the difference in enthalpy between bulk and vicinal water (say between 15 and 30 °C); for comparison, this may be compared to the observed enthalpy changes at each of the thermal transitions (at least T_3, T_4, and T_5 of about 1 to 20 cal/mol (averaged over the total amount of vicinal water).

According to the currently available data and in the view of the model proposed by Etzler, it appears that the properties of water near interfaces may be explained by assuming increasing hydrogen bond probability with decreasing distance from a solid surface. The possibility exists that the thermal anomalies may be explained without invoking geometric, molecular reordering (such as those which occur at the transition between the various ice polymorphs). Instead, nothing more may be required than quantitative (but relatively abrupt) changes — i. e. changes in degree of ordering as opposed to a qualitatively different structural rearrangement. In the absence of a structural transition the heat capacity differential between the interfacial and the bulk water suggests that ΔH between vicinal and bulk water to be an ever increasing function of temperature. Apparently this precarious situation is relieved (apparently periodically) at the structure transition temperatures. At these temperatures, the thickness of the interfacial zone is probably abruptly reduced and the hydrogen bond probability suddenly changes. Our current understanding of interfacial water structure, however, is not sufficient to predict the transition temperatures or the details of such transitions.

VII. SUMMARY AND CONCLUSIONS

Considerable progress has been made over the past decade in confirming the existence of vicinal water. The anomalies in the thermal properties of vicinal water have been particularly well authenticated, and quantitative estimates have been obtained for a number of properties of vicinal water (both equilibrium thermodynamic properties and transport processes). The best current estimates of the thickness of vicinal water is in the range of 0.01 to 0.05 μm. However, the structure and details of the distance dependence of vicinal water remain highly uncertain. A model for vicinal water proposed by Etzler (based on the percolation treatment of liquid water by Stanley and Teixeira) appears promising although presently unable to account for the thermal anomalies. The »Paradoxical Effect«, i. e. the occurrence of vicinal water in most (or all) aqueous interfacial systems (at least, those with solid surfaces) regardless of the specific chemical nature of the surface, is also established quite firmly; although, we can offer no theoretical explanation for its existence at this time.

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SAŽETAK

Novi termodinamički podaci o vicinalnoj vodi sa modelom za njihovu interpretaciju

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Opisani su rezultati novih mjerenja na vicinalnoj vodi (»vicinalnom« se naziva ona voda, čija je struktura modificirana uslijed blizine čvrste površine) i to posebno podaci o gustoći, termičkom koeficijentu ekspanzije i viskozitetu. Proučavanjem ovih rezultata kao i usporedbom s rezultatima prijašnjih proučavanja, dolazi se do zaključka da se vicinalna voda nalazi uz površinu u slojevima debljine 30 do 100 molekularnih promjera. Vrlo je vjerojatno, da se vicinalna voda ne inducira isključivo u blizini čvrstih površina, već i kao voda hidratacije makromolekula, ako su iste veće od neke minimalne veličine, vjerojatno u području između 1000 i 5000 Daltona. Isto su tako primjenom diferencijalne scanning kalorimetrije potvrđene kritičke temperature kod kojih dolazi do anomalija u termičkim svojstvima vicinalne vode. Pokazano je, da su kritičke temperature za te anomalije neovisne o naravi čvrste površine. To je ustanovljeno na osnovi mjerenja na poroznom kvarcu, suspenzijama polistirena i dijamantnog praha. Time se još jednom potvrđuje tzv. »paradoksalni efekt«. Na kraju rada raspravlja se o perkolacijskom modelu vicinalne vode, koji su predložili Stanley i Texeira. Taj model predskazuje gustoću vicinalne vode od 0,97 g/cm³ što se dobro slaže s mjerenom vrijednošću. Model, međutim, ne predviđa postojanje anomalija u termičkim svojstvima.