

CALORIMETRIC EVIDENCE FOR STRUCTURAL TRANSITIONS OF HIGHER ORDER IN THE PORE WATER OF PRESSED SILICIC ACID BY USING DSC

G. Peschel and R. Krämer

Institut für Physikalische und Theoretische Chemie der Universität Essen

Abstract

Structured water near solid surfaces can particularly exhibit structural transitions of higher order at about 15°, 30°, 45°, and 60°C the mechanism of which is still poorly understood.

In the present work compressed samples of silicic acid (Aerosil 200) were wetted with aqueous LiCl and CsCl solutions, respectively, and after heating up and cooling down again subject to DSC tests, which yielded exothermic peaks in ranges around 30° and 45°C. Their location on the temperature scale is discussed in terms of the structure temperature in the pore water.

1. INTRODUCTION

It is a widely accepted view that water near interfaces is affected in its structure and, hence, exhibits physicochemical properties notably different from those of the bulk phase [1-4]. Recent studies with mica and fused silica plates, respectively, as the wetted substrates have revealed that interfacial water structuring can extend up to about 3 nm [5-7].

A particular feature of vicinal water structure might be the occurrence of its obviously abrupt changes at about 15°, 30°, 45°, and 60°C [1-4], which have turned out to be of utmost biological importance [4,5]. With respect to the mechanism it is commonly believed that about these temperatures water contiguous to surfaces undergoes structural transitions of higher order [8].

Clifford [9], however, emphasizes that the occurrence of these anomalies is chiefly dependent on the presence of a microporous substrate. What makes the phenomenon still more puzzling is the fact that the temperatures at which the structural transitions take place are practically independent on the chemical nature of the solid substrate ("paradoxical effect") [2].

Many experimental techniques have been employed to substantiate the existence of such anomalies at the solid/aqueous solution interface [1,2]. A direct approach was tried by Pe-

schel [10] investigating the disjoining force in thin aqueous layers between two fused silica plates. He found significant maxima at about the characteristic temperatures which were obviously due to strong surface hydration effects. These findings were corroborated by examining the surface viscosity of water near fused silica surfaces [12]. Mention must be made, however, of the physical state of the silica surfaces used. They displayed a mean roughness of about 10 nm so that by pressing them in water against each other very small pore openings could be formed which might according to Clifford [9] be the origin of the anomalous thermal effects.

Calorimetric investigations in this special field are very sparse. Ling and Drost-Hansen [12] have attacked the problem in question by a thorough DTA study of the system porous glass/water by varying the average pore diameters from 20 up to 200 nm. They, in fact, detected structural transitions at about the characteristic temperatures but because of experimental difficulties felt unable to analyze the order of the transitions.

Their evidence is founded on endothermic peaks and rather steep aberrations of the baseline. It remains to point out that the apparent heats of transitions were found in the range of 40 up to 410 J/mol water which is believed to reflect the right order of magnitude.

Recent work related to this subject is due to Peschel and Furchtbar [13] who investigated by DSC technique compressed disks of highly disperse silicic acid wetted by different aqueous electrolyte solutions. They likewise found anomalous caloric effects at about the temperatures in question. It must be stressed, however, that simple heating curves lead to minor effects only appearing as "kinks" on the baseline. But first heating up the sample to about 85°C, then rapidly cooling down to about 10°C and heating up again provided rather significant exothermic peaks at about some of the characteristic temperatures.

The essential question concerning these experiments is, how strong the dependence of the anomalous caloric effects on the pressure is, which was applied when producing the disks from disperse silicic acid. The pressure on the other hand, determines the pore size distribution in the test samples. The present work, therefore, aims at carrying on the experiments performed by Peschel and Furchtbar [13] with special focus on the influence of pore size.

2. EXPERIMENTAL

2.1 Method

DSC technique [14,15] (DSC2, Perkin Elmer) was employed to examine the caloric behavior of compressed disks consisting of highly disperse silicic acid (Aerosil 200, Degussa) which were wetted by small amounts of aqueous solutions of selected electrolytes.

In order to study by DSC surface hydration phenomena and to get valuable information about the mechanism it seems preferable to modify the structure of the aqueous phase by the addition of ions according to the lyotropic series [16]. Li^+ among the alkali cations has the extreme position of a strong structure former, followed by Na^+ and K^+ . The position of the strongest structure breaker is occupied by Cs^+ . Therefore, when carrying out experiments with Li^+ and Cs^+ solutions, respectively, it may happen that widely different caloric effects appear which, on the other hand, should facilitate the explanation of the hydration effects.

Let us as a further parameter regard the size of the pore openings in the compressed samples, since Clifford [9] stresses the importance of hydration phenomena in pores and capillaries.

2.2 Measuring Procedure

In a number of cases the test samples were pressed to disks from disperse silicic acid by applying pressures from $1 \cdot 10^8$ up to $4 \cdot 10^8$ Pa. Most of the experiments, however, were run with disks compressed by a constant pressure of $3 \cdot 10^8$ Pa. The surface area of the porous disks was about $2.0 \cdot 10^5$ m^2kg^{-1} (BET with nitrogen). The average size of the primary particles of Aerosil 200 turned out to be 12 nm. Application of electron microscopy showed that the primary particles had formed aggregates with a diameter of about 100 - 200 nm.

When starting an experiment 20 mg of fragments of the pressed disks were weighed in small pans manufactured from stainless steel. Then 10 mg of aqueous solution were dropped on the fragments. Finally the pan was closely sealed. The reference pan was filled with pure compressed silicic acid.

In the first instance, a given sample was heated up from about 10°C to about 85°C with a heating rate of 10 degrees per minute (Procedure I). The result was that the baseline displayed rather insignificant "kinks" only at about the characteristic temperatures. The sensitivity was as in all the following runs adjusted to 0.42 mJ s^{-1} .

In view of the poor evidence a modified procedure was employed when carrying out the following runs. The sample was as stated before heated up to about 80°C , then cooled down to about 10°C by a cooling rate of 10 degrees per minute and finally reheated again. The most interesting features of these experiments were that at about some of the characteristic temperatures rather large exothermic caloric peaks appeared which could well be compared with respect to their localisation on the temperature scale.

2.3 Chemicals

The salts used (LiCl , NaCl , KCl , CsCl) were starting from p.a. grade purified by the "adsubble method" [17,18] in order to remove traces of surfactants. The water used was triple-

distilled.

3. RESULTS

Though thermal anomalies in vicinal water have been reported by numerous authors, it is still rather uncertain if bulk water and bulk aqueous solutions, respectively, can likewise undergo structural transitions of higher order on the common temperature scale. If this were the case it should be worthwhile to look for correlations with respect to the anomalous surface effects.

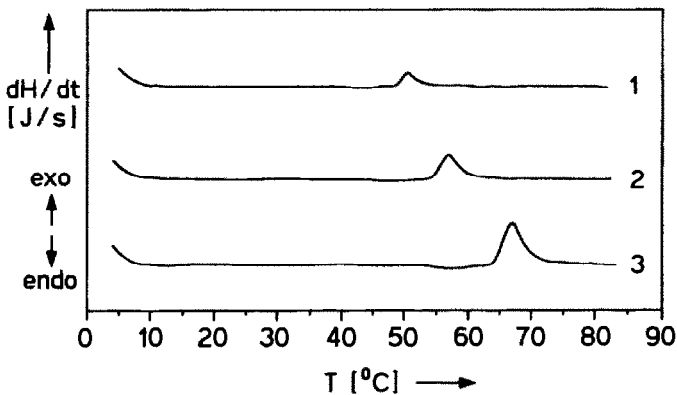


Figure 1. DSC curves of 20 μl 10^{-2} M aqueous NaCl solutions for different reheating rates, 1, $5^{\circ}\text{C min}^{-1}$, 2, $10^{\circ}\text{C min}^{-1}$, 3, $20^{\circ}\text{C min}^{-1}$.

DSC tests with differently concentrated aqueous electrolyte solutions (LiCl, NaCl, KCl, CsCl) in quantities of 20 mg according to Procedure I provided practically no anomalous caloric effects. Employing, however, Procedure II the situation revealed to be quite different. For all selected concentrations (10^{-4} - 10^{-1} M) a moderately large exothermic peak appeared in the temperature range 50° - 65°C . Along with that the peak shifted to higher temperatures and grew larger in its area. Fig. 1 shows the results for a 10^{-2} M NaCl solution. The peak areas correspond to maximally 50 J mol^{-1} . It seems noteworthy that highly concentrated electrolyte solutions (1 M and more) did not display any caloric peak.

In order to check the influence of the pressure applied for producing the silica disks on the caloric effects exerted by the wetting medium, DSC tests were carried out with 1 M

aqueous solutions of LiCl and CsCl, respectively, by varying the pressure.

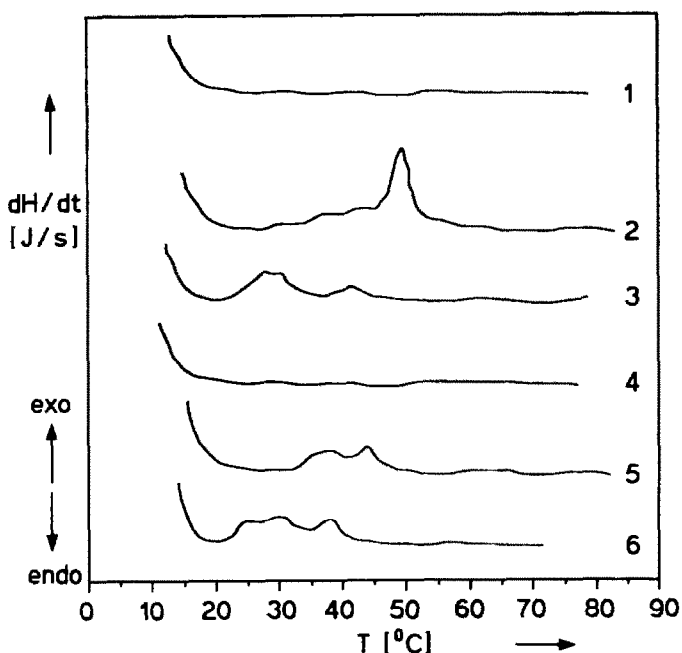


Figure 2. DSC curves of Aerosil 200 wetted with aqueous LiCl and CsCl solutions, respectively, and compressed with various pressures. 1, 1 M LiCl, $1 \cdot 10^8$ Pa; 2, 1 M LiCl, $2 \cdot 10^8$ Pa; 3, 1 M LiCl, $3 \cdot 10^8$ Pa; 4, 1 M CsCl, $1 \cdot 10^8$ Pa; 5, 1 M CsCl, $2 \cdot 10^8$ Pa; 6, 1 M CsCl, $3 \cdot 10^8$ Pa.

The thermograms in Fig. 2 reveal that for the smallest applied pressures no peak can be detected. Regarding LiCl an exothermic deviation from the baseline sets in at about 30°C and clearly changes into a large exothermic peak at about 50°C; by increasing the pressure two peaks appear both lying below 50°C. A similar picture is found for CsCl, irrespective of the occurrence of two peaks for both pressure.

A significant feature of these experiments, however, is that with increasing pressure applied to the silica disks, i.e., with decreasing size of the pore openings, the exothermic peaks are shifted to lower temperatures.

Fig. 3 displays thermograms for the aqueous wetting solutions of LiCl, NaCl, KCl, and CsCl and the constant pressure

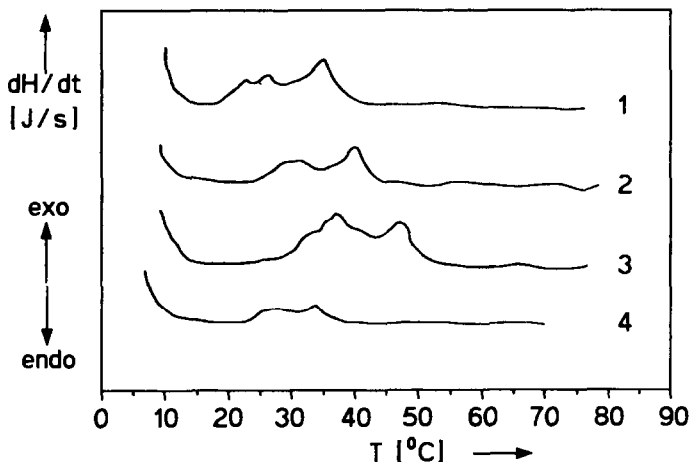


Fig. 3. DSC curves of Aerosil 200 compressed with $3 \cdot 10^8$ Pa and wetted with 0.1 M aqueous solutions of 1, LiCl; 2, NaCl; 3, KCl; 4, CsCl.

$3 \cdot 10^8$ Pa applied to the silica disks. All DSC curves obtained are distinguished by the occurrence of two adjoining exothermic peaks; for LiCl they are localized at about 25°C and 33°C, for NaCl at about 30°C and 38°C, for KCl at about 37°C and 47°C, and for CsCl at about 27°C and 33°C. In the latter case the effect is rather small.

There is no question that the concentration dependence of the caloric effects of aqueous LiCl solutions is particularly intriguing (Fig. 4). With increasing concentration the lower temperature peak is finally shifted down to about 15°C, thereby decreasing its height. The higher temperature peak is subject to a similar shift, but its height grows larger and more.

4. DISCUSSION

It is certainly important to recognize that applying Procedure II only to bulk aqueous solutions of electrolytes provided well detectable caloric (exothermic) effects in contrast to Procedure I. It is, of course, rather difficult to explain this extraordinary behavior at the first attempt. Realizing that water is well-known for its many-sided reactivity let us speculate on the ability of small quantities of

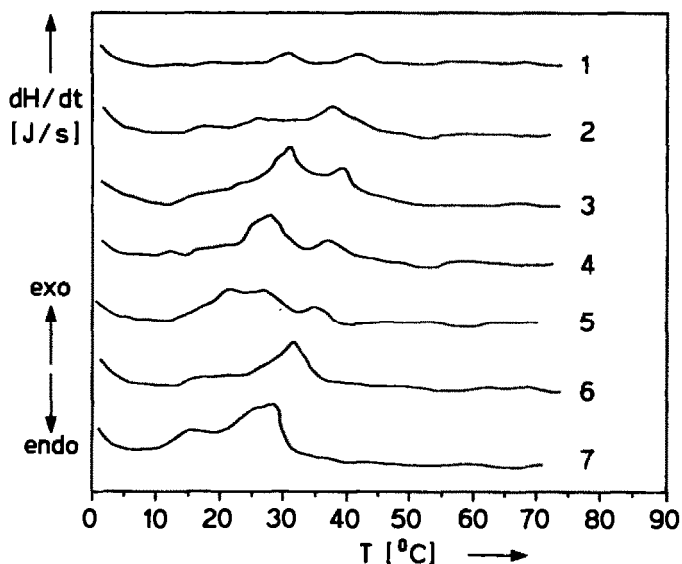


Fig. 4. DSC curves of Aerosil 200 compressed with $3 \cdot 10^8$ Pa and wetted with 1, H₂O, and differently concentrated aqueous LiCl solutions, 2, 10^{-5} M; 3, 10^{-4} M; 4, 10^{-3} M; 5, 10^{-2} M; 6, 10^{-1} M; 7, 1 M.

aqueous solutions to suffer supercooling within the course of Procedure II. When reheating such a sample it might jump into equilibrium in a small temperature range where possibly some sort of structural transition is believed to occur, even if this is practically not detectable by employing Procedure I. This tentative assumption is corroborated by the fact that the transition enthalpies in all tests with aqueous electrolyte solutions turned out to be exothermic contrary to that what was expected.

When in Procedure II after cooling down the temperature was kept for, e.g., five minutes at about 12°C reheating did not provide any caloric effect on the temperature scale. Obviously the system had turned within the period of some minutes from the nonequilibrium into the equilibrium state.

Quite another explanation could be derived from findings due to Krasnogolovets et al. [19]. The authors succeeded in showing by NMR tests that water containing dissolved oxygen exhibited weaker hydrogen bonds. In the present case the first heating up in Procedure II might serve for degassing the solution sample which then by further thermal treatment

might pass into a state which makes structural transitions much easier possible.

In order to understand the results in Fig. 2 let us recall that Luck et al. [20] investigated porous glass exposed to water vapor by infrared technique and provided evidence for a more disorganized structure in pore water than in the bulk. They particularly assigned to pore water a 'structure temperature' which is introduced to be the temperature at which bulk water displays the same state of hydrogen bonding.

Similar considerations were reported by Thompson [21] who speculated that water is present in small clusters in pores. That water in pores of silica can have a rather broken structure has been advocated by Clifford and Pethica [22] who in their NMR-investigations found an appreciable (14 ppm) proton shift upfield and, this is of large importance, a shorter spin-lattice relaxation time than in bulk water.

Commonly the reason for disruption of water structure is believed to be created by space requirement for ordinary water structure, which cannot be fulfilled in small pores.

On the other hand, pore water with a less tough hydrogen bond structure can, as is widely acknowledged, easily be subject to the orienting influence of polar surface groups. Thus the existence of an extended hydration layer on the pore wall can be assumed.

According to Drost-Hansen [2] the hydration sheath adjacent to a solid surface is followed by a disordered transition zone which passes over into bulk structure. Using this picture one can easily imagine that in sufficiently small pores the median part of pore water might be more or less disordered according to the formation of hydration water by the silica surface or adsorbed ions, respectively, when the wetting medium is an aqueous electrolyte solution. This is, of course, another mechanism to disrupt water structure within the pores. The pore radii (determined by nitrogen adsorption) showed a broad distribution with peaks at about 14 nm ($2 \cdot 10^8$ Pa), 12 nm ($3 \cdot 10^8$ Pa), and finally about 6 nm ($10 \cdot 10^8$ Pa). The porous glass investigated by Luck et al. [20] had pore diameters of about 10 nm.

From that, what is said before, follows that smaller pores (micro- or mesopores) imply increasing perturbation of water structure. Hence, pore water can achieve a structure temperature of, say, 60°C though the measurable temperature is not larger than, e.g., 30°C.

The implication is that the structural transition in the range about 60°C (Fig. 1) might occur in sufficiently small pores at about one of the other characteristic temperatures according to the hydrogenbonded water structure in the pores. Increasing the pressure applied to the disks reduces the diameter of the pore openings and along with that the number of hydrogen bonds in the pore water. Consequently the exothermic peaks should show a shift to the low temperature side. But just that was found.

The findings in Fig. 3 lend further support to our idea.

Li^+ ions will in comparison with Na^+ and K^+ ions via adsorption on the pore wall create the strongest hydration sheath and consequently the largest molecular disorder in the median part of the pore. Hence, the exothermic peak for LiCl should in comparison to NaCl and KCl appear at a rather low temperature, when the concept of a structure temperature applied to pore water is right. For CsCl the situation might be quite different since Cs^+ ions completely disrupt surface hydration structure, but at any rate they create disorder and, thus, enhance the structure temperature of pore water.

The question, why at least two adjoining peaks appear cannot be answered promptly. Possibly, two (or more) differently sized pore systems are existent in the compressed disks.

This problem is likewise evident in Fig. 4. What can be deduced from this picture is, that the smaller pore system (on the low temperature side) differs in its behavior from the less smaller pore system (adjoining on the higher temperature side) in that the concentration dependencies of the caloric peaks are reversely directed. May be, that the particular property of Li^+ ions to be excluded from small pores containing hydration water [4,23] is a basis for the explanation of this extraordinary effect. The error in the determination of the transition temperature lies in the order of some degrees because of the rather great heating rate adjusted.

Our concept, to be sure, cannot give any explanation for all the thermal anomalies described in literature which are mostly crowded around the characteristic temperatures. We believe that two essential parameters determine the localization of the anomalies on the temperature scale. These are the pore size of the porous substrate and the strength of the hydration sheaths on the pore walls which by virtue of their volume, particularly in the case of Li^+ -solutions, might additionally impose space limitations for the formation of ordinary water structure. In face of our experimental evidence we cannot exclude the fact that the "paradoxical effect" owes its strange features rather to the presence of pores of appropriate size than to the chemical nature of the substrate.

We believe that our arguments do not contradict the view of Etzler [24] who postulates the existence of an appreciable amount of hydration water in small silica pores.

5. CONCLUSIONS

In the present work we have tried to give an explanation for the appearance of thermal anomalies in highly porous systems in contact with aqueous electrolyte solutions. The disks compressed from silicic acid might in the sense of highly sophisticated experiments serve as very simple samples of biological tissue which is extinguished by the occurrence of multiple thermal anomalies. Our understanding of such phenomena is still very poor; much work has still to be done to reveal all the details of the underlying mechanisms.

6. REFERENCES

- 1 W. Drost-Hansen, *Ind. Eng. Chem.* 61 (1969) 10.
- 2 W. Drost-Hansen, in H.D. Brown (Ed.), *Chemistry of the Cell Interface, Part B*, Academic Press, New York, 1971, pp. 1 - 184.
- 3 B.V. Derjaguin and N.V. Churaev, in C.A. Croxton (Ed.), *Fluid Interfacial Phenomena*, J. Wiley & Sons Ltd., 1986, pp. 663 - 738.
- 4 P.M. Wiggins, *J. Theor. Biol.* 32 (1971) 131.
- 5 J.N. Israelachvili and G.E. Adams, *J. Chem. Soc. Faraday Trans I* 74 (1978) 975.
- 6 R.M. Pashley, *J. Colloid Interf. Sci.* 80 (1981) 153; 83 (1981) 531.
- 7 G. Peschel, P. Belouschek, M.M. Müller, M.R. Müller and R. König, *J. Colloid Polym. Sci.* 260 (1982) 444.
- 8 W. Drost-Hansen, *Colloq. Int. C.N.R.S. (Eau, Syst. Biol.)* 1976, pp. 177-86.
- 9 J. Clifford in F. Franks (Ed.), *Water. A Comprehensive Treatise, Vol. 5*, Plenum Press, 1975, pp. 75-132.
- 10 G. Peschel in O.L. Lange, L. Kappen and E.-D. Schulze (Ed.), *Ecological Studies 19, Water and Plant Life*, Springer-Verlag, Berlin, Heidelberg, New York, 1976, pp. 6-18.
- 11 G. Peschel and K.H. Adlfinger, *Naturwissenschaften* 56 (1969) 558.
- 12 C. Ling and W. Drost-Hansen, in K.J. Mittal (Ed.) *Adsorption at Interfaces*, ACS Symp. Ser. 8, American Chemical Society, Washington, 1975, pp. 129-156.
- 13 G. Peschel and U. Furchtbar, *Progr. Colloid Polym. Sci.* 83 (1990) 216.
- 14 W.W. Wendlandt, *Thermal Analysis*, J. Wiley & Sons, 3rd Ed. 1986.
- 15 W. Hemminger and G. Höhne, *Grundlagen der Kalorimetrie*, Verlag Chemie, Weinheim, New York, 1979.
- 16 B.E. Conway, *Ionic Hydration in Chemistry and Biophysics*, Elsevier, Amsterdam, Oxford, New York, 1981.
- 17 R. Lemlich, *Adsorption Bubble Separation Technique*, Academic Press, New York, London, 1972.
- 18 F. Sebba, *Ion Flotation*, Elsevier Amsterdam, London, New York, 1962.
- 19 V.V. Krasnogolovets, J.D. Zelepukhin and V.D. Zelepukhin, *Z. Naturforsch., Ser. C*, in press (1991).
- 20 W.A.P. Luck, D. Schiöberg and U. Siemann, *J. Chem. Soc. Faraday Trans II*, 76 (1980) 136.
- 21 W.K. Thompson, *J. Chem. Soc.* (1964) 3658.
- 22 J. Clifford and B.A. Pethica, in A.K. Covington and P. Jones (Ed.), *Hydrogen-bonded Solvent Systems*, Taylor and Francis, London (1968) p. 169.
- 23 V. Vlachy and A.D.J. Haymet, *J. Electroanal. Chem.* 283 (1990) 77.
- 24 F.M. Etzler, *J. Colloid Interf. Sci.* 92 (1983) 1.