Institute of Paper Science and Technology
Atlanta, Georgia

IPST TECHNICAL PAPER SERIES

NUMBER 348

TEMPERATURE DEPENDENCE OF THE HEAT CAPACITY

OF WATER IN SMALL PORES

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FEBRUARY, 1990

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Abstract

The temperature dependence of the heat capacity of vicinal water has been measured in 242 Å silica pores. The data are discussed in light of measurements of other physical properties of vicinal (interfacial) water. Notable heat capacity "spikes" were observed at temperatures which may be related to the previously discussed structural transitions in vicinal water. Physiological anomalies have been observed by various authors at these same temperatures. This work will be discussed in light of a statistical thermodynamic model for vicinal water proposed by Etzler. [*J. Colloid Interface Sci.* <u>92</u>(1), 43 (1983).]

Introduction

Because of its significance to biology and various technological processes, the properties of water have been studied for many years. Interfacial water (vicinal water) has properties that differ considerably from those of bulk water. For instance, water in 140 Å diameter silica pores is approximately 3% less dense than the bulk.[5,6] Drost-Hansen, in particular, has written a number of comprehensive reviews on the properties and biological significance of vicinally modified water.[1-4] A considerable body of evidence exists which suggests that water may play significant roles in biology and in various chemical processes at aqueous solution/solid interfaces.

The heat capacity of water near surfaces of a variety of materials has been shown to be greater than that of the bulk. For instance, Braun and Drost-Hansen[7] have measured the heat capacity of water adsorbed on the surfaces of such diverse materials as porous glass, zeolite, diamond, and charcoal. They have found the value of the heat capacity of vicinal water (water near interfaces) to be approximately 1.25 cal/g/K and independent of the surface material. The apparent independence of the properties of vicinal water and the nature of the surface has been called the "paradoxical effect" by Drost-Hansen. Etzler has measured the heat capacity of vicinal water in various pore size silicas.[27,28] The heat capacity of the vicinal water goes through a maximum

value (approximately 25% greater than that of bulk water) in 7 nm radius silica pores.

Other physical properties have been measured and also support the notion that the behavior of vicinal water is altered. Low et al.[11-13] have studied many thermodynamic properties of water in montmorillonite clays. More specifically, they have examined the partial specific volume, partial specific heat capacity, and viscosity of water in these materials. These measurements suggest that vicinal structuring extends to around 5 nm from the surface and decays approximately exponentially. The value that Low measured for the partial specific volume for water in the clays was approximately 1.02 cm^3/g, which corresponds to a density of 0.98 g/cm^3, about the value found by Etzler and Fagundus in their examination of the density of water in silica pores and by Clegg in *Artemia* cysts.[14-17]

Peschel and Adlfinger[8-10] have studied the viscosity and disjoining pressure of water between two quartz plates as a function of temperature and have observed maxima at 15, 30, and 45°C. Etzler and Liles[18] have measured the temperature dependence of the selectivity coefficient (of K$^+$ versus Li$^+$) of ions in silica pores. The selectivity coefficient was found to go through a series of maxima separated by approximately 15°C (ie., 15, 30, 45°C, etc.). These results are in agreement with those of Wiggins[19,20] and Hurtado and Drost-Hansen.[21] Furthermore,

Wiggins showed that the temperature dependence of the selectivity coefficient remained qualitatively the same when rat renal cortex was substituted for silica gel (ie., the temperatures of the maxima remain the same).[20] Etzler and Drost-Hansen[22,23] have reported numerous examples of physiological anomalies which occur at the above temperatures. Nishiyama[24-26] has noted physiological anomalies which occur in a variety of plants at these same temperatures. Drost-Hansen[2,22,35] long ago suggested anomalies in physiological processes reflect structural transitions in the water. In this paper, we will discuss our measurements on the heat capacity of vicinal water and its relation to the temperature dependence of the modification of water by propinquity to solid surfaces.

Etzler[31] has proposed a statistical thermodynamic model for vicinal water. The model discusses the structure of water both in terms of a bond percolation model for bulk water (proposed earlier by Stanley and Teixeira[33]) and a single particle enthalpy distribution calculated earlier by Stey.[32] The model suggests that vicinal water differs from the bulk in that hydrogen bonding between water molecules is enhanced by propinquity to solid surfaces. Vicinal water thus would appear to be similar to water under negative pressures or at supercooled temperatures; that is hydrogen bonding between water molecules is enhanced by proximity to a surface.

In an earlier paper,[27] the heat capacity of water in silica pores has been shown to agree with predictions suggested by Etzler's model and Stey's distribution function. Specifically, the prediction that the heat capacity reached a maximum value near 1.25 cal/g/K was verified experimentally. In the present paper we report measurements of the heat capacity of water in 242 Å diameter silica pores. This present study differs from earlier studies of the heat capacity of vicinal water in that instrumentation now available is capable of measuring heat capacity with higher precision than in previous studies and that measurements were obtained over a significant temperature interval. Two questions concerning the nature of vicinal water which might by answered by such data are:

1. Does vicinal structuring become unimportant at temperatures well below the normal boiling temperature (100°C)?

2. Are heat capacity "spikes" observed at the temperatures where Drost-Hansen and others have observed physiological anomalies and other unusual phenomena which have been attributed to structural changes in vicinal water?

Earlier, Lumry[34] suggested such heat capacity "spikes" might be found if structural transitions indeed occur at the

"Drost-Hansen" temperatures.

Experimental

A differential scanning calorimeter (Setaram DSC-111 G) was used. The Setaram DSC operates on the Calvet principle. Data manipulation and heat capacity calculations were completed with the aid of Astra Plus Thermal Analysis Software (Astra Scientific International, San Jose, CA). Normal calibration procedures were followed. The heat capacity of bulk water was found to be consistent with earlier literature values.

The water used in these experiments was distilled and degassed before use. The silica used in these experiments had a pore volume of 0.89 cm^3/g of silica and an average pore diameter of 242 Å. The silica was dried at 110°C for at least 24 hours prior to use. The dried silica was stored in a desiccator.

Samples for the determination of the heat capacity of pore water were made as follows. Silica was placed in a DSC sample cup and weighed (8-10 mg). To the silica sample, enough water was added to the sample so that approximately 50% of the total mass of water fills all the pores in the silica. After the water was added, the sample was placed under reduced pressure to aid water penetration into the pores. After the sample was removed from the

vacuum chamber, the mass of water in the sample was approximately 15-25 mg. Once the sample was properly prepared, it was sealed and placed in the calorimeter at room temperature.

The calorimeter was then brought to the initial temperature of the scan. The temperature was kept constant until the calorimeter came to equilibrium. Once this occurred, data collection was initiated. The sample was scanned from 1°C to 60°C at a rate of 2°C/min.

Once the heat capacity of the silica/water slurry is determined experimentally, it is possible to calculate the heat capacity of water in the pores. The mean heat capacity of water $C_p(water)$, in the sample is calculated.

$$C_p(sample) = f_{silica}C_p(silica) + f_{water}C_p(water)$$

Here f is the mass fraction of the relevant component. The heat capacity of the pore liquid, $C_p(pore)$, may be calculated by

$$C_p(water) = f_{pore}C_p(pore\ water) + f_{bulk}C_p(bulk)$$

Here f_{pore} is calculated from the known pore volume and pore density. Etzler and Fagundus[5] found that the density of water in 242 Å silica pores is approximately 0.990 g/cm^3 and is independent of temperature (within 2 parts per thousand over

the range of 10-40°C). Small variations in the density with temperature are unlikely to significantly alter the value of the heat capacity. Earlier data collected at 25°C in 7 nm radius silica pores by Cianci,[36] who assumed the pore water density to be 1.00 g/cm^3, and data collected by Etzler in the same pores are within experimental error identical. Also, no correction was made for a change in pore volume. Any variation of the pore volume of the silica with temperature (over the short temperature range studied) should be negligible. The heat capacity of bulk water is calculated by fitting the water heat capacity data from the literature[29] to an equation suggested by Speedy.[30] (See References 27 and 28 for more details regarding the calculation of the heat capacity of water in silica pores.)

Results and Discussion

In these experiments we have measured the temperature dependence of the heat capacity of vicinal water. The temperature variation differs markedly from the temperature dependence of the heat capacity of bulk water.

The silica used in these measurements has an average pore size of 242 Å and a pore volume of 0.89 cm^3/g of silica. The data are presented in Figure 1. This plot shows the average value and the standard error of a total of 8 measurements on different dry silica samples. Notice that the standard error for the measurements is quite small for heat capacity measured by DSC. A linear dependence on temperature is used to model the functional variation of the heat capacity of the silica. Namely :

$$C_p(silica) = A * t(°C) + B$$

where A = 0.000325 K^{-1} and B = 0.18078 cal/g/K for the silica used. The standard deviation of the fit is 0.00015 cal/g/K. At 25°C, the value of the heat capacity of the silica is 0.189 cal/g/K. The weak temperature dependence for the heat capacity of the silica is expected for a solid that is not undergoing any major structural changes.

Etzler has previously determined the heat capacity of water

in 242 Å silica pores to be 1.05±0.02 cal/g/K.[27,28] This earlier value was determined at 25°C on a Perkin-Elmer DSC-7. Based on the present measurements, we find the heat capacity of vicinal water at 25°C to be 1.084±0.005 cal/g/K. Thus, the two determinations are in reasonable agreement.

Figures 2-6 show the data for the heat capacity of the vicinal water in 242 Å silica pores. Figures 2 and 3 show the data over the entire temperature range studied, while Figures 4-6 show various expansions of the temperature axis to highlight certain significant features of the heat capacity data. Figure 2 illustrates that the temperature dependence of the heat capacity of vicinal water is markedly different from that of bulk water in the region studied. The bulk water data shown on this graph are the average of 5 measurements and the standard error of the measurements is ±0.0005 cal/g/K. Using literature values for the heat capacity of bulk water as a function of temperature,[29] we fit the data to a functional form described by Speedy[30] using a singularity temperature of 227.1 K. This function goes through a minimum near 34°C. Notice that the measured bulk water heat capacity agrees well with Speedy's function. Also, this figure shows that the observed vicinal water C_p does not have the temperature dependence described by Speedy. The difference in the behavior of vicinal and bulk water remains significant even at elevated temperatures. For example, at 55°C, the literature value for the C_p of bulk water is 0.999 cal/g/K, while the measured

value of the C_p of pore water in 242 Å silica pores is approximately 1.10 cal/g/K, a difference of about 10%. As ΔC_p remains quite large to rather high temperatures, it appears that significant vicinal structuring exists at elevated temperatures. Presumably, proximity to a surface has the effect of "stabilizing" the liquid structure relative to that of the bulk. The independence of the pore water density observed earlier by Etzler and Fagundus[5] is, in addition, consistent with this observation.

While the vicinal water C_p increases linearly with increasing temperature, it appears that heat capacity "spikes" are observed at certain temperatures (See Figures 4-6). Each heat capacity "spike" displayed appears to be significantly different from the general trend of the heat capacity in the temperature range shown and is reproducible. Indeed, the plotted figures are the average of 4 independent runs. To determine whether the heat capacity "spikes" are significant, a t test was performed in which the average heat capacity value near each peak was compared to the data of the surrounding "baselines". Based on the analysis of the results of the t test, the probability that any of the peaks is the result of random noise in the data is less than 1 per cent. Perhaps more importantly, the apparent heat capacity "spikes" observed in the pore water are seen to occur near the temperatures previously considered to represent structural transitions in vicinal water (ie., 15, 30, 45°C, the

"Drost-Hansen" temperatures). Because the precise molecular details of the structural transitions of vicinal water are unknown, at this time, no explanation for the varying sign of the heat capacity "spikes" is offered. It is probable that the apparent heat capacity "spikes" are related to other physical property changes and physiological anomalies described earlier by Drost-Hansen *et. al.*[1-4,18-26] It will be an important task to measure the heat capacity in still smaller pores. Presumably, the apparent heat capacity "spikes" will be more pronounced in smaller pores.

Conclusion

In this paper, we have reported the heat capacity of water in 242 Å diameter silica pores as a function of temperature. Previous examinations of the heat capacity of water in silica pores have been made at single temperatures. In general, the pore water heat capacity increases linearly with temperature in the temperature interval studied (5-55°C). Heat capacity "spikes" are noted near the "Drost-Hansen" temperatures. The apparent heat capacity "spikes" are consistent with previously published evidence suggesting the existence of structural transitions in vicinal water at the "Drost-Hansen" temperatures. The earlier results also indicate that physiological anomalies occur near the "Drost-Hansen" temperatures. It remains an important task to measure heat capacity in still smaller pores. Presumably, the apparent heat capacity "spikes" will be even more pronounced in smaller pores.

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Figure Captions

Figure 1. Heat capacity of 242 Å pore diameter silica dried at
110°C for 24 hours as a function of temperature. The
error bars represent the standard error of 8
independent measurements.

Figure 2. Heat capacity of bulk water and water in 242 Å silica
pores as a function of temperature. The function drawn
through the bulk water data is the Speedy function
described in the text. The function drawn through the
data for the pore water is a quadratic fit.

Figure 3. Heat capacity of water in 242 Å silica pores as a
function of temperature. The error bars represent the
standard error of 4 independent measurements.

Figure 4. Expansion of the temperature scale of the data shown in
Figure 2. Note the deviation of the heat capacity
around 14.5°C.

Figure 5. Expansion of the temperature scale of the data shown in
Figure 2. Note the deviation of the heat capacity
around 27°C.

Figure 6. Expansion of the temperature scale of the data shown in
Figure 2. Note the deviation of the heat capacity
around 47°C.

Cp (cal/g K) versus Temperature (C)