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A Comparison of the Properties of Vicinal Water in Silica, Clay, Wood, Cellulose and Other Polymeric Materials

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CHAPTER FOR - H. Levine + L. Slade eds
"WATER Relations in Foods"

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ABSTRACT:

The properties of water are known to be significantly modified by propinquity to solid surfaces. This author has previously measured some thermodynamic properties of water in silica gel pores and offered a statistical thermodynamic model for vicinal water which is apparently able to account successfully for the observed properties of water in silica pores. This model suggests that hydrogen bonding between water molecules is enhanced by propinquity to solid surfaces. The experimental work suggests that the structural modification extends at least to distances approaching 5 nm from the surface. In addition to the work of the the present author, Low has conducted an extensive study of the thermodynamic properties of water in clays. Low's results are remarkably similar to those of the present author, suggesting that the state of vicinal water in both systems is similar. In this paper the properties of water adjacent to several surfaces are compared. The properties of water near cellulosic surfaces, including wood, are compared to those in silica. It appears that the properties of vicinal water adjacent to dissimilar surfaces are nearly identical to those in silica gel. Significantly, it appears that the notion of "structure breaking" surfaces suggested earlier by Goring and the notion of dense water near surfaces discussed, for instance, by Stamm are in fact inconsistent with the available thermodynamic data despite their rather frequent mention in the wood and paper literature.

A COMPARISON OF THE PROPERTIES OF VICINAL WATER IN SILICA, CLAYS, WOOD, CELLULOSE AND OTHER POLYMERIC MATERIALS

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I. BACKGROUND

Since antiquity some natural philosophers have realized the fundamental involvement of water in the human body and in a diverse variety of everyday human activities. It has also been recognized for at least 300 years that water possesses a number of unusual physical properties (e.g. the density maximum near 4°C) although, in this century, the uniqueness of water has probably been overstated. A number of other liquids (e.g. SiO_2, Ga, Sn) have a least some of the unusual features of water. Future investigation of some of the more exotic liquids may reveal that water is not an altogether atypical inorganic liquid. At this time the understanding of the bulk liquid state is limited despite the considerable effort of a number of able investigators. The understanding of the state of liquids near surfaces is even more confused. Indeed many fundamental measurements have not, as yet, been made. Ignorance of the state of interfacial liquids has surely hampered the full understanding of many interfacial and colloidal phenomena so important in industry and science. The biological significance of vicinal water appears to have been first recognized by Szent-Gyorgyi [3] and Jacobsen [1,2].

As early as 1912 Hardy [4] recognized that interfacial liquids may be structurally modified. Much of the early literature concerning vicinal liquids has been reviewed by Henniker [5]. From fairly recent investigations it has become clear that the properties of liquid water differ significantly from those of the bulk liquid. Drost-Hansen [6-10], in particular, has reviewed the properties of vicinal (interfacial) water and discussed their

biophysical significance. Low [11-16]has measured and reviewed the properties of water in clays. Peschel and Adlfinger [17-20] have measured the viscosity of water between quartz plates; While, Low [15,16] has measured the viscosity of water in clays by several experimental methods. Both sets of investigators have have found the viscosity to be increased by propinquity to surfaces. Etzler and Fagundus [21,22] have studied the density of water in silica pores and found it to be smaller than the bulk. From the work of Etzler [21,22], Low [11-16] and Peschel [17-20] it appears that vicinal water structure decays in an approximately exponential manner with distance and that significant vicinal structuring extends 3-6 nm from the surface. Braun and Drost-Hansen [23,24] as well as Cianci [25] have measured the heat capacity of water adjacent to a variety of materials including silica and found the heat capacity to be greater than the bulk. Etzler [26,27] has measured the heat capacity of water in silicas of varying pore radius. A maximum in the heat capacity near 7 nm pore radius was observed.

In an attempt to correlate some of the properties of vicinal water, Etzler [28] has proposed a statistical thermodynamic model for vicinal water. This model considers water in terms of a bond percolation model proposed earlier for bulk water by Stanley & Teixeira [29] and a bimodal single particle enthalpy distribution calculated earlier by Stey [30]. This model has been successful in correlating a number of properties of water in silica pores. From the model, which will be explored in detail later in this manuscript, it appears that vicinal water is similar to supercooled or negative pressure water. In other words, hydrogen bonding between water molecules is enhanced by propinquity to solid surfaces.

In addition to the general structural enhancement induced near surfaces it appears that water undergoes structural transitions at the Drost-Hansen transition temperatures (15, 30, 45, 60°C) [6-10]. At present, the molecular details of these transitions are not understood although this author has speculated that the nearly regular periodicity of temperatures may result from the differential heat capacity between the bulk and vicinal zones. Peschel and Adlfinger [17-20] have reported maxima in the viscosity and disjoining pressure of water between quartz plates at the Drost-Hansen transition temperatures. Wiggins [31-32], Hurtado and Drost-Hansen [33] as well as Etzler and Liles [34] have reported similar maxima in the selectivity coefficients (K^+ vs Na^+ or Li^+) by water in silica pores and in rat renal cortex. Recently, Etzler and Conners [71] have observed heat capacity spikes for water in 24 nm silica pores near the Drost-Hansen temperatures. Etzler and Drost-Hansen [6-10] have discussed numerous examples of physiological anomalies at the above temperatures and, as well, the physiological importance of vicinal water.

In this paper, the physical properties of water adjacent to a variety of substances are discussed in relation to a statistical thermodynamic model for vicinal water advanced earlier by this author. In particular, other notions concerning the state of water in wood and near cellulose are contrasted to those suggested by the model.

II. A STATISTICAL THERMODYNAMIC MODEL FOR VICINAL WATER

II.A General Commentary

In order to better aquaint the reader with the essential features of the model for vicinal water published earlier by this author, the model is briefly reviewed. The ideas discussed here have been shown to be relevant to the state of water in silica and clay pores.

As stated earlier, Braun and Drost-Hansen [23,24] have reported elevated heat capacities for water near surfaces while Peschel and Adlfinger [17-20] as well as Low [15-16] have reported increased viscosities for water near surfaces. At first glance these observations seem to present a paradox; large heat capacity is usually associated with a less structured environment (heat capacities of gases are generally larger than those of crystals), while increased viscosities are associated with a more structured environment.

Is vicinal water more or less structured than the bulk ?

II.B Bulk Water

In order to resolve this apparent paradox let us consider, for the moment, some ideas concerning the structure of bulk water which appear to be relevant to the understanding of vicinal water

structure.

Stanley and Teixeira [29] have proposed a bond percolation model for bulk water. This model considers water molecules to be distributed over five hydrogen bonding states (0,1,2,3 or 4 hydrogen bonded). The average number of molecules in each of the hydrogen bonding states is governed by the probability of forming a hydrogen bond between adjacent water molecules. The hydrogen bonding state of a given molecule is, of course, constantly changing as the hydrogen bond lifetime is envisioned to be on the order of 1 psec: no long-lived structures are postulated.

Stey [30] has calculated the distribution of single particle enthalpies for liquids. Stey has argued that it is possible to use the "moments problem" to estimate the distribution of single particle enthalpies. The heat content, H, is related to the single particle components, h_i [here units are energy/molecule], via the relation:

$$H = \Sigma_i h_i \qquad [1]$$

The molar heat content can thus be considered as the mean or first moment of an enthalpy distribution. Higher moments are calculated according to the algorithm:

$$\langle H^n \rangle = [\ \partial/\partial\beta + \langle H \rangle\ ]^{n-1} \langle H \rangle \qquad [2]$$

Here $\langle H^n \rangle$ is the n-th moment, $\langle H \rangle$ the molar heat content or first moment and $\beta = 1/kT$. The estimated probability, P, of finding a molecule with a given enthalpy, H_i [expressed here in units of energy/mole], is according to Stey:

$$P(H,\beta) = \beta \sum_{n=0}^{N} \sum_{l=0}^{n} b_{nl}(\alpha)\ \beta^l\ \langle H^l \rangle \qquad [3]$$

$$L_n^{\alpha}(\beta H)\ (\beta H)\ \exp(-\beta H)$$

where

$$L_n^{\alpha}(u) = \sum_{l=0}^{n} b_{nl}(\alpha)\, u^l \qquad [4]$$

and

$$b_{nl}(\alpha) = [\, -1^l/(l+\alpha)\,] \binom{n}{l} [\, (n+\alpha)!/n!\,]^{(1/2)} \qquad [5]$$

Here N is the number of moments chosen for the calculation and α the degree of the Laguerre polynomial. Stey's probability equation reflects a restricted case of the general moments problem; calculated distribution functions have a Boltzmann tail and thus have thermodynamic meaning [see 30 for details]. When attempting the calculation of P(H) the number of moments, N, used in calculation is arbitrarily selected. Next successive calculations using incremental values of α are performed. For a given N the value of α, which best predicts the next k moments [N+1, N+2 ... N+K] is selected. The calculated P(H) converges rapidly with increasing N; thus $P(H)_N \approx P(H)_{N+1}$ for a sufficiently large N. It appears from both Stey's calculations and our own that N = 4 or 5 is usually large enough to arrive at a limiting result. Stey termed his algorithm as Optimized Weighted Laguerre Expansion (OWLE). Estimated P(H)'s are labeled OWLE(N,K) where N is the number of moments and K is the number of extra moments used in optimizing α. Our experience in reconstructing known distributions from calculated moments, has shown Stey's algorithm to be quite reliable for distributions of similar shape to those calculated in Stey's thesis. Stey's contribution is that he has shown, for the case of statistical thermodynamic parameters and thermodynamically reasonable distributions, that the appropriate distribution function can be estimated using only a relatively small number of moments. It is also significant that Stey's calculations DO NOT rely on any particular model for the liquid state.

Some of Stey's results for H_2O, D_2O and NH_3 are shown in Fig. 1. These calculations show that water, in contrast to "normal" liquids such as benzene and ammonia, exhibits a bimodal distribution of single particle enthalpies. Preliminary calculations performed in this laboratory suggest that water is not entirely unique in this regard; some liquid metals such as liquid Ga and Sn also apparently exhibit a similar distribution. Indeed, Wynne [72], who has also used Stey's algorithm, has shown that the distribution of enthalpies in liquid Ga near the melting temperature is also bimodal. Bimodality may be related, at least

in part, to 4 coordination. The bimodal character of Stey's distribution allows one to consider two fractions of water molecules. It appears that these two fractions represent those molecules which are 4-hydrogen bonded and those *not* 4-hydrogen bonded (i.e. those with 0,1,2 or 3 hydrogen bonds). Note from the figure that the bimodal character diminishes with increasing temperature and has almost disappeared at 353 K. At 298 K nearly 10% of the molecules belong to the low enthalpy fraction.

In order to relate Stey's results to more familiar thermodynamic parameters, a single-particle isobaric partition function, q_P is considered. Here,

$$q_P = \Sigma\, \omega_i \exp(-h_i/kT) = \Sigma\, \Sigma\, \omega_{jk} \exp[-(\epsilon_j + Pv_k)/kT \qquad [6]$$

From q_P and statistical thermodynamics it is possible to show that:

$$\beta_T \equiv -(1/V)(\delta V/\delta P)_T = \sigma^2/VRT^2 \qquad [7]$$

$$\alpha_P \equiv (1/V)(\delta V/\delta T)_P = (\sigma_{\epsilon v}^2 + P^2\sigma_v^2)/VRT^2 \qquad [8]$$

$$C_P = \sigma_h^2/RT^2 \qquad [9]$$

In the case of liquid water $P^2\sigma_V^2 \ll \sigma_{\epsilon v}^2$ thus:

$$\alpha_P \approx \sigma_{\epsilon v}^2/VRT^2 \qquad [10]$$

Here σ^2 is the variance in the appropriate distribution; the h, v subscripts refer to the enthalpy and volume per molecule. $\sigma_{\epsilon v}^2$ is the covariance between energy and volume. As the isobaric expansivity is negative below 4°C, $\sigma_{\epsilon v}^2$ is necessarily also negative suggesting the existence of low-energy high-volume or "ice-like" states in liquid water. Computer simulation results by Stanley [35] suggest that water molecules interacting most strongly with neighboring molecules occupy the largest volumes. σ_v^2 shows a distinct minimum near 290K; the

large increase in σ_v^2 below 290K indicates the existence of states at low temperature which possess a distinctly different volume than those which predominate at high temperature. It is not unreasonable to conclude that the low enthalpy peak in Stey's distribution represents the 4-hydrogen bonded or "ice-like" water molecules.

It may be concluded from Stey's work that his algorithm may serve as a conceptual bridge between macroscopic thermodynamic behavior and microscopic molecular events in a way that remains largely unexplored. Stey's Algorithm is able to convert macroscopic thermodynamic information into distributions of microscopic single particle parameters. Molecular Dynamics simulations convert intermolecular potiential functions into distributions of microstates and, with more difficulty, into macroscopic thermodynamic information. Comparison of the distributions generated from Stey's Algorithm with those generated *via* Molecular Dynamics calculations might prove useful. Etzler, Halcomb and Ross [73] have recently made such a comparison. The single particle enthalpies in Stey's distribution may be thought of as consisting of a volume component and an energy component *via* the conventional relation:

$$h_i = \epsilon_i + Pv_i \qquad [11]$$

Bimodality may thus be induced either through the volume or energy component. Etzler, Halcomb and Ross, using a statistical geometric analysis of SPC/E water (a type of "computer water") have shown that the distibution of Voronoi (molecular) volumes is bimodal. In addition, there appears to be strong correlation between energy and volume. The distribution of single particle energies does not, however, appear to be bimodal. The recent statistical geometric alalysis, indeed, appears to offer support for Roentegen's Hypothesis which states that water must exist in "bulky" and "dense" states in order to account for the density maximum at 4°C. Furthermore, it appears that Stey's results are consistent with molecular dynamics simulations. Some of the results of the statistical analysis are shown in Fig. 2 and 3.

Given the bimodal character of Stey's distribution, it is not unreasonable to consider water as being composed of two fractions of molecules of which one fraction represents the 4-hydrogen bonded molecules. Assuming that these fractions behave as an ideal solution, the enthalpy, H, and volume, V, are given by the following expressions:

$$H = x_1H_1 + x_2H_2 \qquad [12]$$

and

$$V = x_1V_1 + x_2V_2 \qquad [13]$$

For the purposes of the present discussion, component 1 will represent the 4-hydrogen bonded water molecules. Differentiating Eqn 11 or 12 with respect to T or P, the following relations result.

$$Cp = x_1Cp_1 + x_2Cp_2 + x_1x_2\ \Delta H^2/RT^2 \qquad [14]$$

$$\alpha = [1/V][(\delta V_1/\delta T)_P + (\delta V_2/\delta T)_P + x_1x_2\ \Delta V\ \Delta H/(R\ T^2)] \qquad [15]$$

$$B = [1/V]\ [(\delta V_1/\delta P)_T + (\delta V_2/\delta P)_T + x_1x_2\ \Delta V^2/(R\ T)] \qquad [16]$$

From the above expressions, it is clear the thermodynamic properties of such a "mixture" can be calculated if x_1 and the various properties of the two fractions can be estimated.

Consider, for the moment, heat capacity. It is possible to estimate Cp_2 and x_1 *via* several arguments if it is assumed that $Cp_1 = Cp_{ice}$. A fairly straight forward method is to consider the effect of pressure on Cp [36]. As water appears to be composed of two fractions of molecules and one of these fractions (fraction 1) is a high volume fraction, the major effect of pressure, at least for the first few thousand atmospheres, would be to reduce x_1. A plot of Cp vs P at 298K exhibits a limiting value around 16.3 cal/K mole. This limiting value thus provides an estimate of Cp_2. A second approach might to be to consider the partial molar heat capacity of water in mixtures with cosolvents similar to water but lacking the ability to form significant 3 dimensional structures. Replacing the neighbors around a central water molecule should interfere with the formation of high volume states. Angel [37] has measured the heat capacities of hydrazine-water and hydrogen peroxide-water mixtures. The partial molar heat capacity of water in solutions containing a

high mole fraction of cosolvent [x(cosolvent) > 0.3] is constant. The limiting partial molar heat capacity of water in hydrazine is 16.3 cal/K mole. The limiting partial molar heat capcity of water in hydrogen peroxide is 16.9 cal/K mole. Cosolvent addition thus leads one to conclude that Cp_2 is around 16.5 cal/K mole at 298K. The activation energy of the rotational correlation time, H_r, provides a less obvious approach to the calculation of Cp_2. At low temperature (< 300K) H_r is highly sensitive to pressure, while at higher temperatures it is relatively insensitive to pressure. It thus appears that H_r is sensitive to the bimodal character of water. It is possible to show that [27, 38]:

$$x_1 \approx H_r - H_{normal} \qquad [17]$$

where H_{normal} is the extrapolated (from high T) activation energy for rotational motion of water in absence of 4 hydrogen bonded clusters.[see 27 for details of this calculation]. According to this third method x_1 = 0.058 and Cp_2 = 16.8 cal/K mole at 298 K for bulk water. It is probably safe to say that the fraction of 4-hydrogen bonded water molecules in bulk water at 298K is in the range of 5-7%.

II.C Vicinal Water in Silica and Clays

Fig. 4 and 5 show the average heat capcity and density of vicinal water in silica pores. The partial specific heat capacities and volumes of water in clays has been determined by Low [13] and are shown in Fig. 6 & 7.

The paradox posed by the anomalously high viscosity and simultaneously high heat capacity of vicinal water can now be resolved. Fig. 8 shows the hypothetical heat capacity for water and D_2O plotted against x_1 as calculated *via* Eqn 13. From comparison of Fig. 4 & Fig. 8 it is clear that anomalously high heat capacities can result from the enhancement of liquid structure as reflected by the increase in x_1. Simulteanously high heat capacities and viscosities of water in pores thus may result from the bimodal character of Stey's distribution function. An increase in x_1 implies that the density of vicinal

water is lower than the bulk [recall Eqn 12]. Etzler and Fagundus [21-22] have disscussed the density of water in silica pores and have found the density to increase in an approximately exponential manner with distance from the surface. A comparison of Eqns 12 & 13 indicates that the dependences of density and heat capacities with pore radius are both consistent with a continuous rise in x_1 as the surface is approached. The density data, in addition, suggest that vicinal structuring extends to about 5 nm from the surface. Low's data on the water in clays are remarkably similar to water in silica gel pores in that the extent of vicinal structuring exhibits a similar distance dependence. The heat capacity data, particularly as the heat capacity of vicinal water in clays never reaches a maximal value near 1.25 cal/K g, appear to suggest that water in clays is never structured to the extent it is in silica; however, it is none-the-less clear that the same rules regarding vicinal structuring apply to both systems. It is tempting, as Drost-Hansen has done, to suggest that vicinal water in other systems is similar to water in the disscussed model systems. Drost-Hansen has termed the apparent independence of vicinal water properties on the precise physico-chemical details of the substrate the "paradoxical effect".

In the remainder of this paper, the properties of water in other media will be discussed in relation to the author's model for vicinal water and the properties of water adjacent to clay and silica surfaces.

III. WATER IN WOOD AND CELLULOSE

III.A GENERAL

In this section some previous notions regarding vicinal water, which appear to have gained some acceptence in the wood and paper literature, will be contrasted to the notions of the present author. The intention is to correct some possible misconceptions concerning water adjacent to wood and cellulose surfaces as well as to stimulate further research in this area. It should be recognized that water as well as cellulose are both complex substances and thus their interactions may also be quite complex. It does, however, appear that previous experience with model substrates, such as silica, may be valuable in delineating

the individual contributions of each component. No attempt is made to review the structure of cellulose or wood.

III.B CELLULOSE

A recent review of the current understanding of water-cellulose interactions has been given by Caufield [39-40]. Goring *et. al* [41-43] have looked at the partial specific expansivities of both simple and complex carbohydrates, including cellulose, in water and found them to be larger than the pure substance. According to Goring, the "extra" apparent expansivity results from a destructuring of water adjacent to these molecules and surfaces. Goring reasoned, using a mixture model, that the expansivity of the "ice-like" regions would be lower than the "non-ice like" regions; the expansivity of ice is lower than that of bulk water at 25°C. Goring, however, failed to recognize that according the mixture approach the expansivity would not be a sum of the expansivities but rather be modeled as in equation 14. On the basis of this one property, Goring has claimed that surfaces with hydroxyl surfaces such as cellulose and silica are water structure breaking surfaces. Wahaba and Aziz [44] have cautioned earlier against such conclusions. The opening of pores in cellulose upon swelling in water has been discussed [39-40]. Gorings ideas concerning structure breaking surfaces have been reiterated many times in the pulp and paper literature as well as in the wood science literature. The present author's work on silica clearly demonstrates that water adjacent to silica surfaces is more and NOT less structured than that of the bulk. Could vicinal water adjacent to cellulose be in a vastly different form than of water adjacent to silica ?

The expansivity of water in silica pores has not been reliably measured. Derjaguin [45-48] has measured the expansivity of silica and titania slurries in water but has not calculated the expansivity of the pore water. Derjaguin's data do suggest interesting temperature effects for the expansivity of pore water. Etzler and Fagundus [21-22] have measured the density of water in silica pores. From the densities of water in silicas with the smallest pore radii, it appears that the expansivity is small (nearly zero from 10-30°C) with respect to the expansivity of bulk water. This result is quite consistent with Eqn 14 ; At large values of x_1, α will be small or slightly negative assuming α_1 and α_2 are unchanged with the variation in x_1. Machin [49-50] has studied the thermodynamic properties of capillary condensed fluids. He has found the compressibility of water in pores to be greater than the bulk. This result is

consistent with Eqn. 15 and the present author's results for other properties of water in silica pores. It would appear *via* thermodynamic arguments presented earlier by Speedy [51] that the simultaneously elevated compressibility and heat capacity of vicinal water would imply the expansivity should be negative at low temperatures. The expansivity data by Clementz and Low [48] on water in clays suggest that the expansivity at 25°C is slightly larger than the bulk. Low has reasoned that the larger expansivity could be due to less easily broken or bent hydrogen bonds or due to more easily lengthened bonds. This explanation, in contrast to Goring's, is consistent with the observed low densities and high viscosities of vicinal water. It is possible, however, that Low's estimation of the expansivity of the clay from lattice parameters is not an accurate measure of the expansivity in the measured slurries. Drost-Hansen *et al* [70] have, from measurements on polystyrene spheres, also claimed a larger expansivity for vicinal water. Thermal expansion has the potential to be a difficult property to model *via* the somewhat simplistic model advanced earlier by this author. Estimation of $(\delta V_i/\delta T)_P$ may be complicated by the fact that expansivity is strongly temperature and pressure dependent; thus, other factors unrelated to the bimodal character of Stey's distribution may significantly influence the magnitude of the thermal expansion. Indeed the expansivity varies by about 10% per 10K near the boiling point, a temperature region where the 4-hydrogen bonded clusters play a small role. It is quite possible, in the case of expansivity as contrasted to density or heat capacity, that $(\delta/\delta x_i)(\delta V_i/\delta T)_P$ is significantly different from zero so as to affect the calculations. Other molecular packing problems may also be important. It is, however, clear that thermal expansivity should not be used as the primary indicator of vicinal water structure until more knowledge of the expansivity in model systems is aquired. Such data are being collected in this author's laboratory.

As thermal expansion, by itself, should not be used, at present, as an indicator of the state of water adjacent to cellulose surfaces, it is necessary to look elsewhere. Wahaba [52] has studied the thermodynamics of adsorption water by cellulose. The entropies of adsorbtion indicate that the entropy of water near the surface is smaller than that for bulk liquid water. The adsorption data are consistent with the notion water is more structured near cellulose surfaces. Wahaba [54] has studied the heat capacity of water in cellulose. These data suggest that the heat capacity is larger than bulk value; the data are, thus, consistent with the data and ideas concerning water in silica pores as presented previously by this author. Caufield [39, 53], on the basis of NMR and dielectric relaxation data, suggested water adjacent to cellulose is more structured than the bulk.

The thermodynamic properties of water adjacent to cellulose

surfaces suggest that the state of this vicinal water is similar to that found near silica surfaces. Vicinal water near cellulose is thus more structured than the bulk.

III.C WOOD

The state of water in wood has been of considerable interest. Skaar [55]has reviewed the state of water in wood. Stamm[56], for instance, has reviewed the structure and properties of wood.

The heat capacity of water in woods has been investigated by Kelsey & Clarke [57] as well as by Hermon & Burcham [58]. Kelsey & Clarke's data show that the apparent heat capacity of water in wood is rather small at low hydration levels while quite large at higher hydration levels. Hermon & Burcham's data on Beech wood suggest that the heat capacity of water in the wood at the studied hydration levels is 1.15 - 1.20 cal/K g. Any differences between the two sets of data probably can be regarded as being due to differences in structure of the experimental woods as well as the considerable experimental uncertainty (about +/- 0.05cal/K g). Comparison of the heat capacity of water in wood, as presented in Fig 9 with Fig. 4 showing the dependence of the heat capacity of vicinal water with silica pore radius, might lead one to conclude that water is filling small pores in the wood. The heat capacity data suggest that water in wood is similar to that in silica pores. Entropies of adsorption of water by wood also support this notion.

The apparent volume of water adsorbed into wood has been measured on several occasions. The results of these experiments show that the apparent density of water in wood is greater than the bulk. This observation has lead investigators to refer to "densification" of water in wood. Calculations of the apparent specific volume of water, φ_w, in woods from data by Keylwerth [59, 60] appear to show that:

$$\lim_{m \to 0} \varphi_w = 0 \qquad [18]$$

Here m is the mass fraction of water present in the hydrated

wood. The apparent infinite density of this initially adsorbed water suggests that this water enters small pores in the cellulose fibers or elsewhere within the wood. (indeed, the apparent densities at measured hydrations can be 80 - 100% greater than the density of ice VIII! [62]) Weatherwax and Tarkow have previously challenged the notion of "densified" water in wood. [See also Skaar [55], p 76-77 for more details.] These investigators measured the apparent density of wood in various solvents as compared to the density of nonsolvent swollen wood. The apparent densities of water swollen wood in hexane, water, and ethanol were found to be nearly equal but quite a bit larger than the apparent density of non-solvent swollen wood. Weatherwax and Tarkow thus concluded that solvent swelling opens small pores in wood and the apparent high density of water in wood is largely and primarily due to pore filling and not due to vicinal water structuring. Note that this view is consistent with the measured apparent heat capcity of water in wood. Despite the fact that the apparent wood densities in the various solvents are similar, they are none-the-less measurably different. Weatherwax and Tarkow reasoned that the hexane value represented the correct apparent density of solvent swollen wood assuming no structural modification of the pore liquid; thus, the different apparent densities of wood in other solvents were due to the modification of liquid structure. On this basis they calculated that the pore water density was 1.017 g/cc considerably smaller than 1.129 g/cc calculated without considering the porous nature of water swollen wood. If Weatherwax and Tarkow's logic is extended to cover ethanol, one would conclude that ethanol's pore density is more anomalous than water. Data by Etzler and Fagundus [21] on the density of methanol and acetone in silica pores indicate that density of non-aqueous hydrophyllic liquids in silica pores is not modified by propinquity to a surface. Wahaba [45] has suggested that the accessibility to micropores in wood by different sized molecules is not identical. As hexane is larger than either ethanol or water it seems unreasonable to conclude that hexane would fill the pores as extensively as either water or ethanol. Using Weatherwax and Tarkow's data and ethanol as the reference liquid instead of hexane suggests that the density of water in wood pores is about 0.98 consistent with its value in silica or clay pores. Despite much discussion in the literature which would lead the casual reader to conclude that water adjacent to wood or cellulose surfaces differs considerably from that adjacent to silica surfaces, it appears, on more careful consideration of the earlier data, that the state of water adjacent to each of the discussed surfaces is structurally similar. Water adjacent to wood and cellulose surfaces is more structured and hence less dense than the bulk.

IV. WATER IN OTHER POLYMERIC SYSTEMS

While extensive and systematic measurements of the thermodynamic properties of water in the myriad of possible polymer-water systems have not been performed as they have been in the silica and clays, some available measurements suggest that the state of water near a variety of polymeric materials is similar to that in silica pores. Unfortunately and frequently, the thickness of the liquid films adjacent to these various surfaces is unknown; thus, a detailed comparison to Fig. 6, for instance, is not possible. No attempt is made to provide a comprehensive review of the available literature.

The heat capacities of water in gelatin gel [63] and starch [64] slurries at various hydration levels are shown in Fig. 10. Note in particular the heat capacity maxima near 1.27 cal/K g and the similarity of the data to those in Fig 4; presumably the average distance of a water molecule to a surface is related to the hydration level. Stitt and Kennedy [65] have measured the heat capacity of potato, egg, and carrots as a function of hydration. The data suggest elevated heat capacities for surface water but do not appear to be of sufficient quality for a more detailed and quantitative analysis. Braun and Drost-Hansen [24] have measured the heat capacities of water adjacent to a variety of surfaces including diamonds, proteins, zeolite, and *Artemia* (brine shrimp) cysts and found the heat capacities to be approximately 1.25 cal/K g and independent of the substrate material. A heat capacity maximum near 1.25-1.30 cal/K g similar to that observed in starch, gelatin, and silica is also seen when heat capacity versus hydration is plotted for polysulfonated ion exchange resins [66] and for lysozyme [67].

The density of vicinal water is obviously more difficult to study unambigiously in poorly characterized systems as the pore and swelling characteristics may be unknown. However, Bernhardt & Pauly [68] report the partial molar volumes for water in rather concentrated bovine serum albumin and hemoglobin solutions. Their measurements suggest that the density of water near the macromolecular surface is reduced in comparison to the bulk liquid. Ash and Findenegg [69] indicate that water near graphon has reduced density.

V. SUMMARY

In this paper, the author has compared the thermodynamic properties of water in silica and clays to other polymeric and colloidal systems. It appears, on careful inspection, that the properties of water adjacent to the discussed surfaces are similar and consistent with the model for vicinal water advanced earlier by this author. Despite much discussion to the contrary in the paper and cellulose literature, it appears that water in cellulosic systems is more and not less structured than the bulk and is indeed very similar to water in silica pores. The similarity of the properties of water in various polymeric systems suggests:

1. The general importance of further investigations on the properties and structure of water in model systems such as silica..

2. The use of data generated in model systems to help understand less well characterized systems (e.g. cellulosic systems).

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FIGURES

FIGURE 1

Stey's distribution functions. Probability, P(H), vs enthalpy, H. (A) Water at 298 K and NH_3 at 200 K. (B) D_2O at 298 K. (C) H_2O at 313 K. (D) H_2O at 353 K.

FIGURE 2

Distribution of molecules in SPC/E water as a function of Voronoi volume and number of faces on Vornoi polyhedra. Two peaks indicate presence of two classes of molecules.

FIGURE 3

Distribution of molecules in SPC/E water as a function Voronoi volume and interaction energy. Note the two volume classes are apparently seperated in energy.

FIGURE 4

Heat capacities of water in silica pores as a function of pore radius at 298 K: squares H_2O; diamonds, D_2O. Radius in Angstroms (10 A = 1 nm).

FIGURE 5

Mean pore density of water in silica pores as a function of

pore radius at 293 and 303 K. Circles, 293 K; triangles, 303 K. Dashed lines represent bulk density.

FIGURE 6

Heat capacity of water in Na and Li Montmorillonite at 298 K as determined by Low [13]. Solid line - partial specific heat capacity; Dashed line - apparent heat capacity.

FIGURE 7

Partial specific volume of water in Montmorillonite. Dashed line - Na Montmorillonite; Solid line - Li Monmorillonite. Data by Low [13].

FIGURE 8

Hypothetical heat capacity of water and deuterium oxide as a function of x_1 at 298 K. Note similarity to Figure 4. [see 27 for details]

FIGURE 9

Apparent heat capacity of water in woods. Squares - Pine [57]; Circles - Beech [58]. Dashed line - maximum heat capacity as calculed from author's model.

FIGURE 10

Apparent heat capacity of water versus per cent of substrate material in mixture. Squares - gelatin [63]; Circles - Starch[64]. Horizontal line - maximum heat capacity calculated from author's model. Note similarity to Figure 4.

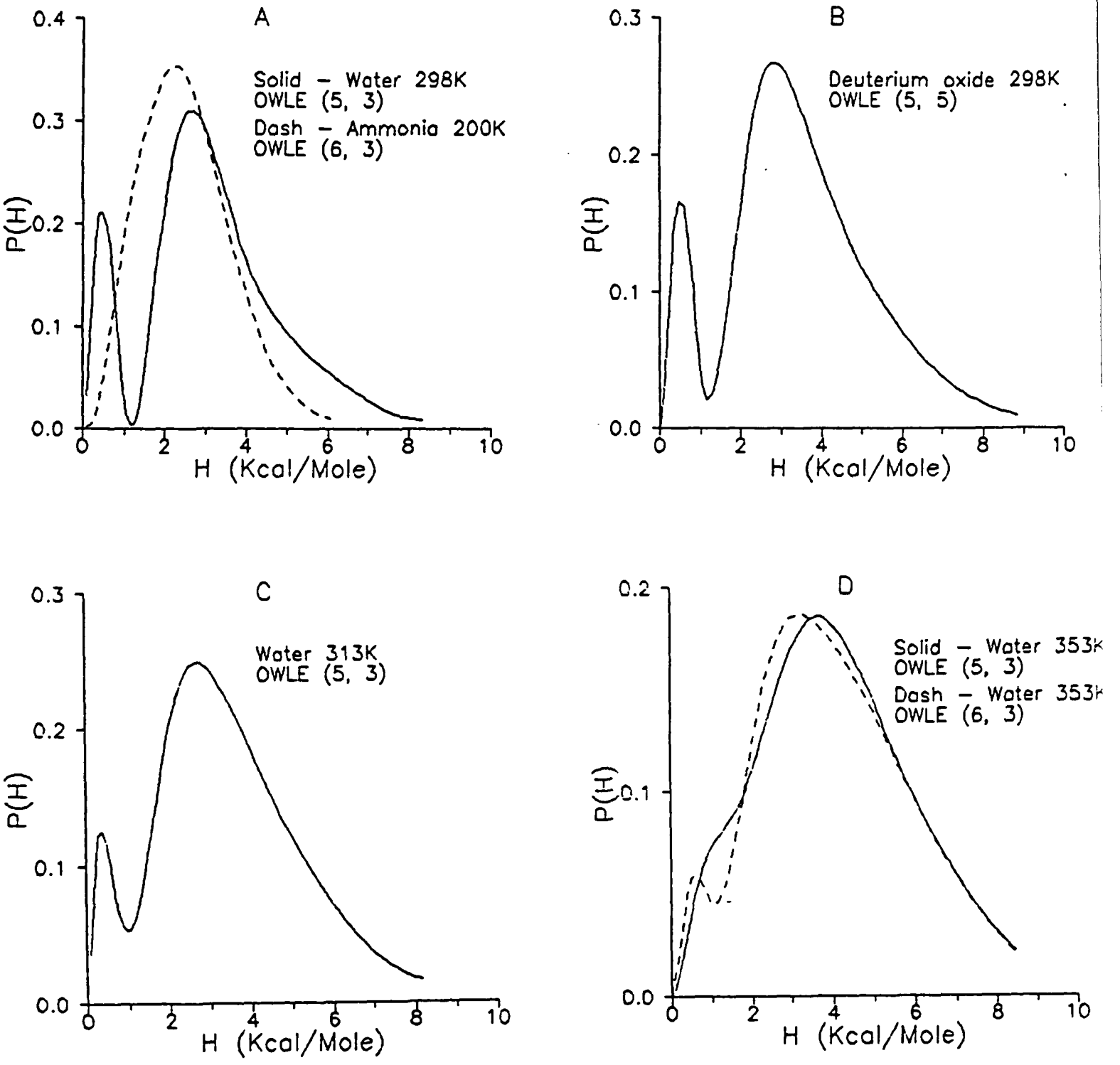

A
Solid – Water 298K
OWLE (5, 3)
Dash – Ammonia 200K
OWLE (6, 3)
P(H)
H (Kcal/Mole)
B
Deuterium oxide 298K
OWLE (5, 5)
P(H)
H (Kcal/Mole)
C
Water 313K
OWLE (5, 3)
P(H)
H (Kcal/Mole)
D
Solid – Water 353K
OWLE (5, 3)
Dash – Water 353K
OWLE (6, 3)
P(H)
H (Kcal/Mole)

Fig #1

SPC WATER – Data Set 2

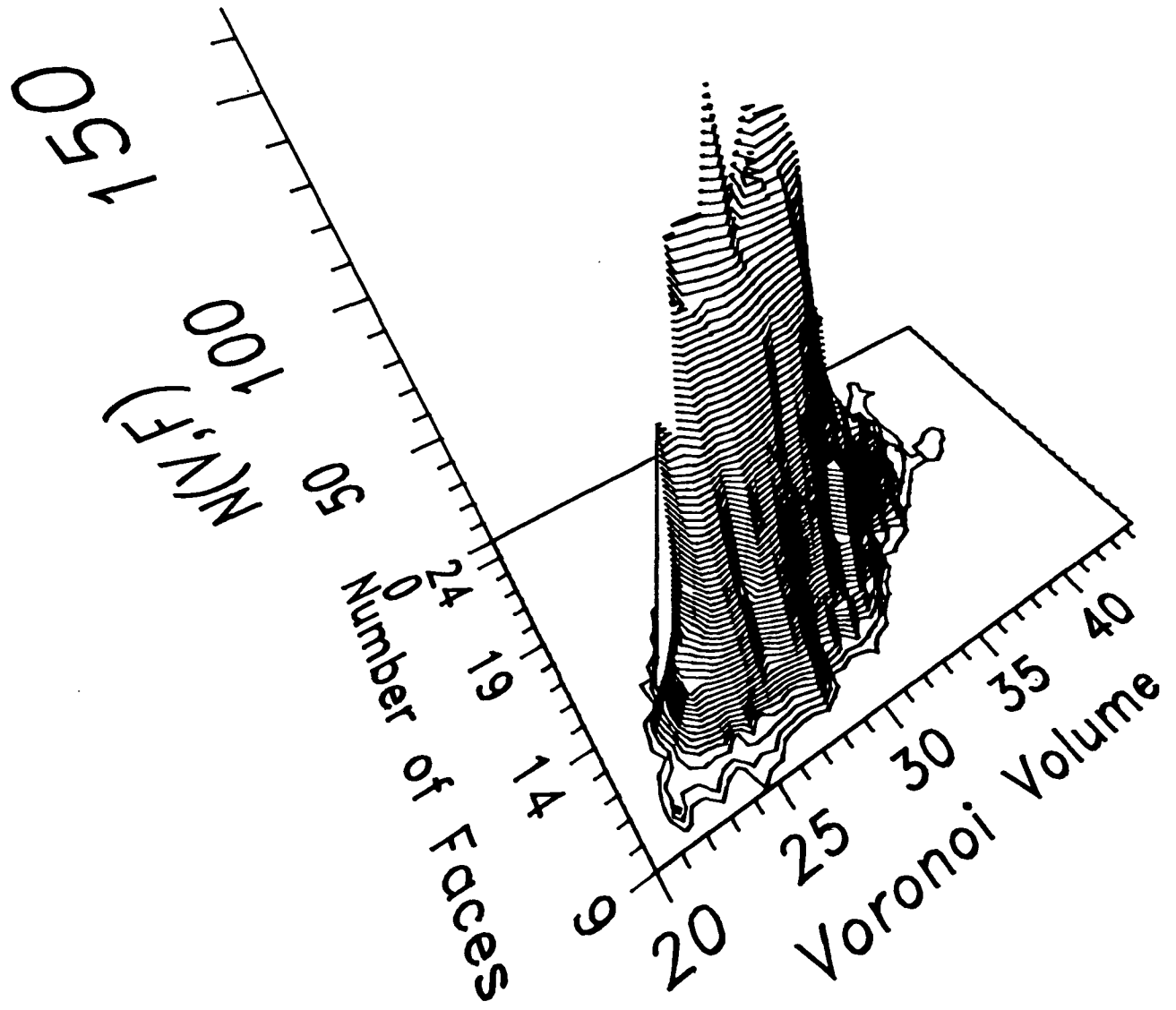


Fig #2

Voronoi Volume (nm^3)
3.77E-002
3.27E-002
2.77E-002
2.27E-002
-1.09E-001
-5.95E-002
-9.50E-003
4.05E-002
9.05E-002
Energy KJ/molecule*10^20
P(V,E)
25
20
15
10
5

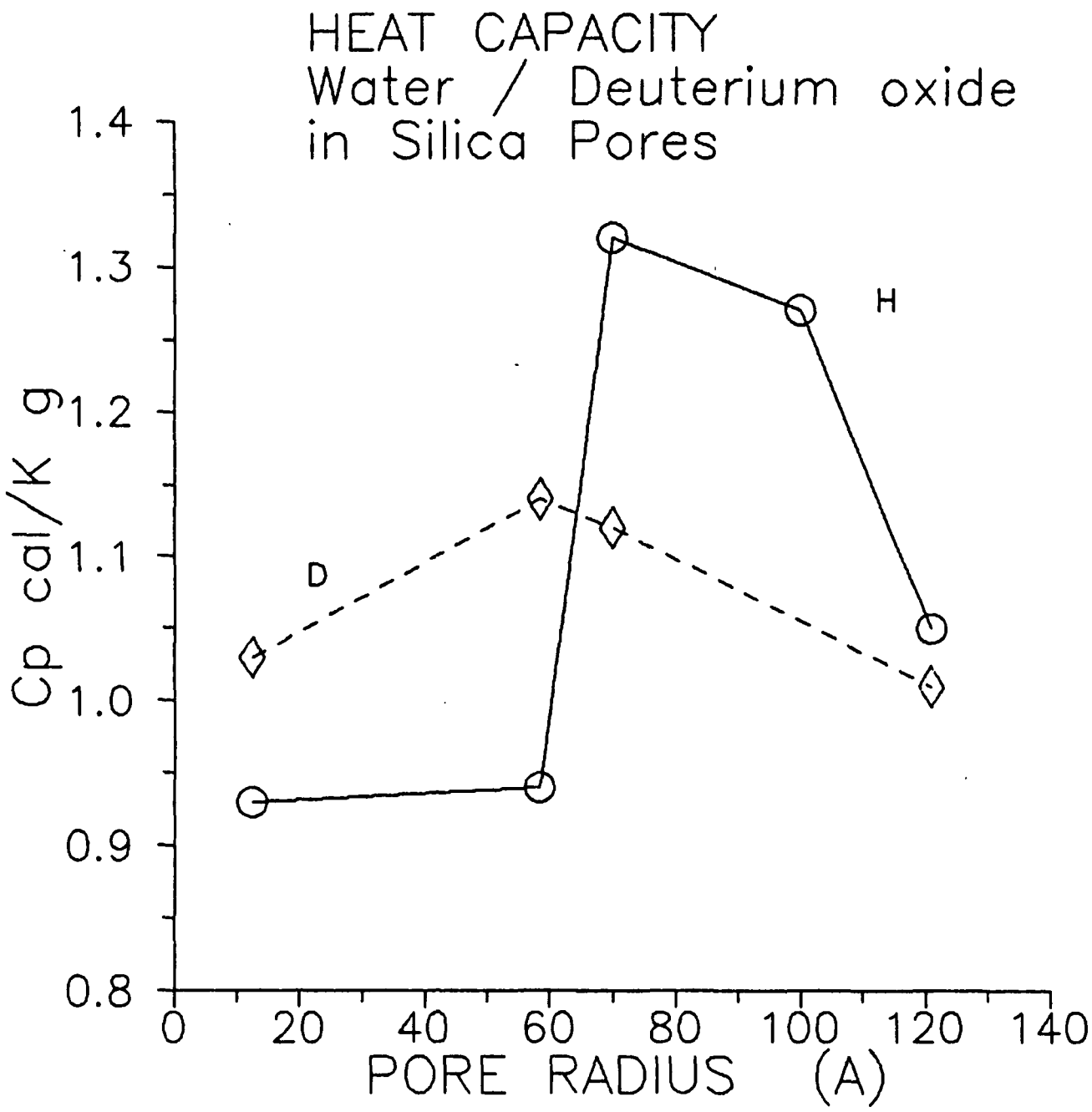

HEAT CAPACITY
Water / Deuterium oxide
in Silica Pores
Cp cal/K g
1.4
1.3
1.2
1.1
1.0
0.9
0.8
0
20
40
60
80
100
120
140
PORE RADIUS (A)
H
D

Fig #4

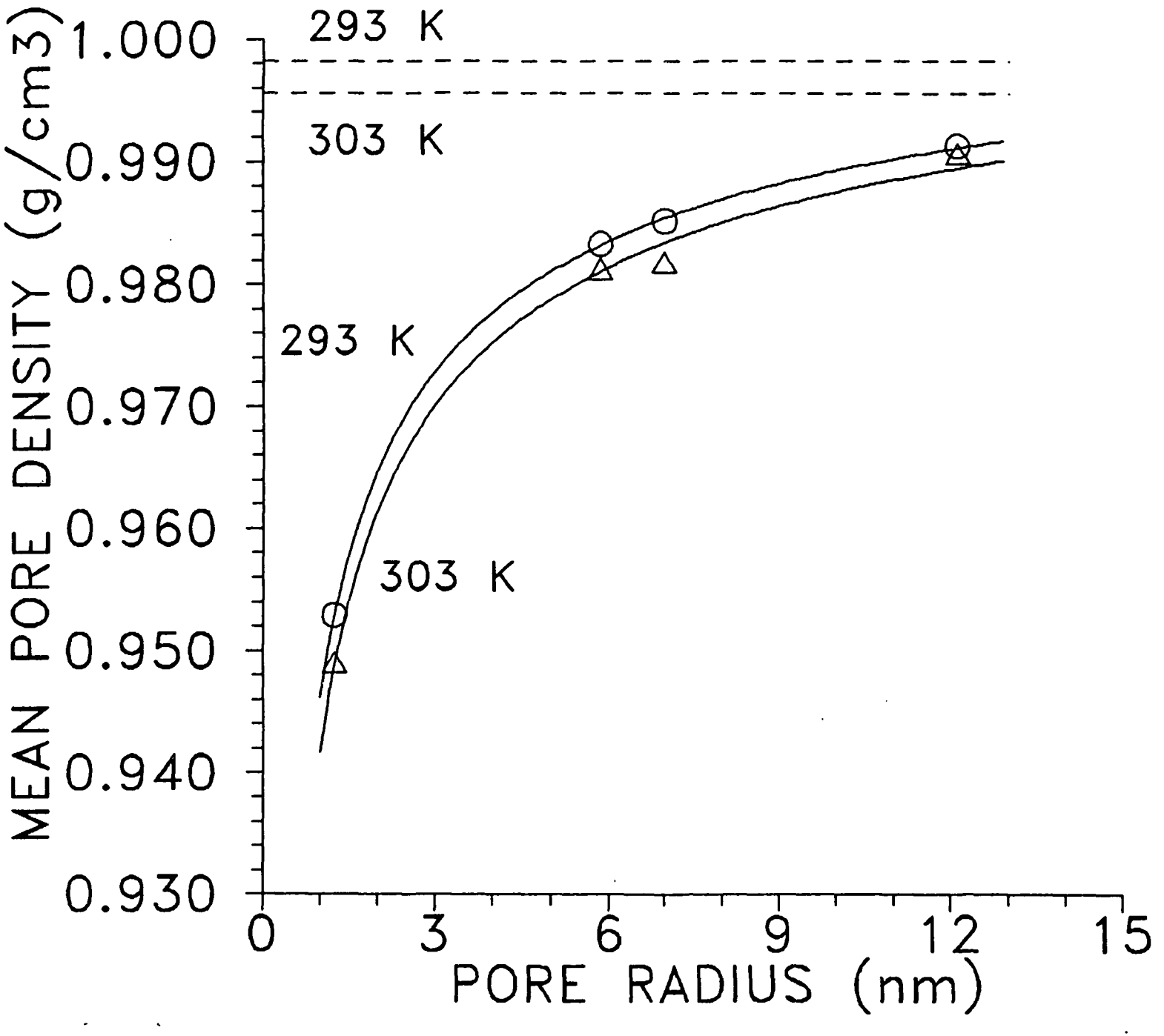

MEAN PORE DENSITY (g/cm3)
1.000
0.990
0.980
0.970
0.960
0.950
0.940
0.930
293 K
303 K
293 K
303 K
0
3
6
9
12
15
PORE RADIUS (nm)

Fig #5

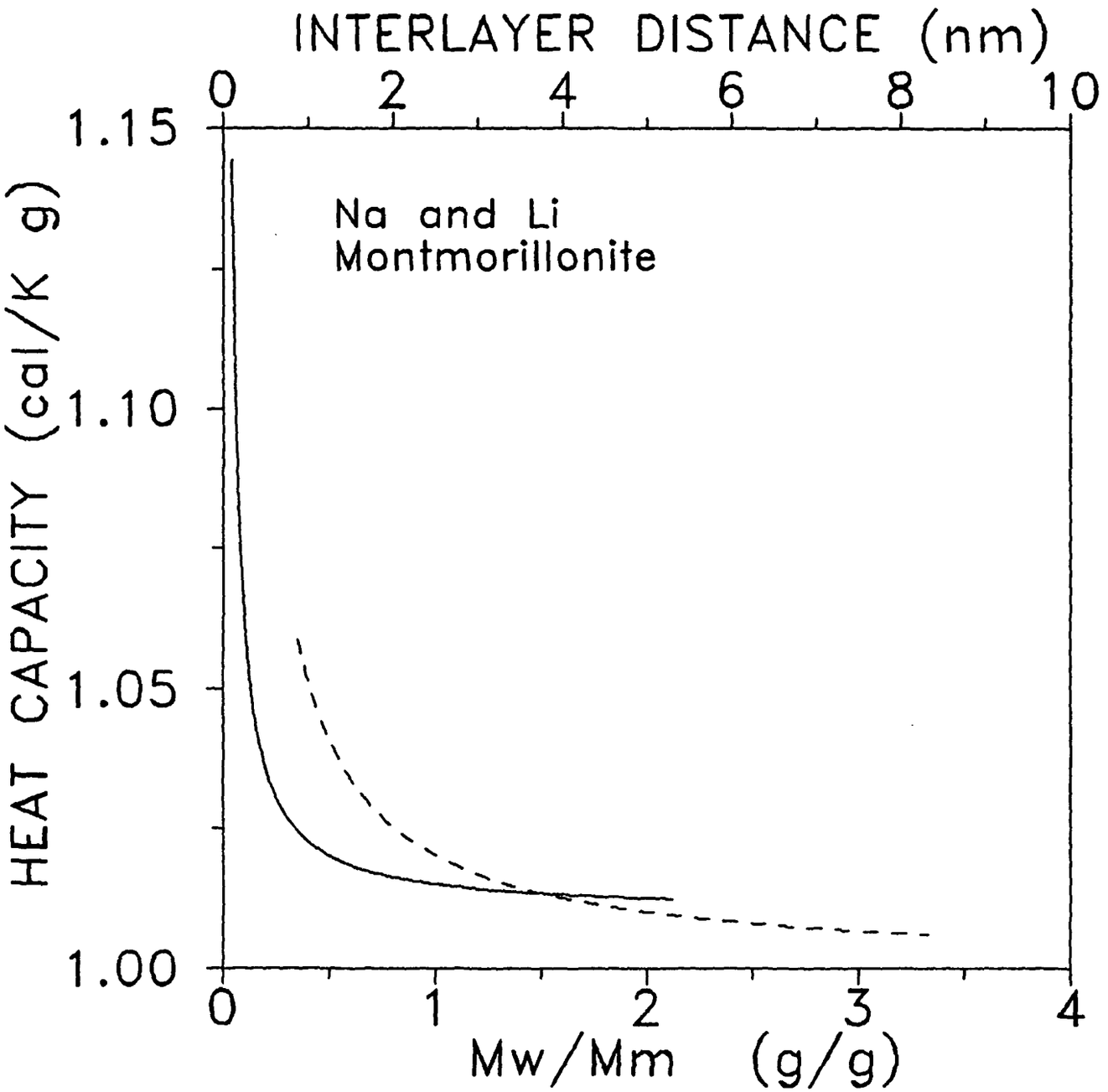

INTERLAYER DISTANCE (nm)
0
2
4
6
8
10
1.15
1.10
1.05
1.00
HEAT CAPACITY (cal/K g)
Na and Li
Montmorillonite
0
1
2
3
4
Mw/Mm (g/g)

Fig #8

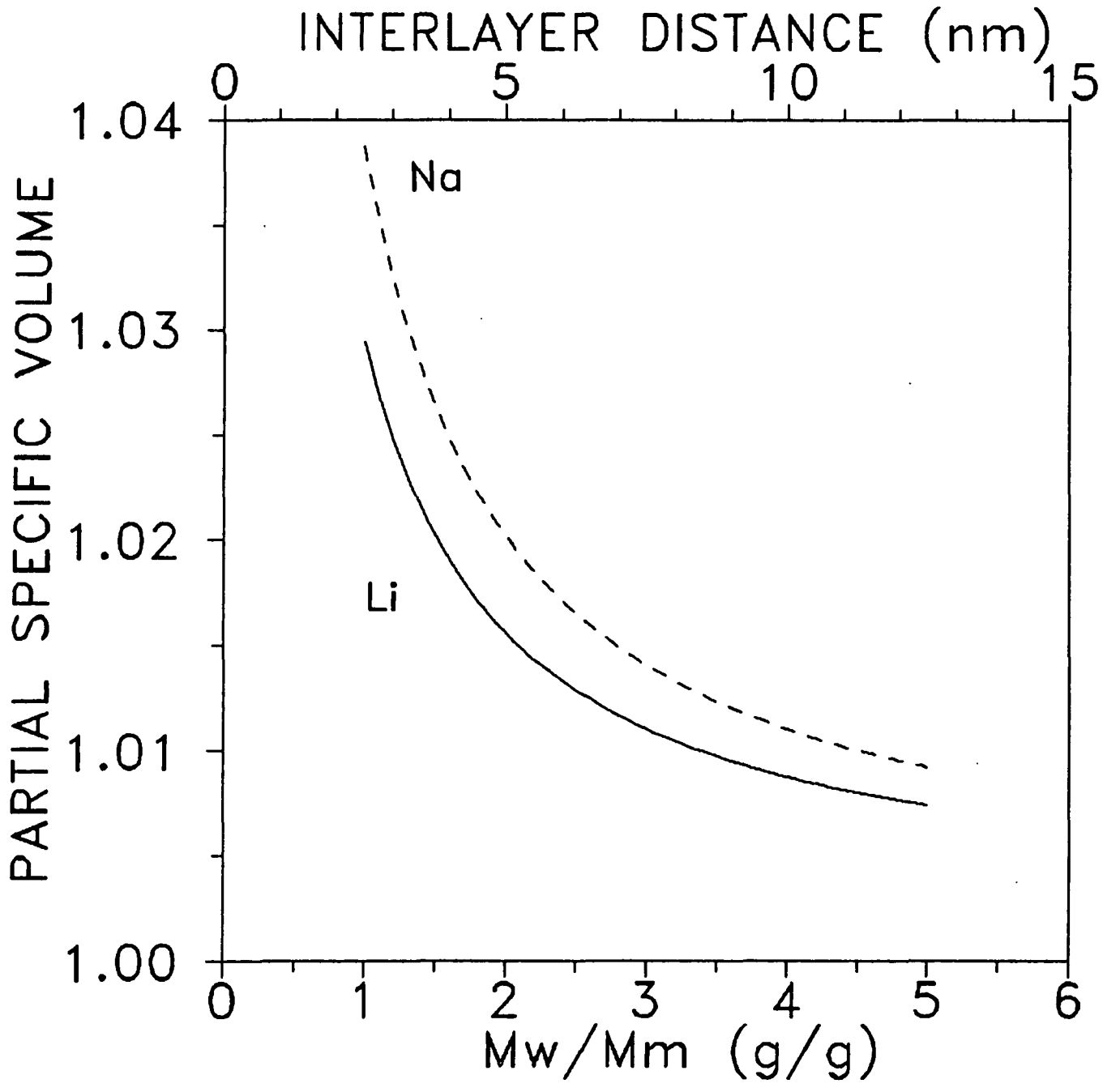
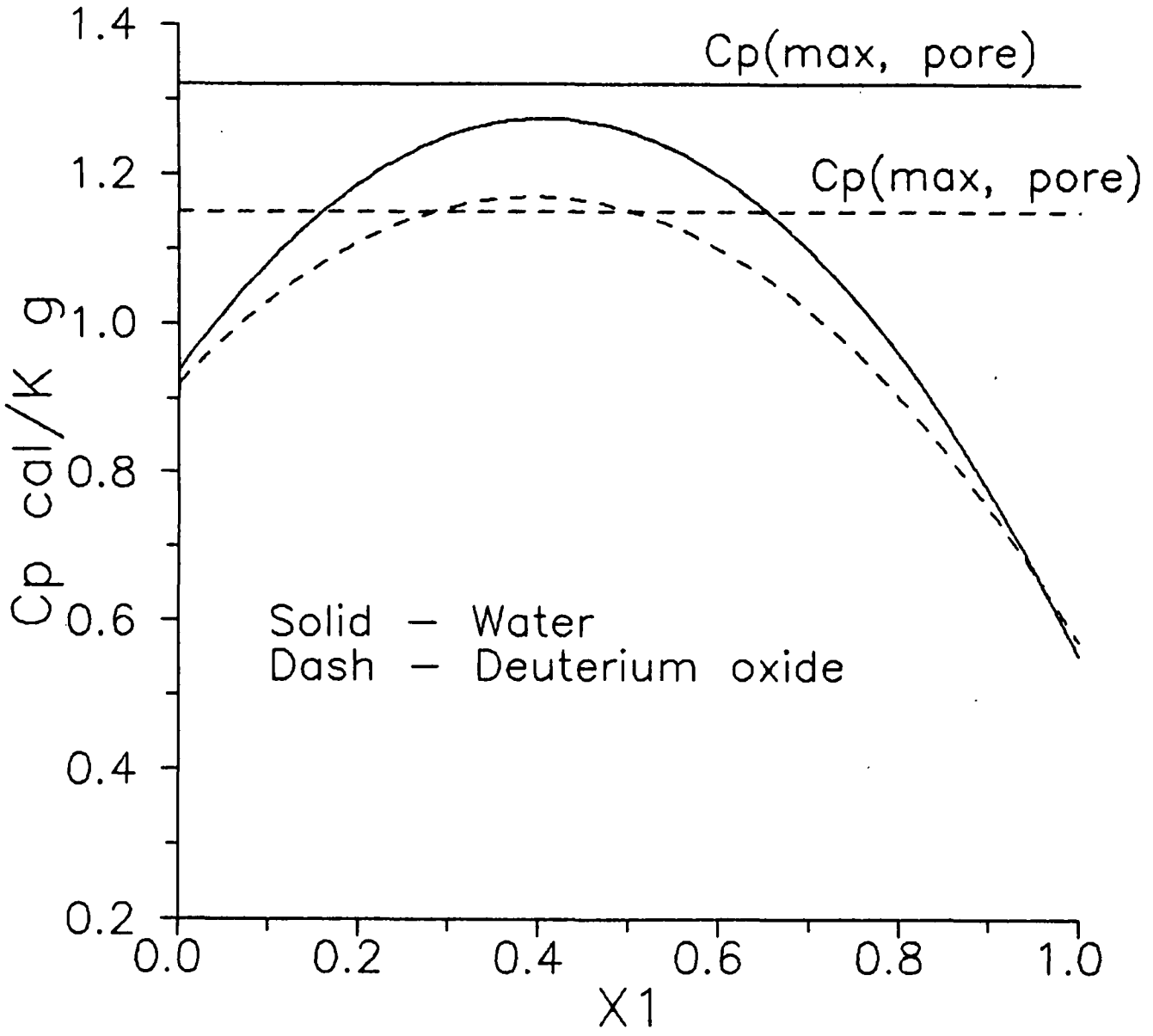

INTERLAYER DISTANCE (nm)
0
5
10
15
1.04
1.03
1.02
1.01
1.00
PARTIAL SPECIFIC VOLUME
Na
Li
0
1
2
3
4
5
6
Mw/Mm (g/g)

Fig #7


1.4
1.2
1.0
0.8
0.6
0.4
0.2
Cp cal/K g
Cp(max, pore)
Cp(max, pore)
Solid – Water
Dash – Deuterium oxide
0.0
0.2
0.4
0.6
0.8
1.0
X1

Fig#8

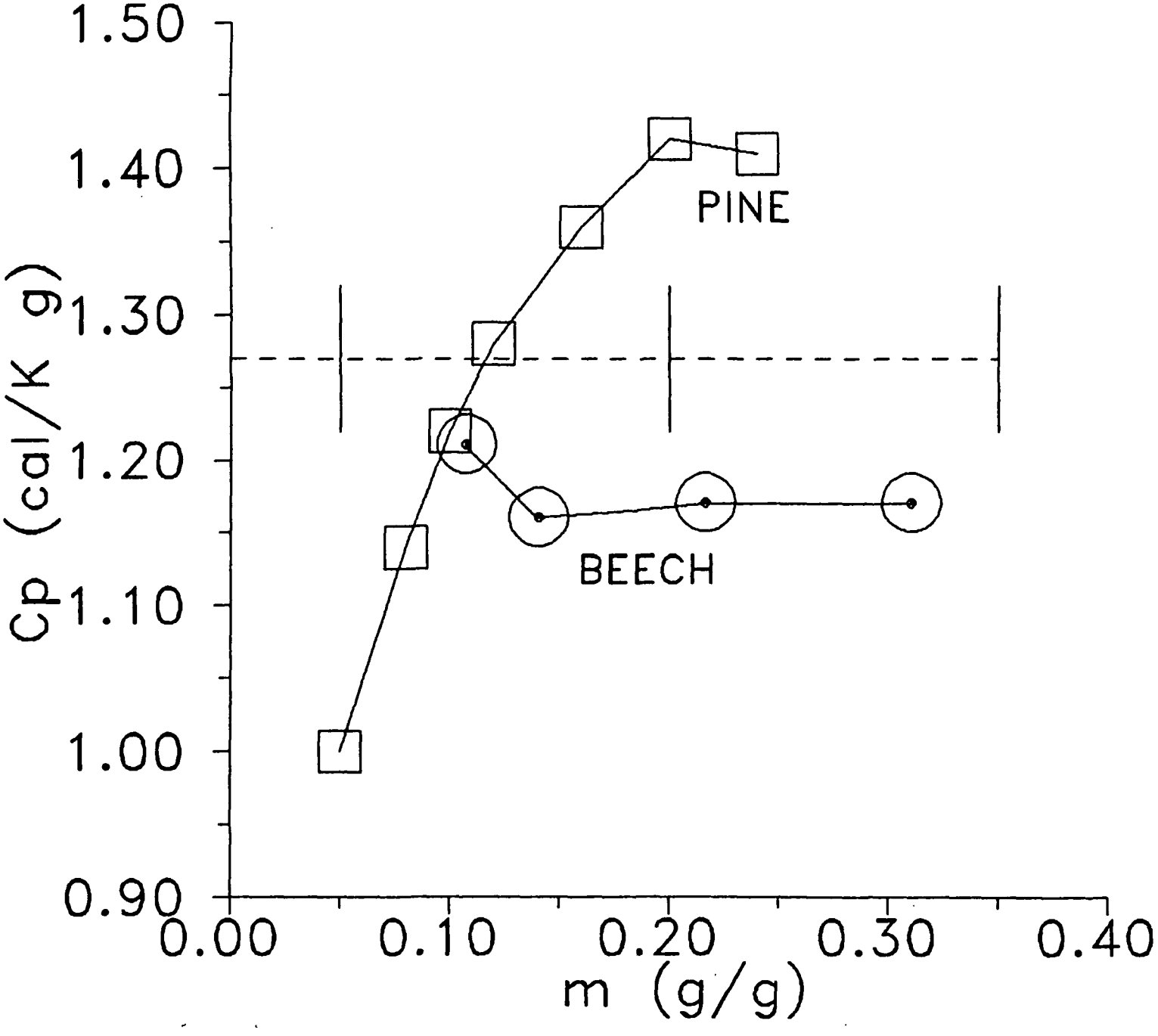

1.50
1.40
1.30
1.20
1.10
1.00
0.90
Cp (cal/K g)
0.00
0.10
0.20
0.30
0.40
m (g/g)
PINE
BEECH

Fig #7

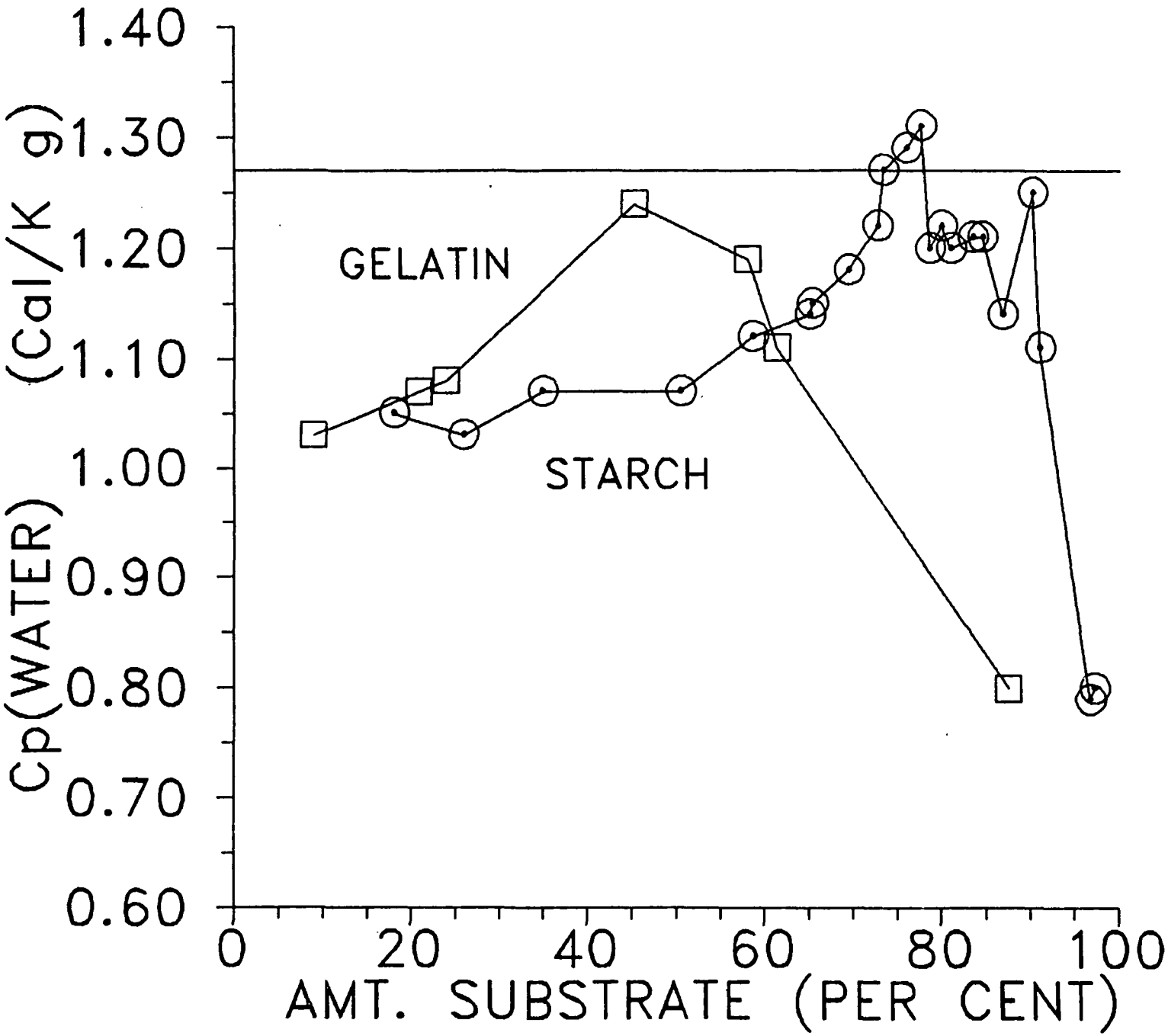

1.40
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
Cp(WATER) (Cal/K g)
GELATIN
STARCH
0
20
40
60
80
100
AMT. SUBSTRATE (PER CENT)

Fig # 10