with the central miscibility gap H_2O–oil. Addition of a less hydrophilic nonionic surfactant or a lyotropic salt lowers the three-phase body temperaturewise, whereas the addition of a more hydrophilic surfactant or a hydrophobic electrolyte raises it. These two effects counteract each other. Accordingly, we suggest representing multicomponent systems in a pseudoquaternary phase tetrahedron (at constant temperature), in which pure (!) H_2O is located in one corner of the basis, the nonpolar liquids are combined into an oil of an effective hydrophobicity in the second corner, the nonionic surfactants and the hydrotropic electrolytes are combined into an amphiphile of an effective hydrophilicity in the third corner, and the lyotropic salts are on top of the tetrahedron. If the phase behavior of the pseudoternary system (i.e., that of the basis) is known as a function of temperature, one can qualitatively predict the phase behavior of the corresponding pseudoquaternary system.

We showed further that ionic detergents, hitherto applied as hydrotropic electrolytes, can be replaced by non-surface-active hydrotropic salts.

Nonionic surfactants can be looked at as "chemical dipoles". The stronger their "dipole moment", i.e., their amphiphilicity, the smaller the central miscibility gap and the closer the 3PT to the H_2O–oil side of the Gibbs triangle. On the other hand, the stronger their amphiphilicity, the stronger the tendency to form micelles and lyotropic mesophases. We claim, however, that the evolution of the three-phase triangle remains essentially similar to that of "simple" systems. This is demonstrated in Figure 14, which shows the phase behavior of three ternary systems. The upper systems with n-C_4E_1[1] as nonionic surfactant shows neither micelles nor anisotropic phases, the central one with C_8E_3[14] shows micelles, but no anisotropic phases, whereas the lower one with $C_{12}E_5$[15] shows both micelles and lamellar mesophases. This comparison shows that the existence of micelles, or of "microemulsions" in the sense of Schulman,[9] or that of lyotropic mesophases is not a prerequisite for this particular phase behavior, although one cannot exclude the possibility that the microstructure of the solutions becomes more complex with increasing amphiphilicity. We further note that with increasing amphiphilicity, the "Schreinemaker groove" appears to become increasingly deeper.

The result that the addition of lyotropic salts is equivalent to decreasing the effective hydrophilicity of nonionic surfactants, whereas that of hydrotropic salts is equivalent to increasing their effective hydrophilicity, holds not only for the upper loop H_2O–surfactant, but for the entire phase diagram, i.e., for the regions of existence of the lyotropic mesophases as well. Figure 15 shows on the left the phase diagrams of the three binary systems H_2O–$C_{12}E_7$, $C_{12}E_6$, $C_{12}E_5$, the two latter taken from ref 16. If one adds the lyotropic NaCl to the H_2O–$C_{12}E_6$ system, the surfactant becomes effectively less hydrophilic. Accordingly, the phase diagram of the (ternary) system becomes similar to that of H_2O–$C_{12}E_5$. If, on the other hand, one adds the hydrotropic $NaClO_4$, the surfactant becomes effectively more hydrophilic and the phase diagram becomes similar to that of H_2O–$C_{12}E_7$. Thus, by adding non-surface-active hydrotropic salts to systems with very amphiphilic nonionic surfactants, one can reduce the regions of existence of the lamellar mesophases.

Acknowledgment. We are indebted to Mr. B. Faulhaber and Mr. T. Lieu for their assistance with the experiments, to Mr. D. Luckmann for drawing the figures, and to the "Max-Buchner-Stiftung" and the "Fond der Chemischen Industrie" for financial support.

Registry No. C_2E_0, 74-84-0; n-C_3E_0, 74-98-6; n-C_4E_0, 106-97-8; C_4E_1, 111-76-2; C_4E_2, 112-34-5; C_4E_3, 143-22-6; $C_{12}E_5$, 23244-49-7; $C_{12}E_6$, 3055-96-7; NaDS, 151-21-3; $(C_6H_5)_4PCl$, 2001-45-8; NaCl, 7647-14-5; $NaClO_4$, 7601-89-0; cyclohexane, 110-82-7; toluene, 108-88-3; decane, 124-18-5; benzene, 71-43-2; p-xylene, 106-42-3; mesitylene, 108-67-8.

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Pentagon–Pentagon Correlations in Water

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We report computer simulation studies on the concentration of pentagonal rings of hydrogen-bonded water molecules (pentagons) and on the spatial correlation of pentagons in liquid water. The pentagon–pentagon correlation function $g_{55}(r)$ has a peak at $r \simeq 3.2$ Å. The results support the idea that the anomalies of water may be related to the self-replicating propensity of pentagons in the random network.

1. Introduction

The unusual properties of water, its expansion below 4 °C, various anomalies displayed by supercooled water,[1-3] and hydrophobic effects in aqueous solution,[4-6] may have a common explanation in terms of the presence in the liquid of some particular structures which are (a) self-replicating, and (b) associated with cavities.[7] Speedy and Angell gave evidence for anomalous density fluctuations in supercooled water and attributed them to some

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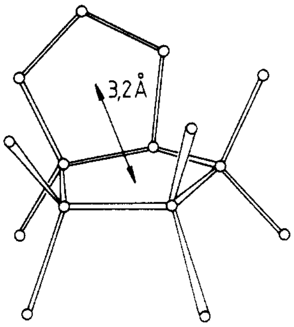

Figure 1. The geometry of a pentagon and its neighbors in a tetrahedral network. Circles locate the oxygen atoms of water molecules and the lines represent hydrogen bonds. The adjoining molecules are constrained to lie (in a tetrahedral network) in positions which favor the presence of more pentagons which share a side. The distance between the centers of mass of such pentagon pairs is 3.2 Å when the O–O separation is 2.9 Å.

form of geometrical cooperativity in the random network.[8] They suggested that the fluctuations might be directly observable by small-angle scattering techniques, and this was confirmed in a small-angle X-ray scattering study by Bosio, Teixeira, and Stanley[9] which showed density flucutations with a correlation length of about 8 Å in water at −20 °C. The identification of the structure of these "low-density patches" will presumably clarify the nature of the cooperative process which underlies the anomalies of water and aqueous solutions.

Computer simulation provides the most promising tool for their identification but, since generalized pattern recognition is not a strong point with computers, it is necessary to speculate about what the structures might be like and then to use the computer to test the speculations. Current contenders for the role of the low-density species are clusters of four-bonded molecules in the Stanely–Teixeira[10,11] model, bulky polyhedral species in Stillinger's picture,[12,13] and pentagonal rings of hydrogen-bonded water molecules (pentagons), as suggested in ref 7.

Tests of the Stanley–Teixeira postulate that a molecule with four intact hydrogen bonds is more bulky than an average molecule have given contradictory results[14,15] which have been shown to be dependent on the potential function and on the H bond definition.[16] These tests have been done on small constant-density systems. More convincing evidence that a particular species is bulky would be provided by an (N, p, T) simulation to measure $\langle \Delta X \Delta V \rangle_{N,p,T}$, where ΔX is the fluctuation in the concentration of the species and ΔV is the fluctuation in the volume.

In ref 7 it was shown that the thermodynamic anomalies of supercooled water and some simple manifestations of the hydrophobic effect can be accounted for by the postulates that pentagons are self-replicating and are associated with cavities. Rahman and Stillinger's early computer simulation study of polygons in water[17] and subsequent studies[18,19] have shown that the most common nonshort-circuited polygons are pentagons and hexagons. Geiger, Stillinger, and Rahman[20] have shown that the molecules in water form a single well-connected network. As water is cooled one expects the local structure in this network to tend toward the stable tetrahedral geometry found in the low-pressure ices and aqueous clathrate crystals.

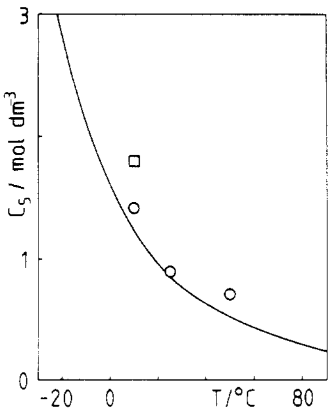

Figure 2. The concentration of pentagons, C_5, vs. temperature. Circles show the values calculated in this work. The square shows a value calculated for ST2 water by using an energetic criterion for a hydrogen bond ($V_{HB} = -4$ kcal/mol) by Rahman and Stillinger.[17] The line shows the concentration of pentagons estimated in ref 7 from the bulk properties of water.

In an approximately tetrahedral network a pentagon is planar and its sides are in the eclipsed conformation such that the bonds which it presents to the surrounding network are aligned in just the right way to be part of an adjoining planar pentagon (Figure 1). As a result, the presence of a planar pentagon may bias adjoining regions of the network in favor of more planar pentagons. Similarly, the sides of a chair-form hexagon (and four and the six sides of a boat-form hexagon) are in the staggered conformation so that the pairs of bonds presented to the adjoining network are nonplanar and are aligned so as to favor more hexagons. However, distortion away from ideal tetrahedrality is needed for a pentagon to bond to a hexagon.

One implication of these observations is that pentagons in water may have a tendency to form correlated clusters in which pairs of pentagons stabilize each other by sharing a side. The simplest manifestation of this effect will be a peak in the pentagon–pentagon radial correlation function $g_{55}(r)$ at the center of mass separation $r \simeq 3.2$ Å, which corresponds to the unstrained side sharing conformation shown in Figure 1. The present work is aimed at testing this prediction.

2. Calculations

The calculations analyzed the same set of configurations of MCY and ST2 water that were used in previous analyses.[21,22] Hydrogen bonds were defined by the geometric criteria for a "strong" bond (cutoff values:[21] O–O separation ≤ 3.3 Å; H(1)–O–O, and LP(1)–O–O angles $\leq 45°$; δ(H(1)–O–O–LP(1) $\leq 90°$).

For MCY water at 50 °C (0.988 g/cm^3, 216 molecules, fcc boundary conditions) results derive from the analysis of 2305 configurations, separated by 1000 Monte Carlo steps. The average number of hydrogen bonds per molecule N_{HB}/N was 1.973 and the average number of pentagons per molecule N_5/N was 0.0129.

For MCY water at 25 °C (0.997 g/cm^3, 125 molecules, simple cubic boundary conditions) 6813 configurations separated by 500 Monte Carlo steps gave $N_{HB}/N = 2.103$ and $N_5/N = 0.0162$.

For ST2 water at 10 °C (1.000 g/cm^3, 216 molecules, simple cubic boundary conditions) 2099 configurations, separated by 1000

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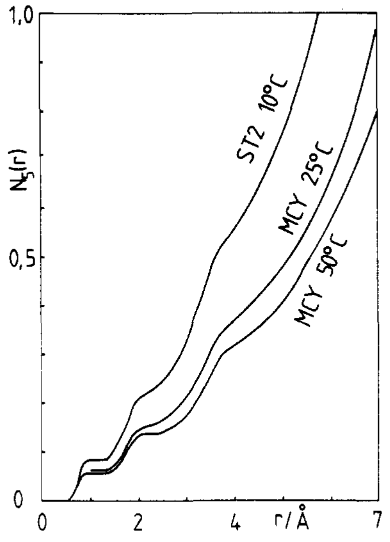

Figure 3. The average number, $N_5(r)$, of pentagons within a sphere of radius r about a reference pentagon.

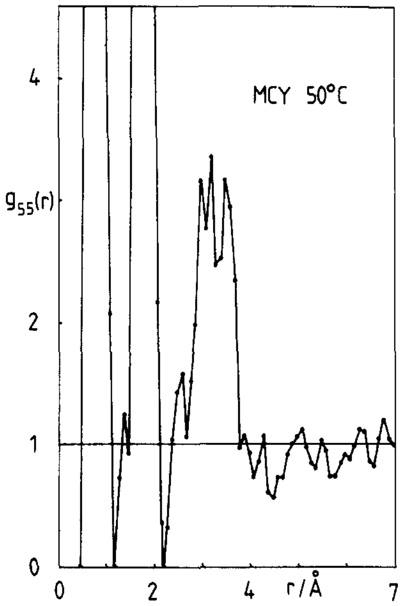

Figure 4. The pentagon–pentagon radial correlation function $g_{55}(r)$ for MCY water at 50 °C.

steps, gave $N_{HB}/N = 2.32$ and $N_5/N = 0.0256$.

Short-circuited[17] pentagons were not counted. The location of a pentagon was defined as the position of the center of mass of the five water molecules. The average number of pentagons in shells of radius r and thickness $\delta r = 0.1$ Å about a given pentagon was also calculated.

3. Results

3.1. Pentagon Concentrations. Figure 2 compares the calculated number of pentagons with the number estimated from the bulk properties of water in ref 7. The predicted values derive from the assumptions that the volume of water is the sum of two parts $V = V_n + V^*$. V_n is the volume of "normal" or pentagon-free water and was estimated, somewhat arbitrarily, by drawing a tangent to the near linear density vs. temperature plot at 100 °C. V^* is the excess volume due to the cavities associated with the pentagons. The average volume of the two cavities associated with a pentagon was taken to be the volume of one molecule, so that $V^* = N_5(V_n/L)$, where L is Avogadro's number, and $N_5/N = V/V_n - 1$.

Despite the crude nature of this estimate, it is in good agreement with the concentrations calculated here. The same assumptions were shown to account semiquantitatively for the anomalous components of the compressibility and heat capacity of supercooled water.[7]

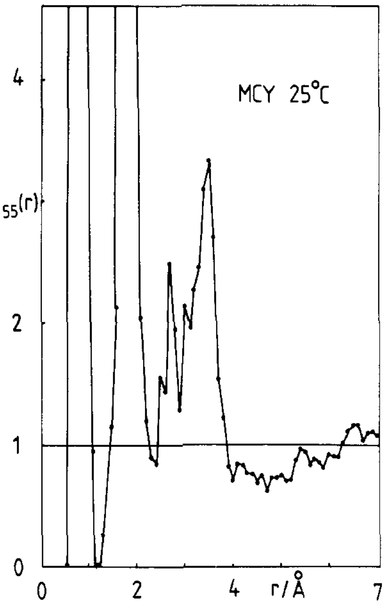

Figure 5. The pentagon–pentagon, radial correlation function $g_{55}(r)$ for MCY water at 25 °C.

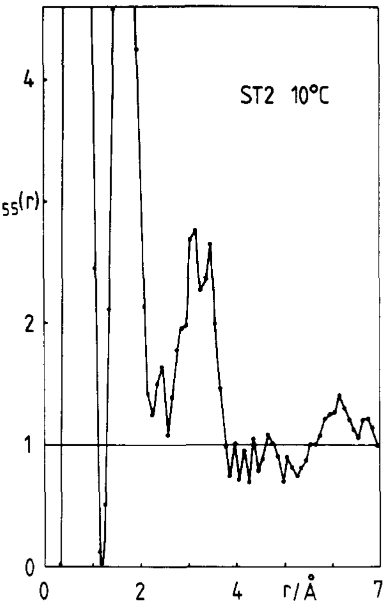

Figure 6. The pentagon–pentagon radial correlation function $g_{55}(r)$ for ST2 water at 10 °C.

3.2. Pentagon–Pentagon Correlations. Figure 3 shows the average number, $N_5(r)$, of pentagons within a sphere of radius r about a reference pentagon. The density of pentagons at r, $\rho_5(r)$, is defined by

$$\rho_5(r) = \Delta N_5(r)/\Delta V(r) \qquad (1)$$

where $\Delta N_5(r)$ is the number of pentagons in the spherical shell of radius r and thickness $\delta r = 0.1$ Å, and $\Delta V(r)$ is the volume of the shell $\Delta V(r) = 4\pi r^2 \delta r$. We define the pentagon–pentagon radial correlation function $g_{55}(r)$ by

$$g_{55}(r) = \rho_5(r)/\rho_5 \qquad (2)$$

where $\rho_5 = N_5/V$ is the average density of pentagons. The form of $g_{55}(r)$ is shown in Figures 4–6. The significant feature is the peak at $r \approx 3.2$ Å. However, the peaks at $r \simeq 0.8$ and 1.8 Å need to be explained, since they tend to dwarf the significant result.

3.3 Overlapping Pentagons. The sharpness of the peaks in $g_{55}(r)$ around 0.8 and 1.6 Å is evidence that they are due to topologically specific structures rather than to the broad flexing of the structure shown in Figure 1. The first peak almost certainly corresponds to the structure shown in Figure 7a because model

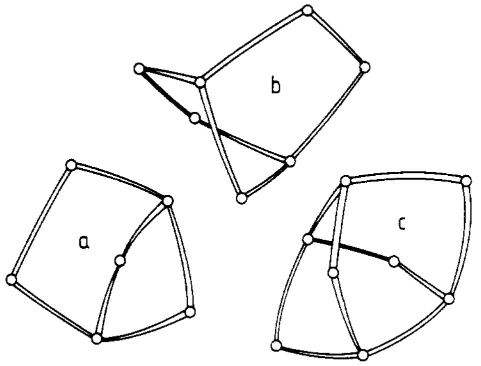

Figure 7. Examples of overlapping clusters of pentagons with pentagon centers of mass separations $r < 2.2$ Å. Approximate separations are (a) 0.8 Å, (b) 1.8 Å, (c) two pairs at 2.2 Å, four pairs at 1.6 Å. These distances were estimated from models in which the O–O separation was taken 2.9 Å.

building experiments show that it is not possible to bring the centers of two pentagons within 0.8 Å, without severe repulsions, unless they overlap by having three sides in common. Similarly, the second peak around 1.6 Å can be attributed to the presence of pairs of pentagons which have two sides in common as shown by b and c in Figure 7. These peaks appear large because r^2 is small but Figure 3 shows that only 10% (MCY, 50 °C) to 20% (ST2, 10 °C) of the pentagons have a neighbor closer than 2 Å.

The total concentration of overlapping pentagons (counted as pairs closer than 2.2 Å) increases with decreasing temperature because more hydrogen bonds are made. However, the rate of increase is about 10% less than that of the structure responsible for the peak between 2.2 and 4 Å, showing that the overlapping structures are somewhat less stable than the structure shown in Figure 1.

The presence of overlapping pentagons complicates the quantitative interpretation of $g_{55}(r)$ because they are likely to be anticorrelated with the planar pentagons. Most of the o–o–o–o tetramers in Figure 7 are nearer to the staggered conformation characteristic of chair-form hexagons than to the eclipsed conformation of the tetramers in a planar pentagon, so, according to the reasoning of ref 7, they are more likely to be bonded to hexagons than to pentagons.

3.4. Unstrained Pentagonal Clusters. The important prediction made in ref 7 is that pentagons are self-replicating, in the sense that a pentagon in the random network will bias adjoining regions of the network in favor of reproductions of itself. The simplest manifestation of this effect will be the occurrence of a greater concentration of side-sharing pairs of pentagons, with their centers of mass separated by ~3.2 Å, than would occur if the pentagons were distributed randomly. This prediction is confirmed by the presence of a substantial peak in $g_{55}(r)$ between ~2.5 and 4 Å. The absence of a peak near 4.2 Å, corresponding to coplanar fused pentagons, argues for the geometry shown in Figure 1.

The same effect would be expected to produce smaller peaks in $g_{55}(r)$ around 5, 6, and 6.8 Å, corresponding to the unstrained clusters shown in Figure 8. However, a quantitative estimate of the amplitude of these peaks shows that they are likely to be smaller than the statistical noise which is evident in $g_{55}(r)$ beyond 4 Å (section 3.6). Before explaining this result we digress to estimate the association constant for pentagons.

3.5. Pentagon Association Constant K. A quantitative measure of the clustering tendency of pentagons is provided by the association constant K defined by

$$K = C_{55}/C_5^2 \qquad (3)$$

where C_{55} is the concentration of associated pentagons, and C_5 is the total concentration of pentagons. To estimate C_{55} we neglect the occurrence of triplets and high-order clusters and we count as associated only those pairs of pentagons whose centers are separated by 2.2 to 4 Å. C_{55} is then given by

$$C_{55} = \tfrac{1}{2}C_5P \qquad (4)$$

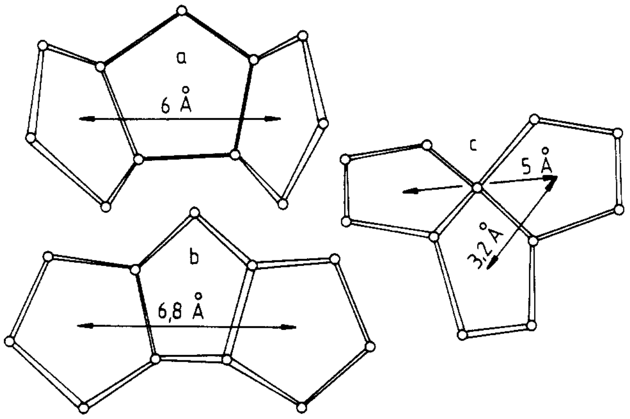

Figure 8. Examples of unstrained clusters of three pentagons. Approximate center of mass separation indicated were estimated from models in which the O–O separation was taken as 2.9 Å.

TABLE I: Concentration of Pentagons C_5, Paired Pentagons C_{55}, and the Equilibrium Constant $K = C_{55}/C_5^2$, Estimated As Discussed in Section 3.5[a]

model	T/°C	N_5/N	C_5/mol dm^{-3}	C_{55}/mol dm^{-3}	K/dm^3 mol^{-1}
MCY	50	0.0129	0.72	0.065	0.13
MCY	25	0.0162	0.90	0.099	0.12
ST2	10	0.0256	1.42	0.23	0.11

[a] The values depend on the definition of a hydrogen bond (section 2).

where P is the probability that a given pentagon has a neighbor in the range 2.2 to 4 Å, and can be read from Figure 3.

$$P = N_5(4\ \text{Å}) - N_5(2.2\ \text{Å}) \qquad (5)$$

The resulting values of K are listed in Table I, which shows that K is independent of temperature to within the likely errors and approximations involved in its definition. This result is consistent with the idea that the association is caused by geometrical (or entropic) factors and involves no energy change.

3.6. Pentagon Triplet Concentrations. To explain why $g_{55}(r)$ shows no clearly defined peaks corresponding to the triplet cluster separations shown in Figure 8, we estimate here the approximate concentration of such triplets and their contribution to $g_{55}(r)$.

Given a reference pentagon at the origin, a second pentagon can be attached to it at any one of ten sites with equal probability. A third pentagon can bond to the second to form the structure labeled (a) in Figure 8, in two equivalent ways. Therefore, other things being equal, the association constant for the formation of (a), defined by

$$K_{(a)} = C_{(a)}/C_5C_{55} \qquad (6)$$

will be related to K by $K_{(a)} = 2K/10$. The same result is obtained for the clusters (b) and (c) in Figure 8.

The area of the peak in $g_{55}(r)$, due to state (a), relative to that at ~ 3.2 Å due to pairs, is therefore expected to be about

$$(C_{(a)}/(6\ \text{Å})^2)/(C_{55}/(3.2\ \text{Å})^2) = \left(\frac{3.2}{6}\right)^2\left(\frac{2K}{10}\right)C_5 \simeq 0.01 \text{ for ST2 at } 10\ ^\circ\text{C} \qquad (7)$$

The oscillations which do appear in $g_{55}(r)$ around 6 Å in Figures 4–6 are somewhat larger than this estimate, but in view of the evident statistical noise, and complications due to the presence of overlapping pentagons (section 3.3), it would be unwise to attach much significance to them.

3.7. Polyhedra. The method of the last section can be extended to make a rough estimate of the concentration of the clathrate-like cages which have been invoked[12,24] to explain the expansion of

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water below 4 °C. A lower bound on the concentration of dodecahedra, C_{20}, is $C_{20} \geq (KC_5)^{11}C_5 = 4 \times 10^{-9}$ mol dm^{-3} for ST2 at 10 °C. This is a lower bound because the completion of the 12-faced polyhedron, once four or five of the faces are in place, may be a highly cooperative process. On this basis an optimistic upper bound is $C_{20} \leq (KC_5)^3C_5 = 5 \times 10^{-3}$ mol dm^{-3} for ST2 at 10 °C. (This estimate was suggested by a referee.)

It therefore seems unlikely that C_{20} is large enough to account for the anomalies of water, which are in evidence well above 10 °C. If C_{20} does approach the upper bound then dodecahedra should be detectable in computer simulation studies, with a sufficiently liberal hydrogen bond definition.

The above estimates of C_{20} do not rule out the presence of a substantial concentration of clathrate-like cages near the stability limits in supercooled or stretched water,[13,23] but they do suggest that the presence of dodecahedra is not a prerequisite for the anomalies.

4. Conclusions

The results support the model in ref 7. They confirm that the concentration of pentagons needed to account for the anomalies in water[7] is close to the actual concentration (Figure 2), and they confirm that there is a significant tendency for the pentagons to cluster together. However, to establish the model more convincingly will require further studies. One would want to show, for example, that hexagons are also correlated and that hexagons and pentagons are anticorrelated.

The other important postulate of ref 7, that pentagons in water are associated with cavities, has not been addressed here. One way to examine that possibility would be to examine the distribution of pentagons about an inert solute;[7] another would be to show that fluctuations in the pentagon concentration are positively correlated with volume fluctuations in an (N, p, T) simulation.

Registry No. Water, 7732-18-5.

Stable Alkaline Earth Metal-Ammonia-Anion Radical Complexes and Their Thermodynamic Stabilities

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A series of compounds with the general formula $M(NH_3)_2^{2+}$(anion radical)$_2$ have been generated by simply reacting the alkaline earth metal (M) with naphthalene, anthracene, tetracene, perylene, or benzophenone in liquid ammonia and distilling off the solvent. These solid complexes react exothermically with water, and this reaction has been studied calorimetrically. The calorimetric results were placed into a thermochemical cycle to obtain the crystal lattice energies and heats of generation (from M, ammonia, and the organic compound in their standard states) of the complexes. These heats of generation of the complexes decrease for the different metals as Ca > Sr > Ba. However, the crystal lattice energies do not vary extensively upon changing the size of the hydrocarbon anion radical. When the nitrobenzene anion radical is used as the anion, only one ammonia is incorporated into the complex, $Ba^{2+}(NH_3)(PhNO_2^{-}\cdot)$. A sample of this green solid detonated upon exposure to sunlight.

Introduction

The "metal-ammonias", as they were called in 1830,[1] were the first derivatives of alkaline earth metal cations with electrically neutral ligating molecules to be reported. Complexes between calcium, strontium, and barium with ammonia were first thought to be hexammonates,[2] but it was later realized that nonstoichiometric amounts of ammonia are combined with the metals.[3] Despite the very early work with alkaline earth metal-ammonia complexes, the coordination chemistry of alkaline earth cations has started to develop rapidly only in the past 15 years.[4] Little importance has been given to the coordination chemistry of the group 2A elements due to the facts that (1) the complexing ability of these cations is weaker than those of the transition metal ions and (2) the complexes of the alkaline earth metals were thought to be simple and understandable in terms of the ionic model.[4,5]

Recently equilibria have been observed to exist between solid strontium and calcium salts suspended in 1-pentanol and gas-phase ammonia, two examples of which are[6]

$$SrCl_2{\cdot}2NH_3(s) \rightarrow SrCl_2{\cdot}NH_3(s) + NH_3(g) \qquad (1)$$

$$CaCl_2{\cdot}8NH_3(s) \rightarrow CaCl_2{\cdot}4NH_3(s) + 4NH_3(g) \qquad (2)$$

Reaction 2 is endothermic by 9.8 kcal/mol,[6] reflecting the high affinity that these salts have for ammonia.

We have made use of the strong affinity of the alkaline earth metal cations for ammonia to generate a new class of solid alkaline earth metal complexes containing hydrocarbon anion radicals which are thermodynamically stable. The first examples, in which anthracene served as the anion radical, were reported in a preliminary communication.[7] Freeman and Hutchinson[8] have very recently reported a compound that is analogous to this series, but it contains the anthracene dianion and tetrahydrofuran (THF) as opposed to the anthracene anion radical and ammonia. Their solid compound $Mg(anth)_2{\cdot}THF$ (anth = anthracene) was the subject of the first report concerning the properties of a solid benzoid aromatic dianion containing other than group 1A metals.[8] Due to the large size and lack of symmetry of the unit cell, Freemen and Hutchinson[8] had to abandon plans for a structure determination.

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