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PHYSICAL CHEMISTRY OF NANOCLUSTERS AND NANOMATERIALS

The Stability and Structure of $(N_2)_j(H_2O)_i$ and $(Ar)_j(H_2O)_i$ Clusters

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Abstract—The stability and structure of water clusters absorbing nitrogen molecules or argon atoms was analyzed by molecular dynamics simulation at 233 K. The $(\partial\mu/\partial i)_{V, T}$ derivative of the chemical potential, a value characterizing the stability of a cluster with respect to its size, depends linearly on the number of molecules i. According to this criterion, the clusters under study become stable near $i = 40$. The average length of H-bonds increases monotonically in the growing cluster of pure water and exhibits oscillatory behavior if the growing cluster contains N_2 molecules or Ar atoms. The number of H-bonds per molecule oscillates between one and six as the cluster size changes. These oscillations are damped in pure water and sustained for clusters containing impurities, especially argon.

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INTRODUCTION

Clusterization affects strongly the energy, radiative, and optical properties of the atmosphere. Computer simulations showed that clusterization of water decreased the greenhouse effect on the Earth [1, 2]. It was found in a series of works [3–7] that water clusters could capture molecules of other atmospheric gases. Depending on the kind of absorbed molecules, the absorption of infrared radiation by cluster systems can both increase and decrease. While flexibility of molecules has no significant effect on the thermodynamic and structural characteristics of disperse systems, it can affect the spectral characteristics strongly [8]. It is interesting to establish at what size atmospheric water clusters become thermodynamically stable, that is, can exist sufficiently long to be detected.

We can characterize clusters by macroscopic parameters that approach the corresponding characteristics of the bulk condensed phase as the size of aggregates increases [9]. The macroscopic parameters of small clusters can depend on the number of constituent molecules nonmonotonically. Stable, including liquid, clusters correspond to a certain type of structure which can be characterized, for example, by the statistical geometry methods [10]. One of the most important characteristics of water clusters is the number of hydrogen bonds per molecule.

The purpose of the present work was to explore the thermodynamic stability of water clusters absorbing nitrogen molecules or argon atoms, analyze the structure of these clusters in detail, and determine changes in the number of hydrogen bonds per molecule as the cluster size increases.

COMPUTER MODEL

We used a modified TIP4P model of water [11]. The dynamics of H_2O molecules was simulated using the Φ_w potential of intermolecular interaction defined as the sum of Lennard–Jones, Coulomb, and polarization interactions [12]. The $\Phi(r)$ function describing nitrogen–water interaction is a 6–12 potential of the Lennard–Jones type [13]. The interaction between argon and water is characterized by very weak attraction proportional to $1/r^6$. The repulsive part of the potential is the sum of the exponential function and the $1/r^{12}$ term [14].

The great advantage of flexible models of water is the possibility to explore the effects of temperature, pressure, and local environment on such characteristics as dipole moments and vibrational frequencies. As concerns the simulation of aqueous systems, they are especially useful for the interpretation of chemical composition effects, elucidation of structural features, and more precise determination of thermodynamic properties. In this work, we used the flexible model of water molecules [15]. The molecular strain is determined by balancing the $\mathbf{f}(\mathbf{q}) = -\dfrac{\partial \mathbf{r}}{\partial \mathbf{q}}\nabla\Phi(\mathbf{r})$ total potential force with the $\mu q\omega^2$ centrifugal force, where μ is the reduced mass, q is the distance between two atoms, ω is the vibrational frequency, and the vector $\mathbf{r}$ determines the point of force application.

Molecular dynamics (MD) simulations [16] and ab initio calculations [17] showed that the energy of the $(H_2O)_{20}$ cluster depended on the model of water used. The difference between the POL1 [18] and SPC/E [19] models is 13.4%. For our model, the energy of the $(H_2O)_{20}$ cluster at $T = 233$ K is –8.66 eV, an intermedi-

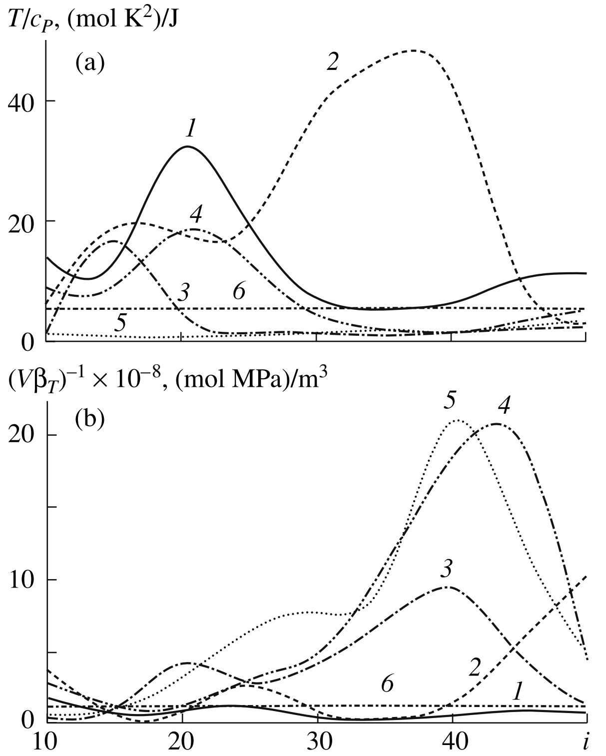

Fig. 1. (a) Thermal and (b) mechanical stability coefficients of clusters (*1*) $(H_2O)_i$, (*2*) $N_2(H_2O)_i$, (*3*) $(N_2)_2(H_2O)_i$, (*4*) $Ar(H_2O)_i$, (*5*) $(Ar)_2(H_2O)_i$ ($10 \le i \le 50$), and (*6*) liquid water (experiment [23]).

ate value between those for the POL1 and SPC/E models. The structures of clusters also differ significantly. While for the POL1 model, the cluster is a cell consisting of four-, five-, and six-membered rings, for the SPC/E model, the minimum energy structure is based on two pentagonal prisms. For our model, the minimum energy structure of $(H_2O)_{20}$ clusters can be interpreted as a strongly distorted pentagonal dodecahedron. The introduction of polarizability and flexible bonds decreases the energy of strained hydrogen bonds.

The simulation of nitrogen and argon absorption by water clusters began with the generation of the initial configuration as an equilibrium cluster of water surrounded with impurity species. The initial equilibrium configurations of water clusters were obtained in separate MD simulations. The kinetic energy of molecules constituting the cluster corresponded to a temperature of 233 K. Initially, the center of mass of impurity species (one or two) was placed at a distance of 0.6–0.7 nm from the nearest water cluster atom, and every argon atom or nitrogen molecule was in the field of molecular interactions. The cutoff radius of all interactions in the model was 0.9 nm. Linear N_2 molecules were oriented along the ray connecting their centers with the center of mass of the cluster. In order to add two molecules (or argon atoms) to the cluster, they were arranged along the same ray but on the opposite sides of the cluster.

The system generated was equilibrated for $6 \times 10^5 \Delta t$ in time steps of $\Delta t = 10^{-17}$ s. The required physicochemical properties were then calculated for $2 \times 10^6 \Delta t$. The fourth-order Gear algorithm was used to integrate the equations of motion for the molecular centers of mass [20]. An analytical solution to the equations of motion for rotations of molecules was obtained using the Rodrigues–Hamilton parameters [21], and the integration scheme in the presence of rotations corresponded to the approach suggested by Sonnenschein [22].

RESULTS AND DISCUSSION

The isobaric heat capacity c_p, isothermal compressibility β_T, and chemical potential μ were calculated as described in [6]. An increase in the number of water molecules in the cluster from 10 to 50 leads to large fluctuations of the T/c_p thermal stability coefficient both for pure water aggregates and clusters containing N_2 molecules or Ar atoms (Fig. 1a). The most prominent peak of the size dependence of the T/c_p isodynamic stability coefficient was observed for the $N_2(H_2O)_{35}$ cluster. The T/c_p coefficient for the water cluster with $i = 20$ was also high. The lowest average T/c_p values were obtained for $(N_2)_2(H_2O)_i$ clusters. At $i > 45$, all water clusters containing impurities (N_2 or Ar) had lower T/c_p coefficients than pure water clusters. A twofold increase in the concentration of N_2 molecules decreased the thermal stability of aggregates over the whole range of i values. The adition of Ar atoms to water clusters decreased the thermal stability coefficients of aggregates of all sizes. At $i < 30$, the thermal stability of clusters decreased as the concentration of Ar increased. The T/c_p coefficient for pure water clusters was virtually always higher than that for liquid water [23] at $T = 373$ K.

In contrast, the $1/V\beta_T$ mechanical stability coefficient was as a rule higher for aggregates containing impurities (N_2 or Ar) than for pure water clusters (Fig. 1b). Especially high $1/V\beta_T$ coefficients were obtained for water clusters of size $i = 40$ and 50 containing absorbed N_2 molecules and water aggregates of size $i = 40$ and 45 containing absorbed Ar atoms. Among the heteroclusters under discussion, water clusters with $i = 15$ and 35 containing one N_2 molecule and clusters with $i = 10$ containing two N_2 molecules had the lowest mechanical stability. Among the clusters containing Ar atoms, the lowest mechanical stability was observed for aggregates of 10–15 water molecules. The mechanical stability coefficient of pure water clusters was as a rule lower than the corresponding experimental characteristic of liquid water [23] at about 373 K (straight line *6* in Fig. 1b).

The behavior of the derivative of the chemical potential μ with respect to the number of particles i is of great interest, because this value characterizes the absorption stability of clusters when their growth is not hindered by the absence of "building blocks." Figure 2 shows the dependence of the $(\partial\mu/\partial i)_{V,T}$ absorption stability coefficient on the number i of water molecules in $(H_2O)_i$, $N_2(H_2O)_i$, and $(N_2)_2(H_2O)_i$ clusters. Similar dependences for water clusters containing Ar atoms (not shown) were close to the corresponding functions for water clusters with N_2 molecules. The $(\partial\mu/\partial i)_{V,T}$ coefficient is positive definite, which corresponds to the cluster state stable with respect to the addition of new molecules, including impurity molecules.

The $(\partial\mu/\partial i)_{V,T}(i)$ functions are linear over the whole range except a segment with low i values. For pure water clusters, the $(\partial\mu/\partial i)_{V,T}$ value becomes positive at larger i than for clusters with N_2 molecules. The larger the number of N_2 molecules absorbed by a cluster, the sooner it becomes stable with respect to the addition of new molecules. This suggests that N_2 molecules (and Ar atoms) organically fit into the structure of a water cluster as its size increases. Note that, in all cases under discussion, water clusters become stable with respect to disturbances related to the absorption of other molecules near the size $i = 40$. Evidently, starting just from this size, a structure corresponding to the structure of liquid water is formed in clusters.

The Voronoi polyhedra (VPs) were constructed for the centers of a half of molecules constituting the cluster. The special feature of these VPs was that their faces were formed by hydrogen atoms. The hydrogen environment of water oxygens and the VPs obtained were used to determine the average length $\bar{L}_b$ and number $\bar{n}_b$ of H-bonds per molecule. For pure water clusters, the $\bar{L}_b$ length increased monotonically as the cluster size grew (Fig. 3). When N_2 molecules or Ar atoms were added, the $\bar{L}_b(i)$ function exhibited oscillatory behavior. As a rule, the $\bar{L}_b$ values were higher for clusters containing one absorbed N_2 molecule than for pure water clusters. When an argon atom was absorbed, the $\bar{L}_b$ values were higher for clusters with $i < 30$ and lower for clusters with $i \geq 30$ than for the corresponding pure water clusters. However, when a cluster absorbed two N_2 molecules or two Ar atoms, the $\bar{L}_b$ value was virtually always lower than the corresponding value for a pure water cluster.

In pure water clusters, the number of H-bonds per molecule decreased until the cluster reached the size $i = 25$ and then oscillated near the $\bar{n}_b = 3.2$ value (Fig. 4). When a cluster absorbed an N_2 molecule, the number of H-bonds per molecule decreased in the majority of cases. When an Ar atom was absorbed, the $\bar{n}_b$ value exhibited significant fluctuations. The highest $\bar{n}_b$ values were observed for the $(H_2O)_{10}$, $N_2(H_2O)_{10}$, and $Ar(H_2O)_{30}$ clusters, and the lowest values, for the $(H_2O)_{25}$, $N_2(H_2O)_{30}$, and $Ar(H_2O)_{20}$ clusters. At $i \geq 45$, the $\bar{n}_b$ values for clusters of different types become closer to each other. Starting with the size $i = 40$, the $\bar{n}_b$

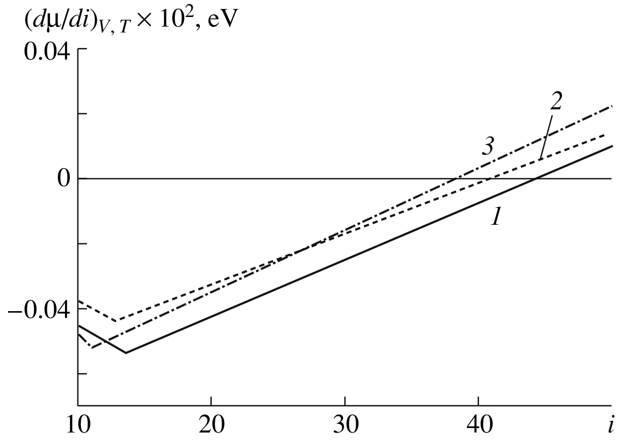

Fig. 2. Stability coefficient $(\partial\mu/\partial i)_{V,T}$ for (1) $(H_2O)_i$, (2) $N_2(H_2O)_i$, and (3) $(N_2)_2(H_2O)_i$ clusters.

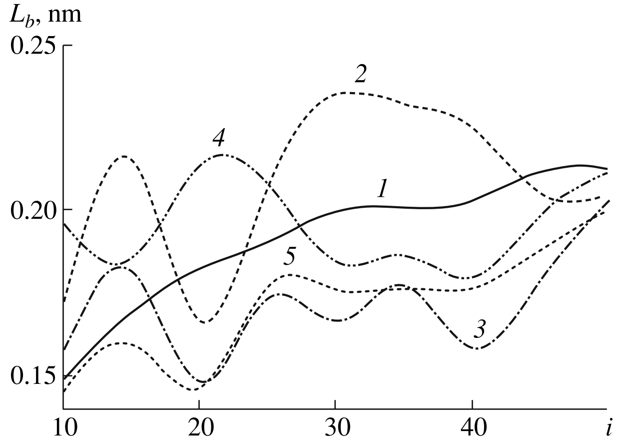

Fig. 3. Average length of H-bonds versus the number of water molecules in clusters (1) $(H_2O)_i$, (2) $N_2(H_2O)_i$, (3) $(N_2)_2(H_2O)_i$, (4) $Ar(H_2O)_i$, and (5) $(Ar)_2(H_2O)_i$ ($10 \leq i \leq 50$).

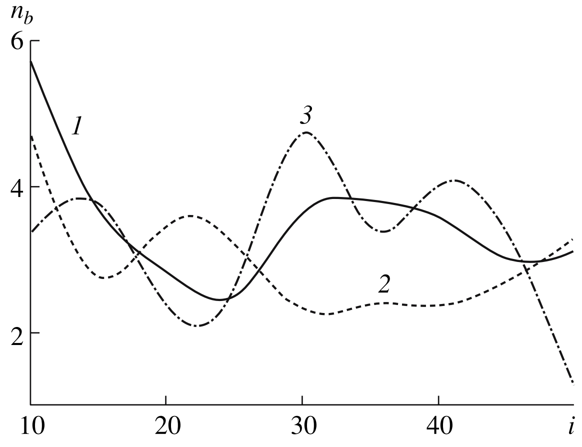

Fig. 4. Average number of bonds per atom for (1) $(H_2O)_i$, (2) $N_2(H_2O)_i$, and (3) $Ar(H_2O)_i$ clusters.

values of clusters with and without impurities approached each other. We can suppose that, starting with this size, a cluster separates into the bulk and surface parts, the structure of the bulk part approaching the structure of liquid water.

CONCLUSIONS

Stable clusterization in water vapor proceeds at low temperatures ($T < 273$ K). Under the conditions of deficiency of molecules for the formation of clusters, the stability of nuclei can be evaluated according to the stability criteria used for the bulk phase. However, difficulties related to large density and temperature fluctuations then appear. As a result, estimates of the mechanical and thermal stability of clusters become ambiguous. In saturated and supersaturated vapor with no deficiency of molecules joining the cluster, we should use the $(\partial\mu/\partial i)_{V,T} > 0$ stability criterion. In our simulations, the $(\partial\mu/\partial i)_{V,T}(i)$ function was linear in the $15 \le i \le 50$ range of aggregate sizes. It predicted the formation of stable clusters containing more then 40 molecules. It is of no importance which molecule (H_2O or N_2) makes the cluster thermodynamically stable in its growth.

However, an increase in the cluster size caused by the addition of an N_2 molecule or Ar atom influences the structure of the whole cluster. The average length of H-bonds, $\bar{L}_b$, changes its behavior as the size of the cluster increases, from monotonic growth characterizing the pure water cluster to oscillations when the cluster contains N_2 molecules or Ar atoms. The largest variance of $\bar{L}_b$ values is observed for clusters containing N_2 molecules. The number of H-bonds per atom, $\bar{n}_b$, changes in a substantially nonmonotonic way depending on the size of the $(H_2O)_i$, $N_2(H_2O)_i$, and $Ar(H_2O)_i$ aggregates. The oscillatory behavior of the $\bar{n}_b(i)$ function becomes more pronounced after the absorption of two N_2 molecules or Ar atoms.

To summarize, the structure of clusters with hydrogen bonds is largely governed by their composition, while their thermodynamic stability is governed by the total number of structural units constituting them.

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