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PHENOMENON OF THE OUSTING OF A MONATOMIC ION FROM ITS HYDRATION SHELL IN FLAT NANOPORES

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The structure and stability of hydrate shells of singly charged sodium and chlorine ions are studied by computer simulations under the conditions of nanoscopic flat pores with the use of the previously proposed detailed force field model containing polarization interactions, transferring charge effects as well as many-body interactions of covalent type. It is found that the effect of ousting a monatomic ion from its hydration shell, which has previously been observed by independent authors in bulk vapor, is also reproduced persistently in nanoscopic pores. Whereas the ousting of the ion from its hydration shell in bulk vapor is accompanied by the loss of thermodynamic stability of the system and at sufficiently high vapor pressure causes avalanche-like condensation, under the conditions of a nanoscopic pore the thermodynamic stability is retained. The obtained data show that the ousting of the ion from its hydration shell is a universal phenomenon covering the majority, if not all, of monatomic and, possibly, some of molecular ions.

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INTRODUCTION

In the natural air atmosphere even under the conditions of extremely low relative humidity, all ions are hydrated and bear from a few to several tens of water molecules [1-4]. In the conductivity and static electricity phenomena in the atmosphere we have to deal with cluster ions representing charged molecular complexes rather than free ions *per se*. A relatively high intrinsic dipole moment of water molecules helps retain them in a strongly heterogeneous electric field of ions and a rapid weakening of the field with distance from the ion prevents the avalanche-like growth of the complex. The state of the atmosphere with respect to its electric properties must be characterized as the cold rarefied cluster plasma whose degree of ionization largely depends on the hydration of charge carriers.

Hydrated charges have a number of characteristic properties that qualitatively distinguish their behavior from the behavior of free charges in the plasma. In the usual plasma, recombination is accompanied by rearrangements in the electron shells of ions as a result of which the ions transform into electrically neutral atoms. In the cluster plasma the hydrated ions with opposite signs can form ionic pairs without electron exchange. As a result of the formation of a hydrated ionic pair the ions do not turn into electrically neutral atoms but continue to exist as charged particles dissolved in microdroplets of water.

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The formation of these electrically neutral complexes in the field of unrecombined ionic pairs is responsible for the accumulation of a vast population of stable clusters of water molecules in the upper layers of the atmosphere and an anomalously intense absorption band in downflows of electromagnetic radiation in the IR range corresponding to vibrational frequencies of hydrogen bonds [1]. The accumulation of unrecombined ionic pairs in the clusters of water molecules is responsible for the anomalously high reflection coefficient of centimetric electromagnetic waves from the radioactive cloud in the natural atmosphere [2, 5]. Ionization in the clusters of water molecules explains the high coefficient of hydrogen chloride adsorption on the ice surface as the key element in the cyclic destruction of the protective ozone layer in the stratosphere [6-12]. The intensive formation of unrecombined hydrated ionic pairs is one of the probable hypotheses for the mechanism of energy accumulation in the ball lightning [13, 14].

The hydration of ions on solid surfaces [15, 16] needs a special investigation. These conditions take place in reactions on catalyst surfaces and electrodes in accumulator batteries. Real surfaces can have a complex relief and multiple crystal defects that are often purposely created to increase the specific surface or provide the contact of three phases: liquid, solid, and gaseous. Even if a liquid electrolyte contacts with a solid surface, depending on its wettability, the saturated vapor pressure at the interface can be insufficient for the electrolyte to penetrate into a pore and the charge hydration in this pore corresponds to the hydration conditions in water vapor.

The ion mobility and reactivity depends on the structure of its hydrate shell. It was initially assumed that the ion hydration in water vapor occurred similarly to the hydration in liquid solutions. It was considered that the ion was uniformly enveloped by molecules from all sides as a result of which a spherically symmetric shell formed. However, the computer simulation performed by independent authors in the 1980-1990’s with different models of intermolecular interactions (see [3, 17, 18] and references therein) showed that the hydration of the chlorine anion in water vapor did not correspond to these representations. When the number of molecules coordinating the ion exceeds 10-15, they gather at one side of the ion, and the ion is ousted from its own hydration shell and the shell is transformed into a compact cluster. In this system the ion takes a position on the cluster surface. The surface states of the chlorine ion were steadily reproduced at room temperatures, however, they were leveled after an increase in the temperature by more than 100°.

The reasons for this phenomenon have been discussed in the literature [19]. Hypotheses based on a high polarizability of the chlorine ion, its relatively large sizes, and also the polarizability and a relatively high intrinsic dipole moment of water molecules were put forward as possible explanations. Each of these factors acts in favor of the observed phenomenon, however, it has remained unclear whether all factors are equally responsible for the observed effect or there is a single key factor among them.

In [4] in the detailed model of interactions that is consistent with the experimental data on the Gibbs free energy of attachment reactions of vapor molecules [20] the effect of ousting from the own hydrate shell was reproduced for the singly charged positive sodium ion and in [21] for the hydroxyl ion. The data obtained provided the assumption that the phenomenon had the universal character and could be observed not only for the chlorine ion but also for the majority of atomic ions. It remained unclear how the hydration conditions could affect this phenomenon. In particular, the question about the possibility of its observation under the hydration conditions on the surfaces and in nanoscopic pores remained unexplored.

This work contains the report about the first results of the observation of this effect under the conditions of a nanoscopic volume in a planar pore. In order to separate the limited volume factor from the factors determined by a particular crystal structure of walls, the hydration under the conditions of a model pore with flat structureless walls is investigated. The aim of the work is to evaluate the effect of a limited volume on the hydration mechanism. A specific task is to elucidate whether the phenomenon of ousting an ion from its own hydrate shell will be observed in a planar nanoscopic pore or not. It is expected to clarify whether the limited volume conditions weaken or strengthen this phenomenon and how it is related to the thermodynamic stability of the hydrate shell in the pore.

MOLECULAR MECHANISMS OF THE PHENOMENON

Although the effect of ousting the chlorine ion from its own hydrate shell was reproduced by independent authors, there were still doubts whether the observed phenomenon was the artifact of the applied model of intermolecular interactions or not [22]. In [23] the traditional model of interactions was tested. The model ability to reproduce the experimental data on the Gibbs free energy and entropy of the first six attachment reactions of water molecules to the ion hydrate shell was examined. The Monte Carlo computer simulation in the bicanonical statistical ensemble showed that the traditional model could not reproduce the experimental data with sufficient accuracy. Divergences in the calculation per reaction were several $k_B T$ and simple corrections of the numerical values of interaction parameters failed to remove these divergences in all reactions simultaneously. The model was unable to correctly reproduce the course of the Gibbs free energy from one reaction to another. Errors of the model accumulated together with an increase in the hydrate shell and in the medium size range resulted in a catastrophically rapid increase in errors in the work of formation and the nucleation rate. The analysis showed that the reasons for the divergences with the experiment consisted in that the non-pair interactions at short distances were insufficiently accurately taken into account.

In order to solve this problem, in [24] a detailed model of interactions was developed and precise statistical test calculations were carried out. Apart from electrostatic, exchange, dispersion, and polarization interactions in the form of the first term of multipole expansions, the model contained in the explicit form non-pair interactions of the covalent type, bond saturation effects, partial screening and excess charge transfer, and for systems containing more than one ion it also involved the effects of partial charge transfer between counterions. Numerical values of the parameters were restored from the consistency condition with the experimental data on the Gibbs free energy of the first six attachment reactions of water molecules with an accuracy of up to a tenth of $k_B T$ (the accuracy of experimental values) and also with the experimental data on the normal vibrational frequencies and quantum mechanical calculations of intermolecular bond lengths and angles in the ground quantum state.

Within the developed model we managed to present the non-pair interactions in the analytical form in which the volume of computer calculations increased linearly with the number of molecule at each step of the statistical simulation rather than quadratically as in the traditional non-pair models. This made it possible to substantially enlarge the volume of collected statistics and to lower the statistical error of calculations up to hundredths of $k_B T$, i.e. to exceed the accuracy of the respective experimental measurements in this part of the calculations.

The results of the computer simulation with the application of the detailed model of interactions show [3] that the ousting of the ion from its own hydrate shell is steadily reproduced at room temperatures, i.e. the observed effect is not the artifact of the insufficiently accurate model used before. The ousting of the ion to the surface of the molecular cluster is not also a consequence of a relatively large size of the chlorine atom. In [4] this effect was also reproduced for a substantially smaller sodium ion.

The analysis shows that one of the significant driving factors of the observed phenomenon is polarization interactions: ion polarization in the reactive field of the hydrate agglomerate. The ion polarization energy E depends quadratically on the molecular field ($-\alpha E^2/2$). If the ion polarizability α is high enough, at the sufficient number of molecules in the system the polarization energy can considerably exceed in absolute value the energy of thermal motion $k_B T$ and in this case, to determine the most energetically favorable configurations of the system. The configurations in which the fields of separate molecules are summed up and the quadratic dependence on the field remarkably enhances the effect have the lowest energy. The most optimal arrangement of molecules, which satisfies this condition, is their location on one side of the ion. In this case, the hydrate agglomerate is polarized in the ion field: the dipole moments of the molecules are oriented mainly towards the ion and own electric fields of the molecules are summed up, thus providing the lower polarization energy of the ion. Otherwise, at the uniform arrangement of molecules around the ion their fields are mutually compensated and do not cause ion polarization.

Out of two possible states the configuration with the asymmetric location of molecules with respect to the ion, but at the same time corresponding to a closer particle packing and a lower entropy S, has a lower energy U. The competition of the energy and entropy components in the Gibbs free energy $F = U - TS$ depends on the temperature T. With a decrease in the temperature the role of the energy component becomes more significant. An enhancement of the effect with a decrease in the temperature and the weakening with an increase in the temperature indicates that it is the energetic effect rather than entropic and its noticeable temperature dependence gives evidence of comparable energy and entropy contributions.

In the early studies one of the driving factors of ion ousting from the hydrate shell remained out of view. This factor is the intensive formation of hydrogen bonds between the molecules in the state when they are located off the ion. On the contrary, in the state when molecules are located uniformly around the ion, they form chains radially diverging from the ion. The repulsion between the chains strongly polarized in the ion field hinders the formation of hydrogen bonds.

The formation of hydrogen bonds after ousting the ion to the cluster surface is accompanied by a decrease in energy and entropy. A stable network of hydrogen bond is formed only after the accumulation of the necessary minimum number of molecules when the average number of the nearest neighbors exceeds some threshold value. If the effect of a decrease in energy exceeds the inverse effect of a decrease in entropy, the Gibbs free energy of the state can turn out to be lower and the state thermodynamically more stable. At least, with a decrease in the temperature this ratio in favor of the energy factor must occur sooner or later.

A significant role of the factor of the intensive formation of hydrogen bonds after ousting the ion from the cluster is confirmed by the results of [4] where the ousting effect was steadily reproduced for the singly charged sodium ion, especially since the sodium ion by no means can be assigned to high polarizability ions: the effective polarizability of the sodium ion in aqueous solutions (7.9×10^{-5} nm^3) is fifty times lower than the polarizability of the chlorine ion (3.59×10^{-3} nm^3).

In [4] in relation to the phenomenon of ousting the ion to the microdroplet surface the reasons for the loss of the thermodynamic stability by the hydrate agglomerate formed near the ion were analyzed. The ousting of the ion from the microdroplet makes it similar by its thermodynamic properties to a homogeneous nucleus of a condensed phase whose avalanche-like growth in water vapor is due to the overcoming of the free energy barrier. It is well known that the thermodynamic instability of homogeneous nuclei is determined by positive surface contributions to their free energies which increase slower ($\propto N^{2/3}$, in the capillary approximation) than the bulk contributions ($\propto N$) with an increase in the number of molecules N in the microdroplet, thus providing a convex shape of the curve of the size dependence of the Gibbs free energy for the microdroplet $\frac{\partial^2 G(N,p,T)}{\partial N^2} < 0$, and in a certain range of vapor pressures p the occurrence of the maximum on the curve of the work of formation $A(N,p,T) = G(N,p,T) - N\mu(p,T)$, where $\mu(p,T)$ is the chemical potential of vapor molecules. The position of this maximum satisfies the condition of the equilibrium between the microdroplet and vapor $\mu_a(N,p,T) = \mu(p,T)$, where $\mu_a(N,p,T) \equiv \frac{\partial G(N,p,T)}{\partial N}$ is the chemical potential of microdroplet molecules and corresponds to the critical nucleus size.

The thermodynamic instability of the equilibrium with vapor is a characteristic property of homogeneous microdroplets. It is natural to expect that the ousting of the ion from the microdroplet must promote the thermodynamic instability of the latter. Indeed, in [4] it is found that during its growth in the ion field the hydrate shell passes from the stable equilibrium state to the unstable state of equilibrium with vapor. This is indicated by a change in the sign of the second derivative of the Gibbs free energy from positive to negative. The stability crisis point N^* separating these two modes in the Gibbs free energy curve is the inflection point $\left.\frac{\partial^2 G(N,p,T)}{\partial N^2}\right|_{N=N^*} = 0.$. Its position does not depend on the vapor pressure and is the characteristic of microdroplets *per se*. In [4] it is supposed that the ousting of the ion to the microdroplet surface shifts the crisis N^* towards smaller sizes, thus increasing the instability of the system.

SIMULATION RESULTS UNDER THE CONDITIONS OF A NANOPORE

Under the conditions of a nanoscopic cavity the configurational volume of the system decreases, which is inevitably accompanied by a decrease in entropy. Therefore it is possible to expect that the energy effect, which is the ousting of the ion from the hydrate shell, can not only not disappear but even enhance under the conditions of a pore. On the other hand, if based on the results of computer simulation [3, 4], it is assumed that the crisis of the stability and the effect of ousting the ion from the microdroplet are the rigorously correlated phenomena, it is possible to expect that the effect of ousting the ion from the molecular cluster under the conditions of a pore facilitates a decrease in the hydrate shell stability.

In order to reveal which of the two factors is dominant, we performed the computer simulation of the hydration of singly charged Cl^- chlorine and Na^+ sodium ions by means of the detailed model of interactions [24]. Molecules within a planar pore with structureless walls placed at distances of up to 2 nm were explicitly modeled. The ion was fixed in the middle between the pore walls. Periodic boundary conditions were not imposed. The thermal equilibrium with vapor was simulated by the statistical ensemble method. The employed method corresponds to the principally accurate consideration of all spatial intermolecular correlations in the system.

The calculation algorithm was based on the successive growth of the number of molecules *N* in the simulation range from 1 to 100 with a step of one molecule. For each *N* value the Gibbs free energy, internal energy, and entropy of the system were numerically calculated by the Monte Carlo method in the bicanonical statistical ensemble [3], the curves of the work of formation were calculated, the spatial correlation functions and the distribution of molecules around the ion were analyzed. Thus, at the molecular level the precise calculation of the thermodynamic functions of the system, without the approximations of continuous media and mean field theory was carried out.

Evolution of the form of the distribution of molecules around the chlorine ion in a nanopore gives evidence of the ousting of the ion from the hydrate shell after it exceeds its threshold size value of 10-15 molecules (Fig.1). Thus, under the conditions of the nanopore the effect of ousting the ion is retained in the same explicit form as that under the conditions of hydration outside the pore. There is no noticeable shift in the cluster minimum size necessary for the formation of ion surface states. The effect is leveled when the temperature increases by approximately 100° relative to ambient ones.

In the range of small sizes the molecules uniformly coordinate the ion from all sides and the calculations of the entropy of attachment reactions at the background of thermal fluctuations show that on average the most rigid construction is formed when the fifth molecule attaches to the chlorine ion: entropy of the fifth molecule attachment is lowest. The sixth molecule attachment is accompanied by a sharp growth of entropy caused by the free space deficit in the first hydrate layer and the attachment of a molecule to one of the five already present in the first layer of molecules. The subsequent attaching molecules form short molecular chains radially diverging from the ion.

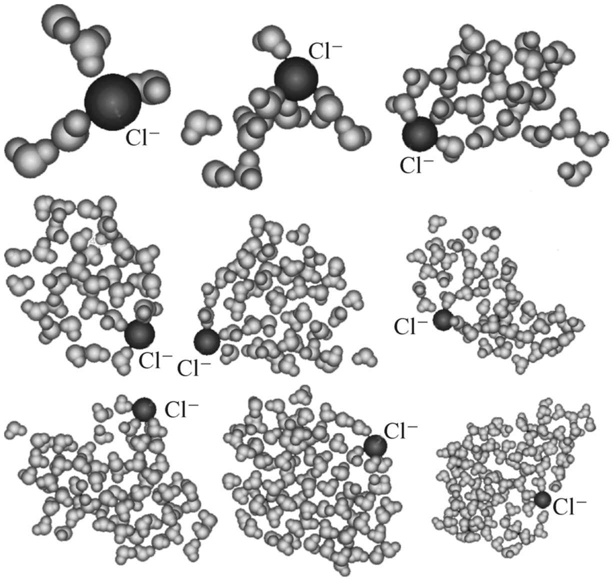

Fig. 1. Cluster of water molecules that grows in the Cl^- ion field in a planar model pore with structureless walls with a width of 0.5 nm at a temperature of 298 K. View in the direction perpendicular to the pore plane.

The ousting of the ion to the cluster surface is accompanied by the formation of a network of hydrogen bonds between the molecules: the cluster becomes more compact and its entropy and energy decrease. Although the energy and entropy components of the free energy at ambient temperatures are comparable; after exceeding the threshold size value of 10-15 molecules, the energy component prevails, making the ion surface states thermodynamically more favorable.

At ambient temperatures the ion returns to the inner part of the cluster when the cluster size reaches the values of several hundreds of molecules. At these sizes there is no space for the formation of strong bonds from the side of the hydrate agglomerate and the occupation of vacancies from the ion side that is free of molecules becomes thermodynamically favorable.

In the first approximation, the conditions of a planar nanopore correspond to a decrease in the cluster size: a transition from a three-dimensional to planar structure. With a decrease in the size the average number of the nearest neighbors decreases together with the possibility to form a dense network of hydrogen bonds. On the other hand, along with the weakening of the factor of hydrogen bonds in the planar cluster it is natural to expect also the weakening of the ion polarization factor. In the planar pore the ratio between them can differ from the conditions outside the pore.

In order to evaluate the role of the factor of high polarizability of the chlorine ion we performed a comparative simulation under the nanopore conditions for the singly charged sodium cation as an ion with low polarizability. We obtained the distributions of molecules around the ion (Fig. 2) that coincide with the distributions obtained for the chlorine anion. When the detailed model of interactions is applied the effect of ousting the ion from the hydrate shell is also reproduced for the ion with low polarizability. This means that the factor of the intensive development of hydrogen bonds in the cluster with the ion ousted from it also acts under the nanopore conditions. It is most likely that the stability of this factor of the transition from a three-dimensional to planar cluster is promoted by a relatively small number of the nearest neighbors (=4) required for the saturation of all hydrogen bonds of water molecules.

The loss of the stability by the hydrate shell of the chlorine ion seems to be a direct consequence of its ousting from the cluster: the system size corresponding to the crisis of the stability is close to the size sufficient for the ousting of the ion to the cluster surface. In bulk water vapor after the ion is ousted to the surface of the microdroplet the latter cannot be in the stable equilibrium with vapor. With an increase in the vapor density the avalanche-like condensation occurs on these nuclei, and with a decrease in it a part of molecules leaves the cluster, the ion returns to its inner region, and the system is stabilized.

In [4] it is assumed that under the hydration conditions in water vapor the ousting of the ion to the microdroplet surface enhances its thermodynamic instability and shifts the crisis point towards smaller sizes. Whether such a relation between the ousting of the ion and the stability of the system is retained under the conditions of a planar nanopore or the state with the ousted ion can be in the pore in the thermodynamic equilibrium with vapor, depends on the result of a combination of many counter factors.

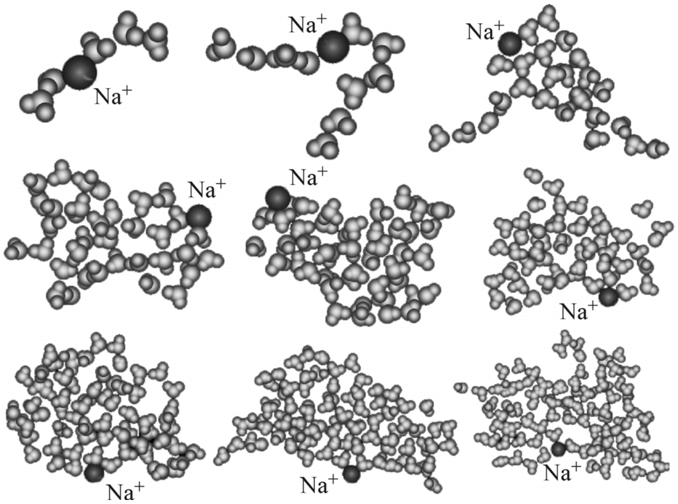

Fig. 2. The same as in Fig. 1 for the Na$^+$ ion.

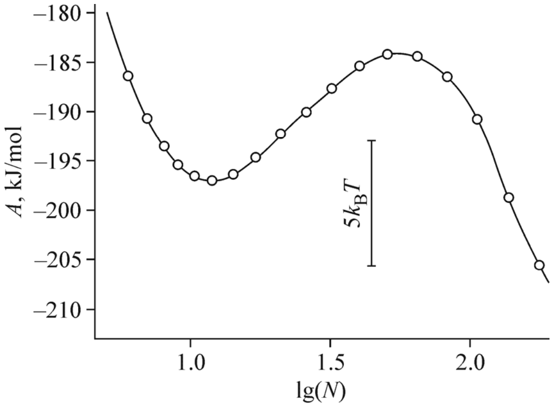

Fig. 3. Work of hydration of the Na^+ ion in water vapor at a temperature of 273 K in the size range of the hydrate agglomerate corresponding to the crisis of stability.

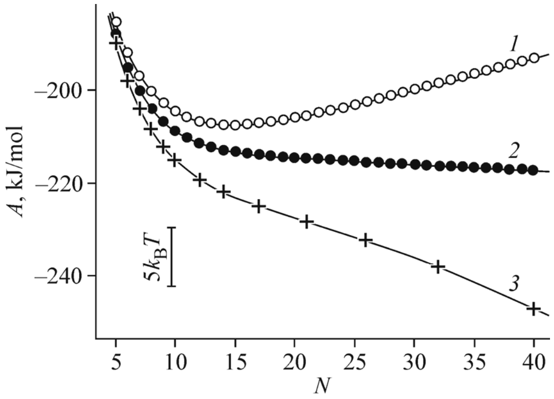

Fig. 4. Work of hydration of the Na^+ ion under the conditions of a planar model pore with structureless walls with widths of 0.5 nm (*1*) and 0.7 nm (*2*), and also in water vapor outside the pore (*3*), at a temperature of 298 K.

The computer simulation [3, 4] shows that the crisis of the hydrate shell stability in bulk water vapor is observed for both high (chlorine anion) and low (sodium cation) polarizability ions. The sign of the crisis of the stability is the occurrence of the inflection point in the size dependence of the Gibbs free energy of the microdroplet, and consequently, the occurrence of two extrema (maximum and minimum) on the curve of the work of hydration at the corresponding vapor pressure. Fig. 3 depicts this curve obtained for the sodium cation. Similar dependences were also obtained for the chlorine anion.

The crisis of the stability was also observed for both ions after an increase in the temperature by more than a hundred degrees when the effect of ousting the ion disappeared. The crisis of the stability, being poorly sensitive to temperature elevation, at the same time disappears under the nanopore conditions. Fig. 4 displays the curves of the work of hydration of the sodium cation in planar pores in the vapor pressure range close to the equilibrium with respect to the hydrate shell. The monotonically decaying curve corresponding to a wider pore complies with avalanche-like condensation and the rising curve corresponding to a narrower pore complies with the stable equilibrium between the hydrate shell and vapor. Hydration in a narrow pore needs a higher vapor pressure.

All curves of the work of formation, which were obtained in such wide pores for both chlorine and sodium ions have no inflection points. The crisis of the stability in pores is absent. The free energy curves are concave in the pore $\left(\frac{\partial^2 G(N,p,T)}{\partial N^2} > 0\right)$, and the hydrate agglomerate formed off the ion is thermodynamically stable. This fact radically distinguishes the mechanism of ion hydration in nanopores from the hydration in bulk water vapor.

CONCLUSIONS

The obtained results can be summarized as follows.

The ousting of the ion from its own hydrate shell in water vapor is likely to be the universal phenomenon encompassing the majority, if not all, of atomic ions as well as some relatively small molecular ions rather than the specific property of the chlorine ion.

In the explanation of the mechanism of ousting the ion from its own hydrate shell the factor of the intensive formation of hydrogen bonds as the force pushing the ion from the inner region of the molecular cluster to its surface has remained underestimated so far whereas the ion polarization factor has been overestimated. The formation of hydrogen bonds should be considered as essential as the ion polarization by the reactive field of the cluster, and for low polarizability ions it is the leading factor.

Under the conditions of a limited volume of a planar nanopore with hydrophobic walls the phenomenon of ousting the ion from its own hydrate shell occurs for both low and high polarizability ions. The threshold boundary of the effect in the pores is practically not shifted.

In planar pores with a width of about one nanometer and smaller the effect of the transition from stable to unstable states of the growing hydrate shell (the crisis of stability) is absent. The thermodynamic stability is maintained in the whole size range.

As opposed to the hydration in bulk water vapor, under the conditions of a planar nanopore the ousting of the ion from the molecular cluster does not cause the loss of its stability.

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