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A molecular dynamics study of Al^{3+} in water: hydrolysis effects

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A molecular dynamics study of Al^{3+} in water was performed. A flexible non-constrained central force model for water molecules was used. This permitted one to take into account a tendency of cation hydrolysis effects. We observed strict octahedral arrangement of neighbours in aluminium cation hydration shell, two of six neighbours being water molecules, the rest four being OH^{-} groups that appeared as a consequence of cation hydrolysis. Four created protons leave the first hydration shell and transfer to the second one. Those protons are strongly bonded to cation hydration shell, which implies that total charge of hydration shell does not change. Structural and dynamical features of the obtained hydration shell of Al^{3+} are reported.

Key words: *molecular dynamics, hydration structure, cation hydrolysis*

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1. Introduction

A concept of cation hydrolysis was introduced about a hundred years ago by Bjerrum [1]. In accordance with this concept the initial steps, which are involved in the hydrolysis of metal ions in aqueous solutions, are considered as a series of removals of protons from water molecules in ion hydration shell. At the next stage there appear polynuclear ions [2,3] caused by condensation reaction between hydrated aqua-ions. However, a mechanism of cation hydrolysis, including the initial steps, is not quite understandable so far. For example, the primary evidence of the existence of such hydrated aqua-ions as $Al(OH)^{2+}$, $Al(OH)_2^+$ or $Al(OH)_3$ in aqueous solutions of aluminium salts appear to be just indirect; they are indispensable to fit solubility data over a broad pH range [4].

For the last three decades an impressive progress has been reached in computer modelling of the structure of hydration shells of monovalent alkaline cations and divalent alkaline earth cations [5]. It was shown that for divalent cations the electrostatic repulsion between cation and protons of water molecules can cause notable modifications of an intramolecular geometry of water molecules in hydration shell. One can suppose that it can be sufficiently strong to repel protons of water molecules from hydration shell causing the hydrolysis effect. However the computer studies of hydration of cations with the hydrolysis effects have not been practically performed. This can be explained by inapplicability of standard water models in treating the hydrolysis effects and by difficulties of quantum-mechanical calculations of hydrated-hydrolyzed complexes with a sufficient degree of reliability in order to be used in further computer simulations [6]. In computer simulations, in order to treat cation hydrolysis effects explicitly, water should be considered in the framework of a non-constrained flexible model. The modelling of cation-water interaction is more complex. It should contain numerous details connected with the treatment of many-body cation-water interactions, the covalent bond effects caused by the specific features of cation electronic configuration etc.

Since the intensity of cation hydrolysis increases with an increase of ion charge and/or decrease of ion size [7], the electrostatic interaction between cation and water molecules plays a prevalent role in this phenomenon. Due to this we recently proposed a model of a primitive cation M^{Z+} [8–10] for the treatment of hydrated-hydrolyzed structure of cation. In this model we use a non-rigid model of water CF1 [11,12] in order to describe the effect of a cation charge Ze (e is the elementary electric charge) on intramolecular structure of water molecules. The interaction of primitive cation M^{Z+} with water molecules is similar to an interaction of the potential of cation Na^+ [13] with water but we also assume that an ion can possess different valency Z. A molecular dynamics study for this model has shown that the increase of cation charge stabilizes an octahedral hydration structure of this cation and significantly modifies the intramolecular geometry of water molecules in hydration shell. For highly charged cations such as M^{4+} and M^{5+}, we observed the effect of some proton loss by water molecules in hydration shell, which was treated as a cation hydrolysis.

In this paper we report a molecular dynamics modelling of hydration structure and dynamical properties of one of the simplest realistic trivalent cations – Al^{3+}. Due to a comparatively small size and high valency of Al^{3+} the electrostatic cation-water interaction is strong enough for hydrolysis initiation. The aqueous speciation of Al^{3+} is very important for many industrial processes such as waste water treatment, pharmaceutical design, catalysis optimization, remediation of wastes from plutonium production etc. [4,14]. For example, the speciation of Al^{3+} hydrolysis products, especially the polynuclear complexes, appear to be a key aspect of aluminum rhizotoxicity [15]. However, in spite of large efforts to describe the cation-water interaction correctly no hydrolysis effects are taken into account directly in previous computer simulations of Al^{3+} in water [16,17].

In present investigation water is considered in the framework of flexible CF1 model [11,12]. The description of cation-water interaction is taken in the form given in [18], which was drawn from quantum-chemical calculations. The results of our investigations demonstrate a strict octahedral configuration of Al^{3+} shell with the tendency for cation hydrolysis. The obtained results for hydration structure and self-diffusion coefficient of Al^{3+} are in good agreement with the results of other computer simulations and experimental data.

2. Model

This study of Al^{3+} aqueous solution was performed in the framework of a mixed model. The interaction between Al^{3+} and water was taken from [18] in the form (energies are given in kJ/mol, distances are in Å):

$$
\begin{aligned}
V_{\mathrm{Al-O}}(r) &= -2750.5/r - 2495.69/r^2 + 266000 \cdot \exp(-3.89948r), &(1)\\
V_{\mathrm{Al-H}}(r) &= 1375.26/r + 160.657/r^2 + 287.456 \cdot \exp(-0.35461r). &(2)
\end{aligned}
$$

The water-water interaction in [18] is described by Bopp-Jancso-Heinzinger model (BJH) [19]. In this study we used the CF1 model for water-water interaction. Both models are identical in the sense of description of intermolecular interaction, but differ for intramolecular part of interaction. The intramolecular terms in BJH are described by anharmonic expansion, which are unfavorable in the sense of water molecule dissociation.

As a first step of our investigation for simplification we neglect the role of three-body cation-water interactions, which was discussed in [18].

3. Results and discussion

3.1. Simulation details

Molecular dynamics simulations were carried out using the standard DL_POLY package [20]. A simulation unit cell (L_x=L_y=33.645 Å, L_z=46.263 Å) with periodic boundary conditions in three directions contained 1727 water molecules and one Al^{3+} ion in the center. The production run over $4 \cdot 10^5$ steps was performed in isotropic NPT ensemble. The density of the solution at temperature 298 K and pressure 1 bar was 1 g/cm^3. Equations of motion were integrated according to Verlet algorithm with time step equal to 10^{-16} s.

For a treatment of Coulombic interactions the Ewald summation procedure (Ewald convergence parameter was 0.285 Å^{-1}, maximal summation parameters for reciprocal lattice were $|n_x| = |n_y| = 9$, $|n_z| = 12$) was used. We also made a pilot simulation with the use of shifted force procedure to manage the long-range interactions. The comparison between those two approaches has shown that shifted force procedure neglects in a special way the long-range part of interaction, which appears in stronger hydrolysis of water molecules in Al^{3+} hydration shell. For short range parts of potentials, a cut-off distance was chosen to be 10 Å.

3.2. Results

It is convenient to explore the hydration shell of aluminium cation by means of radial distribution functions (RDF) $g_{\mathrm{Al-O}}(r)$, $g_{\mathrm{Al-H}}(r)$ and corresponding running coordination numbers:

$$n_{\mathrm{Al}-\beta}(r) = 4\pi\rho_\beta \int_0^r x^2 g_{\mathrm{Al}-\beta}(x)\mathrm{d}x, \tag{3}$$

where β=O, H of water molecules. A function $n_{\alpha\beta}(r)$ indicates the number of species β in the sphere of radius r with species α in the center; ρ_β is the number density of species β.

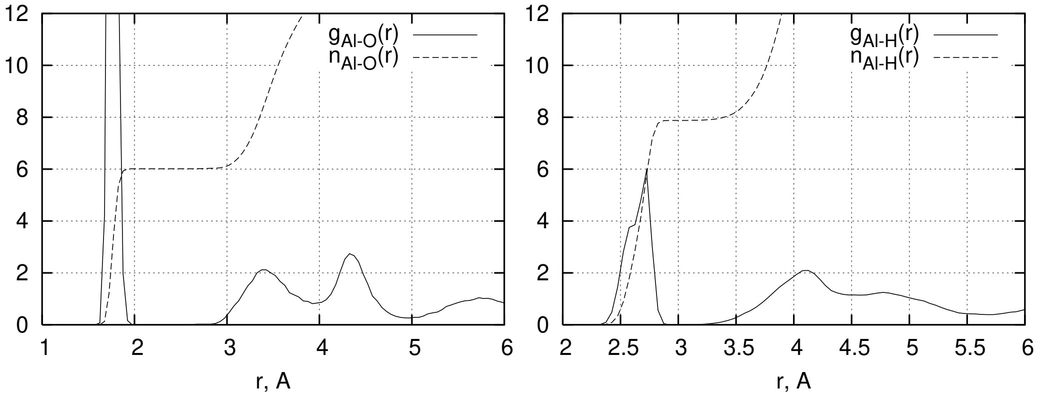

Figure 1. Radial distribution functions (solid lines) $g_{\mathrm{Al-O}}(r)$, $g_{\mathrm{Al-H}}(r)$ and corresponding running coordination numbers (dashed lines) $n_{\mathrm{Al-O}}(r)$, $n_{\mathrm{Al-H}}(r)$.

In figure 1 we present Al^{3+}-water RDFs and coordination numbers. The main peak of $g_{\mathrm{Al-O}}(r)$ distribution is located at 1.78 Å. This result slightly underestimates the value range 1.8–1.97 Å yielded from calculations at various levels of theory in [16,17,22], while the experimental results collected in [21] are within the range 1.87–1.9 Å. However the number of oxygens in the first hydration shell in our calculations coincides with Al–O coordination numbers reported from all mentioned investigations and is equal to 6. A well defined plateau on the $n_{\mathrm{Al-O}}(r)$ indicates that no exchange processes between the first and the second hydration shells were observed during simulation time.

Al–H distribution is characterized by $g_{\mathrm{Al-H}}(r)$, $n_{\mathrm{Al-H}}(r)$ functions. Position of a first peak of Al–H RDF is 2.71 Å. Different theoretical approaches [16,17] yielded a range of values 2.47–2.59 Å for r_{max}. The deviation of our result can be easily explained if one takes into account that our water model is non-rigid (in spite of the ones used in the above references). The strong electrostatic repulsion between Al^{3+} and hydrogens stretches the O–H bonds of the aluminium cation hydration shell neighbours. In [16] a stretching of O–H bonds in water molecules in the first hydration shell was noticed too. Such a deformation was also observed in simulations of the effect of cation charge on intramolecular structure of water in hydration shell of highly charged model cation [9]. The corresponding running coordination number $n_{\mathrm{Al-H}}(r_{\mathrm{min}})$ indicates that the number of protons in the first hydration shell is equal to 8, instead of 12. We treat this result as a cation hydrolysis: strong electrostatic repulsion between Al^{3+} and protons pushes four of them outside the first

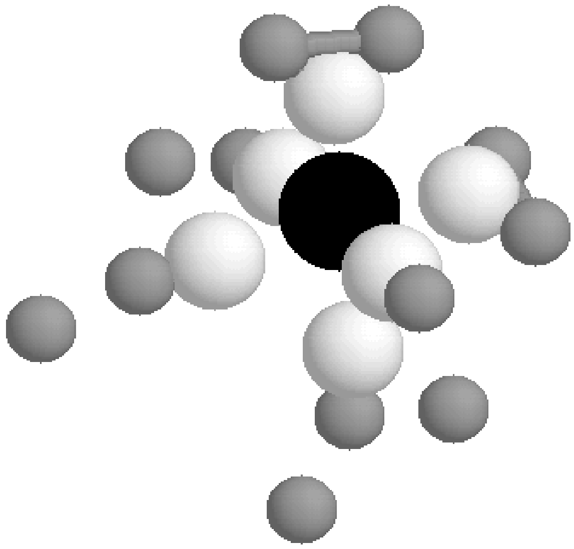

Figure 2. Instantaneous configuration of Al^{3+} cation hydration shell.

hydration shell. However these protons do not move to the bulk water. They stay in the second hydration shell being bonded with cation hydration shell so the total charge of the hydrated cation does not change. After hydrolysis of a few molecules the newly created OH^- groups are preferably positioned in such a way that the angle Al–O–H is close to 180^0, which results in an increase of Al–H distance too. Due to separation of the first hydration shell from the second one both first peaks of $g_{\mathrm{Al-O}}(r)$ and $g_{\mathrm{Al-H}}(r)$ are separated by gaps making well-defined plateaus on the profiles of running coordination numbers. The structural details of hydration shell of Al^{3+} are collected in table 1. A snapshot of aluminium cation first hydration shell

Table 1. Structure of Al^{3+} hydration shell

	r_{max1}, Å	$g(r_{\mathrm{max1}})$	r_{min1}, Å	$n(r_{\mathrm{min1}})$
Al–O	1.78	40.99	2.02-2.52	6
Al–H	2.71	5.95	2.98	8

is presented in figure 2. One can clearly see two water molecules, four OH^- groups and four protons that appeared due to hydrolysis. Four protons are located in the second hydration shell and are strongly bonded to the first one. All the neighbours are octahedrally arranged around the aluminium ion. As it was mentioned before the protons in OH^- groups are oriented outside the hydration shell. The strong electrostatic interactions cause strict octahedral arrangement of Al^{3+} hydration shell. For example, in Na^+ hydration shell there are six neighbours too. However, the charge of sodium ion being lower, the octahedral arrangement is feebly pronounced [9]. A bond-angle distribution O–Al–O in hydration shell is presented in figure 3. This distribution demonstrates two peaks at 0 and –1, which correspond to angles 90^0 and 180^0. This confirms the conclusion that during the simulation time the octahedral arrangement of Al^{3+} neighbours was predominant keeping the coordination number equal to 6.

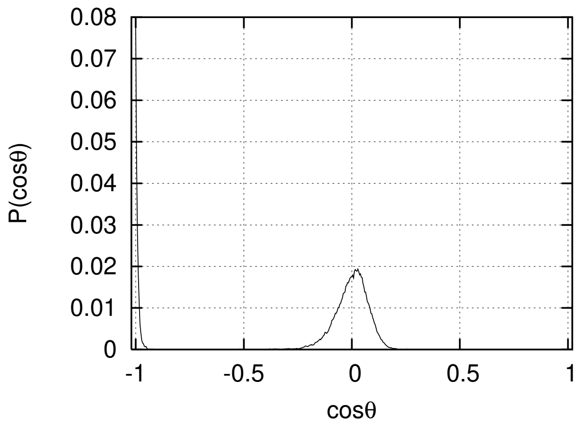

Figure 3. Bond angle distribution O–Al–O in the first hydration shell.

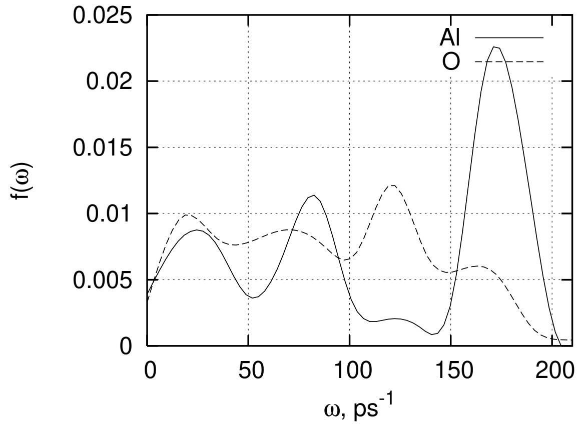

Figure 4. Spectral densities of hindered translation of aluminium cation and oxygens of hydration shell.

Another aspect of our investigation is connected with dynamical properties of Al^{3+} and oxygens in the first hydration shell. We calculated the normalized velocity autocorrelation functions (VACF) for aluminium ion and for oxygens of hydration shell. The spectral densities $f_\alpha(\omega)$ of hindered translational motions were drawn by Fourier transformations of VACFs

$$f_\alpha(\omega) = \int_0^\infty \frac{\langle v_\alpha(0) v_\alpha(t)\rangle}{\langle (v_\alpha(0))^2\rangle} \cos(\omega t) \mathrm{d}t, \tag{4}$$

where $v_\alpha(t)$ is the velocity of particle α =M,O at time t. The functions $f_{\mathrm{M}}(\omega)$, $f_{\mathrm{O}}(\omega)$ are presented in figure 4. The Al^{3+} ion distribution of frequencies is characterized by three main peaks approximately at: 25, 80 and 170 ps^{-1}; one additional peak is located near 120 ps^{-1}. On the spectrum of oxygens one can see four peaks approximately at: 20, 70, 120 and 165 ps^{-1}. Obviously there is correlation between the spectra of central cation and oxygens. Furthermore, the characteristic frequencies coincide, which allows us to conclude that the motion of Al ion is strongly coupled with the motion of water molecules and OH^- groups in hydration shell. The self-diffusion coefficient of aluminium ion, calculated in our study is equal to $0.46 \cdot 10^{-5}$ cm^2/s. In [17] a set of results is reported for the self-diffusion coefficient of aluminium ion for different models. It varies within the range $0.17 - 0.47 \cdot 10^{-5}$ cm^2/s, while the experimental value drawn from [23] is $0.6 \cdot 10^{-5}$ cm^2/s.

4. Conclusions

In the current investigation, a molecular dynamics simulation of Al^{3+} aqueous solution was performed. We made an attempt to take into account a non-rigid origin of water molecules; this permitted us to observe a tendency of a cation hydrolysis effect and to explore how this effects the structural and dynamical properties of aluminium ion first hydration shell. CF1 model makes it possible for the water molecules to dissociate in spite of rigid models, for which the hydrolysis effect is impossible.

The aluminium cation hydration shell demonstrated a stable octahedral arrangement of neighbours. Coordination numbers $n_{\mathrm{Al-O}}(r)$ and $n_{\mathrm{Al-H}}(r)$ indicate the presence of 6 oxygens and 8 hydrogens respectively in the first hydration shell. A snapshot of this configuration shows that aluminium cation neighbourhood consists of two water molecules while four OH^- groups appeared as a consequence of hydrolysis of water molecules due to strong electrostatic repulsion between aluminium cation and hydrogens. 4 protons, which transferred from the first hydration shell to the second one, are still strongly bonded to the cation, which implies that the whole hydrated complex does not change its total charge. The octahedral strict arrangement of neighbours around the cation is confirmed by the O–Al–O bond-angle distribution with two peaks at 90^0 and 180^0. The calculated self-diffusion coefficient of aluminium cation agrees well with other theoretical and experimental results. The characteristic frequencies of both spectra of translational motions of alumunium cation and oxygens in its hydration shell coincide. This fact agrees with the conclusion about the leading role of electrostatic interactions in complexation processes in "highly charged cation+hydration shell" clusters.

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Моделювання Al^{3+} у воді методом молекулярної динаміки. Ефекти гідролізу

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Нами було проведено моделювання водного розчину Al^{3+} методом молекулярної динаміки. Для опису води було використано нежорстку модель центральних сил, що дозволило описати ефекти гідролізу. Отримана гідратна оболонка алюмінію характеризується строгим октаедричним впорядкуванням найближчих сусідів: двох молекул води і чотирьох OH^{-} груп, утворених в результаті катіонного гідролізу. Чотири відірвані протони знаходяться в другій гідратній оболонці, залишаючись тісно зв'язаними з першою гідратною оболонкою, внаслідок чого повний заряд всього гідратного комплексу залишається незмінним. В статті представлено структурні і динамічні властивості гідратної оболонки іона Al^{3+}.

Ключові слова: *молекулярна динаміка, гідратна структура, катіонний гідроліз*

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