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Molecular dynamics simulation of ion sputtering of the solutions of sodium and calcium chlorides

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Abstract. The ionic sputtering of sodium chloride and calcium chloride solutions was studied by classical molecular dynamics method. It is shown that the ions of the solute transferred into the gas phase both in the form of hydrated ions and in the form of ion pairs in water clusters. The threshold character of the ions transfer process is established. The calculated transfer coefficients of water and anions are in a good agreement with the experimental data. The fraction of water molecules sputtered in the form of clusters increases with the energy inputted in the solution. The fraction of water clusters in the gas phase is 40% at the inputted energy is 45 kJ mol$^{-1}$.

1. Introduction
Investigation of gas discharge plasma in contact or in liquids is one of the priority areas in plasma physics [1]. Atmospheric pressure discharges with liquid electrolyte electrodes are of interest as sources of active species for a variety of plasma-chemical applications [2-5]. Furthermore, the plasma-solution system is non-equilibrium in which the processes of formation of active particles in the liquid phase and in the plasma are closely interrelated. The properties of discharges with liquid cathode depend on the transfer of solvent and dissolved substances from the cathode to the gas phase. In discharges with an electrolyte cathode, the surface of the cathode is bombarded by positive ions, which leads to the transfer to the gas phase of the molecules of the solvent and of the components of the solute [6].

There are several possible mechanisms of particles transfer to the gas phase. First, the transfer of particles to the gas phase is similar to cathode sputtering [7]. In this case, the positive ions accelerated by the near-electrode potential drop collide with the surface of the liquid cathode and sputter out drops of liquid from its surface. Cserfalvi and Mezei [8] assumed that the sputtered drop passes through four stages: desolvation, charge stripping, bond breaking, and atomization, sometimes ending in the generation of a free atom of metal. Maksimov et al. [9] suggested that these solvated ions are transferred into the discharge by sputtering of water clusters from the solution cathode. In the discharge, the ions are excited to high vibrational energy levels. The vibrationally excited ionic salts transition from ionic states to covalent states at these high vibrational levels and dissociate as neutral atoms in the discharge. Another possible transfer mechanism is the thermal evaporation of droplets from the surface of the electrolyte cathode, desolvation and further thermal excitation of metal atoms because there is a plasma zone above the surface of the electrolyte cathode where the gas temperature is 1500-3000 K [10]. Finally, electrospray liquid free-jet formation on the solution surface and the formation of a Taylor cone have also been put forth as possible mechanisms [11].
The transfer process can be characterized by a transfer coefficient – the number of particles transferred from liquid to gas phase per one ion bombarding solution surface. In [6, 12] the authors have shown that the transfer coefficients for water are about $200 - 500$ molecule ion$^{-1}$ and for solute these values are $0.01 - 1$ particle ion$^{-1}$. However, a detailed study of the transfer processes is difficult due to the complexity of experimental measurements of transfer coefficients. Nevertheless, it is possible to study the ion sputtering processes of liquid media in a glow discharge at atmospheric pressure by means of numerical simulation methods such as molecular dynamics. For example, the authors [13] investigated the water molecules sputtering from the liquid phase under the falling ion with an initial energy of $50 - 500$ eV. According to the results of the simulation, the authors showed that the value of transfer coefficient of water molecules in the gas phase is about $100 - 500$ molecule ion$^{-1}$. The number of sputtered water molecules, liquid temperature, and ion depth penetration after ions bombardment of O$^+$ with kinetic energies of $10$ eV and $100$ eV on the liquid surface were investigated in [14]. The average number of sputtered water molecules by ion was $0.5$ at $10$ eV and $7.0$ at $100$ eV.

In this context, the aim of our work was to study the process of plasma sputtering more complex systems such as water solution of sodium and calcium chloride by means of the molecular dynamics method. Furthermore, the flow of bombarding positive ions was increased (up to 20 ions) and the transfer coefficients of both solvent and solute were evaluated.

2. Experimental part

The plasma sputtering of sodium and calcium chlorides solution is studied by classical molecular dynamics method, implemented in a software package Gromacs-4.5.4, according to the algorithms described in [15]. The cell with periodic boundary conditions contained 8112 water molecules (SPC/E model), 80 Na$^+$ ions or 40 Ca$^{2+}$ and 80 Cl$^-$ ions, which corresponds to a concentration is $0.5$ mol l$^{-1}$. Cell size $4.9596 \times 4.9596 \times 9.9192$ nm corresponds to the density of solution $1026.8$ kg m$^{-3}$ at $T = 298$ K. Equilibration of the system was carried out in NVT-ensemble for 500 ps with a time step 1 fs. Equilibration achievement determined by analysing of the radial distribution functions, the value of the potential energy and temperature and energy fluctuations during the simulation. The cell obtained in such way then was used to create box consisting of a layer of the solution with thickness $9.9192$ nm, and the vacuum layer with thickness $80.0808$ nm. The ion with atomic mass equals $23$ a.u. and charge $+1$ was selected as the bombarding ion. The solution was bombarded by one, five, eight, nine, thirteen and twenty ions with energies from $60$ eV to $500$ eV. Simulation was performed in NVE-ensemble, bond lengths in the molecules were restricted by the LINCS algorithm. Five simulations of each system were carried out to average statistical error.

3. Results and discussions

Sputtering both the solvent (water) and the solute is observed under the bombardment of the solution by the incident ions. It should be noted that the process of sputtering of the solution surface depends on a number of the bombardment ions and energy of ions (Figure 1). When incident ion collides with the solution surface its energy is transferred to nearest water molecules. Then these molecules interact with neighbouring ones and it results in increasing the kinetic energy of the particles in the region of impact and breaking of hydrogen bonds between water molecules. Having obtained enough kinetic energy some of the water molecules transfer into the gas phase. Thus in the solution cavity is formed due to the intensive destruction of hydrogen bonds and the sputtering of water molecules. Cavity size varies from $0.31$ nm$^3$ at the energy of the incident ion $250$ eV to $1.97$ nm$^3$ at the energy of the incident ion $500$ eV. At the same time, the incident ion overcomes a distance of $2$ to $3.5$ nm in the solution. Simulation results show that the water molecules sputtered due to impact the incident ion with the energy of $250$ eV exist as monomers in the gas phase, whereas dimers, trimers and larger clusters of water molecules can be observed in the gas phase in the case when the initial energy of the incident ion is $500$ eV. When the solution is bombarded only one ion the transition of the solute ions in the gas phase is absent. Mainly monomers of water are transferred into the gas phase at a relatively small
amount of energy inputted in the solution (0.14 – 0.25 eV particle\(^{-1}\), 13.5 – 24 kJ mol\(^{-1}\)). The dimers, trimers and large clusters of water appear in the gas phase at the increasing energy of bombarding ions.

In contrast, the bombardment of the solution surface by several ions results in altering of the sputtering process. The components of the dissolved substance are detected in the gas phase when the threshold value of the input energy (0.3 eV particle\(^{-1}\), 30 kJ mol\(^{-1}\)) is reached. Sputtered of solvent molecules is occurred already along the entire cell surface without cavity formation. Moreover, the sodium and chloride ions exist mainly as ion pairs in a gas phase, and about 30% of all ions are presented separately each other in hydrated complexes. Also, the increasing of the incident ions number leads to increased bombarding ion track in the liquid phase - up to 7.5 nm. On the basis of the results obtained by molecular dynamics, we were able to estimate the amount of ejected into the gas phase ions per one bombarding ion (transfer coefficients). Obtained data are summarized in Table 1 in comparison with experimental ones. The difference between the transfer coefficients for cations and anions is possibly due to the electric field that exists in real plasma cell and which inhibits transferring of positive ions to the condensate. Computer simulation results show that two of the eight solute ions transfer separately into the gas phase under the action of several bombarding ions with a low energy (200 eV). It should be noted that under experimental conditions the transfer of the cluster containing only the cation to the condensate is very difficult because of the presence of interfering electric field. Perhaps such phenomenon can be a reasonable explanation of the stoichiometry violation when the solute transfers to the gas phase. However, in computer simulations the fraction of ions sputtered separately is only 30%. Thus, molecular dynamics simulation results allow concluding that the plasma sputtering of the solution by ion bombardment may cause transfer of the solute ions into the gas phase preferably in the form of ion pairs surrounded by water clusters.

The number of sputtered molecules and the fraction of molecules sprayed into clusters increases with increasing inputted energy. In addition, the water clusters become larger. The geometric criterion of the hydrogen bond was used at the determining the number of molecules in the water cluster. As shown in Figure 2, the water clusters of 5 or more molecules are starting to prevail in the gas phase at the energy reaches ~ 30 kJ mol\(^{-1}\). The maximum fraction of the transferred clusters reaches 40%, and half of them are large clusters with 7 – 10 or more water molecules. Thus, the results of computer simulation by the method of classical molecular dynamics confirm the experimentally observed threshold character of the transfer of cations from the liquid cathode. It has been established that the components of the solute were transferred into the gas phase both in the form of hydrated ions and in the form of ion pairs in water clusters.

![Initial interface](image1)

Figure 1. Configuration of the cell at 10 ps after the impingement of the: A) 1 ion with \(E_i = 500\) eV B) 5 ions with \(E_i = 300\) eV C) 9 ions \(E_i = 300\) eV D) 13 ions with \(E_i = 200\) eV.
Table 1. The transfer coefficients (particle ion$^{-1}$) for water molecules s(H$_2$O) and ions (s) at different numbers of bombarding ions ($N_i$) and energy of ions ($E_i$).

| $N_i$ | $E_i$ (eV) | s(H$_2$O) | s(Cl) | s(Na) | s(Ca) | Experiment$^a$ [16] | MD$^b$ [13] |
|-------|------------|-----------|-------|-------|-------|----------------------|-------------|
| 1     | 250        | 50±5      |       |       |       | 300±50               | 0.213±0.018 | 220±10      |
| 1     | 500        | 450±15    |       |       |       | 350±50               | 0.258±0.025 | 0.019±0.005 |
| 5     | 300        | 270±10    |       |       |       | 440±50               | 0.334±0.027 | 0.029±0.007 |
| 8     | 300        | 310±15    | 0.255 | 0.255 | 0.128 | 480±50               | 0.395±0.032 | 0.038±0.006 |
| 9     | 300        | 405±20    | 0.333 | 0.333 | 0.167 |                       |             |             |
| 13    | 200        | 280±25    | 0.307 | 0.307 | 0.154 |                       |             |             |
| 20    | 60         | 170±25    | 0.305 | 0.305 | 0.152 |                       |             |             |

$^a$ C(NaCl) = 0.5 mol l$^{-1}$, $i = 35$ mA, 40 mA, 45 mA, 50 mA,

$^b$ the energies of bombarding ions are $E_i = 300$ eV and $E_i = 500$ eV.

Figure 2. The number of sprayed water molecules to the gas phase (a), the number of hydrogen-bonded water molecules in the gas phase (b) and the molar fraction (χ) of the water molecules in clusters:

1 – 3-4 molecules in cluster,
2 – 5-7 molecules in cluster,
3 – more than 7 molecules in cluster.

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