Dissolution process of sodium chloride crystal in water

Hitoshi Ohtaki*, Nobuhiro Fukushima, Ei Hayakawa† and Isao Okada

Department of Electronic Chemistry, Tokyo Institute of Technology
at Nagatsuta, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 227 Japan

Abstract — A molecular dynamics simulation has been employed in order to *observe* the disso-
lution process of an NaCl crystal in water at 25 °C. The Tosi-Fumi, Popkie-Kistenmacher-
Clementi and Matsuoka-Clementi-Yoshimine potentials have been used to describe ion-ion,
ion-water and water-water interactions, respectively. The side length of a box assumed was
2000 pm, in which 216 water molecules, 32 Na⁺ and 32 Cl⁻ ions were contained. The length
of the edge of the cubic NaCl crystal having the (100) and the corresponding faces was 1120
pm. The process of dissolution of ions in the crystal was followed over the period of 7 ps
from the beginning of the dissolution. It was *observed* that a chloride ion at a corner of the
crystal first dissolved in water. Then another chloride ion at a different corner left the crystal
surface. The third and fourth ions dissolving were also chloride ions at the other corners. The
velocity of ions leaving from the crystal was estimated from the displacement of the ions with
time. For the first chloride ion, this velocity was about 4×10^2 ms^{-1}. The velocity of other
chloride ions was less than that of the first one owing to electrostatic interactions between a
leaving chloride ion and the crystal skeleton becoming successively positively charged.

INTRODUCTION

Ionic processes of a crystal in solution may be separated into the following steps: *dissolution, solvation* and *complex-
ation*. Ionic association to form undissociated molecules may be included in the process of complexation.
Precipitation, phase separation and *gas evolution* can be regarded as slightly modified reverse reactions of the above
process.

The processes of solvation and complexation have been thoroughly investigated in various systems from the equili-
brium and kinetic points of view. The dissolution process has also been well studied on the basis of equilibrium
thermodynamics. It is well known that the difference between the lattice Gibbs energy of an ionic crystal and the
sum of the Gibbs energies of solvation of each ion at a given temperature determines the solubility of the crystal,
and thus, we know why a crystal can be dissolved in a solvent. However, it has never been considered *how* an ionic
crystal dissolves in a solvent. It is not observable with any apparatus what ion goes first from the crystal surface to
the solution phase. What is the second one? How fast do they leave from the crystal surface? Such questions cannot
be answered by any experimental observation. Only computer simulations may be possible to elucidate the process.
The present work is undertaken to *observe* the dissolution process of a sodium chloride crystal in water by a simula-
tion procedure with the help of a high speed computer.

THE SYSTEM EMPLOYED, PAIR POTENTIALS AND DETAILS OF THE SIMULATION

The system is constructed from a box of the side length of 2000 pm in which 216 water molecules, 32 Na⁺ and 32
Cl⁻ ions are contained. The sodium and chloride ions form a cube having the (100) and the corresponding faces and
the length of the edge of the cube is 1120 pm. The temperature was kept constant at 25 °C during the simulation
process. In fact the temperature calculated from the average kinetic energies of all ions and molecules varied by
only about ± 1 °C. The step was taken to be $\Delta t = 1 \times 10^{-15}$ s and the simulation was carried out over the period of
$t = 0 - 7 \times 10^{-12}$ s.

The pair potential used for describing ion-ion interactions was of the Born-Mayer-Huggins type :

$$\Phi_{ij} = \frac{z_i z_j e^2}{r} + A_{ij} b_{ij} \exp(\frac{\sigma_i + \sigma_j + r}{\rho}) - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8} \tag{1}$$

where z is the charge number, *i.e.*, +1 for Na⁺ and −1 for Cl⁻, e the elementary charge and A the Pauling factor.
The other parameters b, σ, ρ, c and d for each atom (i and j) were given originally by Fumi and Tosi (ref. 1). These
parameter values are listed in Table 1.

---

† Present address: TOPPAN Printing Co. Ltd., 1 Kanda Izumi-cho, Chiyoda-ku, Tokyo, 101

TABLE 1. Parameters used for the pair potentials of ion-ion interactions

parameter	$Na^+ - Na^+$	$Na^+ - Cl^-$	$Cl^- - Cl^-$
A_{ij}	1.25	1.00	0.75
$c_{ij}/10^{-79}Jm^6$	1.68	11.20	116.00
$d_{ij}/10^{-99}Jm^8$	0.8	13.9	233.00
$(\sigma_i + \sigma_j)/10^{-10}$ m	2.340	2.755	3.170
$b_{ij}/10^{-19}J$	0.338	0.338	0.338
$\rho/10^{-10}m$	0.317	0.317	0.317

TABLE 2. Parameters used for the pair potentials of ion-water and water-water interactions

Parameter	$H_2O - H_2O$	$H_2O - Na^+$	$H_2O - Cl^-$
r_{O-H}/pm	95.72	95.72	95.72
r_{O-M}/pm	–	1.79	14.91
r_{O-R}/pm	25.81	16.95	27.19
$\theta/degree$	104.52	104.52	104.52
$\theta'/degree$	0.00	68.68	49.09
$z_H(= -z_R)/e$	0.7517	0.7696	0.3563
$z_M(= -z_O)/e$	0.00	0.2563	0.7840
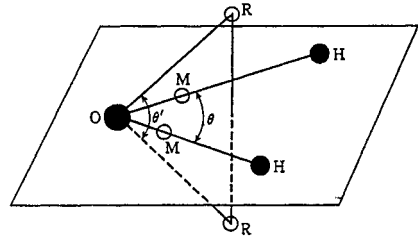
The pair potential function proposed by Popkie, Kistenmacher and Clementi (ref. 2) was employed for describing ion-water interactions. The structure of water molecule and the charge distribution in the water molecule are given in Table 2. The potential function is expressed as follows:

$$\Phi_{ion-water} = z_i\Sigma\{q/r_{ij} - Q/r'_{ij}\} + \Sigma\ a_k\exp(-b_k r_{im}) \tag{2}$$

where $q = \dfrac{z_H}{e} = \dfrac{-z_R}{e}$ and $Q = \dfrac{z_M}{e} = \dfrac{-z_O}{e}$

Water-water intermolecular interactions are described by the potential function given by Matsuoka, Clementi and Yoshimine on the basis of the model proposed by them (see figure in Table 2) (ref. 3). The function is given as follows:

$$\Phi_{water-water} = q^2\{\Sigma\ r_{ij}^{-1} - 2\Sigma\ r_{uv}^{-1}\} + \frac{4q^2}{r_{\alpha\beta}} + \Sigma\ a_\alpha\exp(-b_\alpha r_{\beta\gamma}) \tag{3}$$

In the models polarization of water molecules due to interactions with ions is taken into consideration. However, as we can see from the table, some discreteness can be seen for water molecules which interact with a water molecule on one hand and an ion on the other or with a cation and an anion at the same time. Nevertheless no serious ambiguities have been introduced with the water model of PKC combined with that of MCY in order to describe structures and dynamic properties of electrolyte solution (ref. 4). Therefore, we employed the potential functions of PKC and MCY together with the TF potential in the present simulation.
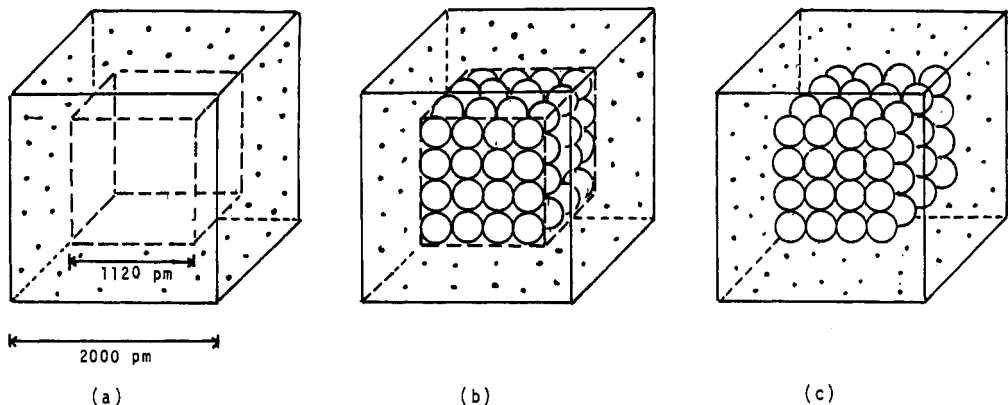

Fig. 1. Simulation procedure before starting the dissolution of sodium chloride crystal in water. (a) Water in the box, (b) water molecules and a crystal having extremely strong ion-ion interactions, (c) the crystal in (b) is replaced to a real crystal and dissolution of it starts.

At the first step of the simulation procedure, we introduced 216 water molecules into the box and the molecular dynamics simulation was performed until the thermal equilibrium was attained in the solvent system. Collision between the walls of the box and water molecules, as well as between the walls and ions, was assumed to be completely elastic at the center of gravity of the water molecule (and ions) (Fig. 1a). After the thermal equilibrium of the solvent molecules was established, a sodium chloride crystal of the given size but having so strong interactions between the ions that they were unable to dissolve in water was placed at the center of the box (Fig. 1b).

The simulation calculations were continued until a new thermal equilibrium was attained. Finally the crystal was replaced to a real one in which ion-ion interaction potential is given by Eq. 1. At this moment dissolution of the sodium chloride crystal started (Fig. 1c). The simulation was then carried out for the dissolution process of the crystal for 7 ps.
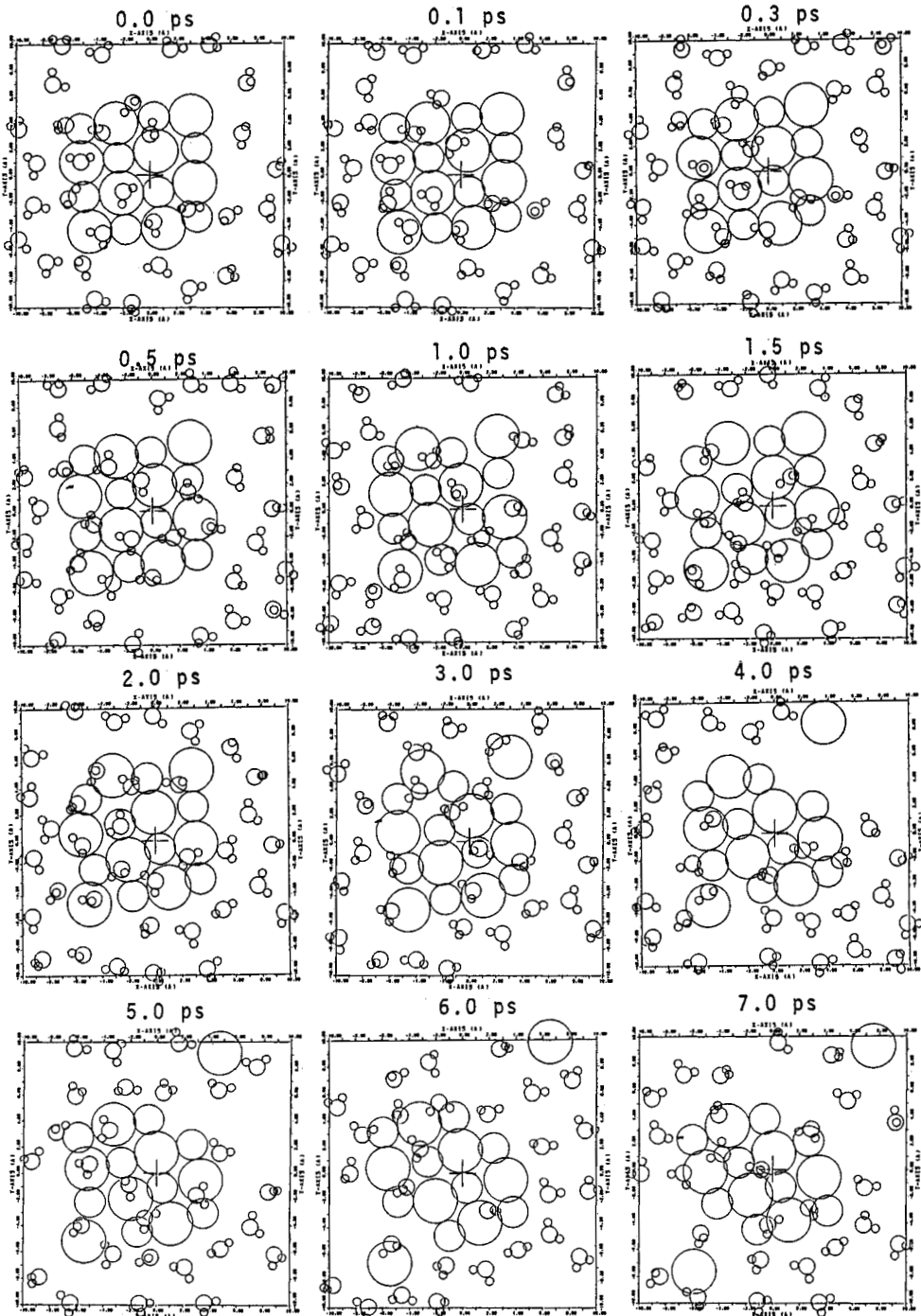

Fig. 2. Shots of the dissolution process of sodium chloride crystal in water with times. Large circle: Cl^-, small circle: Na^+, :H_2O.
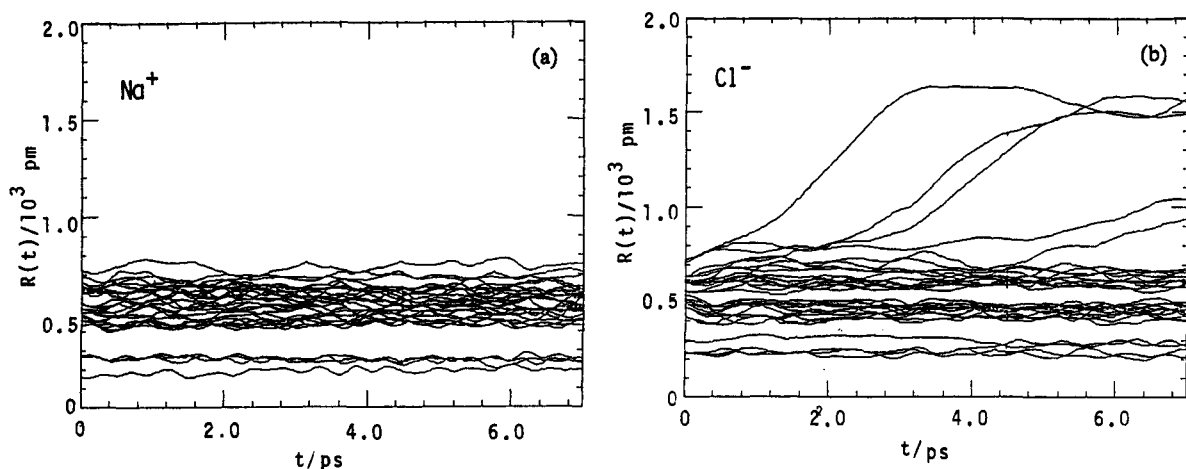
Fig. 3. Displacements R of sodium (a) and chloride (b) ions from the center of the box with time.

RESULTS AND DISCUSSION

At $t = 0$, water molecules prefer to approach sodium ions than chloride ions, as expected from the stronger hydration of the former.

The dissolution process of the sodium chloride crystal is depicted in Fig. 2 as a series of shots with time. The shot was taken from a side of the crystal and water molecules in a layer with the thickness of 280 pm above the surface of the crystal are drawn.

Displacements (R) of sodium and chloride ions from the center of gravity of the crystal with time are plotted in Fig. 3. It is seen from the figure that a chloride ion at a corner first dissolves in water. The second, third, fourth and even fifth ions leaving from the crystal are chloride ions and sodium ions still remain in the crystal. The leaving velocity of ions in the solution can be estimated from the slope of the $R(t)$ vs. t plots of Fig. 3. The first leaving chloride ion has the velocity of about 4×10^2 ms^{-1}. Since the crystal becomes more and more positive due to the escape of chloride ions from it, the velocity of the fifth chloride ion was much smaller than that of the first one, as seen in Fig. 3b.

The reason why chloride ions at the corners first dissolve in water may be interpreted as follows: A chloride ion at a corner is surrounded by sodium ions which can strongly interact with water molecules. Since the water molecules approach the sodium ions by directing the negative site of the water molecule, the chloride ion at the corner may be strongly repulsed by the water molecules and the repulsive force between the chloride ion and the water molecules interacting with sodium ions produces the driving force of separating the chloride ion from the crystal surface.

REFERENCES

1. F. G. Fumi and M. P. Tosi, *J. Phys. Chem. Solids*, **25**, 31 (1964), M. P. Tosi and F. G. Fumi, *J. Phys. Chem. Solids*, **25**, 45 (1964).
2. H. Popkie, H. Kistenmacher and E. Clementi, *J. Chem. Phys.*, **59**, 1325 (1973).
3. O. Matsuoka, E. Clementi and M. Yoshimine, *J. Chem. Phys.*, **64**, 1351 (1976).
4. R. W. Impey, P. A. Madden and I. R. McDonald, *J. Phys. Chem.*, **87**, 5071 (1983).