Usage Report for Fiscal Year 2015

Project Title:

Elucidation of selective chemical binding on cations

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1. Background and purpose of the project, relationship of the project with other projects

Establishing efficient and transgenic-free phytoremediation system for radioactive cesium in eastern Japan, we adopted chemical biology approaches. A chemical library composed of 10,000 small organic compounds have been screened for finding two Cs^+ related properties: Cs^+ tolerance and/or accumulation in Arabidopsis thaliana. Upon phenotype test and quantification of cesium concentrations in plants treated with cesium, 29 chemicals were selected. However, the detailed mechanisms of Cs^+ transport and response in plants are still ongoing subject. Thus, by introducing quantum mechanical calculation, we have evaluated Cs^+ binding property of above 29 chemicals and analyzed a relation between Cs^+ uptake ratio and Cs-chemical binding strength.

2. Specific usage status of the system and calculation method

To evaluate the effective Cs^+ binding strength of the chemicals, thorough quantum mechanical system of the ion-chemical complex in aqueous systems have been constructed. Each system contains a chemical with 20 – 70 atoms including alkali metals, Na^+, K^+, Rb^+ and Cs^+, to observe binding strength difference among the elements. All quantum calculations are calculated by the commercial software, Gaussian 09 which already had been installed on the supercomputing system. At first, we optimized chemical structures using density functional theory (DFT) approach with B3LYP hybrid exchange-correlation energy functional and the atom-centered LanL2DZ basis set for heavy ions, such as Rb^+ and Cs^+. We assumed that the experimental condition is much more likely in water rather than vacuum. Therefore, to mimic the aqueous systems, the Polarizable Continuum Model (PCM) with the integral equation formalism variant have been used. After the chemical only optimization process, electrostatic potential (ECP) maps calculated to find more probable ion binding site. Figure 1 shows the ECP maps of one of candidate chemicals.

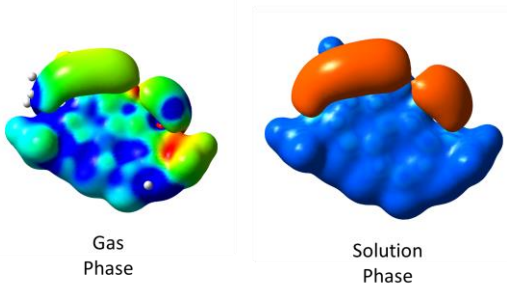

Figure 1. Gas and solution phase electrostatic potential maps of candidate chemical, T0501-3341.

As shown in Figure 1, in the solution phase, electrons are delocalized by surrounding water molecule. Thus we could select more negative positions (in red) which an ion can bind to. After finding the ion bind positions, we placed four different ions, Na+, K+, Rb+ and Cs+, near the site. An example of ion binding structures is shown in the Figure 2.

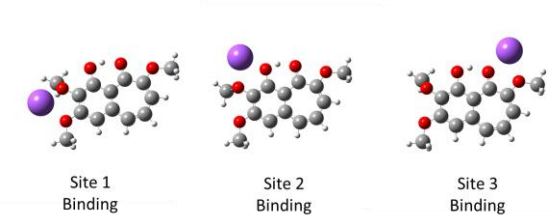

Figure 2. Three different Cs-chemical systems of candidate chemical, T0501-3341.

Again, we optimized ion bind structures of each candidate chemicals in solution phase and obtained energy of ion binding structures.
After the calculation, we could evaluate the ion binding energy by using Eq. 1.

$$E_{binding} = E_{complex} - (E_{chemical} + E_{ion}) \quad \text{(Eq. 1)}$$

Eventually, we could calculate the ion binding energy of 8 chemicals among total 29 candidates.

3. Result

After calculation of the binding energy of all different binding sites, we collected the maximum binding site which has the highest value. Figure 3 is the example of the maximum ion binding energy of the candidate chemical T0501-3341.

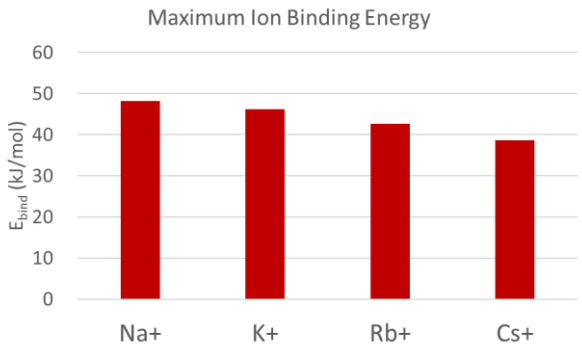

Figure 3. Maximum ion binding energy of 4 different alkali metal with T0501-3341.

As the Figure 3 shows, in most cases, the binding energy of Cs^+ is the lowest and Na^+ is the highest. Due to the highest electronegativity and small ionic radius, it could be predicted that Na^+ has the highest ion binding strength. Thus, we calculated the difference of ion binding energy among 4 elements and obtained Boltzmann population of Cs-complex in different ionic condition in Figure 4 and 5.

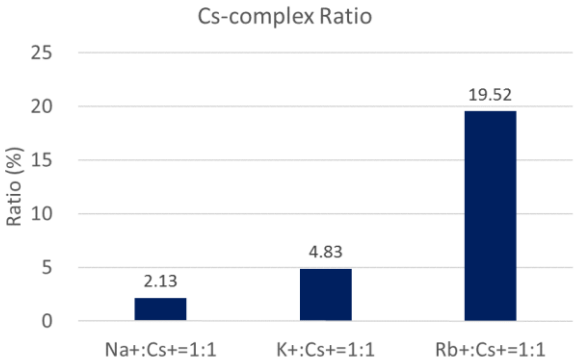

Figure 4(a). Cs-complex ratio calculated based on Boltzmann population of Cs-T0501-3341 complex in Na^+, K^+ and Rb^+:Cs+ =1:1 condition.

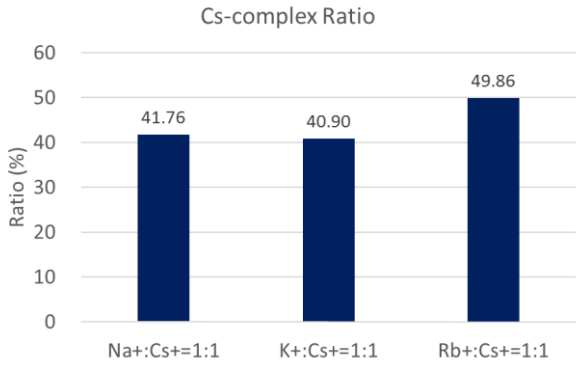

Figure 4(b). Cs-complex ratio calculated based on Boltzmann population of Cs-T0502-0981 complex in Na^+, K^+ and Rb^+:Cs+ =1:1 condition.

As we can see in Figure 4(a) and (b), The chemical T0502-0981 has more strong Cs-binding behavior in other alkali metal solutions. It means the latter one is the more effective Cs binding agent than the former one.

With this approach, as shown in Figure 5, we could obtain Cs^+ binding energies of 8 candidate chemicals.

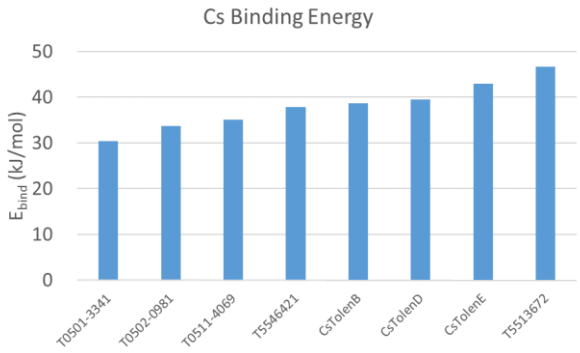

Figure 5. Cs^+ binding energies of 8 candidate chemicals.

All 8 chemicals have relatively high Cs^+ binding energies ranging 30-50 kJ/mol which are near strong hydrogen bonding region. With the result, we could assume that those chemicals effectively bind to Cs^+ and they guide the Cs^+ onto plant surface for Cs^+ uptake.

4. Conclusion

We have performed quantum mechanical calculation of Cs^+ binding energies for 8 candidate chemicals among 29 and obtained optimized structures, ECP maps and Cs^+ binding energies of each chemicals. The results show the candidate chemicals have different Cs+ binding properties in different ionic solution. However, all of them shows relatively high Cs^+ binding strength compare to other supramolecular interactions such as hydrogen bonding. Thus, we could assume that the candidate chemicals help Cs^+ uptake of plants.

5. Schedule and prospect for the future

Most of all, we need to calculate the rest 25 candidate chemicals with the same procedure above. After summarizing the computational and experimental results, we expect that the detail Cs^+ uptake mechanism can be revealed. Also, we are going to use effective method to find optimal ion binding position and get more precise ionic binding strength.