Influence to the Structure and Dynamics of Hydrated Ca^{2+} and Water Molecules in CaCl$_2$ Aqueous Solution Caused by External AC Electric Field: A Mechanism Study by Molecular Dynamics Simulation

Yong Han, Yongping Zhao[*]

School of Electrical Engineering and Automation, Harbin Institute of Technology, 92 West Street, Nan Gang, Harbin 150001, China
[*]E-mail: zhaoyp2590@hit.edu.cn

In the present study systematic long time (1112-2500 ns) non-equilibrium molecular dynamics (MD) simulation have been carried out at the first time to study structural and dynamical properties of hydrated Ca^{2+} and water molecules in CaCl$_2$ aqueous solutions with an external AC electric field produced by the electronic anti-fouling (EAF) system. The result of this study can help to understand some mechanism of electronic anti-fouling. Our simulations reveal the change of structure and dynamics of hydrated Ca^{2+} and water molecules under external AC electric field with different frequencies and amplitude values respectively. Within the range of electric field frequencies and amplitude values in this paper, it was found that radius of the hydrated Ca^{2+} changed smaller. Under the electric field of 400 KHz and 70 v/m, the radius of the hydrated Ca^{2+} had the smallest value. All electric field with different frequencies or amplitude values in our range could make the Ca^{2+}–water coordination number from 4 to 5 for the first water shell, but almost no influence to the second water shell. Self-diffusion coefficient of Ca^{2+} and water molecule changed larger under the external AC electric field. Under the electric field of 400 KHz and 70 v/m, the self-diffusion coefficient of Ca^{2+} had the biggest value. It was also found that changing electric field amplitude values was more effectively to increase the self-diffusion coefficient of water molecule than changing electric field frequencies.

1. INTRODUCTION

Scale problem is a key problem to the heat exchanger, such as cooling tower and boiler, and it roots on using hard water. The electronic anti-fouling (EAF) system is a very useful electromagnetic

field water treatment system to the scale problem. But the anti-fouling mechanism of EAF system is still not all clear as yet. Cho et al. [1] supposed that the induced alternate electric field in the aqueous solution generated by the excitation coil was the leading role to achieve the purpose of anti-fouling. The induced alternate electric field changes the crystallization process of scale and stops precipitate sticking to the water wall. There are many researchers do a lot of experiment researches based on the above-mentioned anti-fouling mechanism of EAF system [2-6]. But the results are always quite different, even opposite because of the different experiment conditions.

At the present stage experiment researches on mechanism of EAF system almost focus on calcium carbonate (magnesium sulfate) crystallization process or the change of scale crystal structure [7-8], but ignore the influence to the change of microcosmic particles structure in the aqueous solutions by AC electric field. Actually, when EAF system is working, there are almost no scale-forming negative ions because of the very low solubility of calcium carbonate (magnesium sulfate). Ca^{2+} (Mg^{2+}) exists in the aqueous solution as hydrated ion, and the hydrated Ca^{2+} (Mg^{2+}) is also combined with other water molecules by hydrogen bonding. Therefore, the study of hydrated Ca^{2+} (Mg^{2+}) is a very important part of the calcium (magnesium) ion solution property research [9-14]. When AC electric field is applied to the aqueous solution, the structure of hydrated Ca^{2+} (Mg^{2+}) cluster and water cluster will get some inevitable changes. Furthermore, these changes will impact the crystallization process of scale. Therefore, the research of influence to the structure and dynamics of hydrated Ca^{2+} and water molecules by AC electric field is very important to the study of anti-fouling mechanism of EAF system.

Various methods have been used to study the microstructure and dynamics properties. Among these methods, molecular dynamics simulation has been proven to be one of the most useful tools for elucidating all kinds of detailed microscopic properties of aqueous solutions. On one hand, this kind of simulations is convenient to do a real-time study to the structure and properties of particles in aqueous solutions, which can avoid the error taken from sampling and detection process. On the other hand, the results from molecular dynamics simulations are more convenient in comparing to experimental results under wide range of concentrations, temperatures and pressures.

In the present study, $CaCl_2$ aqueous solution has be taken as the research object. Non-equilibrium MD simulation is used to study the change of location of the first water shell of Ca^{2+}, the first coordination numbers for Ca^{2+}, location of the second water shell of Ca^{2+}, the second coordination numbers for Ca^{2+}, self-diffusion coefficient of Ca^{2+} and water molecular under external AC electric field with different frequencies and amplitude, and the influence to the crystallization process of scale caused by the changes of these parameters is researched. The results of present study do not only supply a theoretical basis for the research of anti-fouling mechanism of EAF system, but also provide a theoretical guidance for optimization of EAF system in application.

2. SIMULATION DETAILS

2.1. AC electric field wave form and parameters selection

In the present study, AC electric field wave form and parameters are confirmed according to the induced electric field produced in aqueous solution by EAF system.

2.1.1. AC electric field wave form selection

The wave form of excitation current signal produced by EAF system is sinusoid, and the induced electric field in aqueous solution also changes as sinusoid [15]. Therefore, in the MD simulation the external AC electric field wave form should be sinusoid.

2.1.2. AC electric field frequency selection

The induced electric field frequency should be equal to the excitation current signal frequency [15]. In practical application the frequency range of excitation current signal produced by EAF system is from several tens KHz to 1MHz. For the purpose of studying the influence to $CaCl_2$ aqueous solution caused by electric field with different frequency and controlling the MD simulation time within a acceptable range, the external AC electric field frequencies in the present study are chosen as 400 KHz, 500 KHz, 600 KHz, 700 KHz, 800 KHz, 900 KHz。

2.1.3. AC electric field amplitude selection

In practical application the amplitude range of excitation current signal produced by EAF system is from several A to several tens A, and the corresponding induced electric field amplitude is from several tens v/m to 200 v/m. For the purpose of studying the influence to $CaCl_2$ aqueous solution caused by electric field with different amplitude, the external AC electric field amplitudes used in our simulation are chosen as 10v/m, 30v/m, 50v/m, 70v/m, 90v/m, 120v/m, 150v/m.

When researching the influence to $CaCl_2$ aqueous solution caused by electric field with different frequency, the AC electric field amplitude is a constant 10v/m, and the simulation time is a constant 2500ns when the electric field frequency is changed. 2500ns is a cycle time of a signal with 400 KHz frequency. When researching the influence by electric field with different amplitude, the AC electric field frequency is a constant 900 KHz, and the simulation time is a constant 1112ns when the electric field amplitude is changed. 1112ns is a cycle time of a signal with 900 KHz frequency.

2.2. Simulation details

In the present study, the MD simulation in our work is a non-equilibrium MD simulation process because of the external AC electric field applied on the $CaCl_2$ aqueous solution. The MD simulations were performed with the software GROMACS 4.5.4 [16]. *NPT* ensemble is used to perform MD simulations. Temperatures of all simulations were set as 300K. The simulation system consists of a 1.6nm×1.6nm×1.8nm box containing 8 Ca^{2+}, 16 Cl^- and 111 water molecules. SPCE model is used as water model [17-18]. The $CaCl_2$ aqueous solution concentration is 4mol·kg^{-1}, and the concentration errors between simulations and experiments are below 0.5%. Periodic boundary condition is used and the GROMOS force field [19-20] is used for ion–water interactions. For Lennard-Jones interactions, a cutoff at 0.8 nm was applied, while electrostatic interactions were treated

with the particle mesh Ewald (PME) [21] method and a real space cutoff of 0.7 nm. The time step of all the simulations was set as 2.0 fs [19].

3. RESULTS AND DISCUSSIONS

All structural parameters in our study can be classified into two categories: (1) average radii (R) of the first or second shell, including R_{Ca-O}, R^{II}_{Ca-O}; (2) coordination number (n), including n_{Ca-O}, n^{II}_{Ca-O}. Dynamic parameter in our study is Self-diffusion coefficient (D), including D_{Ca}, D_O. R and n are defined according to radial distribution function [g(r)], and D is defined according to the 'Einstein relation' [22].

3.1. Verification for correctness of our MD simulations

For verifying the correctness of our MD simulations, in the present study we calculate structural parameters and dynamic parameter of $CaCl_2$ aqueous solution without external AC electric field. $CaCl_2$ aqueous solution concentration is $4mol \cdot kg^{-1}$. The results are compared with the results from experiment and other references. The comparison is shown in Table 1.

Table 1. Simulation results from our work comparing with other simulation method and experiment

	M1	M2	M3
$D_{Ca}(cm^2 s^{-1} \times 10^{-5})$	0.047	0.058 [a], 0.205 [b]	
$D_O(cm^2 s^{-1} \times 10^{-5})$	0.312	0.309 [a]	
$R_{Ca-O}(Å)$	3.42	3.4 [a], 3.4 [c]	
$R^{II}_{Ca-O}(Å)$	5.6	5.3 [a]	
n_{Ca-O}	4.5	7.7 [a], 5.9 [c]	5.8 [d], 7.3 [e], 5.9 [f]
n^{II}_{Ca-O}	12.8	10.7 [a]	9.2 [f]
Location of first peak of the $g_{CaO}(r)$ (Å)	2.44	2.45 [c]	

Note: M1 is from our work, M2 is the result by other simulate method, M3 is from experiments.
[a] From ref.[19]，by MD simulation; [b] from ref.[23] using tracer method; [c] from ref.[24] using MD simulation;
[d] from ref.[25] using X-ray; [e] from ref.[26]using ND; [f] from ref.[27] using X-ray.

It can be known from Table 1 that the results of D_{Ca}, D_O, R_{Ca-O}, R^{II}_{Ca-O} and $g_{CaO}(r)$ from our work are close to the results from other references. But n_{Ca-O}, n^{II}_{Ca-O} from our work are a little larger than the results from other references and experiments. It may be resulted from the following factors: (a) the small simulation system may lead to more error [28]. The simulation system in our work is smaller than the simulation system in other references. The particles quantity in our simulation system

equals to 50% particles quantity of simulation system in ref. [19] under the same solution concentration. Moreover, in our work the water model is SPCE model, but the other references are not. Using different water model can make errors. For example, a slight revision to charge in the model from SPC to SPCE can make self-diffusion coefficients sharply decreasing [29]. (b) n^{II}_{Ca-O} from our work is larger than the results from ref. [19] and X-ray experiment. It is because that the R^{II}_{Ca-O} from our work is larger, which leads to a larger n^{II}_{Ca-O}.

According to the compare above, our MD simulation method is verified to be reliable, and it can be used to study the properties of CaCl$_2$ aqueous solution with external AC electric field. In the following, the change of the parameters value which is caused by external AC electric field will be discussed on the basis of the result from our MD simulation in Table 1.

3.2. Structure parameters under different AC electric field

In this section, the values of R_{Ca-O}, R^{II}_{Ca-O}, n_{Ca-O}, n^{II}_{Ca-O}, which can be obtained from radial distribution function [g(r)], are discussed under AC electric field with frequency 400KHz, 500 KHz, 600 KHz, 700 KHz, 800 KHz, 900 KHz and with amplitude 10v/m、30v/m、50v/m、70v/m、90v/m 、120v/m、150v/m respectively. The expression of radial distribution function is shown as Eq. (1) [30]:

$$g_{AB}(r) = \frac{\langle \rho_B(r) \rangle}{\langle \rho_B \rangle_{local}}$$
$$= \frac{1}{\langle \rho_B \rangle_{local}} \frac{1}{N_A} \sum_{i \in A}^{N_A} \sum_{j \in B}^{N_B} \frac{\delta(r_{ij} - r)}{4\pi r^2} \tag{1}$$

Where N_A is the quantity of particle A, and N_B is the quantity of particle B; $\langle \rho_B(r) \rangle$ is the particle density of particle B at a distance r around particles A, and $\langle \rho_B \rangle_{local}$ is the particle density of particle B averaged over all spheres around particles A with radius r_{max}. Usually the value of r_{max} is half of the minimum length of box.

The values of n_{Ca-O} and n^{II}_{Ca-O} are calculated using Eq. (2) [24]:

$$n^O_{Ca}(r_s) = 4\pi \rho_O \int_0^{r_s} g_{CaO}(r) r^2 dr \tag{2}$$

When calculating n_{Ca-O}, r_s is the location of the first local minimum of $g_{CaO}(r)$. When calculating n^{II}_{Ca-O}, r_s is the location of the second local minimum of $g_{CaO}(r)$.

Since all of the electric field force applied to CaCl$_2$ aqueous solution by different AC electric field are periodic, and the cycle is the same as the cycle of AC electric field, therefore in our work the whole simulation time is divided into pieces, and the parameters value at the last part of each piece are collected for researching the change of structure parameters during the MD simulation process. The length of one piece is 1/4 cycle of the AC electric field. For example, the whole simulation time is

2500000 ps, when the AC electric field frequency is 400KHz, then the 1/4 cycle of AC electric field is 625000 ps, and the whole simulation time is divided into 4 pieces; when the AC electric field frequency is 500KHz, then the 1/4 cycle of AC electric field is 500000 ps, and the whole simulation time is divided into 5 pieces.

The results of R_{Ca-O} and R^{II}_{Ca-O} under AC electric field with different frequency are shown in Table 2 and Table 3, the corresponding graphs are shown in Figureure. 1. and Figureure. 2.

Table 2. Radii of the first water shell under AC electric field with different frequency

frequency (KHz)	R_{Ca-O}(Å)									Average value
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Time piece 5	Time piece 6	Time piece 7	Time piece 8	Time piece 9	
400	3.20	3.20	3.20	3.18						3.19
500	3.24	3.28	3.28	3.28	3.42					3.30
600	3.34	3.36	3.26	3.32	3.12	3.30				3.28
700	3.43	3.24	3.17	3.29	3.12	3.43	3.24			3.27
800	3.48	3.26	3.28	3.28	3.36	3.30	3.22	3.28		3.31
900	3.28	3.34	3.22	3.38	3.34	3.28	3.32	3.32	3.36	3.32

Table 3. Radii of the second water shell under AC electric field with different frequency

frequency (KHz)	R^{II}_{Ca-O}(Å)									Average value
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Time piece 5	Time piece 6	Time piece 7	Time piece 8	Time piece 9	
400	5.56	5.50	5.52	5.64						5.56
500	5.60	5.74	5.6	5.48	5.72					5.63
600	5.56	5.62	5.60	5.46	5.52	5.58				5.56
700	5.54	5.56	5.60	5.54	5.82	5.48	5.62			5.59
800	5.58	5.60	5.68	5.48	5.66	5.70	5.58	5.64		5.61
900	5.60	5.46	5.76	5.58	5.48	5.68	5.56	5.48	5.52	5.57

According to Table 2 and Figure.1, it is known that: 1 For every frequency, great majority of the R_{Ca-O} value at the end of time pieces is smaller than 3.42 Å — the R_{Ca-O} value obtained under no electric field. 2 Radii of the first water shell R_{Ca-O} is also the radii of hydrated Ca^{2+}. It can be known that under the AC electric field with different frequencies the R_{Ca-O} value does not change regularly during MD simulation process. When the AC electric field frequency is 400KHz, the average R_{Ca-O} value has the minimum 3.19 Å. When the AC electric field frequency is 900KHz, the average R_{Ca-O} value has the maximum 3.32 Å.
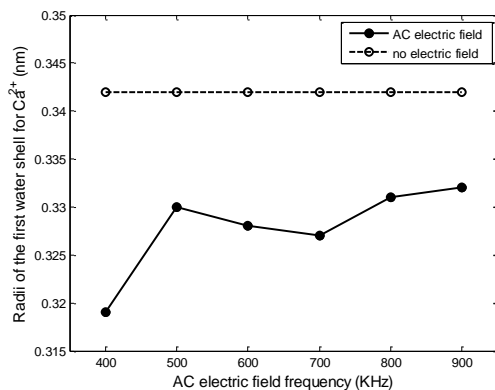
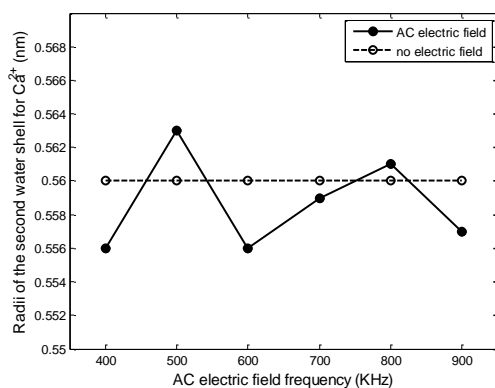**Figure 1.** Average R_{Ca-O} value under AC electric field with different frequency

Figure 2. Average R^{II}_{Ca-O} value under AC electric field with different frequency

Figure 3 shows the distribution of Ca^{2+} and water molecule before and after MD simulation under the AC electric field with 400 KHz frequency. In Figure 3, the cyan atoms are Ca^{2+} and the red ones are oxygen atoms, which stand for water molecules. The hydrogen atoms are leaved out for making it easy to observe the change of the water molecules number around Ca^{2+} after MD simulation. The two pictures of Figure 3 show that the water molecules are more close to Ca^{2+} after the MD simulation. In other word, the radii of hydrated Ca^{2+} changes smaller. The effective radius of water molecule is 1.38 Å, and the distance between Ca^{2+} and the most inner-shell water molecules is 2.0 Å. Therefore, Ca^{2+} is combined with water molecules as hydrated Ca^{2+} by electrostatic interactions [31]. The smaller radii of hydrated Ca^{2+} supports that the external AC electric field enhances the hydration between Ca^{2+} and water molecules. The first water shell of Ca^{2+} has hindering effect to the other negative ion in solution [31]. If some carbonate ions were brought into the solution, the carbonate ions would be more close to the Ca^{2+} with a smaller first water shell than to the Ca^{2+} with a larger one when carbonate ions are hindered by the first water shell of Ca^{2+}, which means that the carbonate ions can more easily product a chemical reaction with the Ca^{2+} with a smaller first water shell. Therefore, the calcium carbonate crystal growth is promoted. This result agrees with the experimental results from

ref. [3] and ref. [32]. More calcium carbonate precipitate is formed in solution instead of being formed on the water wall, and the precipitate in solution will be washed away by running water. Then the scale problem can be prevented. Therefore, making the radii of hydrated Ca^{2+} smaller is an important point of the mechanism of electronic anti-fouling. In the present study, within the range of AC electric field frequency, the radii of hydrated Ca^{2+} has the minimum value when external AC electric field frequency is 400 KHz, which means that using AC electric field with 400 KHz frequency can make the best anti-fouling effect.
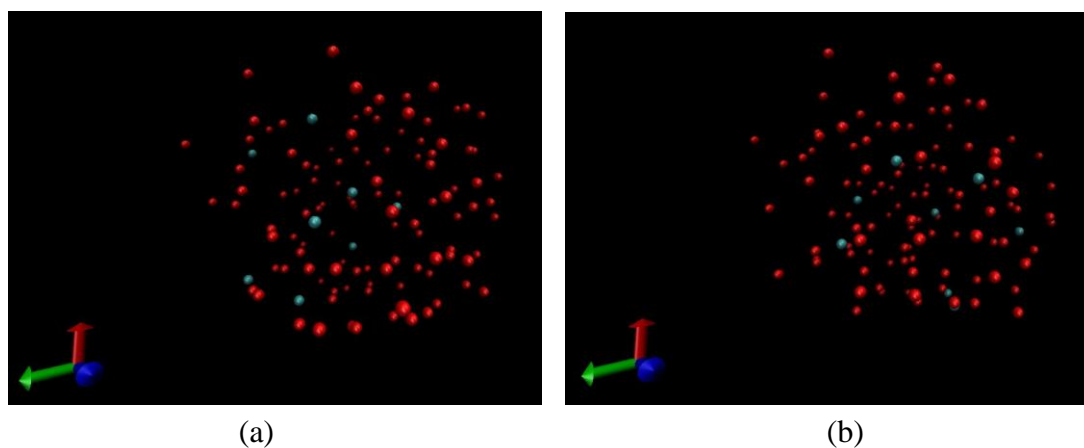

(a)   (b)

Figure 3. The distribution of Ca^{2+} and water molecule before and after MD simulation (a) before MD simulation.(b) after MD simulation

According to Table 3 and Figure 2, it is known that most of the R^{II}_{Ca-O} values obtained under external AC electric field with different frequency are very close to 5.6Å, which has no obvious change according to the R^{II}_{Ca-O} value obtained under no external AC electric field. Therefore, it is supposed that the external AC electric field with different frequency almost has no influence to the location of the second water shell of Ca^{2+}.

The results of n_{Ca-O} and n^{II}_{Ca-O} under AC electric field with different frequency are shown in Table 4 and Table 5, the corresponding graphs are shown in Figure 4 and Figure 5.

Table 4. First water coordination number for Ca^{2+} under AC electric field with different frequency

frequency (KHz)	n_{Ca-O}									
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Time piece 5	Time piece 6	Time piece 7	Time piece 8	Time piece 9	Average value
400	5.72	5.54	5.74	5.76						5.69
500	5.77	5.62	5.77	5.81	5.85					5.76
600	5.62	5.57	5.68	5.73	5.83	5.66				5.68
700	5.50	5.70	5.70	5.80	5.86	5.73	5.71			5.71
800	5.83	5.73	5.65	5.71	5.66	5.73	5.64	5.62		5.70
900	5.48	5.52	5.75	5.90	5.54	5.80	5.69	5.69	5.67	5.67

Table 5. Second water coordination number for Ca^{2+} under AC electric field with different frequency

| frequency (KHz) | n^{II}_{Ca-O} | | | | | | | | | |
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Time piece 5	Time piece 6	Time piece 7	Time piece 8	Time piece 9	Average value
400	12.32	11.84	11.99	13.03						12.30
500	12.68	13.95	12.72	11.66	13.73					12.95
600	12.68	13.95	12.72	11.66	13.73	12.68				12.90
700	12.20	12.42	12.70	12.18	14.71	11.66	12.13			12.57
800	12.46	12.70	13.41	11.64	13.20	13.55	12.48	12.54		12.75
900	12.67	11.43	14.15	12.52	11.65	13.36	13.23	11.64	12.85	12.62
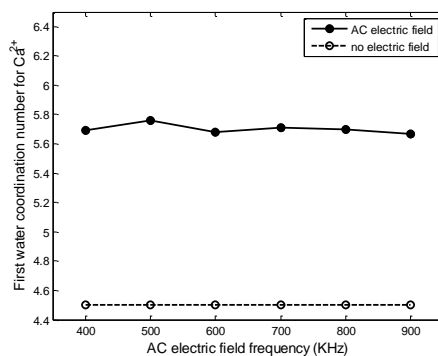
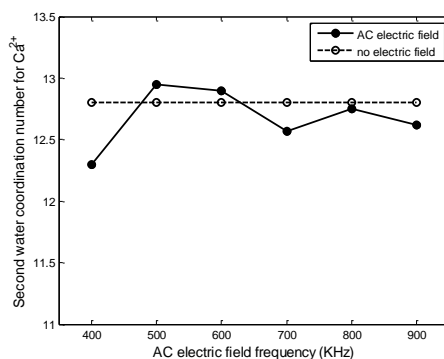**Figure 4.** Average n_{Ca-O} value under AC electric field with different frequency

Figure 5. Average n^{II}_{Ca-O} value under AC electric field with different frequency

According to Table 4 and Figure 4, it is known that the n_{Ca-O} value do not fluctuate obviously during the MD simulation process, and in every time piece the n_{Ca-O} value is larger than the value 4.5 under no electric field. The average n_{Ca-O} value under the electric field with different frequency is similar. The average n_{Ca-O} value has the maximum 5.76 when the electric field frequency is 500 KHz,

and the average n_{Ca-O} value has the minimum 5.67 when the electric field frequency is 900 KHz. All average n_{Ca-O} value in Table 4 have about 1 larger than 4.5, which means that the AC electric field makes the first water coordination number for Ca^{2+} increased 1.

The more first water coordination number for Ca^{2+} is also caused by the enhanced hydration between Ca^{2+} and water molecules. The enhanced electrostatic interaction does not only make hydrated water molecules more close to Ca^{2+}, but also attract one more water molecules as hydrated water molecule. The increase of the first water coordination number for Ca^{2+} enhances the inhibition to carbonate ions, which seems inconsistent against above conclusion that external AC electric field increases the probability of forming calcium carbonate precipitate. Actually, electrostatic interaction is a kind of physical interaction, and during the Ca^{2+} and carbonate ion are associating the interaction between them is chemical interaction. Therefore, the enhancement of chemical interaction caused by reducing the distance between Ca^{2+} and carbonate ion is too much stronger than the inhibition to carbonate ion caused by enhancing electrostatic interaction.

Table 6. Radii of the first water shell under AC electric field with different amplitude

amplitude (v/m)	R_{Ca-O}(Å) Time piece 1	Time piece 2	Time piece 3	Time piece 4	Average value
10	3.28	3.34	3.22	3.38	3.31
30	3.24	3.36	3.32	3.32	3.31
50	3.28	3.28	3.26	3.36	3.29
70	3.22	3.34	3.18	3.28	3.25
90	3.22	3.36	3.24	3.38	3.30
120	3.34	3.50	3.22	3.38	3.36
150	3.34	3.4	3.33	3.38	3.36

Table 7. Radii of the second water shell under AC electric field with different amplitude

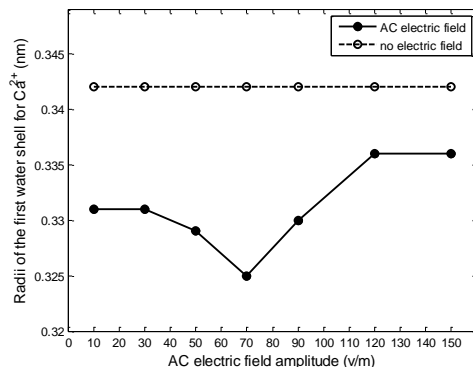| amplitude (v/m)	R^{II}_{Ca-O}(Å) Time piece 1	Time piece 2	Time piece 3	Time piece 4	Average value
10	5.60	5.46	5.76	5.58	5.60
30	5.6	5.68	5.48	5.72	5.62
50	5.64	5.58	5.50	5.48	5.55
70	5.72	5.54	5.54	5.62	5.61
90	5.70	5.58	5.66	5.70	5.66
120	5.56	5.52	5.46	5.64	5.55
150	5.50	5.50	5.58	5.58	5.54

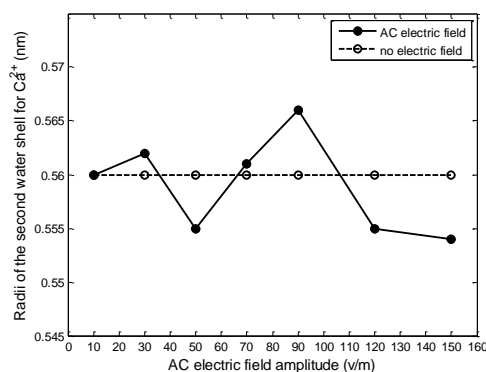**Figure 6.** Average R_{Ca-O} value under AC electric field with different amplitude

Figure 7. Average R^{II}_{Ca-O} value under AC electric field with different amplitude

According to Table 5 and Figure 5, it is known that most of the n^{II}_{Ca-O} values obtained under external AC electric field with different frequency are very close to 12.8, which have no obvious change according to the n^{II}_{Ca-O} value obtained under no external AC electric field. Therefore, it is supposed that the external AC electric field with different frequency almost has no influence to the second water coordination number for Ca^{2+}.

The results of R_{Ca-O} and R^{II}_{Ca-O} under AC electric field with different amplitude are shown in Table 6 and Table 7, the corresponding graphs are shown in Figure 6 and Figure 7.

According to Table 6 and Figure.6, it is known that: 1 For every amplitude, great majority of the R_{Ca-O} value at the end of time pieces is smaller than the R_{Ca-O} value obtained under no electric field. It can be known that under the AC electric field with amplitude 70v/m, 90v/m and 120v/m the R_{Ca-O} value is up and down regularly as the frequency of the AC electric field during MD simulation process. The average R_{Ca-O} values are decrease and then increase with amplitude of AC electric field increasing. When the AC electric field amplitude is 70 v/m, the average R_{Ca-O} value has the minimum 3.25 Å. When the AC electric field amplitude is 150 v/m, the average R_{Ca-O} value has the maximum 3.36 Å. Therefore it is known that using AC electric field with 70 v/m amplitude can make the best anti-fouling effect.

According to Table 7 and Figure 7, it is known that under external AC electric field with different amplitude most of the R^{II}_{Ca-O} values are very close to 5.6, which have no obvious change according to the n^{II}_{Ca-O} value obtained under no external AC electric field. Therefore, it is supposed that the external AC electric field with different amplitude almost has no influence to the second water coordination number for Ca^{2+}.

The results of n_{Ca-O} and n^{II}_{Ca-O} under AC electric field with different amplitude are shown in Table 8 and Table 9, the corresponding graphs are shown in Figure 8 and Figure 9.

Table 8. First water coordination number for Ca^{2+} under AC electric field with different amplitude

n_{Ca-O}					
amplitude (v/m)	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Average value
10	5.48	5.52	5.75	5.90	5.66
30	5.41	5.56	5.69	5.92	5.65
50	5.52	5.31	5.78	5.86	5.62
70	5.48	5.48	5.66	5.83	5.61
90	5.40	5.62	5.87	5.61	5.63
120	5.58	5.53	5.76	5.91	5.69
150	5.72	5.85	5.72	5.49	5.69

Table 9. Second water coordination number for Ca^{2+} under AC electric field with different amplitude

n^{II}_{Ca-O}					
amplitude (v/m)	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Average value
10	12.67	11.43	14.15	12.52	12.69
30	12.69	13.39	11.68	13.78	12.89
50	13.09	12.52	11.82	11.66	12.27
70	13.77	12.17	12.75	12.88	12.89
90	13.67	12.51	13.18	13.66	13.25
120	12.36	11.93	11.53	13.01	12.21
150	11.80	11.82	12.55	12.47	12.16

According to Table 8 and Figure 8, it is known that in every time piece the n_{Ca-O} value is larger than the value 4.5 under no electric field. The average n_{Ca-O} value under the electric field with different amplitude is similar. The average n_{Ca-O} value has the maximum 5.69 when the electric field amplitude is 150v/m, and the average n_{Ca-O} value has the minimum 5.61 when the electric field amplitude is 70v/m. All average n_{Ca-O} value in Table 8 has about 1 larger than 4.5.

According to Table 9 and Figure 9, it is known that most of the n^{II}_{Ca-O} values obtained is very close to 12.8. Therefore, it is supposed that the external AC electric field with different amplitude almost has no influence to the second water coordination number for Ca^{2+}.
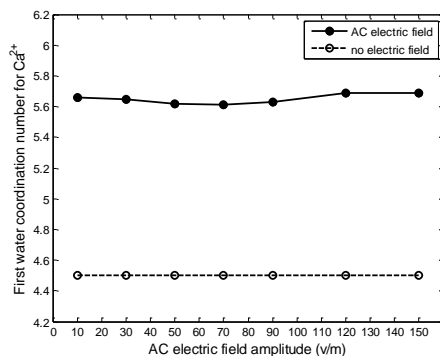
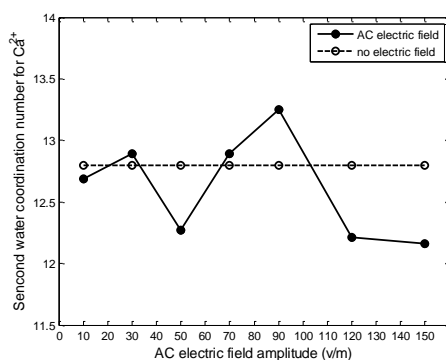**Figure 8.** Average n_{Ca-O} value under AC electric field with different amplitude

Figure 9. Average n^{II}_{Ca-O} value under AC electric field with different amplitude

3.3. Dynamics parameters under different AC electric field

Self-diffusion coefficient of Ca^{2+} and water molecular in $CaCl_2$ aqueous solution as an important dynamic property was experimentally measured by quasi-elastic neutron scattering and NMR measurements [33]. However, these experiments are involved in great uncertainties.

In the present study, our calculation of self-diffusion coefficient is based on the 'Einstein relation' [22]:

$$D = \lim_{t \to \infty} \frac{1}{6t} \left\langle [r_i(t) - r_i(0)]^2 \right\rangle \tag{3}$$

Where $r_i(t)$ is the molecular position i at time t and $r_i(0)$ is the initial position, the bracket denotes ensemble average.

The results of D_{Ca} and D_O under AC electric field with different amplitude are shown in Table 10 and Table 11, the corresponding graphs are shown in Figure 10 and Figure 11.

Table 10. Self-diffusion coefficient of Ca^{2+} under AC electric field with different frequency

frequency (KHz)	D_{Ca} (cm^2 s^{-1}×10^{-5})									Average value
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Time piece 5	Time piece 6	Time piece 7	Time piece 8	Time piece 9	
400	0.125	0.102	0.272	0.122						0.155
500	0.086	0.063	0.069	0.077	0.104					0.080
600	0.163	0.129	0.085	0.091	0.113	0.143				0.121
700	0.168	0.105	0.159	0.105	0.148	0.076	0.113			0.125
800	0.122	0.105	0.166	0.095	0.132	0.088	0.084	0.095		0.111
900	0.089	0.098	0.106	0.154	0.162	0.055	0.104	0.117	0.096	0.099

Table 11. Self-diffusion coefficient of water molecule under AC electric field with different frequency

frequency (KHz)	D_O (cm^2 s^{-1}×10^{-5})									Average value
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Time piece 5	Time piece 6	Time piece 7	Time piece 8	Time piece 9	
400	0.313	0.342	0.422	0.380						0.364
500	0.231	0.312	0.315	0.376	0.390					0.325
600	0.312	0.314	0.376	0.345	0.437	0.474				0.376
700	0.406	0.421	0.402	0.394	0.324	0.387	0.396			0.390
800	0.460	0.360	0.375	0.319	0.405	0.337	0.347	0.412		0.377
900	0.440	0.427	0.350	0.406	0.308	0.401	0.349	0.386	0.413	0.387

According to Table 10 and Figure 10, it is known that in every time piece the D_{Ca} value is larger than the value 0.047 cm^2 s^{-1}×10^{-5} under no electric field. The average D_{Ca} value has the maximum 0.155 cm^2 s^{-1}×10^{-5} when the electric field frequency is 400 KHz, and the average D_{Ca} value has the minimum 0.080 cm^2 s^{-1}×10^{-5} when the electric field frequency is 500KHz. It is known from Table 11 and Figure.11 that D_O value in every time piece is larger than the value 0.312 cm^2 s^{-1}×10^{-5} which is obtained under no electric field. The average D_{Ca} value has the maximum 0.390 cm^2 s^{-1}×10^{-5} when the electric field frequency is 700 KHz, and the average D_{Ca} value has the minimum 0.325 cm^2 s^{-1}×10^{-5} when the electric field frequency is 500 KHz.

Self-diffusion coefficient is an important dynamics parameter of CaCl$_2$ aqueous solution. The change of self-diffusion coefficient can reflect the fluctuation of internal energy and particle's activity in solution. When internal energy of solution is rising, particle's self-diffusion coefficient will change larger, and particle's activity is increasing accordingly. When internal energy of solution is falling, particle's self-diffusion coefficient and particle's activity are decreasing accordingly. According to Table 10 and Table 11, under AC electric field self-diffusion coefficient of Ca^{2+} and water molecules all changes larger, which means their activity increase accordingly. Ca^{2+} with more activity has a higher probability to produce the chemical reaction with carbonate ion. The increase of water molecules activity can lead to the water clusters changing into monomers or dimers, and then the resistance to carbonate ions from water clusters is decreased. So, when self-diffusion coefficient of Ca^{2+} and water molecules changes larger, the Ca^{2+} and carbonate ion will generate precipitation more

easily. Therefore making the self-diffusion coefficient of Ca^{2+} and water molecules larger is the other important point of the mechanism of electronic anti-fouling.
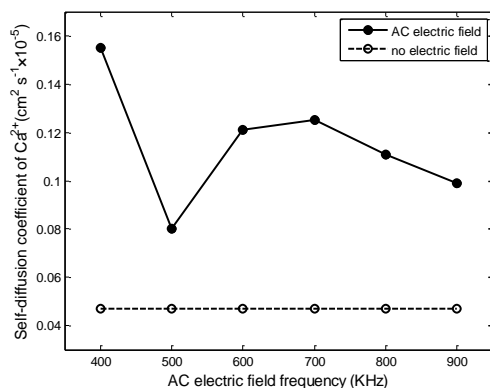

Figure 10. Average D_{Ca} value under AC electric field with different frequency
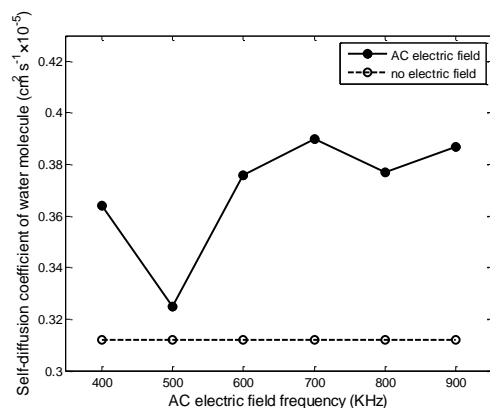

Figure 11. Average D_O value under AC electric field with different frequency

In addition, according to Stokes-Einstein equation, self-diffusion coefficient of particle is inversely proportional to particle radii. Stokes-Einstein equation is shown as Eq. (4).

$$d(H) = \frac{kT}{3\pi\eta D} \qquad (4)$$

Where $d(H)$ is particle radii, k is Boltzmann constant, T is absolute temperature, η is viscosity, D is self-diffusion coefficient of particle. According to Table 10, self-diffusion coefficient of Ca^{2+} under AC electric field with different frequency is larger than the value under no electric field, and according to Table 2, radii of hydrated Ca^{2+} under AC electric field with different frequency is smaller than the value under no electric field. The changes of self-diffusion coefficient of Ca^{2+} and hydrated

Ca^{2+} radii meet exactly with Stokes-Einstein equation. The graphs of average value in Table 2 and Table 10 changing with time are shown in Figure 12.
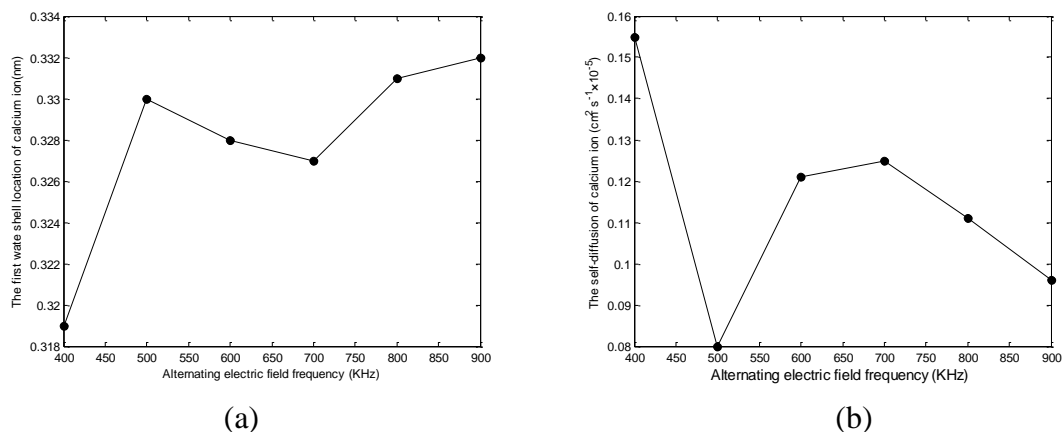

(a)　　　　　　　　　　　　　　　　　(b)

Figure 12. Comparison between the changes of hydrated Ca^{2+} radii and self-diffusion coefficient of Ca^{2+} (a) change of hydrated Ca^{2+} radii (b) change of self-diffusion coefficient of Ca^{2+}

Table 12. Self-diffusion coefficient of Ca^{2+} under AC electric field with different amplitude

amplitude (v/m)	$D_{Ca}(cm^2\,s^{-1}\times10^{-5})$				
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Average value
10	0.096	0.104	0.114	0.160	0.119
30	0.092	0.115	0.130	0.093	0.106
50	0.183	0.149	0.095	0.133	0.140
70	0.092	0.136	0.094	0.241	0.141
90	0.208	0.079	0.105	0.073	0.116
120	0.087	0.071	0.198	0.079	0.109
150	0.088	0.135	0.076	0.053	0.088

Table 13. Self-diffusion coefficient of water molecule under AC electric field with different amplitude

amplitude (v/m)	$D_{O}(cm^2\,s^{-1}\times10^{-5})$				
	Time piece 1	Time piece 2	Time piece 3	Time piece 4	Average value
10	0.440	0.427	0.350	0.406	0.406
30	0.519	0.654	0.555	0.536	0.566
50	0.639	0. 435	0.538	0.565	0.544
70	0.580	0.495	0.481	0.459	0.504
90	0.610	0.485	0.502	0.491	0.522
120	0.649	0.539	0.566	0.437	0.548
150	0.665	0.487	0.537	0.476	0.541

The results of D_{Ca} and D_O under AC electric field with different amplitude are shown in Table 12 and Table 13, the corresponding graphs are shown in Figure 13 and Figure 14.
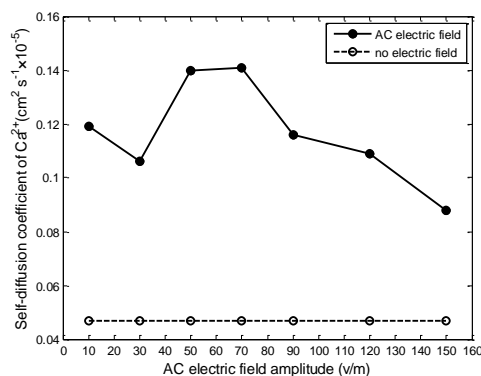

Figure 13. Average D_{Ca} value under AC electric field with different amplitude
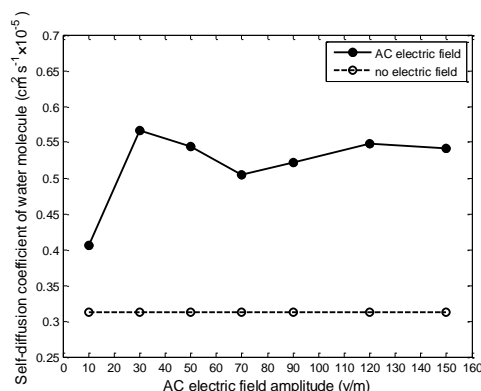

Figure 14. Average D_O value under AC electric field with different amplitude

According to Table 12 and Figure 13, in every time pieces the D_{Ca} value is larger than the value 0.047 $cm^2\,s^{-1}\times10^{-5}$ under no electric field. It also can be known that under the AC electric field with amplitude 70v/m, 90v/m and 120v/m the D_{Ca} value is up and down regularly as the frequency of the AC electric field during MD simulation process. The average D_{Ca} value has the maximum 0.141 $cm^2\,s^{-1}\times10^{-5}$ when the electric field amplitude is 70v/m, and the average D_{Ca} value has the minimum 0.088 $cm^2\,s^{-1}\times10^{-5}$ when the electric field amplitude is 150v/m. Therefore, within the present electric field amplitude range, the D_{Ca} value changes steady and the average D_{Ca} value is biggest when the AC electric field amplitude is 70v/m, which means that using AC electric field with 70v/m amplitude can make the best anti-fouling effect. This result meets exactly with the conclusion obtained in Part B of Sec. III.

According to Table 13 and Figure.14, it is known that in every time piece the D_O value is larger than the value 0.312 $cm^2\,s^{-1}\times10^{-5}$ under no electric field. The average D_O value has the maximum 0.566 $cm^2\,s^{-1}\times10^{-5}$ when the electric field amplitude is 30v/m, and the average D_O value has the minimum

$0.406 \text{ cm}^2 \text{ s}^{-1} \times 10^{-5}$ when the electric field amplitude is 10v/m. Under the AC electric field with amplitude 70v/m, 90v/m and 120v/m, the D_O value is up and down regularly as the frequency of the AC electric field. It also can be known that the average D_O value curve is a multi-extreme curve. When the electric field amplitude is 30v/m, 50v/m, 120 v/m and 150v/m, the average D_O value is larger.

An important result is obtained by comparing Table 10 with Table 13 that the increment of D_O value under AC electric field with different amplitude is larger than the increment under AC electric field with different frequency, which means increasing electric field amplitude is more effective to enhance the self-diffusion coefficient of water molecule than increasing electric field frequency. In other word, increasing electric field amplitude can make better anti-fouling effect.

4. CONCLUSION

For exploring the mechanism of electronic anti-fouling, in the present study the structure and dynamics of hydrated Ca^{2+} and water molecules in $CaCl_2$ aqueous solution under external AC electric field with different frequency and amplitude are researched at first time by systematic long time non-equilibrium molecular dynamics simulation. Within the range of the electric field frequency and amplitude in this paper, some important conclusions obtained as follow that under external AC electric field with different frequency and amplitude:

(1) the radii of hydrated Ca^{2+} is smaller than the radii under no external electric field. When the AC electric field frequency is 400KHz and amplitude is 70v/m, the radii of hydrated Ca^{2+} has the minimum. The smaller radii of hydrated Ca^{2+} means that the hydration between Ca^{2+} and water molecules is enhanced by external AC electric field. When there are carbonate ions appearing in the $CaCl_2$ aqueous solution, a hydrated Ca^{2+} with smaller radii can more easily combine with carbonate ion and form calcium carbonate precipitate. Then the precipitate formed on the water wall is decreased. Therefore making the radii of hydrated Ca^{2+} changing smaller is an important point of the mechanism of electronic anti-fouling.

(2) the first water coordination number for Ca^{2+} changes from 4 to 5. The first water coordination number for Ca^{2+} increasing also can be considered that the hydration between Ca^{2+} and water molecules is enhanced by external AC electric field.

(3) the location of the second water shell of Ca^{2+} and the second water coordination number for Ca^{2+} almost have no change. Therefore, it is considered that the external AC electric field has no obvious impact to the second water shell of Ca^{2+}.

(4) the self-diffusion coefficient of Ca^{2+} is larger than the self-diffusion coefficient under no external electric field. When the AC electric field frequency is 400KHz and amplitude is 70v/m, the self-diffusion coefficient of Ca^{2+} has the maximum. The larger self-diffusion coefficient of Ca^{2+} can be considered that the activity of Ca^{2+} is enhanced. The self-diffusion coefficient of water molecules changes larger, which means that the activity of water molecules is enhanced too. When there are carbonate ions appearing in the $CaCl_2$ aqueous solution, the increase of particles activity can make a higher rate to form calcium carbonate precipitate. Therefore, the increase of particles activity is another important point of the mechanism of electronic anti-fouling.

(5) the increment of self-diffusion coefficient of water molecules under AC electric field with different amplitude is more than the increment under AC electric field with different frequency. Since a larger self-diffusion coefficient of water molecules can make a better anti-fouling effect, therefore in the practical application the anti-fouling effect can be controlled by changing the current strength of excitation signal produced by EAF system.

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