ISSN:2790-1688 DOI: 10.56028/aetr.1.1.75

Molecular Dynamics Simulation on the Corrosion Inhibition Mechanism of Octadecylamine Inhibitor Film

Chao Li[1], Junlin Huang[1,*], Keyi Zhou[1], Qinglan Xu[2],

[1] Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, Jiangsu, China

[2] Science and Technology on Reactor System Design Technology Laboratory, Nuclear Power Institute of China, Chengdu 610213, Sichuan, China

Abstract. Octadecylamine (ODA), a well-known film-forming amine, recently finds increasing application in nuclear pressurized water reactors to protect carbon steel components in the secondary circuit against corrosion. To clarify the inhibition mechanism, molecular dynamics simulations were employed to study the diffusion characteristics of three commonly encountered species, H2O, O2, and Cl-, in the formed inhibitor film. The simulation results revealed that the formed film mitigates corrosion by effectively impeding the diffusion of corrosion species in the film. For various species, the film exhibits markedly different inhibition abilities.

Keywords: Octadecylamine, molecular dynamics, diffusion.

1. Introduction

The secondary circuit of pressurized water reactors (PWRs) contains carbon steel components that may corrode excessively because of the reducing chemistry of the feedwater. Such conditions are imposed to protect the steam generator tubes, which may degrade from corrosion due to the presence of dissolved oxygen, water, and other species[1],[2].

Using octadecylamine(ODA) to protect carbon steel components exposed to corrosive environment has been proved to be an effective method[3]-[4][5][6]. For example, Mao et al.[7] used electrochemical impedance spectroscopy to study the inhibition effect of ODA on type 316SS steel immersed in 348 K, acetic acid solution with a pH of 4.2 and found that the charge transfer resistance was 640945 Ωcm2 with ODA concentration at 0.01 M which was 19973 Ωcm2 when without ODA. Bäßler et al.[8] exposed type AISI 321 steel to ODA-containing 10-1 M chloride ions solutions. Their results, based on electrochemical impedance and Auger electron spectroscopy analysis, suggested that ODA adsorbed onto the steel surface and formed a compact film effectively retarding the diffusion of chloride ions to the metal surface.

All the above studies, relying mainly on experimental investigation, confirmed the protectiveness of ODA as a film-forming corrosion inhibitor in aqueous solutions, supporting a more promising application of ODA in the secondary circuit of PWRs. It is, however, important to understand the details of the inhibition mechanism of ODA at the molecular level in order to improve its efficiency and lay the basis for further application in operating systems.

Recently, molecular dynamics (MD) simulation has become a powerful method for studying the corrosion inhibition mechanism of different inhibitors. In this work, as a part to explain the corrosion inhibition mechanism of ODA, the diffusion coefficients of oxygen molecules, water molecules and chloride ions in ODA inhibitor film were computed by means of MD simulations. To reflect the operating conditions in the secondary circuit of PWRs, the pressure was set to 8 MPa, and the temperature was set to six different values, 298 K, 323 K, 348 K, 373 K, 398 K, and 413 K. The parameters 413K and 8MPa correspond to those of a certain PWR plant.

2. Simulation method

As shown in Fig. 1(b), (c), and (d), three types of cubic and 3D periodic boundary initial structures with 3 water molecules, 3 oxygen molecules, and 3 chloride ions in 50 ODA molecules, were built in simulation boxes. The COMPASS (Condensed-phase Optimized Molecular Potentials

ISSN:2790-1688 DOI: 10.56028/aetr.1.1.75
for Atomistic Simulation Studies) force field[9] was used in all MD simulations. In the MD simulations to get the density of the system, with 1000 ps of total simulation time and 1 fs of time step, the Velocity Scale thermostat and Berendsen barostat were adopted to control the temperature to be at 298 K, 323 K, 348K, 373 K, 398 K, 413K and pressure at 8MPa. In the subsequent 3000 ps MD simulations, the Nosé-Hoover-Langevin thermostat was applied to control the temperature. Table 1 lists the calculated diffusion coefficients of O2, H2O, and Cl- ions.

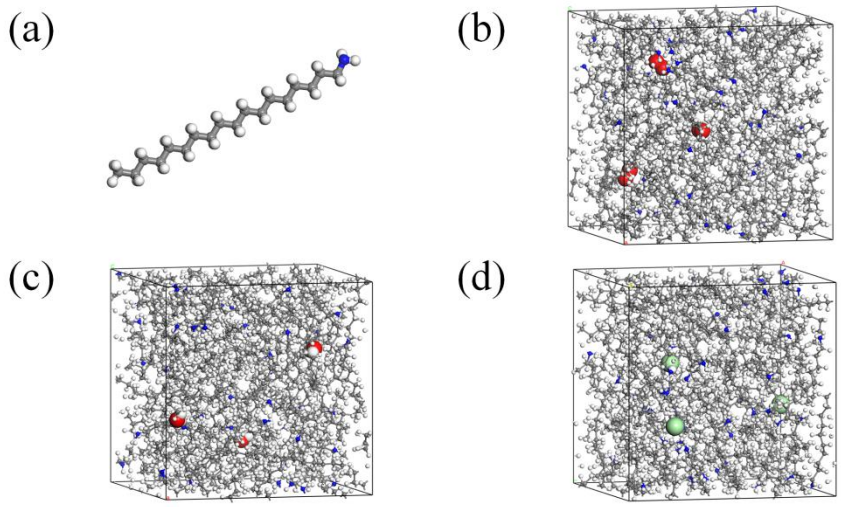

Figure 1. Initial structure of diffusion process: (a) ODA molecule, blue: N atom, grey and white: carbon chain, (b) three oxygen molecules in ODA corrosion inhibitor film, (c) three water molecules in ODA corrosion inhibitor film, (d) three chloride ions in ODA corrosion inhibitor film.

To validate whether using MD simulations to investigate the inhibition mechanism in ODA film is a reliable way, the self-diffusion coefficients of water and the diffusion coefficients of oxygen molecule in water, were calculated at 298 K and 1 atm. Firstly, cubic models of 128 water molecules and one oxygen molecule in 128 water molecules with a 3D periodic boundary were built with the Amorphous Cell module, respectively. Secondly, the smart algorithm was used to optimize the initial structure to avoid high-energy conformations. Thirdly, the MD simulation with 1000 ps was carried out to get the stable density. Finally, the MD simulation with 3000 ps was carried out to obtain diffusion coefficient. Table 2 shows the calculated diffusion coefficients.

3. Results and discussion

3.1 Diffusion coefficient

The calculated diffusion coefficients (D) reflect the migration speeds of H2O, O2, and Cl- in pure water and across the ODA inhibitor film, respectively. The smaller diffusion coefficients represent slower migration speed, meaning the higher inhibition efficiency of the corrosion inhibitor film. Eq. (1) is the so-called Einstein relation:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dx}\sum_i^n \langle |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

Where ri(t) and ri(0) are the positions of corrosion species at time t and 0, respectively, |ri(t)-ri(0)|2 means the mean-square displacement (MSD) which can be obtained with Materials Studio software, and the angle brackets are the ensemble average of MSD.

Table 1 shows the calculated diffusion coefficients of oxygen molecules, water molecules and chloride ions in the ODA inhibitor film. For all species, the diffusion coefficients in the ODA film increase with increasing temperature, as expected. This suggests that the corrosion inhibition of ODA would decrease with temperature - all other parameters remaining the same. At any

ISSN:2790-1688 DOI: 10.56028/aetr.1.1.75
temperature, the diffusion coefficients follow the order of O2 > H2O > Cl-, with that of Cl- being about an order of magnitude less than that of the other two species. This is because of the strong electrostatic interaction between the negatively charged chloride ion and the ODA molecules, which traps it firmly in the ODA matrix and impedes its diffusion to the metal surface. The water and oxygen molecules are electrically neutral and their interaction with ODA molecules is via the weak van der Waals interaction. Water and oxygen molecules, therefore, diffuse more readily in the ODA inhibitor film, oxygen always somewhat faster than water. This is due to the polarity of the water molecule, producing electrostatic interactions with surrounding ODA molecules, while oxygen molecules are non-polar and freer to diffuse. This result, that the diffusion coefficient of charged species (Cl-) is smaller than that of electrically neutral species (O2 and H2O), agrees with the results of other researchers[10].

Table 1 Diffusion coefficients of O2, H2O, and Cl- in ODA corrosion inhibitor film at 8 MPa and different temperatures.

Temperature (K)	Diffusion coefficients in ODA film ($\times 10^{-9}$ m^2/s)		
	O_2	H_2O	Cl^-
298	0.57	0.14	0.026
323	1.49	0.54	0.077
348	2.75	1.02	0.095
373	3.31	2.43	0.18
398	4.18	2.93	0.26
413	4.69	4.41	0.39

Fig. 2 shows the comparison of diffusion coefficients of water molecule, oxygen molecule and chloride ion in pure water and in the ODA inhibitor film, under the conditions of 8 MPa and 413 K; all were obtained via MD simulations. The lower values in ODA than in water reflect the inhibitor properties of the adsorbed film.

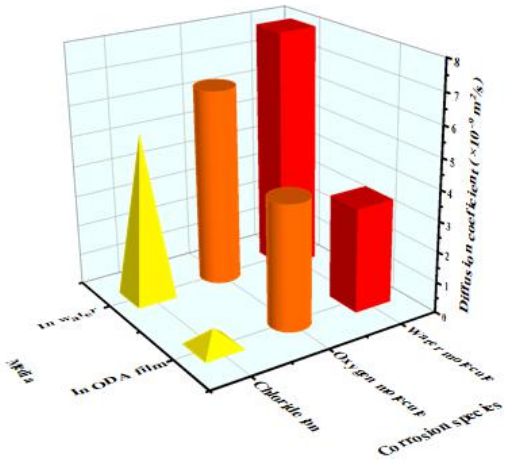

Figure 2. Comparation of diffusion coefficients of O2, H2O and Cl- in pure water and ODA corrosion inhibitor film at 413K, 8MPa.

ISSN:2790-1688 DOI: 10.56028/aetr.1.1.75

The diffusion barrier of ODA is most efficient for chloride ion, reducing its diffusion coefficient from 5.39×10-9 in water to 0.39×10-9 m2/s. The coefficient for water molecules is reduced from 7.93×10-9 to 3.41× 10-9 m2/s and for oxygen molecules from 6.44×10-9 to 4.09×10-9 m2/s. Using the data in Fig.2 to define the barrier performance of ODA for different species, i.e., the difference between the diffusion coefficient in water and that in the ODA inhibitor film, suggests an efficiency of ODA against chloride ions of 92.8 %, against water molecules of 57.0 %, and against oxygen molecules of 36.5 %.

Table 2. Diffusion coefficients of H2O and O2 in pure water at 298 K, 1 atm

Times	Diffusion coefficients of water in pure water ($\times 10^{-9}$ m^2/s)	Diffusion coefficients of oxygen in pure water ($\times 10^{-9}$ m^2/s)
Average	2.28	2.71
Experimental	2.09-2.66	2.42

From Table 2, it can be seen that the calculated self-diffusion coefficients of water in pure water, are well agreed with the value of experiment, which indicates that using MD simulation to calculate the diffusion coefficients of corrosion species in ODA inhibitor film is a reliable method. The calculated diffusion coefficients of oxygen in pure water are not very precise as the calculated diffusion coefficients of water in pure water, however, considering the size of boxe, the selected force field, the thermostat and the barostat, and error inherent of non-bonding interactions and statistical could affect the calculation results, the agreement with the experimental value is acceptable and the MD method is considered reliable for calculating diffusion properties of these species within ODA films.

4. Conclusions

In summary, the diffusion process of three species in an ODA inhibitor film such as would be applied in the secondary circuit of PWR nuclear power plants was investigated by molecular dynamics simulation. The results demonstrated the ability of ODA to inhibit the diffusion of H2O, O2 and Cl-, following the order Cl- > H2O > O2. The corrosion inhibition mechanism of ODA is to protect the metal by inhibiting the diffusive of corrosion soecies in the ODA corrosion inhibiting film.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (52106003, 51676035).

References

[1] C.W. Turner. Fouling of nuclear steam generators: fundamental studies, operating experience and remedial measures using chemical additives[J]. AECL Nucl. Rev, 2013, 2:61-88.

[2] I. Betova, M. Bojinov, T. Saario. Film-forming amines in steam/water cycles-structure, properties, and influence on corrosion and deposition processes[R]. Research Report, 2014, VTT-R-03234-14.

[3] S. Odar. Use of film forming amines (FFA) in nuclear power plants for lay-up and power operation. Advanced Nuclear Technology International Europe AB, ANT International, 2017.

[4] M.A. Rodríguez. Corrosion control of nuclear steam generators under normal operation and plant-outage conditions: a review[J]. Corrosion Reviews, 2020, 38(3):195-230.

[5] J. Baux, N. Pebere, S. Delanunay, et al. Film-forming amines for corrosion protection of carbon steels in PWR secondary circuit conditions[M]. NPC 2018 (Nuclear Plant Chemistry Conference), Sep 2018, San Francisco, United States. Hal-02415481.

ISSN:2790-1688 DOI: 10.56028/aetr.1.1.75
[6] C. Forget, G. Stoianovici, P. Bleriot. Film forming amines for closed cooling/heating water systems[J]. PowerPlant Chemistry: The Journal of ALL Power Plant Chemistry Areas, 2014, 16(6):3361-375.

[7] F. Mao, C. Dong, D.M. Digby. Effect of octadecylamine on the corrosion behavior of Type 316SS in acetate buffer[J]. Corrosion Science, 2015, 98: 192-200.

[8] R. Bäßler, M. Uhlemann, K. Mummert. Inhibiting effect of octadecylamine on pitting corrosion behaviour of stainless steel type 1.4541 up to 250°C[J]. Materials & Corrosion, 2015, 50(3):146-153.

[9] H. Sun. COMPASS: An ab initio force-field optimized for condensed-phase applications-overview with details on alkane and benzene compounds[J]. Journal of Physical Chemistry B, 1998, 102:7338-7364.

[10] Youguo Yan, Xiao Wang, Yang Zhang, et al. Molecular dynamics simulation of corrosion species diffusion in imidazoline inhibitor films with different alkyl chain length[J]. Corrosion Science, 2013, 73:123-129.