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Molecular dynamics simulation of corrosive species diffusion in imidazoline inhibitor films with different alkyl chain length

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ABSTRACT

Diffusion performances of corrosive species in imidazoline derivative film with different alkyl chain length are investigated by molecular dynamics simulation method. The diffusion coefficient is used to evaluate the inhibition efficiency. Calculated results indicate that the diffusion coefficient decreases with the increasing alkyl chain length, and the inferred inhibition efficiency increases with the increasing alkyl chain length, which is well in accordance with reported experimental results. Furthermore, the diffusion process of corrosive species is discussed in detail, and four factors, fractional free volume, interaction energy, displacement period and self-diffusion coefficient, are proposed to illustrate the microscopic diffusion mechanism.

1. Introduction

The application of corrosion inhibitors is one of the most effective and economical methods to protect metal in many fields [1–4]. Among numerous kinds of corrosion inhibitors, the adsorptive inhibitors will take effect by adsorption on metal surface and formation of protective films, which can isolate the metal from corrosive medium [5–11]. The migrating rate of corrosive species in inhibition film is considered as a key factor to evaluate the inhibition efficiency of corrosion inhibitors. Generally, the higher migrating rate means a lower inhibition efficiency [12]. It is approved that the migrating rate is closely related with the structural characteristic of inhibitor film adsorbed on the metal surface [13–17].

In the formation of the inhibitor film, the head groups of inhibitor, i.e. functional group, commonly attach and adsorb onto the metal surface, the alkyl chains will stretch up against Fe surface and pack together to form film. The structural characteristic of inhibitor film is greatly dependent on the structure of inhibitor molecule [18], such as functional group type [19] and chain length [20–23]. Our previous researches indicated that the type of functional group of inhibitor molecule had important influence on the diffusion behaviour of corrosive species [24], and high polarity of functional group would largely hinder the migration of corrosive species and result in high inhibition efficiency. However, the microscopic diffusion performance of corrosive species in inhibitor film with different chain lengths is scarcely investigated.

In this work, six imidazoline derivatives with different alkyl chain length are selected as research objects, which favour to protect metal in CO_2 and H_2S environment via adsorption onto metal surface forming inhibitor film [25–28], Table 1 present their molecular structures. The diffusion performances of corrosive species in six imidazoline film with different alkyl chain lengths are studied by molecular dynamics (MD) simulation. The diffusion coefficient is calculated to evaluate the inhibition efficiency. The diffusion process is discussed at length, and four factors, fractional free volume, interaction energy, displacement period and self-diffusion coefficient, are proposed to illustrate the microscopic diffusion mechanism and provide some useful references in the inhibition efficiency evaluation of other inhibitors.

2. Molecular dynamic simulation details

2.1. Construction of inhibitor film

In the realistic environment, inhibitor molecules would undergo dissolution and diffusion in the solution. As to adsorptive inhibitors, they would adsorb onto the metal surface spontaneously and form inhibitor film. Generally, the structure of formed inhibitor film is complex ascribed to the interaction between inhibitor molecules with metal surface and internal interaction among inhibitor film. Due to the lack of experimental references and limitation of simulation technique, it is difficult to construct realistic inhibitor film. Hence, the simplified amorphous model is adopted in our paper. Similar models [29,30] have been adopted to study the barrier properties of the coatings and hygrothermal aging of the materials,

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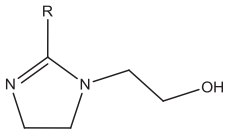
Table 1
Chemical structure and inhibition efficiency of six imidazoline inhibitors.

Molecular structure	R	Name	Abbr.	I (%)[a]
	$-CH_2(CH_2)_5CH_3$	1-(2-Hydroxyethyl)-2-heptyl-imidazoline	IC-7	31.7
	$-CH_2(CH_2)_7CH_3$	1-(2-Hydroxyethyl)-2-nonyl-imidazoline	IC-9	41.3
	$-CH_2(CH_2)_9CH_3$	1-(2-Hydroxyethyl)-2-undecyl-imidazoline	IC-11	48.5
	$-CH_2(CH_2)_{11}CH_3$	1-(2-Hydroxyethyl)-2-tridecyl-imidazoline	IC-13	68.9
	$-CH_2(CH_2)_{13}CH_3$	1-(2-Hydroxyethyl)-2-pentadecyl-imidazoline	IC-15	83.0
	$-CH_2(CH_2)_{15}CH_3$	1-(2-Hydroxyethyl)-2-heptadecyl-imidazoline	IC-17	96.3

[a] I (inhibition efficiency) is taken from Ref. [25].

and their calculated results are well accorded with experimental results.

MD Simulation is carried out using the Discover and Amorphous Cell module in Materials Studio software. A cubic model containing 50 corrosion inhibitors with 3D periodic boundary conditions is built by Amorphous Cell module. The model is firstly minimised by smart minimisation method, followed by a conjugate gradient method until the convergence reaches 0.418 kJ/mol. The density of the inhibitor films are evaluated from 200 ps MD trajectories run under Constant-pressure NPT ensemble, which means that the numbers of molecules, the pressure and the temperature of the model keep constant during simulation.

2.2. Selection of corrosive species

According to the applied environment of H_2S acidic liquid, water (H_2O), hydronium ion (H_3O^+), chloride ion (Cl^-) and hydrogen sulfide ion (HS^-) are selected as corrosive species. Actually, in liquid medium, corrosive ions often appear as hydrated ion, viz. $HS^-\cdot(H_2O)_n$, $Cl^-\cdot(H_2O)_n$, etc. While, the inhibitor film is significantly different with the liquid, it is essential to acquire the status, hydrated or unhydrated, of these corrosive species. Herein, the $Cl^-\cdot(H_2O)_n$ is selected as example, and the diffusion behaviour is studied. First, the molecular dynamics simulation is conducted to investigate the hydrature of $Cl^-\cdot(H_2O)_n$, and the built model contains 1000 water molecules and one Cl^-. After 2 ns molecular dynamics simulation, it is observed that one hydration shell forms around Cl^- (shown in Fig. 1a). Based on the analysis of radical distribution function between Cl^- and oxygen in H_2O (seen in Fig. 1b), it can be found that the first hydration shell forms at 3.17 Å around Cl^-, and six water molecules are contained in the hydration shell. So, the hydrated status of Cl^- should be $Cl^-\cdot(H_2O)_6$.

After that, the model containing $Cl^-\cdot(H_2O)_6$ and inhibitor film is constructed to investigate the diffusion behaviour of $Cl^-\cdot(H_2O)_6$ in inhibitor film. After 2 ns molecular dynamics simulation, it can be observed that the structure of $Cl^-\cdot(H_2O)_6$ is broken (Fig. 2). This result indicates that the interaction between Cl^- and water molecules is weak, and the hydrogen shell could not exist stably in the inhibitor film. As a result, in this work, the unhydrated corrosive species are adopted to investigate the diffusion behaviour in various imidazoline films.

2.3. Simulation details of diffusion models

According to above density calculation, a model composed of 50 inhibitor molecules and one corrosive species is built to investigate the diffusion performance of corrosive species in the inhibitor film. Typical models of four corrosive species in 1-(2-Hydroxyethyl)-2-heptyl-imidazoline (IC-7) inhibitor film are presented in Fig. 3. Each model with corrosive species is then minimised again and conducted with a 2000 ps canonical ensemble NVT (T = 298 K) dynamics simulation to obtain the equilibrium configuration, and the trajectory is recorded every 1 ps.

All simulations mentioned above are carried out with COMPASS force field [31]. The simulation temperature is set at 298 K controlled by Andersen thermostat [32], and the pressure is set at atmospheric pressure (1.01×10^5 Pa) controlled by Berendsen barostat [33]. The long-range coulomb interaction and van der Waals interaction are handled by charge group method, and the cutoff is selected as 1.5 nm (spline width: 0.10 nm, buffer width: 0.05 nm). For all the simulation systems, the initial 500 ps are considered as the building period of equilibration, and the following 1500 ps is used to analyse.

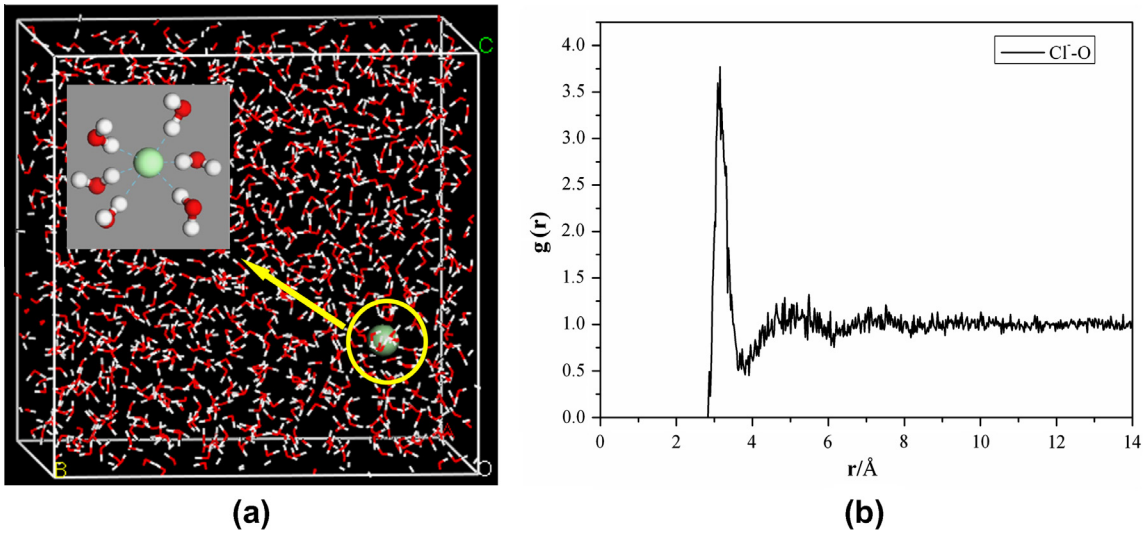


Fig. 1. Simulation model of Cl^- and H_2O molecules: (a) equilibrium configuration after 2 ns; and (b) radical distribution function between Cl^- and oxygen in H_2O (Cl: green; H: white; and O: red). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)