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Molecular dynamics simulation of corrosive particle diffusion in benzimidazole inhibitor films

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ABSTRACT

Diffusion of corrosive particles inside inhibitor films consisting of 2-mercaptobenzimidazole (2-SH-BI), 2-aminobenzimidazole (2-NH_2-BI), 2-methylbenzimidazole (2-CH_3-BI), and benzimidazole (BI) was investigated by molecular dynamics simulation. Diffusion coefficients of various corrosive particles in the films were calculated, following the same order of 2-SH-BI < 2-NH_2-BI < 2-CH_3-BI < BI. Fractional free volume, interaction between corrosive particles and films, and mobility of films were also investigated to illustrate the microscopic diffusion mechanism. As a result, it can be inferred that the order of inhibition efficiency is 2-SH-BI > 2-NH_2-BI > 2-CH_3-BI > BI, which is in good accordance with published experimental results.

1. Introduction

Corrosion inhibition is of great importance in many industries, such as oil and gas extractions, refining and petrochemicals, metallurgy, and construction. Among various corrosion inhibitors, the adsorptive type takes effect by adsorption onto metal surface, formation of protective films, and isolation of metal from corrosive media [1–5]. It has been accepted that the performance of inhibitors is closely related to the properties of inhibitor films [6–8]. Traditionally, efforts have been devoted to shed light on the relationship between inhibition performance and reactivity property of inhibitor [9], adsorption strength of inhibitor molecules on metal surface [10], and adsorption configuration of inhibitor film formed on metal surface [11]. However, these studies have scarcely been focused on the microscopic mechanism of diffusion-preventing of corrosive species by inhibitor films, which is crucial to the effectivity of corrosion inhibitors.

From the experimental point of view, various techniques, such as quasi-elastic neutron scattering, pulsed field gradient NMR, and electrochemical impedance spectroscopy, are hardly used to investigate the diffusion process of corrosive species, because the actual system that reveals diffusion of corrosive species inside inhibitor films is too complicated to be dealt with. Nevertheless, molecular dynamics simulation has become a powerful tool to obtain detailed dynamic information and elucidate physiochemical phenomena at molecular level. Many studies have been carried out on diffusion of small particles by molecular dynamics simulations in various fields, such as transportation in porous media, molecular encapsulation, and separation or purification processes. [12–17]. This method is competent for tracking the diffusion process of particles inside porous and bulk materials, describing the geometrical morphology of films, obtaining data of diffusion coefficient, and so on. Hence, we perform molecular dynamics simulations to investigate the diffusion mechanism of corrosive species inside films of four distinct corrosion inhibitors, for theoretical evaluation of inhibition performance of these compounds.

The selected compounds are different benzimidazole derivatives, which have been widely used as effective corrosion inhibitors [18–20]. The chemical structures of these compounds are described in Table 1, and their inhibition efficiency (IE) for carbon steel in dilute hydrochloric acid environment has been measured using gravimetric and polarization techniques in the previous publications [21]. In accordance with the corrosive environmental, hydronium ion (H_3O^+), water (H_2O) and chlorine ion (Cl^-) are selected as corrosive particles. In this paper, diffusion behaviour of the three corrosive species inside inhibitor films are investigated via molecular dynamics simulations first. Then the inhibition efficiencies of the four inhibitors are evaluated by comparing the ability to hinder diffusion of corrosive particles by various films. And finally the microscopic diffusion mechanism is elucidated by analysis of film fractional free volume, interaction between particle and film, and mobility of the films.

2. Computational details

Diffusion of corrosive particles was modelled in two different systems. First, a bulk liquid system was adopted to investigate

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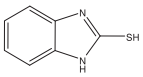
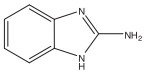
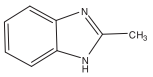
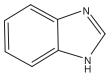
Table 1
Chemical structure and inhibition efficiency of the investigated benzimidazole derivatives.

Structure	Name	Abbreviation	Inhibition efficiency (%)
	2-Mercaptobenzimidazole	2-SH-BI	90.0
	2-Aminobenzimidazole	2-NH_2-BI	88.4
	2-Methylbenzimidazole	2-CH_3-BI	61.7
	Benzimidazole	BI	58.9

the diffusion of corrosive particles in corrosive media consisting of one corrosive particle and 500 water molecules. And second, an inhibitor film system containing one corrosive particle and 80 inhibitor molecules was introduced for investigation of diffusion of corrosive particles in the film, as shown in Fig. 1. Periodic boundary conditions were applied along all the three coordinate axes in the simulation systems. Although these models can barely reflect the real diffusion of corrosive particles, it is still viable for qualitatively comparison of diffusion of corrosive particles in films and corrosive media.

After the initial configurations were built, energy optimization was performed with smart minimizer tool in Materials Studio software package [22], in which iterations were assigned cascade convergence levels of 4180, 41.8, and 0.00418 kJ/(mol Å) for the methods of steepest-descent, conjugated gradient, and Newton method, respectively. And then NPT (constant number of molecules, constant pressure, and constant temperature) ensemble molecular dynamics simulation was carried out for 200 ps to reach the equilibrium status of the simulation system. Consequently, from the endpoint of NPT ensemble simulation, 1000 ps NVT (constant number of molecules, constant volume, and constant temperature) ensemble molecular dynamics simulation was carried out for the subsequent analysis.

All simulations were implemented with Materials Studio 4.0 software, and COMPASS force field [23] was applied. The Berendsen barostat was used to control system pressure at 1 bar, and Andersen thermostat was used to control system temperature at 298 K [24,25]. Van der Waals and Coulomb interactions were calculated by group based method, and the cutoff distance was 10.0 Å (with a spline width of 1.0 Å and a buffer width of 0.5 Å) [26]. Long-tail corrections to the energy due to cutoff were applied during simulation. The time step was 1.0 fs, and atomic trajectory was recorded every 1000 fs.

3. Results and discussion

3.1. Diffusion coefficient of particles in film

The transport of corrosive particle inside inhibitor films can be investigated using mean square distance (*MSD*) functions, which were computed with following equation:

$$MSD = \left\langle |r_i(t) - r_i(0)|^2 \right\rangle \quad (1)$$

Where $r_i(t)$ is the position of atom i at time t, and $r_i(0)$ is the initial position. The diffusion coefficient (D) can be obtained from the slope of their *MSD* in a time interval with Einstein relation [27]:

$$D = \frac{1}{6}\lim_{t\to\infty}\frac{d}{dt}\sum_{i=1}^{Na}\left\langle |r_i(t) - r_i(0)|^2 \right\rangle \quad (2)$$

Double logarithmic coordinate plots of *MSD* for H_3O^+, H_2O, and Cl^- are shown in Fig. 2. To verify the Einstein relation, linear fit for the straight parts of the plot was performed to see if their slopes remain constant. And since the beginning and ending part of *MSD* is relatively chaotic, the fitting was conducted only in the region between 100 and 900 ps for calculation of diffusion coefficient by the Einstein relation.

The values of diffusion coefficients are listed in Table 2. It is worth noting that the calculated diffusion coefficient of pure water is $2.419 \times 10^{-9}\,m^2\,s^{-1}$ at 298 K, which matches well with the experimental value of $2.09 \sim 2.66 \times 10^{-9}\,m^2\,s^{-1}$ [28]. This result implies that it is reliable to use molecular dynamics simulation to estimate the diffusion coefficients of corrosive particles.

From Table 2, it is interesting to note that the diffusion coefficient of each particle in inhibitor film is considerably lower than that in pure water, suggesting that the inhibitor film constrains the diffusion of the particles. It can also be inferred that with the formation of these inhibitor films on metal surface, they can effectively hinder the diffusion of corrosive particles from corrosive medium to metal surface, and thus slow down the corrosion process.Furthermore, for each corrosive particle, the diffusion coefficients inside different films follow the order of 2-SH-BI < 2-NH_2-BI < 2-CH_3-BI < BI. The film with larger diffusion coefficient of particles is weaker in slowing down the diffusion of corrosive particle. As a result, corrosive particle will penetrate the inhibitor film between corrosive medium and metal surface more easily and cause corrosion. Therefore, it can be safely inferred that the inhibition performance of the four inhibitor films should follow the order of 2-SH-BI > 2-NH_2-BI > 2-CH_3-BI > BI, which also agrees well with the previously reported experimental results [21]. Moreover, in the case of various particles diffusion inside the same film, another interesting finding is that the values of diffusion coefficient of the three corrosive particles follow the order of $D_{H_2O} > D_{H_3O^+} > D_{Cl^-}$. This result indicates that the inhibitor film can more effectively hinder the diffusion of charged corrosive particle than that of chargeless particles.

3.2. Diffusion mechanism of particles in film

Diffusion of corrosive particles inside inhibitor films is an extremely complex process, which can be affected by various factors, such as the size and distribution of free volume in the film, interactions between particles and films, and the mobility of film itself. For deeper exploration of the microscopic diffusion mechanism of the corrosive particles, these factors were investigated primarily.

3.2.1. Fractional free volume of inhibitor film

Diffusion of corrosive particles can be explained by the fact that particles will diffuse faster inside a film with larger free volume. To