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Short Communication

Molecular dynamics simulations of dodecylamine adsorption on iron surfaces in aqueous solution

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ABSTRACT

Molecular dynamics (MD) simulations have been used to study the adsorption of dodecylamine (DDA) on iron surfaces in aqueous solution in this paper. In strong acidic solution the protonated form of DDA, DDAH, can adsorb on the iron surface preferentially, while in weak acidic solution containing chloride ions the adsorption of DDA and DDAH forms can occur simultaneously. Different results were obtained when different simulation factors were considered. In order to obtain the correct results, a model close to the realistic inhibition system was fabricated.

1. Introduction

Efficiency of organic inhibitor depends on their chemical/electronic structure of molecules. The relationships between the structure of inhibitor molecule and its efficiency have been investigated using quantum chemical methods, for example, DFT method [1–8]. The studies indicated that quantum chemical parameters could be correlated to experimentally obtained inhibition efficiencies [9–13], and hetero-atoms usually act as main adsorption centres [14,15]. Recently, molecular dynamics (MD) simulations have been used to illustrate the adsorption of the molecules onto the corroding metal surface at a molecular level [16–19]. During the simulation process the geometry optimization of the studied system was carried out using an iterative process, in which the atomic coordinates were adjusted until the total energy of a structure is minimized, i.e., it corresponded to a local minimum in the potential energy surface [20]. Some significant results have been obtained in vacuum systems, which confirmed that MD simulation was an efficient method for the study of mechanism of corrosion inhibition. However, it is still difficult to model the realistic inhibition system where various factors, such as the adsorption of the solvent molecules, the co-adsorption of the electrolyte anions and protonation of the inhibitor molecules, can influence the adsorption of the inhibitor onto the metal surface. Xia et al. [21] investigated the adsorption of imidazoline derivatives on iron surface using MD method and found that the equilibrium configuration of the molecules in vacuum system is quite different from that in aqueous system. Additionally, in our previous publication [22], we reported that if the adsorption of electrolyte anions was considered in the simulation the calculated interaction energy between inhibitor molecules and iron surface could be higher.

Straight-chain amines are well known corrosion inhibitors for carbon steel in aqueous solutions [23–26]. Although many amines inhibitors have been studied, apparently there are still some unanswered questions regarding inhibition mechanism. In this work we attempt to fabricate a model system to investigate the corrosion inhibition mechanism of dodecylamine (DDA) in aqueous solutions. In this system, the effect of solvent molecules, the electrolyte anions and protonation of the inhibitor molecules on the adsorption of DDA onto Fe (0 0 1) surface will be considered.

2. Simulation methods

The molecular dynamics (MD) simulations were performed using the software, Materials Studio 2.2. Fe (0 0 1) surface was chosen for the simulation study. The MD simulation of the interaction between DDA molecule and Fe (0 0 1) surface was carried out in a simulation box (17.20 Å × 17.20 Å × 35.97 Å) with periodic boundary conditions to model a representative part of the interface devoid of any arbitrary boundary effects. The iron substrate with (0 0 1) plane was first optimized to minimum energy, then the addition of the liquid phase with a DDA molecule and 200 H_2O molecules near to the surface was carried out. The MD simulation was performed at 298 K, NVT ensemble, with a time step of 0.1 fs and simulation time of 50 ps using the compass force field. The

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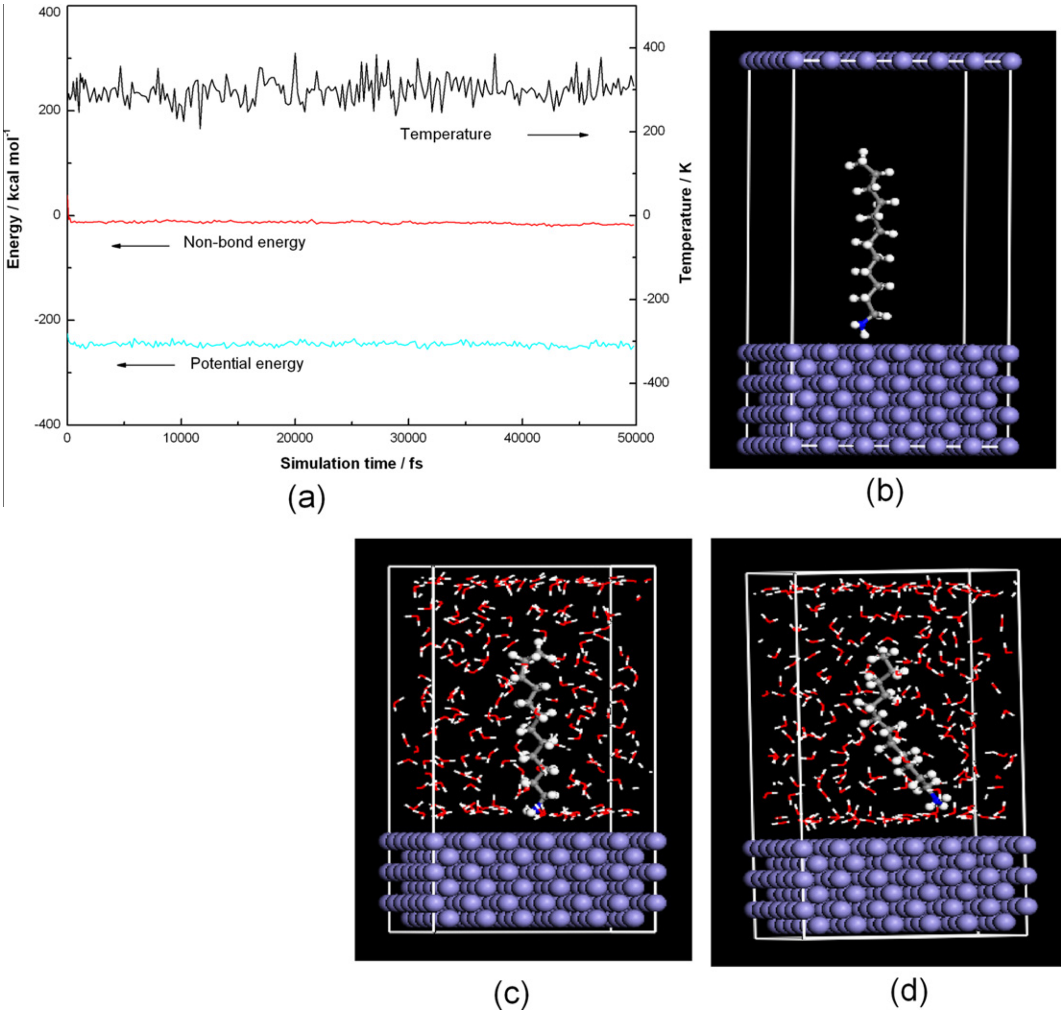

Fig. 1. (a) Representative energy and temperature fluctuation curves and equilibrium configurations of (b) DDA in vacuum, (c) DDA and (d) DDAH in aqueous solution.

interaction energy E_{int} between the iron surface and the DDA molecule was calculated as follows:

$$E_{\text{int}} = E_{\text{total}} - (E_{\text{surf}} + E_{\text{DDA}}) \qquad (1)$$

where E_{total} is the total energy of iron crystal together with the adsorbed DDA molecule, E_{surf} and E_{DDA} are the energy of the iron crystal and free DDA molecule, respectively.

3. Results and discussion

The MD simulation was first performed to model the adsorption behaviour of DDA molecule on the (0 0 1) plane in vacuum system. After the system must have reached equilibrium, criterion of which is that both temperature and energy of the system reach balance (Fig. 1a), calculations of single point energy using the DISCOVER molecular dynamics module were carried out to obtain E_{total}, E_{surf} and E_{DDA}, and then E_{int} was obtained using Eq. (1). The simulation result is shown in Fig. 1b, and the calculated E_{int} is -100.1 kJ mol^{-1} (Table 1). According to the equilibrium configuration of DDA molecule adsorbed on the (0 0 1) plane, we can conclude that the compound can be adsorbed on the iron surface through the nitrogen atom. It is well known that the presence of unoccupied d-orbital on iron surface exhibits a tendency to obtain electrons from the adsorbed molecules, and there is a lone pair of electrons on the nitrogen atom of DDA molecule. Therefore, it is possible that DDA molecule provides electrons to the unoccupied d-orbital on iron surface to form stable co-ordination bonds. It is also evident from Fig. 1b that the alkyl chain of DDA is approximately perpendicular to the iron surface without almost any torsion in the vacuum system. Furthermore, the corrosion inhibition is achieved through the reduction of the exposed part of iron surface by the covering of the nitrogen atom and the blocking layer of the alkyl chain. However, electrochemical corrosion takes place in the liquid phase, so it is relevant to include the effect of solvent in the simulation [19]. Therefore, in the present study a model containing a DDA molecule and 200 water molecules is constructed and then added near to the (0 0 1) plane for the MD simulation. The corresponding simulation result is presented in Fig. 1c, and the calculated interaction energy is -2089.5 kJ mol^{-1}. It can be seen from Fig. 1c that the optimization configuration of DDA in the aqueous solution is similar to that in the vacuum, but the torsion of the alkyl chain is slightly im-

Table 1
Values of interaction energy of different simulation systems.

Systems	E_{int} (kJ mol^{-1})
DDA	-100.1
DDA + H_2O	-2089.5
DDAH + H_2O	-2452.8
DDA + H_2O + Cl^-	-5959.8
DDAH + H_2O + Cl^-	-5992.5