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Synergistic effect of 2-oleyl-1-oleylamidoethyl imidazoline ammonium methylsulfate and halide ions on the inhibition of mild steel in HCl

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ABSTRACT

The effect of 2-oleyl-1-oleylamidoethyl imidazoline ammonium methylsulfate (ODD) and halide ions on corrosion inhibition of mild steel in HCl solution has been studied by experimental and molecular dynamics simulation methods. Synergistic effects were observed between ODD and the halides, and the inhibition efficiency was found to follow the trend ODD–Cl^- < ODD–Br^- < ODD–I^-. In molecular dynamics simulation, the analysis of fractional free volume and diffusion coefficient showed that the synergistic effect increased in the order ODD–Cl^- < ODD–Br^- < ODD–I^-. The molecular dynamics simulation analysis agreed with the experimental results.

1. Introduction

Organic inhibitors have been widely applied to inhibit the corrosion of metals in acidic media. A large number of studies about corrosion inhibition mechanism have emerged over the past few years. Originally, the mechanism of single corrosion inhibitor was studied by the experimental methods. These methods provided some really useful information in explaining the mechanism of single corrosion inhibitor [1–5]. But they were expensive and time consuming. Above all, they were unable to present the mechanism of the corrosion inhibitor from a microscopic level. Afterwards, with the development of computer technology and theoretical process, computer simulation methods had evolved to be an efficient method to study the complex systems at the microscopic level [6–10], and had made it possible to investigate the mechanism of single corrosion inhibitor fundamentally. However, for a single corrosion inhibitor, the selectivity to the environment was so high that the scope of application was too narrow.

The multicomponent corrosion inhibitors showed more excellent performance, such as lower dosage, high efficiency and broad scope of application. Thus, the study on the mechanism of the multicomponent corrosion inhibitors was paid more and more attention to. Many studies had been performed by the experimental methods. Hosseini et al. [11] studied the inhibition effects of sodium dodecylbenzenesulphonate (SDBS) and hexamethylenetetramine (HA) on the corrosion of mild steel in sulphuric acid solution using weight loss, electrochemical impedance and Tafel polarization measurements. Results showed that SDBS and HA presented a synergistic effect within a certain concentration range. Jeyaprabha et al. [12] explored the influence of halide ions on the adsorption of diphenylamine on iron surface in 0.5 M H_2SO_4 solution using electrochemical impedance and polarization methods. It was found that the inhibition efficiency of diphenylamine increased in the presence of halide ions, and the decreasing order of synergistic effect of halide ions was $I^- \gg Br^- > Cl^-$. Tavakoli et al. [13], Pavithra et al. [14] and Gao et al. [15] also investigated the synergistic effect of different additives on the corrosion inhibition of various metals by the experimental methods. However, the studies about synergistic effect of corrosion inhibition mechanism were in a stage of summary and inference from the experimental phenomena.

At present, the theoretical study on the synergistic effect of multicomponent corrosion inhibitors was scarce. Yan et al. [16] studied the corrosion inhibition properties of pyridine and I^- on the aluminum surface in phosphoric acid by weight loss and quantum chemistry method. It showed that there was a synergistic effect between pyridine and I^-. The quantum chemistry calculation method showed that the net energy of synergistic inhibition was the main reason of synergistic effect. Generally, quantum chemistry method is only applied to a system containing no more than 100 atoms or small molecules. But the corrosion process always

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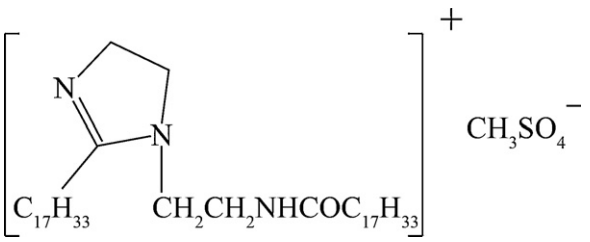

Fig. 1. Schematic molecular structure of ODD.

refers to a big system, which includes a large number of molecules or atoms on the interface between a bulk and metal surface. In fact, molecular dynamics (MD) simulation can be performed to study a complex system, such as a interface and diffusion of particles [17], etc. However, there were few publications on the synergistic inhibition mechanism studied by the MD simulation.

In this paper, the inhibition effects of 2-oleyl-1-oleylamidoethyl imidazoline ammonium methylsulfate (ODD, Fig. 1), halide ions (Cl^-, Br^- and I^-) and their mixture (ODD–Cl^-, ODD–Br^-, and ODD–I^-) on A_3 steel in 0.5 M HCl solution are studied by the weight loss method and potentiodynamic polarization test. Furthermore, we investigate the synergistic mechanism by molecular dynamics simulation to explain the synergistic mechanism from the molecular level.

2. Experimental and computational methods

2.1. Experimental method

2.1.1. Materials

Experiments were carried out using A_3 steel as the specimen with the composition (in wt.%) C 0.17%, Si 0.20%, S 0.03%, P 0.01% and the remainder being iron. The specimens were ground on SiC waterproof abrasive paper up to 2000 mesh grit, and then ultrasonically cleaned in the analytical reagent alcohol and dried in air.

Experiments were undertaken in 0.5 M HCl solution in the absence and presence of different concentrations of ODD (0.1, 0.5, 1.0, 2.0 and 3.0 g l^{-1}, respectively), KX (1.0 g l^{-1} for KCl, KBr and KI, respectively) and ODD–KX mixtures (both 1.0 g l^{-1}) at 50 °C. The temperature was maintained by placing a container in a thermostated water bath.

The aggressive solution of 0.5 M HCl was prepared using AR grade chemicals and distilled water. The active constituent of ODD was 80%, and the concentration of inhibitor solutions were obtained by dissolving it in 0.5 M HCl. The mixed inhibitor solutions (ODD–KX) were prepared by adding specified amount of AR KX to ODD–HCl solution.

2.1.2. Weight loss method

In the weight loss experiment, twelve beakers containing 0.5 M HCl solution were placed in the thermostated bath maintained at 50 ± 0.1 °C. A_3 mild steel specimens in triplicate were suspended in the beakers. All the aggressive acid solutions were open to air. After 24 h, the specimens were taken out, washed, dried and weighed accurately.

2.1.3. Potentiodynamic polarization method

Polarization curve was measured by potentiodynamic technique. A cell was filled with 250 ml of the test solution and a conventional three-electrode cell was used for electrochemical measurements. A platinum was used as the auxiliary electrode, a mercurous sulfate electrode was used as the reference electrode, and A_3 steel sheet with 1.00 cm^2 was used as the working electrode. Prior to each electrochemical measurement, the working electrode was immersed in HCl solution for 1 h to establish a steady open circuit potential (OCP). All potentials are reported versus that of the mercurous sulfate electrode. The potentiodynamic polarization curves were carried out in the potential range of −250 to 1200 mV (vs. Hg/Hg_2SO_4) at a sweep rate of 0.166 mV s^{-1}. The corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were extracted using the Tafel extrapolation method by means of a Princeton Applied Research 352 SoftCorr™ III corrosion measurement system connected to a computer.

Table 1
Description of different simulated models.

Membrane	Number of compositions			$Lx^a = Ly^a = Lz^a$, Å
	X^-	ODD^+	Corrosive particle	
ODD–Cl^-	30	30	H_3O^+	1
			H_2O	1
				33.61
ODD–Br^-	30	30	H_3O^+	1
			H_2O	1
				33.10
ODD–I^-	30	30	H_3O^+	1
			H_2O	1
				31.18

[a] *Lx*, *Ly* and *Lz* represent the length, width and height of the model constructed, respectively.

2.1.4. Scanning electron microscopy (SEM)

Immersion corrosion analysis of A_3 steel samples in 0.5 M HCl solution with KX (1.0 g l^{-1} for KCl, KBr and KI, respectively) and ODD–KX mixtures (both 1.0 g l^{-1}) at 50 °C were performed using SEM. Immediately after the corrosion tests, the samples were subjected to SEM studies to know the surface conditions. S-4800 – the ice emission scanning electron microscope was used for the experiments.

2.2. Molecular dynamics simulation

In order to study the synergistic effect between ODD and halide ion in the same concentration by mean of the inhibition effect of ODD and halides on corrosive particles, the Amorphous Cell module and Discover module in commercial software package Materials Studio 4.4 developed by Accelrys Inc. were used. The Amorphous Cell module allows constructing complex amorphous systems. The first step is to build the amorphous systems. Diffusion model was used to study the synergistic effect between the ODD and halide ion at the molecular scale. Six diffusion models were built by the Amorphous Cell module [18–20] at an initial density of 1.0 g cm^{-3}. The lengths of the model and the compositions of the systems contained in each cell are summarized in Table 1. The initial diffusion models of H_3O^+ in the three inhibitor membrane ODD–Cl^-, ODD–Br^- and ODD–I^- are shown in Fig. 2. The diffusion models of H_2O were similar to those of H_3O^+, so they are not presented in this paper for simplicity.

The discover module incorporates a broad spectrum of molecular mechanics and dynamics methodologies that have demonstrated applicability to molecular design. The discover molecular mechanics module allows optimizing a molecular structure such that its energy is at a minimum by different methodologies. The discover molecular dynamics module allows selecting a thermodynamic ensemble and the associated parameters, defining simulation time, temperature and pressure and initiating a dynamics calculation [21]. In the configuration optimization, the structure of each system with 3D periodic boundary conditions was minimized by a smart minimizer method, which switches from a steepest-descent method to conjugated gradient method, and then the Newton method. Molecular dynamics simulations were carried out for 200 ps to obtain the equilibrium status of systems under NPT (constant number of molecules, constant pressure, and constant