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Regular Article

Synergistic effect of mixing cationic and nonionic surfactants on corrosion inhibition of mild steel in HCl: Experimental and theoretical investigations

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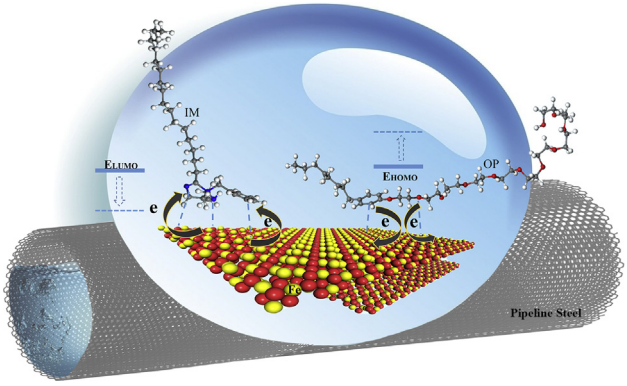
GRAPHICAL ABSTRACT



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ABSTRACT

We studied the inhibition performances of IMB (imidazoline quaternary salt (IM) and benzotriazole (BTAH)) and IMO (IM and octyl phenol ethoxylates (OP)) mixtures as inhibitors of L245 steel placed in 10 vol% HCl solution at 298 K using experimental methods and theoretical calculations. We found that the mixtures adsorb on the steel by an endothermic spontaneous process, and the adsorption model follows Langmuir isotherm. The mixtures exhibit good synergistic inhibition effect, and the inhibition efficiency enhanced in turn (IMB < IMO). The relationship between synergistic effect of organic inhibitors and their energetic position of molecular frontier orbitals was discussed.

1. Introduction

Pipeline steels suffered serious corrosion during oil and gas transportation [1–5]. The addition of inhibitors can effectively protect metals from corrosion. Lately, it has become a widely used

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method in materials corrosion and protection [6–13]. Mixed inhibitors will show good synergistic effect if they are suitably mixed [14–19], e.g., iodide ions works by bridging polyaspartic acid molecules and metal surface, and therefore showed good synergistic effect with polyaspartic acid [20]. However, the physical interactions are so weak that the adsorption stability and durability of inhibitors on metal surface are unsatisfied [21].

Organic inhibitors will chemically adsorb onto a metal surface through heteroatoms (N, O, S, P), double/triple bonds or aromatic rings [22–26]. It has been reported that the frontier orbital distributions of inhibitor molecules will change while inhibitor molecules interact with metal surface. Inhibitor molecule with a higher EHOMO (energy of the highest occupied molecular orbitals) will show larger electron donating ability, while inhibitor molecule with a lower ELUMO (energy of the lowest unoccupied molecular orbitals) will show larger electron accepting ability [27–34], metal surface worked as a platform for the freely flowing of electrons, till the system obtains an energy balance state [35]. While various inhibitor molecules co-adsorbed on a metal surface, it seems that the electron accepting/donating ability of inhibitor molecules can be influenced by other types of inhibitors, synergistically contributing to corrosion inhibition. Despite significant advances regarding the single component inhibitors and their corrosion inhibition mechanism, the mechanism of multiple inhibitor systems on the metal surface remains elusive.

Based on the aforementioned issues, imidazoline quaternary salt (IM), benzotriazole (BTAH) and octyl phenol ethoxylates (OP) were selected as the studying compounds. The inhibition performances of IM/BTAH, IM/OP mixtures were studied. The relationship between synergistic effect of inhibitor mixtures and their energetic position of molecular frontier orbitals was discussed.

2. Material and methods

2.1. Material preparation

Analytical grade OP (purity of 99%, Fig. 1(a)) and BTAH (purity of 99%, Fig. 1b) were used as received. IM (Fig. 1c) was synthesized using oleic acid, diethylene triamine and benzyl chloride with analytical grade as previously reported, and the purity of IM is over 95%[11]. IMO is a mixture of IM (80 wt%) and OP (20 wt%). IMB is a mixture of IM (80 wt%) and BTAH (20 wt%).

L245 pipeline steel with chemical composition (wt%) C (0.13%), Mn (0.76%), S (0.014%), P (0.022%), Si (0.24%) and Fe (balance) was used. The sample dimensions 50 mm × 10 mm × 3 mm were cut from L245 steel for the weight loss measurements. Columned samples sizes of ø12×5 mm were cut for electrochemical measurements. Before each experiment, the working electrode was mechanically abraded with emery paper beginning from 400 # to 2000 #. The electrode was rinsed with double-distilled water and dried in air.

2.2. Electrochemical tests

Electrochemical measurements were carried out in a conventional three-electrode cell, using CHI660E electrochemical workstation. The L245 steel was used as the working electrode. Two graphite rods were used as the counter electrodes. Saturated calomel electrode (SCE) with Luggin capillary salt bridge was used as the reference electrode. The purity of HCl is 38% and the test solution was 10 vol% HCl solution. 50 ppm BTAH, 50 ppm OP, 50 ppm IM, 100 ppm BTAH, 100 ppm OP, 100 ppm IM, 100 ppm IMB and 100 ppm IMO was added in the test solution, respectively. The test solution was bubbled with N_2 (99.999%) for 20 min and the open circuit potential (OCP) was recorded until a stable state reached. EIS measurements were carried out in a frequency range of 100 kHz to 0.1 Hz using a signal amplitude of 5 mV using a.c. mode at open circuit potential. Finally, potentiodynamic polarization tests were performed by polarization from −0.8 V to −0.2 V with a scan rate of 1 $mV{\cdot}s^{-1}$. All potentials reported here are referred to SCE. Three or four measurements were performed for each experimental condition. The linear Tafel segments of the cathodic curves were extrapolated to the corrosion potential to obtain the corrosion current density [36].

2.3. Weight loss tests

10 vol% HCl solution was used as test solution. A serious of weight loss tests were performed as follows,

(a) The effect of temperature (298 K, 313 K and 328 K) on the corrosion rate of L245 in the test solution without inhibitor.
(b) The effect of inhibitor concentration (20 ppm, 50 ppm, 100 ppm and 200 ppm) for IMB and IMO on the corrosion inhibition of L245 in the test solution under various temperatures (298 K, 313 K and 328 K).

Test solution was deoxygenated using high-purity N_2 (99.999%) for 2 h. Then, IMB or IMO was added into the test solution. Samples were immersed in the 10 vol% HCl test solutions for 8 h. Finally, samples were rinsed with double-distilled water and dried in air.

2.4. Scanning electron microscope measurements

L245 samples were immersed in the test solution without inhibitor and in the test solution with the addition of 100 ppm IMB or 100 ppm IMO for 8 h at 303 K. Then samples were rinsed with double-distilled water and dried in air. The microstructures of corroded sample surfaces were observed using scanning electron microscope (SEM, Quanta 200F field, FEI Inc.).

2.5. Calculation procedure

The frontier orbital energies of adsorbed inhibitor molecules were calculated. These calculations were carried out in gas phase by Dmol^3 module in Material Studio (Accelarys Inc.) software, all the calculations were performed using B3LYP function [37,38]. A double numerical basis set with polarization functions (DNP) [39–42] was used during these calculations.

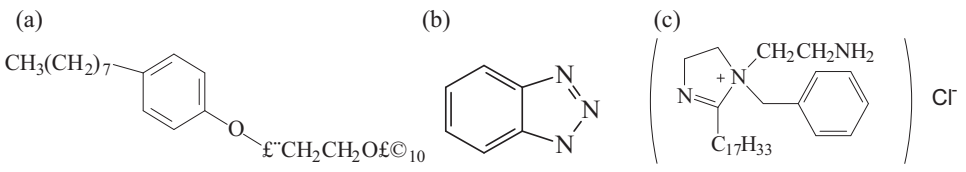

Fig. 1. Molecular structure of (a) OP, (b) BTAH, and (c) IM.