

Corrosion inhibition of a composite inhibitor containing imidazoline on carbon steel in simulated reverse osmosis product water of seawater

S.H. Liu,^{1*} Y.N. Wang,¹ B.X. Yuan,¹ W.T. Dong² and Q.Q. Liao¹

¹Shanghai University of Electric Power, Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, Shanghai 20009, China

²Shanghai Fakai Chemical Industry Co. Ltd., Shanghai 201505, China

E-mail: 15075088709@163.com

Abstract

The synergistic performance of corrosion inhibition of 2-undecyl-*N*-carboxymethyl-*N*-hydroxyethyl imidazoline (UHCI) and ZnSO₄ on 20# carbon steel surface in simulated reverse osmosis product water of seawater was investigated by electrochemical methods, scanning atomic force microscopy (AFM) and X-ray diffraction (XRD). The results show that the composite inhibitor acts as a mixed type inhibitor, reducing the corrosion of carbon steel effectively and the inhibition efficiency reaches the best values when the mass concentration ratio of UHCI and ZnSO₄ is 50 : 50 at the total concentration of the solution is 100 mg·L⁻¹ where the corrosion inhibition efficiency reaches 96.99%. The UHCI molecules adsorbed on metal surfaces, controlling the anodic reaction. ZnSO₄ is deposited on the metal surface in the form of Zn(OH)₂, controlling the cathodic reaction.

Keywords: carbon steel, composite inhibitor, simulated RO product water, polarization, EIS, AFM, XRD.

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1. Introduction

At present, with the increasing shortage of fresh water resource, the study on seawater desalination is attracting more and more attention. Reverse osmosis (RO) has increasingly become one of the main methods of seawater desalination [1, 2]; it has broad application prospects in the high water consuming industries, such as coastal iron and steel enterprises, coastal power plant, chemical factories, and in other fields [3]. However, due to carbon dioxide content, the RO product water presents a weak acid and the pH value is about 6.5, so it still has corrosivity on the water distribution network which uses carbon steel as its main material, threatening the safe operation of the water distribution network [4–7]. Some documents [8, 9] have reported that the corrosion rust layer of carbon steel in RO product water consists of inner layer Fe₃O₄ and outer layer γ -FeOOH. The studies of Yin [10] and Hu [11] show the primary reason for the high-speed corrosion of carbon steel in the RO product water is that the weak acid of the solution causes the γ -FeOOH

transforming into conductive Fe_3O_4 to be accelerated, and the rust layer is discontinuous, thus it cannot hinder the diffusion of oxygen. In order to improve the lifespan of the water distribution network, usually adding corrosion inhibitor in the RO product water [12, 13], exchanging the materials or adjusting the hardness and alkalinity of the RO product water to reduce the corrosion of the metal materials of the water distribution network.

The inhibitor, 2-undecyl-*N*-carboxymethyl-*N*-hydroxyethyl imidazoline (UHCI), used in this study is a kind of environmentally friendly inhibitor, which has been widely used in pickling and the liquid pipeline transportation [14–16]. However, there are few researches about the corrosion inhibition of imidazoline corrosion inhibitor and its composite corrosion inhibitor on carbon steel in RO product water. Therefore, in this paper, the performance of the corrosion inhibition of UHCI and ZnSO_4 on 20# carbon steel surface in simulated RO product water has been studied with electrochemical methods, and the inhibition mechanism is also discussed by surface analysis technique.

2. Experimental methods

2.1 Materials and chemicals

Experimental materials used in this work were 20# carbon steel, and the composition of the metal in wt.-% is C 0.17–0.23, Si 0.17–0.37, Mn 0.35–0.65, $\text{P} \leq 0.035$, $\text{S} \leq 0.035$, $\text{Cr} \leq 0.25$, $\text{Ni} \leq 0.30$, $\text{Cu} \leq 0.25$, bal. Fe. The size of the electrochemical samples was $10 \times 10 \times 2 \text{ mm}^3$, and the samples were welded with copper wires and sealed with an epoxy resin except the working face. The specimens were orderly polished with metallographic silicon carbide abrasive paper from 1# up to 6#. The oil contamination on the surface of the specimens was cleaned with ethanol, distilled water. The surface was then dried before the tests.

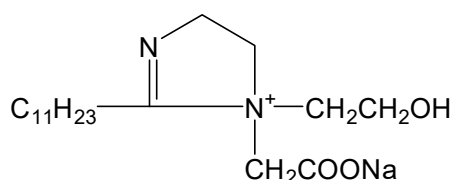


Figure 1. Structure of imidazoline.

The inhibitor, UHCI, used in the experiments, is a sodium salt, which was produced by Shanghai Fakai Chemical Industry Co. Ltd., Shanghai, China. The structure of UHCI is shown in Figure 1. The test solution, which simulated RO product water of seawater, is shown in Table 1.

Table 1. Composition of simulated RO product water.

Na^+ , $\text{mg}\cdot\text{L}^{-1}$	Ca^{2+} , $\text{mg}\cdot\text{L}^{-1}$	Mg^{2+} , $\text{mg}\cdot\text{L}^{-1}$	Fe^{3+} , $\text{mg}\cdot\text{L}^{-1}$	Cl^- , $\text{mg}\cdot\text{L}^{-1}$	SO_4^{2-} , $\text{mg}\cdot\text{L}^{-1}$	HCO_3^- , $\text{mg}\cdot\text{L}^{-1}$	CO_2 , $\text{mg}\cdot\text{L}^{-1}$	Conductivity, $\mu\text{S}\cdot\text{cm}^{-1}$	pH
52.47	0.3000	0.06000	0.09100	79.00	1.578	3.722	2.376	238.0	6.54

2.2 Electrochemical measurements

An EG&G Princeton Applied Research model 2273 Potentiostat/Galvanostat was used to perform the electrochemical experiments, which were done in a conventional three-electrode cell with a saturated calomel electrode (SCE) as the reference electrode (RE), a platinum counter electrode (CE), and 20# carbon steel as the working electrode (WE). The flow conditions in the experimental process were simulated by rotation coupon instrument, with rotating speed of 95 rpm (linear speed 0.4 m/s) [17]. EIS measurements were carried out using a sinusoidal potential perturbation of 5 mV in a frequency range from 0.05 Hz to 100 kHz. Polarization curve was recorded in the potentials region ± 250 mV (vs. OCP) with a sweep rate of $1 \text{ mV} \cdot \text{s}^{-1}$. All the potential values were referred to SCE and the temperature during the measurements was ambient temperature.

2.3 Surface analysis

AFM analysis of the surface was performed with Agilent 5500AFM/SPM. The chemical composition of the surface of the specimens in test solutions was investigated by XRD. BRURER D8 ADVANCE X-ray diffraction instrument was used to determine the composition of the surface film and the result was analysed by Jade 6.0 software.

3 Results and discussion

3.1 Polarization curve measurement

Figure 2 shows the polarization curves of carbon steel electrodes in simulated RO product water with different concentration ratios of UHCl and ZnSO_4 after one day of immersion. The result, corrosion potential (E_{corr}), corrosion current density (i_{corr}) and inhibition efficiency (η_1), fitted by the PowerSuite software, is listed in Table 2. The inhibition efficiency (η_1) is obtained from the corrosion current density according to:

$$\eta_1 = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100\%, \quad (1)$$

where i_{corr}^0 is the corrosion current density of specimens after immersion in simulated RO product water for one day without inhibitor, i_{corr} is the corrosion current density of specimens after immersion in simulated RO product water for one day with different concentration ratios of UHCl and ZnSO_4 .

Compared with the blank sample, both the cathodic polarization curves and the anodic polarization curves are changed after adding the inhibitor, as shown in Figure 2. The current density of cathode and anode are decreased, it indicates that the inhibitor belongs to mixed corrosion inhibitor[18], which can inhibit the cathodic reaction as well as the anodic reaction. According to the Table 2, with the increase of UHCl proportion, the corrosion potential moves to a positive direction, the corrosion current density, however, firstly decreases and reaches the minimum when the mass concentration ratio of UHCl and

ZnSO₄ is 50:50; then increases with the concentration of UHCl continue increases to 100 mg·L⁻¹. It suggests that the inhibitor has the best inhibition effect when the ratio of UHCl and ZnSO₄ is 50:50. In the case of equal total concentration, the corrosion current density of the composite inhibitor is smaller than that of single UHCl or ZnSO₄, it can be explained by the synergistic effect of UHCl and ZnSO₄.

Table 2. The fitting results of polarization curves.

UHCl : ZnSO ₄ , mg·L ⁻¹	E_{corr} , mV (vs. SCE)	i_{corr} , $\mu\text{A}\cdot\text{cm}^{-2}$	η , %
0	-654.8	64.79	0
100 UHCl	-399.9	20.80	67.89
100 ZnSO ₄	-661.9	58.75	9.320
20 : 80	-647.4	49.98	22.86
40 : 60	-624.7	8.360	87.09
50 : 50	-580.1	1.945	96.99
60 : 40	-569.2	3.951	93.90
80 : 20	-515.9	4.889	92.45

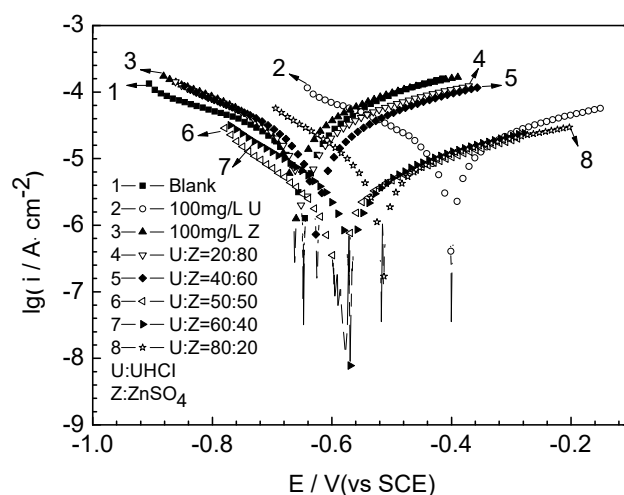


Figure 2. Polarization curves of carbon steel electrodes in simulated RO product water with different ratios of UHCl and ZnSO₄.

3.2 EIS studies

The Nyquist plots and Bode plots of carbon steel electrodes in simulated RO product water for one day with different mass concentration ratios of UHCl and ZnSO₄ are shown in Figure 3. Table 3 gives the fitting results of the Zsimpwin software. The inhibition efficiency (η_2) is calculated using charge transfer resistance (R_{ct}) as follows:

$$\eta_2 = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100\%, \quad (2)$$

where R_{ct} and R_{ct}^0 are the charge transfer resistance in different mass concentration ratios of UHCl and $ZnSO_4$ and blank solution after one day immersion, respectively.

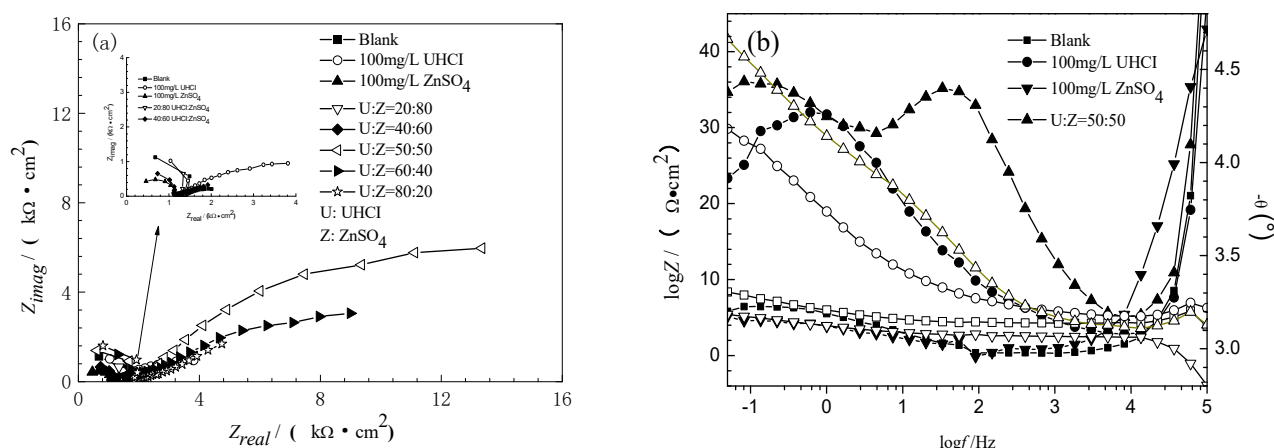


Figure 3. The Nyquist plots and Bode plots of carbon steel electrodes in simulated RO product water with different ratios of UHCl and $ZnSO_4$

Table 3. Electrochemical parameters of the equivalent circuits obtained by fitting the experimental results of EIS.

Concentration, $mg \cdot L^{-1}$	$R_s,$ $k\Omega \cdot cm^2$	$R_f,$ $k\Omega \cdot cm^2$	$CPE_f,$ $\mu\Omega^{-1} \cdot cm^{-2} \cdot s^n$	$R_{ct},$ $k\Omega \cdot cm^2$	$CPE_{dl},$ $\mu\Omega^{-1} \cdot cm^{-2} \cdot s^n$	$\eta_2,$ %
0	1.365	–	–	1.011	1116	–
100 UHCl	1.265	–	–	4.102	1067	75.35
100 $ZnSO_4$	1.447	–	–	1.121	2039	9.810
20 : 80	1.526	1.210	536.2	1.480	79.83	31.69
40 : 60	1.484	1.094	385.4	3.804	69.24	73.42
50 : 50	1.225	1.640	21.55	27.21	62.36	96.28
60 : 40	1.539	1.097	11.07	12.30	127.2	91.78
80 : 20	1.168	5.705	7.317	10.03	47.27	89.92

As shown in Figure 3(a), with an increase in the ratio of UHCl and $ZnSO_4$, the capacitive impedance loops initially increase and then reduce when the concentration of the solution is 100 mg L^{-1} , which indicates that the composite inhibitor has good corrosion inhibition for carbon steel in simulated RO product water. Among all the impedance loops,

it is the biggest when the mass concentration ratio of UHCl and ZnSO_4 is 50:50, indicating that the inhibition effect reaches the best as the ratio is 50:50. Figure 3(b) shows that there is only one time constant in the Bode diagram of blank solution and the single presence of UHCl and ZnSO_4 , while there are two time constants after adding the composite inhibitor. Therefore, it can be explained by the equivalent circuit models of EIS in Figure 4(a) and (b). R_s represents the solution resistance, constant phase angle element CPE is used to replace capacitance because of the exist of dispersion effect, the parameter CPE_f represents the capacitive behavior of the film formed by the action between the corrosion inhibitors and metal surface, coupled with a film resistance R_f . CPE_{dl} describes the electric double-layer capacitance, in parallel with charge transfer resistance R_{ct} . The fitted parameters of the Nyquist plots are listed in Table 3. The data in Table 3 illustrates that adding UHCl and ZnSO_4 , the inhibitive efficiency for carbon steel are 75.35% and 9.81%, respectively, on condition that the total concentration is $100 \text{ mg}\cdot\text{L}^{-1}$. Comparing the two data, it can be found that UHCl has certain corrosion inhibition for carbon steel in simulated RO product water, but only to add ZnSO_4 , the corrosion inhibition is not obviously. The inhibitive efficiency is improved visibly after adding the UHCl and ZnSO_4 simultaneously, and as the proportion of UHCl increased, the value of the inhibitive efficiency firstly increased, continuously come up to a peak value (96.28%), when the concentration of UHCl is $50 \text{ mg}\cdot\text{L}^{-1}$, then let up while the concentration is increased. It tells that the best ratio of UHCl and ZnSO_4 is 50:50, which shows a good consistency with Figure 3.

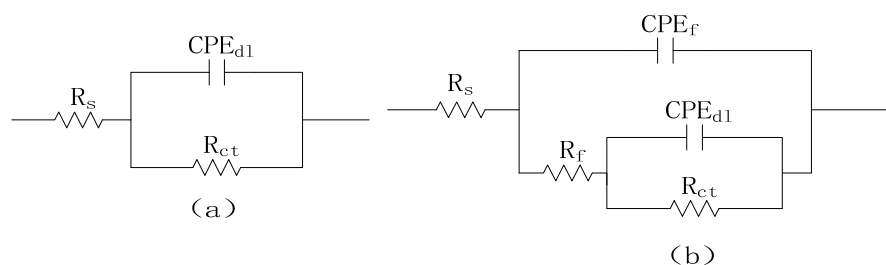


Figure 4. Equivalent circuit models of EIS.

3.3 Surface analysis

Figure 5 demonstrates the AFM images of carbon steel specimen immersed in simulated RO product water for one day without additives and with the mass concentration ratio of $\text{UHCl}:\text{ZnSO}_4 = 50:50$, respectively. As shown in Figure 5(a), after immersion in the blank solution for one day, severe corrosion occurred on the surface of the electrode, and the surface was rough, while, in the solution with composite inhibitor, the surface of the electrode was smooth and almost no corrosion phenomenon happened. This is due to the composite inhibitor prevented the mass of the charge transfer, slowing down the corrosion of carbon steel effectively.

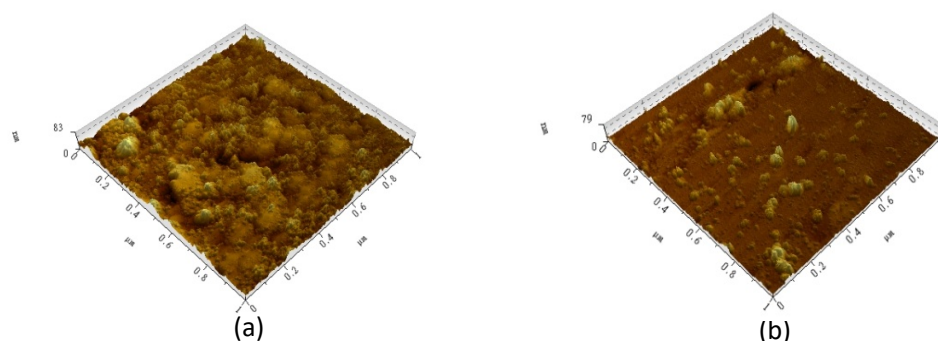


Figure 5. AFM images of the carbon steel specimens immersed in simulated RO product water for 1 day with different additives: (a) blank, (b) UHCl : ZnSO₄ = 50 : 50.

3.4 XRD analysis

Figure 6 presents XRD spectra of carbon steel specimen after immersion in simulated RO product water with 100 mg·L⁻¹ ZnSO₄ for one day. It clearly shows that the surface of the metal contains ZnCl₂ and Zn(OH)₂, from which it can be inferred that the corrosion inhibition of ZnSO₄ for carbon steel is owing to the formation of Zn(OH)₂ on the surface.

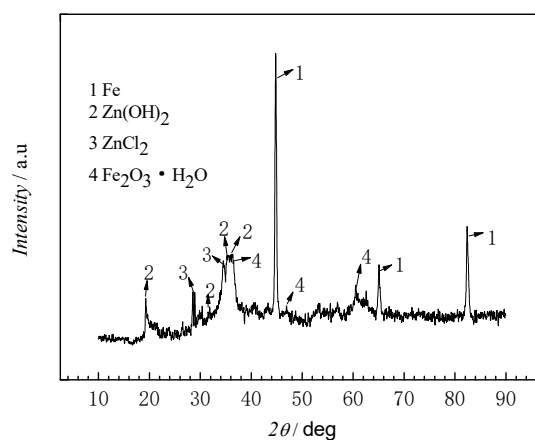


Figure 6. XRD spectra of carbon steel specimens immersed in simulated RO product water for 1 day with 100 mg·L⁻¹ ZnSO₄.

4. Conclusions

When the total concentration is 100 mg·L⁻¹ and the ratio of UHCl and ZnSO₄ is 50 : 50, the corrosion inhibition for carbon steel immersed in simulated RO product water is best. The conclusions made from polarization curve measurements and EIS studies have good consistency.

The composite inhibitor is a mixed corrosion inhibitor. UHCl inhibits anode reaction and adsorbs on the metallic surface, preventing corrosion medium diffusion to the metallic surface while ZnSO₄ inhibits the reaction of cathode in the form of Zn(OH)₂ deposits on the metallic surface.

Acknowledgements

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