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Study on the Synthesis and Corrosion Inhibition Performance of Mannich-Modified Imidazoline

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Abstract

A novel Mannich-modified imidazoline (MMI) as cationic emulsifier was synthesised for corrosion harm reduction, through three steps — acylation, cyclization, and Mannich reaction. The surface activity was characterized by determination of surface tensions and critical micelle concentration (CMC). The corrosion inhibition performance of five types of steels in the simulated corrosion solution in the presence of the MMI was investigated by static weight loss tests. The results showed that the MMI had good surface activities, with CMC of 19.8 $\mu g\,g^{-1}$ and surface tension of 36.4 $mN\,m^{-1}$. The corrosion test results indicated that the corrosion rates of different materials were decreased significantly, and degrees of corrosion inhibition were always higher than 80.0 %. The main inhibition mechanism was most likely due to the adsorption of the corrosion inhibitor on the steel surface, leading to the prevention of corrosion medium from the metal surface.

Keywords

Mannich, emulsifier, imidazoline, CMC, corrosion inhibition

1. Introduction

As environmental awareness is increasing and energy costs are rising, many industries are seeking solutions for pollutant emissions and energy consumption. The asphalt industry and its agency partners are also constantly seeking ways to improve pavement performance, increase construction efficiency, conserve resources, and advance environmental stewardship. Emulsified asphalt has the advantages of convenient construction, higher energy-efficiency, and less emissions compared with hot-mix asphalt.[1] Taking into account these benefits, the requirements of saving energy and reducing pollution have been satisfied under the situations and circumstances of the energy shortage and environmental crisis.[2,3]

As the core technology, the emulsifier plays a crucial role in the performance of emulsified asphalt.[4,5] It is well known that cationic emulsifier is one of the most important types of asphalt emulsifier, because of its ability to bond well with the aggregate.[6,7] However, the issue here is that the current widespread cationic asphalt emulsifiers are usually used in acidic systems by adjusting the pH value to less than 5 with hydrochloric acid before the preparation of the emulsion. The steel, which is the main material of the emulsification equipment, is exposed to the corrosive medium in the process of adding hydrochloric acid. We investigated the corrosion problem and found that the corrosion rate of N80 steel in the hydrochloric acid solution with pH = 1 at 90 °C was 63.45 $g\,m^{-2}\,h^{-1}$. Although many kinds of cationic emulsifiers have a certain corrosion inhibition performance because of the nitrogen-containing group,[8–10] the effect was not satisfying, especially if the local concentration of HCl and the temperature are much higher. In this paper, a novel modified imidazoline as cationic emulsifier was synthesised for corrosion harm reduction. The corrosion problem was investigated in a simulated asphalt-emulsion-producing process. The corrosion test was undertaken to elucidate the inhibiting effect of the emulsifier on different kinds of steel in HCl solutions under varied corrosion conditions. Further, the surface of the test steel was analysed by scanning electron microscopy (SEM), and the adsorption mechanism of the emulsifier on the N80 steel surface was discussed.

2. Experimental

2.1 Materials

Tetraethylenepentamine, lauric acid, methanal, acetone, hydrochloric acid, petroleum ether, xylene, and anhydrous alcohol, were chemically pure and provided by Sinopharm Chemical Reagent Co., Ltd.

2.2 Methods

2.2.1 Synthesis of the MMI

The modified imidazoline emulsifier investigated in this study was synthesized in our laboratory. Lauric acid (0.40 mol), tetraethylenepentamine (0.44 mol), and xylene (80 cm^3) were added to a round-bottomed flask equipped

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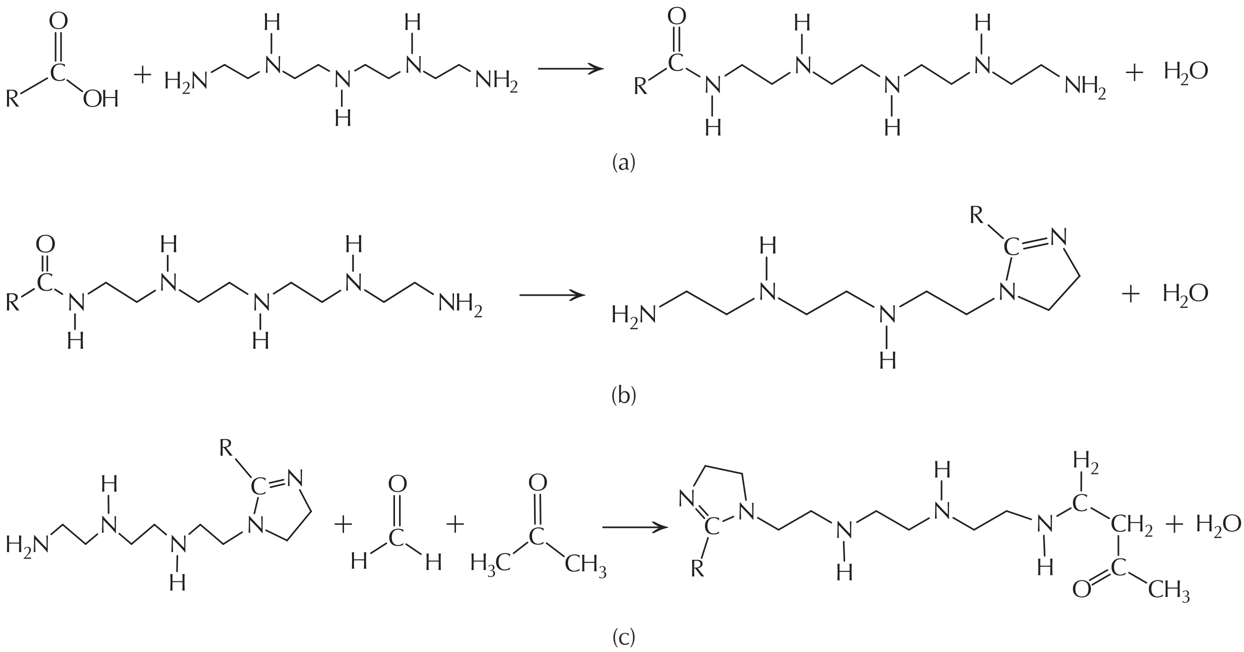


Fig. 1 – Schematic of synthetic steps (a: acylation, b: cyclization, c: Mannich reaction)
Slika 1 – Shematski prikaz koraka sintetiziranja (a: acilacija, b: ciklizacija, c: Mannichova reakcija)

with a magnetic stirrer, temperature thermocouple, and backflow apparatus. Upon being heated under reflux at 150 °C, the whole reaction mixture was stirred for 3.5 h, and 6.8 cm^3 of the water produced in the reaction was collected, which indicated that the acylation reaction was 94 % complete. After xylene was distilled, the temperature of the reaction system was elevated to 240 °C, and the vacuum degree was kept at 0.096 MPa using vacuum pump for 4 h. The cyclization reaction occurred in the process. The reaction process was monitored by the on-line infrared test system (React IR ic10). This system is based on the principle of infrared (IR) spectroscopy, through the determination of characteristic absorption peak strength change in real-time monitoring of the reaction process.

Finally, the Mannich reaction occurred with addition of methanal (0.4 mol) and acetone (0.4 mol) to the intermediate, and the final product 4-((2-((2-((2-(2-undecyl-4,5-dihydro-1H-imidazol-1-yl)ethyl)amino)ethyl)amino)ethyl) amino)butan-2-one coded as MMI was gained. The schematic of synthetic steps is shown in Fig. 1.

2.2.2 IR and surface activity determination of the MMI

The infrared absorption spectrums of the intermediate and the final products were monitored by Thermo Nicolet NEXUS FT-IR spectrometer at 2 cm^{-1} resolution. The measurement of surface tension and the critical micelle concentration (CMC) at 25 °C were carried out by TX500C interfacial tension meter.

2.2.3 The corrosion inhibition performance of the MMI

The corrosion inhibition performance of the MMI was investigated by static weight loss tests in the simulated corrosion solutions. The surface morphologies of specimens after immersion in HCl solution for 4 h, in the absence and presence of the MMI at different temperatures, were performed by SEM. The accelerating voltage was 20.0 kV.

3. Results and Discussion

3.1 Synthesis of the MMI

The synthetic installation is shown in Fig. 2. After the substrates were added into the reactor, the infrared-line testing system (React IR ic10) probe was put into the reaction system to monitor the characteristic infrared absorption peaks of the reaction system in real-time, and the data were recorded on the computer.

The three-dimensional stack plot of the IR spectra in the reaction process of lauric acid and tetraethylenepentamine is shown in Fig. 3. The x, y and z axes were, respectively, for wave-number, absorption intensity, and reaction time. The wavenumber of 1708 cm^{-1}, 1555 cm^{-1}, and 1609 cm^{-1} were respectively the absorption peaks of HO−C=O, O=C−NH and C=N.[11,12] It can be seen in Fig. 3 that the characteristic wavenumbers of the absorption peaks were changing along with the reaction time, indicating material concentration changes. The characteristic peak at

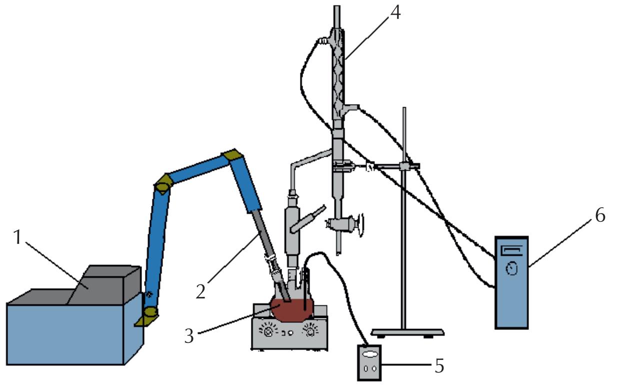


Fig. 2 – Experimental device for emulsifier synthesis
1 – ReactIR ic10 online IR spectroscopy detector; 2 – IR detector probe; 3 – reaction system; 4 – reflux condenser system; 5 – thermocouple thermometer; 6 – cooling water circular system

Slika 2 – Eksperimentalni uređaj za sintezu emulgatora
1 – *on-line* IR-spektroskop ReactIR ic10; 2 – IR-spektroskopska sonda; 3 – reakcijski sustav; 4 – povratno hladilo; 5 – termoparni termometar; 6 – vodeno hlađenje

1708 cm^{-1} is the peak of stretching vibration of carbonyl groups in the organic acid. When organic amine was added, the 1708 cm^{-1} wavenumber rapidly disappeared and the amide (O=C−NH) absorption peak at 1555 cm^{-1} appeared at the same time. This result indicated that the amidation reaction of organic acids and organic amine was a rapid reaction, and that synthesis had proceeded between lauric acid and tetraethylenepentamine after the latter had been added. Then, rising the reaction temperature to 240 °C for 4 h, the absorption peak intensity of O=C−NH at 1555 cm^{-1} decreased and C=N at 1609 cm^{-1} increased gradually. This indicated that the amide was transformed into imidazoline. After 4 h, the absorption peak intensity of C=N became flat and the reaction basically reached equilibrium.

The infrared absorption spectrums of the intermediates and the final product MMI are shown in Fig. 4. With an identified result of the infrared-line test, it was observed that there was no 1609 cm^{-1} absorption peak during the acylation reaction, indicating that the cyclization reaction could not occur at the relatively low temperature, and was independent of the acylation reaction. At the end of the cyclization reaction, the 1555 cm^{-1} and 1630 cm^{-1} absorption peaks, which were characteristic peaks of in-plane bending vibration of amine group, were rarely found in the imidazoline product, while the 1609 cm^{-1} peak was found, revealing that the amide had completely transformed into imidazoline. The wavenumber of 1739 cm^{-1} was the characteristic absorption peaks of C=O, which was found in the final product, demonstrating that the Mannich reaction had occurred, and the target product of the MMI had been gained.

3.2 Surface activity determination of the MMI

The surface tensions of emulsifier aqueous solution of different concentrations were determined at 25 °C and the critical micelle concentration (CMC) was calculated.

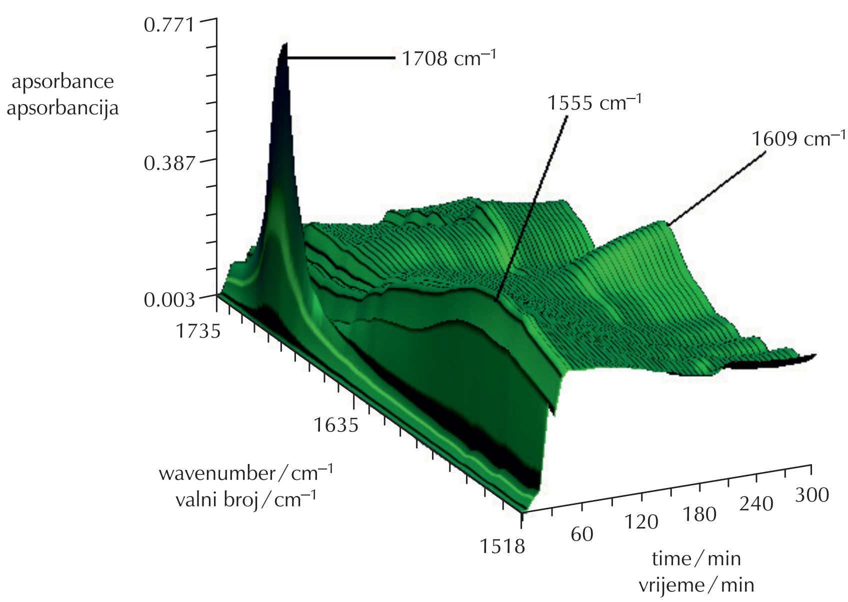


Fig. 3 – Three-dimensional stack plot of the IR spectra from 1800 cm^{-1} to 1500 cm^{-1}

Slika 3 – Trodimenzionalni prikaz IC spektra od 1800 cm^{-1} do 1500 cm^{-1}

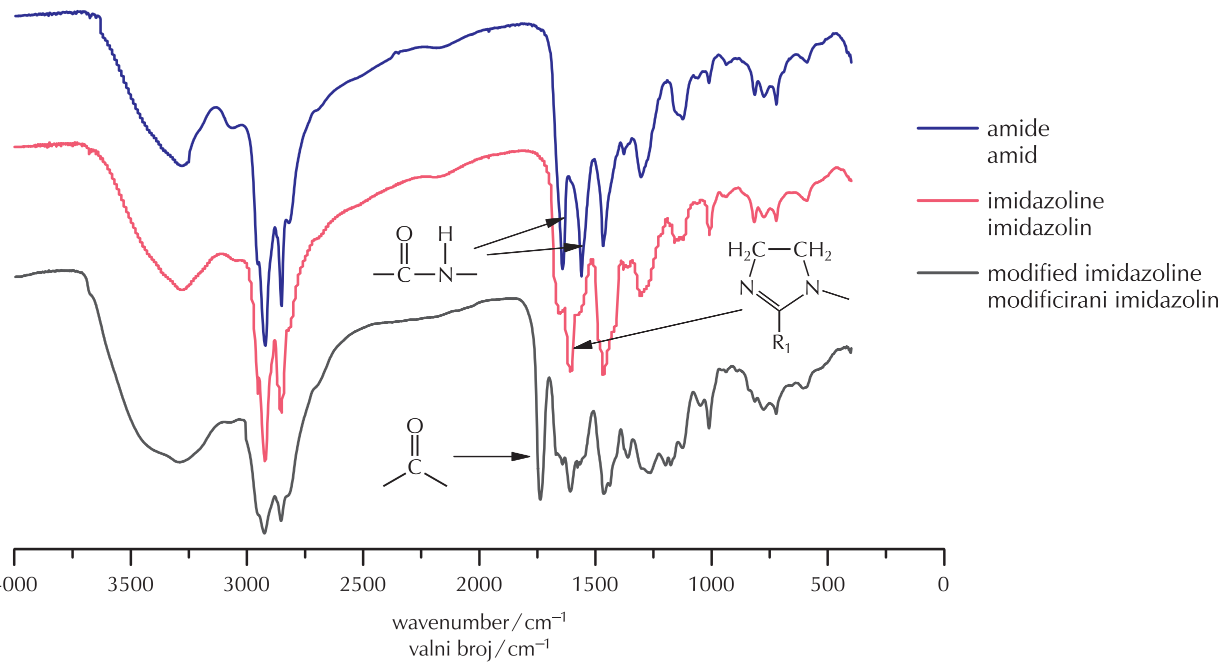


Fig. 4 – Infrared spectrum of the intermediates and the final products
Slika 4 – Infracrveni spektar međuprodukata i konačnih produkata

The results are shown in Fig. 5. It can be seen from Fig. 5 that the MMI was able to reduce the surface tension to 36.4 mN m^{-1} and the CMC was 19.8 μg g^{-1}, indicating that the synthetic asphalt emulsifier had good surface activity and performance.

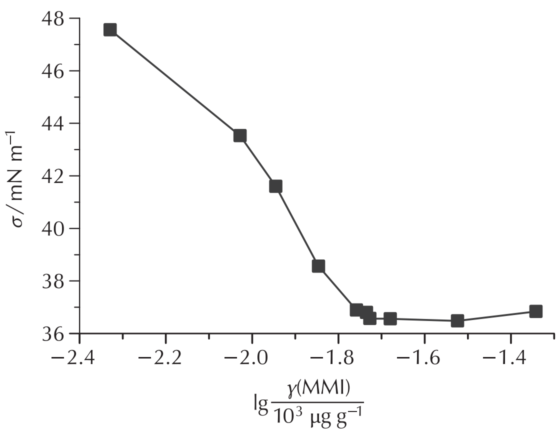


Fig. 5 – Plot of the lg γ(MMI) *vs.* σ
Slika 5 – Odnos logaritma koncentracije MMI-ja i površinske napetosti

3.3 Corrosion inhibition performance of the MMI

The current widespread cationic asphalt emulsifiers are usually adjusted to pH value of 2–5 with hydrochloric acid before the preparation of the emulsion. Only under such conditions could the emulsifiers be converted to cationic, and play an effective role in the emulsion system. Therefore, the potential risk of corrosion may occur in the process of asphalt emulsion production, such as in the emulsifier aqueous solution storage tank at pH adjustment, in the colloid mill, pump, and the pipeline during asphalt emulsion preparation. The corrosion inhibition performance of the MMI was investigated by static weight loss tests under the simulated corrosion situations of the emulsion manufactory. The results are summarized in Table 1.

It can be seen from Table 1 that the corrosion rate v_{corr} of the blank test was very high (63.45 g m^{-2} h^{-1}, when the pH value was 1.0). However, the corrosion rates had decreased significantly in the presence of the MMI. All of the degrees of corrosion inhibition η at various pH value were higher than 86.00 %. The MMI showed a satisfactory performance of corrosion inhibition.

Table 1 – Corrosion inhibition performance of MMI in aqueous solution (N80 steel, temperature 90 °C, and corrosion time 4 h)
Tablica 1 – Inhibicija korozije u vodenoj otopini MMI-ja (čelik N80, temperatura 90 °C, trajanje korozije 4 h)

pH	w(MMI) / %	v_{corr} / g m^{-2} h^{-1}	η / %
1.0	0	63.45	97.23
	1.5	1.76	
2.0	0	18.14	96.42
	1.5	0.65	
3.0	0	3.55	87.04
	1.5	0.46	
4.0	0	1.65	86.06
	1.5	0.23	

The corrosion inhibition performance of the modified imidazoline emulsifier on the different materials is shown in Table 2. It can be observed from Table 2 that the corrosion resistance of N80 was the worst in the absence of the MMI, while that of 022Cr17Ni12Mo2, which is a kind of stainless steel, was the best. Q345A and Q235 had similar abilities of corrosion resistance because of the similar chemical composition. The corrosion rates had decreased significantly in the presence of MMI, indicating good corrosion inhibition on different materials.

Table 2 – Corrosion inhibition performance of MMI on different materials in aqueous solution (pH = 1.0, temperature 90 °C, and corrosion time 4 h)

Tablica 2 – Inhibicije korozije različitih materijala u vodenoj otopini MMI-ja (pH = 1,0, temperatura 90 °C, trajanje korozije 4 h)

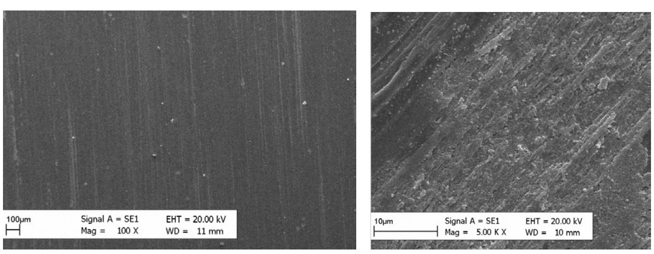
Material* Materijal*	w(MMI) / %	v_{corr} / $g\,m^{-2}\,h^{-1}$	η / %
N80	0	63.45	97.23
	1.5	1.76	
Q345A [Gr.50]	0	10.52	83.93
	1.5	1.69	
Q235 [A283GRC]	0	9.66	86.44
	1.5	1.31	
20 [1020]	0	8.61	85.37
	1.5	1.26	
022Cr17Ni12Mo2 [S31603]	0	3.03	81.19
	1.5	0.57	

* Designations in brackets are the ASTM designations

* U uglatim zagradama navedene su oznake ASTM-a

3.4 Surface analysis of the steel and the mechanism discussion

Fig. 6 presents the surface morphologies of the original steel and the steel immersed in HCl solution for 4 h in the presence of MMI. The original steel showed a clean surface, while the steel immersed in HCl solution in the presence of MMI (w = 1.5 %) showed only a few corrosion products and an adsorption film.



(a) (b)

Fig. 6 – SEM images of the steel surface (a: original steel; b: steel immersed in HCl solutions of pH = 1.0 in the presence of MMI, w = 1.5 %)

Slika 6 – SEM slike površine čelika (a: početni čelik; b: čelik uronjen u otopinu HCl, pH = 1,0, uz MMI, w = 1.5 %)

This was mainly due to the hydrophilic group which was composed of imidazoline ring and carbonyl group.[13–15] The MMI was easily absorbed on the surface of the steel through N atom and C=O with lone pair electrons. Furthermore, the long chains of nonpolar lipophilic group extended toward water to prevent the corrosion medium from the metal surface.

4. Conclusion

In this paper, a novel Mannich-modified imidazoline (MMI) was synthesized and used as asphalt emulsifier for the first time. The MMI investigated in this work was proved to decrease the corrosion risk in the asphalt emulsion preparation process. The MMI exhibited a superior surface activity and inhibition performance in the simulated corrosion solution. It was able to significantly decrease the corrosion rate and effectively increase the corrosion resistance of the different steels in the HCl solution. The SEM analysis showed that a film had formed on the steel surface after 4 h of immersion in the presence of MMI, w(MMI) = 1.5 %. This organic adsorption film prevented the corrosion medium from the metal surface.

List of symbols and abbreviations
Popis simbola i kratica

CMC – critical micelle concentration, $\mu g\,g^{-1}$
– kritična micelizacijska koncentracija, $\mu g\,g^{-1}$

MMI – Mannich-modified imidazoline
– imidazolin modificiran Mannichom reakcijom

v_{corr} – corrosion rate, $g\,m^{-2}\,h^{-1}$
– brzina korozije, $g\,m^{-2}\,h^{-1}$

w – mass fraction, %
– maseni udjel, %

γ – mass concentration, $\mu g\,g^{-1}$
– masena koncentracija, $\mu g\,g^{-1}$

η – degree of corrosion inhibition, %
– stupanj inhibicije korozije, %

σ – surface tension, $mN\,m^{-1}$
– površinska napetost, $mN\,m^{-1}$

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SAŽETAK

Sinteza i inhibicija korozije imidazolina modificiranog Mannichovom reakcijom

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Radi smanjenja oštećenja od korozije, Mannichovom reakcijom sintetiziran je kationski emulgator, derivat imidazolina (MMI), u tri stupnja: acilacija, ciklizacija i Mannichova reakcija. Površinska aktivnost određena je površinskom napetošću i kritičnom micelizacijskom koncentracijom (CMC). Inhibicija korozije uz MMI istražena je u korozivnoj otopini preko gubitka mase na pet vrsta čelika. MMI pokazuje dobru površinsku aktivnost, pri CMC = 19,8 $\mu g\, g^{-1}$ površinska napetost iznosi 36,4 $mN\, m^{-1}$. Brzine korozije različitih materijala značajno su se smanjile, a stupanj inhibicije korozije uvijek je bio iznad 80 %. Inhibicija korozije najvjerojatnije se događa zbog adsorpcije inhibitora na površinu čelika čime je spriječen kontakt otopine i metalne površine.

Ključne riječi

Mannichova reakcija, emulgator, imidazolin, CMC, inhibicija korozije

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