Corrosion Science 50 (2008) 2166–2171

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Corrosion inhibition of dibenzo [1,4,8,11] tetraaza [14] annulene nickel on steel in 1 M HCl

Peng Zhao *, Cheng Zhong, Lei Hunag, Lihong Niu, Fushi Zhang

The Key Lab of Organic Photoelectrons and Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, 100084 Beijing, China

ARTICLE INFO

Article history:
Received 1 December 2007
Accepted 12 June 2008
Available online 20 June 2008

Keywords:
Acid inhibition
Steel
EIS
Potentiodynamic
XPS

ABSTRACT

Dibenzo [1,4,8,11] tetraaza [14] annulene nickel (TAA-Ni) has been synthesized and its inhibitive behavior on mild steel in 1 M HCl was firstly investigated by gravimetric, potentiodynamic and impedance method. The potentiodynamic curves indicate the TAA-Ni mainly acted as mixed type inhibitor on electrochemistry in acid media. The weight loss result indicates TAA-Ni is good inhibitor in acid solution with the temperature changing from 303 K to 333 K. The XPS experiment indicates the protonation of TAA-Ni and its chemical adsorption on steel surface.

1. Introduction

Corrosion inhibitor can effectively reduce the corrosion rate of metallic materials in acid solution and has been widely applied in acidic cleanout, crude oil refine, electrochemical and chemical etching [1]. In order to avoid excessive corrosion and the risk of stress crack caused by longtime immersion in Cl^- and H^+ solution [2–3], high temperature and short time condition are desirable in acidic cleaning. The equipment in crude oil refine production also encounters high temperature acidic media and need inhibitor working at high temperature. In many researches, attention has been paid to inhibitors [4–7] which can be working at 313 K or 333 K. However, the corrosion rate may accelerate at 10–100 times with 10–20 K temperature increasing when using unfitted inhibitors, because the organic inhibitor usually takes effect by forming adsorptive layer on metal surface. The strength of this adsorption is at the intervenient of physical adsorption and chemical binding [8–9]. The layer would be extensively destroyed by temperature elevation and make the inhibitor unavailable.

Furthermore, the temperature elevation can improve the protonation of nitro-contained compounds in acid solution; some amine compounds [10–11] exhibit good inhibitive effect in acid solution with increasing temperature. Compared to hexa or penta heterocyclic compounds, larger conjugated system compounds, phthalocyanine [12–13] has already been investigated by previous work but its inhibitive effect is limited to its bad solubility and self-aggregation in solution. Dibenzo annulene compound [14] has moderate conjugated system with 14 π electrons and high electric density on molecular orbital. Also the annulene has higher capability to protonate and lower aggregation trend than phthalocyanine, which perhaps facilitates its inhibitive effect at high temperature. From another point, dibenzo [1,4,8,11] tetraaza [14] annulene nickel (TAA-Ni) only dissolves in acidic solution below pH 2 (0.01 M HCl or 0.005 M H_2SO_4). When the pH value increases to more than 5, it will precipitate out. It is convenient for the recycle of the inhibitor in repeating application. So far as we know, no corrosion inhibitive behavior of annulene compounds has been ever reported in any document.

In this article, we tried to investigate the inhibitive effect of TAA-Ni on mild steel in 1 M HCl at different temperatures. The weight loss, potentiodynamic and impedance methods were employed to determine the corrosion rate and inhibited mechanism. The protonation of TAA-Ni in adsorption layer with temperature varying was also probed by XPS analysis. We expect the result would be helpful to evaluate more inhibitor from macrocyclic aza compounds.

2. Materials and methods

Dibenzo [1,4,8,11] tetraaza [14] annulene nickel (TAA-Ni) was synthesized and characterized based on the references of previous literature (shown in Scheme 1) [14].

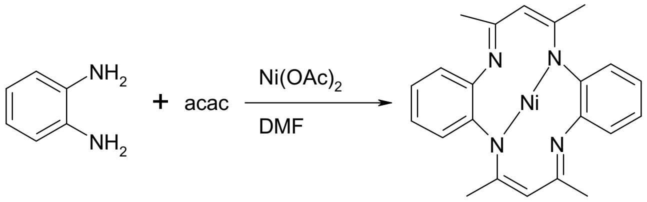
Mild steel samples, whose chemical composition includes C 0.17, Si 0.78, Mn 0.85, S 0.017, Fe bal., were used for experiments.

1 M HCl solutions were prepared by dilution of 37% HCl in bi-distilled water. The concentration of TAA-Ni was 1.0×10^{-5}–5.0×10^{-3} M.

---

* Corresponding author. Tel.: +86 10 62782456; fax: +86 10 62770304.
E-mail address: alfred9807@hotmail.com (P. Zhao).

0010-938X/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.corsci.2008.06.015



Scheme 1. The synthesis of dibenzo [1,4,8,11] tetraaza [14] annulene nickel.

Specimens used in the weight loss experiment were cut into desired dimension and polished with SiC paper 400, 600 grit. The specimens in triplicate for each inhibitor concentration were immersed in the test acid solutions for 3 h at 303 K, 313 K and 333 K, respectively. A semi-sealed refluxed flask was employed to avoid the volatilization of HCl at 333 K. The temperature was controlled by an aqueous thermostat. After treatment of the samples, the loss in weight was determined by analytic balance. The inhibition efficiency IE%, surface coverage degree θ and corrosion rate V_{corr} were obtained by

$$\mathrm{IE\%} = (W_0 - W)/W_0 \times 100 \quad (1)$$

$$\theta = (W_0 - W)/W_0 \quad (2)$$

$$V_{\mathrm{corr}} = (W_0 - W)/st \quad (3)$$

W_0 and W are the weight losses in the absence and presence of the inhibitor, respectively, S is samples surface area, t is immersion time, the unit of V_{corr} converses to g m^{-2} h^{-1} and mm y^{-1}.

In electrochemical measurement the steel specimen was sealed by epoxy resin with exposure surface (10.8 mm × 10.8 mm) as working electrode. The working surface was polished with SiC emery papers to 1000 grit. Electrochemical experiments were performed on a conventional three-electrode cell. The measurement used a CHI 6600 (Shanghai Chenhua) Electrochemical Station. EIS measurement was carried out on steady state open circuit potential disturbed with amplitude of 10 mV a.c. sine wave. The frequency range is 100 kHz–10 mHz. The potentiodynamic polarization curves were obtained from −300 mV vs. OCP to +300 mV vs. OCP with scan rate of 0.5 mV s^{-1}.

The XPS measurements were performed using a PHI Quantera SXM Scanning X-ray Microscope with an Al Kα monochromated source ($h\nu$ = 1 486.6 eV). The energy analyzer was using 25 eV pass energy with 0.5 eV step^{-1}. The contaminated C1s peak (282.45 eV) was used as internal reference for calibration of the binding energy scale. The spectrum of adsorptive inhibitor on aluminum surface was obtained after a 3 nm depth sputter by Ar^+ to avoid the affection of surface oxygen adsorption. The data fitness was used Origin 7.0 with a PFM module pack as literature [15].

3. Results and discussion

3.1. Weight loss

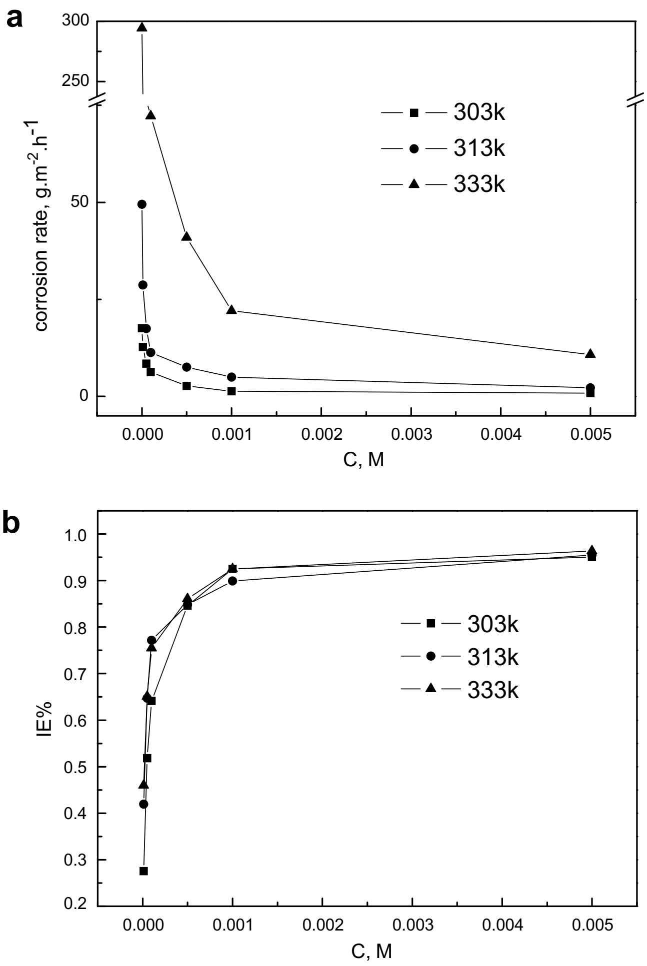


Fig. 1. The correlation between concentration of TAA-Ni and corrosion rate (a), inhibitive efficiency (b) of mild steel in 1 M HCl at different temperature.

Table 1
Corrosion rate of mild steel in 1 M HCl without and with TAA-Ni at different temperature

C (TAA-Ni)/M	Corrosion rate (303 K)/g m^{-2} h^{-1}	Corrosion rate (313 K)/g m^{-2} h^{-1}	Corrosion rate (333 K)/g m^{-2} h^{-1}
Blank	17.57	49.50	294.30
10^{-5}	12.73	28.73	158.96
10^{-4}	8.46	17.46	102.86
10^{-3}	6.30	11.30	72.24
10^{-4}	2.71	7.53	40.96
10^{-3}	1.32	4.99	22.07
0.005	0.87	2.22	10.80

The weight loss experiment results are shown in Fig. 1 indicating the relation between corrosion rate and inhibitive efficiency with TAA-Ni concentration, respectively. Correlated data is shown in Table 1. The corrosion rate reduces largely after the addition of TAA-Ni with the temperature varying from 303 K to 333 K. At 313 K, the corrosion rate is still about 2 g m^{-2} h^{-1} (lower than 2 mm y^{-1}) with TAA-Ni concentration at 5×10^{-3} M. Mild steel in this solution is still corrosion-resistant. With 5×10^{-3} M TAA-Ni solution, the corrosion rate is 10.80 g m^{-2} h^{-1} (lower than 10 mm y^{-1}) during 3 h at 333 K. It is enough to be used in acid cleaning for steel [16]. The inhibitive efficiency of TAA-Ni at different temperatures did not decrease largely with temperature elevation. According to other documents [4,7–8], TAA-Ni is indicated to be an excellent inhibitor for steel in high temperature acid solution from 303 K to 333 K.

The highest inhibitive corrosion rate on steel in 1 M HCl was 1.32 g m^{-2} h^{-1} (1.21 mm y^{-1}) at 303 K with 10^{-3} M TAA-Ni. This value is a little higher comparing to the data of 3-mino-1-H-isoindole [15] (1.18 mm y^{-1}, 303 K, potentiodynamic test), 3,5-bis(3-thienyl) 1,3,4-hiadiazole [17] (1.1 g m^2 h^{-1}, 303 K, weight loss test), and better than 3-amino-1,2,4-triazole [18] (4.1 g m^2 h^{-1}, 300 K, weight loss test). It indicated that TAA-Ni is an effective inhibitor comparable with azole compounds in its inhibitive ability.