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Synthesis of *N*-alkyl-4-(4-hydroxybut-2-ynyl) pyridinium bromides and their corrosion inhibition activities on X70 steel in 5 M HCl

Sheng Tu [a], Xiaohui Jiang [a,*], Limei Zhou [a], Ming duan [b], Hu Wang [b], Xiaomin Jiang [c]

[a] Chemical Synthesis and Pollution Control Key Laboratory of Sichuan Province, China West Normal University, Nanchong, Sichuan 673002, PR China
[b] State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, Sichuan 610500, PR China
[c] Southwest Electric Power Design Institute, Chengdu, Sichuan 610021, PR China

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N-alkyl-4-(4-hydroxybut-2-ynyl) pyridinium bromides (designated as P-*n*) have been synthesized and characterized. The corrosion inhibition efficiency of P-*n* on X70 steel in 5 M HCl was evaluated via weight loss and electrochemical methods. The results indicated that the combination of good inhibition moieties, such as alkylpyridinium and acetylenic alcohol, promoted P-*n* to be efficient inhibitors. Although the inhibitory efficiency of P-*n* decreased with elevating temperature, less reduction of the efficiency was found for the P-*n* with longer chain. P-*n* molecules were adsorbed on X70 surface by replacing water, which blocked the active sites and elevated the energy barrier for corrosion.

1. Introduction

Industrial acid cleaning, acid descaling, acid pickling and oil-well acidizing are usually carried out in acid solutions, and thus anticorrosive reagents are generally required to restrain the acid erosion of metallic materials by acids [1,2]. Most of the well-known acid inhibitors are organic compounds containing N, O or S heteroatoms with lone pair electrons and aromatic rings with π electrons [3–6]. Normally, the inhibition efficiency of organic compounds is related to their adsorption properties. It is well known that the adsorption of an inhibitor on metal surface depends on the nature and the surface charge of the metal, the chemical structure of the inhibitor, as well as the type of the electrolyte solution type [7]. The interaction of between the lone pair electrons and π-orbital electrons of in the inhibitor molecules and the d-orbital of the metal surface atoms may be the most crucial factor during adsorption [8].

A number of research interests have been focused on synthetic organic inhibitors that can protect steel under acidic condition [9–14]. Among those employed organic compounds, quaternary ammonium salts have showed effective anticorrosive ability for steel protection in acidic medium [15–18]. For example, the protective effect of cetyl pyridinium chloride/bromide (CPC/CPB) on carbon steel has been evaluated in 20% HCl at 25 °C [19]. It was reported that both CPC and CPB could reduce the corrosion current of carbon steel, and correspondingly the anticorrosive efficiency of CPB reached 92% which was higher than that of CPC at a concentration of 5 mM of the inhibitors. In addition, it was found that the anticorrosive efficiency could be enhanced by KI. On the other hand, Kumar studied the inhibition effect of cetyl pyridinium chloride on mild steel in 1 M HCl medium [20]. The results manifested that CPC had very good anticorrosive efficacy by the fact that the inhibitory efficiency was as high as 98.86% at a concentration of 0.1 mM of CPC at 45 °C. Notably, the efficiency increased with increasing temperature in the range of 25–45 °C, and then decreased with further increasing temperature.

It is also well recognized that many of acetylenic alcohols have shown good corrosion inhibition for ferrous metals in acid solutions [21–23]. Babic-Samardzija evaluated the protection of iron with 2-butyn-1-ol (2B), 3-butyn-1-ol (3B), 3-pentyn-1-ol (3P) and 4-penyn-1-ol (4P) in 1 M HCl by Tafel extrapolation method, linear polarization resistance and EIS [24]. The results showed that 4P gave the highest inhibition efficiency of 94.14% at the concentration of 0.1 mM, and the efficiencies were in a descending order of 4P > 3B > 3P > 2B. Besides, Jayaperumal reported the inhibitory performance of propargyl alcohol on mild steel in 15% HCl at 30 °C and 105 °C by gravimetric and electrochemical methods [25]. The inhibition efficiency of propargyl alcohol was 100% and 99% at a concentration of 0.107 M at 30 and 105 °C, respectively.

Therefore, both alkyl pyridinium salts and acetylenic alcohols exhibited good anticorrosive property. Moreover, acetylenic alcohols performed very well at high temperature in strong acidic medium. Thus, we envisioned that the combination of alkyl pyridinium and acetylenic alcohol moieties in the same molecule might enhance the anticorrosive efficacy. In the present work, P-*n*

* Corresponding author. Tel.: +86 817 2314508; fax: +86 817 2582029.
E-mail address: jxh2314508@163.com (X. Jiang).

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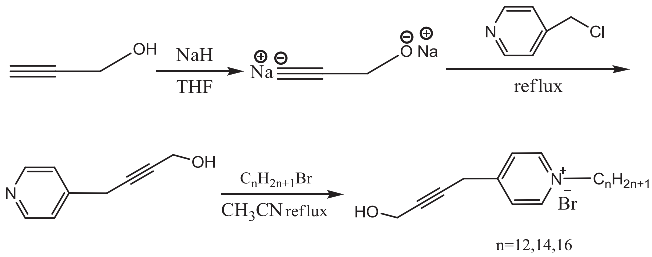

Scheme 1. The preparation of *N*-alkyl-4-(4-hydroxybut-2-ynyl) pyridinium bromides.

containing both alkyl pyridinium and acetylenic alcohol moieties were designed and prepared (see Scheme 1), and their anticorrosive efficacy on X70 steel in 5 M HCl was studied by means of weight loss, Tafel polarization and electrochemical impedance spectroscopy (EIS). In addition, the surface morphology of inhibited/uninhibited X70 steel was investigated by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD).

2. Experimental

2.1. Materials and instruments

4-Chlormethylpyridine (99%), propargyl alcohol (98%), sodium hydride (99%), bromoalkane (C12–14) (99%) were all purchased from Chengdu Kelong Company, China. All reagents were used as supplied except propargyl alcohol which was distilled before use. Bruker-400 NMR spectrometer, Nicolet-6700 FTIR spectrometer, D/MAXUltima IV X-ray diffraction and JSM-6510 scanning electron microscopy (SEM) were employed to confirm the structure of P-*n* or to character the surface morphology of the tested samples. CHI 660D (CH Instruments, USA) was used for electrochemical measurement.

The X70 steel sheets (3 cm × 1.5 cm × 0.2 cm, from PetroChina Southwest Oil & Gasfield Company) were abraded with a series of emery papers (grade 400#–1200#), and then successively washed with acetone and distilled water. The chemical composition of X70 steel was listed in Table 1.

2.2. Synthesis of N-alkyl-4-(4-hydroxybut-2-ynyl) pyridinium bromides

P-*n* was synthesized according to the following procedure described in Scheme 1.

2.2.1. Preparation of 4-(4-hydroxybut-2-ynyl) pyridine

Sodium hydride (0.15 mol) was suspended in THF (50 ml) and stirred under nitrogen atmosphere at room temperature. To the solution was added propargyl alcohol (0.12 mol) and the mixture was stirred for 3 h. Afterwards 4-chloromethylpyridine (0.1 mol) was added and the mixture was agitated for another 24 h. And then the excess NaH was slowly quenched with water and the mixture was extracted with Et_2O for at least three times. The organic layers were separated and combined. After Et_2O was evaporated, the residue was passed through a silica gel column (petroleum ether/ethyl acetate = 20/1). As a result, 4-(4-hydroxybut-2-ynyl) pyridine was obtained in a yield of 50%, and its structure was confirmed by NMR spectroscopy.

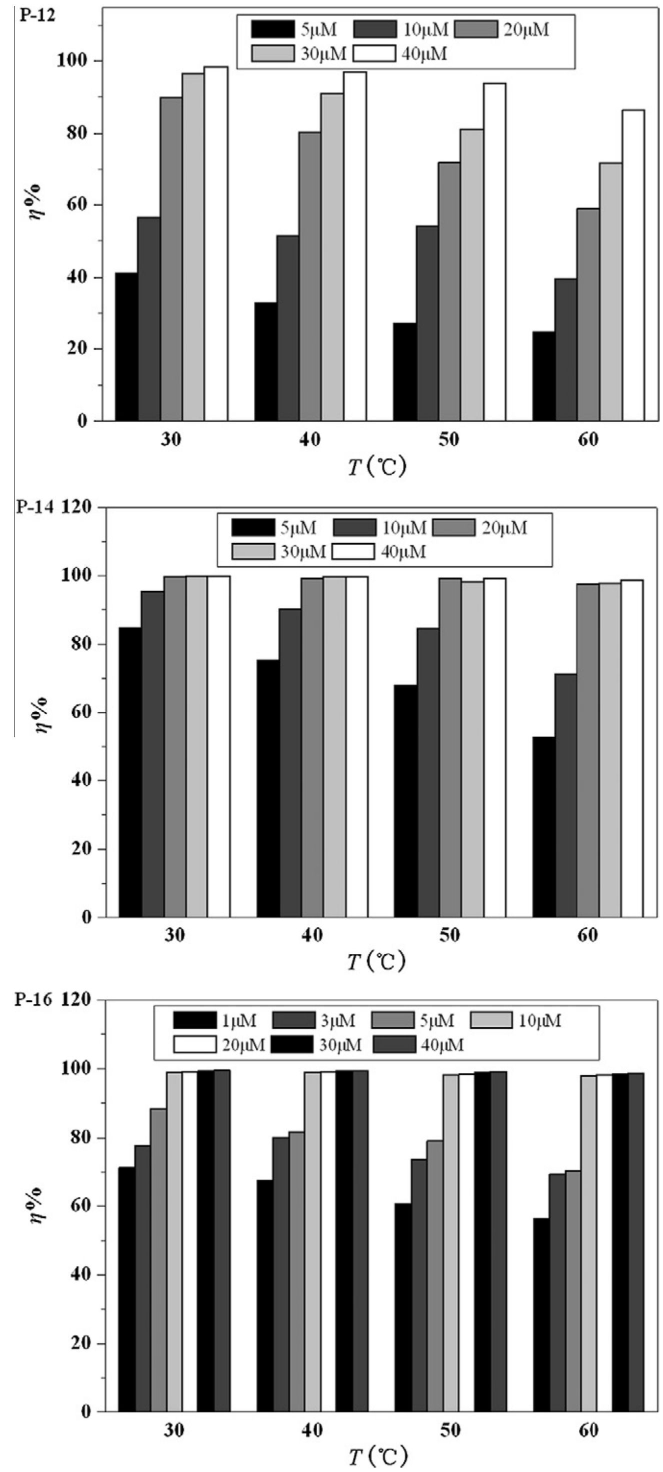

Fig. 1. Weight loss results of X70 steel corrosion with different concentration of P-*n* in 5 M HCl at 30–60 °C.

Table 1
Chemical composition of X70 steel sample.

Element	C	Si	Mn	P	S	V	Nb	Ti	Mo	Fe
Weight (%)	0.16	0.45	1.70	0.02	0.01	0.06	0.05	0.06	0.35	97.14