Further study on the inclusion complex of 2-phosphonobutane-1,2,4-tricarboxylic acid with β-cyclodextrin: A new insight of high inhibition efficiency for protecting steel corrosion

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\textbf{A B S T R A C T}

The present studies were performed to further investigate the inclusion reaction of 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) with β-cyclodextrin (β-CD) and the inhibition performance of the inclusion complex of PBTCA with β-CD (β-CD-PBTCA). The inclusion behavior of PBTCA with β-CD was investigated by UV–vis absorption spectrum and the formation of the inclusion complex was proved by Fourier transform infrared spectroscopy (FT-IR). The results showed that the PBTCA characteristic absorption band at 221.5 nm in inclusion complexes was strengthened and functional groups portion of PBTCA have penetrated the cavity of β-CD, due to the formation of β-CD-PBTCA inclusion complex. The study of thermodynamics indicated that the inclusion reaction of β-CD with PBTCA can spontaneously carry on and the inclusion process is exothermic. In addition, the inhibition performance was evaluated by potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and scanning electronic microscopy (SEM). The results of potentiodynamic polarization and EIS measurements on the corrosion inhibition of Q235 carbon steel in the 0.1 M sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) solution revealed that the highest inhibition efficiency of it over 90% is obtained, which means that the inclusion complex can act as a more efficient corrosion inhibitor for carbon steel. Also, SEM observations of the electrode surface confirmed that the presence of the inclusion complex better achieves the anti-corrosion property in aggressive medium than is the case with PBTCA alone.

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1. Introduction

Acid treatment (Willkwns et al., 1979; Dilullo and Rae, 1996; Kume et al., 1999; Hibbeler and Chavez, 2003; Zou et al., 2011), one of the significant stimulation techniques can dissolve layer minerals and foreign materials such as drilling mud, which is a preferred approach to enhance oil production in reservoirs. However, corrosion of the pipeline and facility is a serious problem existing in the course of the oil-gas field development, which imposes a great threat to the safe operation and also causes huge economic losses. Fortunately, corrosion inhibitor technology (Benabdellah et al., 2007; Oguzie et al., 2007; Al-Sarawy et al., 2008; Hosseini et al., 2008; Umoren et al., 2009; Fu et al., 2010; Gopi et al., 2010; Hosseini et al., 2010; Solmaz, 2010; Kosaria et al., 2011; Li et al., 2011), as an effective and economic way of protecting metal from corrosion, has been widely used in many industries. With the purpose of reducing corrosive rate of the pipeline and facility, oil-gas field corrosion inhibitors which are a class of especial additives, are injected into the oil-gas field corrosive medium.

PBTCA (Fig. 1) form organic phosphonate corrosion inhibitor family has been employed in the applications of scale inhibition and corrosion inhibition, but single composition of PBTCA used as a corrosion inhibitor barely achieves the desired anti-corrosion effect (Zhang et al., 2007; Abulkibash et al., 2008). It is well known, some co-inhibitors and different metal ions which could effectively improve inhibition efficiency of organic phosphonate corrosion inhibitor had been investigated by many researchers (Rajendra et al., 1998, 2003). Nevertheless, a new insight of high inhibition efficiency for protecting steel corrosion, based on the formation of β-CD-PBTCA inclusion complex, will be presented in this paper.

A study on acidizing effect of β-CD-PBTCA inclusion compound with sandstone has its potential application to enhance oil production
2.2. Preparation of β-CD-PBTCA inclusion complexes

Preparation of β-CD-PBTCA inclusion complexes was performed according to the method described previously (Zou et al., 2011). Aqueous solutions containing PBTCA and β-CD, in a 1:1 M ratio, were obtained by dissolving β-CDs in distilled water. All experiments were performed under the atmospheric ambient, the reacting temperature at \((40 \pm 1) ^\circ C\) controlled by Electro-Thermostatic Water Bath (Nanjing Instrumentation Manufacture Co., Ltd, China), the stir speed was restricted at 150 r/min and the reaction time continued for 12 h, which have been proved to be sufficient reaction conditions. UV–vis absorption spectrum (Shanghai Spectrotech Instruments Co., Ltd, China) was applied to study the inclusion behavior of PBTCA with β-CD at room temperature (25 °C). And then, the solid β-CD-PBTCA inclusion complexes were prepared by freeze drying method (Ramos et al., 2011).

2.3. Characterization of the inclusion complex

PBTCA, β-CD, and β-CD-PBTCA inclusion complexes spectra were recorded by using a Nicolet 170SX spectrometer (Nicolet, USA). Spectra acquisitions were performed directly in powder samples with the application of 16 scans at a resolution of 4 cm\(^{-1}\) over the range 4000–400 cm\(^{-1}\).

2.4. Electrochemical experiments

Prior to all experimental measurements, the exposed surface of Q235 carbon steel specimens was ground with different emery papers (grade 400, 600, 800, 1000, and 1200), rinsed with double distilled water, degreased in absolute ethanol, and dried by compressed air at room temperature (25 °C). Appropriate concentrations of acid and corrosion inhibitor were prepared using double distilled water. The corrosive solutions were made of AR grade 95% H\(_2\)SO\(_4\) and the concentration was 0.1 M. The concentration range of the β-CD-PBTCA inclusion complex employed was 80–100 mg/L in the acid solution. The inhibition performance of single composition of PBTCA was also evaluated previously.

Electrochemical tests were performed using a computer-controlled system CHI 604D (Shanghai Chenhua Instrument Co. Ltd, China). Carrying out the whole process of these, a three-electrode arrangement was used for electrochemical studies. The homemade working electrode was prepared from a Q235 carbon steel sheet, mounted in polyester so that the area exposed to the aggressive solution was 1 cm\(^2\). The reference electrode was a saturated calomel electrode, which was separated from the solution by a bridge compartment filled with the saturated solution of KCl. A platinum disc electrode was used as a counter electrode. For potentiodynamic polarization measurements, the polarization curve was performed at a scan rate of 0.3 mV s\(^{-1}\). The impedance measurements were carried out in the frequency range of 100 kHz to 0.05 Hz at the open circuit potential, by applying an amplitude vibration of 5 mV sine wave ac voltage. The immersion time before each test was 60 min in order to access an equilibrium potential.

All experiments were performed under the atmospheric ambient, the temperature at \((25 \pm 1) ^\circ C\) was controlled by Electro-Thermostatic Water Bath (Nanjing Instrumentation Manufacture Co., Ltd, China). Besides, the inhibition performance of β-CD-PBTCA inclusion complex was evaluated at the temperature range \((25 \pm 1)–(55 \pm 1) ^\circ C\). The polarization curve and the EIS were both calculated by ZView software.

2.5. Scanning electronic microscopy studies

The surface morphologies of Q235 carbon steel samples exposed to 0.1 M H\(_2\)SO\(_4\) solutions in the absence and presence of corrosion inhibitors over 24 h were examined by scanning SEM using a Philips XL30-EDAX electron microscope (Philips, Holland). To remove loosely adsorbed ions, the Q235 carbon steel samples were finally washed thoroughly and submitted to 15 min of ultrasonic cleaning.
3. Results and discussion

3.1. UV–vis spectroscopy analysis

UV–vis absorption spectra for the pure PBTCA and the β-CD-PBTCA inclusion complex have been studied in distilled water. As it can be seen from Fig. 3, the results of UV–vis spectra show the absorption spectrum of inclusion complexes aqueous solution coincides with the pure PBTCA, the maximum peaks appears at 221.5 nm, and the absorbance of the PBTCA solution increases with the addition of β-CDs. The similarity of the changes reveals that the inclusion complexes have been formed between β-CD and PBTCA (Zou et al., 2011).

3.2. Thermodynamics of inclusion process

The study of thermodynamics is conduced to further analyze the interactions of inclusion process between β-CD and PBTCA. The inclusion constants (K) value of different temperature (T) was calculated by using the Hildebrand–Benesi Equation, which has been previously reported (Zou et al., 2011). The change of enthalpies (ΔH) and the change of entropies (ΔS) of inclusion reaction for the formation of inclusion complex were determined from temperature dependence of inclusion constants, by employing the classical Van’t Hoff Eq. (1), and then plotting lnK versus 1/T (Tong, 2001).

\[
\ln K = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}
\]

The corresponding enthalpy and entropy calculated from the slop and intercept (Fig. 4) are shown in Table 1, respectively. The changes of Gibbs free energy (ΔG) for the interactions that take place during the inclusion process were also calculated by Eq. (2), as given in Table 1.

\[
\Delta G = -RT\ln K
\]

In general, the main driving forces for forming inclusion complex are hydrogen binding between the hydroxyl groups of β-CD and the guest, Van der Waals force interactions between host and guest molecules, hydrophobic interaction, and the release of “high energy water” molecules from the cavities of β-CD to bulk water, which have been broadly accepted. Essentially, hydrophobic interaction involves favorable positive entropy together with a slightly positive enthalpy change, while the other forces involve negative ΔH and ΔS (Tong, 2001). The negative values of enthalpy changes indicate that the interaction processes of β-CD with PBTCA are exothermic. The enthalpy of the system is largely decreased, which implies that the main driving forces of inclusion reaction are Van der Waals force and the extrusion of “high energy water” molecules from the cavities of β-CD. The changes of entropy are also negative in these processes. This behavior can be explained considering that the complex causes a decrease in translational and rotational degrees of freedom of the complex molecule as compared with the free ones, giving a more ordered system. These results can indicate that the complex of β-CD with PBTCA has occurred (Tong, 2001).

3.3. Fourier transform infrared spectroscopy analysis

The structures of the free guest PBTCA, host β-CD and the β-CD-PBTCA inclusion complex were characterized by using FT-IR. FT-IR spectrum of the inclusion complex (Fig. 5) shows changes from parent spectra (i.e. pure PBTCA and β-CD). The obtained FT-IR data supports formation of the inclusion complex.

The PBTCA FT-IR spectrum shows the presence of the characteristic peaks: 3450 cm\(^{-1}\) (–OH); 1720 cm\(^{-1}\) (–C═O); 1411 cm\(^{-1}\) (–C–OH); 1203 cm\(^{-1}\) (–P═O); 1052, 1014 and 929 cm\(^{-1}\) (–P–OH). The FT-IR spectrum of β-CD shows absorption bands at: 3358 cm\(^{-1}\) (O–H stretching vibration); 2928 cm\(^{-1}\) (O–H stretching); 1649 and 1642 cm\(^{-1}\) (OH bending); 1356 and 1376 cm\(^{-1}\) (OH deformation); 1156 and 1090 cm\(^{-1}\) (C–O–C stretching and OH banding); 1028–1006 cm\(^{-1}\) and 1056–1028 cm\(^{-1}\) (C–O–C stretching). In the FT-IR spectra of β-CD-PBTCA inclusion complexes, the presence or absence of characteristic peaks associated with specific structural groups of the PBTCA molecule was observed. By contrast, the characteristic peak of PBTCA portion such as 1203 cm\(^{-1}\) (–P═O) cannot be detected and the other peaks of PBTCA like 1411 cm\(^{-1}\) (–C–OH), 1014 and 929 cm\(^{-1}\) (–P–OH), etc. are superposed over β-CDs’ peaks because of a strong interaction between the PBTCA and β-CD, indicating the formation of inclusion complex.

3.4. Evaluation of inhibition performance using EIS

Fig. 6 shows the Nyquist diagrams of Q235 carbon steel in 0.1 M H\(_2\)SO\(_4\) at (25 ± 1) °C containing various concentrations of PBTCA and β-CD-PBTCA inclusion complex after 60 min
immersion, respectively. All the impedance spectra exhibit one single depressed semicircle, and the diameter of semicircle increases with the increase of PBTCA and β-CD-PBTCA inclusion complex concentration. It is apparent, from these plots that, the impedance response of Q235 carbon steel in uninhibited H2SO4 solution has significantly changed after addition of β-CD-PBTCA in the corrosive solution. Furthermore, compared with PBTCA, the greater diameter of semicircle of β-CD-PBTCA inclusion complex at the same concentration reveals that the inclusion complex achieves better performance in decreasing corrosive rate.

The EIS parameters, i.e. charge transfer resistance (Rt) with inhibitors were calculated by ZView software, as shown in Fig. 7a. The values of Rt calculated from EIS can visually display the inhibition effects of PBTCA and β-CD-PBTCA inclusion complex. The inhibition efficiency (η) was calculated by using the charge transfer resistance as Eq. (3) (Solmaz, 2010; Kosaria et al., 2011).

\[
\eta = \left( \frac{R_{t(\text{inh})} - R_t}{R_{t(\text{inh})}} \right) \times 100\%
\]

where \(R_t\) and \(R_{t(\text{inh})}\) are the charge transfer resistance values without and with an inhibitor, respectively. The inhibition efficiencies calculated from Eq. (3) are presented in Fig. 7b. The β-CD-PBTCA inclusion complex exhibits the highest inhibition efficiency of 93.10%. Therefore, the results demonstrate that the novel corrosion-inhibiting system can improve inhibition efficiency of PBTCA to reduce the corrosion of carbon steel, which may be attributed to the mass of β-CD-PBTCA inclusion complexes.

**Table 1**

Determined thermodynamic parameters of β-CD-PBTCA inclusion complex.

<table>
<thead>
<tr>
<th>Inclusion complex</th>
<th>(\Delta H) (kJ mol(^{-1}))</th>
<th>(\Delta S) (J mol(^{-1}) K(^{-1}))</th>
<th>(\Delta G_{303.15} ) (kJ mol(^{-1}))</th>
<th>(\Delta G_{313.15} ) (kJ mol(^{-1}))</th>
<th>(\Delta G_{318.15} ) (kJ mol(^{-1}))</th>
<th>(\Delta G_{323.15} ) (kJ mol(^{-1}))</th>
</tr>
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**Fig. 5.** FT-IR spectra of pure PBTCA, β-CD and β-CD-PBTCA inclusion complex.

**Fig. 6.** Nyquist diagrams of the corrosion of Q235 carbon steel in 0.1 M H2SO4 at 25 ± 1°C containing various concentrations of PBTCA and β-CD-PBTCA inclusion complex (inserted) after 60 min immersion.

**Fig. 7.** \(R_t\) (a) and inhibition efficiency (b) calculated from EIS at the range of concentration employed. The maximum inhibition efficiency of PBTCA and β-CD-PBTCA inclusion complex is 74.69% and 93.10%, respectively.
3.5. Evaluation of inhibition performance using polarization curve

The polarization curve was used to investigate the quality of PBTCA and β-CD-PBTCA inclusion complex on protecting Q235 carbon steel from corrosion in 0.1 M H₂SO₄ solution and the results are shown in Figs. 8 and 9. Electrochemical corrosion parameters, i.e., corrosion current densities \( i_{\text{corr}} \) were obtained by extrapolation of the Tafel lines, as shown in Fig. 10a. It is clear that the corrosion current densities decreased with the addition of PBTCA and β-CD-PBTCA inclusion complex. However, corrosion current densities of β-CD-PBTCA inclusion complex have the marked tendency to decrease in corrosion media, which indicates that the inclusion complex as a more effective inhibitor are better than PBTCA at anti-corrosion. The inhibition efficiency calculated from polarization curve \( \eta_p \) could be calculated as follows (Solmaz, 2010; Kosaria et al., 2011):

\[
\eta_p = \left( \frac{i_0 - i_{\text{corr}}}{i_0} \right) \times 100\% \tag{4}
\]

where \( i_0 \) and \( i_{\text{corr}} \) are the corrosion current densities without and with an inhibitor, respectively. The values of \( \eta_p \) are shown in Fig. 10b and the inhibition efficiencies calculated from polarization curves also show the same trend as those observed from EIS measurements.

3.6. Scanning electronic microscopy analysis

The formation of a protective surface film of inhibitor on the electrode surface was investigated by SEM observations after 24 h immersion in uninhibited and inhibited sulfuric acid solutions. The SEM photographs are shown in Fig. 11. The morphology of the Q235 carbon steel specimen surface in Fig. 11a reveals that in the absence of inhibitors the surface is highly corroded. However, in presence of the inhibitor (Fig. 11b and c), the rate of corrosion is suppressed. The electrode surface is almost free from corrosion, which may be due to the adsorption of the inhibitor on the carbon steel surface. In contrast, inspection of Fig. 11c shows that the inhibited metal surface is smoother than the inhibited surface with PBTCA indicating a more dense and protective layer of adsorbed inhibitor preventing acid attack. In accordance, it could be concluded that in the presence of β-CD-PBTCA inclusion complex the adsorption film can more efficiently inhibit the corrosion of steel, decreasing the extent of corrosion.

3.7. Influence of temperature

Temperature, as is well known, can modify the interaction between the carbon steel electrode surface and the acidic corrosion media without and with inhibitors. Influence of temperature
Fig. 11. SEM images of the surface for Q235 carbon steel specimens after 24 h of immersion in 0.1 M H$_2$SO$_4$: (a) without, (b) with 100 mg/L of PBTCA and (c) with 100 mg/L of β-CD-PBTCA.

Fig. 12. Nyquist diagrams of the corrosion of Q235 carbon steel (a–d), $R_t$ (e) and inhibition efficiency (f) in 0.1 M H$_2$SO$_4$ at the range of 25–55°C containing 100 mg/L of β-CD-PBTCA inclusion complex after 60 min immersion.
on the inhibition efficiency of the β-CD-PBTCA inclusion complex was investigated by EIS. Fig. 12a–d shows the Nyquist diagrams of Q235 carbon steel in 0.1 M H2SO4 at the temperature range (25 ± 1)–(55 ± 1) °C containing 100 mg/L of the inclusion complex after 60 min immersion. As shown in Fig. 12e, the value of $R_t$ decreases slightly with increasing temperature in the absence of the inclusion complex. In the presence of the inclusion complex, however, the value of $R_t$ (Fig. 12e) decreases rapidly with increasing temperature. More particularly, it can be observed that the $\eta$ (Fig. 12f) decreases slightly with temperature, which suggests that inhibition efficiency of the inclusion complex is independent of temperature. Thus, these results indicate that the temperature has a few impacts on inhibition efficiency in the range of temperature employed.

4. Conclusion

β-CD-PBTCA inclusion complexes were prepared by freeze-drying method in a molar ratio 1:1. The inclusion behavior of β-CD and PBTCA was investigated by UV–vis absorption spectrum and the formation of the inclusion complex was proved by FT-IR. From UV–vis spectra, it was observed that the PBTCA characteristic absorption band at 221.5 nm in inclusion complexes was strengthened. FT-IR spectra showed that the PBTCA penetrates the β-CD cavities and the inclusion complex was stabilized due to hydrogen bonding between β-CD and PBTCA. The study of thermodynamics indicated that the inclusion reaction of β-CD with PBTCA can spontaneously carry on and the inclusion process is exothermic. The results of EIS and polarization curve studies revealed that β-CD-PBTCA inclusion complexes exhibited the higher inhibition efficiency, which suggests the active effect of the inclusion complex on improving inhibition efficiency of PBTCA. The results of SEM were in good agreement with the results obtained from potentiodynamic polarization and EIS. Taking into account these results, it can be concluded that the novel corrosion-inhibiting system of β-CD-PBTCA inclusion complexes leads to a new approach to enhance inhibition efficiency of PBTCA as well.

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