Analysis of Protective Film Formed on Carbon Steel Immersed in Seawater by Diethylenetriamine Penta (methylene phosphonic acid) – Zn^{2+} System

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Abstract: The inhibition efficiency of diethylenetriamine penta (methylene phosphonic acid) (DTPMP) - Zn^{2+} system in controlling corrosion of carbon steel in natural sea water has been evaluated by weight-loss and electrochemical method. The formulation consisting of 250 ppm of DTPMP and 50 ppm of Zn^{2+} has 98% IE. Polarization study reveals that DTPMP–Zn^{2+} formulation functions as a mixed inhibitor controlling the anodic reaction and cathodic reaction to the same extent. The protective film has been analyzed by FTIR and the surface morphology of the metal surface has been analyzed by an atomic force microscopy.
Keywords: Corrosion inhibition, Carbon steel, Sea water, Atomic force microscopy (AFM) and Fourier transform infrared spectroscopy (FTIR).

Introduction

Corrosion is the gradual destruction of material, usually metal, by chemical reaction with its environment. Seawater is a complex natural electrolyte. Seawater contains many corrosive electrolytes such as sodium chloride, magnesium chloride, calcium chloride, etc.; hence, carbon steel immersed in seawater is corroded slowly because of chemical reactions between the metal and the electrolytes [1-3]. The corrosion is severe due to the presence of chloride ions and dissolved oxygen. Seawater has been used as cooling fluid in various industries. Carbon steel is widely used in infrastructure in marine environments [4]. It is one of the major constituents in structural steel applications including body of a ship, offshore platforms, foundation piling, sheet piling, and coastal facilities. It is also used in industry where the metal is exposed to acid corrosion. So, it is imperative to study the corrosion aspect and find out suitable corrosion inhibitors to be used in seawater. Inhibition of corrosion and scaling can be done by the application of inhibitors, which is one of the most practical and economic methods for protection against metallic corrosion [5,6]. Corrosion inhibitors disclose that most organic substances used as corrosion inhibitors can adsorb on the metal surface employed through heteroatoms such as nitrogen, oxygen, sulphur, and phosphorus, multiple bonds or aromatic rings and block the active sites decreasing the corrosion rate [15]. Several phosphonic acids have been used as corrosion inhibitor [7-11]. Phosphonic acids are organic compounds containing $R\text{-}PO(OH)_2$ or $R\text{-}PO(OR)_2$ groups. They are effective chelating agents that are used in cooling water and desalination systems to inhibit scale formation and corrosion. Phosphonic acids are extensively used now-a-days due to their complex forming abilities, high stability under harsh conditions, and low toxicity [12,13]. The inhibition efficiency of phosphonates depends on the number of phosphono groups in a molecule and also on different substituents. Compounds with a phosphonic functional group are considered to be the most effective chemical for inhibiting the corrosion process and it is well known that short-chain-substituted phosphonic acids are good corrosion inhibitors for iron and low-alloyed steels [14].

The present work is undertaken (i) to evaluate the inhibition efficiencies of diethylenetriamine penta (methylene phosphonic acid) (DTPMP) – Zn $^{2+}$ system in controlling corrosion of carbon steel in sea water by weight-loss method (ii) electrochemical techniques provide information on the corrosion rate, as well as on processes at interfaces affected by additives (iii) to analyze the protective film by FT1R spectra, (iv) to analyse the surface morphology by AFM, and (v) to propose a suitable mechanism of corrosion inhibition based on the results from the above study.

Experimental

Preparation of specimens

Carbon steel specimens [0.0267 % S, 0.06 % P, 0.4 % Mn, 0.1 % C and the rest iron] of dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight-loss method

Carbon steel specimens in triplicate were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion was determined using a Shimadzu balance, model AY62. The corrosion products were cleansed with Clarke's solution [16]. The inhibition efficiency (IE) was then calculated using the equation.

IE = 100 [1- (W$_2$/ W$_1$)] %

where W_1 = corrosion rate in the absence of the inhibitor, and W_2 = corrosion rate in the presence of the inhibitor.

Polarization Study

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode.

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimens was analysed for surface analysis technique by FTIR spectra and AFM.

(i) FTIR spectra

The film formed on the metal surface was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in a perkin Elmer 1600 spectrophotometer.

(ii) Atomic Force Microscopy

Atomic Force Microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before. The microscope used for the present study was PicoSPM Molecular Imaging, USA make. Polished specimens prior to the initiation of all corrosion experiments were examined through an optical microscope to find out any surface defects such as pits or noticeable irregularities like cracks, etc. Only those specimens, which had a smooth, pit-free surface were subjected for AFM examination. The protective film formed on the carbon steel specimens after immersion in the inhibitor systems for different time durations were examined for a scanned area of 30 x 30 μm^2 and 15 x 15 μm^2. The two-dimensional and three-dimensional topography of surface films gave various roughness parameters of the film.

Results and Discussion

Weight-Loss Method

The physicochemical parameters of seawater are given in **Table 1**. **Table 2** gives values of the corrosion inhibition efficiencies and the corresponding corrosion rates of diethylenetriamine penta (methylene phosphonic acid) (DTPMP) – Zn^{2+} in controlling corrosion of carbon steel in seawater for a period of 24 hours at room temperature. The DTPMP alone has high rate of corrosion. The inhibition efficiency of DTPMP is improved by adding various concentrations of Zn^{2+}. Similar observations have been made by Umamathi et al [17] where they have improved the inhibition efficiency of Na_3PO_4 on EDTA by addition of Zn^{2+} ion; Mary Anbarasi and Rajendran [18] have improved the inhibition efficiency of heptane sulphonic acid by addition of Zn^{2+} ion. However, increasing the concentration of DTPMP as well as $Zn^{2+,}$ the maximum inhibition is achieved and the corrosion rate is decreased. It is found that 250 ppm of DTPMP and 50 ppm of Zn^{2+} has 98% inhibition efficiency. The inhibition efficiency increases with the increase of concentration of inhibitors. This behavior could be attributed to the increase of the surface area covered by the adsorbed molecules of phosphonic acid with the increase of its concentration. It is generally assumed that the adsorption of the inhibitor at the metal/solution interface is the first step in the mechanism of inhibition in aggressive media.

Table 1. The physicochemical parameters of natural seawater collected in Mandapam, Tamilnadu, India.

Parameter	Value
Total dissolved salts (mg/L)	78136
Electrical conductivity (micro mhos/cm)	70788
pH	7.82
Total Hardness ($CaCO_3$ equivalent)	24500
Calcium as Ca (mg/L)	2200
Magnesium as Mg (mg/L)	1800
Sodium as Na (mg/L)	9600
Chloride as Cl (mg/L)	23100
Fluoride as F (mg/L)	1.2
Free ammonia as NH_3 (mg/L)	900
Sulphate as SO_4 (mg/L)	2350

Table 2. The inhibition efficiency (IE%) and the corrosion rate (mm/y) of DTPMP–Zn^{2+} system are determined by weight-loss method.

| DTPMP pm	Zn^{2+} (ppm)					
	0		25		50	
	IE/%	CR (mm/y)	IE /%	CR (mm/y)	IE/%	CR (mm/y)
0	-	0.1858	15	0.1579	23	0.1431
50	20	0.1486	65	0.0650	72	0.0520
100	28	0.1338	68	0.0595	83	0.0316
150	39	0.1133	75	0.0465	90	0.0186
200	46	0.1003	80	0.0372	95	0.0093
250	50	0.0929	85	0.0279	98	0.0037

Potentiodynamic Polarization Study

Polarization study has been used to detect the formation of protective film on the metal surface[19,20]. The polarization curves of carbon steel immersed in various test solutions are shown in Fig.1. The cathodic branch represents the oxygen reduction reaction, while the anodic branch represents the iron dissolution reaction. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), Tafel slopes (b_c and b_a) and linear polarization resistance (LPR) are given in Table 3.

When carbon steel is immersed in sea water, the corrosion potential is -746 mV vs SCE. The formulation consisting of 250 ppm of DTPMP and 50 ppm of Zn^{2+} in sea water, the corrosion potential is -745 mV vs SCE. The corrosion potential shift is nearly equal. This suggests that the DTPMP–Zn^{2+} formulation functions as a mixed inhibitor controlling the anodic reaction and cathodic reaction to the same extent. The corrosion current density value and LPR value for sea water are 6.351×10^{-6} A cm^{-2} and 6.356×10^{3} ohm cm^{2}. For the formulation of 250 ppm of DTPMP and 50 ppm of Zn^{2+}, the corrosion current density value has decreased to 5.243×10^{-6} A cm^{-2} and the LPR value has increased to 7.570×10^{3} ohm cm^{2}. The fact that the LPR value increases with decrease in corrosion current density indicates adsorption of the inhibitor on the metal surface to block the active sites and inhibit corrosion and reduce the corrosion rate with the formation of a protective film on the metal surface.

Table 3.

| System	E_{corr} mV vs SCE	I_{corr} A/cm^2	b_a mV/dec	b_c mV/dec	LPR Ω cm^2
Sea water	- 746	6.351×10^{-6}	228	157	6.356×10^{3}
Sea water + DTPMP (250 ppm) + Zn^{2+} (50 ppm)	- 745	5.243×10^{-6}	220	156	7.570×10^{3}
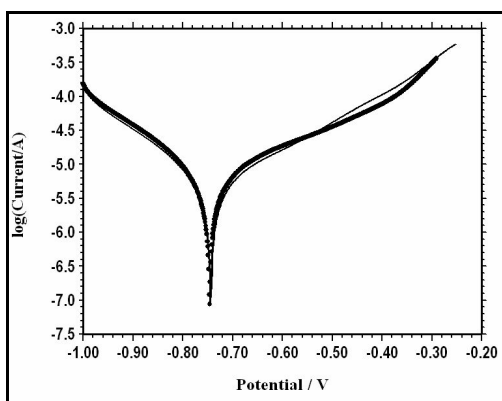
Fig.1. Polarization curves of carbon steel immersed in various test solutions
a) Sea water
b) Sea water containing 250 ppm of DTPMP and 50 ppm of Zn^{2+}

FTIR spectra

FTIR spectra have been used to analyze the protective film formed on the metal surface [21,22]. FTIR spectrum (KBr) of pure DTPMP is shown in Fig.2a. The P-O stretching frequency appears at 1058 cm^{-1} and the C-N stretching frequency appears at 1111 cm^{-1}. The FTIR spectrum of the film formed on the metal surface after immersion in sea water containing 250 ppm of DTPMP and 50 ppm of Zn^{2+} is shown in Fig.2b. The P-O stretching frequency has shifted from 1058 cm^{-1} to 1098 cm^{-1} and the C-N stretching frequency has shifted from 1111 cm^{-1} to 1220 cm^{-1}. The shift indicates that the oxygen and nitrogen atoms of phosphonic acid are coordinated to form Fe^{2+}–DTPMP complex on the anodic sites of the metal surface. The possibility of formation of Zn^{2+}–DTPMP complex to some extent, on the metal surface cannot be ruled out. The peak at 3420 cm^{-1} is due to –OH stretching. The band due to Zn-O appears at 1383 cm^{-1}. These results confirm the presence of $Zn(OH)_2$ deposited on the cathodic sites of the metal surface. Thus, FTIR spectral study leads to the conclusion that the protective film consists of Fe^{2+}–DTPMP complex, Zn^{2+}–DTPMP complex and $Zn(OH)_2$.
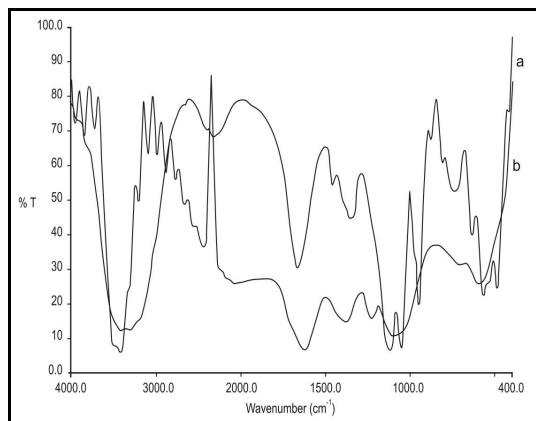
Fig.2. FTIR Spectra
a) Pure DTPMP
b) Film formed on metal surface after immersion in sea water containing 250 ppm of DTPMP and 50 ppm of Zn^{2+}

Atomic Force Microscopy

Atomic force microscopy (AFM) is a powerful technique for gathering of roughness statistics from a variety of surfaces. AFM is becoming an accepted method of roughness investigation [23-25].

The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel immersed in sea water (blank sample) and the carbon steel surface immersed in sea water containing 250 ppm of DTPMP and 50 ppm of Zn^{2+} are shown in Fig.3. (a,d,g), (b,e,h), (c,f,i) respectively.

Root-mean-square roughness, average roughness and peak-to-valley value

AFM image analysis was performed to obtain the average roughness, R_a (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, R_q (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights). R_q is much more sensitive than R_a to large and small height deviations from the mean [25].

The R_q, R_a and P-V values for carbon steel surface immersed in different environment are summarized in Table 4.

Fig.3 (a,d,g) displays the surface topography of non-corroded metal surface. The values of R_q, R_a and P-V height for the polished carbon steel surface (reference sample) are 4.33 nm, 3.41 nm and 35.28 nm respectively. This shows that the surface is more homogeneous in some place where the height is lower than the average depth. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion.

Fig.3 (b,e,h) shows corroded metal surface with few pits in the absence of inhibitor immersed in sea water. The R_q, R_a and P-V height values for the carbon steel surface are 17.67 nm, 13.51 nm and 71.08 nm respectively. These values suggest that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher due to the corrosion of the carbon steel in sea water environment.

Fig.3 (c,f,i) shows the carbon steel surface after immersion in sea water containing DTPMP (250 ppm) – Zn^{2+} (50 ppm). The R_q, R_a and P-V height values for the carbon steel surface are 7.94 nm, 5.89 nm and 35.76 nm respectively. These values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+}–DTPMP complex, Zn^{2+}–DTPMP complex and $Zn(OH)_2$ on the metal surface, thereby inhibiting the corrosion of carbon steel.

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Table 4. AFM data for carbon steel surface immersed in inhibited and uninhibited environments.

Samples	RMS (R_q) Roughness (nm)	Average (R_a) Roughness (nm)	Maximum Peak-to-Valley height (P-V) (nm)
Polished carbon steel (control)	4.33	3.41	35.28
Carbon steel immersed in sea water (blank)	17.67	13.51	71.08
Carbon steel immersed in sea water + DTPMP (250 ppm) + Zn^{2+} (50 ppm)	7.94	5.89	35.76
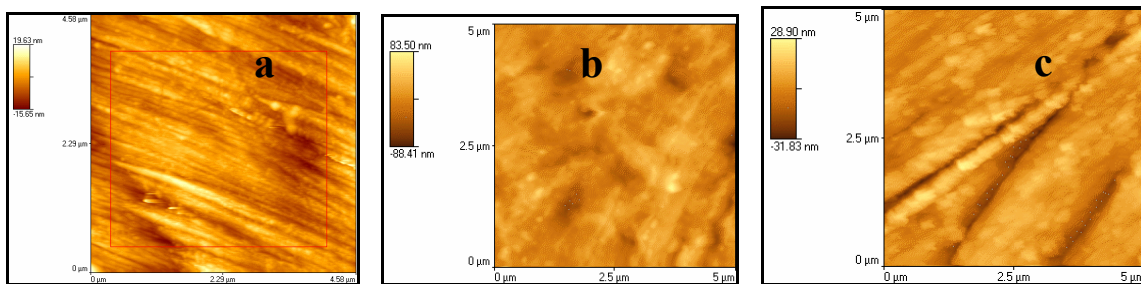
Fig.3. Two dimensional AFM images of the surface of
a) Polished carbon steel (control)
b) Carbon steel immersed in sea water (blank)
c) Carbon steel immersed in sea water containing DTPMP (250 ppm) + Zn^{2+} (50 ppm)
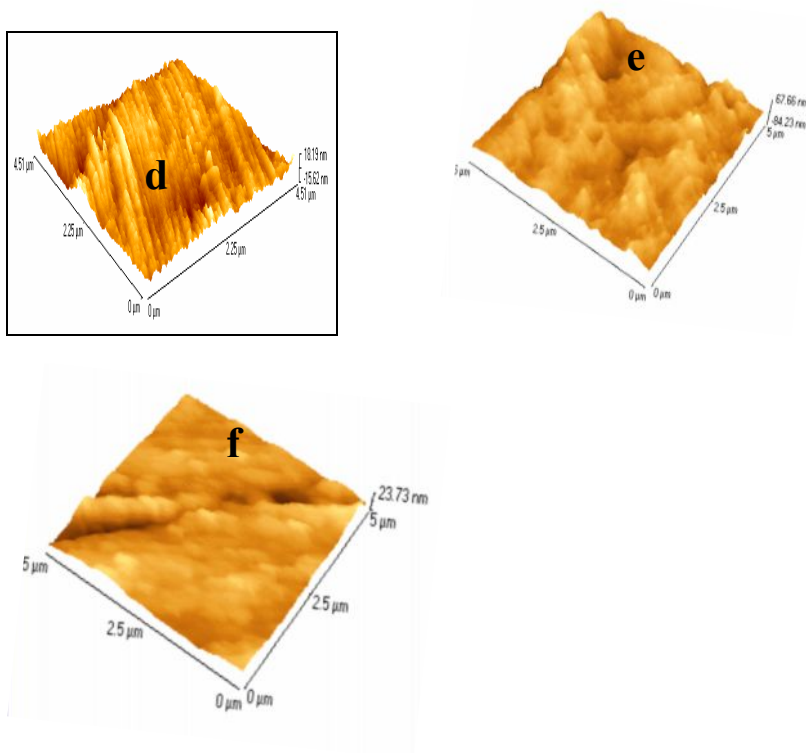
Fig.3. Three dimensional AFM images of the surface of
d) Polished carbon steel (control)
e) Carbon steel immersed in sea water (blank)
f) Carbon steel immersed in sea water containing DTPMP (250 ppm) + Zn^{2+} (50 ppm)
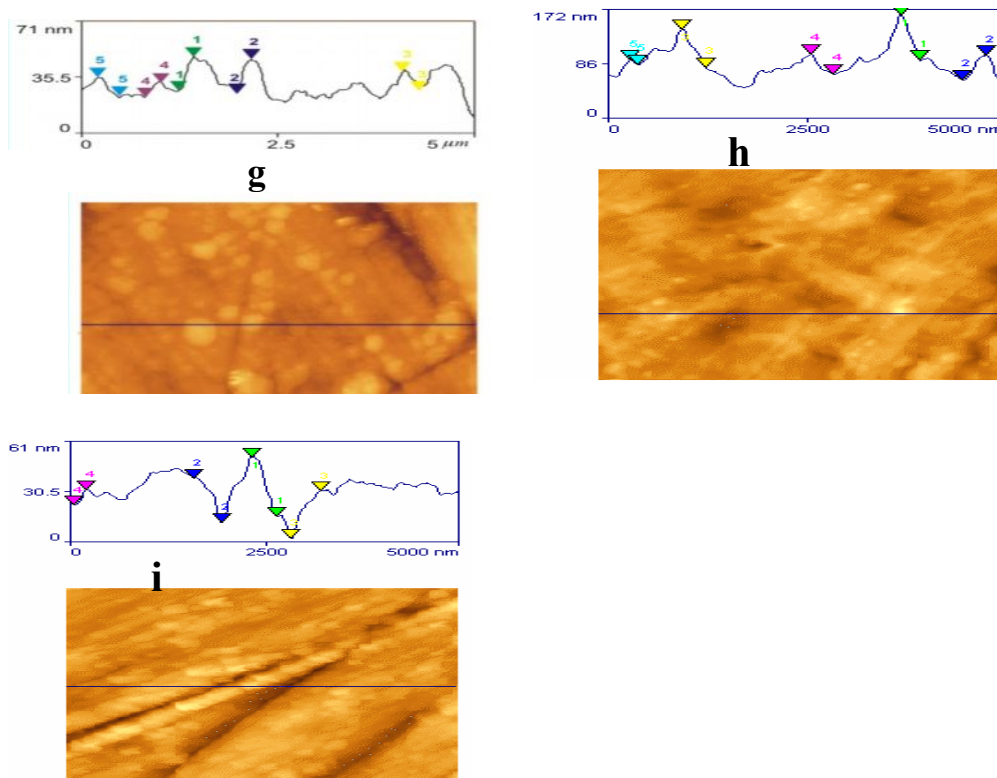
Fig.3. AFM cross-sectional images of the surface of
g) Polished carbon steel (control)
h) Carbon steel immersed in sea water (blank)
i) Carbon steel immersed in sea water containing DTPMP (250 ppm) + Zn^{2+} (50 ppm)

Mechanism of corrosion inhibition

Analysis of the results of weight loss method reveals that the formulation consisting of sea water, 250 ppm of DTPMP and 50 ppm of Zn^{2+} offers an IE of 98%. FTIR spectra reveal that the protective film consists of Fe^{2+}–DTPMP complex, Zn^{2+}–DTPMP complex and $Zn(OH)_2$.

In order to explain all these observations in a holistic way the following mechanism of corrosion inhibition is proposed.

➢ When carbon steel specimen is immersed in an aqueous solution, the anodic reaction is. $Fe \rightarrow Fe^{2+} + 2e^-$ And the cathodic reaction is
  $2H_2O + O_2 + 4e^- \rightarrow 4\ OH^-$.
➢ When carbon steel is immersed in this solution, the DTPMP–Zn^{2+} complex diffuses from the bulk of the solution towards the metal surface. DTPMP–Zn^{2+} complex is converted into DTPMP–Fe^{2+} complex on the anodic sites of the metal surface with the release of Zn^{2+} ion.
  Zn^{2+}–DTPMP + $Fe^{2+} \rightarrow Fe^{2+}$–DTPMP + Zn^{2+}
➢ The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$ on the cathodic sites of the metal surface.
  $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \downarrow$
➢ The possibility of formation of Zn^{2+}–DTPMP complex to some extent on the metal surface cannot be ruled out. Thus, the protective film consists of Fe^{2+}–DTPMP complex, Zn^{2+}–DTPMP complex and $Zn(OH)_2$.

Conclusions

The present study leads to following conclusions:

➢ The formulation consisting of 250 ppm of DTPMP and 50 ppm offers 98% IE to carbon steel immersed in sea water.
➢ Polarization study reveals that DTPMP–Zn^{2+} formulation functions as a mixed inhibitor.
➢ FTIR spectra show that the protective film consists of Fe^{2+}–DTPMP complex, Zn^{2+}–DTPMP complex and $Zn(OH)_2$.

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> AFM images confirm the formation of protective layer on the metal surface.

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