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Quantum chemical calculations, synthesis and corrosion inhibition efficiency of ethoxylated-[2-(2-{2-[2-(2-benzenesulfonylamino-ethylamino)-ethylamino]-ethylamino}-ethylamino)-ethyl]-4-alkyl-benzenesulfonamide on API X65 steel surface under H_2S environment

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The effect of four novel nonionic surfactants based on sulphonamide as corrosion inhibitors for X-65 type carbon steel in oil well formation water under H_2S environment was investigated by electrochemical measurements. The obtained results revealed that synthesized surfactants perform as acceptable corrosion inhibitors. Scanning electron microscopy (SEM) was used to examine surface morphology in the absence and presence of inhibitors molecules. It was found that the inhibition efficiency depends on the ethylene oxide content in the molecule. The quantum chemical calculations were carried out to study the molecular geometry and electronic structure of obtained derivatives. The energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital has been calculated using the theoretical computations to reflect the chemical reactivity and kinetic stability of compounds.

1. Introduction

Carbon steel has been widely employed as construction material for pipe work in oil and gas production facilities such as down hole tubular, piping systems and transmission pipelines [1–5]. Carbon steel has remarkable economic attractive properties for engineering applications owing to its low cost, easy availability and high mechanical strength. Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Thus, the search for new and efficient corrosion inhibitors has become a necessity to protect metallic installations against corrosion [6]. To be effective, an inhibitor must displace water from the metal surface, interact with anodic or catholic reaction sites to retard the oxidation and reduction corrosion reaction, prevent transportation of water and corrosion active species on the surface [7]. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media [8]. To prevent the attack of the corrosive species on the metallic surface, it is very important to add a corrosion inhibitor to decrease the rate of metal dissolution in such solutions. Thus, many studies concerning the inhibition of carbon steel corrosion using corrosion inhibitors of nonionic surfactants are conducted in the medium [9–13]. Corrosion inhibitors can be divided into three kinds: (i) inorganic inhibitors, (ii) organic inhibitors and (iii) mixed material inhibitors [14]. Most well-known inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms [15–18]. Surfactants are special type of organic compounds and exhibit unique properties due to their amphiphilic properties. The mechanism of corrosion process of carbon steel in aqueous medium containing H_2S was discussed in former literatures [19–24].

The adsorption of the surfactant on the metal surface can markedly change the corrosion resisting property of the metal [25], so the study of the relationship between the adsorption and corrosion inhibition is of great importance. The present work aimed to synthesis four nonionic surfactants based on sulphonamide and evaluates their performance of corrosion inhibition X 65 type carbon steel in oil well formation water under H_2S environment.

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2. Experimental

2.1. Chemical composition of X-65 type carbon steel alloy

X-65 type carbon steel specimens used in this investigation were cut from unused petroleum pipeline. The chemical composition (weight%) of carbon steel is C 0.09, Si 0.22, Mn 1.52, P 0.01, S 0.05, Ni 0.04, Cr 0.02, Mo 0.004, V 0.002, Cu 0.02, Al 0.04 and reset is Fe.

2.2. Deep oil well formation water

Deep oil well formation water naturally exists in the reservoir rocks before drilling. Most oil field water contains a variety of dissolved organic and inorganic compounds. The major elements usually present are sodium, calcium, magnesium, chloride, bicarbonate and sulfate. The chemical composition of the oil well formation water used in this investigation and its physical properties are shown in Table 1.

2.3. Synthesis of the inhibitors

2.3.1. Preparation of sulfonamide

In 500 ml three-necked flask equipped with mechanical stirrer, condenser, Den-Stark Trap and dropping funnel, 2 mol of linear alkyl benzene sulphonic acid (LABS) was reacted with 1 mol triethylenetetramine, tetraethylene pentamine in the presence of (100 ml) xylene as a solvent and 2% ZnO as a catalyst for 4 h reflux at 140°C. Then, after complete removal of the theoretical amount of water (36 ml), the solvent was stripped out using a rotary evaporator. The product was then dissolved in (30 ml) isopropanol as shown in Scheme 1.

2.3.2. Ethoxylation of amide

In 250 ml four-neck flask equipped with condenser, magnetic stirrer, thermometer, ethylene oxide gas inlet and outlet nozzles, 2–3 droplets of triethylamine were added to 1 mol sulphonamide derivatives with stirring at 80–90°C for about 15 min., then ethylene oxide gas was allowed to pass over the sulphonamide derivatives melt under a controlled pressure of around 86–88 cm Hg with stirring [26–27].

The temperature was raised gradually up to reflux temperature and then the reaction mixture was refluxed for about 3 h. After that it was cooled and flashed off every 0.5 h. The progress of the reaction was evaluated by monitoring the gained weight as a result of insertion of ethylene oxide units till reaching to the weight equivalent to insertion of ten ethylene oxide units to the sulphonamide derivatives as shown in Scheme 2.

Table 1
Chemical composition and physical properties of deep oil well formation water used in this investigation.

Physical properties	Unit	Value
Density	g/cm^3	1.044
Turbidity	FAU	263
PH		6.38
Salinity NaCl	mg/l	12,029
Conductivity	µs/cm	29,220
Total hardness	mg/l	2910

Ionic species		Value
Sulfate	(mg/l)	6.5
Phosphate	(mg/l)	0.771
Bi-carbonte	(mg/l)	143
Chloride	(mg/l)	7300
Sulfide	(mg/l)	450
Iron ferrous	(mg/l)	23
Iron, total	(mg/l)	42
Calcium	(mg/l)	800
Magnesium	(mg/l)	364
Barium	(mg/l)	105
Potassium	(mg/l)	250
ZINC	(mg/l)	1.359
TDS	(mg/l)	15,520

2.3.3. FTIR spectroscopic analysis

The appearance of new characteristic absorption band for compound II at 3434.23 cm^{-1} assigned to the primary alcohol (−OH) of ethylene oxide units. The ethereal band (C—O—C) appeared at 1123.82 cm^{-1} which confirms that the ethoxylated derivatives were successfully prepared. Fig. 1 shows the appearance of new characteristic absorption bands for compound IV at 2922.25 and 2857.57 cm^{-1} for the asymmetric and symmetric (−CH$_2$), 727 cm^{-1} for (CH$_2$)$_n$, 2900, 1303 cm^{-1} for CH$_3$.

2.3.4. ^{1}H NMR spectrum spectroscopic analysis

All the above chemical shifts confirm the cationic compound IV was successfully prepared as showed in Fig. 2 The chemical shifts at б (2.7) for ^{1}H proton (a) of the —CH$_2$ group in the first ethylene oxide unit attached to 3°rd N, the chemical shift б (3.8) for ^{1}H protons (b) —CH$_2$ group of repeated ethylene oxide units and the chemical shift at б (3.96) for ^{1}H protons (c) —CH$_2$ group of ethylene oxide unit near terminal (−OH). The chemical shifts at б (3.24) for ^{1}H proton of the —CH$_2$ group in the aliphatic group dodecyl.

2.4. Testing solution

The test solution for this work is deep oil well formation water. H$_2$S gas was generated in situ by addition of equivalent amount of 0.5 M H$_2$SO$_4$ and 0.5 M Na$_2$S. The precise concentration of H$_2$S was determined by the iodometric titration method three times to make sure the results were reproducible and reliable.

2.5. Open circuit potential measurements

All electrochemical experiments were carried out by Volta lab80 (Tacussel-radiometer PGZ402) controlled by Tacussel corrosion analysis software model (Volta master 4) attached to traditional three-electrode cell. The working electrode (WE) was a rod of API X65 steel pipeline embedded in PVC holder using epoxy resin so that the flat surface of the electrode (1.0 cm^2) was the only exposed area to the corrosive media the electrode was abraded with emery paper (grade 320–400–600–800–1000–1200) on the test face, rinsed with distilled water, degreased with acetone and dried.

A platinum wire electrode with (0.63 cm^2 surface area) and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. All potential data reported were referred to SCE reference electrode. Before starting the experiments, the working electrode was immersed in test solution for 30 min at open circuit potential (OCP). All experiments were carried out at 298 K.

2.6. Potentiodynamic polarization measurements

Polarization curves were recorded at a constant sweep rate of 2 mV s^{-1}. The values of corrosion current densities were calculated using Tafel extrapolation method by taking the extrapolation interval of 250 mV with respect to E$_{corr}$.

2.7. Electrochemical impedance spectroscopy (EIS)

Impedance spectra were obtained in the frequency range between 100 kHz and 50 mHz using 10 steps per frequency decade at open circuit potential after 3 h of immersion time. AC signal with 10 mV amplitude peak to peak was used to perturb the system. EIS diagrams are given in Nyquist and Bode representations [28].