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Novel cationic surfactants for corrosion inhibition of carbon steel pipelines in oil and gas wells applications

M.A. Hegazy^{a,*}, A.Y. El-Etre^b, M. El-Shafaie^a, K.M. Berry^b

^a Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt

^b Chemistry Dept., Faculty of Science, Benha University, Benha, Egypt

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ABSTRACT

A novel series of cationic surfactants namely: 1-dodecyl-2-(phenethylimino)-1-methylpyrrolidin-1-ium bromide (A), 1-dodecyl-2-((2-hydroxyethyl)imino)-1-methylpyrrolidin-1-ium bromide (B) and 1-dodecyl-2-((4-hydroxyphenyl)imino)-1-methylpyrrolidin-1-ium bromide (C), were evaluated as corrosion inhibitors for carbon steel pipelines in oil and gas wells applications by weight loss, potentiodynamic polarization and electro-chemical impedance spectroscopy techniques. Surface parameters of the cationic surfactants were determined using surface tension and conductivity techniques. The results of the surface tension measurements showed good surface behavior of these compounds in their aqueous solutions. The prepared cationic surfactants showed a good ability to act as corrosion inhibitors for the tested system. It was found that the inhibition efficiency of three cationic surfactants follows the order: C > A > B.

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1. Introduction

Oil and gas wells applications are the general terms describing an operation performed on a well to improve its productivity through opening up new channels in the rock for the oil and gas stimulation by dissolving materials from a well. A basic requirement for wellbore cleanout is that the scale must be acid soluble. If a well is plugged with an acid soluble scale such as carbonate scale, then the acid can be very effective at the scale removal and production restoring. The acid will not dissolve paraffin deposits, but it will be very effective at removing iron scales such as iron sulfide. Hydrochloric acid is generally used in the oil and gas wells applications [1–4]. Carbon steel is the most widely used as the constructional material in many industries due to its excellent mechanical and low cost. It is used in large tonnages in marine applications, chemical processing, petroleum production and refining, construction and metal processing equipment. The corrosion of steel in such environments and its inhibition constitute a complex problem of processes [5,6]. Using inhibitors is one of the most practical methods for protection metals against corrosion, especially in acidic media. Heterocyclic organic compounds containing nitrogen, sulfur and/or oxygen atoms are often used for this purpose [6-10].

In this work the inhibition efficiencies of 1-dodecyl-2-(phenethylimino)-1-methylpyrrolidin-1-ium bromide (cationic surfactant A), 1-dodecyl-2-((2-hydroxyethyl)imino)-1-methylpyrrolidin-

Corresponding author.
E-mail address: mohamed_hgazy@yahoo.com (M.A. Hegazy).

http://dx.doi.org/10.1016/j.molliq.2015.11.047 0167-7322/© 2015 Elsevier B.V. All rights reserved. 1-ium bromide (cationic surfactant B) and 1-dodecyl-2-((4-hydroxyphenyl)imino)-1-methylpyrrolidin-1-ium bromide (cationic surfactant C) toward carbon steel corrosion in 1 M HCl solution were determined. A comparative study of the prepared inhibitors with some of the previously reported compounds shows that the prepared surfactants are comparable or superior in respect of the inhibition efficiency.

2. Material and experimental methods

2.1. Carbon steel

The chemical composition of carbon steel was the following: 0.080 C, 0.025 P, 0.020 Si, 0.026 Al, 0.015 Ni, 0.010 S, 0.004 Mo, 0.003 V, 0.280 Mn, 0.003 Co, 0.005 Cu, 0.008 N, 0.007 Cr and the remainder iron which determined by an ARLTM 4460 Optical Emission Spectrometer (USA).

2.2. Preparation of novel cationic surfactants

The cationic surfactants were prepared by quaternization reaction [11,12] of three Schiff bases: (0.02 mol, 4.0430 g) N-(1-methylpyrrolidin-2-ylidene)-2-phenylethanamine, (0.02 mol, 2.8440 g) 2-((1-methylpyrrolidin-2-ylidene)amino)ethanol and (0.02 mol, 3.8048 g) 4-((1-methylpyrrolidin-2-ylidene)amino)phenol with (0.02 mol, 4.9848 g) 1-bromododecane in 100 ml ethanol as solvent in 250 ml flask at 70 °C for 24 h. These mixtures were allowed to cool down, and the obtained materials were further purified by diethyl

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ether then recrystallized by ethanol to produce 1-dodecyl-2-(phenethylimino)-1-methylpyrrolidin-1-ium bromide (cationic surfactant A), 1-dodecyl-2-((2-hydroxyethyl)imino)-1-methylpyrrolidin-1-ium bromide (cationic surfactant B) and 1-dodecyl-2-((4hydroxyphenyl)imino)-1-methylpyrrolidin-1-ium bromide (cationic surfactant C) respectively. The final products were dried under vacuum. The chemical structures of the prepared cationic surfactants (Fig. 1) were confirmed by ¹H NMR and Mass spectroscopy.

2.3. The surface tension measurements

Surface tension was measured with a Du Nouy Tensiometer (Kruss Type 6) for different concentrations of synthesized cationic surfactants. Bidistilled water from an all-glass apparatus with a surface tension of 72 mN m⁻¹ at 25 °C was used to prepare all solutions.

2.4. Conductivity measurements

An electrical conductivity meter (Type 522; Crison Instrument, S.A.) was used to measure the conductivity of the different concentrations of synthesized cationic surfactants.

2.5. Weight loss technique

The test specimens were cut into $3 \text{ cm} \times 6 \text{ cm} \times 0.5 \text{ cm}$ were abraded with a series of emery paper (grade 320-400-600-800-1000-1200), cleaned successively with distilled water, ethanol, and acetone then finally dried in dry air before use. The samples were allowed to stand for 24 h in 1 M HCl solution in the absence and presence of different

concentrations of the inhibitors. Triplicate specimens were exposed for each experiment and the mean weight losses were reported.

2.6. Electrochemical technique

Electrochemical experiments were carried out using a Voltalab 40 Potentiostat PGZ 301 in a conventional electrolytic cell with threeelectrode arrangement: saturated calomel reference electrode (SCE), platinum rod as a counter electrode and the carbon steel rod as working electrode (WE). The electrode potential was allowed to stabilize for 30 min before starting the measurements. The exposed electrode area to the corrosive solution is 0.34 cm^2 . All experiments were conducted at 20 °C. Potentiodynamic polarization curves were obtained by changing the electrode potential automatically (from -800 to -300 mV vs.SCE) at open circuit potential with scan rate of 0.2 mV s^{-1} . EIS measurements were carried out in a frequency range of 100 kHz to 50 mHz with amplitude of 10 mV peak-to-peak using ac signals at open circuit potential.

3. Results and discussion

3.1. Structure confirmation of the prepared cationic surfactants

3.1.1.¹H NMR spectroscopy

¹H NMR spectrum of cationic surfactant C shown in Fig. 2 is a representative figure of the surfactants A and B presented in the supplementary materials as Figs. S1 and S2, respectively. ¹H NMR (DMSO-d6) spectrum of cationic surfactant (A) showed that δ , ppm at: $\delta = 0.797-0.840$ ppm (t, 3H, CH₃(CH₂)₁₀CH₂); $\delta = 1.144-1.298$ ppm (m, 20H, CH₃(CH₂)₁₀CH₂); $\delta = 1.488-1.555$ ppm (m, 2H, CH₃NCH₂CH₂CH₂C); $\delta = 2.113-2.208$ ppm





(cationic surfactant A)



1-dodecyl-2-((2-hydroxyethyl)imino)-1-methylpyrrolidin-1-ium bromide

(cationic surfactant B)



1-dodecyl-2-((4-hydroxyphenyl)imino)-1-methylpyrrolidin-1-ium bromide

(cationic surfactant C)

Fig. 1. The chemical structure of the prepared cationic surfactants.

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